

57300086

NOVEL FLUORINE OXIDIZERS

PART A. COPYRIGHT ARTICLES*

Karl O. Christe
William W. Wilson

3/9/3

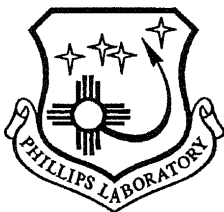
Rockwell International
Rocketdyne Division
6633 Canoga Avenue
Canoga Park CA 91309

February 1994

Final Report

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

* COPIES AVAILABLE FROM COPYRIGHT HOLDERS



PHILLIPS LABORATORY
Propulsion Directorate
AIR FORCE MATERIEL COMMAND
EDWARDS AIR FORCE BASE CA 93524-7001

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (MM/DD/YYYY) February 1994		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) Jul 1990 – Aug 1993	
4. TITLE AND SUBTITLE Novel Fluorine Oxidizers Part A: Copyright Articles				5a. CONTRACT NUMBER F04611-90-C-0011	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Karl O. Christie; William W. Wilson				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER 573000LQ	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Rockwell International Rocketdyne Division 6633 Canoga Avenue Canoga Park, CA 91309				8. PERFORMING ORGANIZATION REPORT NO. RI/RD 93-176	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Phillips Laboratory OLAC PL/RKFE 9 Antares Road Edwards AFB, CA 93524-7680				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) PL-TR-93-3058A	
12. DISTRIBUTION / AVAILABILITY STATEMENT DISTRIBUTION STATEMENT A. Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES Part A is a companion to ADA279480					
14. ABSTRACT Appendix A through Appendix R are copyright articles provided by the copyright holders.					
15. SUBJECT TERMS Energy storage; fluorides; energetic compounds; oxidizers; azides; high coordination numbers; oxidizer strength scale					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 123	19a. NAME OF RESPONSIBLE PERSON
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NO (include area code)

The IOF_6^- Anion: The First Example of a Pentagonal Bipyramidal AX_5YZ Species[†]

K. O. Christe,^{*1} D. A. Dixon,² A. R. Mahjoub,³ H. P. A. Mercier,⁴ J. C. P. Sanders,⁴ K. Seppelt,^{*3} G. J. Schrobilgen,^{*4} and W. W. Wilson¹

Contribution from Rocketdyne, A Division of Rockwell International, Canoga Park, California 91309, the Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada, the Central Research and Development Department, E.I. du Pont de Nemours and Company, Inc., Experimental Station, Wilmington, Delaware 19880-0328, and the Institut für Anorganische und Analytische Chemie der Freien Universität, Berlin, Germany

Received October 16, 1992

Abstract: The IOF_6^- anion, which is the first example of a pentagonal bipyramidal AX_5YZ type species, was prepared in the form of its stable $\text{N}(\text{CH}_3)_4^+$ salt. Its X-ray crystal structure was determined at -93° and -155°C (tetragonal, space group $P4/nmm$, $Z = 2$, $a = 8.8590$ (10) and 8.8151 (10) Å, $c = 6.3690$ (10) and 6.3213 (10) Å, $R = 0.0373$ and 0.0291 for 876 [$I > 3\sigma(I)$] and 885 [$I > 3\sigma(I)$] reflections, respectively). In addition to two perfectly ordered $\text{N}(\text{CH}_3)_4^+$ cations, the structure contains two IOF_6^- anions of approximate C_{5v} symmetry which are subject to a positional 4-fold disorder for the equatorial plane. The $\text{O}-\text{I}-\text{F}_{\text{ax}}$ angle is constrained by symmetry to be 180° , whereas there are no constraints on the positions of the equatorial fluorines. The $\text{I}-\text{O}$ bond length indicates substantial double bond character, and the axial $\text{I}-\text{F}$ bond length is significantly shorter than the five equatorial $\text{I}-\text{F}$ bond lengths. The mean $\text{O}-\text{I}-\text{F}_{\text{eq}}$ bond angle is slightly larger than 90° , due to the doubly bonded oxygen atom being more repulsive than the singly bonded axial fluorine ligand. The equatorial IF_5 plane is puckered to alleviate its congestion. In contrast to the highly fluxional, free IF_7 molecule, in which the equatorial fluorines undergo a very rapid, dynamic, pseudorotational ring puckering and a slower intramolecular equatorial-axial ligand exchange, the puckering of the IOF_6^- anion in its $\text{N}(\text{CH}_3)_4^+$ salt is frozen out due to anion-cation interactions, and the equatorial-axial ligand exchange is precluded by the more repulsive oxygen ligand which occupies exclusively axial positions. Therefore, the IOF_6^- anion is ideally suited for studying the nature of the equatorial puckering in species of 5-fold symmetry. The puckering in IOF_6^- is of the C_s symmetry type, and the deviations from the ideal equatorial plane are relatively small and decrease with decreasing temperature. Furthermore, the axial $\text{I}-\text{O}$ bond length decreases and the mean $\text{O}-\text{I}-\text{F}_{\text{eq}}$ bond angle increases with decreasing temperature. These findings demonstrate that in agreement with our results from ab initio calculations and contrary to the VSEPR concept of repelling points on a sphere, the minimum energy structures of these main group heptacoordinated fluorides or oxyfluorides are those of pentagonal bipyramids with an unpuckered equatorial plane and not those of either monocapped octahedra or monocapped trigonal prisms. Whereas in solid $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$ the equatorial ring puckering of IOF_6^- is frozen out, in the dissolved free ion this puckering becomes dynamic, as demonstrated by ^{19}F NMR spectroscopy which shows five equivalent equatorial fluorine ligands. Contrary to IF_7 and TeF_7^- , the IOF_6^- anion does not undergo an intramolecular equatorial-axial ligand exchange on the NMR time scale because of the more repulsive, doubly bonded oxygen. The vibrational spectra of $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$ in both the solid state and CH_3CN solution were recorded and assigned with the help of ab initio calculations on IOF_6^- using effective core potentials and local density functional theory. Normal coordinate analyses were carried out for the pentagonal bipyramidal series IF_7 , IOF_6^- , XeF_5^- which show that the equatorial, in-plane deformation force constants (f_α) are a good measure for the degree of congestion in the equatorial plane. Puckering increases with decreasing bond lengths, increasing ligand and decreasing central atom sizes, and increasing temperature. The pentagonal bipyramidal structures of these molecules and the coplanarity of their equatorial ligands, which are found for their minimum energy structures, are explained by a bonding scheme involving delocalized p_{xy} hybrid orbitals of the central atom for the formation of a coplanar, semi-ionic, 6-center 10-electron bond system for the five equatorial bonds and of an sp_2 hybrid orbital for the formation of two, more covalent, colinear, axial bonds. This bonding scheme can account for all the observed structural features and also the bond length differences.

Introduction

In main group element chemistry, coordination numbers in excess of six are relatively rare, but they are of considerable interest due to special features caused by steric crowding of the ligands, free valence electron pairs being sterically either active or inactive, and the propensity of the molecules to exhibit fluxionality. Of particular interest are heptacoordinated species which could exist either as a monocapped octahedron, a mono-

capped trigonal prism, or a pentagonal bipyramid.⁵ According to the VSEPR model of "repelling points on a sphere",⁵ the preferred structures should be the monocapped octahedron or trigonal prism. However, for main group elements and relatively low repulsive forces, the pentagonal bipyramid is favored⁶ and has been found for species such as IF_7 ,^{7,8} or TeF_7^- .⁹⁻¹¹ In pentagonal bipyramidal structures, the pentagonal equatorial plane is highly congested which results in increased repulsion

[†] Dedicated to Professor Jean'ne Shreeve on the occasion of her 60th birthday.

(1) Rocketdyne International, Rocketdyne Division.

(2) E.I. du Pont de Nemours and Company, Inc.

(3) Freie Universität, Berlin.

(4) McMaster University.

(5) Gillespie, R. J.; Hargittai, I. In *The VSEPR Model of Molecular Geometry*; Allyn and Bacon, A Division of Simon & Schuster, Inc.: Needham Heights, MA, 1991; p 58.

(6) Thompson, H. B.; Bartell, L. S. *Inorg. Chem.* **1968**, *7*, 488.

(7) Adams, W. J.; Thompson, H. B.; Bartell, L. S. *J. Chem. Phys.* **1970**, *53*, 4040.

among the equatorial ligands and, as a result, in increased bond lengths and usually some kind of puckering.⁵⁻⁸ In the case of 5-fold symmetry, this puckering presents a special problem. The odd number of ligands does not allow for a highly symmetric arrangement in which all five equatorial ligands can be placed into equivalent positions, i.e. with identical displacements alternately above and below the equatorial plane. One way to achieve equivalency of the equatorial ligands is a fast, dynamic, pseudorotational ring puckering, as found for IF_7 ,^{7,8} which results in a highly fluxional molecule. In addition, the pentagonal bipyramidal XF_7 molecules generally exhibit a second kind of fluxionality, i.e. a slower, intramolecular, axial-equatorial ligand exchange.⁸ The combination of these two types of fluxionality makes it experimentally very difficult to characterize and describe the structures of these molecules. Many of the difficulties with the fluxionality of the XF_7 species might be overcome by studying ionic XOF_6^- salts. The presence of one doubly bonded oxygen which is more repulsive than the fluorine ligands should preempt a facile axial-equatorial ligand exchange, and the dynamic puckering of the equatorial plane could be frozen out by anion-cation interactions. Therefore, an effort was undertaken to prepare and characterize a salt containing an XOF_6^- anion. Examples of pentagonal bipyramidal XOF_6^- species had previously been unknown and only recently been reported^{10,11} in two separate preliminary notes from our laboratories. In this paper, a full account and analysis of our work on the IOF_6^- anion is given.

Experimental Section

Caution: IOF_5 is a strong oxidizer, and its combination with organic materials, such as CH_3CN or $\text{N}(\text{CH}_3)_4^+$ salts, could be potentially hazardous. Although no difficulties were encountered in the present study, appropriate safety precautions and shielding should be used, particularly when working on a larger scale with these materials.

Materials. The CH_3CN (Baker, Bio-analyzed, having a water content of 40 ppm) was treated with P_2O_5 and freshly distilled prior to use, thereby reducing its water content to <4 ppm. Literature methods were used for the syntheses of IOF_5 ¹²⁻¹⁴ and anhydrous $\text{N}(\text{CH}_3)_4^+\text{F}^-$.¹⁵

Synthesis of $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$. The salt $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$ was prepared by condensing gaseous IOF_5 (6.40 mmol) from the calibrated volume of a nickel and stainless steel vacuum line at room temperature onto anhydrous $\text{N}(\text{CH}_3)_4^+\text{F}^-$ (0.4473 g, 5.779 mmol) in 8 mL of dry CH_3CN at -196°C . The mixture was warmed and allowed to react, with frequent agitation, at -35°C for 30 min. The solvent and unreacted IOF_5 were pumped off at -35°C leaving behind $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$ as a very pale yellow crystalline solid in essentially quantitative yield (1.8298 g, 5.772 mmol). Anal. Calcd for $\text{C}_4\text{H}_{12}\text{F}_6\text{IO}$: C, 14.50; H, 3.63; F, 33.00; I, 38.35; N, 4.23. Found: C, 14.62; H, 3.66; F, 32.4; I, 38.51; N, 4.33.

Vibrational Spectroscopy. Raman spectra were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer using the 488-nm exciting line of an Ar ion or the 647.1-nm line of a Kr ion laser, respectively. Baked-out Pyrex melting point capillaries or thin-walled Kel-F tubes were used as sample containers. A previously described¹⁶ device was used for recording the low-temperature spectra.

Infrared spectra were recorded by using either AgCl or AgBr disks on a Perkin-Elmer Model 283 spectrophotometer. The finely powdered samples were sandwiched between two thin disks and pressed together in a Wilks minipress inside the drybox.

Nuclear Magnetic Resonance Spectroscopy. The ^{19}F NMR spectra were recorded at McMaster University unlocked (field drift < 0.1 Hz

h^{-1}) on a Bruker AM-500 spectrometer equipped with an 11.744 T cryomagnet and an Aspect 3000 computer. The spectra were obtained using a 5-mm combination $^1\text{H}/^{19}\text{F}$ probe operating at 470.599 MHz. The spectra were recorded in a 32K memory. A spectral width setting of 62 500 Hz was employed, yielding a data point resolution of 3.8 Hz/data point and an acquisition time of 0.262 s. No relaxation delays were applied. Typically, 40 000 transients were accumulated. The pulse width corresponding to a bulk magnetization tip angle, θ , of approximately 90° was equal to 1 μs . Line broadening parameters used in the exponential multiplication of the free induction decays were 3–4 Hz.

The low-temperature study was carried out by the use of a Bruker temperature controller. The temperature was measured with a copper-constantan thermocouple inserted directly into the sample region of the probe and was accurate to $\pm 1^\circ\text{C}$.

The spectra were referenced to a neat external sample of CFCl_3 . The chemical shift convention used is that a positive (negative) sign signifies a chemical shift to high (low) frequency of the reference compound.¹⁷

Computational Methods. The electronic structure calculations were done at the ab initio molecular orbital level using either local density function (LDF) theory¹⁸⁻²¹ or effective core potentials (ECP). The LDF calculations were carried out with the program system DMol,²² as previously described,⁸ with a double-numerical basis set augmented by d polarization functions. This can be considered in terms of size as a polarized double- ζ basis set. However, because exact numerical solutions are employed for the atom, this basis set is of significantly higher quality than a normal molecular orbital polarized double- ζ basis set. The fitting functions have an angular momentum number one greater than that of the polarization function, resulting in a value of $l = 3$ for the fitting functions.

The ECP calculations were done with all electrons on the F and O and with an effective core potential replacing all of the core electrons on the I. The valence basis set is of polarized double- ζ quality. The fluorine and oxygen basis set is from Dunning and Hay,²³ and the ECP from Hay and Wadt²⁴ including relativistic corrections. The valence basis set of Hay and Wadt²⁴ was used augmented by a d function on I with an exponent of 0.266.²⁵ The geometries were optimized by using gradient techniques,²⁶ and the force fields were calculated analytically.^{27,28} The ab initio MO calculations were done with the program GRADSCF,²⁹ as implemented on a Cray YMP computer system.

Crystal Structure Determinations of $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$. Two independent crystal structure determinations were carried out for this compound at McMaster University and the Freie Universität Berlin.

(17) *Pure Appl. Chem.* **1972**, 29, 627; **1976**, 45, 217.

(18) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(19) Salahub, D. R. In *Ab Initio Methods in Quantum Methods in Quantum Chemistry*, 2nd ed.; Lawley, K. P., Ed.; J. Wiley & Sons: New York, 1987; p 447.

(20) (a) Wimmer, E.; Freeman, A. J.; Fu, C.-L.; Cao, P.-L.; Chou, S.-H.; Delley, B. In *Supercomputer Research in Chemistry and Chemical Engineering*; Jensen, K. F.; Truhlar, D. G., Eds.; ACS Symp. Ser.; American Chemical Society: Washington, DC, 1987; p 49. (b) Dixon, D. A.; Andzelm, J.; Fitzgerald, G.; Wimmer, E.; Delley, B. In *Science and Engineering on Cray Supercomputers. Proceedings of the Fifth International Symposium*; Cray Research: Minneapolis, MN, 1990; p 285.

(21) Jones, R. O.; Gunnarsson, O. *Rev. Mod. Phys.* **1989**, 61, 689.

(22) Delley, B. *J. Chem. Phys.* **1990**, 92, 508. DMol is available commercially from BIOSYM Technologies, San Diego, CA.

(23) Dunning, T. H., Jr.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Chapter 1.

(24) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, 82, 299.

(25) Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio, E.; Sakai, Y.; Tatasaki, H. *Gaussian Basis Sets of Molecular Calculations*; Elsevier: Amsterdam, 1984.

(26) (a) Komornicki, A.; Ishida, K.; Morokuma, K.; Ditchfield, R.; Conrad, M. *Chem. Phys. Lett.* **1977**, 45, 595. (b) Melver, J. W., Jr.; Komornicki, A. *Chem. Phys. Lett.* **1971**, 10, 202. (c) Pulay, P. In *Applications of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; p 153.

(27) (a) King, H. F.; Komornicki, A. *J. Chem. Phys.* **1986**, 84, 5465. (b) King, H. F.; Komornicki, A. In *Geometrical Derivatives of Energy Surfaces and Molecular Properties*; Jorgenson, P.; Simons, J., Eds.; NATO ASI Series C; D. Reidel: Dordrecht, 1986; Vol. 166, p 207.

(28) Breidung, J.; Thiel, W.; Komornicki, A. *Chem. Phys. Lett.* **1988**, 153, 76.

(29) GRADSCF is an ab initio program system designed and written by A. Komornicki at Polyatomics Research.

(8) Christe, K. O.; Curtis, E. C.; Dixon, D. A. *J. Am. Chem. Soc.* **1993**, 115, 1520.

(9) Selig, H.; Sarig, S.; Abramowitz, S. *Inorg. Chem.* **1974**, 13, 1508.

(10) Christe, K. O.; Sanders, J. C. P.; Schrobilgen, G. J.; Wilson, W. W. *J. Chem. Soc., Chem. Commun.* **1991**, 837.

(11) Mahjoub, A. R.; Seppelt, K. *J. Chem. Soc., Chem. Commun.* **1991**, 840.

(12) Holloway, J. H.; Selig, H.; Claassen, H. H. *J. Chem. Phys.* **1971**, 54, 4305.

(13) Schack, C. J.; Pilipovich, D.; Cohz, S. N.; Sheehan, D. F. *J. Phys. Chem.* **1968**, 72, 4697.

(14) Schack, C. J.; Christe, K. O. *J. Fluorine Chem.* **1990**, 49, 167.

(15) Christe, K. O.; Wilson, W. W.; Wilson, R. D.; Bau, R.; Feng, J. J. *Am. Chem. Soc.* **1990**, 112, 7619.

(16) Miller, F. A.; Harney, B. M. *Appl. Spectrosc.* **1969**, 23, 8.

At McMaster, only one type of crystal was observed, tetragonal $P4/nmm$ crystals which have IOF_6^- with a positional 4-fold disorder for the puckered equatorial plane. The structure of one of these crystals was determined at -93°C and is given in this paper.

At Berlin, originally a very similar, orthorhombic crystal was studied at -163°C , and the data were refined either in $P4/nmm$ with 4-fold disorder or $Pmmn$ with systematic twinning; however, no puckering of the equatorial plane was observed.¹¹ In repeat experiments, exclusively crystals identical to those found at McMaster were obtained. The structure of one of these crystals was determined at -155°C and is given in this paper.

Single crystals of $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$ were grown at McMaster by making a saturated solution of $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$ in CH_3CN in a Teflon-FEP tube at room temperature and warming it to 45°C whereupon it completely dissolved to give a pale yellow solution. The sample tube was then positioned horizontally above a dewar containing water at 60°C , covered with aluminum foil, and slowly allowed to cool overnight. This resulted in the growth of transparent crystals which could be described as tetragonal prisms. At McMaster, the crystals were sealed in Lindemann quartz capillaries and centered on a Siemens R3m/v diffractometer. Accurate cell dimensions were determined at $T = -93^\circ\text{C}$ from a least-squares refinement of the setting angles (χ , ϕ , and 2θ) obtained from 25 accurately centered reflections (with $34.71^\circ \leq 2\theta \leq 38.05^\circ$) chosen from a variety of points in reciprocal space. Examination of the peak profiles revealed that they were single.³⁰ Integrated diffraction intensities were collected using a θ - 2θ scan technique with scan rates varying from 1.5 to $14.65^\circ/\text{min}$ (in 2θ) and a scan range of $\pm 0.6^\circ$, so that the weaker reflections were examined slowly to minimize counting errors. Data were collected in four steps since the crystal was diffracting very strongly. In the first step, the data were collected with $-15 \leq h \leq 15$, $0 \leq k \leq 15$, and $0 \leq l \leq 11$ and with $3^\circ \leq 2\theta \leq 45^\circ$, using silver radiation monochromatized with a graphite crystal ($\lambda = 0.56087 \text{ \AA}$). During data collection, the intensities of three standard reflections were monitored every 97 reflections to check for crystal stability and alignment. A total of 1583 reflections were collected out of which 16 were standard reflections. At this stage, the distribution of the reflections in the reciprocal space indicated that the crystal was diffracting at relatively high angles, consequently a second data set was recorded with $45^\circ \leq 2\theta \leq 55^\circ$. This time a total of 1163 reflections were collected out of which 12 were standard reflections. Finally, a third data set was recorded with $55^\circ \leq 2\theta \leq 60^\circ$ giving rise to 712 reflections out of which 8 were standard reflections. These data sets were recorded with the maximum intensity (i.e. 1.5 kW Ag X-rays), without attenuation, and as a consequence, the strongest reflections at very low angles were not recorded. In order to record these missing reflections, the power had to be decreased to 750 W. Another set of data was collected with $-3 \leq h \leq 3$, $0 \leq k \leq 3$, and $0 \leq l \leq 2$. A total of 31 reflections were collected, out of which 6 were standard reflections. No crystal decay was observed. In total, 3136 reflections were collected and 876 unique reflections remained after averaging of equivalent reflections. A total of 780 reflections, satisfying the condition $l \geq 3\sigma(I)$, were used for the structure solution. These reflections exhibited systematic absences for $h k 0$: $h + k = 2n$ and $h 0 0$: $h = 2n$. Corrections were made for Lorentz and polarization effects. Absorption corrections were applied by using the program DIFABS.³¹ The transmission factors ranged from 0.728 to 1.117.

The XPREP program³² was used to determine the correct cell and space group. It confirmed that the original cell was correct and that the lattice was tetragonal primitive ($R_{\text{int}} = 0.028$). The structure was shown to be centrosymmetric by an examination of the E -statistics (calculated, 0.616; theoretical, 0.736). The two space groups which were consistent with the systematic absences (n -glide and C_2) were the centrosymmetric $P4/n$ and $P4/nmm$ space groups.

A first solution was obtained without absorption corrections; it was achieved in the space group $P4/nmm$ (129) by conventional heavy-atom Patterson methods which located the positions of the iodine, nitrogen, and carbon atoms on special positions (i.e. $4mm$, $-4m2$, $.m.$). The full-matrix least-squares refinement of their positions and isotropic thermal parameters gave a conventional agreement index $R = (\sum |F_o| - |\sum F_c|) / \sum |F_o|$ of 0.12. A subsequent difference Fourier synthesis revealed the positions

Table I. Summary of Crystal Data and Refinement Results for $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$ at -93 and -155°C

T ($^\circ\text{C}$)	-93	-155
space group	$P4/nmm$ (tetragonal)	
a ($\text{\AA}$)	8.8590(10)	8.8151(10)
c ($\text{\AA}$)	6.3690(10)	6.3213(12)
V ($\text{\AA}^3$)	499.85(11)	491.20(10)
molecules/unit cell	2	
molecular weight	331.0	
cryst dimens (mm)	$0.4 \times 0.5 \times 0.2$	$0.4 \times 0.4 \times 0.4$
calcd density (g cm^{-3})	2.199	2.238
color	very faintly yellow	
cryst decay (%)	no	no
abs coeff (mm^{-1})	3.259	3.326
wavelength ($\text{\AA}$) used for data collection	0.56086	0.71069
$\sin \theta / \lambda$ limit ($\text{\AA}^{-1}$)	0.8915	0.9045
total no. of refltns measd	3136	3489
no. of independent refltns	876	887
no. of refltns used in structural analysis, $I > 3\sigma(I)$	780	885
no. of variable parameters	28	34
final agreement factors		
R	0.0373	0.0291
R_w	0.0350	0.0255

of two atoms located on special positions, above and below the iodine. It was possible to distinguish a fluorine from an oxygen atom from the difference in bond lengths (i.e., 1.83 and 1.74 $\text{\AA}$). The introduction of these positions gave a residual factor R of 0.10. A further difference Fourier synthesis clearly showed the presence of three atoms in the equatorial environment of the iodine. Two of these atoms were positioned on general positions, while the third one was positioned on a special position ($.m$). Consequently, the model implied a 4-fold disorder in the "pseudo"-equatorial plane consisting of a superposition of four molecules with identical I, axial F, and O positions. Consequently, the site occupancy factors of the equatorial fluorine atoms were set equal to 0.25 and 0.125 (general and special positions, respectively) instead of 1.00 and 0.5. The introduction of these positions and isotropic thermal parameters for the equatorial F atoms (all set equal) resulted in a drop of the residual factor R to 0.057. Another improvement of the structure was achieved by introducing anisotropic thermal parameters for the I, N, C, F_{ax} , and O atoms (the F_{eq} were kept isotropic because of the presence of the 4-fold disorder), and the positions of the hydrogen atoms located from a difference Fourier map ($U(\text{H})$ fixed to $0.08 \text{ \AA}^2$), as well as a weighting factor ($w = 1/\sigma^2(F) - 0.0003F^2$), dropping the R factor to 0.044 ($R_w = 0.041$).

The structure was solved a second time using data that had been corrected for absorption. The initial model used the atomic coordinates and isotropic thermal parameters defined previously for all the atoms. The solution obtained ($R = 0.043$) indicated a slight improvement over that obtained without absorption corrections ($R = 0.057$). The final refinement was obtained by introducing anisotropic thermal parameters for the I, F_{ax} , O, N, and C atoms and a weighting factor ($w = 1/\sigma^2(F) + 0.0000F^2$) and gave rise to a residual R of 0.0373 ($R_w = 0.0350$). In the final difference Fourier map, the maximum and the minimum electron densities were 1.5 and $-1.6 \text{ \AA}^{-3}$.

All calculations were performed using the SHELXTL PLUS³² determination package for structure determination molecular graphics.

At Berlin, the crystal was mounted, with the help of a special apparatus,³³ on an Enraf Nonius CAD 4 diffractometer at -155°C . Oscillating crystal photographs were used to check the reflection quality. There were 25 reflections in the θ range 12 – 25° that were used to obtain the orientation matrix and lattice constants. Space group determination: The lattice constants indicated no deviation from tetragonal symmetry. Reflection intensities obeyed the rules $F(hkl) = F(\bar{h}k\bar{l}) = F(kh\bar{l})$ with $R_{\text{int}} = 0.0204$. Extinction of $hk0 \neq 2n$ left only space group $P4/nmm$ (No. 129), which enforces the 4-fold disorder model. Calculations in orthorhombic space groups $Pmmn$ (No. 59) or $P2_1mn$ (No. 31) generated the same disorder of the equatorial fluorine atoms. Three reflections were used to check for crystal decay and standard reflections orientation. Further details of the measurement routine are given in Tables I and S1 (supplementary material). After applying Lorentz and polarization

(30) Despite the fact that all the peaks proved to be single, the possibility of twinning was checked by verifying that the hkl values associated with the very weak and very strong reflections at low $\sin \theta / \lambda$ refined using the same orientation matrix.

(31) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(32) Sheldrick, G. M. (1990); SHELXTL PLUSTM Release 4.21/V. Siemens Analytical X-Ray Instruments, Inc., Madison, Wisconsin.

(33) Keith, M.; Bärnighausen, H. A. *Kristallogr.* **1985**, *170*, 5. Schumann, H.; Genthe, W.; Hahn, F.; Hossein, M. B.; d. Helin, D. V. *Organomet. Chem.* **1986**, *229*, 67.

Table II. Bond Lengths, Bond Angles, Average Equatorial Plane Angle, and Deviations from the Average $\text{O}-\text{I}-\text{F}_{\text{eq}}$ Bond Angle for $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$ at -93 and -155 °C

	bond lengths (Å)		deviations (deg) from the mean $\text{O}-\text{I}-\text{F}_{\text{eq}}$ bond angle	
	-93 °C	-155 °C	-93 °C	-155 °C
I-O	1.772(8)	1.745(4)		
I-F(1)	1.822(6)	1.823(3)		
I-F(2)	1.899(9)	1.894(5)	-0.8(2)	-0.4(1)
I-F(3)	1.852(10)	1.868(7)	5.2(2)	3.7(2)
I-F(4)	1.880(14)	1.868(9)	-8.7(4)	-6.6(3)
N-C	1.483(4)	1.491(3)		

	bond angles (deg)	
	-93 °C	-155 °C
O-I-F(2)	94.3(2)	95.9(1)
O-I-F(3)	88.3(2)	91.8(2)
O-I-F(4)	102.4(4)	102.1(3)
F(1)-I-F(2)	85.7(2)	84.1(1)
F(1)-I-F(3)	91.7(2)	88.2(2)
F(1)-I-F(4)	77.8(4)	77.9(3)
F(3)-I-F(2e)	68.7(4)	69.9(3)
F(4)-I-F(3)	78.6(3)	76.1(2)
F(2c)-I-F(2e)	66.8(5)	67.5(3)
mean O-I-F _{eq}	93.5(3)	95.5(2)
mean pucker angle ^a	4.14(30)	2.96(20)

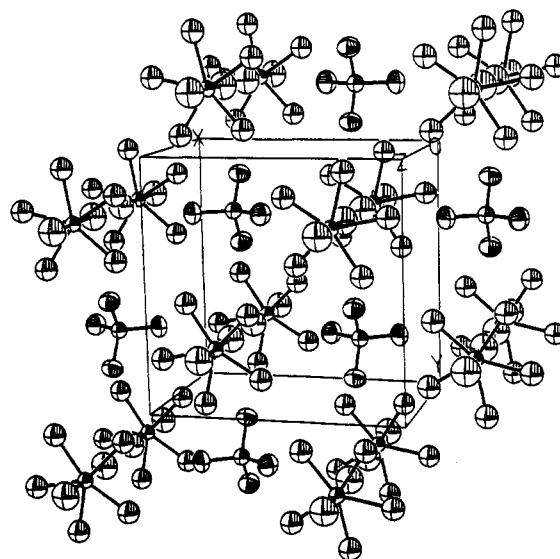
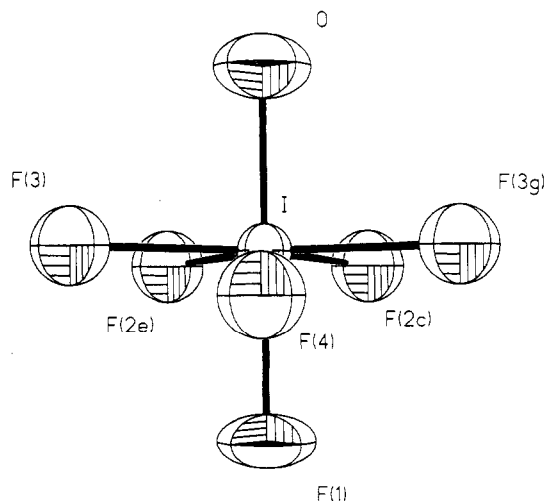
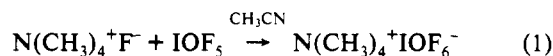
^a Mean deviation of the equatorial fluorine ligands from the mean $\text{O}-\text{I}-\text{F}_{\text{eq}}$ angle.

corrections, the data were used for refinement of the previously published¹¹ model with the program SHELXS 76.³⁴ Atomic form factors were taken from the Kynoch tables.³⁵ The atoms I, O, F(1), N, and C were refined anisotropically and F(2)–F(4) isotropically which resulted in $R = 0.045$. Absorption correction was introduced at this stage. Optical measurements were not possible because of the embedding of the colorless crystal in paraffin oil. The ψ scan method gave no better results. Finally the method DIFABS³¹ was used. Maximal and minimal corrections of 1.28 and 0.85 were applied. At this stage, hydrogen atoms were found in difference Fourier maps and refined with fixed isotropic U . This model refined to $R = 0.0291$ and $R_w = 0.0255$ (see Table I). The 4-fold disordered atoms F(2)–F(4) were then treated anisotropically. This resulted in $R = 0.020$ and $R_w = 0.0171$. The F(2), F(3), and F(4) atoms became quite disk-like, with a considerable bond shrinkage effect. Since it is unclear whether or not it is advisable to refine these 4-fold disordered atoms anisotropically because of overlap of these atoms with each other, the calculations with isotropic F(2), F(3), F(4) atoms is regarded as the best solution.

Summaries of the data collection parameters and other crystallographic information for both data sets are given in Table I. The final atomic coordinates, thermal parameters, interatomic distances, bond angles, and deviations from the average $\text{O}-\text{I}-\text{F}_{\text{eq}}$ angles are listed in Tables II and S4–S5 (supplementary material). Summaries of the structure determinations and the observed and calculated structure factors are given in Tables S1–S3.

Results and Discussion

Synthesis and Properties of $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$. In a previous study,³⁶ it was shown that at room temperature, CsF does not react with a large excess of IOF_5 , while at higher temperatures it tends to undergo deoxygenation. In the same paper it was speculated that the failure to observe fluorine–oxygen exchange in the IF_7 – CsNO_3 system might be due to the lack of formation of an intermediate IOF_6^- salt. The present study clearly demonstrates that under suitable reaction conditions, i.e. using a soluble anhydrous fluoride of a large cation in a compatible solvent, IOF_6^- salts are readily formed according to

**Figure 1.** Packing diagram of $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$ viewed along the c axis.**Figure 2.** The structure of the IOF_6^- anion showing the puckering pattern of the equatorial fluorine ligands.

The resulting $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$ is a very pale yellow solid which is thermally stable up to about 137 °C where it starts to decompose to IOF_4 , CF_4 , and COF_2 as the major products. It was characterized by elemental analysis, a crystal structure determination, and vibrational and ^{19}F NMR spectroscopy (see below).

X-ray Crystal Structure of $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$. The crystal structure of $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$ at -93 °C was determined at McMaster University and confirmed at the Freie Universität Berlin for a crystal kept at -155 °C. Although the gross features of both structures are very similar, they exhibit an extremely interesting temperature dependence of the degree of puckering and, therefore, both data sets are given in full detail.

The crystal structure of $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$ consists of well-separated $\text{N}(\text{CH}_3)_4^+$ and IOF_6^- ions. The packing of the ions (see Figure 1) can be described as a cubic close packing of alternating layers of IOF_6^- anions and $\text{N}(\text{CH}_3)_4^+$ cations in which the alternating orientation of the tetrahedral cations results in a cuboctahedral³⁷ unit cell with $Z = 2$. While the cation is perfectly ordered with the expected bond lengths, the IOF_6^- anion is subject to a positional 4-fold disorder in the equatorial plane. The model results from the superposition of four anions in which the central I atom and the axial O and F(1) atoms occupy identical positions.

(34) Sheldrick, G. M. *Program for Crystal Structure Determination*; Göttingen, 1976.

(35) *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, 1968; Vol. III.

(36) Christie, K. O.; Wilson, W. W.; Wilson, R. D. *Inorg. Chem.* **1989**, *28*, 904.

(37) Hyde, B. G.; Anderson, S. *Inorganic Crystal Structures*; John Wiley & Sons: New York, 1989; p 7.

One of these anions is shown in Figure 2. There are no significant contacts to iodine other than the directly bonded oxygen and six fluorine ligands, and the anion exhibits a gross pentagonal bipyramidal geometry. The O–I–F_{ax} angle is constrained by symmetry to be 180°, while there are no constraints on the positions of the equatorial fluorines. The equatorial fluorines are bent away from the axial oxygen ligand, as expected for a doubly bonded oxygen being more repulsive than a singly bonded fluorine ligand.⁵

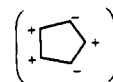
The I–O bond length (1.75–1.77 Å) indicates significant double bond character for the I–O bond.^{38–43} Its temperature dependence will be discussed below. The greater I–O bond length in IOF₆[−], when compared with that in IOF₅ (1.715(4) Å),³⁸ is consistent with the placement of some of the negative charge on oxygen, thereby increasing the polarity and decreasing the bond order of the I–O bond. The axial I–F bond (1.823(3) Å) is, within experimental error (±3σ), significantly shorter than all of the equatorial I–F bonds (average 1.88 Å), and both types of I–F bonds in IOF₆[−] are significantly longer than the corresponding bonds in IF₇ (1.786(7) and 1.858(4) Å, respectively).⁷ These differences can be attributed again to the formal negative charge on IOF₆[−], which leads to greater I^{δ+}–F^{δ−} bond polarities and consequently longer bonds. The greater length of the equatorial bonds in IOF₆[−] and IF₇ relative to their axial ones is due to the increased mutual repulsion of the fluorine ligands in the highly congested equatorial plane and their higher ionicity (see below).

Nature and Temperature Dependence of the Equatorial Puckering in IOF₆[−]. As mentioned above, the equatorial fluorine atoms in IOF₆[−] are bent away from the doubly bonded oxygen atom by about 5°. Furthermore, the plane of the equatorial fluorine atoms is puckered and its I–F bonds are elongated in order to lessen the high degree of ligand–ligand repulsion encountered for these fluorines. Contrary to the rapid dynamic puckering in free, pentagonal-bipyramidal molecules, such as IF₇,⁸ the puckering in solid N(CH₃)₄⁺IOF₆[−] is frozen out by hydrogen...fluorine bridging between the two F(2) atoms of IOF₆[−] and hydrogen atoms from two different cations. This bridging results in two close F...C contacts of 3.175(9) and 3.271(9) Å, while the remaining closest F...C contacts occur at 3.317(9), 3.473(9), and 3.416(9) Å and are very close to the accepted sum of the van der Waals radii of CH₃ (2.00 Å)⁴⁴ and F (1.35–1.40 Å)^{44,45} which is 3.35–3.40 Å.

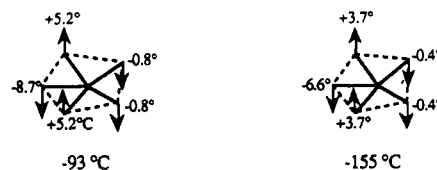
A pentagonal plane can be puckered in two ways resulting in structures of either C_s or C₂ symmetry, respectively.



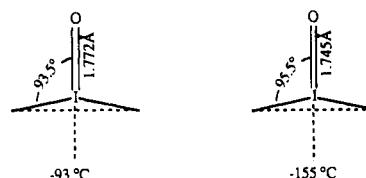
As mentioned above, the doubly bonded, axial oxygen ligand in IOF₆[−] is more repulsive than the singly bonded, axial fluorine ligand. Therefore, the average equatorial plane, which can be defined as a plane perpendicular to the O–I–F_{ax} axis containing all five equatorial fluorine ligands at the averaged F_{eq}–I–O bond angle, drops below the center of the iodine atom. As can be seen from Table II and Figure 2, the puckered plane of IOF₆[−] definitely exhibits C_s symmetry.



Furthermore, the relative displacements of the equatorial fluorine ligands from the average equatorial plane decrease with decreasing temperature, i.e. the degree of puckering decreases with decreasing temperature.



This decrease in the degree of puckering at lower temperatures causes additional important structural changes. Thus, the I–O bond length is significantly shortened and the angle between the oxygen ligand and the average equatorial plane is increased.



These temperature effects can be explained by a decreasing population of the higher vibrational states of the ring puckering motion which, due to its low frequency of about 141 cm^{−1}, is, even at low-temperatures, still highly populated. The resulting decrease in the thermal motion of the equatorial fluorines diminishes their mutual repulsion and allows the equatorial fluorines to become more coplanar and less repulsive which, in turn, results in a shortening of the I–O bond length. It would therefore be of great interest to determine the crystal structure of N(CH₃)₄⁺IOF₆[−] at a very low temperature at which the puckering motion is completely frozen out and to compare the resulting structure with those of the present study. Such a study could establish beyond a doubt that in their minimum energy structures these normally puckered, pentagonal bipyramidal molecules indeed possess unpuckered equatorial planes.

¹⁹F NMR Spectrum of the IOF₆[−] Anion. The ¹⁹F NMR spectrum (obtained at McMaster University) of N(CH₃)₄⁺IOF₆[−] was recorded at −40 °C in CH₃CN solution and is in agreement with a pentagonal bipyramidal structure for the IOF₆[−] anion. This structure is expected to have an average C_{5v} point group symmetry with the oxygen in the axial position. Accordingly, the ¹⁹F NMR spectrum (Figure 3) displays a broad doublet (Δν_{1/2} ≈ 170 Hz) at 166.0 ppm, assigned to the equatorial fluorines, and a broad binomial sextet (Δν_{1/2} ≈ 360 Hz) at 111.1 ppm, assigned to the axial fluorine *trans* to oxygen. The weak triplet observed at 114.5 ppm [²J(F_{eq}–F_{ax}) = 200 Hz] is attributed to the F-*trans*-to-O environment of *cis*-IO₂F₄[−]⁴⁶ which probably arose from adventitious hydrolysis of IOF₆[−] during synthesis or NMR sample preparation. The observation of separate ¹⁹F resonances for the axial and equatorial ligand environments of IOF₆[−] is unusual for a pentagonal bipyramidal species and demonstrates that the IOF₆[−] anion does not undergo intramolecular ligand exchange (i.e., pseudorotation) in solution, in contrast with the related TeF₇[−] anion^{10,11} and IF₇ molecule.⁴⁷ This is not surprising because any plausible intermediate in the pseudorotation process for IOF₆[−] would require the doubly bonded oxygen ligand to move into an

(38) Bartell, L. S.; Clippard, F. B.; Jacob, J. E. *Inorg. Chem.* **1976**, *15*, 3009.

(39) Smart, L. E. *J. Chem. Soc., Chem. Commun.* **1977**, 519.

(40) Selte, K.; Kjekshus, A. *Acta Chem. Scand.* **1970**, *24*, 1912.

(41) Kálmán, K.; Cruickshank, D. W. J. *Acta Crystallogr.* **1970**, *B26*, 1782.

(42) Feikeman, Y. D. *Acta Crystallogr.* **1961**, *14*, 315.

(43) Feikeman, Y. D. *Acta Crystallogr.* **1966**, *20*, 765.

(44) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960; p 260.

(45) Bondi, A. J. *Phys. Chem.* **1964**, *68*, 441.

(46) Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Chem.* **1981**, *20*, 2104.

(47) (a) Gillespie, R. J.; Quail, J. W. *Can. J. Chem.* **1964**, *42*, 2671. (b) Bartlett, N.; Beaton, S.; Reeves, L. W.; Wells, E. J. *Can. J. Chem.* **1964**, *42*, 2531. (c) Alexakos, L. G.; Cornwell, C. D.; Pierce, S. B. *Proc. Chem. Soc.* **1964**, 86, 293. (d) Gutowski, H. S.; Hoffmann, C. F. *J. Chem. Phys.* **1951**, *19*, 1259.

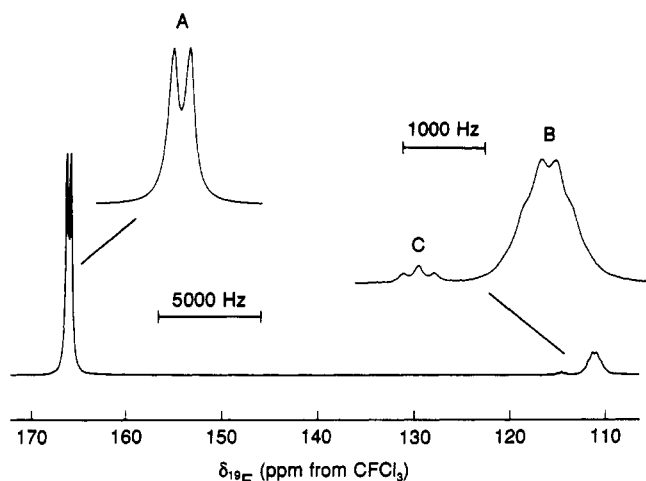


Figure 3. The ^{19}F NMR spectrum (470.599 MHz) of a saturated solution of $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$ in CH_3CN at -40°C : (A) F_{eq} environment of IOF_6^- ; (B) F_{ax} environment of IOF_6^- ; (C) F-trans-to-O environment of $\text{cis-IO}_2\text{F}_4^-$ impurity.

equatorial position. The greater space requirement of the oxygen double bond domain, compared with that of a fluorine single bond domain, would render the placement of the oxygen ligand in the more sterically crowded equatorial position energetically unfavorable, thereby creating a high activation barrier for the process. Although the X-ray crystal structure reveals that, in the solid state, the equatorial fluorine ligands of the IOF_6^- anion are unevenly puckered, only a single resonance is observed for these ligands in the ^{19}F NMR spectrum of the solution. Clearly, the puckering, which is frozen out in the solid state, becomes a dynamic process in solution which is fast on the NMR time scale.

It is of interest to compare the ^{19}F chemical shifts of IOF_6^- with those of other related iodine(VII) oxofluoro species. The ^{19}F chemical shifts of the F-trans-to-F environments in $\text{trans-IO}_2\text{F}_4^-$, $\text{cis-IO}_2\text{F}_4^-$,⁴⁶ and IOF_5 ⁴⁷ occur in a specific region at 65.1, 66.0, and 68 ppm, respectively. Similarly, the ^{19}F chemical shifts of the F-trans-to-O environments in $\text{cis-IO}_2\text{F}_4^-$ and IOF_5 also occur in a distinct region at 112.8⁴⁶ and 107 ppm,⁴⁸ respectively. In the IOF_6^- anion it can be seen that the F-trans-to-O environment (111.1 ppm) also resonates in this region but that the resonance of the five equatorial fluorines (166.0 ppm) is strongly deshielded (i.e., by ca. 100 ppm) from the F-trans-to-F environments of IOF_5 and $\text{cis-/trans-IO}_2\text{F}_4^-$. This phenomenon has also been noted for the XeF_5^- anion in which the fluorines in the pentagonal plane resonate 56.8 ppm to high frequency of the fluorine ligands in square-planar XeF_4 .⁴⁹ In the cases of the pentagonal bipyramidal TeF_7^- anion and IF_7 molecule, even at low temperature^{10,11,47} only average ^{19}F chemical shifts can be obtained owing to their fluxional behavior. Nevertheless, the fact that these average chemical shifts occur at significantly higher frequency than those of the related octahedral TeF_6 ⁵⁰ and IF_6^+ ⁵¹ species indicates that the five equatorial fluorines have a higher frequency ^{19}F chemical shift than the two axial fluorine ligands, since the former will contribute the largest weighting to the average chemical shift.

The large chemical shift differences between fluorine ligands in a square plane and those in a pentagonal plane in the aforementioned species are indicative of the dominance of the paramagnetic contribution to the ^{19}F shielding constant. In the theory developed by Pople and Karplus,⁵² the paramagnetic contribution to the shielding constant of an atom A bonded to

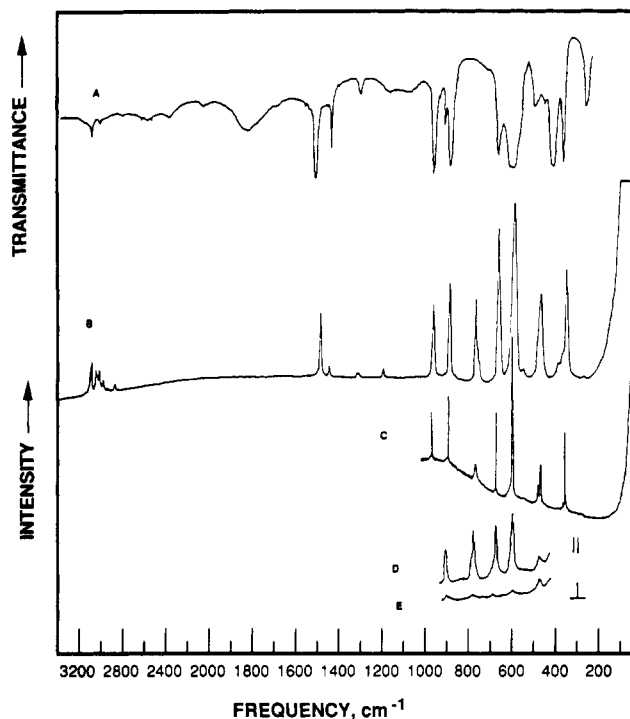


Figure 4. Vibrational spectra of $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$. Trace A, infrared spectrum of the solid as an AgBr disk; traces B and C, Raman spectra of the solid at 25 and -146°C ; traces D and E, Raman spectra of the CH_3CN solution with parallel and perpendicular polarization, respectively.

another atom B is given by eq 2

$$\sigma_p^A = \frac{-e^2 \hbar^2 \langle r^{-3} \rangle_{2p}}{2m^2 c^2 \Delta E} [Q_{AA} + \sum_{B \neq A} Q_{AB}] \quad (2)$$

where $\langle r^{-3} \rangle_{2p}$ is the mean inverse cube of the 2p-orbital radial function on atom A, Q_{AA} is the charge density term for atom A, Q_{AB} is the bond order term for the A–B bond, and ΔE is the mean excitation energy.

Compared with the bonds in the corresponding octahedral or pseudooctahedral precursors, $\text{MO}_y\text{F}_{x-n}$, those in the $\text{MO}_y\text{F}_{x+1}^{n-1}$ species, which contain a pentagonal plane of M–F bonds (where $\text{M} = \text{Xe}, \text{I}, \text{Te}$), exhibit greater ionic character, as indicated by their longer bond lengths and lower vibrational stretching frequencies. This greater ionic character would be expected to bring about a decrease in the $\langle r^{-3} \rangle_{2p}$ and charge density–bond order terms of eq 2. This would result in a decrease in σ_p and a more shielded chemical shift and does not account for the experimentally observed trend. Consequently, it would appear that the origin of the observed deshielding most likely lies in the ΔE term. Unfortunately, the nature of the excited states is unknown at present; however, it is interesting to note that comparison of the HOMO energies in XeF_4 and XeF_5^- ⁴⁹ as well as IOF_5 and IOF_6^- reveals that the anions have significantly lower values than the neutral molecules and may facilitate excitation to a higher excited state, i.e., ΔE is smaller for XeF_5^- and IOF_6^- than for XeF_4 and IOF_5 .

The two-bond fluorine–fluorine scalar coupling $^2J(^{19}\text{F}_{\text{ax}}-^{19}\text{F}_{\text{eq}})$ in IOF_6^- has a value of 205 Hz and is almost identical in magnitude to that measured previously for $\text{cis-IO}_2\text{F}_4^-$ in CH_3CN [$^2J(^{19}\text{F}_{\text{ax}}-^{19}\text{F}_{\text{eq}}) = 204 \text{ Hz}$].⁴⁶ The couplings in both anions are smaller than the corresponding coupling in the related IOF_5 molecule [$^2J(^{19}\text{F}_{\text{ax}}-^{19}\text{F}_{\text{eq}}) = 271\text{--}280 \text{ Hz}$],⁵³ which may reflect the anticipated greater ionic character in the bonds of the anionic species.⁵⁴ In the ^{19}F NMR spectrum of IOF_6^- , both the doublet and sextet

(48) Remeasured for this work in CH_3CN at -40°C .

(49) Christe, K. O.; Curtis, E. C.; Dixon, D. A.; Mercier, H. P.; Sanders, J. C. P.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **1991**, *113*, 3351.

(50) This work; chemical shift determined as $\delta = -51.3 \text{ ppm}$ for TeF_6 in CH_3CN at -40°C .

(51) Brownstein, M.; Selig, H. *Inorg. Chem.* **1972**, *11*, 656.

(52) Karplus, M.; Pople, J. A. *J. Chem. Phys.* **1963**, *38*, 2803.

(53) Brownstein, M.; Gillespie, R. J.; Krasznai, J. P. *Can. J. Chem.* **1978**, *56*, 2253.

Table III. Vibrational Spectra of $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$ and Their Assignment

obsd freq, cm ⁻¹ (rel intensity)					
IR 25 °C	Ra		CH ₃ CN sol 25 °C	assignments (point group)	
	solid			N(CH ₃) ₄ ⁺ (T _d)	IOF ₆ ⁻ (C _{5v})
3045 mw	3043 (20)	3045 (5)		ν ₅ (E)	
2970 w	2996 (13)	2970 (4)		ν ₁₄ (F ₂)	
	2965 (13)			ν ₁ (A ₁) + combin bands	
	2927 (6)				
	2819 (5)				
1489 vs				ν ₁₅ (F ₂)	
1418 m	1464 (46)	1466 (15)		ν ₂ (A ₁), ν ₆ (E)	
1285 mw	1417 (6)	1416 (3)		ν ₁₆ (F ₂)	
	1288 (3)			ν ₁₇ (F ₂)	
949 vs	1173 (6)	1174 (4)		ν ₇ (E)	
873 vs	948 (41)	949 (28)	ν ₁₈ (F ₂)		
	874 (53)	873 (37)	880 (50) p		ν ₁ (A ₁)
	752 (45)	753 (15)		ν ₃ (A ₁)	
	740 sh	742 sh			
649 s	649 (88)	658 (57)	656 (75) p		ν ₂ (A ₁)
585 vs					ν ₅ (E ₁)
	578 (100)	584 (100)	581 (100) p		ν ₃ (A ₁)
535 w,sh	530 (4)	530 (3)			ν ₉ (E ₂)
490 m		466 (15)		ν ₁₉ (F ₂)	
475 sh					
	457 (49)	456 (23)	457 (20) dp		ν ₁₀ (E ₂)
405 vs					ν ₆ (E ₁)
	373 sh	377 (5)		ν ₈ (E)	
359 s		354 (4)			ν ₄ (A ₁)
	341 (62)	344 (52)			ν ₇ (E ₁)
		335 (5)		ν ₁₂ (F ₁)	
255 s	260 (2)	260 (2)			ν ₈ (E ₁)

are significantly broadened owing to partially collapsed scalar coupling to the quadrupolar ^{127}I ($I = 5/2$) nucleus. The ^{19}F NMR spectra of *cis*- IO_2F_4^- ⁴⁶ and IOF_5 ^{47a} also show broadening attributed to the same cause. Interestingly, the line width of the sextet of IOF_6^- is substantially broader than that of the doublet, indicating that $^1J(^{19}\text{F}_{\text{ax}}-^{127}\text{I})$ is larger than $^1J(^{19}\text{F}_{\text{eq}}-^{127}\text{I})$ and therefore less quadrupole collapsed. If it is assumed that the Fermi-contact mechanism provides the dominant coupling contribution, then this observation is consistent with the relatively more covalent (i.e., greater s-character) bond between iodine and the axial fluorine as compared with those between iodine and the equatorial fluorines.⁵⁴ The X-ray crystallographic data and vibrational spectra for $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$ support this idea in that the $\text{I}-\text{F}_{\text{ax}}$ bond distance is shorter than the average $\text{I}-\text{F}_{\text{eq}}$ bond distance and the $\text{I}-\text{F}_{\text{ax}}$ force constant is larger than the $\text{I}-\text{F}_{\text{eq}}$ one (see below).

Vibrational Spectra. The infrared and Raman spectra of solid $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$ and the Raman spectra of its CH_3CN solution were recorded and are shown in Figure 4. The observed frequencies, together with their assignments, are summarized in Table III. A comparison of the observed and calculated (see below) frequencies of IOF_6^- with those of the closely related pentagonal IF_7 molecule⁸ and XeF_5^- anion,⁴⁹ together with their approximate mode descriptions, is given in Table IV. After subtraction of the well-known^{15,55} bands of the $\text{N}(\text{CH}_3)_4^+$ cation (see Table III), the remaining bands, which are due to IOF_6^- , can be readily assigned based on the data given in Table IV. Since the vibrational spectra of IOF_6^- in solid $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$ do not appear to be noticeably affected by the slight equatorial puckering, they were assigned (see Table IV) in point group C_{5v} , which is the lowest energy structure of the free anion (see below).

Ab Initio Calculations and Normal Coordinate Analyses. The electronic structure of IOF_6^- was calculated at the ab initio level

by using both local density functional (LDF) theory and molecular orbital theory with an effective core potential (ECP) for the core electrons of iodine. Both types of calculations resulted in minimum energy structures of C_{5v} symmetry with the ECP calculations duplicating the experimentally observed geometry (see Table V) and vibrational frequencies (see Table IV) much better than the LDF calculations. In view of the superiority of the ECP calculations, we have also recalculated the structure of the closely related XeF_5^- anion, for which previously⁴⁹ only LDF values had been available. As can be seen from Tables IV and V, the ECP calculations are in excellent agreement with the observed values, after scaling of the calculated frequencies by empirical factors to maximize their fit with the experimental data, and therefore are invaluable for the correct assignments of the vibrational spectra. For XeF_5^- , for example, they clearly indicate that the previous assignments⁴⁹ for $\nu_2(\text{A}_2'') = 274 \text{ cm}^{-1}$ and $\nu_4(\text{E}_1') = 290 \text{ cm}^{-1}$ should be reversed. In view of the closeness of these two frequencies, the reversal of their assignments has very little or no impact on the conclusions previously reached⁴⁹ for XeF_5^- .

The eleven fundamental vibrations of a pentagonal bipyramidal AX_5YZ species in point group C_{5v} can be classified as $\Gamma = 4\text{A}_1 + (\text{IR}, \text{Ra}) + 4\text{E}_1(\text{IR}, \text{Ra}) + 3\text{E}_2(\text{Ra})$. The internal coordinates, symmetry coordinates, and approximate mode descriptions for IOF_6^- are summarized in Figure 5 and Table S6, respectively. The tentative assignments given in our preliminary communication¹⁰ for IOF_6^- and IF_7 have been significantly improved resulting in revised assignments for ν_6, ν_7, ν_8 , and ν_{10} of IOF_6^- and for ν_9 and ν_{10} of IF_7 .

By the use of the scaled ECP frequencies, force fields were calculated for IOF_6^- (see Table VI) and XeF_5^- (see Table VII). The potential energy distribution (PED) for IOF_6^- is given in Table VIII. As can be seen from Table VIII, the IF_5 in-plane deformation motions, due to their high frequencies, mix considerably with some of the other symmetry coordinates, and the $\nu_7(\text{E}_1)$ and $\nu_8(\text{E}_1)$ modes are antisymmetric and symmetric combinations, respectively, of S_7 and S_8 . Consequently, ν_7 and ν_8 are better described as an $\text{O}-\text{I}-\text{F}_{\text{ax}}$ rocking motion

(54) Jameson, C. J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; Chapter 4, pp 97-101.

(55) Christe, K. O.; Wilson, W. W.; Bau, R.; Bunte, S. W. *J. Am. Chem. Soc.* 1992, 114, 3411 and references cited therein.

and an O—I— F_{ax} scissoring motion



respectively, than as separated $\text{I}=\text{O}$ and $\text{I}-\text{F}_{\text{ax}}$ wagging motions. The only deficiency of the ECP calculation for IOF_6^- was the low-frequency value and resulting force constant for the scaled I—O stretching mode, $\nu_1(\text{A}_1)$. Consequently, we prefer to use for this mode the unscaled value of 860 cm^{-1} which is in much better agreement with the observed value of 873 cm^{-1} . The low value calculated for this stretching frequency is surprising as the calculated I—O bond length is shorter than the experimental value. Due to the larger number of symmetry species for XeF_5^- , its PED (see Table VII) is highly characteristic and requires no further comment. It should be noted, however, that the symmetry coordinates and internal force constants, previously published⁴⁹ for XeF_5^- , contained two typographical errors. S_{5b} should read $(2/5)^{1/2} [\sin 2\alpha (\Delta r_2 - \Delta r_3) - \sin \alpha (\Delta r_3 - \Delta r_4)]$, and subscripts had been omitted from the last two internal force constants in Table VIII which should read $f_{\gamma\gamma} - f_{\gamma\gamma'}$ and $f_{\gamma} - f_{\gamma\gamma'}$, respectively.

The internal force constants of greatest interest are those involving the stretching of the axial and the equatorial fluorine bonds and the equatorial in-plane deformation constants. These data are summarized for the IF_7 , IOF_6^- , XeF_5^- series in Table IX. As can be seen from this table, the X— F_{ax} bonds are considerably stronger than the X— F_{eq} ones for a given compound, as expected from the bonding scheme proposed below. Furthermore, the stretching force constants decrease significantly on going from IF_7 to IOF_6^- and XeF_5^- , as expected from an increasing ionicity of the X—F bonds caused by the formal negative charge in the anions and the reduction in the formal oxidation state of the central atom from +VII in IF_7 and IOF_6^- to +IV in XeF_5^- . The large increase in the value of $f_{rr'}$, the coupling to opposite bonds, from IOF_6^- to XeF_5^- , is analogous to those previously observed⁴⁶ for going from either *trans*- IO_2F_4^- ($f_{rr'} = 0.27\text{ mdyn/\AA}$) to IOF_4^- ($f_{rr'} = 0.45\text{ mdyn/\AA}$) and IF_4^- ($f_{rr'} = 0.47\text{ mdyn/\AA}$) or IOF_5^- ($f_{rr'} = 0.18\text{ mdyn/\AA}$) to IF_5 ($f_{rr'} = 0.38\text{ mdyn/\AA}$) and, hence, appears to be associated with the introduction of a sterically active, free valence electron pair into the ligand sphere around the central atom.

The in-plane deformation constants, f_{α} , are a measure for the strength of the mutual repulsion of the equatorial ligands and hence for the degree of congestion in this plane which, in turn, is responsible for the puckering. As can be seen from Table IX, the value of f_{α} decreases markedly on going from IF_7 to IOF_6^- and XeF_5^- . In IF_7 , the in-plane deformation constant, f_{α} , is about five times larger than the out-of-plane deformation constant, f_{β} , and accounts for the puckering of the equatorial plane in IF_7 . On the other hand, in XeF_5^- the f_{α} value has become much smaller and approaches the range of values expected for the out-of-plane deformation constants, f_{β} . This is in good agreement with the X-ray crystal structure of $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$ which showed⁴⁹ that XeF_5^- is planar and not puckered. Hence, it appears that the value of the in-plane deformation force constant, f_{α} , is a useful parameter for measuring the degree of congestion and the likely occurrence of puckering in the equatorial ligand plane.

It must be pointed out that the problem of calculating the internal deformation constants from the corresponding symmetry force constants is underdetermined (more unknowns than available equations) and, hence, requires additional assumptions. For the calculation of f_{α} in our compounds, the pure vibrational force field⁵⁶ condition of Kuczera, adapted to 5-fold symmetry, $f_{\alpha} +$

Table IV. Comparison of Observed and Calculated Frequencies of IOF_6^- , IF_7 , and XeF_5^- , Together with Their Approximate Mode Descriptions

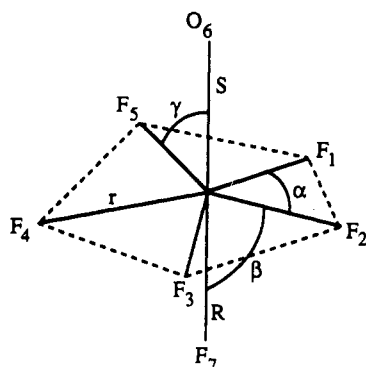
assign	approx mode description	$\text{IOF}_6^- (\text{C}_{5v})$			$\text{IF}_7 (\text{D}_{5h})^e$			$\text{XeF}_5^- (\text{D}_{5h})$		
		obsd freq, cm^{-1} int (IR,Ra)	calcd freq, cm^{-1} ECP ^a	LDF	approx mode description	obsd freq, cm^{-1} int (IR,Ra)	calcd freq, cm^{-1} ECP ^a	approx mode description	obsd freq, cm^{-1} int (IR,Ra)	calcd freq, cm^{-1} ECP ^a
A_1, ν_1	$\nu \text{ I}=\text{O}$	873 (vs, 53p)	860 ^b	870	$\nu_3(\text{A}_2'')$	746 (s, -)	753	$\nu_1(\text{A}_1')$	502 (-, 100)	498
ν_2	$\nu \text{ IF}_{\text{ax}}$	649 (s, 88p)	625	599	$\nu_1(\text{A}_1')$	676 (-, 20p)	673	$\nu \text{ sym XeF}_5$	290 (m, sh, -)	301
ν_3	$\nu \text{ sym IF}_5$	584 (ν_5 , 100p)	566	537	$\nu \text{ sym IF}_5$	635 (-, 100p)	644	$\delta \text{ umbrellae XeF}_5$	450 (vs, -)	449
ν_4	$\delta \text{ umbrellae IF}_5$	359 (s, 4)	371	314	$\nu_4(\text{A}_2'')$	365 (s, -)	368	$\nu \text{ as XeF}_5$	274 (s, -)	273
E_1, ν_5	$\nu \text{ as IF}_5$	585 (vs, ν_3)	583	568	$\nu_5(\text{E}_1')$	670 (vs, -)	681	$\delta \text{ as XeF}_5 \text{ in plane}$		
ν_6	$\delta \text{ as IF}_5 \text{ in plane}$	405 (vs, -)	415	365	$\nu_6(\text{E}_1')$	425 (vs, -)	441			
ν_7	$\delta \text{ rock O}=\text{I}-\text{F}_{\text{ax}}$	341 (-, 62)	340	292	$\nu_8(\text{E}_1'')$	319 (-, 6)	320			
ν_8	$\delta \text{ sciss O}=\text{I}-\text{F}_{\text{ax}}$	260 (s, 2)	273	233	$\nu_7(\text{E}_1')$	257 (w, -)	265			
E_2, ν_9	$\delta \text{ sciss IF}_5 \text{ in plane}$	530 (-, 4)	530	486	$\nu_9(\text{E}_2')$	596 (-, 2)	605	$\nu \text{ as XeF}_5$	423 (-, 16)	420
ν_{10}	$\nu \text{ as IF}_5$	457 (-, 49)	446	421	$\nu_{10}(\text{E}_2')$	510 (-, 17)	515	$\delta \text{ sciss XeF}_5 \text{ in plane}$	377 (-, 23)	373
ν_{11}	$\delta \text{ pucker IF}_5$	not obsd	141	111	$\nu_{11}(\text{E}_2'')$	[68]	59	$\delta \text{ pucker XeF}_5$	not obsd	105
							50i			79

^a Frequency values were scaled by an empirical factor of 0.9038. ^b Unscaled frequency value; scaled frequency value is 789 cm^{-1} . ^c Frequency values were scaled by an empirical factor of 0.932. ^d Frequency values were scaled by an empirical factor of 0.8618. ^e Data from ref 8. ^f Data from ref 49.

(56) (a) Kuczera, K.; Czerninski, R. *J. Mol. Struct.* **1983**, *105*, 269. (b) Kuczera, K. *J. Mol. Struct.* **1987**, *160*, 159.

Table V. Observed and Calculated Geometries of IOF_6^- and the Closely Related IF_7 and XeF_5^-

IOF ₆ ⁻				IF ₇				XeF ₅ ⁻			
		calcd ^a				calcd ^c				calcd	
	exp ^a	ECP	LDF		exp ^b	ECP	LDF		exp ^d	ECP	LDF
rI-O (Å)	1.75-1.77	1.7255	1.791	rI-F _{ax}	1.781	1.7705	1.870	rXe-F _{eq}	2.012	1.9924	2.077
rI-F _{ax} (Å)	1.82	1.8087	1.913	rI-F _{eq}	1.857	1.8333	1.918				
rI-F _{eq} (Å)	1.88	1.8819	1.969	F _{ax} -I-F _{eq}	90	90	90				
O-I-F _{eq} (deg)	94-96	95.76	96.0								

^a Data from this study. ^b Data from ref 7. ^c Data from ref 8. ^d Data from ref 49.**Figure 5.** Internal coordinates for IOF_6^- .**Table VI.** Symmetry Force Constants^a of IOF_6^- Calculated from the Scaled ECP Frequencies of Table IV

		F_{11}	F_{22}	F_{33}	F_{44}
A_1	F_{11}	6.077 ^b (4.967) ^c			
	F_{22}	0.057	3.899		
	F_{33}	-0.041	0.169	3.656	
	F_{44}	-0.164	0.332	0.078	1.725
		F_{55}	F_{66}	F_{77}	F_{88}
E_1	F_{55}	3.040			
	F_{66}	-1.079	3.246		
	F_{77}	0.230	-0.234	1.087	
	F_{88}	0.176	-0.271	0.085	0.891
		F_{99}	$F_{10,10}$	$F_{11,11}$	
E_2	F_{99}	2.844			
	$F_{10,10}$	0.407	2.478		
	$F_{11,11}$	-0.007	-0.064	0.395	

^a Stretching constants in mdyne/Å, deformation constants in mdyne/Å², and stretch-bend interaction constants in mdyne/rad. ^b Unscaled value (see text). ^c Scaled value.

$2f_{\alpha\alpha} + 2f_{\alpha\alpha'} = 0$, was used. Since for f_{β} the case is even more complex, no explicit values were calculated for f_{β} of IOF_6^- and XeF_5^- ; however, we estimate f_{β} of IOF_6^- to be slightly larger than and that of XeF_5^- to be similar to that of IF_7 .

Structure and Bonding in IOF_6^- and Related Molecules and Ions. The pentagonal bipyramidal structure and the co-planarity of the equatorial ligands in the minimum energy configuration of IOF_6^- , which cannot be accounted for by either "repelling points on a sphere" VSEPR arguments⁵ or classical, directionally localized molecular orbitals, can be rationalized in terms of a bonding scheme, outlined⁴⁹ for XeF_5^- and elaborated on in more detail⁸ for IF_7 . In this scheme, the structure and bonding of XeF_5^- are explained by a simple model derived from XeF_4 . The bonding in the square-planar XeF_4 can be described by two semi-ionic, 3-center 4-electron (3c–4e) bonds⁵⁷ for the four Xe–F bonds and two lone valence electron pairs on Xe ($s^2p_z^2$ hybrids). The 3c–4e bonds involve the p_x^2 and p_y^2 orbitals of xenon. Addition

(57) (a) Pimentel, G. C. *J. Chem. Phys.* **1951**, *10*, 446. Hach, R. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 4321. Rundle, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 112. (b) Burdett, J. K. In *Molecular Shapes: Theoretical Models of Inorganic Stereochemistry*; Wiley: New York, 1980.

Table VII. Revised Assignments, ECP Force Field,^a and Potential Energy Distribution^b for XeF_5^-

assign	approx mode description	freq cm ⁻¹		symmetry force constants	PED
		calcd (ECP)	obsd ^c		
A_1	ν_1	ν sym XeF_5	498	502	$F_{11} = 2.775$ 100(1)
A_2''	ν_2	δ umbrella	301	290	$F_{22} = 1.191$ 100(2)
E_1'	ν_3	ν asym XeF_5	449	450	$F_{33} = 1.6714$ 97(3) + 3(4)
					$F_{34} = -0.193$
E_2'	ν_4	δ asym in plane	273	274	$F_{44} = 1.940$ 99(4) + 1(3)
					$F_{55} = 1.938$ 92(5) + 8(6)
E_2''	ν_5	ν asym XeF_5	420	423	$F_{56} = 0.1191$
					$F_{66} = 1.7505$ 91(6) + 9(5)
	ν_6	δ in-plane	373	377	$F_{77} = 0.2498$ 100(7)
	ν_7	δ pucker	105		

^a Force constants calculated with the ECP frequencies; stretching constants in mdyne/Å, deformation constants in mdyne/Å², and stretch-bend interaction constants in mdyne/rad. ^b PED in percent. ^c Data from ref 49.**Table VIII.** Potential Energy Distribution for IOF_6^-

		freq, cm ⁻¹	PED, %
A_1	ν_1	860	87(1) + 7(2) + 5(4)
	ν_2	625	83(2) + 10(3) + 4(1) + 2(4)
	ν_3	566	88(3) + 12(2)
	ν_4	371	100(4)
E_1	ν_5	583	97(5) + 2(8)
	ν_6	415	44(6) + 26(8) + 25(7) + 5(5)
	ν_7	340	58(8) + 42(7)
	ν_8	273	43(8) + 40(7) + 16(6)
E_2	ν_9	530	73(9) + 27(10)
	ν_{10}	446	72(10) + 28(9)
	ν_{11}	141	100(11)

Table IX. Internal Force Constants^{a,b} (mdyne/Å) of IF_7 , IOF_6^- , and XeF_5^-

	IF_7	IOF_6^-	XeF_5^-
f_R	5.005	3.897	
f_t	3.947	2.938	2.062
$f_{rr'}$	0.326	0.306	0.198
$f_{rr'}$	0.0265	0.0536	0.317
f_{α}	0.847	0.690	0.364
$f_{\alpha\alpha}$	-0.183	-0.147	-0.081
$f_{\alpha\alpha'}$	-0.240	-0.198	-0.102
f_{β}	0.163		

^a The deformation constants have been normalized for the following bond distances: IF_7 , $r_{\text{I-F}_{\text{eq}}} = 1.857$ Å; IOF_6^- , $r_{\text{I-F}_{\text{eq}}} = 1.877$ Å; XeF_5^- , $r_{\text{Xe-F}} = 2.0124$ Å. ^b $f_{rr'}$ and $f_{rr'}$ denote coupling to adjacent and opposite bonds, respectively, and $f_{\alpha\alpha}$ and $f_{\alpha\alpha'}$ coupling to adjacent and opposite bond angles, respectively.

of an F^- ion to the equatorial plane in XeF_4 results in pentagonal-planar XeF_5^- and the formation of a semi-ionic, 6-center 10-electron (6c–10e) bond involving the delocalized p_x^2, p_y^2 hybrid orbitals of Xe and 6 electrons on the 5 F ligands.⁴⁹ The two lone valence electron pairs on Xe in XeF_5^- are analogous to those in XeF_4 .

Now let us consider the bonding in IF_7 and IOF_6^- . Their planar IF_5 fragments have essentially the same bonding as XeF_5^- , as shown by the atomic population calculations given in Table X. As expected for the replacement of two free valence electron pairs on the central atom by two bonded ligands, each of which

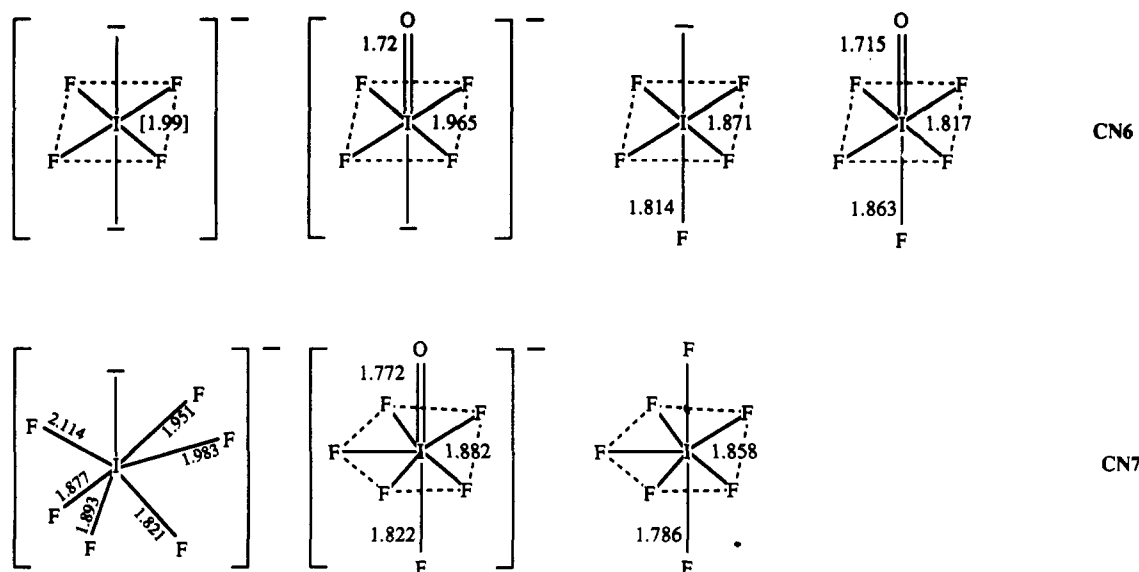


Figure 6. A comparison of the structure of IOF_6^- with those of closely related hexa- and heptacoordinated iodine fluorides and oxyfluorides.

Table X. Atomic Populations (e) in the Valence Electron Orbitals and Total Charge Distributions for XeF_5^- , IF_7 , and IOF_6^-

	XeF_5^-	IF_7	IOF_6^-
Central Atom			
s	2.22	1.35	1.43
$p_x = p_y$	0.61	0.64	0.64
p_z	2.02	0.60	0.71
d_{z^2}	0.03	0.11	0.14
$d_{x^2-y^2} = d_{y^2-z^2}$	0.06	0.12	0.09
d_{xy}	0.14	0.20	0.16
$d_{xz} = d_{yz}$	0.04	0.14	0.15
d total	0.37	0.83	0.78
Equatorial Fluorines			
s	1.98	1.93	1.94
p bond	1.70	1.57	1.64
p in plane	1.98	1.96	1.97
p_z	1.97	1.94	1.95
d	0	0.03	0.02
Axial Fluorines and Oxygens			
s		1.92	1.92 (F), 1.86 (O)
p_z		1.54	1.57 (F), 1.16 (O)
$p_x = p_y$		1.94	1.95 (F), 1.83 (O)
d		0.04	0.03 (F), 0.04 (O)
Total Charges			
central atom	2.15	2.94	2.81
F_{eq}	-0.63	-0.43	-0.53
F_{ax}		-0.39	-0.44
O_{ax}			-0.74

contributes one electron to its bond, the population of the s^2 and p_z^2 orbitals of I in IF_7 and IOF_6^- has decreased by about two electrons, compared to XeF_4 and XeF_5^- . The higher oxidation state of the central atoms in IF_7 and IOF_6^- (+VII) results in I having a higher positive charge than Xe (+IV) in XeF_5^- . This causes the effective electronegativity differences between the central atoms and the ligands in IF_7 and IOF_6^- to be smaller than those in XeF_4 and XeF_5^- and results in an increased covalency and a shortening of the central atom-fluorine bonds. Furthermore, the axial fluorine ligands in IF_7 and IOF_6^- carry less of a negative charge than the equatorial ones which accounts for the axial I-F bonds being more covalent and, hence, shorter than the equatorial ones. The total charge distributions in IF_7 and IOF_6^- (see Table X) also demonstrate the effect of replacing an F ligand in IF_7 by an O- ligand. The oxygen substitution results in the release of electron density into the IF_6 part of the molecule which increases the negative charges on the six fluorines and weakens the I-F bonds in IOF_6^- relative to those in IF_7 .

Of course, the above model does not account for the fact that the electrons will try to minimize their mutual repulsions and occupy all of the available orbitals to do so. This results in the participation of some d functions. Although we are not proposing a d hybridization model, the population in the d orbitals does suggest a redistribution into these orbitals beyond that expected if the d orbitals were to act solely as polarization functions.

The above atomic population and total charge distribution analysis qualitatively confirms our simple bonding model for pentagonal-bipyramidal molecules. This model involves the use of delocalized p_x^2 and p_y^2 hybrid orbitals of the central atom for the formation of a semi-ionic, 6c-10e bond with the five equatorial ligands and of an sp_z hybrid orbital for the formation of two, more covalent, axial bonds. This bonding scheme can account for all the observed structural features and also the observed bond length differences. The planarity of the p_x^2 and p_y^2 hybrid orbitals of the central atom also explains why these heptacoordinated main group fluorides and oxyfluorides prefer pentagonal-bipyramidal structures and not the monocapped octahedral or trigonal prismatic ones expected from VSEPR arguments.

As far as the puckering of the equatorial plane in pentagonal bipyramidal molecules is concerned, the data given above for IOF_6^- strongly suggest that the congestion in its equatorial plane and hence the driving force toward puckering is intermediate between those of puckered IF_7 and planar XeF_5^- . Therefore, it might be possible that by a reduction of the thermal motion of the ligands, the mutual repulsion among the equatorial ligands will be sufficiently diminished to allow for the observation of a temperature-dependent transition from a puckered to a planar configuration. Our two crystal structure determinations of $\text{N}(\text{CH}_3)_4^+\text{IOF}_6^-$ at different temperatures clearly demonstrate such a temperature dependency of the degree of puckering, and the ab initio calculations point to a minimum energy structure with coplanar equatorial ligands.

A comparison of the structure of IOF_6^- with those^{7,38,58-61} of other hexa- and heptacoordinated iodine fluorides and oxyfluorides is shown in Figure 6 and suggests the following general effects: (i) If the central iodine atom possesses a free valence electron pair, this pair seeks high s character, i.e. sp^n hybridization. If the number of ligands is larger than four, then as many F ligands

(58) The bond length in IF_4 is a value estimated from a normal coordinate analysis: Christie, K. O.; Naumann, D. *Inorg. Chem.* **1973**, *12*, 59.

(59) Ryan, R. R.; Asprey, L. B. *Acta Crystallogr. Part B* **1972**, *B28*, 979.

(60) Balicki, B.; Brier, P. N. *J. Mol. Spectrosc.* **1981**, *89*, 254.

(61) Majhoub, A. R.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 323.

form semi-ionic, 3-center 4-electron (3c-4e)^{57a} or similar multi-center bonds^{57b} as are required to allow the free electron pairs to form an sp^n hybrid with any remaining ligands. The resulting semi-ionic, multi-center bonds are considerably longer than the more covalent sp^n hybrid bonds.⁶² This effect accounts for the long equatorial I-F bonds in IF_4^- ,⁵⁸ IOF_4^- ,⁵⁹ and IF_5 ,⁶⁰ and the short axial I-F bond in IF_5 .⁶⁰ (ii) If the central atom does not possess any free valence electron pair, the ionicity of the bonds and, as a result, their lengths are influenced by the following secondary effects: (a) An increase in the oxidation state of the central atom generally increases its effective electronegativity and results in increased covalency and, hence, shorter bonds. It must be kept in mind, however, that the addition of two fluorine ligands results in a considerably stronger electron density withdrawal from the central atom than that caused by the addition of one doubly bonded oxygen ligand. Thus, for extremely electronegative central atoms, such as chlorine in ClF_2^+ or ClF_4^- , the addition of an oxygen ligand may even result in the reverse effect, i.e. the release of electron density to the central atom.^{62,63} (b) In the case of coordination number (CN) seven, steric crowding and, hence, repulsion effects also become important. The increased congestion in the equatorial planes of IF_7 and IOF_6^- , for example, results in increased mutual repulsion and increased lengths of the equatorial bonds. Thus, the nearest-neighbor $F_{eq} \cdots F_{eq}$ contacts in the IOF_6^- anion at $-93^\circ C$ are 2.090(16)–2.362(12) Å and are significantly less than twice the nominal van der Waals radius for fluorine, i.e., 2.70–2.80 Å,^{44,45} while in hexacoordinated IF_5 ,³⁸ the nearest neighbor $F_{eq} \cdots F_{eq}$ contacts are 2.571 Å and are still at the limit of the sum of the fluorine van der Waals radii. Similarly, the increased repulsion from the sterically active, free valence electron pair on iodine in hepta-coordinated IF_6^- causes an elongation of the three neighboring I-F bonds.⁶¹ (c) A formal negative charge, as found in an anion, enhances the $F^\delta - I^{\delta+}$ bond polarity and hence the ionicity of a bond and, thereby, increases the bond lengths.⁶²

The combination of these effects can explain the features of the compounds shown in Figure 6. For IOF_6^- , the relative length of equatorial I-F bonds can be explained by semi-ionic, multi-center bonding, which is enhanced by the formal negative charge and the repulsion effects caused by the steric crowding in the equatorial plane, while the lengthening of the I-O bond is attributed mainly to the formal negative charge and the repulsion effects. There is one piece of data in Figure 6, however, which does not fit the overall picture. This is the axial I-F bond length in IOF_5 . The published³⁸ value of 1.863 Å appears too long and, based on the fact that the axial IF stretching force constant in IOF_5 is larger than the equatorial one⁶⁴ and by analogy with the isoelectronic $TeOF_5^-$ anion ($Te-F_{ax} = 1.854$ Å, $Te-F_{eq} = 1.853$ Å),⁶⁵ the axial bond distance in IOF_5 should be similar to or shorter than the equatorial ones. A cursory examination⁶⁶ of the

experimental data^{38,64,67-69} available for IOF_5 revealed that these bond distances are not well-determined and are very sensitive to the choice of the O-I- F_{eq} bond angle. Thus, a decreasing angle lengthens the I-O and shortens the I- F_{ax} bond. Furthermore, a lengthening of the I- F_{eq} bond distance results in a shortening of the I- F_{ax} bond distance. Obviously, additional experimental data are required for a more precise structure determination of IOF_5 .

Conclusions. The IOF_6^- anion provides unique information on the nature of heptacoordinated molecules. The high degree of fluxionality, which is normally encountered for free heptacoordinated molecules, is absent. Dynamic puckering of the equatorial ligand plane is frozen out by crystal forces, and axial-equatorial ligand exchange is precluded by the incorporation of the more repulsive, axial oxygen ligand. It is shown that the statically puckered, equatorial fluorine plane exhibits C_s symmetry in the crystal. Furthermore, it is demonstrated by ab initio calculations and the crystal structure of XeF_5^- that the lowest energy structures of these molecules are pentagonal bipyramids with coplanar equatorial ligands. This coplanarity is explained by a bonding scheme involving delocalized, planar $p_x^2-p_y^2$ hybrid orbitals of the central atom for the formation of a semi-ionic, 6-center 10-electron system for the five I- F_{eq} bonds which also accounts for their increased lengths. The degree of puckering of the equatorial ligand plane increases with increasing mutual repulsion of the equatorial ligands and, therefore, is temperature dependent as demonstrated for IOF_6^- .

Acknowledgment. The work at Rocketdyne was financially supported by the U.S. Air Force Phillips Laboratory and the U.S. Army Research Office, that at McMaster University by the U.S. Air Force Phillips Laboratory and the Natural Sciences and Engineering Research Council of Canada, and that at Freie Universität Berlin by the Deutsche Forschungsgemeinschaft. We also thank Professor Neil Bartlett, Dr. A. J. Arduengo, Dr. C. J. Schack and Mr. R. D. Wilson for helpful discussions and Professor S. Kukolich for the calculations on the structure of IOF_5 .

Supplementary Material Available: A structure determination summary (Table S1), final atomic coordinates, equivalent isotropic displacement coefficients, and site occupancy factors (Table S4), anisotropic displacement coefficients (Table S5), and symmetry coordinates (Table S6) (6 pages); calculated and observed structure factor amplitudes (Tables S2 and S3) (16 pages). Ordering information is given on any current masthead page.

(64) Smith, D. F.; Begun, G. M. *J. Chem. Phys.* **1965**, *43*, 2001. Holloway, J. H.; Selig, H.; Claassen, H. H. *J. Chem. Phys.* **1971**, *54*, 4305.

(65) Miller, P. K.; Abney, K. D.; Rappé, A. K.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1988**, *27*, 2255.

(66) Kukolich, S. G., private communication of unpublished results.

(67) Brier, P. N. *J. Mol. Spectrosc.* **1987**, *125*, 233.

(68) Brier, P. N.; Winrow, M. J. *J. Mol. Spectrosc.* **1984**, *107*, 21.

(69) Pierce, S. B.; Cornwell, C. D. *J. Chem. Phys.* **1967**, *47*, 1731.

(62) Christe, K. O.; Schack, C. J. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 331. Christe, K. O. *XXIVth Int. Congr. Pure Appl. Chem.* **1974**, *4*, 115.

(63) Christe, K. O.; Curtis, E. C. *Inorg. Chem.* **1972**, *11*, 2209.

Table I. Details of the Data Collection and Structure Refinement for $\text{H}_2\text{N}_3^+\text{SbF}_6^-$ at 20 K

formula	$\text{H}_2\text{N}_3\text{SbF}_6$
fw	279.78
cryst system	orthorhombic
space group	$Pmc2_1$
cryst dims, mm	$0.15 \times 0.30 \times 0.50$
cryst color	colorless
cryst habit	irregular
a, Å	5.794 (3)
b, Å	5.113 (2)
c, Å	9.919 (5)
Z	2
V, Å ³	293.88
ρ (calcd), g/cm ³	1.79
radiation (λ , Å)	Mo K α (0.7107)
abs coeff (μ), cm ⁻¹	2.42
abs cor type	empirical
abs factor range (intensity)	1.14–1.00
F(000), e	154
temp, K	20
diffractometer	Huber (Crystal Logic)
scan mode; speed, deg/min	θ -2 θ ; 12.0
2 θ range, deg	1–65
total no. of reflns measd	2095 (+h, $\pm k$, $\pm l$)
no. of unique reflns	649
R_{int}	0.024
no. of reflns used in refinement	587 ($I > 3\sigma(I)$)
no. of params refined	58
final shift/error: max, av	0.021, 0.002
max residual density, e/Å ³	1.55 (0.75 Å from Sb)
$R = \sum F_o - F_c / \sum F_o $	0.015
$R_w = (\sum w(F_o - F_c)^2 / \sum w(F_o)^2)^{1/2}$	0.022
$\text{GOF} = (\sum w(F_o - F_c)^2 / (N_o - N_v))^{1/2}$	1.024
isotropic extinction param ($\times 10^5$)	1.883

Crystal Structure Determination of $\text{H}_2\text{N}_3^+\text{SbF}_6^-$. Single crystals of $\text{H}_2\text{N}_3^+\text{SbF}_6^-$ were obtained by recrystallization from anhydrous HF solution. Suitable crystals were selected under a microscope inside the glovebox and sealed in quartz capillaries. Initial data collection was carried out at room temperature on a Siemens P2₁ diffractometer. The structure was solved and refined to an agreement factor of $R = 0.049$ for 409 reflections. This structure revealed an asymmetric H_2N_3^+ cation with two poorly-defined H atoms attached to one of the terminal N atoms. Since the hydrogen positions in this room-temperature X-ray analysis were not entirely satisfactory, it was decided to re-collect data at low temperature.

Low-temperature diffraction data were collected on a four-circle Huber diffractometer equipped with a closed-cycle helium refrigerator.¹¹ The crystal was slowly cooled, over a period of 4 h, to 20 (5) K. Accurate unit cell parameters at this temperature were obtained by least-squares refinement of 15 centered reflections and are listed in Table I together with other details of data collection and structure refinement. Intensity data at 20 K were collected with the θ -2 θ step scan technique, up to a maximum 2θ of 65°. Three standard reflections measured after every 97 reflections showed no decay. A total of 2095 reflections were measured over one hemisphere of reciprocal space and were then averaged for multiple observations to give a set of 649 unique reflections. $R(\text{av})$ was 0.024. Corrections for Lorentz and polarization effects were made, and an empirical absorption correction was applied using the ψ -scan procedure.

The position of antimony was determined from a Patterson map, and the remaining non-hydrogen atom positions were obtained from the initial difference Fourier map. The structure was then refined using 587 reflections with $I > 3\sigma(I)$, first with isotropic and later with anisotropic thermal parameters. At this point, a difference electron density map revealed the positions of the hydrogen atoms at a distance of 0.85 Å from N(1). In the final cycles of least-squares refinement, the hydrogen atom positions were also refined with a fixed isotropic temperature factor. The assigned thermal parameter for the hydrogen atoms was 30% higher than the average isotropic thermal parameters of the rest of the atoms, excluding Sb. Refinement converged with final agreement factors of $R(F) = 0.015$ and $R_w(F) = 0.022$ and $\text{GOF} = 1.024$. In the final difference map, except for two ripples associated with Sb (1.55 and 1.51 e/Å³ about 0.68 and 0.75 Å away, respectively), the maximum residual electron

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å²) with Esd's of the Refined Parameters in Parentheses for $\text{H}_2\text{N}_3^+\text{SbF}_6^-$ at 20 K

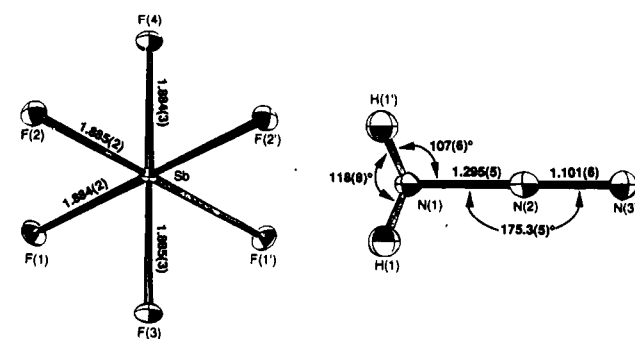
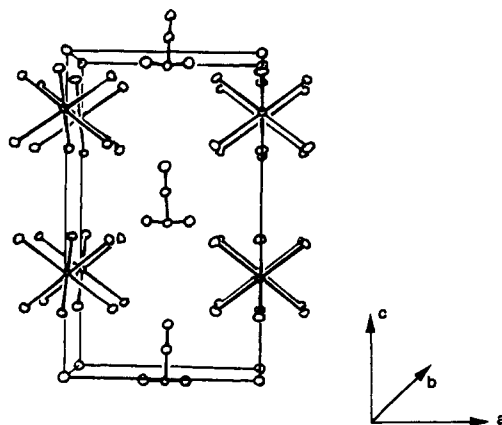
atom	x	y	z	$10^4 U_{\text{eq}}^a$
Sb	0.0000	0.13576 (3)	0.1873 ^b	40 (1)
F(1)	-0.2303 (3)	-0.0176 (3)	0.0790 (2)	85 (6)
F(2)	0.2311 (3)	0.2909 (3)	0.2946 (2)	88 (6)
F(3)	0.0000	0.4289 (5)	0.0720 (3)	84 (10)
F(4)	0.0000	-0.1618 (5)	0.2993 (4)	83 (11)
N(1)	0.5000	-1.4511 (7)	1.0250 (4)	83 (14)
N(2)	0.5000	-1.6211 (6)	0.9282 (5)	85 (18)
N(3)	0.5000	-1.7781 (7)	0.8523 (4)	111 (15)
H(1)	0.388 (13)	-1.3753 (65)	1.020 (11)	127 ^c

^a $U_{\text{eq}} = [1/(6\pi^2)] \sum_i \sum_j \beta_{ij} a_i^* a_j^*$. ^b z coordinate held constant to define origin. ^c Assigned isotropic temperature factor held constant.

Table III. Interatomic Distances (Å) and Angles (deg) with Esd's in Parentheses for $\text{H}_2\text{N}_3^+\text{SbF}_6^-$ at 20 K^a

H_2N_3^+			
N(1)–N(2)	1.295 (5)	N(1)–H(1)	0.76 (7)
N(2)–N(3)	1.101 (6)	H(1)–H(1')	1.30 (16)
N(1)–N(2)–N(3)	175.3 (5)	H(1)–N(1)–N(2)	107 (6)
H(1)–N(1)–H(1')	118 (8)		
SbF_6^-			
Sb–F(1)	1.884 (2)	Sb–F(3)	1.885 (3)
Sb–F(2)	1.885 (2)	Sb–F(4)	1.884 (3)
F(1)–Sb–F(1')	90.20 (1)	F(2)–Sb–F(2')	90.5 (1)
F(1)–Sb–F(2)	89.65 (8)	F(2)–Sb–F(3)	90.46 (8)
F(1)–Sb–F(2')	179.58 (9)	F(2)–Sb–F(4)	90.4 (1)
F(1)–Sb–F(3)	89.15 (9)	F(3)–Sb–F(4)	178.8 (1)
F(1)–Sb–F(4)	90.00 (9)		

^a Room-temperature parameters: N(1)–N(2) = 1.36 (5) Å, N(2)–N(3) = 1.06 (5) Å, N(1)–N(2)–N(3) = 173 (5)°.

**Figure 1.** Atom numbering schemes, bond lengths (Å), and bond angles (deg) for H_2N_3^+ and SbF_6^- at 20 K.**Figure 2.** Packing diagram of $\text{H}_2\text{N}_3^+\text{SbF}_6^-$ viewed along the b axis.

density was less than 0.75 e/Å³. No significant correlations were observed. All data reduction, structure solution and refinement, and graphics were executed using the UCLA crystallographic package.¹²

(11) Strouse, C. E. *Rev. Sci. Instrum.* **1976**, *47*, 871–876.

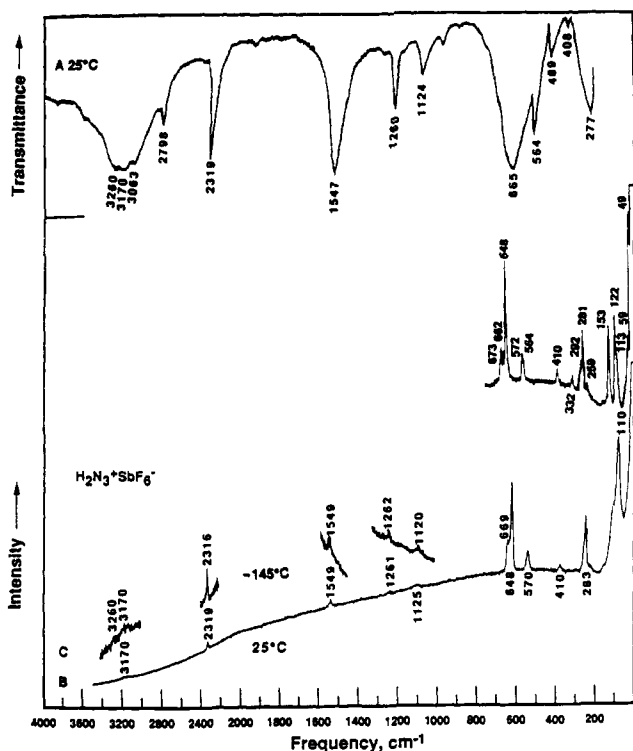


Figure 3. Vibrational spectra of solid $\text{H}_2\text{N}_3^+\text{SbF}_6^-$: trace A, infrared spectrum of a sample pressed between AgBr windows; traces B and C, Raman spectra recorded at 25 and -145°C , respectively.

Final atomic coordinates with equivalent isotropic thermal parameters are listed in Table II. Interatomic distances and angles are given in Table III, and the anisotropic temperature factors are listed in Table 1S in the supplementary material. An Ortep plot of the molecule is shown in Figure 1, and unit cell packings along the b and a axes are shown in Figures 2 and 3, respectively.

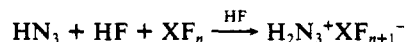
Crystal Structure Determination of $\text{H}_2\text{N}_3^+\text{AsF}_6^-$. This compound crystallizes in the orthorhombic space group $Pma2$ (No. 28), with $a = 20.056 \text{ \AA}$, $b = 5.468 \text{ \AA}$, $c = 5.523 \text{ \AA}$, $V = 604.7 \text{ \AA}^3$, and $Z = 4$. Data were collected at room temperature, and the structure was refined to an agreement factor of $R = 0.057$ for 387 nonzero reflections. The structure shows a linear and apparently almost symmetric H_2N_3^+ cation [$\text{N}-\text{N} = 1.16(2)$ and $1.19(2) \text{ \AA}$; $\text{N}-\text{N}-\text{N} = 177(2)^\circ$]. However, the structure analysis was marred by extensive disordering of the AsF_6^- anion, and it is quite possible that the H_2N_3^+ cation suffers from a 2-fold packing disorder as well. The H atoms in $\text{H}_2\text{N}_3^+\text{AsF}_6^-$ could not be located.

Computational Methods. The geometry, vibrational frequencies, and force field of H_2N_3^+ were calculated, as previously described,¹³ in the local density functional (LDF) approximation by using the program system DMol with a polarized double numerical basis set.

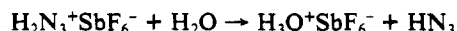
Results and Discussion

Syntheses and Properties of H_2N_3^+ Salts. Protonation of HN_3 by mixtures of HF and the strong Lewis acids SbF_5 , AsF_5 , and BF_3 , followed by removal of solvent and unreacted starting ma-

terial at room temperature, produces the H_2N_3^+ salts of SbF_6^- , AsF_6^- , and BF_4^- , respectively.

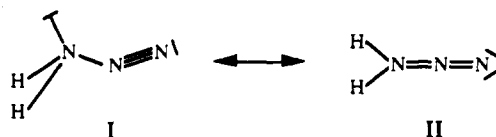


Although the existence of the H_2N_3^+ cation in these solutions had previously been established by multinuclear NMR spectroscopy,⁶ the actual salts had not been isolated and characterized. All salts are white, crystalline solids that are stable at room temperature. They are strongly hygroscopic and, when exposed to moisture, form the corresponding H_3O^+ salts¹⁴



as expected from H_2O being a stronger base than HN_3 and, therefore, being able to displace HN_3 from its salts.

X-ray Crystal Structure of $\text{H}_2\text{N}_3^+\text{SbF}_6^-$. The crystal structure of $\text{H}_2\text{N}_3^+\text{SbF}_6^-$ was determined both at room temperature and at 20 K. The structures were almost identical at both temperatures (see Table III and footnote), but the low-temperature data were of much better quality. The structure consists of well-separated H_2N_3^+ and SbF_6^- ions (see Figure 1). The SbF_6^- anion is a nearly perfect octahedron with angles ranging from $89.15(9)$ to $90.5(1)^\circ$ and identical Sb-F bond lengths of $1.885(3) \text{ \AA}$. The H_2N_3^+ cation is asymmetric, with both hydrogens attached to the same nitrogen. Furthermore, the two N-N bond distances are very different, the N-N-N group is slightly distorted from linearity ($\text{N}(1)-\text{N}(2)-\text{N}(3) = 175.3^\circ$), and the NH_2 group is pyramidal. These findings demonstrate that the structure of H_2N_3^+ is best described by I, with little contribution from resonance structure



II. The fact that the repulsion from the free valence electron pair on N(1) is larger than those from the two hydrogen ligands can account for N(2) being slightly bent away from this free pair. The observed N-N bond lengths are in good agreement with our expectations for an N-N single and an N≡N triple bond, and their differences are more pronounced than those found for other covalent azides such as CF_3N_3 ($\text{N}(1)-\text{N}(2) = 1.252(5) \text{ \AA}$, $\text{N}(2)-\text{N}(3) = 1.118(3) \text{ \AA}$)¹⁵ or FN_3 ($\text{N}(1)-\text{N}(2) = 1.253(10) \text{ \AA}$, $\text{N}(2)-\text{N}(3) = 1.132(10) \text{ \AA}$).¹⁶ The observed N-H bond length of $0.76(7) \text{ \AA}$ is unrealistically short due to the fact that hydrogen does not possess any core electrons, and therefore, the X-rays are being diffracted by the binding electrons. This results in an artificially short N-H bond length, which is no surprise in view of the well-known difficulties of obtaining reliable hydrogen bond lengths by X-ray diffraction. On the basis of the ab initio calculation (see below), a realistic N-H bond distance in H_2N_3^+ is about $1.01 \text{ \AA}$. The H-N-H and H-N-N bond angles, on the other hand, should not be affected, as the binding electrons are located along the N-H bond axes, and, therefore, are considered more reliable.

A packing diagram of $\text{H}_2\text{N}_3^+\text{SbF}_6^-$ is shown in Figure 2. The anion and the cation are located on crystallographic mirror planes. The anionic mirror plane passes through the atoms F(3)-Sb-F(4) whereas the cationic mirror plane passes through all three nitrogen atoms and bisects the H-N-H angle. The cations are stacked parallel to each other down the crystallographic b axis (see Figure 2) but are oriented perpendicular to each other in the b - c plane, causing a doubling of the repeat distance along the c axis. The nearest anion-cation interactions are $\text{N}(1) \cdots \text{F}(1)$ at $2.765 \text{ \AA}$ and $\text{H}(1) \cdots \text{F}(1)$ at $2.127 \text{ \AA}$, which are significantly shorter than the

(12) The programs used in this work included modified versions of the following programs: REDUCE (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation, full-matrix least-squares refinement; ORFEE (Busing, Martin, and Levy), distance, angle, and error calculations; ORTEP (Johnson), figure plotting. Scattering factors and corrections for anomalous dispersion were taken from: *International Tables for X-ray Crystallography*; Kynoch Press; Birmingham, England, 1974; Vol. IV. All calculations were performed on a DEC VAX 3100 cluster.

(13) (a) Christe, K. O.; Wilson, R. D.; Wilson, W. W.; Bau, R.; Sukumar, S.; Dixon, D. A. *J. Am. Chem. Soc.* 1991, 113, 3795. (b) Dixon, D. A.; Andzelm, J.; Fitzgerald, G.; Wimmer, E.; Jasien, P. In *Density Functional Methods in Chemistry*; Labanowski, J., Andzelm, J., Eds.; Springer Verlag: New York, 1991; p 33. (c) Dixon, D. A.; Christe, K. O. *J. Phys. Chem.* 1992, 96, 1018. (d) Delley, B. *J. Chem. Phys.* 1990, 92, 508. Dmol is available commercially from BIOSYM Technologies, San Diego, CA. A FINE grid was used. The multipolar fitting functions for the model density used to evaluate the effective potential have angular momentum numbers of 3 for N and 2 for H.

(14) Christe, K. O.; Schack, C. J.; Wilson, R. D. *Inorg. Chem.* 1975, 14, 2224.

(15) Christe, K. O.; Christen, D.; Oberhammer, H.; Schack, C. J. *Inorg. Chem.* 1984, 23, 4283.

(16) Christen, D.; Mack, H. G.; Schatte, G.; Willner, H. *J. Am. Chem. Soc.* 1988, 110, 707.

Table IV. Calculated and Observed Geometries of Isoelectronic H_2N_3^+ and H_2NCN

	[$\text{H}_2\text{N}-\text{N}\equiv\text{N}$] $^+$			$\text{H}_2\text{N}-\text{C}\equiv\text{N}$			
	expt ^a	LDF	3-21G ^b	expt ^c	LDF	6-31G* ^d	STO-3G ^d
Bond Distances, Å							
r_1, r_2 (N—H)	<i>e</i>	1.043	1.008	1.001	1.031	0.998	1.031
r_3 (N—X)	1.295 (5)	1.276	1.305	1.346	1.341	1.344	1.399
r_4 (X≡N)	1.101 (6)	1.126	1.088	1.160	1.172	1.138	1.158
Bond Angles, deg							
α (H—N—H)	118 (8)	117.9	<i>f</i>	113.5	110.5	113.2	108.8
β_1, β_2 (H—N—X)	107 (6)	114.5	<i>f</i>	115.6	113.6	114.5	110.4
$\sum(\alpha + \beta_1 + \beta_2)^g$	332 (20)	346.9	360 ^h	344.7	337.7	342.2	329.6
N—X≡N	175.3 (5)	175.2	<i>f</i>	[180] ^h	176.1	178.2	176.7

^a Data from crystal structure of $\text{H}_2\text{N}_3^+\text{SbF}_6^-$ at 20 K. ^b Data from ref 6. ^c Data from refs 24 and 30. ^d Data from ref 22. ^e The value of 0.76 (7) from Table III is much too short because of the shortcomings of X-ray diffraction methods for the determination of exact hydrogen bond distances and should not be used. ^f No angles were given in ref 6; however, from the stated planarity and C_{2v} symmetry of H_2N_3^+ $\sum(\alpha + \beta_1 + \beta_2)$ must equal 360°. ^g This sum of the angles is a measure for the planarity of the NH_2 group, with 360° being planar and 328.5° being an ideal trigonal pyramid. ^h Assumed value.

Table V. Calculated and Observed Vibrational Frequencies (cm^{-1}) of Isoelectronic H_2N_3^+ and H_2NCN

Approx description of mode in point group C_4	Symmetry coordinates	[$\text{H}_2\text{N}-\text{N}\equiv\text{N}$] $^+$			$\text{H}_2\text{N}-\text{C}\equiv\text{N}$					
		obsd	calcd		obsd	calcd			PED	
			LDF	PED ^a LDF		LDF	6-31G* ^f	4-31G* ^g	LDF	4-31G* ^g
A' ν_1 v sym NH_2	$S_1 = \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r_2)$	3170	3248	98S ₁ + 1S ₃	3420 ^b	3375	3787	3722	100S ₁	100S ₁
ν_2 v X≡N	$S_2 = \Delta r_4$	2318	2350	69S ₂ + 31S ₄	2270 ^b	2301		2611	66S ₂ + 34S ₄	90S ₂ + 14S ₄
ν_3 δ sciss NH_2	$S_3 = \frac{1}{\sqrt{6}}(2\Delta\alpha - \Delta\beta_1 - \Delta\beta_2)$	1547	1526	100S ₃	1595 ^b	1556	1804	1818	100S ₃	102S ₂
ν_4 vN—X	$S_4 = \Delta r_3$	1129	1190	88S ₄ + 8S ₂ + 4S ₆	1055 ^b	1092	1159	1170	85S ₄ + 8S ₂ + 5S ₃ + 2S ₆	79S ₄ + 10S ₂
ν_5 δNXXN in plane	$S_5 = \text{N}(-), \text{X}(+), \text{N}(-)$ in plane	530	516	79S ₅ + 20S ₆	(538) ^d	477	531	554	85S ₅ + 15S ₆	74S ₅ + 23S ₆
ν_6 δNH_2 wag (inversion at N)	$S_6 = \frac{1}{\sqrt{3}}(\Delta\alpha + \Delta\beta_1 + \Delta\beta_2)$	489	479	72S ₆ + 24S ₅ + 3S ₃	(714, 670) ^e (414, 364) ^e	622	691	688	86S ₆ + 13S ₅ + 1S ₄	96S ₆ + 27S ₅ + 21S ₄
A'' ν_7 v as NH_2	$S_7 = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_2)$	3280	3372	98S ₇ + 2S ₈	3480 ^b	3469	3890	3829	98S ₇ + 1S ₈	100S ₇
ν_8 δ as NH_2	$S_8 = \frac{1}{\sqrt{2}}(\Delta\beta_1 - \Delta\beta_2)$	1259	1232	99S ₈ + 1S ₉	(1055 or 1150) ^c	1151	1323	1343	98S ₈ + 2S ₉	93S ₈
ν_9 δNXXN out of plane	$S_9 = t_1 + t_2$ ^h	418	429	85S ₉ + 14S ₈	(437) ^d	408	463	485	85S ₉ + 15S ₈	99S ₉

(a) in percent; (b) infrared gas phase frequencies from ref. 21; (c) see text; (d) Raman of the liquid (ref. 28) and solid (ref. 32); (e) components of the inversion splitting (see refs. 21, 24, 27); (f) data from ref. 22; (g) data from ref 24; (h) t_1 = angle of C(2)—N(3) with respect to the plane H(1)—C(2)—N(1); t_2 = angle of C(2)—N(3) with respect to the plane H(2)—C(2)—N(1); see also comments made in the discussion of the results of the normal coordinate analysis.

sums of their Pauling van der Waals radii.¹⁷ Although these short distances suggest appreciable hydrogen—fluorine bridging, they do not result in a significant distortion of the SbF_6^- octahedron (see above).

The above crystal structure demonstrates that H_2N_3^+ has indeed the asymmetric aminodiazonium structure. This is not surprising in view of a previous *ab initio* calculation which indicated that the aminodiazonium structure is 49.8 kcal mol⁻¹ more favorable than the symmetric diazenium structure.⁶ It must be pointed out, however, that, in spite of the good agreement between the predicted⁶ and our observed N—N bond lengths (1.305 and 1.088 Å versus 1.295 (5) and 1.101 (6) Å), the previous calculation⁶ predicted a planar NH_2 group whereas the crystal structure and our LDF calculations (see below) show that the NH_2 group in H_2N_3^+ is pyramidal. This was due to the lack of polarization functions on the nitrogens at the 3-21G level.

Computational Results. To support our analysis of the vibrational spectra of the H_2N_3^+ cation, the structure, vibrational frequencies, and force field of the free H_2N_3^+ cation in the gas phase were calculated using local density functional (LDF) theory. To test the quality of these computations, the electronic structure of the known,^{18–32} isoelectronic cyanamide molecule, H_2NCN , was

Table VI. Symmetry Force Constants (mdyn/Å) of H_2N_3^+ and H_2NCN Calculated by the LDF Method

H_2N_3^+										
A'	1	2	3	4	5	6	A''	7	8	9
1	6.04	-0.20	0.01	0.24	0.02	0.25	7	6.11	0.08	0.04
2		20.17	0.01	0.57	0.06	-0.20	8		0.74	-0.11
3			0.54	-0.47	-0.03	-0.14	9			1.94
4				9.53	0.18	0.99				
5					0.56	-0.14				
6						0.54				
H_2NCN										
A'	1	2	3	4	5	6	A''	7	8	9
1	6.48	-0.14	0.07	0.18	0.04	0.32	7	6.53	0.17	-0.02
2		17.58	-0.01	0.39	0.04	-0.11	8		0.64	-0.13
3			0.57	-0.33	-0.03	-0.03	9			1.04
4				7.98	0.09	0.65				
5					0.51	-0.03				
6						0.45				

also calculated. The results are summarized in Tables IV–VI and demonstrate that, for this type of molecule, LDF theory duplicates

(18) Brown, R. D.; Godfrey, P. D.; Head-Gordon, M.; Wiedenmann, K. H.; Kleibömer, B. *J. Mol. Spectrosc.* **1988**, *130*, 213.

(19) Hunt, R. D.; Andrews, L. *J. Phys. Chem.* **1987**, *91*, 2751.

(20) Read, W. G.; Cohen, E. A.; Pickett, H. M. *J. Mol. Spectrosc.* **1986**, *115*, 316.

(17) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, **1960**; p 260.

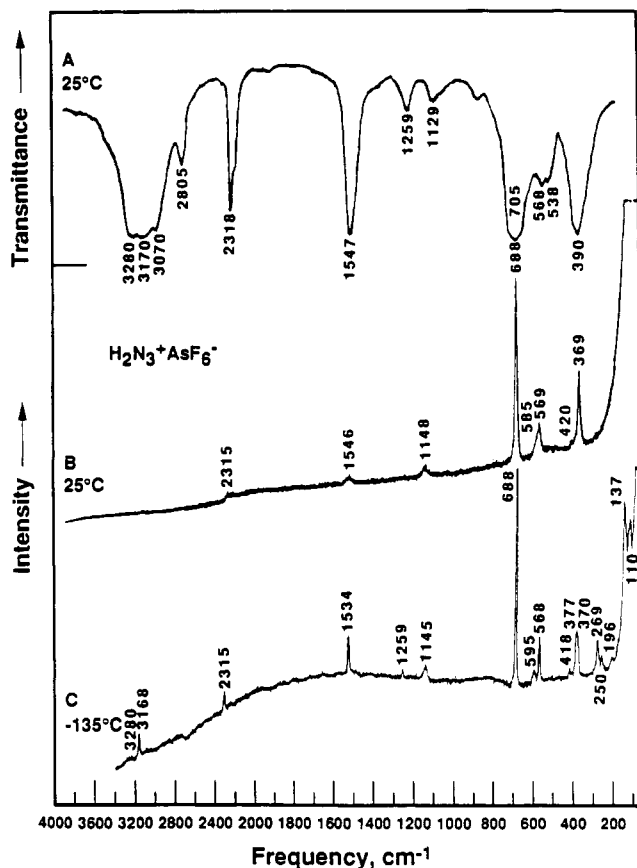


Figure 4. Vibrational spectra of solid $\text{H}_2\text{N}_3^+\text{AsF}_6^-$: trace A, infrared spectrum of a sample pressed between AgBr windows; traces B and C, Raman spectra recorded at 25 and -135°C , respectively.

the experimental frequency values better than calculations at either the $4\text{-}31\text{G}^{*24}$ or $6\text{-}31\text{G}^{*22}$ level. In agreement with previous calculations at the $4\text{-}31\text{G}^{*24}$ or higher levels²² for H_2NCN , the lowest energy structure found for H_2N_3^+ by using LDF theory is nonplanar (C_s symmetry) with a pyramidal amino group. The planar C_{2v} structure previously calculated for H_2N_3^+ at the $3\text{-}21\text{G}$ level⁶ is due to the lower level of theory used and, for isoelectronic H_2NCN , represents a saddle point on the potential energy surface.²² It should also be pointed out that LDF theory predicts the $\text{H}_2\text{N}-\text{N}$ group in H_2N_3^+ to be considerably flatter than the $\text{H}_2\text{N}-\text{C}$ group in H_2NCN . This should result in a lower inversion barrier for the NH_2 group in H_2N_3^+ , which is also apparent from the lowering of the frequency of the NH_2 wagging mode, $\nu_6(\text{A}')$, which, on the basis of its symmetry coordinate and potential energy distribution, represents the inversion motion (see below).

Vibrational Spectra. Infrared and Raman spectra were recorded for $\text{H}_2\text{N}_3^+\text{SbF}_6^-$, $\text{H}_2\text{N}_3^+\text{AsF}_6^-$, and $\text{H}_2\text{N}_3^+\text{BF}_4^-$ (see Figures 3–5). Table VII shows the observed frequencies and their assignments.

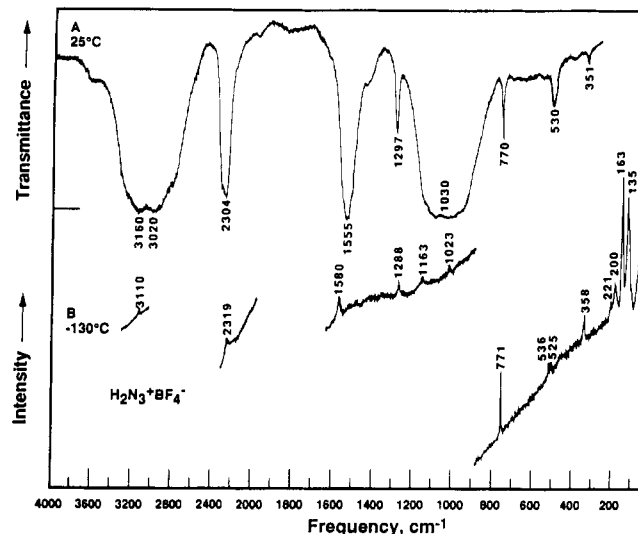


Figure 5. Vibrational spectra of solid $\text{H}_2\text{N}_3^+\text{BF}_4^-$: trace A, infrared spectrum of a sample pressed between AgBr windows; trace B, Raman spectra recorded at -130°C .

Approximate mode descriptions, symmetry coordinates, and potential energy distributions for H_2N_3^+ and isoelectronic H_2NCN are included in Table V. The LDF force fields for H_2N_3^+ and H_2NCN were calculated in terms of internal coordinates and are given in Table VI.

Although cyanamide, H_2NCN , is a simple molecule of great industrial importance and its structure is well-known from microwave spectroscopy,^{20,30,31} its vibrational analysis is still incomplete. This is partially due to experimental difficulties, i.e. its low vapor pressure and tendency to polymerize, and to complications caused by its low inversion barrier at the nitrogen atom.

The H_2NCN molecule and the isoelectronic H_2N_3^+ cation possess symmetry C_s , and their nine fundamental vibrations are classified as $\Gamma = 6\text{A}' + 3\text{A}''$ (see Table V). Of the nine fundamental vibrations of H_2NCN , the antisymmetric NH_2 deformation, $\nu_8(\text{A}'')$, has not been experimentally observed, the two NCN bending modes, $\nu_5(\text{A}')$ and $\nu_9(\text{A}'')$, have been observed only in the liquid phase²⁸ or solution,²⁴ and the NH_2 wagging mode, $\nu_6(\text{A}')$, is complicated by inversion splittings.²¹ Nevertheless, H_2NCN served as a good case for testing the accuracy of the LDF calculations. As can be seen from Table V, our LDF results for H_2NCN are in good agreement with the experimental frequencies. Consequently, the LDF values for H_2N_3^+ should be equally good and were used as a guide for the following assignments for H_2N_3^+ .

The assignment of the two NH_2 stretching modes, $\nu_1(\text{A}')$ and $\nu_7(\text{A}'')$, the $\text{N}\equiv\text{N}$ stretching mode, $\nu_2(\text{A}')$, and the NH_2 scissoring mode, $\nu_3(\text{A}')$, to the bands at about 3170, 3280, 2318, and 1547 cm^{-1} , respectively, is unambiguous. In the $1100\text{--}1300\text{-cm}^{-1}$ region, two bands are observed at about 1129 and 1259 cm^{-1} , respectively, which, on the basis of the LDF predictions, should represent the $\text{N}-\text{N}$ stretching mode, $\nu_4(\text{A}')$, and the antisymmetric NH_2 deformation, $\nu_8(\text{A}'')$, respectively. This choice of assignments is also supported by the observations that the 1259-cm^{-1} mode is more intense in the infrared and less intense in the Raman spectra and that, in the room-temperature Raman spectrum of $\text{H}_2\text{N}_3^+\text{SbF}_6^-$, it is broadened so much that it is no longer observable. A similar broadening of the Raman bands at ambient temperature has also been observed for the remaining NH_2 -group modes in the $\text{H}_2\text{N}_3^+\text{SbF}_6^-$ spectrum. This positive identification of the antisymmetric NH_2 deformation vibration for H_2N_3^+ suggests that, in H_2NCN , this mode should occur in a similar frequency range and might either be assigned to the broad band at about 1150 cm^{-1} in the infrared spectrum of liquid H_2NCN ,²⁷ or, in the gas phase, coincide with the $\text{N}-\text{C}$ stretching mode at 1055 cm^{-1} .

The remaining three, yet unassigned, fundamental vibrations are the NH_2 wagging mode, $\nu_6(\text{A}')$, and the two N_3 skeletal deformation modes, $\nu_5(\text{A}')$ and $\nu_9(\text{A}'')$. On the basis of the LDF calculations, these three modes are expected to occur in the

(21) Birk, M.; Winnenwiser, M. *Chem. Phys. Lett.* **1986**, *123*, 382.

(22) Saebo, S.; Farnell, L.; Riggs, N. V.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5047.

(23) Khaikin, L. S.; Mochalov, V. I.; Grikin, O. E.; Pentin, Yu. A. *Vestn. Mosk. Univ., Ser. 2: Khim.* **1983**, *24*, 536.

(24) Ichikawa, K.; Hamada, Y.; Sugawara, Y.; Tsuboi, M.; Kato, S.; Morokuma, K. *Chem. Phys.* **1982**, *72*, 301.

(25) Daoudi, A.; Pouchan, C.; Sauvatre, H. *J. Mol. Struct.* **1982**, *89*, 103.

(26) King, S. T.; Strobe, J. H. *J. Chem. Phys.* **1971**, *54*, 1289.

(27) Jones, T. R.; Sheppard, N. *J. Chem. Soc. D* **1970**, 715.

(28) Fletcher, W. H.; Brown, F. B. *J. Chem. Phys.* **1963**, *39*, 2478.

(29) Wagner, G. D.; Wagner, E. L. *J. Chem. Phys.* **1960**, *34*, 1480.

(30) Tyler, J. K.; Sheridan, J.; Costain, C. C. *J. Mol. Spectrosc.* **1972**, *43*, 248.

(31) Johnson, D. R.; Suenram, R. D.; Lafferty, W. J. *Astrophys. J.* **1976**, *208*, 245.

(32) Durig, J. R.; Walker, M.; Baglin, F. G. *J. Chem. Phys.* **1968**, *48*, 4675.

Table VII. Vibrational Spectra for Solid $\text{H}_2\text{N}_3^+\text{SbF}_6^-$, $\text{H}_2\text{N}_3^+\text{AsF}_6^-$, and $\text{H}_2\text{N}_3^+\text{BF}_4^-$ and Their Assignments

obsd freq, cm ⁻¹ (rel intens)										
H ₂ N ₃ ⁺ SbF ₆ ⁻			H ₂ N ₃ ⁺ AsF ₆ ⁻			H ₂ N ₃ ⁺ BF ₄ ⁻		assignt (point group)		
IR 25 °C	Raman		IR 25 °C	Raman		IR 25 °C	Raman -130 °C	H ₂ N ₃ ⁺ (C _s)	XF ₆ ⁻ (O _h)	BF ₄ ⁻ (T _d)
	25 °C	-144 °C		25 °C	-135 °C					
3260 vs		3260 (0+)	3280 vs		3280 (0+)	3160 vs		ν ₇ (A'')		
3170 vs	3170 (0+)	3170 (0.5)	3170 vs		3168 (0.9)	3020 vs	3110 (0.2)	ν ₁ (A')		
3063 m			3070 m					2ν ₃ (A')		
2798 m			2805 m			2850 sh		(ν ₃ + ν ₈)(A'')		
2319 s	2319 (0.7)	2316 (2)	2318 s	2315 (0.3)	2315 (0.7)	2304 s	2319 (0.7)	ν ₂ (A')		
1958 vw			1960 vw			1995 vw		(ν ₃ + ν ₉)(A'')		
1547 vs	1549 (0.8)	1549 (0.6)	1547 vs	1546 (0.4)	1534 (1.6)	1555 vs	1580 (1.5)	ν ₃ (A')		
1310 vw			1400 vw						(ν ₁ + ν ₃)(F _{1u})	
1260 m	1261 (0.4)	1262 (0.4)	1259 m		1259 (0.4)	1297 m	1288 (1)	ν ₈ (A'')		(ν ₁ + ν ₄)(F ₂)
1220 vw									(ν ₂ + ν ₃)(F _{1u} + F _{2u})	
1124 mw	1125 (0.5)	1120 (0.5)	1129 mw	1148 (0.5)	1145 (0.7)			ν ₄ (A')		ν ₃ (F ₂)
1025 vw						1030 vs	1023 (0.2)			
								(ν ₅ + ν ₆)(A')		
						770 mw	771 (4.8)			ν ₁ (A ₁)
665 vs	669 (3)	673 (2) } 662 (1) }	705 vs						ν ₃ (F _{1u})	
	648 (10)	648 (10)		688 (10)	688 (10)				ν ₁ (A _{1g})	
	570 (2.3)	572 (2.4) }		585 sh }	595 (0.5) }				ν ₂ (E _g)	
564 m		564 (1) }	568 m	569 (1.6) }	568 (2) }					
530 sh			538 m			530 mw	536 (0.5) 525 (0.5)	ν ₂ (A')		ν ₄ (F ₂)
489 mw								ν ₆ (A')		
408 vw	410 (0.8)	410 (1.0)		420 sh	418 (0.3)	420 m		ν ₉ (A'')		
277 s			390 s						ν ₄ (F _{1u})	
		332 (0.8)							F...H bridge	
		292 (2) }			377 (1.9) }				ν ₅ (F _{2g})	
	283 (6.2)	281 (5.8) }		369 (4)	370 (1.7) }					
		259 (0.5)							F...H bridge	
						351 w	358 (1.9)			ν ₂ (E)
					269 (1.5) }				ν ₆ (F _{2u})	
					250 (0.5) }					
	150 sh	153 (8) }			196 (0.2) }		221 (0.5) }			
	110 (10)	122 (8.5) }			137 (4) }		200 (2) }			
		113 (2) }			110 (3.5) }		163 (10) }			
		59 (2) }					135 (8) }			
		49 (8) }							lattice vibrations	

400–500-cm⁻¹ frequency range, which is complicated by bands due to the anions. Furthermore, the A'' skeletal bending mode, ν_9 , is expected to be of very low infrared intensity,²³ and the NH₂ wagging mode, ν_6 (A'), should not exhibit any inversion splittings since in the crystalline salts the hydrogens are locked into fixed positions by fluorine bridges (see X-ray crystal structure section).

Inspection of the low-temperature Raman spectra of H_2N_3^+ , SbF_6^- and $\text{H}_2\text{N}_3^+\text{AsF}_6^-$ reveals a reasonably intense band at $410\text{--}420\text{ cm}^{-1}$, which has a very weak counterpart in the infrared spectra and is only slightly broadened at room temperature. Hence, this vibration should belong to one of two skeletal bending modes of H_2N_3^+ . Since, in the Raman spectra of liquid^{24,28} or dissolved²⁴ H_2NCN , the out-of-plane NCN deformation mode has by far the highest intensity of the three modes in question and the $410\text{--}420\text{ cm}^{-1}$ frequency value is very close to that of 429 cm^{-1} calculated by us for the out-of-plane N_3 deformation mode of H_2N_3^+ , this $410\text{--}420\text{ cm}^{-1}$ band can be assigned with confidence to the $\nu_9(\text{A}'')$ mode of H_2N_3^+ .

The two remaining A' modes, ν_5 and ν_6 , are more difficult to assign. In view of their similar predicted frequencies (530 and 489 cm^{-1}) and related motions, we expect their symmetry coordinates to be strongly mixed (see PED of Table V), i.e. to be symmetric and antisymmetric combinations of S_5 and S_6 . Both modes are expected to be of low Raman³² but significant infrared intensity²⁴ and, therefore, should be detectable in the infrared spectra. The infrared spectrum of $\text{H}_2\text{N}_3^+\text{SbF}_6^-$ shows a shoulder at 530 cm^{-1} and a medium weak band at 489 cm^{-1} , and that of $\text{H}_2\text{N}_3^+\text{AsF}_6^-$ shows a medium band at 538 cm^{-1} . In $\text{H}_2\text{N}_3^+\text{BF}_4^-$, the 530- cm^{-1} region is obscured by the antisymmetric BF_4^- deformation, $\nu_4(\text{F}_2)$. Consequently, the ν_5 and ν_6 modes of H_2N_3^+ are tentatively assigned to the bands at about 530 and 489 cm^{-1} , respectively.

The above assignments can account for all the observed features in the vibrational spectra of the H_2N_3^+ salts, except for a medium weak band at 900 cm^{-1} and a shoulder at 820 cm^{-1} in the infrared spectrum of $\text{H}_2\text{N}_3^+\text{AsF}_6^-$. These two features are of variable intensity and show no counterparts in the IR spectrum of $\text{H}_2\text{N}_3^+\text{SbF}_6^-$. Therefore, they are judged to be due to an unknown impurity.

In the low-temperature Raman spectra of $\text{H}_2\text{N}_3^+\text{SbF}_6^-$ and $\text{H}_2\text{N}_3^+\text{AsF}_6^-$, the anion bands become much more complex than those in the room-temperature spectra. This is attributed to the freezing out of ion rotation, which for the anions causes splittings into degenerate components and violations of the O_h selection rules, as shown by the observation of the ν_6 mode for AsF_6^- . In addition, the low-temperature Raman spectrum of $\text{H}_2\text{N}_3^+\text{SbF}_6^-$ shows two bands at 332 and 259 cm^{-1} , which probably are not due to the SbF_6^- anion but represent H...F bridge bonds. This temperature effect on the vibrational spectra might also cause a significant broadening of the NH_2 wagging band, ν_6 , at room temperature and, thereby, contribute to the difficulty of observing this mode in our infrared spectra.

In summary, the nine fundamental vibrations of H_2N_3^+ have been observed with frequencies which are in very good agreement with our LDF calculations. This confirms the asymmetric non-planar aminodiazonium structure of H_2N_3^+ , found by the X-ray crystal structure determination. The previous failure⁵ to observe most of these bands for $\text{H}_2\text{N}_3^+\text{SbCl}_6^-$ is attributed to their relatively low infrared intensities and relative broadness at room temperature.

Normal-Coordinate Analysis. To support our vibrational assignments for H_2N_3^+ , normal-coordinate analyses were carried out for H_2N_3^+ and isoelectronic H_2NCN (see Tables V and VI) with the LDF force fields. The corresponding frequencies and

symmetry coordinates are listed in Table V. Our LDF force field for H_2NCN is in good general agreement with that previously published²⁴ by Ichikawa et al. at the 4-31G* level of theory, if it is kept in mind that the frequencies at the 4-31G* level are on average about 10% higher than the experimental ones. The potential energy distributions are given in Table V and support the given mode descriptions.

A special comment is required on the magnitudes of F_{99} in our force fields, which are given in Table VI. The listed F_{99} values are clearly too high and should be comparable to those of F_{55} . The $\nu_5(\text{A}')$ and $\nu_9(\text{A}'')$ modes represent the in-plane and out-of-plane deformations of the nearly linear NXN groups, which, therefore, should be almost degenerate and exhibit similar frequencies and force constants. Whereas the frequencies of ν_9 are comparable to those of ν_5 , the F_{99} values in Table VI are about 2–4 times larger than those of F_{55} . This is an artifact caused by the inability to exactly describe with our computer input code the S_9 symmetry coordinate of the out-of-plane NXN deformation for these molecules when they possess a slightly bent NXN group. Our program to convert the Cartesian second derivatives to symmetry-adapted internal coordinates allows for only four kinds of internal motions: bond stretching, angle bending, a dihedral angle between two planes, and the minimum angle that a bond

forms with a plane. Thus, the $\nu_9(\text{A}'')$ mode had to be defined as the sum of the angles formed between the X–N(2) bond and the two planes defined by H(1)N(1)X and H(2)N(1)X. By making the NXN bonds linear, we were able to properly describe S_9 with this code and obtain values for F_{99} (H_2N_3^+ , 0.47 mdyne/Å; H_2NCN , 0.44 mdyne/Å) that are in excellent agreement with our expectations (see above) and those previously reported.²⁴ The PED ($94S_9 + 6S_8$) for the revised F_{99} values was similar to those given in Table V, while the remainder of the A'' force field remained practically unchanged.

Acknowledgment. The authors thank Dr. C. J. Schack and Mr. R. D. Wilson for their help, Dr. R. Minkwitz for bringing his unpublished studies on $\text{H}_2\text{N}_3^+\text{SbCl}_6^-$ to our attention, and the U.S. Army Research Office and the U.S. Air Force Phillips Laboratory for financial support of the work at Rocketdyne. T.M. thanks the Deutsche Forschungs Gemeinschaft for the provision of a postdoctoral fellowship.

Supplementary Material Available: Table 1S, listing anisotropic temperature factors (1 page); Table 2S, listing observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

The Vanadium(IV) Enterobactin Complex: Structural, Spectroscopic, and Electrochemical Characterization¹

Timothy B. Karpishin, Torin M. Dewey, and Kenneth N. Raymond*

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. Received August 24, 1992

Abstract: The siderophore enterobactin (H_6ent) has been crystallized as the vanadium(IV) complex in the compound $\text{K}_2[\text{V}(\text{ent})]\cdot 3\text{DMF}$ from dimethylformamide (DMF) solution. The pseudooctahedral coordination of the metal ion is through the three catechol groups and has approximate C_3 molecular point symmetry. The geometry is intermediate between trigonal prismatic and octahedral, with a twist angle of 28° . For comparison, the unconstrained complex of *N*-ethyl-2,3-dihydroxybenzamide (H_2eba) has been determined. The twist angle in $[\text{V}(\text{eba})_3]^{2-}$ is 36° , somewhat larger than in the constrained enterobactin complex. The other metrical parameters are essentially identical between the two. Both the stability and the Δ chirality of the enterobactin complex are explained as due to the conformation of the triserine backbone. Molecular modeling calculations correctly predict this chiral preference as well as that for the complex of the (linear trimer) enterobactin hydrolysis product. The V–O bond distances in $[\text{V}(\text{ent})]^{2-}$ average 1.946(7) and 1.939(5) Å to the ortho and meta catechol oxygens, respectively. Hydrogen bonding between the amide proton and the ortho catechol oxygen is an important feature of the structure. Comparison of the conformation of the trilactone serine ring in the vanadium enterobactin complex with two related trilactones shows that the conformation seen is characteristic of this triserine structure and is not a result of the metal complexation or of hydrogen bonding within the triserine ring. This also implies that the free ligand has a conformation similar to that seen in the metal complex. The potassium cations are partially coordinated by the meta catechol oxygens. Molecular modeling indicates that a smaller cation such as calcium cannot fit in the cavity formed between the octahedral catechol coordination site and the triserine ring. The UV/vis spectrum of $[\text{V}(\text{ent})]^{2-}$ has been assigned on the basis of earlier quantitative spectroscopic studies. The spectroscopic parameters indicate that the M–O bonding is stronger in the vanadium complex than in the iron complex of enterobactin, partially due to strong π bonding. A quasi reversible reduction potential (in DMF vs SCE) is found for the $\text{V}^{\text{V}}/\text{V}^{\text{IV}}$ couple of +0.39 V. For $\text{K}_2[\text{V}(\text{ent})]\cdot 3\text{DMF}$, space group $P2_1$, $a = 13.164(3)$, $b = 10.001(1)$, $c = 16.600(2)$ Å, $\beta = 93.96^\circ$, $z = 2$, $V = 2180(1)$ Å³. For 5551 unique data with $F_o^2 > 3\sigma(F_o^2)$ $R = 0.049$, $R_w = 0.062$. For $\text{K}_2[\text{V}(\text{eba})_3]\cdot 3\text{DMF}$, space group $Pa\bar{3}$, $a = 20.632(5)$ Å, $z = 8$, $V = 8783(5)$ Å³. For 2526 unique data with $F_o^2 > 3\sigma(F_o^2)$ $R = 0.051$, $R_w = 0.058$.

Introduction

Most aerobic and anaerobic bacteria synthesize and excrete low molecular weight compounds (siderophores) for the solubilization and transport of iron.^{2–4} Since the iron supply is often a limiting factor in the growth of these microbes, siderophores and their corresponding transport systems play an important role in bacterial virulence.⁵ Of the approximately 200 siderophores now discovered, enterobactin (Figure 1), produced by enteric bacteria such as *Escherichia coli*, has received considerable at-

tention. Since its discovery in 1970,^{6,7} the synthesis,^{8–10} biosynthesis,¹¹ microbial transport,^{5,12–14} and solution thermodynamics^{15–17}

(1) Paper number 49 in the series Coordination Chemistry of Microbial Iron Transport. The previous paper (number 48) in this series: Abu-Dari, K.; Raymond, K. N. *J. Coord. Chem.* 1992, 26, 1–14. [Note that the series number cited in that article is incorrect. Papers 47 and 46 in the series are ref 31 and 28 of this paper, respectively.]

(2) Matzanke, B. F.; Müller-Matzanke, G.; Raymond, K. N. In *Iron Carriers and Iron Proteins*; Loehr, T. M., Ed.; VCH Publishers: New York, 1989; p. 1.

(3) Raymond, K. N.; Müller, G.; Matzanke, B. F. *Top. Curr. Chem.* 1984, 123, 49.

* To whom correspondence should be addressed.

On the Problem of Heptacoordination: Vibrational Spectra, Structure, and Fluxionality of Iodine Heptafluoride

Karl O. Christe,^{*1} E. C. Curtis,¹ and David A. Dixon²

Contribution from Rocketdyne, A Division of Rockwell International Corporation, Canoga Park, California 91309, and the Central Research and Development Department, E. I. du Pont de Nemours and Company, Inc., Experimental Station, Wilmington, Delaware 19880-0328.
Received August 17, 1992

Abstract: Iodine heptafluoride, the most studied prototype of a heptacoordinated molecule, had presented many mysteries concerning its spectroscopic and structural properties. It is shown by ab initio calculations and a reexamination of the vibrational spectra and their normal coordinate analysis that most of the previously implied abnormalities were due to incorrect assignments. All the available structural data for IF₇ are consistent with a highly fluxional, dynamically distorted pentagonal-bipyramidal molecule possessing *D*_{5h} symmetry in the ground state. The fluxionality of IF₇ can be attributed to (i) a rapid dynamic puckering of the highly congested pentagonal equatorial plane involving a very low frequency, large amplitude puckering mode which induces a small axial bend and (ii) a much slower intramolecular exchange of the axial and equatorial fluorines resulting in their equivalence on the NMR time scale. The high degree of ligand congestion in the equatorial plane of the pentagonal bipyramid, combined with a semi-ionic, 6-center 10-electron bonding scheme, results in the equatorial I-F bonds being significantly longer than the axial ones and the equatorial in-plane deformation force constants being much larger than the out-of-plane ones. It is shown that the VSEPR model of repelling points on a sphere cannot account for either the pentagonal-bipyramidal structure of heptacoordinated molecules or the planarity of their equatorial fluorine belts. These features can be explained, however, by a bonding scheme involving a planar, delocalized p_{x,y} hybrid on the central atom for the formation of five equatorial, semi-ionic, 6-center 10-electron bonds and an sp₂ hybrid for the formation of two mainly covalent axial bonds.

Introduction

Inorganic fluorides offer a unique opportunity to study unusually high coordination numbers and problems associated with them, such as steric activity of free valence electron pairs, steric crowding of the ligands, and fluxionality.³ Of particular interest in this respect are structures involving five-fold symmetry, i.e. structures in which a central atom possesses five equatorial ligands. Whereas four equatorial ligands can generally be accommodated in a plane around a central atom without difficulty, five of them at reasonably short bond distances are usually subject to severe steric crowding.⁴ The steric crowding and the resulting mutual repulsion between these ligands can be relieved by puckering. In the case of five-fold symmetry, however, this puckering presents a special problem. The odd number of ligands does not allow for a highly symmetric rigid arrangement in which all five equatorial ligands can be placed in equivalent positions, with identical displacements alternately above and below the equatorial plane. This poses several interesting questions, such as (i) are the five equatorial ligands equivalent and, if so, how is this equivalency achieved; (ii) are these molecules rigid or fluxional and, if they are fluxional, on what time scale; and (iii) what causes heptacoordinated molecules to adopt, contrary to the "repelling points on a sphere" VSEPR concepts, pentagonal-bipyramidal structures with either planar or only slightly puckered equatorial fluorine belts?

Until now, only a very few simple molecules with five-fold symmetry had been known. The simplest and most thoroughly studied example of a molecule of five-fold symmetry is IF₇. During an ongoing study of the closely related TeF₇⁻, IF₆O⁻, TeF₆O²⁻, and XeF₅⁻ anions,^{3,4} however, it became apparent that the vibrational assignments and some of the structural features proposed^{5,6} for IF₇ were seemingly incompatible with our results for these anions. Therefore, we decided to reinvestigate IF₇.

IF₇ has been known for 61 years,⁷ and many papers dealing with its properties and structure have been published. The following paragraph summarizes the salient features and conclusions from the previous studies: (i) Crystal structure determinations of solid IF₇ were inconclusive due to disorder problems.⁸⁻¹³ (ii) In the liquid and gas phases, all seven fluorine ligands were shown to be magnetically equivalent on the time scale of NMR spectroscopy due to an intramolecular exchange of equatorial and axial fluorines.¹⁴⁻¹⁸ (iii) Gaseous IF₇ at room temperature does not possess a permanent dipole moment, as shown by the absence of microwave transitions¹⁹ and of deflections in inhomogeneous electric fields.²⁰ (iv) Gas-phase electron diffraction data^{5,21,22} show that IF₇ closely approaches *D*_{5h} symmetry with a misfit in the 2.1-2.7 Å region which is not much larger than common amplitudes of vibration. The breadth and skewing of the 2.5-Å nonbonded F_{ax}...F_{eq} radial distribution peak were explained by an asymmetric molecule involving fluxionality and a dynamic pseudorotational ring puckering which resulted in average displacements of 7.5° for the equatorial fluorines and of 4.5° for the axial fluorines.⁵ (v) At least nine studies of the vibrational spectra of IF₇ have previously been reported,²³⁻³² and although all nine studies ana-

- (1) Rockwell International, Rocketdyne Division.
- (2) E. I. du Pont de Nemours and Company, Inc.
- (3) See for example: Christe, K. O.; Sanders, J. C. P.; Schrobilgen, G. J.; Wilson, W. W. *J. Chem. Soc., Chem. Commun.* **1991**, 837 and references cited therein.
- (4) Christe, K. O.; Curtis, E. C.; Dixon, D. A.; Mercier, H. P.; Sanders, J. C. P.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **1991**, *113*, 3351.
- (5) Adams, W. J.; Thompson, B. H.; Bartell, L. S. *J. Chem. Phys.* **1970**, *53*, 4040.
- (6) Bartell, L. S.; Rothman, M. J.; Gavezzotti, A. *J. Chem. Phys.* **1982**, *76*, 4136.

- (7) Ruff, O.; Keim, R. Z. *Anorg. Chem.* **1931**, *201*, 245.
- (8) Burbank, R. D.; Bensey, F. N., Jr. *J. Chem. Phys.* **1957**, *27*, 981.
- (9) Donohue, J. *J. Chem. Phys.* **1959**, *30*, 1618.
- (10) Burbank, R. D. *J. Chem. Phys.* **1959**, *30*, 1619.
- (11) Lohr, L. L., Jr.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2225.
- (12) Burbank, R. D. *Acta Crystallogr.* **1962**, *15*, 1207.
- (13) Donohue, J. *Acta Crystallogr.* **1965**, *18*, 1018.
- (14) Gutowski, H. S.; Hoffmann, C. J. *J. Chem. Phys.* **1951**, *19*, 1259.
- (15) Muetterties, E. L.; Packer, K. J. *J. Am. Chem. Soc.* **1964**, *86*, 293.
- (16) Alexakos, L. G.; Cornwell, C. D.; Pierce, St. B. *Proc. Chem. Soc., London* **1963**, 341.
- (17) Bartlett, N.; Beaton, S.; Reeves, L. W.; Wells, E. J. *Can. J. Chem.* **1964**, *42*, 2531.
- (18) Gillespie, R. J.; Quail, J. W. *Can. J. Chem.* **1964**, *42*, 2671.
- (19) Kukolich, S. G. Private communication, 1991.
- (20) Kaiser, E. W.; Muentert, J. S.; Klemperer, W.; Falconer, W. E. *J. Chem. Phys.* **1970**, *53*, 53.
- (21) Thompson, H. B.; Bartell, L. S. *Trans. Am. Crystallogr. Assoc.* **1966**, *2*, 190.
- (22) La Villa, R. E.; Bauer, S. H. *J. Chem. Phys.* **1960**, *33*, 182.
- (23) Lord, R. C.; Lynch, M. A.; Schumb, W. C.; Slowinski, E. J. *J. Am. Chem. Soc.* **1950**, *72*, 522.

Table I. Mesh Parameters Used for the LDF Calculations

parameter	FINE ^a	XFINE ^a
<i>A</i>	1.2	1.5
<i>R</i> _{max}	12.0	15.0
threshold ^b	0.00001	0.000001
max <i>l</i>	29	35
<i>N</i> points	302	434

^a Mesh parameter in DMol. ^b Angular sampling threshold.

lyzed the observed spectra in point group *D*_{5h}, all sets of assignments were different and none was able either to duplicate the experimental mean square amplitudes of vibration⁵ or to assign the observed infrared combination bands without violations of the *D*_{5h} selection rules. (vi) Results from a pseudopotential SCF-MO study⁶ yielded a minimum-energy structure with *D*_{5h} symmetry and an alternative assignment for the vibrational spectra; however, the agreement between calculated and observed frequencies was poor, and a complete vibrational spectrum was not calculated at that time due to the lack of analytic second-derivative methods for pseudopotentials.

Experimental Section

Materials and Apparatus. The preparation and purification of IF₇ have previously been described.³³ For its handling, a well-passivated (with ClF₃) stainless-steel vacuum line,³⁴ equipped with Teflon-FEP U-traps, was used. Raman spectra were recorded on a Spex Model 1403 spectrophotometer using the 647.1-nm line of a Kr ion laser for excitation and a Miller-Harney-type³⁵ cooling device. Flamed-out quartz tubes were used as sample containers in the transverse-viewing-transverse-excitation mode. Infrared spectra of the gas were recorded on a Perkin-Elmer Model 283 spectrophotometer using a 5 cm path length Teflon cell equipped with AgCl windows. The ¹⁹F NMR spectra of IF₇ in CFCI₃ solution either with or without NaF as an HF getter were recorded at 84.6 MHz on a Varian Model EM390 spectrometer equipped with a variable-temperature probe.

Computational Methods. The electronic structure calculations were done at the ab initio molecular orbital (MO) and local density functional (LDF) levels. The ab initio MO calculations were done both with all electrons and with an effective core potential (ECP) replacing all of the core electrons on the iodine. In both cases, the valence basis set was of polarized double ζ quality. The fluorine basis set for both calculations is from Dunning and Hay.³⁶ The all-electron basis set for iodine is from Huzinaga et al.,³⁷ and the ECP calculations were done with the ECP of Hay and Wadt³⁸ including relativistic corrections. The geometries were optimized by using gradient techniques,³⁹ and the force fields were calculated analytically.^{40,41} The ab initio MO calculations were done with

the program GRADSCF⁴² as implemented on a Cray YMP computer system.

The LDF calculations⁴³ were done with the program system DMol⁴⁴ on a Cray YMP computer. A polarized double numerical basis set was used for the calculations; the atomic basis functions are given numerically on an atom-centered, spherical-polar mesh. Since the basis sets are numerical, the various integrals arising from the expression for the energy need to be evaluated over a grid. The radial portion of the grid is obtained from the solution of the atomic LDF equations by numerical methods. The number of radial points *N_R* is given as

$$N_R = 14A(Z + 2)^{1/3} \quad (1)$$

where *Z* is the atomic number. The maximum distance for any function is *R*_{max}. The angular integration points *N_l* are generated at the *N_R* radial points to form shells around each nucleus. The value of *N_l* ranges from 14 to *N_{max}* depending on the behavior of the density and the maximum *l* value for the spherical harmonics, *L*_{max}. These quantities for the two meshes used in this study are given in Table I.

The conversion of the Cartesian second derivatives to symmetry-adapted internal coordinates was done with the BMATRIX program⁴⁵ using Khanna's symmetry coordinates. The axial and equatorial bond lengths used were 1.76 and 1.86 Å,²¹ respectively. The mean amplitudes of vibration were calculated by using the NORCORL program,⁴⁶ which follows the definitions given by Cyvin.⁴⁷

Results and Discussion

Ab Initio Calculations. As our recent results on the vibrational spectra and structures of the pentagonal-planar XeF₅⁺ and pentagonal-bipyramidal IF₆O⁻ anions^{3,4} substantially differed from those^{5,6,23-32} previously reported for pentagonal-bipyramidal IF₇, ab initio calculations were carried out for IF₇ at the following levels of theory: (i) local density functional (LDF) theory with numerical functions; (ii) all-electron MO calculations; and (3) MO calculations with an effective core potential (ECP) for iodine. All three calculations resulted in a pentagonal bipyramid of *D*_{5h} symmetry as the lowest energy structure. The calculated geometries and vibrational frequencies are summarized in Table II and compared to the revised (see below) experimental values. The IF₇ structure obtained by the LDF method with a FINE grid had a degenerate imaginary frequency of 50i cm⁻¹ for the equatorial puckering mode. Very low frequency, degenerate modes in highly symmetrical structures are very sensitive to the nature of the grid in numerical basis set LDF calculations, as shown previously for Ni(CO)₄.⁴⁸ Improving the mesh quality (XFINE in Table I) did not change the structure or change the frequencies except to reduce the magnitude of the imaginary E₂' mode to 40i cm⁻¹. Reducing the symmetry to C₂ or C₁ resulted in structures with only one component of the E₂' mode being imaginary and having smaller values but led to structures that were higher in energy by <0.05 kcal/mol and with the remaining frequencies, excluding the E₂' mode, within 10 cm⁻¹ of those for the LDF *D*_{5h} structure. As can be seen from Table II, the resulting changes in the frequencies and geometries for the C₂ and C₁ structures from the *D*_{5h} structure are rather small and demonstrate the great similarities between the ideal *D*_{5h} structure and the other structures which are somewhat deformed by equatorial puckering and slight axial bending. This is in accord with the previous conclusion that the potential energy well for IF₇ at *D*_{5h} is very flat and shallow

(24) Nagarajan, G. *Curr. Sci.* **1961**, 30, 413; *Bull. Soc. Chim. Belg.* **1962**, 71, 82.

(25) Khanna, R. K. *J. Mol. Spectrosc.* **1962**, 8, 134.

(26) Arighi, L. S. Ph.D. Thesis, University of Wisconsin, 1965.

(27) Claassen, H. H.; Gasner, E. L.; Selig, H. *J. Chem. Phys.* **1968**, 49, 1803.

(28) Ramaswamy, K.; Muthusubramanian, J. *Mol. Struct.* **1970**, 6, 205.

(29) Wendling, E.; Mahmoudi, S. *Bull. Soc. Chim. Fr.* **1972**, 33.

(30) Eysel, H. H.; Seppelt, K. *J. Chem. Phys.* **1972**, 56, 5081.

(31) Mohan, S. *Acta Cienc. Indica* **1978**, 1, 31.

(32) Bernstein, L. S. Ph.D. Thesis, University of California, Berkeley, 1974.

(33) Schack, C. J.; Pilipovich, D.; Cohz, S. N.; Sheehan, D. F. *J. Phys. Chem.* **1968**, 72, 4697.

(34) Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Synth.* **1986**, 24, 5.

(35) Miller, F. A.; Harney, B. M. *Appl. Spectrosc.* **1969**, 23, 8.

(36) Dunning, T. H., Jr.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Chapter I.

(37) Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio, E.; Sakai, Y.; Tatasaki, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984.

(38) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, 82, 299.

(39) (a) Komornicki, A.; Ishida, K.; Morokuma, K.; Ditchfield, R.; Conrad, M. *Chem. Phys. Lett.* **1977**, 45, 595. (b) McIver, J. W., Jr.; Komornicki, A. *Chem. Phys. Lett.* **1971**, 10, 202. (c) Pulay, P. In *Applications of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; p 153.

(40) (a) King, H. F.; Komornicki, A. *J. Chem. Phys.* **1986**, 84, 5465. (b) King, H. F.; Komornicki, A. In *Geometrical Derivatives of Energy Surfaces and Molecular Properties*; Jorgenson, P., Simons, J., Eds.; NATO ASI Series C, Vol. 166, D. Reidel: Dordrecht, The Netherlands, 1986; p 207.

(41) Breidung, J.; Thiel, W.; Komornicki, A. *Chem. Phys. Lett.* **1988**, 153, 76.

(42) GRADSCF is an ab initio program system designed and written by Komornicki, A. at Polyatomics Research.

(43) Dixon, D. A.; Andzelm, J.; Fitzgerald, G.; Wimmer, E.; Jasien, P. In *Density Functional Methods in Chemistry*; Labanowski, J., Andzelm, J., Eds.; Springer-Verlag: New York, 1991; p 33.

(44) Delley, B. *J. Chem. Phys.* **1990**, 92, 508. DMol is available commercially from BIOSYM Technologies, San Diego, CA. The multipolar fitting functions for the model density used to evaluate the effective potential have angular momentum numbers of 3 for F and I.

(45) Komornicki, A. Private communication. This program was developed to help in analyzing the results from the GRADSCF program system.

(46) Christen, D.; Oberhammer, H. Private communication.

(47) Cyvin, S. J. *J. Mol. Struct.* **1978**, 15, 189.

(48) Sosa, C.; Andzelm, J.; Wimmer, E.; Elkin, B.; Dobbs, K. D.; Dixon, D. A. *J. Phys. Chem.*, in press.

Table II. Observed and Calculated Vibrational Frequencies and Geometries for IF₇

assignments and approximate mode descriptions in point group D_{5h}			obsd frequencies (cm ⁻¹)		calculated frequencies (cm ⁻¹)				
			IR	R	ECP ^a	SCF	LDF		
					D_{5h}	D_{5h}	D_{5h}	C_2	C_1
A_1'	ν_1	ν sym XF ₂ ax		676 (2) p	673	743	630	629	625
	ν_2	ν sym XF ₅ eq		635 (10) p	644	704	598	596	596
A_2''	ν_3	ν as XF ₂ ax	746 s		753	834	710	708	703
	ν_4	δ umbrella XF ₅ eq	365 s		368	366	304	310	305
E_1'	ν_5	ν as XF ₅ eq	670 vs		681	761	647	644	646
	ν_6	δ as XF ₅ in plane	425 vs		441	454	377	375	376
E_1''	ν_7	δ sciss XF ₂ ax	257 w		265	261	213	211	212
	ν_8	δ rock XF ₂ ax		319 (0.6) ^b	320	321	259	268	282
E_2'	ν_9	mixture of δ sciss XF ₅ in plane		596 (0.2)	605	651	561	559	560
	ν_{10}	and ν as XF ₅ eq		510 (1.7)	515	555	467	464	458
E_2''	ν_{11}	δ pucker XF ₅ eq		[68] ^c	59	39	50i	4133i	4223i

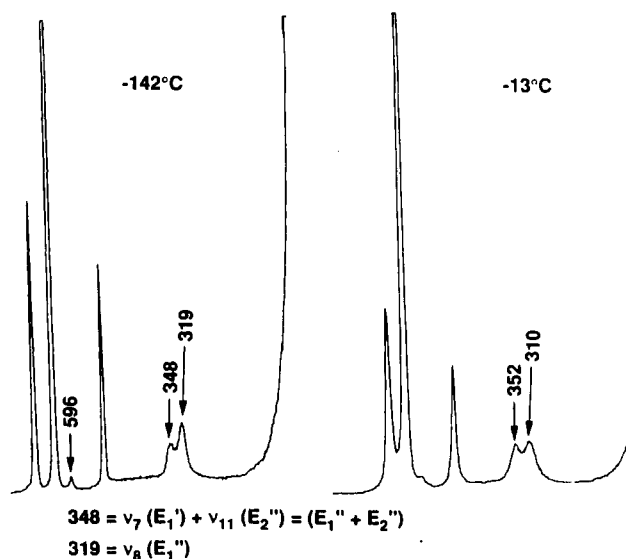
geometry values		obsd ^d		calculated				
		C_2-C_5	D_{5h}	ECP ^a	SCF	LDF		
$r(\text{I-F}_{ax})$ (Å)	$r(\text{I-F}_{eq})$ (Å)	1.786 (7)	1.781	1.7705	1.807	1.870	1.874	1.874
		1.858 (4)	1.857	1.8333	1.862	1.918	1.917	1.917
average eq puckering angle (deg)		7.5	0	0 ^d	0 ^d	0 ^d	4.0 ^e	4.0 ^e
deviation of ax bonds from 180°		4.5	0	0	0	0	1.7 ^e	1.7 ^e

^a The ECP frequencies were scaled by a factor of 0.932. ^b This frequency value was derived from the two Raman bands at 310 (0.6) and 352 (0.6) cm⁻¹ by correction for Fermi resonance (see text). ^c Estimated from the ($\nu_7 + \nu_{11}$) combination band (see text). ^d Although D_{5h} symmetry requires the equatorial plane in the average to be planar, the low frequency of ν_{11} combined with the large $F_{ax} \cdots F_{eq}$ amplitude of vibration makes the effective equatorial puckering comparable to that found for the lower symmetries (see text). ^e The actual displacements of the five equatorial fluorines from the ideal plane in a clockwise sense were +0.35°, -3.15°, +6.65°, -6.65°, and +3.25° with the axial fluorines being bent toward the equatorial fluorine with the smallest (0.35°) equatorial displacement.

and has a nearly quartic contour for buckling along either a C_2 or a C_5 symmetry coordinate.⁴⁹ It seems likely that the out-of-plane potential would be quadratic when the repulsion of the fluorine atoms is neglected. Including the fluorine repulsions adds a double minimum term which adds up to a quartic well near the minimum and undoubtedly has a complex shape. Table II shows that the effective core potential data set, after scaling by a factor of 0.932, duplicates best the experimental frequencies^{27,30} with an average frequency deviation of only 7 cm⁻¹. This small deviation is excellent considering that the calculated values are harmonic, gas-phase frequencies, while the observed values are anharmonic frequencies measured in some cases even in liquid or solid phases.

Raman Spectrum of Solid IF₇. A comparison between the calculated (see Table II) and previously reported²³⁻³² vibrational frequencies, irrespective of their detailed assignments, revealed the following general problems: (i) a Raman active mode having a predicted frequency of about 605 cm⁻¹ was missing; (ii) there was one excess fundamental vibration in the 300–400-cm⁻¹ region; and (iii) the puckering mode of the equatorial plane, which should be inactive in both the Raman and infrared spectra, should have a very low frequency of about 60 cm⁻¹ and be observable only indirectly in the form of combination bands.

For these reasons, the Raman spectrum of solid IF₇ was reinvestigated at different temperatures. As can be seen from Figure 1, at -142 °C a distinct Raman band is observed at 596 cm⁻¹, exhibiting about the right intensity for the missing equatorial IF₅ antisymmetric stretching or in-plane scissoring modes. At higher temperature, this band becomes hidden in the foot of the intense 635-cm⁻¹ band due to the increased line widths. In the 300–360-cm⁻¹ region, two fundamental vibrations had previously been identified²⁷ at 310 and 352 cm⁻¹. Figure 1 shows that, on cooling from -13 to -142 °C, the frequency separation of these two bands decreases from 42 to 29 cm⁻¹ while at the same time the relative intensity of the higher frequency band decreases markedly. This behavior is characteristic for a Fermi resonance between a fundamental vibration and a combination band where the population of the combination band decreases with decreasing temperature. Therefore, the 352-cm⁻¹ Raman band does not represent a fundamental vibration. It is due (see below) to a combination band

Figure 1. Raman spectra of solid IF₇ recorded at -142 and -13 °C.

which involves the inactive equatorial ring-puckering mode and confirms the predicted low-frequency value of the latter.

Vibrational Assignments. In view of the above findings, the vibrational assignments for IF₇ (see Table II) can now be easily made by comparison with the calculated ECP frequencies. All bands strictly follow the selection rules for D_{5h} symmetry, $2A_1'(\text{Ra}) + 2A_2''(\text{IR}) + 3E_1'(\text{IR}) + 1E_1''(\text{R}) + 2E_2'(\text{R}) + 1E_2''(\text{ia})$, and exhibit the expected relative intensities, infrared gas-phase band contours, and Raman polarization. The agreement between calculated and observed frequencies (average $\Delta\nu = 7$ cm⁻¹) is excellent and supports the present assignments.

The difficulty of assigning the vibrational spectra of IF₇ without the help of reliable ab initio calculations is best reflected by the failures of the previous vibrational analyses,²³⁻³² in which no more than four out of the eleven fundamental vibrations had been correctly assigned, a disappointing result if one considers the large number of studies and the expertise of the previous investigators. The only significant improvement over these poor results had previously been achieved by Bartell and co-workers, who, with the aid of pseudopotential SCF-MO calculations, correctly located

Table III. Combination Bands Observed in the Infrared Spectrum of Gaseous IF₇ and Their Assignment

frequency (cm ⁻¹), rel int	assignment
1417 m	676 (A ₁ ') + 746 (A ₂ '') = 1422 (A ₂ '')
1380 sh	635 (A ₁ ') + 746 (A ₂ '') = 1381 (A ₂ '')
1345 vw	676 (A ₁ ') + 670 (E ₁ ') = 1346 (E ₁ ')
1302 m	635 (A ₁ ') + 670 (E ₁ ') = 1305 (E ₁ ')
1258 mw	596 (E ₂ ') + 670 (E ₁ ') = 1266 (E ₁ ' + E ₂ ')
1177 mw	670 (E ₁ ') + 510 (E ₂ ') = 1180 (E ₁ ' + E ₂ ')
1100 w	676 (A ₁ ') + 425 (E ₁ ') = 1100 (E ₁ ')
1058 w	635 (A ₁ ') + 425 (E ₁ ') = 1060 (E ₁ ')
1000 sh	635 (A ₁ ') + 365 (A ₂ '') = 1000 (A ₂ '')
934 vw	676 (A ₁ ') + 257 (E ₁ ') = 933 (E ₁ ')
886 vw	635 (A ₁ ') + 257 (E ₁ ') = 892 (E ₁ ')
839 w	510 (E ₂ ') + 331 (E ₁ ' + E ₂ '') = 841 (A ₁ ' + A ₂ ' + E ₁ '')
518 vw	596 (E ₂ ') - 74 (E ₂ '') = 522 (A ₁ ' + A ₂ ' + E ₁ '')

seven of the eleven fundamental vibrations and predicted the right frequency range for two additional ones.⁶ Most of these difficulties can be attributed to the fact that the previous investigators did not realize that the equatorial in-plane bending modes of IF₇ have such unusually high frequencies.

In several of the previous studies, the inability to assign the observed infrared combination bands of IF₇ without violations of the *D*_{5h} selection rules had been explained by a strong coupling between the E₂' and E₁' modes which should make the E₂' overtones and the pseudoradial, pseudoangular combination bands slightly infrared active, with intensity borrowed from the induced E₁' displacements.^{5,30,50} As can be seen from Table III, the revised assignments for IF₇ given in Table II permit the assignment of all the observed infrared overtones and combination bands without any violations of the *D*_{5h} selection rules, thus eliminating one of the arguments previously advanced^{6,30} against IF₇ having an average symmetry of *D*_{5h}.

The above mentioned, Raman active combination band at 352 cm⁻¹, which is in Fermi resonance with ν₈ (E₁'') requires some special comment. First of all, Fermi resonance requires this band to have the same E₁' symmetry as ν₈; secondly, the band cannot be assigned using any of the remaining fundamental vibrations of IF₇; and thirdly, there are only two fundamental vibrations, ν₇ (E₁') and ν₁₁ (E₂''), that have frequencies lower than that of ν₈. Therefore, the 352-cm⁻¹ band can only be due to a combination of ν₇ (E₁') with the inactive equatorial ring-puckering mode, ν₁₁ (E₂''), which results in the required E₁' symmetry for the ensuing combination band. After a correction for the Fermi resonance induced frequency shift,⁵¹ a frequency of about 68 cm⁻¹ is obtained for the ring-puckering mode, ν₁₁, which is in good agreement with the value of 59 cm⁻¹ predicted by our ECP calculations. Furthermore, this [ν₇ (E₁') + ν₁₁ (E₂'')] combination band represents the mode proposed^{5,6} by Bartell for the pseudorotation in IF₇.

Force Constants and Mean Square Amplitudes of Vibration. Another problem in the previous IF₇ studies²²⁻³² was the discrepancy between the mean square amplitudes of vibration from the electron diffraction study⁵ and those derived from normal coordinate analyses of the vibrational spectra. Since all the previous normal coordinate analyses for IF₇ had been carried out with partially incorrect assignments, such an analysis was repeated using our ab initio (ECP) force field. The resulting symmetry force constants, the explicit F matrix, and the potential energy distribution (PED) are summarized in Table IV. The listed frequencies and force constants were scaled by factors of 0.932 and 0.932² = 0.8686, respectively, to maximize the frequency fit with the observed spectra. As can be seen from the PED in Table IV, most of the fundamental vibrations are highly characteristic and well described by the approximate mode descriptions given in Table II. The only exceptions are (i) the equatorial, antisym-

metric in-plane bending vibration, ν₆ (E₁'), which contains a strong contribution from axial bending and (ii) the two E₂' modes, ν₉ and ν₁₀, which have similar frequencies and, therefore, are almost equal mixes of equatorial stretching and in-plane bending.

Inspection of the internal force constants of IF₇ (see Table V) reveals several interesting features: (i) The stretching force constant of the axial bonds, *f*_D, is considerably larger than that of the equatorial bonds, as expected from the observed bond lengths⁵ and general valence shell electron pair repulsion (VSEPR)⁵² arguments which attribute the longer equatorial bonds to the congestion and increased mutual repulsion of the ligands in the equatorial plane. The absolute value of *f*_D, 5.01 mdyn/Å, is lower than that of 5.42 mdyn/Å previously found for the IF₆⁺ cation,⁵³ as expected for going from a fluorocation to its parent molecule, and (ii) the values of the equatorial angle deformation constants, *f*_α and *f*_β, exhibit a huge difference. As expected, the in-plane deformation, *f*_α, is very large (0.84 mdyn/Å) due to the severe crowding in the equatorial plane, while the out-of-plane deformation, *f*_β, is very small (0.16 mdyn/Å) because of the ease of equatorial ring puckering. These force constants lend strong support to our model of the bonding and fluxionality in IF₇ (see below).

For our calculation of the mean square amplitudes of vibration from the force field, internal force constants were required. For this purpose, the explicit F matrix (see Table IV) and a set of internal force constants (see Table V) were derived for IF₇. Since there are more internal force constants than symmetry force constants, additional relations, such as the procedures of the pure vibrational force field by Kuczer⁵⁴⁻⁵⁸ and molecular-orbital-following arguments, were used for the estimation of the internal force constants.

The previous electron diffraction study⁵ had resulted in two different sets of mean square amplitudes of vibration which, depending on the choice of the structural model, strongly differed in their value for the nonbonded ℓ(F_{ax}...F_{eq}) amplitude. For a static *D*_{5h} model, this amplitude had a value of 0.169 Å, whereas for the statically or dynamically distorted C₂ (50% C₂ + 50% C_v) or C_v models, values ranging from 0.104 to 0.107 Å were obtained. Since the analysis of the vibrational spectra provides an independent experimental set of mean square amplitudes for IF₇, this set can be used to distinguish between the two structural models which were proposed⁵ on the basis of the electron diffraction data. As can be seen from Table VI, the mean square amplitudes from the vibrational spectra are in good agreement with the *D*_{5h} but not the other models. It must be kept in mind, however, that the unusually large vibrational amplitude of 0.16 Å for ℓ(F_{ax}...F_{eq}) in the *D*_{5h} model corresponds to a 6.9° displacement of a fluorine ligand from the equatorial plane and is very close to the average equatorial puckering angle of 7.5° deduced from the electron diffraction data for the distorted models.⁵ The good agreement between the mean square amplitudes of vibration derived from our force field and those deduced for the *D*_{5h} model from the electron diffraction data,⁵ is very gratifying and attests to the correctness of our revised assignments.

Axial-Equatorial Ligand Exchange. In addition to the above described, very fast dynamic exchange of the pentagonal equatorial fluorine plane which requires very little energy (ν₁₁ = 59 cm⁻¹ = 0.17 kcal mol⁻¹) and hence is thermally populated at higher vibrational levels even at low temperatures,⁵⁹ a second type of

(52) Gillespie, R. J. *Molecular Geometry*; Van Nostrand Reinhold Co.: London, 1972.

(53) Christe, K. O.; Wilson, R. D. *Inorg. Chem.* **1975**, *14*, 694.

(54) Kuczer, K.; Czerminski, R. *J. Mol. Struct.* **1983**, *105*, 269.

(55) Kuczer, K. *J. Mol. Struct.* **1987**, *160*, 159.

(56) Lopez Gonzalez, J. J.; Fernandez Gomez, M.; Martinez Torres, E. *J. Mol. Struct.* **1992**, *265*, 397.

(57) Fernandez Gomez, M.; Lopez Gonzalez, J. J. *J. Mol. Struct.* **1990**, *220*, 287.

(58) Lopez Gonzalez, J. J.; Fernandez Gomez, M. *J. Mol. Struct.* **1990**, *216*, 297.

(59) The vibrational partition function terms for ν₁₁ are 3.6 and 1.9 at 20 and -142 °C, respectively, which means that, at these temperatures, only 21% and 34% of the molecules are in the ground state.

(50) Jacob, E. J.; Bartell, L. S. *J. Chem. Phys.* **1970**, *53*, 2235.

(51) Weidlein, J.; Müller, U.; Dehnicke, K. *Schwingungsspektroskopie*; Georg Thieme Verlag: Stuttgart, Germany, 1982; p 37.

Table IV. F Matrix and Scaled ab Initio Effective Core Potential Force Field and Potential Energy Distribution for IF₇ of Symmetry D_{5h}

assignment	freq (cm ⁻¹)	symmetry force constants ^a	potential energy distribution (%) ^b
A ₁ ' ν ₁	673	F ₁₁ = f _D + f _{DD}	5.063 100 (1)
		F ₁₂ = √10 f _{Dd}	-0.0058
ν ₂	644	F ₂₂ = f _d + 2f _{dd} + 2f _{dd'}	4.651 100 (2)
A ₂ ' ν ₃	753	F ₃₃ = f _D - f _{DD}	4.947 92 (3) + 8 (4)
		f ₃₄ = √5(f _{DB} - f _{DB'})	0.342
ν ₄	368	F ₄₄ = f _β + 2f _{ββ} - f _{ββ'} + 2f _{ββ''} - 2f _{ββ'''} - 2f _{ββ''''}	1.624 100 (4)
E ₁ ' ν ₅	681	F ₅₅ = f _d + 2f _{dd} cos α + 2f _{dd'} cos 2α	4.105 97 (5) + 3 (7)
		F ₅₆ = f _{dα} + 2f _{dα'} cos α + 2f _{dα''} cos 2α	-1.427
		F ₅₇ = √2(f _{δβ} + 2f _{δβ'} cos α + 2f _{δβ''} cos 2α)	0.231
ν ₆	441	F ₆₆ = f _α + 2f _{αα} cos α + 2f _{αα'} cos 2α	3.879 62 (6) + 33 (7) + 5 (5)
		F ₆₇ = √2(f _{αβ} + 2f _{αβ'} cos α + 2f _{αβ''} cos 2α)	-0.318
ν ₇	265	F ₇₇ = f _β + 2f _{ββ} cos α + f _{ββ'} + 2f _{ββ''} cos 2α + 2f _{ββ'''} cos α + 2f _{ββ''''} cos 2α	0.980 93 (7) + 7 (6)
E ₁ ' ν ₈	320	F ₈₈ = f _β + 2f _{ββ} cos α - f _{ββ'} + 2f _{ββ''} cos 2α - 2f _{ββ'''} cos α - 2f _{ββ''''} cos 2α	0.823 100 (8)
E ₂ ' ν ₉	605	F ₉₉ = f _d + 2f _{dd} cos 2α + 2f _{dd'} cos α	3.436 57 (10) + 43 (9)
		F _{9,10} = f _{dα} + 2f _{dα'} cos 2α + 2f _{dα''} cos α	0.531
ν ₁₀	515	F _{10,10} = f _α + 2f _{αα} cos 2α + 2f _{αα'} cos α	3.375 61 (9) + 39 (10)
E ₂ ' ν ₁₁	59	F _{11,11} = f _β + 2f _{ββ} cos 2α - f _{ββ'} + 2f _{ββ''} cos α - 2f _{ββ'''} cos 2α - 2f _{ββ''''} cos α	0.0647 100 (11)

^a Stretching constants in mdyn/Å, deformation constants in mdyn Å/rad², and stretch-bend interaction constants in mdyn/rad. ^b The symmetry coordinates used for our normal coordinate analysis of IF₇ were taken from ref 25, but the sequence of S₁ and S₂ was interchanged and the E₁' coordinate was placed ahead of the E₂' block.

Table V. Internal Force Constants^a (mdyn/Å)^b of IF₇

f _D = 5.005	f _β = 0.163
f _{DD} = 0.058	f _{ββ} = 0.078
f _{Dd} = -0.0018	f _{ββ'} = -0.042
f _d = 3.947	f _{ββ''} = -0.038
f _{dd} = 0.326	f _{ββ'''} = -0.044
f _{dd'} = 0.0265	f _{ββ''''} = -0.058
f _α = 0.841	f _{δβ} = 0.090
f _{αα} = -0.187	f _{dβ} = f _{dβ'} = 0
f _{αα'} = -0.243	f _{αβ} = f _{αβ'} = -f _{αβ''} = -0.021
f _{dα} = f _{dα'} = -f _{dα''} = -0.238	f _{Dβ} = -f _{Dβ'} = 0.042

^a D = I-F_{ax}, d = I-F_{eq}, α = ZF_{eq}-I-F_{eq}, β = ZF_{ax}-I-F_{eq}, dd = coupling to adjacent d, dd' = coupling to opposite d, αα = adjacent α, αα' = opposite α, dα = α opposite to d, dα' = remote α, dα'' = adjoining α, ββ = common D and adjoining d, ββ' = noncommon D and common d, ββ'' = common D and remote d, ββ''' = noncommon D and adjoining d, ββ'''' = noncommon D and remote d, dβ = common d, dβ' = adjoining d, dβ'' = remote d, αβ = opposite d, αβ' = adjoining d, αβ'' = common d, Dβ = common D, Dβ' = opposite D. ^b The internal force constants have been normalized for distance assuming D = 1.781 Å and d = 1.857 Å.

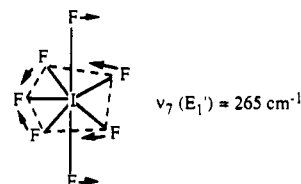
Table VI. Comparison of the Mean Square Amplitudes (Å) of Vibration of IF₇ Obtained from the Vibrational Spectra with Those Derived from the Electron Diffraction Study under the Assumption of Different Structural Models

	vibrational spectra (D _{5h})	electron diffraction ⁵	
		D _{5h}	50% C ₂ -50% C _s
ℓ(I...F _{ax})	0.039	0.042 ^a	0.043 ± 0.003
ℓ(I...F _{eq})	0.043	0.044	0.045 ± 0.003
ℓ(F _{eq} ...F _{eq}) short	0.061	0.061	0.061 ± 0.005
ℓ(F _{eq} ...F _{eq}) long	0.060		
ℓ(F _{ax} ...F _{ax})	0.053	0.093 ^b	0.091 ± 0.006 ^b
ℓ(F _{eq} ...F _{ax})	0.163	0.169	0.106 ± 0.008

^a Obtained from constraint ℓ(I...F_{ax}) = ℓ(I...F_{eq}) - 0.002 Å. ^b Overlapping peak which could not be resolved into its two components.

fluxionality is possible for IF₇. This second type of fluxionality involves an intramolecular exchange of axial and equatorial fluorines. This was shown by the magnetic equivalence of all seven fluorine ligands of IF₇¹⁴⁻¹⁸ or the isoelectronic TeF₇⁻ anion⁴ on the NMR time scale. This exchange process, with an estimated¹⁷ lifetime of a given configuration of ~2.5 × 10⁻³ s, is considerably slower than that for ring puckering and involves higher vibrational levels of ν₇ (E₁'). This motion can best be described as an antisymmetric combination of the axial and equatorial bending symmetry coordinates, S₆ and S₇, which is accompanied by an

out-of-plane twisting motion of the three remote equatorial fluorine ligands.



This axial-equatorial exchange mechanism is analogous to that previously proposed by Berry⁶⁰ for trigonal-bipyramidal molecules, such as PF₅ or SF₄, and involves a substantial energy barrier of several vibrational levels of ν₇.

The previous reports¹⁴⁻¹⁸ for the ¹⁹F NMR spectra of IF₇ were confirmed by our study. Spectra of IF₇ in CFCl₃ solution, in the presence or absence of NaF, showed at -110 °C only one broad line at δ = 173.5 with a line width of ~1150 Hz, which at higher temperatures became extremely broad, as expected from the large ¹²⁷I-¹⁹F spin-spin coupling of about 2100 Hz,¹⁸ the 5/2 spin of iodine, and a quadrupolar mechanism.¹⁷

Structure of IF₇. Whereas the results of the ab initio calculations, the microwave study, and the normal coordinate analysis are best interpreted in terms of a structural model of average D_{5h} symmetry that undergoes a rapid dynamic puckering of the equatorial plane with very large vibrational amplitudes, the previous electron diffraction data⁵ favored a pseudorotational C₂-C_s model with an equilibrium structure that is distorted from D_{5h} symmetry. The question then arises whether one of these seemingly different models is incorrect or if the differences are only due to semantics of how to best describe a highly fluxional and dynamically distorted molecule.

First of all, one must understand what type of information can be gained from the different methods of investigation. Electron diffraction results generally describe the average structure of vibrating molecules and not the minimum-energy geometries.⁶¹ If a highly fluxional molecule, such as IF₇, undergoes a large dynamic distortion at low energy, then electron diffraction will only see a distorted molecule. A classic example for such a case is the linear CO₂ molecule, which, according to its electron diffraction data, would be bent because in the vibrating molecule the average nonbonded O...O distance becomes shorter than twice

(60) Berry, R. S. J. Chem. Phys. 1960, 32, 933.

(61) Bartell, L. S. In Physical Methods of Chemistry; Weissberger, A., Rossiter, B. A., Eds.; Wiley Interscience: New York, 1972; Vol. I, Part IIID, p 125.

the bonded C–O distance.⁶¹ Returning to the electron diffraction data for IF₇, the conclusions^{5,6} reached by Bartell and co-workers are compelling by their logic and thoroughness: The plane of the five equatorial fluorines of IF₇ is highly congested. This congestion can be relieved by a large-amplitude, dynamic puckering. For a five-fold symmetry, the five ligands cannot be displaced from the equatorial plane in a manner which renders them at any given time equivalent and equidistant from the ideal equatorial plane as shown by the previously published⁵ geometries of the C₂ or C_s models of IF₇. As a consequence of these uneven equatorial ligand displacements, the axial ligands experience an uneven repulsion from the equatorial plane and will bend away from those ligands which exhibit the largest displacements from the equatorial plane.⁵² Since the experimental evidence overwhelmingly suggests that all the equatorial ligands are equivalent, a rapid dynamic pseudorotation of the puckering motion must be invoked which is phase-coupled to a precession of the slightly bent axial FIF group (i.e. Bartell's pseudorotational model).⁵ Due to the short time scale of the electron diffraction technique, it detects at all times a distorted IF₇ molecule that exhibits a strong and uneven equatorial puckering and, as a consequence, also an axial bend which results in an equilibrium symmetry lower than D_{5h}.

On the other hand, ab initio calculations and vibrational spectroscopy generally describe the symmetry of the minimum-energy geometry, which for IF₇ would be D_{5h} if the distortions are only dynamic in nature and not static. Although the knowledge of the exact potential energy curve of IF₇ would be desirable to distinguish between a distorted and an undistorted ground-state configuration, the absence of a permanent dipole moment²⁰ and microwave transitions¹⁹ and the results from this study strongly favor an undistorted D_{5h} ground state which undergoes facile dynamic distortion, most likely by Bartell's pseudorotation mechanism.⁵ This signifies that both the D_{5h} and the dynamically distorted model descriptions for IF₇ are, in principle, correct because they describe different time domains. The undistorted D_{5h} model describes the nonvibrating ground state whereas the distorted, dynamically puckered, pseudorotational model depicts the vibrating molecule.

Corroborating evidence that heptacoordinated molecules, with either fluorine, oxygen, or free valence electron pairs as ligands, possess in their ground states pentagonal-bipyramidal structures with an unpuckered equatorial plane comes from ongoing ab initio calculations and two recent X-ray crystal structure determinations. It has experimentally been shown that in XeF₅[−], in which the longer Xe–F bond distances of 1.979 (2)–2.034 (2) Å lessen the equatorial ligand–ligand repulsions (*f*_α = 0.364 mdyn/Å), the equatorial fluorines are essentially coplanar.⁴ It has also been shown that in IF₆O[−] (*f*_α = 0.690 mdyn/Å), which has considerably shorter (1.88 Å) equatorial bonds than XeF₅[−], the equatorial fluorines are puckered, but that with decreasing temperature the degree of puckering strongly decreases.⁶²

The fact that heptacoordinated species in their ground states exhibit pentagonal-bipyramidal structures with an unpuckered equatorial plane cannot be rationalized by VSEPR theory⁶³ in terms of a "repelling points on a sphere" (POS) model which should result in either a monocapped octahedron or a monocapped trigonal prism. Furthermore, it cannot be explained by conventional bonding schemes involving localized electron orbitals of the central atom to enforce the coplanarity of a central atom and five equatorial ligands. The best explanation to account for this planarity is the bonding scheme first proposed⁴ for XeF₅[−] based on an ab initio calculation of the molecular orbital population. In this scheme, the structure and bonding of XeF₅[−] are explained by a simple model derived from XeF₄. The bonding in the square-planar XeF₄ can be described by two semi-ionic, 3-center 4-electron (3c-4e) bonds⁶⁴ for the four Xe–F bonds and two lone

Table VII. Atomic Populations (e) in the Valence Electron Orbitals and Total Charge Distributions for XeF₅[−] and IF₇

	XeF ₅ [−]	IF ₇
Central Atom		
s	2.22	1.35
p _x = p _y	0.61	0.64
p _z	2.02	0.60
d _z ²	0.03	0.11
d _x ² − d _y ²	0.06	0.12
d _{xy}	0.14	0.20
d _{xz} = d _{yz}	0.04	0.14
d total	0.37	0.83
Equatorial Fluorines		
s	1.98	1.93
p bond	1.70	1.57
p in plane	1.98	1.96
p _z	1.97	1.94
d	0	0.03
Axial Fluorines		
s		1.92
p _z		1.54
p _x = p _y		1.94
d		0.04
Total Charges		
central atom	2.25	2.94
F _{eq}	−0.63	−0.43
F _{ax}		−0.39

valence electron pairs on Xe (s²p_z² hybrids). The 3c-4e bonds involve the p_x² and p_y² orbitals of xenon. Addition of an F[−] ion to the equatorial plane in XeF₄ results in pentagonal-planar XeF₅[−] and the formation of a semi-ionic, 6-center 10-electron (6c-10e) bond involving the delocalized p_x²p_y² hybrid orbitals of Xe and six electrons on the five F ligands.⁴ The two lone valence electron pairs on Xe in XeF₅[−] are analogous to those in XeF₄.

The planar IF₇ fragment of IF₇ has essentially the same bonding as XeF₅[−], as shown by the atomic population calculations given in Table VII. As expected for the replacement of two free valence electron pairs on the central atom by two bonded ligands, each of which contributes one electron to its bond, the population of the s² and p_z² orbitals of I in IF₇ has decreased by about two electrons, compared to those in XeF₄ and XeF₅[−]. The higher oxidation state of the central atom in IF₇ (+VII) results in I having a higher positive charge than Xe (+IV) in XeF₅[−]. This causes the effective electronegativity difference between the central atom and the ligands in IF₇ to be smaller than those in XeF₄ and XeF₅[−] and results in an increased covalency and a shortening of the central atom–fluorine bonds. Furthermore, the axial fluorine ligands in IF₇ carry less of a negative charge than the equatorial ones and their bonds have higher s-character, which accounts for the axial I–F bonds to be more covalent and, hence, shorter than the equatorial ones.

Of course, the above model does not account for the fact that the electrons will try to minimize their mutual repulsions and occupy all of the available orbitals to do so. This results in the participation of some d functions. Although we are not proposing a d hybridization model, the population in the d orbitals does suggest a redistribution into these orbitals beyond that expected if the d orbitals were to act solely as polarization functions.

The above atomic population and total charge distribution analysis qualitatively confirms our simple bonding model for pentagonal-bipyramidal molecules. This model involves the use of delocalized p_x² and p_y² hybrid orbitals of the central atom for the formation of a semi-ionic, 6c-10e bond with the five equatorial ligands and of an sp_z hybrid orbital for the formation of two, more covalent, axial bonds. This bonding scheme can account for all the observed structural features and also the observed bond length differences. The planarity of the p_x² and p_y² hybrid orbitals of

(62) Christe, K. O.; Dixon, D. A.; Mahjoub, A. R.; Mercier, H. P.; Sanders, J. C. P.; Seppelt, K.; Schrobilgen, G. J.; Wilson, W. W. *J. Am. Chem. Soc.*, in press.

(63) Gillespie, R. J.; Hargittai, I. In *The VSEPR Model of Molecular Geometry*; Allyn and Bacon, A Division of Simon & Schuster, Inc.: Needham Heights, MA, 1991; p 58.

(64) Pimentel, G. C. *J. Chem. Phys.* **1951**, *10*, 446. Hach, R. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 4321. Rundle, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 112.

the central atom also provides the explanation of why the heptacoordinated main group fluorides prefer pentagonal-bipyramidal structures and not the monocapped octahedral or trigonal prismatic ones expected from VSEPR arguments.⁶³

The possible puckering of the equatorial plane in pentagonal-bipyramidal molecules is due to the high degree of congestion in this plane. While in XeF_5^- ($r(\text{Xe}-\text{F}) \approx 2.00 \text{ \AA}$)⁴ the congestion is relatively low and, therefore, the anion is still planar, the considerably shorter equatorial I-F bonds ($r = 1.857 \text{ \AA}$)⁵ in IF_7 result in increased repulsion and significant puckering.

Conclusion

The problems previously encountered with the vibrational spectra and normal coordinate analyses of IF_7 have been resolved and were caused by partially incorrect assignments. It is shown that the lowest energy structure of IF_7 is a pentagonal bipyramid of D_{5h} symmetry that can undergo a facile, rapid, dynamic, low-frequency equatorial ring puckering with very large vibrational amplitudes. Equivalence of the five equatorial ligands in species of five-fold symmetry is most likely achieved by Bartell's pseudorotational mechanism,⁵ which can also account for the deviations from D_{5h} symmetry observed by electron diffraction studies of the molecules at room temperature in the gas phase. The pentagonal-bipyramidal structures of heptacoordinated fluoride or oxyfluoride complexes, the planarity of their equatorial ligands in their minimum-energy structures, and the large differences in their equatorial and axial bond lengths are attributed to a bonding scheme which involves a planar, delocalized $\text{P}_{x,y}$ hybrid orbital of the central atom for the formation of five equatorial, semi-ionic, 6-center 10-electron bonds and an sp_2 hybrid for the formation

of two mainly covalent axial bonds. The apparent puckering of the fluorine ligands in the equatorial plane is due to their wide vibrational amplitudes involving large vibrational quantum numbers. This effect depends strongly on the relative sizes of the central atom and its ligands and the temperature. Thus, XeF_5^- , which is least congested, is, within experimental error, planar,⁴ while IF_6O^- is strongly puckered, but its degree of puckering significantly decreases with decreasing temperature.⁶² In IF_7 , the I-F bonds are the shortest and, hence, the puckering is most pronounced. These data suggest that a wide spectrum of structures should exist for pentagonal-bipyramidal molecules which range from complete planarity to a strong puckering of the equatorial ligands.

Acknowledgment. The authors thank Drs. H. Oberhammer, L. Bartell, C. J. Schack, W. W. Wilson, and R. D. Wilson for helpful discussions and the Air Force Phillips Laboratory and the U.S. Army Research Office for financial support of the work carried out at Rocketdyne. We also thank Dr. Oberhammer for a copy of his program for the calculation of mean square amplitudes of vibration.

Note Added in Proof: The Coriolis ζ constants of the E_1' block of IF_7 were calculated from the force field and have the following values: $\zeta_{55} = -0.113$, $\zeta_{66} = 0.201$, $\zeta_{77} = 0.913$. Using these values, Dr. L. Bernstein has calculated the infrared band contour of ν_5 . It exhibits a PQR structure similar to that observed for the 670 cm^{-1} band. The absence of pronounced PQR structure for the 746-cm^{-1} band is attributed to interference from hot bands. A high resolution study would be required to better understand the details of the observed band contours.

Molecular Dynamics Simulation of the Hydrated d(CGCGAATTCGCG)₂ Dodecamer

Karol Miaskiewicz,[†] Roman Osman,* and Harel Weinstein

Contribution from the Department of Physiology and Biophysics, Mount Sinai School of Medicine, New York, New York 10029. Received July 24, 1992

Abstract: A 150-ps MD simulation of the DNA dodecamer d(CGCGAATTCGCG)₂ surrounded by 22 sodium counterions and 1431 water molecules was performed with the AMBER force field. The trajectory of the simulation shows that the DNA structure was stable in the first 60 ps, it changed continuously in the interval 60–100 ps, and it stabilized again in the interval 100–150 ps. The structure was analyzed in the two time periods of simulation, 20–60 and 100–150 ps, in which the structure fluctuated around a stable average. The averaged DNA structure in the 100–150 ps of the simulation is highly distorted. Kinks are observed near the C3,G4 and C9,G10 residues. The helix is significantly unwound in the central AATT region. The base pairing and stacking interactions are also disturbed. The analysis of the trajectories of the counterions shows that they are quite mobile. They distribute equally between two types of configurations: in one the Na^+ reside in a direct coordination with the phosphate group, in the other the coordination to the phosphate is through a hydration sphere. The water molecules distribute in two solvation domains. The first solvation domain is very stable during the dynamics, while the rest undergoes a small expansion. The main hydration site in DNA is the phosphate group. The average number of water molecules hydrating a G–C base pair is 21.38, while the A–T pair is solvated by an average of 20.45 water molecules. The results raise the question whether a longer MD simulation would result in a "unique" stable structure of DNA.

Introduction

Early information on DNA structure was obtained from diffraction studies of oriented high molecular weight fibers.¹ The two basic families of DNA structures that were derived from these data are the A-DNA and the B-DNA. However, subsequent single crystal X-ray studies have shown that DNA structure is not uniform and shows many sequence dependent features. Sequence dependence of structure was especially well established for the

d(CGCGAATTCGCG)₂ dodecamer by Dickerson et al.^{2,3} Also, models have been proposed for sequence specific local deformations of the DNA double helix such as Calladine purine–purine clash⁴ or the Trifonov wedge.^{5,6} Recent crystallographic studies have

[†] Present address: Battelle, Pacific Northwest Laboratories, Richland, WA 99352.

(1) Franklin, R. E.; Gosling, R. G. *Acta Crystallogr.* **1953**, *6*, 673.
(2) Dickerson, R. E. *J. Mol. Biol.* **1981**, *149*, 761–786.
(3) Dickerson, R. E. *J. Mol. Biol.* **1983**, *166*, 419–441.
(4) Calladine, C. R. *J. Mol. Biol.* **1982**, *161*, 343–352.
(5) Trifonov, E. N.; Sussman, J. L. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 3816–3820.

The correlation line of the His117Gly type-2 proteins runs below the line of the other type-2 copper centers in Figure 7. This can be attributed to the presence of the sulfur in the Cu coordination shell in the His117Gly type-2 proteins.^{37,38} The smaller values of the $g_{\parallel}$ of His117Gly(His) and -(Hista) compared to those of His117Gly(H₂O) and -(ImAc) may reflect the aromaticity of the His and Hista ligands and the replacement of the less electron-rich oxygens of one or two water molecules or of the carbonyl of ImAc by one or two coordinating more electron-rich nitrogens.³⁷

In the case of His117Gly(H₂O), one or two hydroxide ions could coordinate instead of water molecules. However, this seems less likely because the change in $g_{\parallel}$ upon incubation of His117Gly-(H₂O) by His is much larger than expected for a replacement of OH⁻ by His.³⁵

Concluding Remarks

The replacement of the His117 ligand of azurin by a glycine apparently does not change the structure of the protein noticeably or the pocket which contains the copper ion. However, the important contribution of His117 to the biological function of azurin is best illustrated by the observation that the His117Gly(L) species that cluster around B in Figure 6 behave spectroscopically virtually identical to the wild type but are not functional in reversible electron transfer.

Geometrical changes of the copper center could be induced by various exogenous ligands and cause this one mutant to spectroscopically encompass the known range of type-1 and part of the range of the type-2 copper proteins. An interesting observation is that the His117Gly points in Figure 6 are not scattered more or less evenly along the correlation line connecting regions A and C but cluster in three areas. We tentatively interpret this as indicating a preference by the protein for a few discrete adaptations around the Cu site instead of a continuous variation.

In conclusion, it is interesting to note that a large variety of external ligands appear compatible with a metal center that retains the basic features of a type-1 or type-2 Cu site. It opens the attractive possibility of obtaining deeper insight into the correlation between copper site geometry and spectroscopic and mechanistic features by means of further detailed structural studies.

Acknowledgment. The authors thank Drs. S. J. P. Albracht for recording the S- and Q-band EPR spectra and A. C. F. Gorren for assisting with the stopped-flow measurements. They thank Prof. E. I. Solomon for valuable comments. For stimulating discussions they thank Profs. J. Reedijk, J. Sanders-Loehr, and T. M. Loehr and Drs. C. W. G. Hoitink and M. Ubbink. This research was supported by the Technology Foundation (STW), which is subsidized by the Department of Economic Affairs.

Tetrafluorosulfate(1-) and Tetrafluorooxosulfate(1-) Radical Anions (SF₄⁻ and SF₄O⁻)^{‡,§}

K. O. Christe,^{*4} D. A. Dixon,³ I. B. Goldberg,² C. J. Schack,⁴ B. W. Walther,^{1,§} J. T. Wang,¹ and F. Williams^{*1}

Contribution from the Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600, Science Center, Rockwell International Corporation, Thousand Oaks, California 91360, Central Research Department, Experimental Station, E.I. DuPont de Nemours and Company, Wilmington, Delaware 19880-0328, and Rocketdyne Division, Rockwell International, Canoga Park, California 91309-7922. Received August 10, 1992

Abstract: The novel radical anions SF₄⁻ and *trans*-SF₄O⁻ were generated by γ -irradiation of CsSF₅ and CsSF₅O, respectively, at -196 °C and characterized by their isotropic EPR spectra at +27 °C. The SF₄⁻ anion ($g = 2.0045$, $a_{33S} = 12.85$ mT, $a_{19F} = 9.75$ mT) has a square-planar structure close to D_{4h} symmetry derived from a pseudo-octahedron in which the two axial positions are equally occupied by a total of three sterically active valence electrons. Accordingly, the greatest portion of the unpaired electron spin is localized in a sulfur p_z orbital. The *trans*-SF₄O⁻ anion ($g = 2.0027$, $a_{33S} = 36.26$ mT, $a_{19F} = 18.95$ mT) has a closely related, pseudo-octahedral structure of C_{4v} symmetry in which the equatorial positions are occupied by four equivalent fluorines, one axial position is occupied by a doubly bonded oxygen, and the second axial position is occupied by the sterically active free valence electron. Accordingly, the greatest portion of the unpaired electron spin is localized in an axial sp -hybrid orbital of sulfur. The structures and electron spin density distributions of SF₄⁻ and *cis*- and *trans*-SF₄O⁻ were analyzed by a local density functional study which also provided vibrational frequencies and charge distributions for these radical anions. For comparison, the closely related SF₅ radical, the *cis*- and *trans*-PF₄O²⁻ radical anions, and the SF₄, SF₄O, and SF₆ molecules were also calculated by this method. These calculations show that the exclusive formation of *trans*-SF₄O⁻ under our experimental conditions is probably due to both energetic and reaction mechanistic reasons and that the agreement between the LDF calculations and the experimental data is good.

Introduction

Previous studies have demonstrated that γ -irradiation of salts containing complex fluoro ions can result in the loss of one fluorine atom and in the formation of new complex fluoro radical ions that contain one fluorine atom less than the parent ion. Thus, the

radical ions PF₅⁻⁵⁻⁸, AsF₅^{-8,9} and NF₃^{+10,11} have been obtained from PF₆⁻, AsF₆⁻, and NF₄⁺ containing salts, respectively, and

[‡] Dedicated to Professor Felix Aubke on the occasion of his 60th birthday.

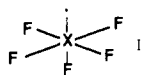
[§] Based in part on the PhD. dissertation of B. W. Walther, University of Tennessee, 1984. A preliminary report of this work was presented at the 186th ACS National Meeting, Washington, D.C., August 28–September 2, 1983; Abstract FLUO 31.

[§] Present address: Dow Chemical Co., Louisiana Research & Development, P.O. Box 400, Plaquemine, LA 70765-0400.

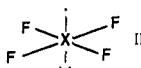
- (1) University of Tennessee.
- (2) The Science Center, Rockwell International Corp.
- (3) E.I. DuPont de Nemours and Co.
- (4) The Rocketdyne Division, Rockwell International Corp.
- (5) (a) Morton, J. R. *Can. J. Phys.* **1963**, *41*, 706. (b) Atkins, P. W.; Symons, M. C. R. *J. Chem. Soc.* **1964**, 4363.
- (6) Morton, J. R.; Preston, K. F. In *Fluorine-Containing Free Radicals*; Root, J. W., Ed.; ACS Symposium Series 66, American Chemical Society: Washington, D.C., 1978; p 386.
- (7) Mishra, S. P.; Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* **1974**, 279.

characterized by electron paramagnetic resonance (EPR) spectroscopy.

Characterization by EPR is not always unambiguous. For example, the pseudo-octahedral XF_5 radicals PF_5^{-7} and SF_5^{12}



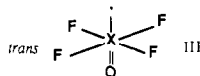
exhibited detectable hyperfine splittings (hfs) only for the four equatorial fluorine atoms but, surprisingly, not for the axial fluorine atom. For PF_5 this led originally to an incorrect identification as PF_4 .⁵ In this respect, it seemed interesting to prepare the yet unknown SF_4^- radical. By comparison with the known isoelectronic ClF_4 radical,¹³⁻¹⁵ a pseudo-octahedral structure with a square-planar XF_4 moiety



can be expected for SF_4^- . Therefore, the EPR spectrum of SF_4^- should, in general appearance, resemble that of the SF_5 radical,¹² but the g -factor and ^{19}F and ^{33}S hyperfine splittings should be significantly different.

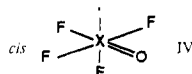
After completion of this work, the results of a theoretical investigation on the molecular and electronic structure of the SF_n ($n = 1-5$) and their singly charged negative ions using density functional theory was published which also predicted an approximately square-planar structure for SF_4^- .¹⁶

Similarly, the preparation of the yet unknown SF_4O^- radical anion should be interesting. Its structure is expected to be similar to that of SF_4^- , except for the replacement of the axial free valence electron pair by an oxygen ligand.



Since ^{16}O does not possess a nuclear spin, the EPR pattern of SF_4O^- should again resemble those of SF_5 and SF_4^- in general appearance, but with a different g -factor and hyperfine splittings.

For SF_4O^- , additional interest comes from the fact that the isoelectronic PF_4O^{2-} and $\text{AsF}_4\text{O}^{2-}$ radical anions⁸ exhibit two stereoisomers (III and IV). Isomer III, labeled trans, has one axial oxygen ligand opposite to the orbital containing the unpaired electron. Isomer IV has one equatorial oxygen ligand adjacent to the orbital containing the unpaired electron. It would be interesting to examine whether such isomerism is also observable for SF_4O^- .



Experimental Section

The samples of CsSF_5 and CsSF_5O were prepared as previously described,^{17,18} from dry CsF and SF_4 or SF_4O . On the basis of the observed

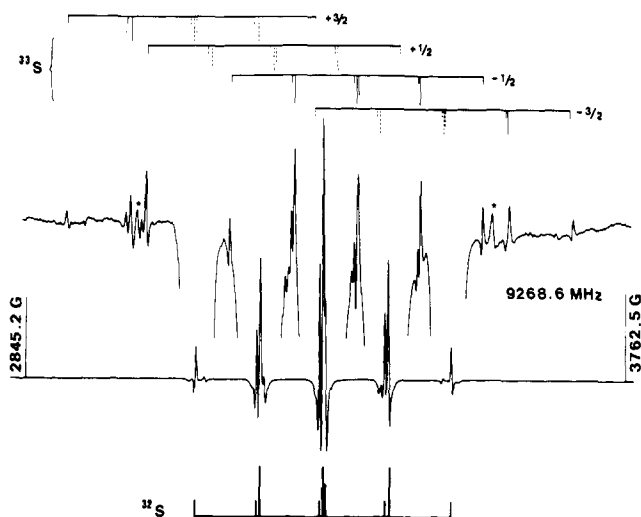


Figure 1. EPR spectrum and spectral analysis of the SF_4^- anion radical. The upper trace was obtained by signal averaging from 30 scans and recorded at 500 times the gain of the lower trace. The lines marked by an asterisk do not belong to the pattern of SF_4^- .

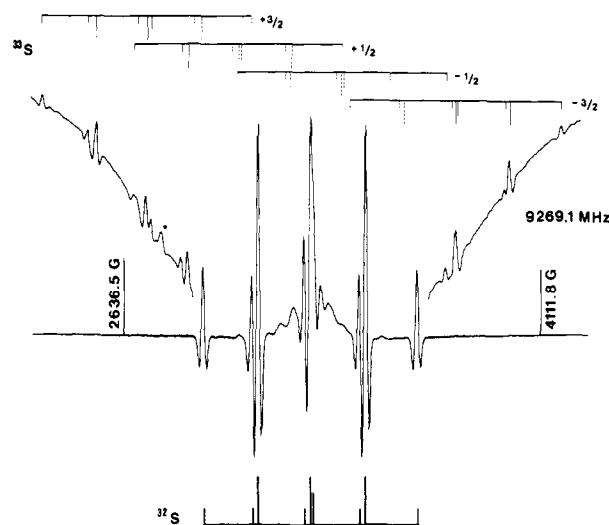


Figure 2. EPR spectrum and spectral analysis of the SF_4O^- anion radical. The upper trace was obtained by signal averaging from 30 scans and recorded at 500 times the gain of the lower trace. The line marked by an asterisk does not belong to the pattern of SF_4O^- .

material balances, the conversion of CsF was 50% for CsSF_5 and 85% for CsSF_5O . The purity of the compounds was verified by Raman spectroscopy, which showed only the bands characteristic^{17,18} of SF_5^- and SF_5O^- , respectively. In the dry nitrogen atmosphere of a glovebox, the samples were loaded into flamed-out 4-mm o.d. Suprasil EPR sample tubes (Wilma Glass Co.) that were flame-sealed under vacuum. These tubes were then irradiated in a ^{60}Co γ -radiation source (Gammacel 200, Nordion International, Inc., Kanata, Ontario, Canada) at a dose rate of 1.03×10^5 rad/h for a total dose of 4 Mrad (4×10^4 J/kg). The EPR spectra were recorded at sample temperatures ranging from -190 to 90°C . Since the spectral features did not sharpen up any further above room temperature and a slight amount of decay was observed above 60°C , the reported spectra were recorded at ambient temperature. Preliminary work with a Varian V4302-15 EPR spectrometer led to the detection of the main ^{33}S spectra of the subject radicals while the ^{33}S satellite lines in natural abundances were only revealed by optimization of microwave power (4 dB $\approx$ 79 mW) and modulation amplitude (1.25–2.5 mT) using a more sensitive Bruker ER 200D SRC instrument.

Computations were carried out in the local density functional (LDF) approximation¹⁹ by using the program system DMol,^{20,21} as previously

(8) Morton, J. R.; Preston, K. F.; Strach, S. J. *J. Magn. Reson.* **1980**, *37*, 321.

(9) Symons, M. C. R. *Int. J. Radiat. Phys. Chem.* **1976**, *8*, 643.

(10) Mishra, S. P.; Symons, M. C. R.; Christe, K. O.; Wilson, R. D.; Wagner, R. I. *Inorg. Chem.* **1975**, *14*, 1103.

(11) Goldberg, I. B.; Crowe, H. R.; Christe, K. O. *Inorg. Chem.* **1978**, *17*, 3189.

(12) (a) Morton, J. R.; Preston, K. F. *Chem. Phys. Lett.* **1973**, *18*, 98. (b) Hasegawa, A.; Williams, F. *Chem. Phys. Lett.* **1977**, *45*, 275.

(13) (a) Morton, J. R.; Preston, K. F. *J. Chem. Phys.* **1973**, *58*, 3112. (b) Nishikida, K.; Williams, F.; Mamantov, G.; Smyrl, N. *J. Am. Chem. Soc.* **1975**, *97*, 3526.

(14) Gregory, A. R. *J. Chem. Phys.* **1974**, *60*, 3713.

(15) (a) Ungemach, S. R.; Schaefer, H. F. *J. Am. Chem. Soc.* **1976**, *98*, 1658. (b) So, S. P.; Richards, W. G. *J. Chem. Soc., Faraday Trans. II* **1979**, *75*, 55.

(16) Ziegler, T.; Gutsev, G. L. *J. Chem. Phys.* **1992**, *96*, 7623.

(17) Christe, K. O.; Curtis, E. C.; Schack, C. J.; Pilipovich, D. *Inorg. Chem.* **1972**, *11*, 1679.

(18) Christe, K. O.; Schack, C. J.; Pilipovich, D.; Curtis, E. C.; Sawodny, W. *Inorg. Chem.* **1973**, *12*, 620.

Table I. Hyperfine Splittings, g-Factors, and s-Orbital Electron Spin Densities of SF₄⁻ and SF₄O⁻ and Related Radicals Calculated from the Observed Hyperfine Splittings

radical	a_x (mT)	n_F^b	a_F (mT)	g-factor	$\rho_s^{X,c}$	$\rho_s^{F,c}$	ref
³³ SF ₄ ⁻	12.85	4	9.75	2.0045	0.104	0.0052	a
³⁵ ClF ₄	28.82	4	7.87	2.0117	0.141	0.0042	13
³³ SF ₄ O ⁻	36.26	4	18.95	2.00274	0.293	0.0105	a
³³ SF ₅	30.68	4	14.30	2.0044	0.248	0.0076	12, 23, 24a
⁷⁵ SeF ₅	187.7	4	11.80	2.0072	0.261	0.0063	24a
³¹ PF ₅ ⁻	135.6	4	19.8	2.0017	0.286	0.0105	7, 8
			0.3			0.0002	
⁷⁵ AsF ₅ ⁻	182.9	4	18.3	1.9996	0.350	0.0097	8
			0.5			0.0003	
³¹ PF ₄ O ²⁻							8
trans	139.0	4	21.2	2.0019	0.293	0.0112	
cis ^d	124.3	2	22.4	2.0025	0.261	0.0119	
		1	17.6			0.0093	
⁷⁵ AsF ₄ O ²⁻							8
trans	185.0	4	19.3	1.9998	0.354	0.0102	
cis ^d	165.1	2	21.9	2.0011	0.316	0.0116	
		1	15.4			0.0082	

^a This work. ^b Number of equivalent fluorine atoms. ^c Calculated based on parameters given in ref 24b. ^d No splittings due to interactions with the apical fluorine ligand were observed.

described in more detail.²²

The SCF equations for the triplet states were solved by spin unrestricted methods similar to those employed in unrestricted Hartree-Fock (UHF) calculations. Geometries were optimized by using analytic gradient methods.²¹ There are two problems with evaluating gradients in the LDF framework which are due to the numerical methods that are used. The first is that the energy minimum does not necessarily correspond exactly to the point with a zero derivative. The second is that the sum of the gradients may not always be zero, as required for translational invariance. These tend to introduce errors on the order of 0.001 Å in the calculation of the coordinates if both a reasonable grid and basis set are used. This gives bond lengths and angles with reasonable error limits. The difference of 0.001 Å is about an order of magnitude smaller than the accuracy of the LDF geometries as compared to experiment. The frequencies were determined by numerical differentiation of the gradient. A two-point difference formula was used with a displacement of 0.01 au.

Results and Discussion

EPR Spectra. The second-derivative isotropic EPR spectra of the SF₄⁻ and SF₄O⁻ radical ions are shown in Figures 1 and 2, respectively. Each spectrum shows the satellite lines due to naturally abundant ³³S. At sample temperatures from -50 to 90 °C, the spectra gave only slight indications of residual anisotropy, suggesting that, in this range, the radicals rotate freely at their lattice positions. Because the hyperfine splittings are large, the azimuthal nuclear spin quantum number, M_I , lines for ¹⁹F exhibit "second-order" splittings^{23,24} and the M_I lines for ³³S exhibit shifts, making the separation between lines nonlinear in M_I . The analyses of the spectra of the ³²S-centered radicals, including the higher

Table II. Geometry, Unscaled Vibrational Spectrum, Spin Populations, and Atomic Charges Calculated for SF₄⁻ by the LDF Method

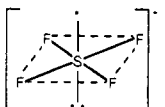
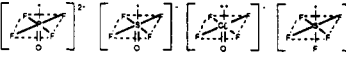
			
Geometry		C _{4v}	D _{4h}
r S-F (Å)		1.793	1.803
∠ FSF (deg)		89.2	90
∠ FS-C _{4v} axis (deg)		83.3	90
Vibrational Frequencies (cm ⁻¹)			
approx. mode description			
v sym SF ₄ in phase	A _{1g} v ₁	547	A _{1g} v ₁ 516
δ sym SF ₄ out of plane, in ph.	v ₂	299	A _{1u} v ₂ 245i
v sym SF ₄ out of phase	B _{1g} v ₃	425	B _{1g} v ₃ 406
δ sym SF ₄ out of plane, out of ph.	v ₄	130	B _{1u} v ₄ 121
δ sciss SF ₄	B _{2g} v ₅	274	B _{2g} v ₅ 258
v as SF ₄	E v ₆	612	Eu v ₆ 604
δ as SF ₄ in plane	v ₇	227	v ₇ 210
Spin Populations			
atom	orbital		
S	3s	0.033	-0.014
S	3p _{x,y}	0.013	
S	3p _z	0.602	0.627
S	3d _{xy,x²-y²}	0.001	
S	3d _{xz,yz}	0.003	0.026
S	3d _{z²}	0.019	0.021
F	2p _{x,y}	0.016	
F	2p _z	0.045	0.078
Atomic Charges			
S			0.725
F			-0.431

Table III. Geometries, Unscaled Vibrational Spectra, Spin Populations, and Atomic Charges Calculated for the *trans*-PF₄O²⁻, SF₄O⁻, and SF₅ Radicals and the Observed Vibrational Spectrum of ClF₄O⁻

					
Geometry		C _{4v}	C _{4v}	C _{4v}	C _{4v}
r X-Y (Å)		1.530	1.464		1.587
r X-F (Å)		1.841	1.770		1.645
∠ YXF (deg)		100.3	101.6		91.7
Vibrational Frequencies (cm ⁻¹)					
approx. mode description					
A ₁ v ₁ v _{X-Y}		1096	1211	1203	837
v ₂ v sym XF ₄		422	503	456	605
v ₃ δ sym in phase XF ₄ out of plane		354	361	339	461
B ₁ v ₄ sym XF ₄ out of phase		333	421	345	563
v ₅ δ sym out of phase XF ₄ out of plane		159	148		201
B _{2v} δ sciss XF ₄		267	315	283	403
E v ₇ v as XF ₄		538	635	578	809
v ₈ δ as XF ₄ in plane		329	375	406	453
v ₉ δ as XF ₄ in plane		203	250	204	311
Spin Populations					
atom	orbital				
X	3s	0.412	0.258		0.258
X	3p _{x,y}	0.227	0.239	0.169	0.201
X	3p _z		0.166		
X	3d _{xy,x²-y²}	0.001	-0.002		
X	3d _{xz,yz}	0.039	0.002	0.027	0.075
X	3d _{z²}	0.030	0.024		0.069
F	2s	-0.004	-0.002		-0.001
F	2p _{x,y}	0.037	0.067		0.046
F	2p _z	0.002	0.004	0.136	0.026
Y	2s	-0.005	-0.003		-0.004
Y	2p _{x,y}	0.027	-0.005	0.016	-0.001
Y	2p _z		0.023		-0.002
Atomic Charges					
X		0.610	0.864		0.996
F		-0.304	-0.376		-0.212
Y		-0.593	-0.360		-0.148

^a X = P, S, or Cl; Y = O or the unique F.

order effects for the fluorine hyperfine lines, are given below the spectra, and those for the ³³S-centered radicals are given above the spectra. The EPR parameters were determined using a least-squares matrix diagonalization program,²⁵ and the isotropic hyperfine splittings and g-factors of these radicals and other analogous species^{7,8,12,13,23,24} are given in Table I. Spin densities in the s orbitals of the central atoms or fluorine, X, were calculated according to

$$\rho_{sX} = a_X/a_X^0$$

(25) Hasegawa, A.; Hayashi, M.; Kerr, C. M. L.; Williams, F. J. *Magn. Reson.* **1982**, *48*, 192.

(19) (a) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989. (b) Salahub, D. R. In *Ab Initio Methods in Quantum Chemistry*; Lawley, K. P., Ed.; J. Wiley & Sons: New York, 1987; Vol. II, p 447. (c) Wimmer, E.; Freeman, A. J.; Fu, C.-L.; Cao, P.-L.; Chou, S.-H.; Delley, B. In *Supercomputer Research in Chemistry and Chemical Engineering*; Jensen, K. F., Truhlar, D. G., Eds.; ACS Symposium Series, American Chemical Society: Washington, D.C., 1987; p 49. (d) Jones, R. O.; Gunnarsson, O. *Rev. Mod. Phys.* **1989**, *61*, 689. (e) Zeigler, T. *Chem. Rev.* **1991**, *91*, 651. (f) Dixon, D. A.; Andzelm, A.; Fitzgerald, G.; Wimmer, E.; Delley, B. In *Science and Engineering on Supercomputers*; Pitcher, E. J., Ed.; Computational Science Publications: Southampton, England, 1990; p 285. (g) Dixon, D. A.; Andzelm, J.; Fitzgerald, G.; Wimmer, E.; Jasien, P. In *Density Functional Methods in Chemistry*; Labanowski, J., Andzelm, J., Eds.; Springer-Verlag: New York, 1991; p 33.

(20) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508. DMol is available commercially from BIOSYM Technologies, San Diego, CA.

(21) Delley, B. In *Density Functional Methods in Chemistry*; Labanowski, J., Andzelm, J., Eds.; Springer-Verlag: New York, 1991; p 101.

(22) Christie, K. O.; Curtis, E. C.; Dixon, D. A.; Mercier, H. P.; Sanders, J. C. P.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **1991**, *113*, 3351.

(23) Fessenden, R. W. *J. Magn. Reson.* **1969**, *1*, 277.

(24) (a) Morton, J. R.; Preston, K. F.; Tait, J. C. *J. Chem. Phys.* **1975**, *62*, 2029. (b) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577.

where a_X and a_X° are respectively the isotropic hyperfine splitting of atom X in the radical and the hyperfine splitting of the atom assuming that there was one unpaired electron in the outermost s orbital of that atom.²⁵

EPR spectra showing varying degrees of ^{19}F hyperfine anisotropy were obtained in each case with sample temperatures below -50°C . In particular, the spectrum of SF_4^- between -190 and -170°C consisted of a strong central absorption at $g = 2.005$ flanked by three pairs of broad features separated by ca. 40.0, 47.0, and 55.0 mT. The two outer pairs of wing features must be anisotropic components, since the total width of the $^{32}\text{SF}_4^-$ anisotropic spectrum is only 29.0 mT. Between -170 and -80°C , these outer features gradually weakened while an additional pair of lines, separated by ca. 20 mT and destined to become the $M_1 = \pm 1$ lines of the isotropic spectrum at higher temperatures, developed considerable intensity. The low-temperature spectra of SF_4O^- recorded below -70°C revealed a pair of anisotropic features, separated by ca. 90.1 mT, in addition to broad resonances at the isotropic positions, but otherwise the spectra were not very informative in this low-temperature region.

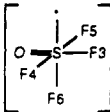
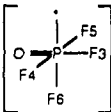
Local Density Functional Calculations. The geometries, vibrational spectra, spin populations, and atomic charges for the SF_4^- , *cis*- and *trans*- SF_4O^- , *cis*- and *trans*- PF_4O^{2-} , and SF_5 radicals were calculated using local density functional theory. The results are summarized in Tables II–IV.

For SF_4^- , a C_{4v} structure, which deviates from the planar configuration by 6.7° and has an FSF bond angle of 89.2° , was found to be the energy minimum on the potential energy surface, in excellent agreement with the results from an independent LDF calculation.¹⁶ The planar D_{4h} structure is 1.51 kcal mol $^{-1}$ higher in energy and is a transition state characterized by an imaginary frequency (ν_2 in Table II). Since the axial positions in SF_4^- are occupied by free valence electrons which can rapidly move from one side of the SF_4 plane to the other, thereby creating the possibility for inversion, the potential energy curve of the C_{4v} model of SF_4^- has two minima, one at 6.7° above and one at 6.7° below the plane. The planar D_{4h} structure represents the inversion barrier, and the energy difference of 1.51 kcal mol $^{-1}$ between the C_{4v} and the D_{4h} structures is the barrier height. The inversion mode is the symmetric out of plane deformation, $\nu_2(A_1)$, with a zero-point energy of one half of 299 cm $^{-1}$ or 0.43 kcal mol $^{-1}$. In view of the small energy required for inversion, the assumption of a D_{4h} ground-state symmetry for SF_4^- under normal conditions is not unreasonable. As can be seen from Table II, the properties of SF_4^- do not change much between the C_{4v} and the D_{4h} configurations. As expected, the largest change involves the inversion mode, i.e. the symmetric out of plane deformation mode, ν_2 .

For SF_4O^- and isoelectronic PF_4O^{2-} , the lowest energy structures are configuration III of symmetry C_{4v} (see Introduction), in which the sterically active unpaired electron is trans to the oxygen ligand. According to our calculations, the *trans* isomers of SF_4O^- and PF_4O^{2-} are 8.6 and 5.6 kcal mol $^{-1}$, respectively, lower in energy than their *cis* isomers (IV), and both isomers are minima on the potential energy surfaces. The exclusive formation of *trans*- SF_4O^- in our study is favored from energetic considerations. From reaction mechanistic arguments both isomers are about equally favored. Although the exact lengths of the axial and the equatorial fluorine bonds in SOF_5^- are unknown,^{26a} those in closely related TeOF_5^- and IOF_5^{26b} are about equal. Therefore, breakage of either fluorine bond should be about equally likely. In the previous study on PF_4O^{2-} , in which both isomers were observed,⁸ these radical anions were generated from unidentified hydrolysis products of PF_6^- and, therefore, may have involved intramolecular HF elimination from hydroxy-substituted phosphorus fluoride anions. Since such an HF elimination would involve neighboring *cis* ligands, the formation of some *cis*- PF_4O^{2-} could be readily explained.

The fact that, in the *trans*- XF_4O radical anions, the F–X–O angles are about 101° and are significantly larger than 90° demonstrates that a doubly bonded oxygen ligand is more repulsive than a sterically active unpaired valence electron. As expected, a singly bonded fluorine ligand is much less repulsive than a doubly

Table IV. Calculated Geometries, Unscaled Vibrational Spectra, Spin Populations, and Atomic Charges for the *cis*- SF_4O^- and *cis*- PF_4O^{2-} Radical Anions

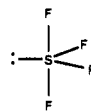
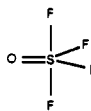
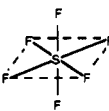
			
Geometry		C_s	C_s
rX-O (Å)		1.490	1.558
rX-F3		1.860	1.945
rX-F4, rX-F5		1.753	1.822
rX-F6		1.656	1.704
∠F3-X-O (deg)		169.0	174.1
∠F4-X-O		96.0	96.8
∠F6-X-O		103.1	101.1
∠F4-X-F6		88.2	88.7
∠F4-X-F5		168.0	166.5
∠F3-X-F4		84.2	83.3
∠F3-X-F6		87.9	84.8
Spin Populations ^a			
atom	orbital		
X	3s	0.238	0.387
X	3py	0.042	0.055
X	3pz	0.082	0.078
X	3px	0.007	0.078
X	3dxy		0.008
X	3dyz	0.010	0.008
X	3dz ²	0.029	0.008
X	3dxz	0.007	0.028
X	3dx ² -y ²		0.016
O	2s	0.002	-0.004
O	2py	0.106	0.080
O	2pz	0.070	0.028
O	2px	0.004	0.028
F3	2s		-0.002
F3	2py	0.215	0.103
F3	2pz	0.011	0.004
F3	2px		0.004
F4	2s	-0.001	-0.004
F4	2pz	-0.001	0.007
F4	2px	0.086	0.044
F5	2s	-0.001	-0.004
F5	2pz	0.086	0.044
F5	2px	-0.001	0.007
F6	2s	-0.003	-0.005
F6	2pz	0.013	0.003
F6	2px	0.001	0.003
Vibrational Frequencies (cm ⁻¹)			
		1101	991
		708	655
		644	545
		498	434
		451	405
		427	366
		399	334
		367	316
		318	279
		283	242
		270	239
		158	152
Atomic charges			
X		0.80	0.54
O		-0.37	-0.59
F3		-0.41	-0.55
F4		-0.37	-0.49
F5		-0.37	-0.49
F6		-0.28	-0.41

^aThe X–O axis is approximately the y axis, and F4, F5, and F6 are approximately in the x,z plane.

bonded oxygen but still slightly more so than an unpaired valence electron. This is shown by the F_{ax} –S– F_{eq} bond angle of 91.7° calculated for the SF_5 radical (see Table III).

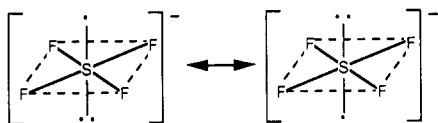
Since no experimental geometries nor vibrational frequencies are known for these radicals, with the exception of two infrared bands attributed²⁷ to SF_5 in a matrix, it was important to test the accuracy of our LDF calculations for closely related, well-known molecules. For this purpose, the geometries and vibrational spectra of SF_4 ,^{28–32} SF_4O ,^{29,30,33–36} and SF_6 ^{37,38} were calculated by the LDF method and, in Table V, are compared to the experimental data. As can be seen from this table, LDF theory duplicates well the observed geometries and vibrational frequencies, particularly if it is kept in mind that, for these types of fluorides,²² LDF theory generally predicts bond lengths which are about 0.04-Å longer than the observed ones. Therefore, the values calculated for the radicals of this study are also deemed to be good approximations to the true values, particularly if the calculated bond lengths are corrected (shortened) by about 0.04 Å. Of the two infrared bands previously reported for SF_5 in an Ar matrix,²⁷ the very intense

Table V. Calculated and Experimental Geometries and Unscaled Vibrational Spectra of SF₄, SF₄O, and SF₆

								
	calcd	obsd [29,31]	calcd	obsd [29,33, 34,36]	calcd	obsd [37,38]		
Geometry	C_{2v}		C_{2v}		O_h			
r S-F _{ax} (Å)	1.679	1.646	1.628	1.593	1.593	1.564		
r S-F _{eq}	1.607	1.545	1.590	1.535				
r S-O	...	...	1.437	1.406				
∠ F _{ax} -S-F _{ax} (deg)	172.9	173.1	163.3	164.4	180	180		
∠ F _{eq} -S-F _{eq}	100.6	101.6	112.3	114.9	90	90		
Vibrational Frequencies (cm⁻¹)								
A ₁ v ₁	826	892	A ₁ v ₁	1340	1380	A _{1g} v ₁	713	774
v ₂	560	558	v ₂	730	796	E _g v ₂	627	642
v ₃	453	532	v ₃	582	588	F _{1u} v ₃	934	948
v ₄	193	228	v ₄	511	566	v ₄	556	616
A ₂ v ₅	402	[437]	v ₅	136	174	F _{2g} v ₅	472	525
B ₁ v ₆	811	867	A ₂ v ₆	505	...	F _{2u} v ₆	309	347
v ₇	305	353	B ₁ v ₇	870	924			
B ₂ v ₈	782	730	v ₈	508	566			
v ₉	464	475	v ₉	232	265			
			B ₂ v ₁₀	837	815			
			v ₁₁	574	640			
			v ₁₂	497	447			

one at 812 cm⁻¹ is in excellent agreement with our calculated value of 809 cm⁻¹ for ν₇(E), but the frequency of the weak band observed at 552 cm⁻¹ appears somewhat high when compared to the value of 453 cm⁻¹ calculated for ν₇(E). This raises a question as to whether the 552-cm⁻¹ band belongs to SF₅.

SF₄⁻ Radical Anion. The paramagnetic species generated by γ-irradiation of Cs⁺SF₅⁻ is attributed to the novel SF₄⁻ radical anion for the following reasons. Its EPR spectrum shows the presence of four equivalent nuclei with spin *I* = 1/2 attributed to ¹⁹F, and the satellite lines reveal the presence of a nucleus of spin *I* = 3/2 at the 0.2% intensity expected for naturally abundant ³³S. Furthermore, the s-orbital spin densities on sulfur, ρ_s, and on fluorine, ρ_f, derived from the hyperfine splittings, and the *g*-factor are similar to those of the known,¹³ isoelectronic ClF₄ radical (see Table I). As shown by the LDF calculations for SF₄⁻ (see Table II) and the CNDO and INDO calculations for ClF₄,¹⁴ the most stable geometry for these two XF₄ radicals is a near-square-planar structure of approximate D_{4h} symmetry in which the electron densities above and below the plane are about equal, as depicted by the two mesomeric structures.

The small C_{4v} distortions, suggested for SF₄⁻ and ClF₄ by the LDF

(26) (a) Although the crystal structure of (Me₂N)₃S⁺SF₅O⁻ has recently been published (Heilemann, W.; Mews, R.; Pohl, S.; Saak, W. *Chem. Ber.* **1989**, 122, 427), no reliable individual bond lengths were obtained for SF₅O⁻ due to disorder of the anion. (b) In TeOF₅, the axial and the equatorial fluorine bonds are of almost equal length (see: Miller, P. K.; Abney, K. D.; Rappé, A. K.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1988**, 27, 2255), and a recent study of IOF₅ (Christe, K. O.; Curtis, E. C.; Dixon, D. A. *J. Fluorine Chem.*, in press) has shown that the same applies to this molecule and that the previously reported (Bartell, L. S.; Clippard, F. B.; Jacob, E. J. *Inorg. Chem.* **1976**, 15, 3009) structure should be revised.

(27) Smardzewski, R. R.; Fox, W. B. *J. Chem. Phys.* **1977**, 67, 2309.

(28) Sawodny, W.; Birk, K.; Fogarasi, G.; Christe, K. O. *Z. Naturforsch.*, **B 1980**, 35B, 1137.

(29) Christe, K. O.; Willner, H.; Sawodny, W. *Spectrochim. Acta, Part A* **1979**, 35A, 1351.

(30) Kimura, K.; Bauer, S. H. *J. Chem. Phys.* **1963**, 39, 3172.

(31) Tolles, W. M.; Gwinn, W. D. *J. Chem. Phys.* **1962**, 36, 1119.

(32) Inoue, H.; Naruse, A.; Hirota, E. *Bull. Chem. Soc. Jpn.* **1976**, 49, 1260.

(33) Oberhammer, H.; Boggs, J. E. *J. Mol. Struct.* **1979**, 56, 107.

(34) Gundersen, G.; Hedberg, K. J. *Chem. Phys.* **1969**, 51, 2500.

(35) Hencher, J. L.; Cruickshank, D. W. J.; Bauer, S. H. *J. Chem. Phys.* **1968**, 48, 518.

(36) Christe, K. O.; Schack, C. J.; Curtis, E. C. *Spectrochim. Acta, Part A* **1977**, 33A, 323.

(37) Shimanouchi, T. *Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.)* **1972**, 39, 33.

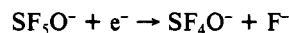
(38) McDowell, R. S.; Aldridge, J. P.; Holland, R. F. *J. Phys. Chem.* **1976**, 80, 1203.

and INDO calculations, respectively, for the minimum energy structures, are insignificant and result in inversion energy barriers which are comparable to the zero-point energies of the inversion modes in the ground states.

A comparison between the observed (see Table I) and calculated (see Table II) s-orbital spin densities of SF₄⁻ shows qualitative agreement. Although the value of 0.033 calculated for the sulfur 3s-orbital spin density of the C_{4v} structure of SF₄⁻ is smaller than that of 0.103 derived from the observed ³³S hyperfine splitting, it should be noted that the former is very sensitive to small changes in the bond angle (see Table II). A slightly larger distortion of SF₄⁻ from D_{4h} symmetry could significantly increase the calculated 3s-orbital spin density on sulfur. In view of the relatively small energy difference between the C_{4v} and the D_{4h} structures (see above), the C_{4v} distortion and hence the hfs and spin densities could, in theory, be strongly temperature dependent. However, the experimental ³³S hyperfine splitting showed virtually no difference between 20 and 70 °C. Unfortunately, precise measurements at lower temperatures were precluded by anisotropic line broadening.

Comparison of SF₄⁻ with isoelectronic ClF₄ (see Table I) shows that SF₄⁻ has a slightly smaller *g*-factor than ClF₄, as expected from the smaller spin-orbit coupling of sulfur. Comparison of SF₄⁻ with SF₅¹² shows a marked difference (see Tables I-III). In SF₄⁻ the unpaired electron is concentrated mainly in the sulfur p_z orbital, whereas in SF₅ it is mainly located in an sp-hybrid orbital, which accounts for the much larger ³³S hfs of the latter.

SF₄O⁻ Radical Anion. By analogy to the generation of the SF₄⁻ radical anion by γ-irradiation of Cs⁺SF₅⁻ (see above), the novel SF₄O⁻ radical anion was generated by γ-irradiation of Cs⁺SF₅O⁻. In both cases, the probable reaction mechanism involves the loss of a fluorine ligand due to secondary electron capture.³⁹



The observed EPR spectrum exhibits hyperfine splittings due to four equivalent fluorine atoms, with weak satellite lines of 0.2% intensity due to the naturally occurring ³³S isotope. The fact that four equivalent fluorine atoms are present in the radical leaves no doubt that the observed radical is the trans isomer (III) rather than the cis isomer (IV). By analogy with cis-PF₄O²⁻ (see Table I), cis-SF₄O⁻ would be expected to exhibit three fluorine atoms, not necessarily equivalent, with large hfs and one fluorine atom with a very small hfs. As discussed above, the exclusive formation of the trans-SF₄O⁻ isomer is probably due to both energetic and reaction mechanistic reasons. If the fluorine atom were eliminated from the SF₅O⁻ precursor by random electron capture, the cis isomer would be four times more likely to form than the trans isomer.

As can be seen from Tables I and III, the orbital spin densities in isoelectronic trans-SF₄O⁻ and trans-PF₄O²⁻ are similar to those in SF₅ but deviate significantly from those in SF₄⁻. This indicates that in trans-SF₄O⁻ and SF₅ the unpaired electron is concentrated mainly in an axial sulfur sp-hybrid orbital, which accounts for their large ³³S hfs (see Table I). The experimentally found, high values of the 3s-orbital spin densities on sulfur in trans-SF₄O⁻ and SF₅ are also supported by the results from the LDF calculations (see Table III). However, the relatively large changes in the spin densities between isoelectronic trans-SF₄O⁻ and trans-PF₄O²⁻, predicted by the LDF calculations (see Table III), are not substantiated by the experimental data given in Table I. As indicated by the LDF calculations (see Table III), the axial oxygen or fluorine ligands in trans-SF₄O⁻ or SF₅ have little spin density, contrary to the case of cis-SF₄O⁻, for which the calculated total spin density on oxygen is 0.184 (see Table IV).

Bonding in SF₄⁻ and SF₄O⁻. For SF₄⁻, the LDF calculated and corrected (-0.04 Å) S-F bond length of about 1.75 Å suggests

(39) This mechanism has been demonstrated for electron capture by F₃NO and FClO₃, since their radical anions were observed by EPR to dissociate into F₂NO and ClO₃, respectively, on annealing to higher temperature. Nishikida, K.; Williams, F. J. *Am. Chem. Soc.* **1975**, 97, 7166. Hasegawa, A.; Hudson, R. L.; Kikuchi, O.; Nishikida, K.; Williams, F. J. *Am. Chem. Soc.* **1981**, 103, 3436. Hasegawa, A.; Williams, F. J. *Am. Chem. Soc.* **1981**, 103, 7051.

long and weak bonds, when compared to normal S-F single bonds, which have values ranging from about 1.53 to 1.56 Å (see Table V). These long S-F bonds in SF_4^- , combined with the above analysis of the electron spin density distribution, suggest the following idealized bonding scheme for SF_4^- . The four equatorial fluorines are bound to sulfur by two semi-ionic, three-center-four-electron bond pairs⁴⁰⁻⁴³ involving the p_x and p_y orbitals of sulfur. The third p orbital of sulfur, the p_z orbital, accommodates primarily the unpaired free electron, while the remaining sulfur free valence electron pair is localized mainly in its s orbital.

For $\text{trans-SF}_4\text{O}^-$, the bonding of the four equatorial fluorines (calculated bond length = $1.77 - 0.04 = 1.73$ Å) is similar to that proposed above for SF_4^- , i.e. weak, semi-ionic, three-center-four-electron bonds involving the sulfur p_x and p_y orbitals. The LDF calculated S-O bond length ($1.464 - 0.04 = 1.42$ Å) is comparable to normal S=O double bonds (r_{SO} in $\text{SF}_4\text{O} = 1.406$ Å),³⁴ supporting, for oxygen, a predominantly covalent bonding scheme through a sulfur sp_z hybrid, which also accommodates, to a large extent, the unpaired free electron. The bonding scheme in SF_4O^- is completed by the formation of an additional double bond between sulfur and oxygen.

In SF_5 , the basic bonding scheme somewhat resembles that in $\text{trans-SF}_4\text{O}^-$, but the ionic character of the four equatorial bonds is less pronounced. This is not surprising in view of the lack of a formal negative charge (neutral radical versus radical anion) which strongly enhances semi-ionic bonding. This interpretation

is nicely supported by the atomic charges calculated by the LDF method for these radicals. As predicted from the above analysis, the negative charges on the four equatorial fluorine ligands decrease from -0.431 in SF_4^- to -0.376 in $\text{trans-SF}_4\text{O}^-$ to -0.212 in SF_5 .

Conclusions

The novel SF_4^- and $\text{trans-SF}_4\text{O}^-$ radical anions⁴⁴ were prepared by γ -irradiation of SF_5^- and SF_5O^- containing salts, respectively, and were characterized by their isotropic EPR spectra, which permitted the determination of the s -orbital electron spin densities. Although anisotropic EPR data were not available for a complete electron spin density analysis, the nature and bonding of these interesting radical anions were elucidated using local density functional calculations. LDF theory was also used to predict the geometries and vibrational spectra of these and other closely related radicals. The reliability of these calculations was confirmed by comparison with experimental data from several well-known sulfur fluorides and oxyfluorides.

Acknowledgment. The work at Rocketdyne was financially supported by both the U.S. Army Research Office and the Air Force Phillips Laboratories. The work at the University of Tennessee was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (Grant #DE-FG05-88ER13852).

(40) Pimentel, G. C. *J. Chem. Phys.* **1951**, *19*, 446.

(41) Hach, R. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 4321.

(42) Rundle, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 112.

(43) Wiebenga, E. H.; Havinga, E. E.; Boswijk, K. H. *Adv. Inorg. Chem. Radiochem.* **1961**, *3*, 158.

(44) Morton and Preston have noted in ref 6 that for isoelectronic pairs of radicals the F^{19} hyperfine interaction is always larger in the radical anion than in the neutral species. The results of the present study are in accord with this generalization, since the F^{19} splittings for SF_4^- and SF_4O^- are greater than those for ClF_4 and SF_5 , respectively (see Table I).

Motional Processes in Solid Organotin Polymers Investigated by One- and Two-Dimensional ^{13}C and ^{119}Sn NMR Spectroscopy

Jörg Kümmerlen and Angelika Sebald*

Contribution from the Bayerisches Geoinstitut, Universität Bayreuth, Postfach 10 12 51, W-8580 Bayreuth, Germany. Received August 24, 1992

Abstract: Variable-temperature one- and two-dimensional ^{13}C CP/MAS spectroscopy of a series of six crystalline trimethyltin compounds has demonstrated that the rate of Me_3Sn reorientation is significant on the NMR time scale. The combination of line shape analyses of the exchange-broadened ^{13}C CP/MAS spectra with rates obtained from 2D exchange spectra yields activation energies in the range of 38.6–72.5 kJ mol⁻¹ for this series of compounds. Comparison of our NMR results with information from X-ray diffraction measurements leads us to postulate a $2\pi/3$ propeller-like jump around the tin-oxygen or tin-nitrogen bond, respectively, as the reorientation mechanism. Rotor-synchronized ^{119}Sn 2D magnetization-transfer experiments strongly support this view and indicate a rigid backbone for these chainlike polymers.

Introduction

Nuclear magnetic resonance (NMR) spectroscopy has proved to be a powerful tool for the elucidation of various types of molecular nonrigidity and fluxional behavior of organometallic complexes and molecules, both in solution and in the solid state.¹⁻³ Coherent averaging of anisotropic spin interactions by magic angle spinning (MAS), in combination with high power proton decou-

pling and cross-polarization (CP) techniques, enables the adoption of a variety of solution-state NMR techniques for the investigation of dynamic processes in solids, exploiting the properties of heteronuclei like ^{13}C or others. In line with the development of high-resolution solid-state NMR spectroscopy, experimental methods for the investigation of such processes have become available, ranging from wide line and relaxation measurements on abundant nuclei to magnetization-transfer experiments in one, two, and three dimensions.^{4,5} This wide range of experimental

(1) Andrew, E. R.; Eades, R. G. *Proc. Roy. Soc. London* **1953**, *A218*, 537–552.

(2) Andrew, E. R. *J. Chem. Phys.* **1950**, *18*, 607–618.

(3) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London and New York, 1982.

(4) Blümich, B.; Spiess, H. W. *Angew. Chem.* **1988**, *100*, 1716–1734; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1655.

(5) Spiess, H. W. *Chem. Rev.* **1991**, *91*, 1321–1338.

Integrating eq 3, with the aid of the integral $Ei(-x) = -\int_{\infty}^x (e^{-x}/x) \approx e^{-x}(x^{-2} - x^{-1})$ for $x \gg 1$, yields

$$\chi = \frac{K}{\alpha} \left(\frac{RT}{\Delta H_s} \right) \exp \left[-\frac{\Delta H_s}{RT} \right] \dots \quad (5)$$

The heat of sublimation ΔH_s is determined by plotting the TGA data as shown in Figure 4. From the slopes of $\ln(\chi/T)$ versus $1/T$ curves, we obtain $\Delta H_s = 30, 35$, and 39 kcal/mol for $\alpha = 0.3, 1.2$, and 5 °C/min, respectively. Also from $\ln(\alpha/T)$ vs $1/T$ plots for a given χ , e.g., 0.1 , we obtain $\Delta H_s = 40$ kcal/mol.

The heat of sublimation of C_{60} powders has been reported previously to be 40 kcal/mol.¹⁴ Our result of $\Delta H_s = 39$ kcal/mol, determined at a scan rate of 5.0 °C/min, is in a good agreement with the reported data. The cause of the lower values, e.g., 30 and 35 kcal/mol obtained at lower rates of 0.3 and 1.2 °C/min, is not clear. Haufler et al.¹ reported a much lower value of $\Delta H_s \sim 22$ kcal/mol. It has been suggested¹⁴ that the low values of ΔH_s observed may be due to the less structurally ordered C_{60} powders which undergo a change during the experiment. Alternatively, we proposed here that the presence of nonuniform defective microstructure, such as stacking fault and grain boundary, is

responsible for the lower heats of sublimation derived from TGA measurements. C_{60} molecules at such defective structures sublime at lower temperature than does those in a bulk crystal grain, and in TGA scan it contributes to the weight loss in the low-temperature regime. This results in the drastic reduction in the slope of χ/T vs $1/T$ curve and thus in the apparent heat of sublimation determined. To test this viewpoint, we prepared a new batch of C_{60} powders sublimed from a purified C_{60} extract at a slower rate. The new sample showed sharp X-ray diffraction lines, indicating a good crystallinity. The new sample shows no detectable structural relaxation in TGA scan up to 450 °C. The TGA curve at 0.3 °C/min of this new sample diverges starting ≤ 400 °C and merges again ~ 620 °C with that of the less ordered structural sample (see Figure 4). Although the deviation is small, the heat of sublimation of the new sample, ~ 35 kcal/mol, is higher by 5 kcal/mol. We may conclude that the heats of sublimation obtained are of the lower limiting values. The $\Delta H_s \sim 40$ kcal/mol of C_{60} powders is low as compared with that of graphites ($\Delta H_s \sim 170$ kcal/mol). This reflects the weak van der Waals bonding among C_{60} molecules in the fcc structure.^{15,16}

(14) Pan, C.; Sampson, M. P.; Chai, Y.; Hauge, R. H.; Margrave, J. L. *J. Phys. Chem.* 1991, 95, 2944.

(15) Fischer, J. E.; Heiney, P. A.; McGhie, A. R. *Science* 1991, 252, 1288.

(16) Fleming, R. M.; Hessen, B.; Kortan, A. R.; Siegrist, T.; Marsh, P.; Murphy, D. W.; Haddon, R. C.; Tycho, R.; Dabbagh, G.; Muijsce, A. M.; Kaplan, M. L.; Zahurak, S. M. *Mater. Res. Soc. Symp. Proc.* 1991, 206, 691.

Nitrosyl Hypofluorite: Local Density Functional Study of a Problem Case for Theoretical Methods†

David A. Dixon*‡ and Karl O. Christe§

Central Research and Development Department, E. I. du Pont de Nemours and Company, Inc., Experimental Station, Wilmington, Delaware 19880, and Rocketdyne, A Division of Rockwell International Corporation, Canoga Park, California 91303 (Received: October 21, 1991; In Final Form: December 17, 1991)

Local density functional (LDF) theory can successfully reproduce the previously published vibrational spectra and the salient geometrical parameters derived from them for FONO for which conventional ab initio methods (CISD/6-31G*) fail. LDF theory was used to calculate the geometries, vibrational spectra, force fields, and charge distributions for the three isomers *cis*-FONO, *trans*-FONO, and FNO₂. It is shown that FNO₂ is 40.8 kcal mol⁻¹ more stable than *cis*-FONO, which in turn is favored by 25.2 kcal mol⁻¹ over the *trans* isomer. It is shown that the previously published approximate mode descriptions for FONO are correct but that the observed spectra must be due to *cis*-FONO and not to the *trans* isomer as previously proposed. The bonding in *cis*-FONO is best rationalized in terms of an F atom loosely bonded through an oxygen atom to an NO₂ molecule, resulting in the following structural parameters: $r_{F-O} = 1.673$ Å, $r_{FO-N} = 1.216$ Å, $r_{N-O} = 1.190$ Å, $\angle FON = 118.0^\circ$, and $\angle ONO = 135.2^\circ$.

Introduction

Although much progress has been made during the past 20 years in the field of ab initio calculations of the geometries and energetics of molecules, there have been a number of cases which have been extremely difficult to compute with conventional methods. A classic example for such a "problem" molecule is FOOF, for which very high level calculations (CAS/CCI or CCSD(T)) with a large basis set were required to duplicate the experimental geometry.^{1a} An even more difficult test is the duplication of the observed vibrational spectra. In a recent study,^{1b} it has been shown that density functional theory (which is an ab initio method) in the local density approximation (LDF)² can predict both the structure and harmonic frequencies of FOOF.

TABLE I: Geometry Parameters for FNO₂^a

param	LDF	expt ¹³
N-F	1.487	1.467
N-O	1.190	1.180
$\angle(F-N-O)$	111.8	112
$\angle(O-N-O)$	136.4	136

^a Bond distances in angstroms, bond angles in degrees.

Noble has recently called attention³ to another similar "problem" molecule, FONO, or nitrosyl hypofluorite. This

† Contribution No. 6018.

‡ E. I. du Pont de Nemours and Co., Inc.

§ Rocketdyne Division, Rockwell International Corp.

(1) (a) See: Scuseria, G. E. *J. Chem. Phys.* 1991, 94, 442, for the most recent ab initio molecular orbital calculations. (b) See: Dixon, D. A.; Andzelm, J.; Fitzgerald, G.; Wimmer, E. *J. Phys. Chem.* 1991, 95, 9197, for the LDF calculations on FOOF and a discussion of previous calculations.

TABLE II: Vibrational Frequencies, Potential Energy Distribution, and Assignments for FNO₂

mode designation in point group C _{2v}	approx description of mode	frequency, cm ⁻¹		potential energy distribution LDF
		expt ^{11,12}	LDF	
A ₁ ν ₁	ν sym NO ₂	1310	1361	-0.730 (1)-0.347 (2)-0.589 (3)
A ₁ ν ₂	ν NF	568	590	0.042 (1)-0.816 (2)+0.577 (3)
A ₁ ν ₃	δ sciss NO ₂	822	821	-0.027 (1)-0.504 (2)-0.864 (3)
B ₁ ν ₄	ν asym NO ₂	1792	1892	-0.808 (4)+0.590 (5)
B ₁ ν ₅	δ FNO ₂ in plane	560	541	0.037 (4)+0.999 (5)
B ₂ ν ₆	δ FNO ₂ out of plane	742	740	-1.0 (6)

^aThe following symmetry coordinates were used for the PED: (1) N-O1 + N-O2; (2) N-F; (3) O1-N-O2; (4) N-O1 - N-O2; (5) F-N-O1 - F-N-O2; (6) F-NO₂.

molecule has been observed only in a matrix by infrared spectroscopy.⁴ A force constant analysis of these spectra suggested a planar trans configuration with a weak F-O bond⁵ which could not be duplicated by traditional ab initio molecular orbital methods.³ In view of the excellent results^{1b} of LDF theory for FOOF, which has a structure similar to that of FONO, it was interesting to examine whether this theory can also master the FONO problem.

Computational Methods

The calculations described below were done in the local density functional approximation² by using the program system DMOL.^{6,7} The atomic basis functions are given numerically on an atom-centered, spherical-polar mesh. The radial portion of the grid is obtained from the solution of the atomic LDF equations by numerical methods. The use of exact spherical atom results offers some advantages. The molecule will dissociate exactly to its atoms within the LDF framework, although this does not guarantee correct dissociation energies. Furthermore, because of the quality of the atomic basis sets, basis set superposition effects should be minimized and correct behavior at the nucleus is obtained.

Since the basis sets are numerical, the various integrals arising from the expression for the energy need to be evaluated over a grid. The integration points are generated in terms of radial functions and spherical harmonics. The number of radial points N_R is given as

$$N_R = 1.2 \times 14(Z + 2)^{1/3}$$

where Z is the atomic number. The maximum distance for any function is 12 au. The angular integration points N_θ are generated at the N_R radial points to form shells around each nucleus. The value of N_θ ranges from 14 to 302 depending on the behavior of the density.⁸ The Coulomb potential corresponding to the electron repulsion term is determined directly from the electron density by solving Poisson's equation. In DMOL, the form for the exchange-correlation energy of the uniform electron gas is that derived by von Barth and Hedin.⁹

TABLE III: Symmetry Force Constants (mdyn/Å) of FNO₂

	1	2	3	4	5	6
1	13.97					
2	1.13	3.03				
3	0.56	-0.71	1.82			
4				11.44		
5				0.51	1.26	
6						0.40

All of the DMOL calculations were done with a double numerical basis set augmented by polarization functions. This can be considered in terms of size, for comparison to traditional molecular orbital calculations, as a polarized double- ζ basis set. However, because of the use of exact numerical solutions for the atom, this basis set is of significantly higher quality than a normal molecular orbital polarized double- ζ basis set. The multipolar fitting functions for the model density used to evaluate the effective potential have angular momentum numbers, l , one greater than that of the polarization function. Since all of the atoms have d polarization functions, the value of l for the fitting function is 3.

Geometries were optimized by using analytic gradient methods.⁷ There are two problems with evaluating gradients in the LDF framework which are due to the numerical methods that are used. The first is that the energy minimum does not necessarily correspond exactly to the point with a zero derivative. The second is that the sum of the gradients may not always be zero as required for translational invariance. These tend to introduce errors on the order of 0.001 Å in the calculation of the coordinates if both a reasonable grid and basis set are used. This gives bond lengths and angles with reasonable error limits. The difference of 0.001 Å is about an order of magnitude smaller than the accuracy of the LDF geometries as compared to experiment. The frequencies were determined by numerical differentiation of the gradient. A two point difference formula was used and a displacement of 0.01 au. The force constant analysis was done with the BMATRIX program of Komornicki.¹⁰

Results and Discussion

Nitryl Fluoride, FNO₂. Since nitryl fluoride, FNO₂, is isomeric with FONO and well characterized,¹¹⁻¹³ the quality of the LDF calculation was first examined for this molecule. As shown in Table I, the agreement between the calculated and experimental structures¹³ is very good, with the LDF bond distances being 0.01-0.02 Å longer than the experimental values as found for other similar compounds.^{2f,s} The vibrational spectrum and the assignments in terms of internal coordinates are given in Table II and the symmetry force constants in Table III. The agreement between theory and experiment^{11,12} is also quite good considering that the calculated values correspond to harmonic values and the experimental ones include the effects of anharmonicity.

(2) (a) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989. (b) Salahub, D. R. In *Ab Initio Methods in Quantum Methods in Quantum Chemistry-II*; Lawley, K. P., Ed.; Wiley: New York, 1987; p 447. (c) Wimmer, E.; Freeman, A. J.; Fu, C.-L.; Cao, P.-L.; Chou, S.-H.; Delley, B. In *Supercomputer Research in Chemistry and Chemical Engineering*; Jensen, K. F., Truhlar, D. G., Eds.; ACS Symposium Series; American Chemical Society: Washington, D.C., 1987; p 49. (d) Jones, R. O.; Gunnarsson, O. *Rev. Mod. Phys.* **1989**, *61*, 689. (e) Zeigler, T. *Chem. Rev.* **1991**, *91*, 651. (f) Dixon, D. A.; Andzelm, A.; Fitzgerald, Wimmer, E.; Delley, B. In *Science and Engineering on Supercomputers*; Pitcher, E. J., Ed.; Computational Science Publications: Southampton, England, 1990; p 285. (g) Dixon, D. A.; Andzelm, J.; Fitzgerald, G.; Wimmer, E.; Jasien, P. In *Density Functional Methods in Chemistry*; Labanowski, J., Andzelm, J., Eds.; Springer-Verlag: New York, 1991; p 33.

(3) Noble, P. N. *J. Phys. Chem.* **1991**, *95*, 4695.

(4) Smardzewski, R. R.; Fox, W. B. *J. Chem. Phys.* **1974**, *60*, 2980.

(5) Sorenson, S. A.; Noble, P. N. *J. Chem. Phys.* **1982**, *77*, 2483.

(6) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508. DMOL is available commercially from BIOSYM Technologies, San Diego, CA.

(7) Delley, B. In *Density Functional Methods in Chemistry*; Labanowski, J., Andzelm, J., Eds.; Springer-Verlag: New York, 1991; p 101.

(8) This grid can be obtained by using the FINE parameter in DMOL.

(9) von Barth, U.; Hedin, L. *J. Phys. C* **1972**, *5*, 1629.

(10) Komornicki, A. Private communication. This program was developed to help in analyzing the results from the GRADSCF program system.

(11) Christe, K. O.; Schack, C. J.; Wilson, R. D. *Inorg. Chem.* **1974**, *13*, 2811.

(12) Bernitt, D. L.; Miller, R. H.; Hisatsune, I. C. *Spectrochim. Acta, Part A* **1967**, *23*, 237.

(13) Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref Data* **1979**, *8*, 619.

TABLE IV: Geometry Parameters^a Computed by Different Methods for FONO

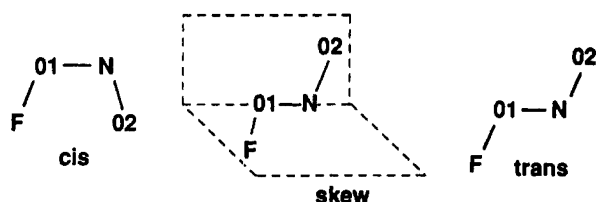
param	computational method						
	LDF		force field analysis ⁵ trans	HF/6-31+G ³		CISD/6-31+G ³	
	cis	trans		cis	trans	cis	trans
F-O1	1.673	1.888	1.57	1.365	1.360	1.405	1.398
N-O1	1.216	1.163	1.27	1.366	1.381	1.399	1.425
N-O2	1.190	1.193	1.18	1.141	1.143	1.159	1.161
∠F-O1-N	118.0	106.5	110	111.3	104.7	110.6	104.0
∠O1-N-O2	135.2	152.1	160	116.0	108.9	115.9	108.0

^a Bond distances in angstroms, bond angles in degrees.

TABLE V: Mulliken Charges (e) for FONO

atom	cis	trans	atom	cis	trans
O1	0.08	0.06	F	-0.30	-0.41
N	0.29	0.42	O2	-0.07	-0.07

Nitrosyl Hypofluorite, FONO. Whereas the FNO₂ molecule is not particularly difficult to calculate by conventional ab initio methods, its FONO isomer is a real "problem" molecule³ and a challenge to almost any computational method. The FONO molecule could exist either as a cis, a skew, or a trans isomer:



LDF calculations starting with a skew structure and a dihedral angle of 90° led to the cis configuration. The cis isomer was found to be 25.2 kcal mol⁻¹ more stable than the trans and 40.8 kcal mol⁻¹ less stable than FNO₂. The geometry parameters calculated by the LDF method for cis- and trans-FONO are shown in Table IV and are compared to those either derived from the force field analysis⁵ of the observed vibrational spectra⁴ or calculated by conventional ab initio methods.³ As can be seen, only the LDF values approximate the "experimental" bonding parameters derived from the force-field analysis⁵ with the cis isomer resulting in a better agreement. The latter fact is no surprise as the cis isomer is energetically favored over the trans isomer by 25.2 kcal mol⁻¹. For the LDF computed trans isomer, the F-O bond is very long and also the N-O1 bond is shorter than the terminal N-O bond, which is not expected as two atoms are bonded to this oxygen (O1) as compared to a single atom bonded to the terminal oxygen. Unfortunately, the previous force-field analysis⁵ has been carried out only for the trans isomer using vibrational frequencies which belong to the cis isomer (see below). If the force-field analysis⁵ had been carried out with the more likely cis geometry, the agreement with the cis isomer LDF values would certainly have been better.

The geometry calculated by the LDF method for cis-FONO is very plausible. The F-O bond length is 0.1 Å longer than that in FOOF (1.575 Å experimental¹³ and 1.563 Å calculated¹), as expected from the lower thermal stability of FONO. The two N-O bond distances are quite similar with oxygen bonded to the F having an N-O bond distance 0.026 Å longer than the terminal N-O distance. The structure of the NO₂ fragment is very similar

to that of the free NO₂ radical which has an N-O distance of 1.197 Å and an O-N-O bond angle of 133.8°. The F-O1-N bond angle is near 120° and is somewhat larger than the tetrahedral OOF bond angle in FOOF. These results show that the FONO structure is significantly different from that of cis-nitrous acid¹³ and more closely resembles that of FOOF. Furthermore, the data in Table IV demonstrate that in agreement with the findings¹ for FOOF, the molecular orbital CISD/6-31G* calculations based on a single configuration³ fail to predict the correct structure for FONO.

The main differences between the cis and the trans configurations of FONO are the following. In trans-FONO, the F-O bond length has increased by 0.2 Å. At the same time the average N-O bond length has shortened by about 0.02 Å and the O-N-O bond angle has significantly increased by 17°. These changes demonstrate that in trans-FONO the contributions from the ionic [O=N=O]⁺F⁻ structure have significantly increased. This interpretation is confirmed by the Mulliken populations given in Table V, which show that the ionic character increases from cis-FONO to trans-FONO.

The vibrational frequencies were calculated for both cis- and trans-FONO and, together with their assignments and potential energy distributions, are summarized in Table VI. As can be seen from this table, the experimentally observed⁴ frequencies must belong to the energetically favored cis isomer and not, as previously assumed,⁵ to the trans isomer. The agreement between the computed and experimental frequencies is quite good considering the difficulty of this problem. As for FNO₂ (see above), most of the fundamental vibrations of FONO are not pure vibrations but strong mixtures of several symmetry coordinates. The present analysis confirms the approximate mode descriptions previously proposed⁵ on the basis of the observed⁴ isotopic shifts. Thus, the 1716-cm⁻¹ transition is mainly an antisymmetric combination of the two N-O stretching coordinates with a larger contribution from the terminal N-O2 stretch. The 1200-cm⁻¹ transition is mainly a symmetric combination of the two N-O stretching coordinates with a larger contribution from the internal N-O1 stretch. The two bending motions, ν₄ and ν₅, also contribute significantly to these two transitions. The 412-cm⁻¹ transition involves mainly the stretching of the O-F bond and therefore is properly assigned as the O-F stretching mode, whereas the 702-cm⁻¹ transition is mainly due to the ONO scissoring mode. The fact that for FONO the computed O-F stretching frequency is 115 cm⁻¹ higher than the observed one is consistent with the previous findings¹ for FOOF, where the calculated stretches (749 and 715 cm⁻¹) were also about 110 cm⁻¹ higher than the observed ones (630 and 615 cm⁻¹).¹⁴ The lowest frequency vibration

TABLE VI: Vibrational Frequencies, Potential Energy Distribution,^a and Assignments for FONO

mode in designation	approx description of mode	expt ⁴	PED frequencies, cm ⁻¹					
			LDF					
			cis			trans		
A' ν ₁	ν NO ₂	1716	1810	0.75 (1)-0.52 (2)-0.21 (4)+0.34 (5)	2090	0.67 (1)-0.72 (2)		
A' ν ₂	ν NO1	1200	1217	-0.38 (1)-0.83 (2)+0.25 (4)+0.32 (5)	1264	-0.63 (1)-0.54 (2)+0.16 (3)+0.30 (4)+0.43 (5)		
A' ν ₃	ν OF	412	527	-0.16 (2)+0.76 (3)+0.44 (4)-0.45 (5)	470	-0.66 (3)+0.58 (4)+0.48 (5)		
A' ν ₄	δ ONO in plane	702	721	-0.14 (2)-0.10 (3)+0.85 (4)-0.48 (5)	148	0.13 (3)+0.97 (4)-0.17 (5)		
A' ν ₅	δ FNO in plane	166	0.13 (3)+0.50 (4)+0.86 (5)	254	0.17 (3)+0.77 (4)+0.61 (5)			
A'' ν ₆	torsion	522	1.0 (6)	380	1.0 (6)			

^a The following symmetry coordinates were used for the PED: (1) N-O2; (2) N-O1; (3) O1-F; (4) O1-N-O2; (5) F-O1-N; (6) F-O1-N-O2.

TABLE VII: Symmetry Force Constants (mdyn/Å) for FONO

	1	2	3	4	5	6
LDF Cis						
1	13.02					
2	1.38	9.29				
3	0.23	1.03	1.95			
4	0.46	1.14	-0.53	1.12		
5	-0.09	-0.48	0.16	-0.25	0.57	
6						0.23
LDF Trans						
1	12.78					
2	0.55	14.34				
3	0.40	0.14	1.08			
4	0.51	0.85	-0.09	0.19		
5	-0.16	0.11	0.16	-0.09	0.48	
6						0.09
Experimental, Using Cis Frequencies and Trans Configuration and Assuming $\nu_5 = 205 \text{ cm}^{-1}$ (refs 4, 5) ^a						
1	13.06					
2	2.52	8.48				
3	0	0	1.01			
4	0.90	-0.27	0.43	1.32		
5	0	0	0	0	0.30	

^aIn the "experimental" force field, the deformation and stretch-bend interaction constants have been normalized for distance and have dimensions of mdyn Å rad⁻² and mdyn rad⁻¹, respectively.

predicted (166 cm⁻¹) is below the spectrometer cutoff of the previous experimental study⁴ and, therefore, would not have been observed. Thus, the calculations for *cis*-FONO can account for all the observed features, and the approximate mode descriptions previously given⁵ by Sorenson and Noble are correct, although made for the incorrect trans isomer. In view of the ab initio CISD/6-31G* calculations failing to yield a correct geometry for FONO (see above), it is also not surprising that they could not reproduce³ the experimentally observed frequencies.

The force constants calculated by the LDF method for *cis*- and *trans*-FONO are given in Table VII and are compared to the force

field previously reported⁵ for *trans*-FONO using the experimental⁴ *cis*-FONO frequencies and isotopic shifts for ν_1 - ν_4 and assuming a frequency of 205 cm⁻¹ for ν_5 . In spite of the obvious shortcomings of this "experimental" force field, it can be seen that it agrees much better with the LDF *cis*-isomer force field than with the *trans*-isomer one. This lends further support to our conviction that the previously reported infrared spectrum must be due to the *cis* and not to the *trans* isomer of FONO.

The force field of *cis*-FONO (see Table VII) is in good agreement with our expectations¹ for such a molecule. It shows significant coupling between the two NO stretches and between the internal N-O1 stretch and the O-F stretch and ONO scissoring mode. The suggested large difference of 3.73 mdyn/Å between the two N-O stretching force constants is somewhat surprising in view of their relatively small difference in bond lengths of only 0.026 Å. This force constant difference strongly depends on the values of the interaction force constants which are quite large in FONO. The calculated LDF force field and geometry, together with the available experimental isotopic shifts,⁴ could be used to fine tune the force field and to verify the large difference in the N-O stretching force constants. This large difference could be caused by strong perturbations in the electronic structure of the ONO fragment of FONO due to the weakly bonded fluorine atom.

Conclusion

The LDF method is well suited for the prediction of the structures and vibrational spectra of "problem" compounds such as FOF and FONO for which conventional ab initio molecular orbital methods at the CISD/6-31G* level fail. Furthermore, the vibrational spectra previously reported⁴ for FONO and attributed to its *trans* isomer are compatible only with the *cis* isomer. The bonding in *cis*-FONO resembles that in FOF and consists of a fluoride ligand loosely coupled through an oxygen atom to the NO₂ molecule, thus resulting in weak F-O and strong NO₂ bonds.

Acknowledgment. K.O.C. is grateful to the U.S. Army Research Office and the U.S. Air Force Phillips Laboratory for financial support.

(14) Kim, K. C.; Campbell, G. M. *J. Mol. Struct.* **1985**, *129*, 263.

Forced Electrochemical Nonlinear Oscillator Assembled on Rotating Ring-Disk Electrodes

Seiichiro Nakabayashi and Akira Kira*

The Institute of Physical and Chemical Research (RIKEN), Wako-shi, Saitama 351, Japan
(Received: November 12, 1991)

Self-sustained potential oscillation was observed on a polycrystalline platinum ring electrode under the galvanostatic (constant current) electrochemical oxidation of formaldehyde in a rotating ring-disk electrode cell. When a pulsed stream of hydrogen was supplied to the ring electrode from the disk electrode, the self-sustained oscillation changed to the forced oscillation under certain conditions.

Introduction

Some chemical reactions oscillate. The Belousov-Zhabotinski reaction is famous along oscillating homogeneous reactions.¹ In heterogeneous reactions, the catalytic oxidation of carbon mon-

oxide on the platinum surface is an established oscillating reaction.^{2,3} Recently, instabilities in electrochemical systems have attracted great interest.⁴⁻⁹ Some of them show transition into

(1) Scott, S. K. *Chemical Chaos*; Clarendon Press: Oxford, U.K., 1991; and references cited therein.

(2) Fink, T.; Imbihl, R.; Ertl, G. *J. Chem. Phys.* **1989**, *91*, 5002.
(3) Rotermund, H. H.; Jakubith, S.; von Oertzen, A.; Ertl, G. *J. Chem. Phys.* **1989**, *91*, 4942.
(4) Basset, M. R.; Hudson, J. L. *J. Phys. Chem.* **1988**, *92*, 6963.

Nitrogen Pentafluoride: Covalent NF_5 versus Ionic NF_4^+F^- and Studies on the Instability of the Latter

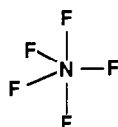
Karl O. Christe* and William W. Wilson

Contribution from Rocketdyne, A Division of Rockwell International Corporation, Canoga Park, California 91039-7922. Received June 9, 1992

Abstract: Recent ab initio calculations suggesting that covalent NF_5 and even NF_6^- are vibrationally stable and might be experimentally accessible prompted us to critically evaluate the presently available theoretical and experimental data for NF_5 and to carry out experiments on the stability of ionic NF_4^+F^- . It is shown that covalent NF_5 of D_{3h} symmetry and crystalline NF_4^+F^- should be of comparable energy but that covalent NF_5 should suffer from severe ligand-crowding effects that would make its synthesis experimentally very difficult. On the other hand, crystalline NF_4^+F^- should be readily accessible from the well-known solvated NF_4^+ and F^- ions. The recent discoveries of a convenient synthesis of truly anhydrous $\text{N}(\text{CH}_3)_4\text{F}$ as a source of soluble "naked" fluoride ions and of solvents which possess sufficient kinetic stability toward strong oxidizers allowed us to carry out experiments on the thermal stability of NF_4^+F^- . It is shown that at temperatures as low as -142°C crystalline NF_4^+F^- is unstable toward decomposition to NF_3 and F_2 , a process which is calculated to be exothermic by about 32 kcal mol^{-1} .

Introduction

Ever since the first successful synthesis of the NF_4^+ cation in 1966,¹ the possible existence of its parent molecule, NF_5 , has been a challenge to both experimental chemists²⁻¹⁰ and theoreticians.¹¹⁻¹⁴ Although the experimentalists have so far failed to isolate NF_5 , interest in its synthesis was renewed by recent ab initio calculations which suggested that NF_5 is a vibrationally stable molecule^{13,14} and that even NF_6^- might be structurally stable.¹⁵ Since NF_5 could exist either as a covalent, trigonal pyramidal molecule of D_{3h} symmetry

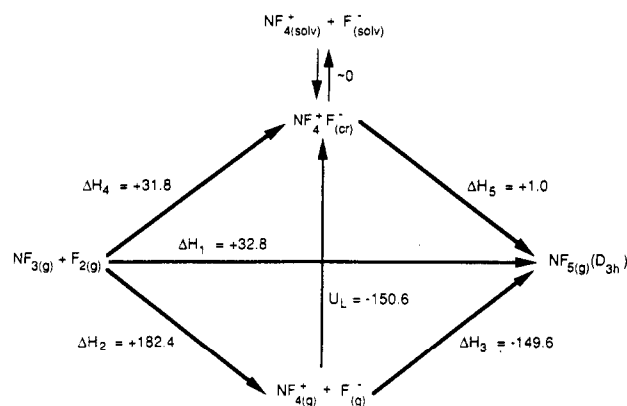


or as an ionic NF_4^+F^- salt, it was necessary to evaluate the relative energies of the two forms and their synthetic accessibility in view of previously published²⁻¹⁴ and new experimental data.

Results and Discussion

The relative energies of covalent NF_5 and ionic NF_4^+F^- with respect to each other and to NF_3 and F_2 can be estimated from a Born-Haber cycle using the following data:

- (1) Christe, K. O.; Guertin, J. P.; Pavlath, A. E. *Inorg. Nucl. Chem. Lett.* **1966**, 2, 83; U.S. Patent 3503719, 1970.
- (2) Miller, A. R.; Tsukimura, R. R.; Velten, R. *Science (Washington, D.C.)* **1967**, 688.
- (3) Goetschel, C. T.; Campanile, V. A.; Curtis, R. M.; Loos, K. R.; Wagner, C. D.; Wilson, J. N. *Inorg. Chem.* **1972**, 11, 1696.
- (4) Solomon, I. J.; Keith, J. N.; Snelson, A. *J. Fluorine Chem.* **1972/73**, 2, 129.
- (5) Olah, G. A.; Donovan, D. J.; Shen, J.; Klopman, G. *J. Am. Chem. Soc.* **1975**, 97, 3559.
- (6) Christe, K. O.; Schack, C. J.; Wilson, R. D. *Inorg. Chem.* **1976**, 15, 1275.
- (7) Keith, J. N.; Solomon, I. J.; Sheft, I.; Hyman, H. *Inorg. Nucl. Chem.—Herbert H. Hyman Mem. Vol.* **1976**, 143.
- (8) Christe, K. O.; Wilson, R. D.; Goldberg, I. B. *Inorg. Chem.* **1979**, 18, 2572.
- (9) Bougon, R.; Bui Huy, T.; Burgess, J.; Christe, K. O.; Peacock, R. D. *J. Fluorine Chem.* **1982**, 19, 263.
- (10) Christe, K. O.; Wilson, W. W.; Schrobilgen, G. J.; Chirakal, R. V.; Olah, G. A. *Inorg. Chem.* **1988**, 27, 789.
- (11) Murrell, J. N.; Scollary, C. E. *J. Chem. Soc., Dalton Trans.* **1976**, 818.
- (12) Peters, N. J. S. Dissertation, Princeton University, 1982. Peters, N. J. S.; Allen, L. C. In *Fluorine Containing Molecules*; Liebman, J. F., Greenberg, A., Dolbier, W. R., Eds.; VCH Publishers: Weinheim, Germany, 1988; pp 252-4.
- (13) Ewig, C. S.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1989**, 111, 4172.
- (14) Michels, H. H.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1990**, 93, 1805.
- (15) Ewig, C. S.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1990**, 112, 109.

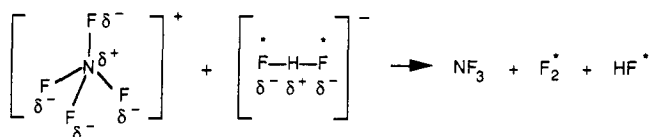


Taking the average of two values of 30.1 and 35.5 kcal mol^{-1} calculated^{13,14} for ΔH_1 at the MP2/6-31++G** and MP2/6-311+G* levels of theory, respectively, the formation of covalent NF_5 from NF_3 and F_2 is endothermic by about 32.8 kcal mol^{-1} . Furthermore, the enthalpy of formation, ΔH_2 , of the free gaseous NF_4^+ and F^- ions from NF_3 and F_2 can be estimated as +182.4 kcal mol^{-1} by taking the average between the values of 183.7 and 181.1 kcal mol^{-1} obtained by the MP2/6-31G* calculation and from a combination of the experimental values for the dissociation energy of F_2 and the first ionization potential and electron affinity of the F atom^{16,17} and the calculated F^+ affinity of NF_3 ,¹⁸ respectively. From $\Delta H_1 - \Delta H_2$, the enthalpy of formation of covalent NF_5 from gaseous free NF_4^+ and F^- ions becomes $\Delta H_3 = -149.6$ kcal mol^{-1} . The value of ΔH_4 , the enthalpy of formation of crystalline NF_4^+F^- from NF_3 and F_2 , is given by the sum of ΔH_2 and the lattice energy U_L of NF_4^+F^- . The value of U_L is the average of two previous estimates (-150.6 and -147.0 kcal mol^{-1})^{9,19} and a value of -154.1 kcal mol^{-1} obtained by Barlett's empirical equation,²⁰ U_L (kcal/mol) = $556.3(V_m)^{-1/3} + 26.3$, where V_m is the sum of the molar volumes of NF_4^+ and F^- that were estimated as 64.9 and 17.5 $\text{\AA}^3$, respectively, from known crystal structures.^{21,22} From $\Delta H_1 - \Delta H_4$, the energy difference between crystalline NF_4^+F^- and covalent NF_5 can then be estimated to be rather small and be of the order of about 1 ± 6 kcal mol^{-1} ,

- (16) Berkowitz, J.; Wahl, A. C. *Adv. Fluorine Chem.* **1973**, 7, 147.
- (17) Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data, Suppl.* **1985**, 14, 1011-3.
- (18) Christe, K. O.; Dixon, D. A. *J. Am. Chem. Soc.* **1992**, 114, 2978.
- (19) Wilson, J. N. *Adv. Chem. Ser.* **1966**, 54, 30.
- (20) Richardson, T. J.; Tanzella, F. L.; Bertlett, N. J. *Am. Chem. Soc.* **1986**, 108, 4937.
- (21) Christe, K. O.; Lind, M. D.; Thorup, N.; Russell, D. R.; Fawcett, J.; Bau, R. *Inorg. Chem.* **1988**, 27, 2450.
- (22) Christe, K. O.; Wilson, W. W.; Wilson, R. D.; Bau, R.; Feng, J. J. *Am. Chem. Soc.* **1990**, 112, 7619.

considering the uncertainties in the values used for ΔH_1 , ΔH_2 , and U_1 .

The following conclusions concerning the stability and synthesis of NF_5 can be drawn from the above Born-Haber cycle: (i) covalent NF_5 and ionic NF_4^+F^- are similar in energy and (ii) the formation of NF_5 from NF_3 and F_2 is endothermic by about 33 kcal mol⁻¹, an amount of energy which is slightly lower than the dissociation energy of molecular fluorine,¹⁷ i.e., 37.9 kcal mol⁻¹. The latter point suggests that, from strictly energetic considerations, covalent NF_5 should be accessible from NF_3 and two fluorine atoms. This approach has been experimentally tested using low temperature and either UV photolysis⁶ or irradiation with 3-MeV bremsstrahlung³ as the F atom sources but provided no evidence for the formation of NF_5 . This failure to produce NF_5 from NF_3 and F atoms is probably due to the steric problem of accommodating more than four fluorine ligands around the nitrogen central atom at the short N-F bond distances of 1.365 Å in NF_3 ²³ and 1.29 Å in NF_4^+ .²¹ This difficulty has been demonstrated by a previous radiotracer study¹⁰ of the thermal decomposition of $\text{NF}_4^+\text{HF}_2^-$ containing ¹⁸F-labeled HF_2^- . It was shown that, contrary to the predictions based on bond polarities, the linear F-H-F anion exclusively attacked the fluorine ligands and not the central nitrogen atom of NF_4^+ .



This result was taken¹⁰ as evidence that at the given bond distances in NF_4^+ (~1.29 Å)²¹ the maximum coordination of nitrogen(+V) toward fluorine is 4. The accommodation of a fifth fluorine ligand at the nitrogen atom would require a significant lengthening of all N-F bonds in NF_4^+ to create enough room for a fifth fluorine ligand. The plausibility of this argument is also borne out by the results of ab initio calculations,^{13,14} which show that for more than four fluorine ligands the average N-F bond lengths increase with increasing coordination numbers. Thus, the bond lengths calculated at the MP2/6-31++G** level of theory were $\text{NF}_4^+ = 1.32$ Å,¹³ $\text{NF}_5(\text{ax}) = 1.57$ Å,¹³ $\text{NF}_5(\text{eq}) = 1.41$ Å,¹³ and $\text{NF}_6^- = 1.58$ Å,¹⁵ with the NF_5 and NF_6^- bond lengths being surprisingly long for highly covalent nitrogen(+V) compounds.

Further evidence for the excessive ligand crowding in NF_5 comes from the vibrational frequencies calculated¹⁴ for covalent NF_5 of D_{3h} symmetry. Depending on the level of theory used for these calculations, the frequency of the antisymmetric axial NF_2 stretching mode, ν_3 , becomes very low or even imaginary. This indicates either a small barrier along the S_3 displacement coordinate or even a spontaneous transition to an ionic C_{3v} or C_{4v} structure with one very long or ionic N-F distance. This is not surprising in view of the above Born-Haber cycle, which suggests that covalent NF_5 and ionic NF_4^+F^- should be of comparable energy. The fact that, at the higher level of theory calculations, the ionic C_{3v} structure lies higher in energy than the covalent D_{3h} structure is probably due to the fact that in these calculations only an NF_4^+F^- ion pair was considered and not a crystalline NF_4^+F^- with its full lattice energy of about 150 kcal mol⁻¹ (see above).

This situation, then, implies that for the successful syntheses of either covalent NF_5 or NF_6^- from NF_3 or NF_4^+ one would first have to lengthen all the existing N-F bonds to make room for the incoming fifth and sixth ligands. This means that the synthesis of NF_5 from ground-state NF_3 or NF_4^+ , although thermodynamically feasible, should not proceed because of steric hindrance. An alternate approach would involve the use of an excited-state N-F_x precursor with longer N-F bonds.

As crystalline NF_4^+F^- is comparable in energy to covalent NF_5 but at the same time does not suffer from the steric hindrance problems of the latter, crystalline NF_4^+F^- should experimentally be easier to prepare than covalent NF_5 of D_{3h} symmetry. Since,

for a salt which is partially soluble in a given solvent, the solvation energy of its ions is comparable to its lattice energy, $\text{NF}_4^+\text{F}^-(\text{cr})$ might be accessible from solvated NF_4^+ and F^- ions in an essentially thermally neutral reaction. This approach avoids the endothermicity of its synthesis from NF_3 and F_2 (see above) but requires a common solvent in which both the NF_4^+ cation and the F^- anion are soluble and chemically inert. Previously, such a solvent had not been identified. The solvents generally used for NF_4^+ salts were Lewis acids, such as HF, BrF_3 , or IF_5 , that react with the strongly basic F^- anion, resulting in the formation of the corresponding complex fluoro anions.²⁴ On the other hand, the simple alkali metal fluorides are practically insoluble in all nonacidic anhydrous solvents, and only recently, the successful synthesis²² of truly anhydrous $\text{N}(\text{CH}_3)_4^+\text{F}^-$ has provided a source of highly soluble "naked" fluoride ion in combination with an oxidizer-resistant cation.^{25,26} The preferred, oxidizer-resistant solvents for $\text{N}(\text{CH}_3)_4^+\text{F}^-$ are CH_3CN and CHF_3 .²² It was therefore interesting to examine whether NF_4^+ salts could also be handled in these organic solvents and, if so, whether NF_4^+ cations and F^- anions can coexist in these solutions or will undergo the possible, exothermic ($-\Delta H_4 = -31.8$ kcal mol⁻¹) reaction to give NF_3 and F_2 . If solvated NF_4^+ and F^- will react with each other, then crystalline NF_4^+F^- should also decompose under these conditions because solvation spheres should increase the ion separation and result in an increased activation energy barrier for the fluorine elimination reaction.

The following experiments were carried out. At ambient temperature, compatibility tests of NF_4^+ salts of BF_4^- , AsF_6^- , and SbF_6^- with dry CH_3CN resulted in gentle NF_3 evolution, but at lower temperatures, good solubility and compatibility were observed by NMR spectroscopy. The lower boiling (-82.0°C) and melting (-155°C) CHF_3 was also found to be compatible with NF_4^+ salts, although their solubilities in this solvent were quite low. In the absence of a solvent, equimolar mixtures of NF_4BF_4 and $\text{N}(\text{CH}_3)_4\text{F}$ did not interact at 25°C , but in CH_3CN at -31°C or CHF_3 at -78°C , they underwent quantitative NF_3 evolution within relatively short time periods. The F_2 evolution was not quantitative, probably due to side reactions with either the solvents or the $\text{N}(\text{CH}_3)_4^+$ cation. A reaction in CHF_3 was also carried out at -142°C and resulted in about 10% NF_3 evolution over a time span of about 3 h. This decrease of the reaction rate at -142°C might be partially due to the very low solubility of NF_4BF_4 in CHF_3 at this low temperature and does not necessarily reflect a substantial activation energy barrier for the $\text{NF}_3 + \text{F}_2$ elimination reaction.

Conclusions

This study allows the following conclusions to be drawn: (i) ionic and covalent NF_5 are of comparable energy; (ii) ionic NF_5 , i.e. NF_4^+F^- , should be experimentally more accessible than covalent NF_5 ; (iii) at temperatures as low as -142°C , metathetical experiments involving solvated NF_4^+ and F^- ions resulted in NF_3 and F_2 elimination, indicating that NF_4^+F^- is unstable at or above -142°C .

Experimental Section

Caution: Mixtures of strong oxidizers, such as NF_4^+ salts, with organic materials, such as CH_3CN or $\text{N}(\text{CH}_3)_4^+$ salts, are potentially explosive. Although no explosions were incurred in the present study, work with these materials should be carried out on a small scale with appropriate safety precautions!

Materials and Apparatus. The syntheses of anhydrous $\text{N}(\text{CH}_3)_4\text{F}^{22}$ and NF_4^+ salts^{6,24} have previously been described. CH_3CN (Baker, Bio-analyzed, having a water content of 40 ppm) was stored over P_2O_5 and freshly distilled on the vacuum line prior to its use which lowered the water content to <4 ppm. CHF_3 (Matheson) was used as received. Volatile materials were handled in a flamed-out Pyrex vacuum line equipped with greaseless Kontes Teflon valves. Solids were handled in

(24) Christe, K. O.; Wilson, W. W.; Schack, C. J.; Wilson, R. D. *Inorganic Syntheses*; Wiley-Interscience: New York, 1987; Vol. 24, p 39.

(25) Wilson, W. W.; Christe, K. O. *Inorg. Chem.* 1989, 28, 4172.

(26) Christe, K. O.; Wilson, W. W.; Chirakal, R. V.; Sanders, J. C. P.; Schrobilgen, G. J. *Inorg. Chem.* 1990, 29, 3506.

(23) Otake, M.; Matsumura, C.; Morino, Y. *J. Mol. Spectrosc.* 1968, 28, 316.

the dry nitrogen atmosphere of a glovebox. Reactions involving NF_4^+ salts were carried out in $3/4$ in. o.d. Teflon-FEP ampules closed by a stainless steel valve.

The ^{19}F and ^1H NMR spectra were measured at 84.6 and 90 MHz, respectively, on a Varian Model EM390 spectrometer, with 4-mm Teflon-FEP tubes (Wilmad Glass Co.) as sample containers and CFCl_3 and TMS, respectively, as internal standards, with negative shifts being upfield from the standards. Raman spectra were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer by use of the 488-nm exciting line of an Ar ion or the 647.1-nm line of a Kr ion laser, respectively. Baked-out Pyrex melting point capillaries were used as sample holders. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer as AgCl disks that were pressed in a Wilks minipress inside the drybox.

The $\text{NF}_4\text{BF}_4\text{-N}(\text{CH}_3)_4\text{F-CH}_3\text{CN}$ System. NF_4BF_4 (0.54 mmol) and $\text{N}(\text{CH}_3)_4\text{F}$ (0.60 mmol) were loaded inside the drybox into a $3/4$ in. Teflon-FEP ampule. On the vacuum line, dry CH_3CN (3 mL liquid) was added at -196°C , and the mixture was warmed to -31°C for 30 min. The ampule was cooled to -78°C , and the volatile material (0.45 mmol) was expanded into the vacuum line and shown by fractional condensation at -210°C and infrared spectroscopy to consist mainly of NF_3 (0.40 mmol). The mixture in the ampule was then warmed for 3 h to -31°C and for 1 h to room temperature, and an additional amount of NF_3 (0.13

mmol) was evolved. The solid residue (90.9 mg, weight calculated for 0.54 mmol of $\text{N}(\text{CH}_3)_4\text{BF}_4$ and 0.06 mmol of unreacted $\text{N}(\text{CH}_3)_4\text{F}$ = 92.9 mg) was shown by vibrational spectroscopy to consist mainly of $\text{N}(\text{CH}_3)_4\text{BF}_4$. When the reaction was repeated using a 5-fold excess of $\text{N}(\text{CH}_3)_4\text{F}$ at -31°C , the NF_3 evolution was 95% complete after 30 min.

The $\text{NF}_4\text{BF}_4\text{-N}(\text{CH}_3)_4\text{F-CHF}_3$ System. NF_4BF_4 (2.19 mmol) and $\text{N}(\text{CH}_3)_4\text{F}$ (2.24 mmol) were combined in a Teflon ampule, and CHF_3 (50.26 mmol) was added at -196°C . The mixture was warmed to -78°C for 3 h and then cooled again to -196°C , and the noncondensable gases (0.45 mmol of F_2) were measured. Subsequently, the ampule was warmed to the melting point of CHF_3 (-155°C), and the volatile material was removed in a dynamic vacuum by fractional condensation through traps kept at -186 and -210°C . The -210°C trap contained NF_3 (2.16 mmol). The solid residue, after being pumped on at room temperature (360 mg), consisted mainly of $\text{N}(\text{CH}_3)_4\text{BF}_4$ (weight calculated for 2.19 mmol of $\text{N}(\text{CH}_3)_4\text{BF}_4$ and 0.05 mmol $\text{N}(\text{CH}_3)_4\text{F}$ = 357 mg). When the reaction was repeated at -142°C , only 10% of the theoretical amount of NF_3 was evolved in 3 h.

Acknowledgment. The authors are grateful to Dr. Carl J. Schack and Mr. R. D. Wilson for help and to the Air Force Phillips Laboratory and the U.S. Army Research Office for financial support.

Conformation of Two 4'-Thio-2'-deoxynucleoside Analogs Studied by 500-MHz ^1H NMR Spectroscopy and X-ray Crystallography

Leo H. Koole,[†] Janez Plavec,[†] Hongying Liu,[†] Beverly R. Vincent,[†] Michael R. Dyson,[§] Paul L. Coe,[§] Richard T. Walker,[§] George W. Hardy,[‡] S. George Rahim,[‡] and Jyoti Chattopadhyaya^{*,†}

Contribution from the Department of Bioorganic Chemistry, Box 581, Biomedical Centre, University of Uppsala, S-751 23 Uppsala, Sweden, Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, Texas 77381, School of Chemistry, University of Birmingham, Birmingham B15 2TT, England, and The Wellcome Research Laboratories, Beckenham, Kent BR3 3BS, England. Received December 23, 1991

Abstract: An integrated conformational study is reported on the structurally modified nucleosides 4'-thiothymidine (**1**), an isoelectronic analogue of natural thymidine, and (*E*)-5-(2-bromovinyl)-2'-deoxy-4'-thiouridine (**2**). The conformation of **1** and **2** in D_2O solution was inferred from the vicinal proton-proton NMR coupling constants and nuclear Overhauser (nOe) contacts. Significant adaptations of the conventional routines for *J*-coupling analysis in nucleos(t)ide structures were necessary due to the presence of sulfur instead of $\text{O}4'$ in the thiofuranose ring. A pseudorotational equation of the form $\nu_j = a_j \nu_m \cos(P + \epsilon_j + 144^\circ(j - 2))$ was used to account for the nonequilateral nature of the 4'-thiofuranose ring. The parameter sets $a_0, \dots, a_4$ and $\epsilon_0, \dots, \epsilon_4$ were deduced from a set of ab initio (HF/3-21G level) molecular orbital calculations. Analysis of the *J*-coupling constants measured for **1** and **2** revealed that (i) the $\text{C}4'\text{-C}5'$ bond is primarily in the γ^+ or γ' conformation and (ii) the 4'-thiofuranose ring has a preference for a South-type ($\text{C}2'\text{-endo}/\text{C}3'\text{-exo}$) puckered conformation. The preference for the South conformation is slightly larger for **1** (73% at 300 K) than for **2** (66% at 300 K). The pseudorotational parameters of the South conformer are as follows: $P = 177^\circ$, $\nu_m = 43^\circ$ for **1**, and $P = 177^\circ$, $\nu_m = 44^\circ$ for **2**. The results reveal that another conformer with a North-type puckered conformation of the 4'-thiofuranose ring is also present in solution, to an extent of $\approx 27\%$ for **1** and 34% for **2** at ambient temperature. The pseudorotational parameters describing the thiofuranose conformation of the minor conformer are as follows: $P = 13^\circ$, $\nu_m = 45^\circ$ for **1**, and $P = 9^\circ$, $\nu_m = 45^\circ$ for **2**. The characterization of the minor conformer must be regarded as an essential complement to the results of X-ray crystallographic analyses. One-dimensional nOe measurements indicated a predominant anti conformation of the thymine base in **1** and the modified uridine base in **2**. The crystal structures of **1** and **2** were found to be grossly similar. The most important characteristics are as follows: compound **1**, $P = 177.7^\circ$, $\nu_m = 47.9^\circ$, $\chi = -144.7^\circ$, $\gamma = 179.5^\circ$; compound **2**, $P = 179.5^\circ$, $\nu_m = 48.6^\circ$, $\chi = -140.0^\circ$, and $\gamma = 174.1^\circ$. Furthermore, it is concluded that the preferred conformation of **1** and **2** in solution is in close agreement with the X-ray crystal structure. The present results indicate that it is dangerous to rely solely on X-ray crystallographic information in attempts to explain or predict biological activity of modified nucleosides. The best basis for formulating structure-activity relationships for modified nucleosides is probably a combined interpretation of solid state and solution conformational data.

Introduction

The ongoing search for more active and more specific anti-(retro)viral agents has stimulated many investigations on struc-

turally modified nucleosides and nucleotides. A plethora of these compounds is known today.¹ A general conclusion emerging from

[†] University of Uppsala.

[‡] Molecular Structure Corporation.

[§] University of Birmingham.

^{*} The Wellcome Research Laboratories.

(1) (a) Proceedings of the 9th International Round Table on Nucleosides, Nucleotides and Their Biological Applications, Uppsala, Sweden, 1990: *Nucleosides and Nucleotides* 1991, 10, 3-737. (b) *Nucleoside Analogues. Chemistry, Biology and Medical Applications*; Walker, R. T., de Clercq, E., Eckstein, F., Eds.; Plenum Press: New York, 1979.

The Pentabromine(1+) Cation, Br_5^+ . Local Density Functional Calculations and Vibrational Spectra

K. O. Christe

Canoga Park, CA (USA), Rocketdyne Division, Rockwell International

D. A. Dixon

Wilmington, DE (USA), Central Research and Development, Du Pont¹⁾

R. Minkwitz

Dortmund, Institut für Anorganische Chemie der Universität

Received November 11th, 1991.

Abstract. The geometry, vibrational spectra and charge distribution of Br_5^+ were calculated by the use of the local density functional (LDF) method. The results show that for free Br_5^+ the lowest energy configuration is a skew structure with the three central Br atoms forming an angle of 168.6° and the two terminal Br atoms exhibiting a dihedral angle of 82° . This skew configuration is in contrast to the planar trans configuration of C_{2h} symmetry found for Br_5^+ in solid $\text{Br}_5^+\text{MF}_6^-$ ($M = \text{As}, \text{Sb}$). The small energy difference of $1.2 \text{ kcal mol}^{-1}$ between the skew and the trans configurations, combined with crystal packing effects, can account for the planar trans configu-

ration of Br_5^+ in solid $\text{Br}_5^+\text{MF}_6^-$. The computed vibrational spectra were used to select the most likely set from three sets of previously published and widely diverging spectra. Contrary to previous STO-3G calculations for Cl_5^+ , the present LDF calculations for Br_5^+ and Cl_5^+ result in charge distribution which agree with a previously proposed simple valence bond model for pentahalogen(1+) cations.

Key words: Pentabromine(1+) cation; local density functional calculations; Vibrational spectra

Das Pentabrom(1+)-Kation, Br_5^+ . Berechnungen mit der Dichtefunktional-Methode und Schwingungsspektren

Inhaltsübersicht. Für das Br_5^+ -Kation werden mit der Dichtefunktional-Methode Geometrie, Schwingungsspektren und Ladungsverteilung berechnet. Das freie Ion hat in der gauche-Konfiguration die niedrigste Energie. Die drei mittleren Br-tome bilden danach einen Winkel von $168,8^\circ$ und der Diederwinkel der beiden terminalen Br-tome beträgt 82° . Diese Konfiguration steht damit im Gegensatz zu der planaren trans-Konfiguration mit C_{2h} -Symmetrie, die für Br_5^+ im $\text{Br}_5^+\text{MF}_6^-$ ($M = \text{As}, \text{Sb}$) durch Röntgenbeugung gefunden wurden. Die geringe Energiedifferenz von $1,2 \text{ kcal mol}^{-1}$ zwischen der

gauche- und trans-Konfiguration, verbunden mit Kristallpackungseffekten, könnten für die trans-Konfiguration von Br_5^+ im festen $\text{Br}_5^+\text{MF}_6^-$ verantwortlich sein.

Um den Wahrscheinlichsten, der bereits publizierten sich stark unterscheidenden Frequenzsätze, zu bestimmen, wurden die berechneten Schwingungsspektren herangezogen.

Im Gegensatz zu früheren STO-3G-Rechnungen für Cl_5^+ , können mit diesen LDF-Rechnungen für Br_5^+ und Cl_5^+ Ladungsverteilungen wiedergegeben werden, die mit einem früher vorgeschlagenen einfachen „valence-bond-model“ für Pentahalogen(1+)-Kationen übereinstimmen.

¹⁾ Du Pont Contribution No. 6044

Introduction

The first report on the existence of the Br_5^+ cation was published in 1980 by Lee and Aubke who prepared its $\text{Au}(\text{SO}_3\text{F})_4^-$ salt and published its vibrational spectra [1]. The only other reports on Br_5^+ are two recent papers by Hartl, Nowicki and Minkwitz on the crystal structures and vibrational spectra of $\text{Br}_5^+\text{MF}_6^-$ ($\text{M} = \text{As}, \text{Sb}$) [2] and by Christe, Bau and Zao on the Raman spectrum of $\text{Br}_5^+\text{AsF}_6^-$ [3]. Although the existence and structure of Br_5^+ are firmly established, the three sets of vibrational spectra published [1–3] for Br_5^+ diverge strongly. This is not surprising because the recording of vibrational spectra for these compounds is very difficult. The compounds are of marginal stability, difficult to handle, intensely colored, photolytically unstable, and often contain impurities which can give rise to very intense resonance Raman spectra. Since local density functional (LDF) calculations are well suited for computations involving large molecules and heavy atoms [4], we performed LDF calculations for the Br_5^+ cation to resolve some of the problems surrounding this interesting cation.

Computational Method

The calculations described below were done in the local density functional approximation [4–11] by using the program system DMol [12, 13]. The atomic basis functions are given numerically on an atom-centered, spherical-polar mesh. The radial portion of the grid is obtained from the solution of the atomic LDF equations by numerical methods. Since the basis sets are numerical, the various integrals arising from the expression for the energy need to be evaluated over a grid. The integration points are generated in terms of angular functions and spherical harmonics. The number of radial points N_R is given as

$$N_R = 1.2 \times 14 (Z + 2)^{1/3}$$

where Z is the atomic number. The maximum distance for any function is 12 a. u. The angular integration points N_θ are generated at the N_R radial points to form shells around each nucleus. The value of N_θ ranges from 14 to 302 depending on the behavior of the density [14]. The Coulomb potential corresponding to the electron repulsion term is determined directly from the electron density by solving Poisson's equation. In DMol, the form for the exchange-correlation energy of the uniform electron gas is that derived by von Barth and Hedin [15].

All of the DMol calculations were done with a double numerical basis set augmented by polarization functions. This can be considered in terms of size, for comparison to traditional molecular orbital calculations, as a polarized double zeta basis set. However because of the use of exact numerical solutions for the atom, this basis set is of significantly higher quality than a normal molecular orbital polarized double zeta basis set. The fitting functions have angular momentum numbers, l , one greater than

that of the polarization function. Since all of the atoms have d polarization functions, the value of l for the fitting function is 3.

Geometries were optimized by using analytic gradient methods [16]. There are two problems with evaluating gradients in the LDF framework which are due to the numerical methods that are used. The first is that the energy minimum does not necessarily correspond exactly to the point with a zero derivative. The second is that the sum of the gradients may not always be zero as required for translational invariance. These tend to introduce errors on the order of 0.001 Å in the calculation of the coordinates if both a reasonable grid and basis set are used. This gives bond lengths and angles with reasonable error limits. The difference of 0.001 Å is about an order of magnitude smaller than the accuracy of the LDF geometries as compared to experiment. The frequencies were determined by numerical differentiation of the gradient. A two point difference formula was used and a displacement of 0.01 a. u.

Results and Discussion

Structure of Br_5^+

The geometries and vibrational spectra of Br_5^+ were computed by the LDF method for two symmetries (see Tables 1 and 2). The first one is C_{2h} , as found [2] by the crystal structure determination, and is shown in Figure 1.

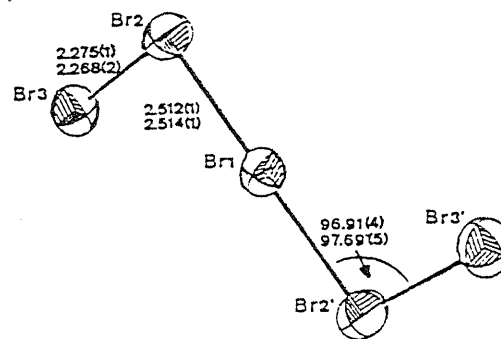


Fig. 1 ORTEP plot of Br_5^+ according to ref. [2]

In C_{2h} symmetry, Br_5^+ is planar, i.e. the terminal Br3 atoms are in trans position, and the three central bromine atoms are linear. The second structure (see Figure 2) which is the energy minimum at the LDF level, has no symmetry and is 1.2 kcal mol $^{-1}$ more stable than the C_{2h} structure.

In this optimized structure, the three central Br atoms slightly deviate from linearity by 11.4°, and the terminal Br atoms form a dihedral angle of 82° about the Br2—Br2' axis, similar to the angles found for *Foof* and *Hooh* [17]. This skewing is caused by the repulsive interactions between the bonded atoms and the sterically active free valence electron pairs on the central atoms and of

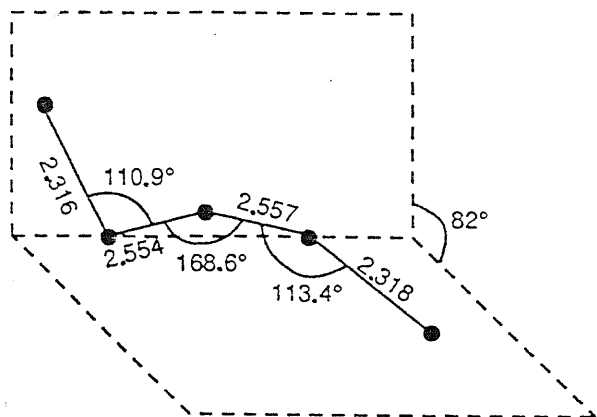


Fig. 2 Optimizing Structure of the Free Br_5^+ Cation

Table 1 Computed and Experimental Bond Distances (Å) and Bond Angles (deg) for Br_5^+ and Cl_5^{+a}

Bond Lengths				
	Expt [2]	Br_5^+ LDF C_{2h}	LDF opt	Cl_5^+ LDF C_{2h}
X1—X2	2.512(1)	2.572	2.554	2.295
X1—X2'	2.514(1)	2.572	2.557	2.295
X2—X3	2.275(1)	2.310	2.316	1.991
X2'—X3'	2.268(2)	2.310	2.318	1.991
Bond Angles				
		Br_5^+		Cl_5^+
X2—X1—X2'	180	180	168.6	180
X1—X2—X3	96.91(4)	108.9	110.9	108.4
X1—X2'—X3'	97.69(5)	108.9	113.4	108.4

^a) For Cl_5^+ no experimental values are known. The C_{2h} geometry was chosen to match that used in [22]

ten can vary over a wide range. For example, in various solid phases containing *Hoo*, the dihedral angle can span a complete range from 90° to 180° [18]. In view of these analogies and the small energy difference of only $1.2 \text{ kcal mol}^{-1}$ between the trans and the optimized skew

configurations of Br_5^+ , the existence of trans $-\text{Br}_5^+$ in its $\text{Br}_5^+\text{MF}_6^-$ salts is not surprising and can be explained by crystal packing effects. Evidence for such an effect is also provided by the frequency shifts observed for the Raman bands of $\text{Br}_5^+\text{AsF}_6^-$ on going from the solid state to the HF solution [3].

As can be seen from Table 1, the geometry computed for Br_5^+ of C_{2h} symmetry agrees well with the experimentally observed one [2], particularly if it is kept in mind that for similar molecules and ions, such as XeF_4 , XeF_5^- [19], Br_3^+ , and Br_3^- (see below), the computed bond lengths are also about 0.05 Å longer than the experimentally observed ones.

Vibrational Spectra

The computed vibrational frequencies are summarized in Table 2. Since the C_{2h} configuration is not an energy minimum, it has two negative directions of curvature which result in imaginary frequencies of 24 and 49 cm^{-1} . Rotation about the Br2—Br2' axis leads to a structure with

Table 3 Computed and Experimental Geometries and Vibrational Frequencies for Br_3^+ and Br_3^-

	Br_3^+ experim [3]	com- puted ^a)	Br_3^- experim [20–22]	computed
r (Å)	2.270(5)	2.322	2.536(2)	2.593
$\angle$ (deg)	102.5(2)	110.8	180	180
asym.stretch	297	295	203	216
sym.stretch	293	280	163	158
deformation	124	75	80	81

^a) The vibrational frequencies of Br_3^+ were also computed using the experimental geometry of 2.27 Å and 102.5° . As expected, the frequencies of the two stretching modes increased somewhat to 328 and 325 cm^{-1} , respectively, but that of the bending mode remained essentially unchanged at 76 cm^{-1} . Hence the discrepancy between the observed and the computed deformation frequencies is not caused by the slightly different geometries

Table 2 Computed and Experimental Vibrational Frequencies (cm^{-1}) for Br_5^+

assignment in point group C_{2h}	experimental $\text{Br}_5^+\text{Au}(\text{SO}_3\text{F})_4^-$ solid [1]	$\text{Br}_5^+\text{AsF}_6^-$ solid [2]	$\text{Br}_5^+\text{AsF}_6^-$ [3] solid	HF solut.	computed LDF C_{2h}	LDF opt ^a)
A_g ν_1 vsym term	304.295 ^b)	272	309	309	307	303*
ν_2 vsym centr	267	220	174	182	139	161
ν_3 δ sym in plane	205	170	84	108	24	45**
A_u ν_4 δ centr out of plane					63	94
ν_5 torsion					24i	26
B_u ν_6 ν as term	305.295 ^b)	290.275 ^b)			307	300*
ν_7 ν as centr	260	185			172	180
ν_8 δ centr in plane					129	105
ν_9 δ as term in plane					49i	33**

^a) The LDF opt configuration has no symmetry, and the motions marked by asterisks and double asterisks mix

^b) Assuming a splitting of these bands due to solid state effects

lower energy and to all positive directions of curvature. The resulting structure [LDF opt] is a true minimum of the LDF potential energy surface and has all real frequencies. Since this configuration has no symmetry, the C_{2h} selection rules no longer apply and all fundamentals can be active in both the infrared and the Raman spectra.

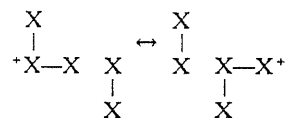
A comparison of the computed vibrational frequencies with the observed ones [1–3] is given in Table 2. To test how well these LDF computations for a free ion can duplicate the observed frequencies in similar, closely related solids, the vibrational spectra of the known Br_3^+ [3] and Br_3^- [20–22] ions were also calculated. As can be seen from Table 3, the agreement is very good for all the modes, except for the deformation mode of Br_3^+ for which the calculated frequency is considerably lower than the observed one. Since in Br_5^+ the three central atoms mimic the Br_3^- anion and the two terminal ones resemble those in Br_3^+ [3], their computed and observed stretching frequencies should also be in good agreement. As can be seen from Table 2, only the Raman spectrum given in [3] satisfies the computed stretching frequencies and, therefore, is the preferred choice.

The exact reasons for the large discrepancies among the three observed data sets [1–3] are not clear at the present time, but should caution future investigators against relying too heavily on vibrational spectra for the identification of these polybromine cations.

The frequency changes observed in [3] on going from solid $Br_5^+AsF_6^-$ to its HF solution, might be due to Br_5^+ having C_{2h} symmetry in the solid and a skew conformation in HF solution. This could also cause the 108 cm^{-1} Raman band observed [3] for the HF solution being possibly due to one of the other modes, (ν_4 or ν_8), which are Raman inactive under C_{2h} symmetry. When judging the quality of the agreement, it must be also kept in mind that the computed values are harmonic frequencies for the free gaseous species, whereas the observed values are anharmonic frequencies recorded for either ionic solids or solvated ions.

Charge Distribution

The charge distribution in Br_5^+ has also been calculated and is given in Table 4. As has been pointed out previously [23] in a study of I_5^+ , the structure and bonding in pentahalogen ($1+$) cations can be simply rationalized in terms of the following valence bond structures,



resulting in weak three-centered four-electron bonds for the three central halogen atoms and “normal” terminal halogen-halogen bonds with a bond order of about one. According to this model, the halogen atoms 2 and 2' should carry most of the positive charge. In the previous

Table 4 Computed Charge Distributions for Br_5^+ and Cl_5^+

atom	atomic charge (e)		Cl_5^+ LDF C_{2h}
	Br_5^+ LDF C_{2h}	LDF opt	
X1	0.09	0.11	0.08
X2	0.25	0.25	0.26
X2'	0.25	0.25	0.26
X3	0.20	0.20	0.20
X3'	0.20	0.19	0.20

paper [23] on I_5^+ , a charge distribution could be calculated only for Cl_5^+ due to computational limitations. Surprisingly, the central Cl atom in Cl_5^+ was found to carry most of the positive charge ($+0.3\text{ e}$) with Cl2 and Cl2' carrying each only $+0.15\text{ e}$ charges. This result was in contrast to the findings for the crystal structure of I_5^+ in its AsF_6^- salt where the absence of iodine-fluorine contacts for the central iodine atom indicated that it carried little positive charge [23]. Our results for Br_5^+ with Br1 carrying only a $+0.10\text{ e}$ charge and the two Br2 atoms carrying a total charge of $+0.50\text{ e}$ is in good agreement with the findings for I_5^+ and the above valence bond model. To test whether the charge distribution and bonding in Cl_5^+ and Br_5^+ are indeed different, we have also computed Cl_5^+ by the LDF method. The results from this computation (see Tables 1 and 4) show that the charge distribution and hence the bonding in Cl_5^+ and Br_5^+ are very similar. These results suggest that the previous calculations of the charges [23] did not give an appropriate charge distribution, probably due to the use of a basis set that was too small.

One of us (K.O.C.) thanks the U.S. Army Research Office and the U.S. Air Force Phillips Laboratory for financial support of the work at Rocketdyne.

References

- [1] K. C. Lee, F. Aubke, *Inorg. Chem.* **19** (1980) 119
- [2] H. Hartl, J. Nowicki, R. Minkwitz, *Angew. Chem. Int. Ed. Engl.* **30** (1991) 328
- [3] K. O. Christe, R. Bau, D. Zhao, *Z. anorg. allg. Chem.* **593** (1991) 46
- [4] R. O. Jones, *Angew. Chem. Int. Ed. Engl.*, **30** (1991) 630
- [5] R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York 1989
- [6] D. R. Salahub, *Ab Initio Methods in Quantum Chemistry-II*, ed. K. P. Lawlwy, J. Wiley & Sons, New York 1987, p. 447
- [7] E. Wimmer, A. J. Freeman, C.-L. Fu, P.-L. Cou, S.-H. Chou, B. Delley, “Supercomputer Research in Chemistry and Chemical Engineering”, K. F. Jensen, D. G. Truhlar, Eds., ACS Symposium Series, American Chemical Society, Washington, D.C., 1987, p. 49
- [8] R. O. Jones, O. Gunnarsson, *Rev. Mod. Phys.* **61** (1989) 689
- [9] T. Zeigler, *Chem. Rev.* **91** (1991) 651

- [10] D. A. Dixon, A. Andzelm, G. Fitzgerald, E. Wimmer, B. Delley, "Science and Engineering on Supercomputers", Ed. E. J. Pitscher, Computational Science Publications, Southampton/England 1990, p. 285
- [11] D. A. Dixon, J. Andzelm, G. Fitzgerald, E. Wimmer, P. Jasien, "Density Functional Methods in Chemistry", Ed. J. Labanowski, J. Andzelm, Springer-Verlag, New York 1991, p. 33
- [12] B. Delley, J. Chem. Phys. 92 (1990) 508. Dmol is available commercially from BIOSYM Technologies, San Diego, CA
- [13] B. Delley, "Density Functional Methods in Chemistry", Ed. J. Labanowski, J. Andzelm; Springer-Verlag: New York 1991, p. 101
- [14] This grid can be obtained using the FINE parameter in DMol
- [15] U. von Barth, L. Hedin, J. Phys. C 5 (1972) 1629
- [16] (a) I. Versiuis, T. Ziegler, J. Chem. Phys. 88 (1988) 3322; (b) J. Andzelm, E. Wimmer, D. R. Salahub, "The Challenge of d and f Electrons, Theory and Computation"; D. R. Salahub, M. C. Zerner, Eds., ACS Symposium Series 394, American Chemical Society; Washington, DC 1989, p. 228; (c) R. Fournier, J. Andzelm, D. R. Salahub, J. Chem. Phys. 90 (1989) 6371
- [17] M. D. Harmony, V. W. Laurie, R. L. Kuczkowski, R. M. Schwendeman, D. A. Ramsay, F. J. Lovas, W. J. Lafferty, A. G. Maki, J. Phys. Chem. Ref. Data 8 (1979) 619
- [18] N. N. Greenwood, A. Earnshaw, "Chemistry of the Elements", Pergamon Press, Oxford 1984, p. 744
- [19] K. O. Christe, E. C. Curtis, D. A. Dixon, H. P. Mercier, J. C. P. Sanders, G. J. Schrobilgen, J. Amer. Chem. Soc. 113 (1991) 3351
- [20] A. W. Coleman, C. M. Means, S. G. Bott, J. L. Atwood, J. Cryst. Spectr. Res. 20 (1990) 199
- [21] W. B. Person, G. R. Anderson, J. N. Fordemwalt, H. Stammreich, R. Forneris, J. Chem. Phys. 35 (1961) 908
- [22] G. R. Burns, R. M. Renner, Spectrochim. Acta 47A (1991) 991
- [23] A. Appleby, F. Grein, J. P. Johnson, J. Passmore, P. S. White, Inorg. Chem. 25 (1986) 422

Korrespondenzanschrift:

Dr. O. Christe
 Rocketdyne Division, Rockwell Intern. Corpor.,
 6633 Canoga Avenue,
 Canoga Park, CA 91303/U.S.A.

Osmium Tetrafluoride Dioxide, OsF₄O₂: a New Osmium(VIII) Oxide Fluoride

Karl O. Christe^a and Roland Bougon^b

^a Rocketdyne, A Division of Rockwell International Corporation, Canoga Park, California 91303, USA

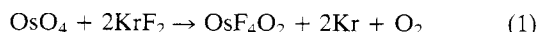
^b SCM-URA CNRS 331, CEA—Centre d'Etudes Nucléaires de Saclay, 91191 Gif-sur-Yvette, France

The reaction of OsO₄ with KrF₂ in anhydrous HF produces *cis*-OsF₄O₂ and not OsF₆O as previously reported.

Of the three possible mononuclear oxide fluorides of osmium in its +VIII oxidation state, OsF₆O, OsF₄O₂ and OsF₂O₃, only the latter had been well known and characterized.^{1–3} Attempts to prepare the other two oxide fluorides had not only failed, but also suggested that such compounds will disproportionate readily.^{2,4,5} Very recently, a new osmium(VIII) oxide fluoride was prepared at Saclay and identified as OsF₆O by elemental analysis, X-ray powder data and vibrational spectroscopy.⁶

During an ongoing effort at Rocketdyne on highly coordinated, high oxidation state compounds, including several XF₆O type ions,⁷ a poor agreement between the vibrational spectra of the alleged OsF₆O and the other XF₆O ions was noticed, and the Saclay experiments were repeated at Rocketdyne. The following results establish that the new osmium(VIII) oxide fluoride, discovered at Saclay, is not OsF₆O but *cis*-OsF₄O₂. Further characterization of the material carried out independently at Saclay also led to this conclusion.

The synthesis of the new osmium(VIII) oxide fluoride was carried out from OsO₄ and an excess of KrF₂ in anhydrous HF solution, as previously described.⁶ A careful separation, measurement and identification of all reactants and reaction products by both pressure–volume–temperature measurements for the volatile species and weights for all of them established the following quantitative 1:2 reaction (1). The excess of KrF₂ used was recovered unchanged.



The physical properties of the osmium oxide fluoride prepared in this manner (burgundy-red solid, m.p. 90 °C, vapour pressure ~ 1 Torr at room temperature), its X-ray powder diffraction pattern and vibrational spectra were within

experimental error identical to those previously reported⁶ and leave no doubt that the two compounds are the same.[†]

One of the authors (K. O. C.) thanks the US Air Force Phillips Laboratory and the US Army Research Office for financial support.

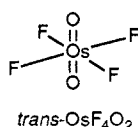
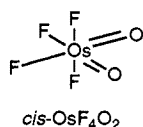
Received, 1st May 1992; Com. 2/02263J

References

- M. A. Hepworth and P. L. Robinson, *J. Inorg. Nucl. Chem.*, 1957, **4**, 24.
- Nguyen-Nghi and N. Bartlett, *C. R. Acad. Sci. Paris Sec. C*, 1969, **269**, 756.
- E. G. Hope, W. Levason and J. S. Ogden, *J. Chem. Soc., Dalton Trans.*, 1988, 61 and 997.
- W. E. Falconer, F. J. Dissalvo, J. E. Griffiths, F. A. Stevie, W. A. Sunder and M. J. Vasile, *J. Fluorine Chem.*, 1975, **6**, 499.
- J. H. Holloway and D. Laycock, *Adv. Inorg. Chem. Radiochem.*, 1984, **28**, 85.
- R. Bougon, *J. Fluorine Chem.*, 1991, **53**, 419.
- K. O. Christe, J. C. P. Sanders, G. J. Schrobilgen and W. W. Wilson, *J. Chem. Soc., Chem. Commun.*, 1991, 837.
- K. O. Christe, R. D. Wilson and C. J. Schack, *Inorg. Chem.*, 1985, **20**, 2104.

[†] Vibrational spectra: The IR and Raman spectra of the solid and the Raman spectrum of an HF solution were recorded. The general pattern of these spectra resembles that⁸ of *cis*-IF₄O₂[–] more closely than those⁷ of IF₆O[–] and TeF₆O^{2–}. Furthermore, two Raman bands at 942 and 932 cm^{–1} are observed for the solid in the Os=O stretching region that had previously been interpreted⁶ as being due to a crystal field splitting of an Os=O group containing a single oxygen atom. The present study, however, shows that in HF solution this splitting is retained and suggests the presence of more than one oxygen atom in the molecule.

¹⁹F NMR spectrum: The ¹⁹F NMR spectrum of the new osmium oxide fluoride in HF solution was recorded and exhibits an A₂B₂ pattern, *i.e.* two almost identical 1:2:1 triplets at δ 61.3 and 14.7 downfield from external CFCl₃ with J_{FF} 136 Hz. No other signals were observed. This clearly establishes that the new osmium oxide fluoride contains only four and not five fluorine atoms and must be OsF₄O₂ and not OsF₆O. Furthermore, the observation of two nonequivalent sets of two fluorine atoms each shows that the OsF₄O₂ is present exclusively as the *cis*- and not as the *trans*-isomer. For *trans*-OsF₄O₂, only a single resonance should be observed with no signs of splittings due to F–F coupling.



CHAPTER 2

Controlled Replacement of Fluorine by Oxygen in Fluorides and Oxyfluorides

KARL O. CHRISTE, WILLIAM W. WILSON, and CARL J. SCHACK

- 2.1. Introduction
- 2.2. Reactions of the Nitrate Anion
 - 2.2.1. Xenon(VI) Fluoride and Oxyfluorides
 - 2.2.2. Chlorine Fluorides and Oxyfluorides
 - 2.2.3. Bromine Pentafluoride
 - 2.2.4. Iodine Fluorides and Oxyfluorides
 - 2.2.5. Carbonyl Fluoride
 - 2.2.6. Mechanism of the Fluorine–Oxygen Exchange Involving Nitrates
- 2.3. Reactions of the Sulfate Anion
 - 2.3.1. Bromine Pentafluoride
 - 2.3.2. Iodine Fluorides
 - 2.3.3. Xenon Fluorides
- 2.4. Summary
 - Acknowledgments
 - References

2.1. INTRODUCTION

Fluorine–oxygen exchange reactions play an important role in synthetic chemistry. Although numerous methods and reagents have been described for these exchange reactions, the emphasis of these studies has been almost exclusively on the selective replacement of oxygen by fluorine. For example, SF_4 ¹ and its derivatives, such as $\text{SF}_3\text{N}(\text{CH}_3)_2$,² have been widely used to convert carbonyl groups to CF_2 groups, and inorganic oxides can be transformed into fluorides by reagents such as HF , F_2 , or halogen fluorides.³ However, much less attention has been paid to the opposite reaction, that is, the conversion of fluorides to oxyfluorides. This is not surprising because generally

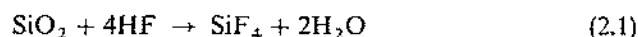
Synthetic Fluorine Chemistry.

Edited by George A. Olah, Richard D. Chambers, and G. K. Surya Prakash.

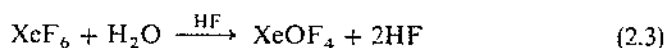
ISBN 0-471-54370-5 © 1992 John Wiley & Sons, Inc.

oxides are more readily preparable than fluorides, and many fluorides undergo facile hydrolysis to the corresponding oxyfluorides and oxides.

For the replacement of fluorine by oxygen, hydrolysis is the most frequently used method. For highly fluorinated compounds of the more electronegative elements, however, these hydrolysis reactions often present significant experimental difficulties, particularly when a controlled and stepwise replacement of fluorine by oxygen is desired. The hydrolysis reactions of these compounds are often violent, as found for XeF_6 ^{4,5} or ClF_3 ,⁶ and require careful moderation. Thus, SiO_2 combined with a trace of HF can be used for the slow formation of water (Eq. 2.1), followed by a continuous regeneration of the HF during the hydrolysis of the fluoride starting material (Eq. 2.2). This approach has been demonstrated previously for compounds such as IF_7 .⁷⁻¹⁰

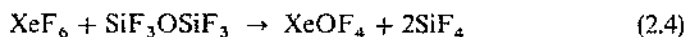


Another approach to moderate otherwise violent or uncontrollable hydrolysis reactions involves the use of suitable solvents, such as HF, and of stoichiometric amounts of water, as reported for XeF_6 ⁵ (Eq. 2.3).

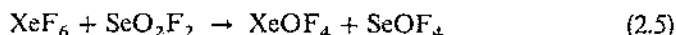


In spite of the above improvements in the techniques of hydrolyzing highly reactive fluorides, these reactions remain experimentally challenging and often are dangerous⁵ and difficult to scale up. Consequently, alternate reagents that allow the safe, easily controllable, and stepwise replacement of fluorine by oxygen, are highly desirable.

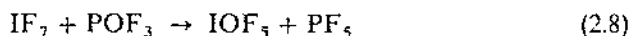
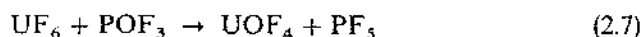
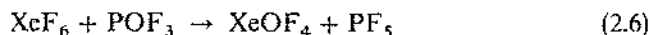
Previously investigated examples for such alternate reagents include $\text{SiF}_3\text{OSiF}_3$, SeO_2F_2 , POF_3 , and several oxides. Most of these alternate reagents exhibit drawbacks. Thus, $\text{SiF}_3\text{OSiF}_3$ reacted with XeF_6 (Eq. 2.4),



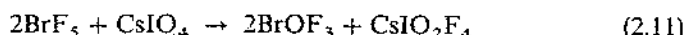
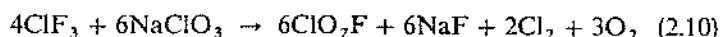
but did not work for IF_7 , BrF_5 , and so on.¹¹ Similarly, the highly toxic SeO_2F_2 was demonstrated only for XeF_6 (Eq. 2.5).¹²



The most versatile of these alternate reagents appears to be POF_3 , which reacted with XeF_6 (Eq. 2.6),¹³ UF_6 (Eq. 2.7),¹⁴ ClF_5 ,¹⁴ and IF_7 (Eq. 2.8).¹⁵



Most of the previously reported, oxide based fluorine-oxygen exchange reactions, such as (Eqs. 2.9,¹⁰ 2.10,¹⁶ or 2.11¹⁷



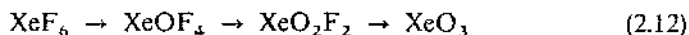
represent useful syntheses for specific compounds, but the exchange reagents have not been studied systematically.

Several years ago, while studying the compatibility of the nitrate and sulfate anions with various halogen fluorides,¹⁸ we surprisingly found that these anions are excellent, general reagents for fluorine-oxygen exchange. Since then, we have systematically investigated the scope of these reactions and we present a summary of our results in this chapter.

2.2. REACTIONS OF THE NITRATE ANION

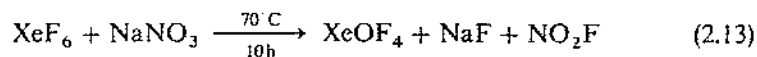
2.2.1. Xenon(VI) Fluoride and Oxyfluorides

Xenon hexafluoride is an ideal test case for the general usefulness of a fluorine-oxygen exchange reagent since it can undergo stepwise fluorine replacement (Eq. 2.12). When preparing XeOF_4 and XeO_2F_2 ,



precise control of the stepwise exchange is of utmost importance because of the shock sensitivity of the potential by-product XeO_3 . Other important aspects, besides high yields and ready availability of the exchange reagent, are the ease of product separation and mild reaction conditions to avoid product decomposition.

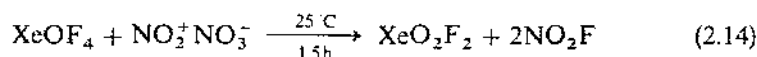
In our studies¹⁹ it was found that NaNO_3 is best suited for the conversion of XeF_6 to XeOF_4 (Eq. 2.13).



The formation of XeO_2F_2 can be suppressed by the use of a moderate excess of XeF_6 . The excess of XeF_6 is readily separable from the desired XeOF_4 because at the reaction temperature it forms stable NaXeF_7 and Na_2XeF_8 salts with the NaF by-product. The only other volatile by-product is NO_2F , which is much more volatile than XeOF_4 and can be separated easily from the XeOF_4 by fractional condensation through traps kept at -78 and -196°C . The yields of XeOF_4 are about 80% based on the limiting reagent NaNO_3 . The use of other alkali metal nitrates is less desirable. In the case of CsNO_3 the resulting CsF

complexes XeOF_4 with formation of CsXeOF_5 ²⁰⁻²² and for LiNO_3 the resulting LiF does not complex any unreacted XeF_6 starting material.

For the conversion of XeOF_4 to XeO_2F_2 , the use of alkali metal nitrates is possible but, due to the relative involatility of XeO_2F_2 and its ease of forming stable XeO_2F_3^- salts, N_2O_5 is the preferred reagent.²³ In the solid state, N_2O_5 has the ionic structure $\text{NO}_2^+\text{NO}_3^-$ ^{24,25} and reacts with XeOF_4 according to (Eq. 2.14).

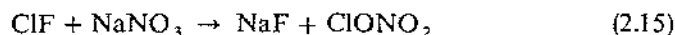


In this manner and by the use of an excess of XeOF_4 , the only product of low volatility is XeO_2F_2 , thus allowing for an efficient product separation. Again, the formation of XeO_3 was suppressed by the use of a slight excess of XeOF_4 starting material, and the yield of XeO_2F_2 was essentially quantitative. The only minor complication in this XeO_2F_2 synthesis is the formation of an unstable $\text{NO}_2^+[\text{XeO}_2\text{F}_3 \cdot n\text{XeO}_2\text{F}_2]^-$ type adduct between NO_2F and XeO_2F_2 , which requires prolonged pumping on the product at room temperature to ensure complete NO_2F removal from the XeO_2F_2 .²³

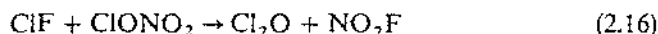
Conversion of either XeF_6 , XeOF_4 , or XeO_2F_2 to the highly explosive XeO_3 can be achieved by their reactions with excess N_2O_5 .²³ However, no detailed studies were carried out on these systems due to the sensitivity of XeO_3 .

2.2.2. Chlorine Fluorides and Oxyfluorides

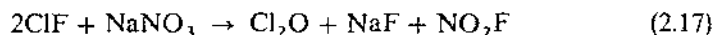
Excess NaNO_3 readily reacts with ClF at subambient temperatures to give NaF and ClONO_2 (Eq. 2.15).²⁶



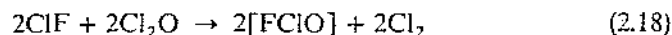
The yield of ClONO_2 , however, was only about 75% because of the competing reaction (Eq. 2.16) which is favored by an excess of ClF .

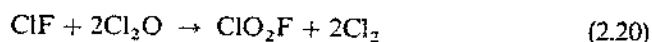
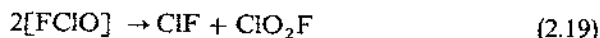


With a sufficiently large excess of ClF , the overall reaction then becomes (Eq. 2.17).



In addition to the NaF , ClONO_2 , and NO_2F products, smaller amounts of Cl_2 and ClO_2F were also observed as by-products due to the side reactions (Eqs. 2.18 and 2.19), which result in the following net reaction (Eq. 2.20).



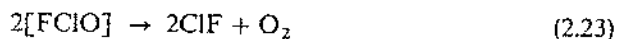
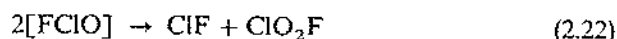


Thus, CIF readily undergoes fluorine-oxygen exchange with the NO_3^- anion with the ratio of the major products, ClONO_2 and Cl_2O , depending on the stoichiometry of the reactants. Smaller amounts of Cl_2 and ClO_2F formed in this system are due to side reactions.

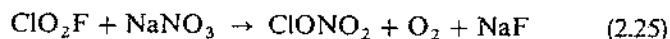
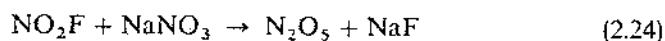
In the case of ClF_3 , the main reaction with the NO_3^- anion is again a facile fluorine-oxygen exchange (Cl. 2.21)²⁶



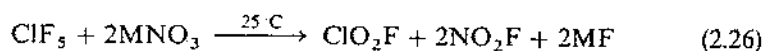
with the thermally unstable FCIO either undergoing disproportionation (Eq. 2.22) or decomposition (Eq. 2.23).



The formation of CIF, ClO_2F , O_2 , and NO_2F is favored by the use of an excess of ClF_3 . If, however, a large excess of NaNO_3 is used, side reactions (Eqs. 2.15, 2.24, 2.25) are also observed.



The compound ClF_5 also reacts readily at room temperature with nitrates.²⁶ Even in the presence of a large excess of ClF_3 , the fluorine-oxygen exchange cannot be stopped at the ClOF_3 stage but proceeds all the way to ClO_2F (Eq. 2.26).



(M = Li, Na, K, Rb, and Cs)

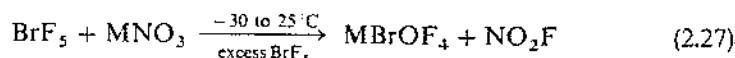
This is in marked contrast to BrF_5 and IF_5 (see below) and is due to the extraordinary reactivity of ClOF_3 , which is much more reactive than ClF_5 .²⁷ Attempts to trap the intermediately formed ClOF_3 as $\text{M}^+\text{ClOF}_3^-$ salts were also unsuccessful indicating that the complexation of ClOF_3 with MF is slower than its fluorine-oxygen exchange with the nitrate anion.

When a large excess of nitrate is used in the reaction of ClF_5 with MNO_3 (Eq. 2.26), the ClO_2F product can undergo further fluorine-oxygen exchange with NO_3^- (Eq. 2.25). This was confirmed by separate experiments between ClO_2F and either LiNO_3 or $\text{NO}_2^+\text{NO}_3^-$.²⁶

Thus, all the chlorine fluorides and oxyfluorides, except for the highly unreactive ClO_3F ,²⁷ undergo rapid fluorine–oxygen exchange with the nitrate anion. Due to the high reactivity of ClOF_3 and in contrast to BrF_5 and IF_5 , a controlled single step fluorine–oxygen exchange in ClF_3 could not be realized (see note added in proof).

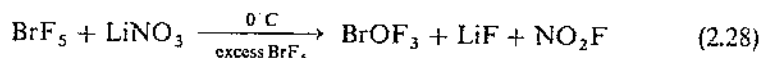
2.2.3. Bromine Pentafluoride

The reactions of BrF_5 with M^+NO_3^- serve as excellent examples of how the nature of the products can be influenced by the appropriate choices of the M^+ cation and the reaction stoichiometries.^{18,28} With an excess of BrF_5 and M being either Na, K, Rb, or Cs, the corresponding $\text{M}^+\text{BrOF}_4^-$ salts can be prepared in 70–100% yield under very mild (-30 to 25°C) conditions (Eq. 2.27).



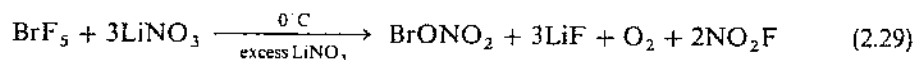
($\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{and Cs}$)

Since lithium does not form a stable LiBrOF_4 salt, the reaction of LiNO_3 with excess BrF_5 (Eq. 2.28) can be used for a convenient synthesis of free BrOF_3 .

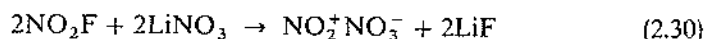


Since BrOF_3 is considerably less volatile than BrF_5 , the two can be separated readily by fractional condensation or distillation.

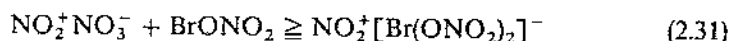
While the use of an excess of BrF_5 results in the single-step replacement of two fluorines by one oxygen, the application of a 1:3 mol ratio of $\text{BrF}_5:\text{LiNO}_3$ causes complete fluorine–oxygen exchange with BrONO_2 formation (Eq. 2.29).²⁸



If the $\text{BrF}_5:\text{LiNO}_3$ mole ratio is further changed to 1:5 or greater, N_2O_5 is produced (Eq. 2.30)

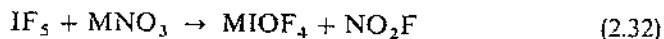


which can react with BrONO_2 (Eq. 2.31).²⁸



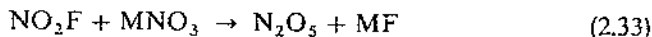
2.2.4. Iodine Fluorides and Oxyfluorides

The reactions of IF and IF₃ with nitrates were not studied since IF and IF₃ are relatively unstable and easily disproportionate to I₂ and IF₅. With excess IF₅, the alkali metal nitrates undergo a controlled, single-step fluorine-oxygen exchange to form the corresponding MIOF₄ salts (Eq. 2.32).²⁹



(M = Li, K, Cs)

However, these reactions are more sluggish than the corresponding BrF₅ reactions. As a consequence, the side reaction (Eq. 2.33)

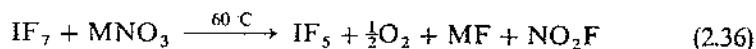


becomes faster than the previous reaction (Eq. 2.32) resulting in an equal consumption of MNO₃ by its reactions with IF₅ and NO₂F (Eqs. 2.32 and 2.33). Furthermore, the following reactions (Eqs. 2.34 and 2.35) also become competitive,



and some of the N₂O₅ decomposes to N₂O₄ + O₂ under these conditions. Consequently, the MIOF₄ salts prepared in this manner, usually contain substantial amounts of IF₆⁻ and I₃F₁₆⁻ salts as by-products.

From the reaction of excess IF₇ with either LiNO₃ or NaNO₃, no IOF₅ is isolated. Instead, IF₅ and O₂ are obtained (Eq. 2.36),



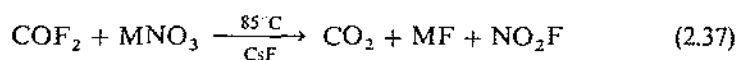
indicative of a competing deoxygenation reaction.²⁹ In the case of CsNO₃, the same deoxygenation occurs but the CsF product reacts with IF₅ and IF₇ to give CsI₃F₁₆ and CsIF₈, respectively. If an excess of MNO₃ is used, the IF₅ product can react further with MNO₃ and form MIOF₄ salts (Eq. 2.32). It was further experimentally confirmed that IOF₅ does not undergo fluorine-oxygen exchange giving IO₂F₃, but loses oxygen giving IF₅, which then undergoes fluorine-oxygen exchange with formation of IOF₄⁻ salts (Eq. 2.32).²⁹

The fact that IF₇ readily undergoes fluorine-oxygen exchange either during controlled hydrolysis⁷⁻¹⁰ or with POF₃,¹⁵ but not with the NO₃⁻ anion remains somewhat a puzzle. It has previously been speculated²⁹ that this lack of fluorine-oxygen exchange in the IF₇-nitrate system might be due to either the instability of an intermediate IOF₆⁻ anion or the lack of a free valence electron

pair on the iodine central atom of IF_7 . Since then, however, we have synthesized and characterized stable IOF_6^- salts³⁰; thus, the first explanation can be ruled out.

2.2.5. Carbonyl Fluoride

The nitrate anion can also exchange carbon bonded fluorine for oxygen. This was demonstrated³¹ for carbonyl fluoride, COF_2 (Eq. 2.37).

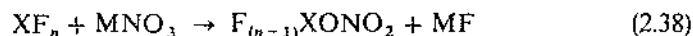


(M = Li and Na)

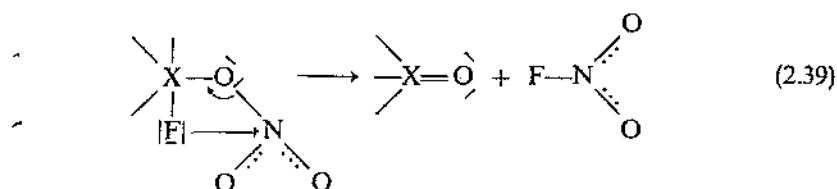
The reactions were carried out in a steel cylinder and, in this manner, essentially quantitative yields of NO_2F are obtainable. This reaction is remarkable because it is a very rare example for the formation of a nitrogen-fluorine bond using a fluorinating agent as mild as COF_2 . Furthermore, it is interesting that the heavier alkali metal nitrates, such as CsNO_3 , do not react under these conditions with COF_2 . This was explained³¹ by thermochemical calculations, which show that for Li and Na the ΔH values are still favorable but become increasingly more positive for the heavier alkali metals. It should be noted that all the ΔH values given in Ref. 31 are slightly in error³² by $-11 \text{ kcal mol}^{-1}$, but that the general trend remains the same for the different alkali metals.

2.2.6. Mechanism of the Fluorine-Oxygen Exchange Involving Nitrates

Of the nitrate based fluorine-oxygen exchange reactions studied so far, the simplest case is that of MNO_3 and ClF , which yields MF and ClONO_2 (Eq. 2.15).²⁶ Assuming for the more highly fluorinated starting materials an analogous first reaction step (Eq. 2.38),



the formation of an intermediate $\text{F}_{(n-1)}\text{XONO}_2$ is expected. This intermediate could easily undergo an internal nucleophilic substitution (S_{Ni}) reaction,¹⁸ accompanied by NO_2F elimination (Eq. 2.39).



Such a mechanism could account for the generally observed reaction products, MF, NO₂F, and the corresponding oxyfluoride. If the oxyfluoride end product is amphoteric and can form a stable salt with the cogenerated alkali metal fluoride, then this salt is observed as the final product (Eq. 2.40).

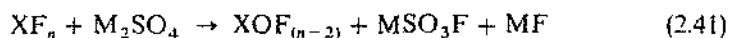


If, as for the ClF + NO₃⁻ reaction (Eq. 2.15), the resulting nitrate intermediate no longer contains a fluoride ligand, NO₂F elimination becomes impossible, and the halogen nitrate becomes the final product.

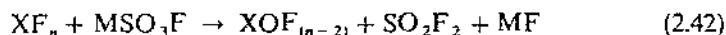
All the nitrate reactions studied so far seem to follow this pattern, except for the IF₇ case where deoxygenation of the expected IOF₅ product occurred (Eq. 2.36). Since the IF₇ + MNO₃ reactions require elevated temperatures and conditions under which IOF₅ can undergo deoxygenation,²⁹ the latter might be a secondary reaction, and the IF₇ + MNO₃ reaction might involve the same primary steps as all the other nitrate reactions.

2.3. REACTIONS OF THE SULFATE ANION

The reactions of the sulfate anion with highly fluorinated compounds of the more electronegative elements resemble those of the nitrate anion. Again, fluorine-oxygen exchange occurs but this exchange generally stops at the SO₃F⁻ level (Eq. 2.41),



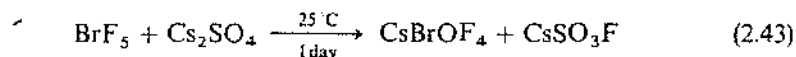
and does not proceed further to the SO₂F₂ stage (Eq. 2.42).³³



Since MSO₃F is a nonvolatile solid, whereas NO₂F is a volatile gas, the use of M₂SO₄ may be more convenient than that of MNO₃ if the desired product is volatile but either complexes with NO₂F or is difficult to separate from it. Compared to the nitrate anion, the sulfate anion is less reactive and requires longer reaction times and/or higher temperatures. Consequently, the reactions of the sulfate anion were not studied as extensively as those of the nitrate anion and were limited to the following examples.

2.3.1. Bromine Pentafluoride

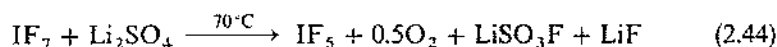
At room temperature Cs₂SO₄ readily undergoes fluorine-oxygen exchange with BrF₅ (Eq. 2.43).³³



Even with an 80-fold excess of BrF_5 , the fluorine–oxygen exchange did not proceed past the CsSO_3F stage. Attempts were made to use this reaction for the synthesis of free BrOF_3 by the replacement of Cs_2SO_4 with Li_2SO_4 since lithium does not form a stable BrOF_4^- salt. Under conditions (0°C , 1 day), which worked well for LiNO_3 ²⁸, no reaction was observed for Li_2SO_4 . This shows that the SO_4^{2-} anion is less reactive than NO_3^- .

2.3.2. Iodine Fluorides

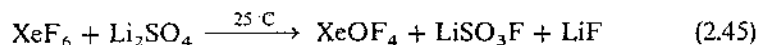
Reaction temperatures in excess of 70°C were required to initiate a slow reaction between IF_7 and Li_2SO_4 . Even at this temperature, the conversion of the Li_2SO_4 was only about 6–7%. As in the case of NO_3^- , deoxygenation of the IOF_5 occurred and IF_5 and O_2 were the observed products (Eq. 2.44).³⁴



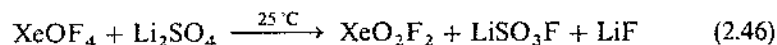
Attempts to convert IOF_5 with Li_2SO_4 to IO_2F_3 at 75°C were, as in the case of NO_3^- , also unsuccessful.³⁴

2.3.3. Xenon Fluorides

At room temperature, excess XeF_6 reacts with Li_2SO_4 to give the expected XeOF_4 in high yield (Eq. 2.45).³⁴



The XeOF_4 can be reacted further with Li_2SO_4 to give XeO_2F_2 in modest yield (Eq. 2.46).³⁴



As in the case of NO_3^- , care must be taken to use excess XeOF_4 to avoid the formation of explosive XeO_3 .

2.4. SUMMARY

Oxoanions, such as NO_3^- or SO_4^{2-} , are effective, readily available, nontoxic, and low cost reagents for controlled, stepwise fluorine–oxygen exchange in highly fluorinated compounds of the more electronegative elements. Product separations can be facilitated greatly by appropriate choices of the anion, the counteranions and the mole ratios of the reagents. The reactions appear to be quite general, controllable, safe, and scalable.

ACKNOWLEDGMENTS

The authors are indebted to Mr. R. D. Wilson for help and to the Army Research Office, the Air Force Astronautics Laboratory, and the Office of Naval Research for financial support of this work.

REFERENCES

1. Burmakov, A. I., Kunshenko, B. V., Alekseeva, L. A., and Yagupolskii, L. M., in *New Fluorinating Agents in Organic Synthesis* (L. German and S. Zemskov, Eds.), Springer-Verlag, Berlin, 1989, pp. 197-253.
2. Hudlicky, M., in *Organic Reactions*, Wiley, New York, 1988, pp. 513-637.
3. Many examples for these types of reactions can be found in Vols. 3 and 4 of *Inorganic Reactions and Methods* (I. J. Zuckerman and A. P. Hagen, Eds.), VCH Publishers, New York, 1989.
4. Chernik, C. L., Claassen, H. H., Malm, J. G., and Plurien, P. L., in *Noble-Gas Compounds* (H. H. Hyman, Ed.), University of Chicago Press, 1963, p. 106.
5. Schumacher, G. A. and Schrobilgen, G. J., *Inorg. Chem.*, **23**, 2923 (1984).
6. Bougon, R., Carles, M., and Aubert, J., *C. R. Acad. Sci. Ser. C*, **265**, 179 (1967).
7. Gillespie, R. J. and Quail, J. W., *Proc. Chem. Soc.*, 278, (1963).
8. Schack, C. J., Pilipovich, D., Cohz, S. N., and Sheehan, D. F., *J. Phys. Chem.*, **72**, 4697 (1968).
9. Alexakos, L. G., Cornwell, C. D., and Pierco, S. B., *Proc. Chem. Soc.*, 341 (1963).
10. Bartlett, N. and Levchuck, L. E. *Proc. Chem. Soc.*, 342 (1963).
11. Jacob, E., *Z. Naturforsch.*, **35b**, 1095 (1980).
12. Seppelt, K. and Rupp, H. H., *Z. Anorg. Allg. Chem.*, **409**, 331 (1974).
13. Nielsen, J. B., Kinkcad, S. A., and Eller, P. G., *Inorg. Chem.*, **29**, 3621 (1990).
14. Kinkcad, S. A. and Nielsen, J. B., paper 47 presented at the ACS Ninth Winter Fluorine Conference, St. Petersburg, FL (February, 1989).
15. Schack, C. J. and Christe, K. O., *J. Fluorine Chem.*, **49**, 167 (1990).
16. Christe, K. O., Wilson, R. D., and Schack, C. J., *Inorg. Nucl. Chem. Lett.*, **11**, 161 (1975).
17. Christe, K. O., Wilson, R. D., and Schack, C. J., *Inorg. Nucl. Chem. Lett.*, **20**, 2104 (1981).
18. Wilson, W. W. and Christe, K. O., *Inorg. Chem.*, **26**, 916 (1987).
19. Christe, K. O. and Wilson, W. W., *Inorg. Chem.*, **27**, 1296 (1988).
20. Selig, H., *Inorg. Chem.*, **5**, 183 (1966).
21. Waldman, M. C. and Selig, H., *J. Inorg. Nucl. Chem.*, **35**, 2173 (1973).
22. Schrobilgen, G. J., Martin-Rovet, D., Charpin, P., and Lance, M., *J. Chem. Soc. Chem. Commun.*, 894 (1980).
23. Christe, K. O. and Wilson, W. W., *Inorg. Chem.*, **27**, 3763 (1988).
24. Grison, E., Eriks, K., and De Vries, J. L., *Acta Crystallogr.*, **3**, 290 (1950).
25. Wilson, W. W. and Christe, K. O., *Inorg. Chem.*, **26**, 1631 (1987).

26. Christe, K. O., Wilson, W. W., and Wilson, R. D., *Inorg. Chem.*, **28**, 675 (1989).
27. Christe, K. O. and Schack, C. J., *Adv. Inorg. Chem. Radiochem.*, **18**, 319 (1976).
28. Wilson, W. W. and Christe, K. O., *Inorg. Chem.*, **26**, 1573 (1987).
29. Christe, K. O., Wilson, W. W., and Wilson, R. D., *Inorg. Chem.*, **28**, 904 (1989).
30. Christe, K. O., Sanders, J. C. P., Schrobilgen, G. J., and Wilson, W. W., *J. Chem. Soc. Chem. Commun.*, 837 (1991).
31. Schack, C. J. and Christe, K. O., *Inorg. Chem.*, **27**, 4771 (1988).
32. The authors are grateful to Dr. W. Jolly for bringing the error to their attention.
33. Christe, K. O., Wilson, W. W., and Schack, C. J., *J. Fluorine Chem.*, **43**, 125 (1989).
34. Wilson, W. W. and Christe, K. O., unpublished results.

Note added in proof: The controlled replacement of two fluorines by one oxygen atom in ClF_5 has recently been achieved by B. B. Chaivanov, Y. B. Sokolov and S. N. Spirin, "Researchers in the Field of Inorganic Fluorine Chemistry," Preprint IAE-4936/13, Moscow, 1989, by the reaction of ClF_5 with $\text{H}_3\text{O}^+\text{BF}_4^-$ according to



A Quantitative Scale for the Oxidizing Strength of Oxidative Fluorinators^{†,‡}

Karl O. Christe^{*,§} and David A. Dixon^{*,||}

Contribution from Rocketdyne, A Division of Rockwell International Corporation, Canoga Park, California 91303, and The Central Research and Development Department, E. I. du Pont de Nemours and Company, Inc., Experimental Station, Wilmington, Delaware 19880.

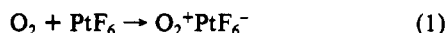
Received August 21, 1991

Abstract: A quantitative scale for the oxidizing strength of oxidative fluorinators has been developed for the first time. This scale is based on relative F^+ detachment energies, which were obtained by local density functional calculations, and is anchored to its F^+ zero point by an experimental value for KrF^+ . The oxidizing strength of 36 oxidizers was determined in this manner and shown to be consistent with all of the previously available qualitative experiments. An analysis of the trends in the calculated data reveals some expected but also some highly unexpected features. Thus, the oxidizer strength depends not only on the number of fluorine ligands and the oxidation state and electronegativity of the central atom but also on the presence of free valence electron pairs on the central atom and the geometry of the oxidizer. The heats of formation of these oxidizers were also determined from their F^+ detachment energy values.

Introduction

The synthesis of fluorine-containing strong oxidizers generally requires powerful fluorinating agents. In this context, the question as to which agent is most powerful and which agent can oxidize a given substrate frequently arises. The ranking of these fluorinating agents according to their strength is very difficult. Direct electrochemical measurements of their oxidation potentials are not possible because the latter generally exceed the decomposition voltages of the available solvents. Therefore, no oxidizer strength scales exist at the present time, and the only data available are isolated observations¹⁻⁴ that some compounds can oxidize certain substrates while others cannot. Frequently, however, a lack of reaction is due to the choice of unfavorable reaction conditions or high activation energies and not necessarily to an insufficient oxidation potential, a thermodynamic measure.

Strong oxidizers can be separated into two main classes. The first one consists of one-electron oxidizers such as PtF_6 or UF_6 , and the second one of oxidative fluorinators such as KrF^+ , ClF_6^+ , or N_2F^+ . The case of one-electron oxidizers has previously been analyzed by Bartlett and is best exemplified by his classic example of the reaction of PtF_6 with O_2 (eq 1).⁵ The reaction enthalpy,



ΔH° , of (1) can be derived from the Born-Haber cycle given in Figure 1, where IP, EA, and U_L stand for the first ionization potential of O_2 , the electron affinity of PtF_6 , and the lattice energy of solid $O_2^+PtF_6^-$, respectively. Neglecting entropy changes, ΔH° must be negative for the reaction to occur spontaneously. Since the ionization potentials of the substrates are usually known and the lattice energies of the solid products can be estimated quite accurately, the occurrence or lack of spontaneous reaction with different substrates was used⁴ to place upper and lower limits on the electron affinity of the oxidizing species. This method allows one to estimate rough electron affinity values which in turn can be taken as a measure for the oxidizing power of these one-electron oxidizers. Since these electron-transfer reactions do not involve significant activation energies, the "go-no go" reaction approach works rather well.

The case of oxidative fluorinators, such as KrF^+ or N_2F^+ , is more complex and has not been analyzed previously. The oxidizer strengths of these species is not a simple function of the electron affinity or ionization potential of the atom or molecule to which the formal " F^+ " unit is attached. This was exemplified by a recent qualitative study¹ which showed that N_2F^+ ($IP_{N_2} = 360.6$ kcal

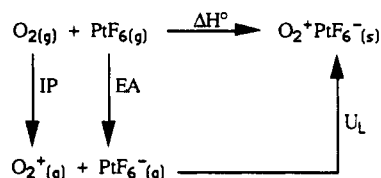


Figure 1. Born-Haber cycle for a typical one-electron oxidation reaction.

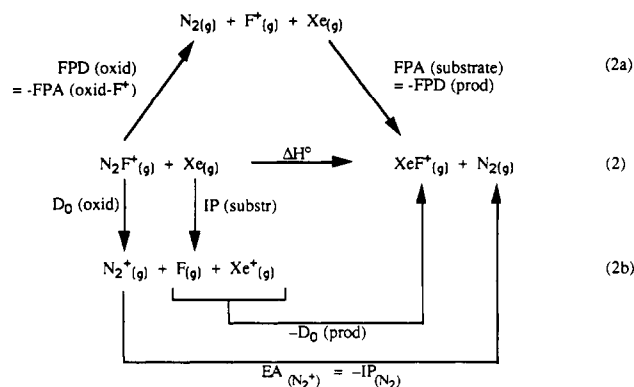


Figure 2. Two Born-Haber cycles which can be used for the description of a typical oxidative fluorination reaction, in this case the oxidative fluorination of Xe by N_2F^+ .

mol^{-1})⁶ is a weaker oxidative fluorinator than KrF^+ ($IP_{Kr} = 324.2$ kcal mol^{-1}).⁶ Therefore, we have undertaken efforts to analyze this case and to define, if possible, a quantitative oxidizer strength scale.

Results and Discussion

Born-Haber Cycles for Oxidative Fluorination Reactions. The case of oxidative fluorination reactions is more complex than that of one-electron oxidations. In addition to the transfer of a positive charge, an existing bond must be broken and a new one must be formed. Furthermore, the bond breaking can require a substantial

(1) Christe, K. O.; Wilson, R. D.; Wilson, W. W.; Bau, R.; Sukumar, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 3795.

(2) Christe, K. O.; Wilson, W. W.; Wilson, R. D. *Inorg. Chem.* **1984**, *23*, 2058.

(3) Sokolov, V. B.; Dobrychevskii, Yu. V.; Prusakov, V. N.; Ryzhkov, A. V.; Koroshev, S. S. *Dokl. Akad. Nauk SSSR* **1976**, *229*, 641.

(4) Bartlett, N. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 433.

(5) Bartlett, N.; Lohmann, D. H. *Proc. Chem. Soc.* **1962**, 277; *J. Chem. Soc.* **1962**, 5253.

(6) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schuman, R. H.; Halow, I.; Bailey, S. M.; Churney, K. A.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, (Suppl. 2).

[†] Dedicated to Prof. Neil Bartlett on the occasion of his sixtieth birthday.

[‡] Du Pont Contribution No. 5889.

[§] Rocketdyne.

^{||} Du Pont.

activation energy and, therefore, complicates experiments aimed at the determination of relative oxidizer strengths based on the observation or lack of observation of a reaction.

Consider the reaction between N_2F^+ and Xe in HF solution¹ as a typical example of an oxidative fluorination reaction. Assuming that the solvation energies of N_2F^+ and Xe are about the same as those of XeF^+ and N_2 , this reaction can be expressed by eq 2. Figure 2 shows two Born–Haber cycles, (2a) and (2b), which can be used to describe reaction 2.

As in the case of the one-electron oxidations, ΔH° must be negative for a spontaneous reaction and, for the cycles 2a and 2b, is given by eq 3a and 3b, respectively, where FPA is the F^+ affinity

$$\Delta H^\circ = \text{FPA}(\text{subst}) - \text{FPA}(\text{oxid} - \text{F}^+) \quad (3a)$$

$$\Delta H^\circ = \text{IP}(\text{subst}) - \text{IP}(\text{oxid} - \text{F}^+) + D_0(\text{oxid}) - D_0(\text{prod}) \quad (3b)$$

($=\Delta H$ of the reaction $\text{A} + \text{F}^+ \rightarrow \text{AF}^+$), FPD is the F^+ detachment energy, IP is the first adiabatic ionization potential, D_0 is the bond dissociation energy, and EA is the electron affinity. Until now, neither cycle 2a nor 2b had been used for the determination of ΔH° values since the F^+ affinities and bond dissociation energies were generally unknown.

Calculations. If one considers reaction 2 as the transfer of F^+ from one compound to another, it is very similar to the transfer of a proton from one base to another (reaction 4). Such pro-



ton-transfer reactions can be calculated quite accurately by molecular orbital methods for both relative values and absolute values.⁷ The agreement with experiment for proton-transfer processes is usually excellent if one employs good geometries and if adequate basis sets with some consideration of the correlation energy are included in the calculations. Absolute values can be obtained with somewhat larger basis sets.

Such a theoretical model could also be employed for the calculation of relative FPAs. However, most of the compounds under consideration as strong oxidants contain atoms predominantly from the right-hand side of the periodic table, and contrary to H^+ , F^+ has a significant number of electrons. Thus, some method is needed which, even for describing the geometries, includes correlation effects. Since there are a significant number of compounds, all of which need to have their geometries optimized, one also requires a computationally efficient method. Rather than using traditional Hartree–Fock methods (scaling as N^4 with N as the number of basis functions) including correlation corrections (scaling as N^m , $m \geq 5$), we chose the local density functional (LDF) method (scaling as N^3).⁸

The calculation of absolute proton affinities by theoretical methods is simplified because the dissociation of BH^+ results in two closed-shell species, B and H^+ , where B and BH^+ have the same number of electron pairs. However, the calculation of absolute F^+ affinities is complicated because (1) the generated F^+ is not a closed-shell singlet but a ground-state triplet⁹ and (2)

the number of electron pairs is different in B and BF^+ . It is also well-established that the LDF method overestimates binding energies. Thus, instead of calculating absolute FPAs, we have calculated relative FPAs.

The LDF method is based on the Hohenberg–Kohn theorem,¹⁰ which states that the total energy E_1 is a functional of the charge density ρ as follows:

$$E_1[\rho] = T[\rho] + U[\rho] + E_{\text{xc}}[\rho] \quad (5)$$

where T is the kinetic energy of the noninteracting electrons of density ρ , U is the classical Coulomb electrostatic energy, and E_{xc} includes all of the many-body contributions to the energy. The first two terms can be evaluated using straightforward techniques. The most important contributions to E_{xc} are the exchange energy and the correlation energy, and it is in the final term where the local density approximation is introduced. A good approximation for the final term is derived from the exchange–correlation energy of the uniform electron gas by following the assumption that the charge density varies slowly on the scale of exchange and correlation effects. The form of the exchange–correlation energy employed in our calculations is that of von Barth and Hedin.¹¹

The calculations were done with the program DMol¹² on a CRAY-YMP computer system. DMol employs numerical functions for the atomic basis sets. These atomic basis sets are exact spherical solutions to the density functional equations. All of the calculations were done with a double numerical basis set augmented by d ($l = 2$) polarization functions. Because exact numerical solutions are employed, the basis set is of higher quality than a normal molecular orbital basis set of the same size. Furthermore, basis set superposition errors should be minimized because of the quality of the basis set.

The various integrals required for the solution of eq 5 need to be evaluated on a grid due to our use of numerical basis functions.¹³ The number of radial points is given by

$$N_R = (1.2)14(Z + 2)^{1/3} \quad (6)$$

where Z is the atomic number and the maximum distance for any function is 12 au. The angular integration points N_Ω are generated at the N_R radial points to form shells around each nucleus with N_Ω ranging from 14 to 302 depending on the density. Fitting functions for the spherical harmonics were all done with an angular momentum number $\ell' = \ell + 1 = 3$.

Geometries were optimized by using analytic gradient methods.^{14,15} Because numerical methods are used, the error in atomic coordinates determined by the optimization is on the order of 0.001 Å, which gives bond lengths and angles with errors at least 1 order of magnitude smaller than the differences between calculated and experimental values. The spin state of each structure is a singlet except for those of O_2 and F^+ , which are triplets.

Oxidizer Strength Scale. Although a knowledge of the relative FPAs allows the prediction of whether a certain reaction is thermodynamically feasible and which oxidizer is stronger with respect to another one, it provides only a relative oxidizer strength scale. To obtain an absolute scale, one must identify the thermodynamic property governing the oxidizer strength, define a zero point for the scale, and then anchor the relative oxidizer strength values derived from the LDF calculations to the chosen zero point by an experimentally known number since LDF theory overes-

(7) Dixon, D. A.; Lias, S. G. In *Molecular Structures and Energies*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: Deerfield Beach, FL, 1987; Vol. 2, Chapter 7, p 269.

(8) (a) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989. (b) Salahub, D. R. In *Ab Initio Methods in Quantum Chemistry*; Lawlwy, K. P., Ed.; J. Wiley and Sons: New York, 1987; Vol. II. (c) Wimmer, E.; Freeman, A. J.; Fu, C. L.; Cao, P. L.; Chou, S. H.; Delley, B. In *Supercomputer Research in Chemistry and Chemical Engineering*; Jensen, K. F., Truhlar, D. G., Eds.; ACS Symposium Series 353; American Chemical Society: Washington, DC, 1987; p 49. (d) Jones, R. O.; Gunnarsson, O. *Rev. Mod. Phys.* **1989**, *61*, 689. (e) Dixon, D. A.; Andzelm, J.; Fitzgerald, G.; Wimmer, E.; Delley, B. *Science and Engineering on Supercomputers*; Pitcher, E. J., Ed.; Computational Mechanics Publications: Southampton, England, 1990; p 285. (f) Dixon, D. A.; Andzelm, J.; Fitzgerald, G.; Wimmer, E.; Jasien, P. In *Density Functional Methods in Chemistry*; Labanowski, J. K., Andzelm, J., Eds.; Springer-Verlag: New York, 1991; Chapter 3, p 33.

(9) Calculations of the F^+ cation affinities of some simple organic bases have recently been reported. These ab initio molecular orbital calculations were done at the STO-3G(*PS) level and the reported affinities are for an excited state of $\text{F}^+(\text{S})$: Alcamí, O.; Yáñez, M.; Abboud, J.-L. M. *J. Phys. Org. Chem.* **1991**, *4*, 177.

(10) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 184.

(11) von Barth, U.; Hedin, L. *Physica C* **1972**, *5*, 1629.

(12) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508. DMol is available commercially from Biosym Technologies, San Diego, CA.

(13) This grid can be obtained by using the FINE parameter in DMol.

(14) For a discussion of Hartree–Fock methods, see: (a) Komornicki, A.; Ishida, K.; Morokuma, K.; Ditchfield, R.; Conrad, M. *Chem. Phys. Lett.* **1977**, *45*, 595. (b) Pulay, P. In *Applications of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; p 153. (c) Jorgensen, P.; Simons, J., Eds. *Geometrical Derivatives of Energy Surfaces and Molecular Properties*; NATO ASI Ser. C **1986**, *166*, 207.

(15) (a) Delley, B. In *Density Functional Methods in Chemistry*; Labanowski, J. K., Andzelm, J. W., Eds.; Springer-Verlag: New York, 1991; Chapter 11, p 101. (b) Fournier, R.; Andzelm, J.; Salahub, D. R. *J. Chem. Phys.* **1989**, *90*, 6371. (c) Versluis, I.; Ziegler, T. *J. Chem. Phys.* **1988**, *88*, 3322.

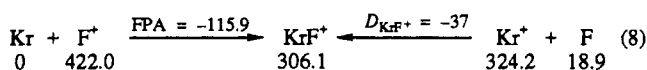
timates absolute binding energies.

According to the Born-Haber cycle 2a and eq 3a, the reaction enthalpy ΔH° equals the difference between the F^+ affinities of the substrate and of the oxidizer minus F^+ . Hence, F^+ affinities are a useful criterion for an oxidizer strength scale. Since the F^+ affinity (FPA) of a substrate equals the negative value of the F^+ detachment energy (FPD) of the corresponding product, eq 3a can be rewritten as eq 7, and an oxidative fluorination reaction

$$\Delta H^\circ = \text{FPD}(\text{oxid}) - \text{FPD}(\text{prod}) \quad (7)$$

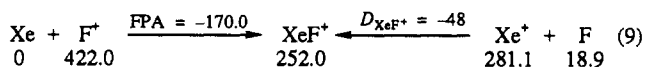
can be considered as the formal transfer of an F^+ cation from an oxidizer to a substrate. Since the F^+ detachment energy for F^+ itself obviously is zero, F^+ is the ideal zero point for an oxidizer strength scale based on F^+ detachment energies. On this scale, then, increasing FPD values signify decreasing oxidizer strength.

The third objective, i.e., the anchoring of the relative FPD values to the F^+ zero point, was accomplished by calculating the F^+ affinity of Kr from experimental data. From the known heat of formation of KrF_2 , the appearance potential of KrF^+ from KrF_2 , and the first adiabatic ionization potential of Kr, the bond energy and heat of formation of gaseous KrF^+ have been estimated¹⁶ to be 37 and 306.1 kcal mol⁻¹, respectively, as shown by the right half of eq 8. [Numbers beneath the equations are ΔH_f° (kcal

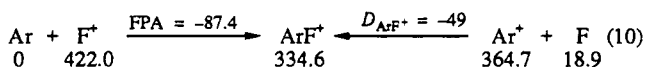


mol⁻¹]. From the known heats of formation of gaseous KrF^+ and F^+ ,⁶ the F^+ affinity of Kr can then be estimated as -115.9 kcal mol⁻¹, as shown by the left half of (8). The combination of this experimentally derived value with the F^+ affinity differences obtained by our LDF calculations permits the construction of the absolute oxidizer strength scale given in Table I.

The quality of the values in Table I was cross-checked for XeF^+ . Using the previously published experimental data,¹⁶ the FPD of XeF^+ was estimated (9) as 170.0 kcal mol⁻¹, in fair agreement with our computed value of 164.8 kcal mol⁻¹ given in Table I.



An additional cross-check was made for the yet unknown ArF^+ cation for which recent ab initio calculations¹⁷ have yielded an Ar-F bond energy value of 49 ± 3 kcal mol⁻¹. Using this value, the F^+ affinity of Ar can be estimated as -87.4 kcal mol⁻¹ (10) which is in good agreement with our FPD value of 84.3 kcal mol⁻¹ from Table I.



Heats of Formation of the Oxidizers. The knowledge of the F^+ detachment energies of the oxidizers (see Table I) also provides a convenient source for their heats of formation ΔH_f° . The latter are given by eq 11, where $\Delta H_f^\circ(F^+_{g})$ equals 422.0 kcal mol⁻¹;

$$\Delta H_f^\circ(XF^+_{g}) = \Delta H_f^\circ(X_g) + \Delta H_f^\circ(F^+_{g}) - \text{FPD}(XF^+_{g}) \quad (11)$$

$\Delta H_f^\circ(X_g)$, the heat of formation of the parent molecule, is usually known, and the FPD values are taken from Table I. The resulting $\Delta H_f^\circ(XF^+_{g})$ values have been included in Table I. Only few experimental estimates are available for these formation enthalpies. For example, the value of 204 kcal mol⁻¹ previously reported¹⁸ for $\Delta H_f^\circ(NF_4^+_{g})$ is in fair agreement with our value of 210 kcal mol⁻¹ given in Table I.

Characteristics of the Oxidizer Strength Scale. The following comments can be made about the data given in Table I.

(16) Bartlett, N.; Sladky, F. In *Comprehensive Inorganic Chemistry*; Pergamon Press: Oxford, UK, 1973; Vol. 1, pp 213-330. The appearance potentials are from J. Berkowitz, unpublished work.

(17) Frenking, G.; Koch, W.; Deakne, C. A.; Liebman, J. F.; Bartlett, N. *J. Am. Chem. Soc.* **1989**, *111*, 31.

(18) Goetschel, C. J.; Campanile, V. A.; Curtis, R. M.; Loos, K. R.; Wagner, D. C.; Wilson, J. N. *Inorg. Chem.* **1972**, *11*, 1696.

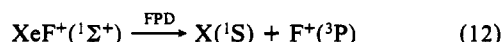
Table I. Absolute Oxidizer Strength Scale and Formation Enthalpies for Oxidative Fluorinators

oxidative fluorinator ^a XF ⁺	F ⁺ detachment energy (kcal mol ⁻¹) ^b FPD(XF ⁺ _g)	formation enthalpy ^c (kcal mol ⁻¹)	
		$\Delta H_f^\circ(XF^+_{g})$	ref for $\Delta H_f^\circ(X)$
(HeF ⁺) (³ π)	-1.6	423.6	6
(HeF ⁺) (¹ Σ ⁺)	(-16.2)	(438.2)	6
(F ⁺)	0	422.0	6
(NeF ⁺) (³ π)	0.6	421.4	6
(NeF ⁺) (¹ Σ ⁺)	(-19.6)	(441.6)	6
(F ₃ ⁺)	60.0	362.0	6
(ArF ⁺)	84.3	337.7	6
KrF ⁺	115.9	306.1	6
(XeF ₇ ⁺)	116.7	222.2	15
(OF ₃ ⁺)	122.2	305.7	6
(BrF ₄ O ⁺)	131.1		
(O ₂ F ⁺) ^f	133.8	288.2	6
(ClF ₄ O ⁺)	135.6	251.0	d
N ₂ F ⁺	139.3	282.7	6
(XeF ₅ O ⁺)	139.8	276.2	e
BrF ₆ ⁺	140.8	178.7	6
(XeF ₃ O ₂ ⁺)	141.7	336.3	16
ClF ₆ ⁺	147.3	215.5	d
XeF ₃ ⁺	152.4	243.7	15
ClF ₄ ⁺	158.7	224.3	6
XeF ₅ ⁺	158.9	200.6	6
ClF ₂ O ₂ ⁺	161.0	228.4	d
(IF ₄ O ⁺)	164.0		
XeF ⁺	164.8	257.2	6
ClF ₂ ⁺	167.1	241.9	6
XeF ₃ O ⁺	173.1		
BrF ₄ ⁺	174.0	187.0	6
IF ₆ ⁺	175.0	40.4	6
NF ₂ O ⁺	175.3	230.8	6
Cl ₂ F ⁺	179.1	242.9	6
NF ₄ ⁺	180.1	210.5	6
(XeFO ⁺)	182.4	290.1	16
BrF ₂ ⁺	182.4	217.2	6
ClF ₂ O ⁺	193.0		
XeFO ₂ ⁺	195.3		
BrF ₂ O ⁺	200.5		
IF ₄ ⁺	212.1	93.9	15
IF ₂ ⁺	213.5	185.7	6
(IF ₂ O ⁺)	230.0		

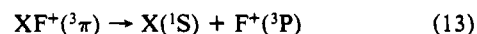
^aThe cations listed in parentheses have so far not been isolated in the form of stable salts. ^bAll FPD values were computed for XF⁺ and X being singlet ground states and F⁺ being a triplet ground state, except for HeF⁺ and NeF⁺, which have triplet ground states (see text) and O₂F⁺ (see footnote f). ^cCalculated by eq 7, using $\Delta H_f^\circ(X)$ values from refs 6 and 15c,d. ^dBarberi, P.; Carre, J.; Rigny, P. *J. Fluorine Chem.* **1976**, *7*, 511. ^eGunn, S. R. *J. Am. Chem. Soc.* **1965**, *87*, 2290. ^fCalculated for the singlet state of O₂F⁺ going to the triplet state of O₂.

(i) F^+ detachment energies are a good measure for the oxidizing power of an oxidative fluorinator. The oxidizing power of a compound decreases with an increase in its F^+ detachment energy.

(ii) A negative value for the F^+ detachment energy of an XF⁺ species signifies a species that is unstable with respect to decomposition to ground-state X(¹S) and F(³P). The negative F^+ detachment energy values for NeF⁺ and HeF⁺, listed in parentheses in Table I, are due to the fact that for all of our calculations the following spin states were used (12).

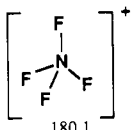
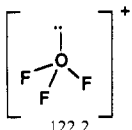
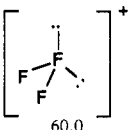
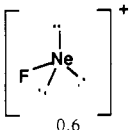
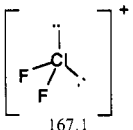
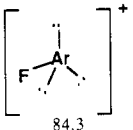
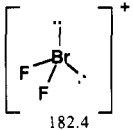
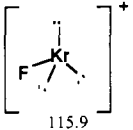
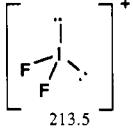
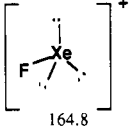


Whereas for XeF⁺, KrF⁺, and ArF⁺ a ¹Σ⁺ state is the ground state; NeF⁺ and HeF⁺ have a ³π ground state. Their ¹Σ⁺ states are excited states which are calculated to lie 30.3 and 23.8 kcal mol⁻¹, respectively, above their ground states.¹⁷ If for NeF⁺ and HeF⁺ the FPDs are computed for their ³π ground states (13)



slightly positive values of about 4.0 and 1.2 kcal mol⁻¹, respectively, are obtained. This was shown by recent high-level ab initio

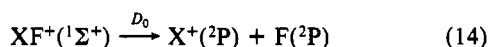
Table II. Relative Oxidizer Strengths (FPD Values)^a of the Electronically Isovalent Series of Tetrahedral and Pseudotetrahedral Binary Fluoride Cations

group in periodic system formal oxidation state of central atom	V A +V	VI A +IV	VII A +III	VIII A +II
	 180.1	 122.2	 60.0	 0.6
			 167.1	 84.3
			 182.4	 115.9
			 213.5	 164.8

^a Numbers below each structure are calculated values (kcal mol⁻¹).

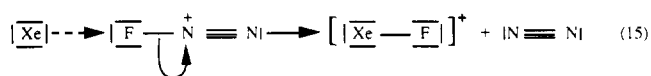
calculations^{17,19} which suggest that in their ground states these cations are only weakly bound.

(iii) Except for NeF⁺ and HeF⁺, the F⁺ detachment energies listed in Table I do not represent the X-F bond dissociation energies, *D*₀. Since usually the first ionization potential of X is lower than that of the F atom (422 kcal mol⁻¹),⁶ the lowest energy bond dissociation process becomes the one which yields X⁺ and F atoms (14).



(iv) The previously reached² conclusion that KrF⁺ is the strongest presently known oxidative fluorinator was confirmed.

(v) The oxidative fluorination reactions can be considered as a formal transfer of F⁺ from the oxidizer to a substrate and involve the breaking of an existing and the formation of a new bond. Even when proceeding through a probable intermediate activated complex, as shown by eq 15 for the Xe + N₂F⁺ reaction, such



a reaction could require a substantial activation energy. Hence, it is not surprising that some of the reactions, deemed possible from the rankings in Table I, have so far experimentally not been observed. Of the previously observed oxidative fluorination reactions,^{1-3,20-27} none violates the rankings given in Table I, thus supporting our results. The only somewhat ambiguous case is a previous report²⁷ which indicated that Cl₂F⁺AsF₆⁻ oxidized Xe

to Xe₂F₃⁺. Although Table I implies that Cl₂F⁺ is not capable of oxidizing Xe to XeF⁺, this does not allow any conclusions concerning the oxidation of Xe to Xe₂F₃⁺. Because Xe₂F₃⁺ contains an extra XeF₂ molecule and, generally, the oxidizing power of a species decreases with decreasing positive charge, Xe₂F₃⁺ is a weaker oxidizer than XeF⁺ and probably also Cl₂F⁺.

(vi) Among the yet unknown oxidizers which are listed in Table I and rank in oxidizing power below KrF⁺ are XeF₅O⁺ and ClF₄O⁺. Previous attempts to oxidatively fluorinate XeF₄O^{24,25,28} or ClF₃O²⁹ have always resulted in oxidation of the oxygen ligand, i.e., O₂ evolution, instead of XeF₅O⁺ or ClF₄O⁺ formation, respectively. These results indicate that in the case of high-oxidation-state oxyfluorides, the oxygen ligand might become easier to oxidize than the central atom, thus foiling attempts aimed at their oxidative fluorination.

General Trends of Oxidizer Strength within the Periodic System.

A systematic analysis of the data of Table I indicates the following general trends, some of which are quite obvious and fully expected but others are rather surprising.

I. Binary Fluorides. (i) Within a group of electronically isovalent³⁰ species, such as the series of tetrahedral and pseudotetrahedral cations shown in Table II, the oxidizing power increases on going from the left to the right and from the bottom to the top of the periodic table. Thus, NeF⁺ is the strongest oxidative fluorinator within this group, and the electronegativity of the central atom appears to be more important than its formal oxidation state, i.e., the number of fluorine ligands. The only minor exception to the above rule is BrF₆⁺ which, by analogy with the known BrO₄⁻-ClO₄⁻ case,³¹ is a slightly stronger oxidative fluorinator than ClF₆⁺.

(ii) For a given central atom, the oxidizing power generally increases with an increase in its formal oxidation state, as shown in Tables III and IV. For chlorine as a central atom, the oxidizing power increases from ClF₂⁺ to ClF₄⁺ to ClF₆⁺ by roughly equal amounts. Going to the heavier central atoms, bromine and iodine, the oxidizer strength gaps between XF₂⁺ and XF₄⁺ become increasingly smaller and those from XF₄⁺ to XF₆⁺ become increasing

(19) (a) Frenking, G.; Koch, W.; Cremer, D.; Gauss, J.; Liebman, J. F. *J. Phys. Chem.* **1989**, *93*, 3397, 3410. (b) Deakyne, C. A.; Liebman, J. F.; Frenking, G.; Koch, W. *J. Phys. Chem.* **1990**, *94*, 2306.

(20) Gillespie, R. J.; Schrobilgen, G. J. *J. Chem. Soc.* **1974**, *13*, 1230.

(21) Artyukhov, A. A.; Khoroshev, S. S. *Koord. Khim.* **1977**, *3*, 1478.

(22) Christe, K. O.; Wilson, W. W.; Curtis, E. C. *Inorg. Chem.* **1983**, *22*, 3056.

(23) Stein, L. *Chemistry* **1974**, *47*, 15.

(24) McKee, D. E.; Adams, C. J.; Zalkin, A.; Bartlett, N. J. *Chem. Soc., Chem. Commun.* **1973**, 26.

(25) Holloway, J. H.; Schrobilgen, G. J. *J. Chem. Soc., Chem. Commun.* **1975**, 623.

(26) Meinert, H.; Gross, U. Z. *Chem.* **1968**, *8*, 345.

(27) Christe, K. O.; Wilson, R. D. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 845.

(28) Christe, K. O.; Wilson, R. D. *J. Fluorine Chem.* **1976**, *7*, 356.

(29) Christe, K. O.; Wilson, W. W.; Wilson, R. D., unpublished results.

(30) Haas, A. *Adv. Inorg. Chem. Radiochem.* **1984**, *28*, 167.

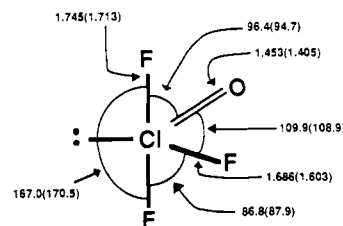
(31) Greenwood, N. N.; Earnshaw, A. In *Chemistry of the Elements*; Pergamon Press: Oxford, UK, 1984; p 1020.

Table III. Relative Oxidizer Strengths (FPD Values) of the Binary Halogen Fluoride Cations as a Function of the Formal Oxidation State of the Central Atom

formal oxidn state of central atom	structure of cation	calcd FPD values (kcal/mol)		
+VII		ClF ₆ ⁺ 147.3	BrF ₆ ⁺ 141.7	IF ₆ ⁺ 175.0
+V		ClF ₄ ⁺ 158.7	BrF ₄ ⁺ 174.0	IF ₄ ⁺ 212.1
+III		ClF ₂ ⁺ 167.1	BrF ₂ ⁺ 182.4	IF ₂ ⁺ 213.5

Table IV. Relative Oxidizer Strengths (FPD Values) of the Binary Xenon Fluoride Cations as a Function of the Formal Oxidation State of the Xenon Central Atom

formal oxidn state of Xe	structure of the cation	calcd FPD value (kcal/mol)
+VIII		116.7
+VI		158.9
+IV		152.4
+II		164.8

**Figure 3.** Geometry of ClF₃O (bond lengths in angstroms, angles in degrees) as calculated by the LDF method. The experimentally observed³² values are given in parentheses.

larger (see Table III). For the xenon fluorides (see Table IV), a similar trend is observed. The FPD gap between XeF⁺ and XeF₅⁺ is only 5.9 kcal mol⁻¹ whereas that between XeF₅⁺ and XeF₇⁺ is 42.3 kcal mol⁻¹.

These features are best explained by the increased mobility of the free valence electron pair on the central atom with increasing atomic weight and by the replacement of the last free valence electron pair by two fluorine ligands, which causes a large decrease in the fluorine plus detachment (FPD) energy values. It is very plausible that the availability of a highly mobile free valence electron pair should counteract the removal of an electron-deficient F⁺ cation from these species, thereby increasing the FPD values.

There appears to be a considerably weaker secondary effect, which is also apparent from the oxyfluoride cations (see below). Trigonal-bipyramidal species seem to exhibit slightly lower FPD values than the energetically more favored pseudotetrahedral or pseudooctahedral species. This causes the FPD value of XeF₃⁺ to be slightly lower than those of XeF⁺ and XeF₅⁺ (see Table IV) and also accounts for the very small difference of 1.4 kcal mol⁻¹ between IF₂⁺ and IF₄⁺.

The low FPD value of XeF₇⁺, which is almost identical to that of KrF⁺ (see Table I), also explains the failure of our previous attempts²⁹ to prepare the yet unknown XeF₇⁺ cation from XeF₆ and KrF⁺.

II. Oxyfluorides. The case of oxyfluorides is not quite as transparent as that of the binary fluorides. A priori, one might have predicted that the replacement of one free valence electron pair on a central atom by one doubly bonded oxygen ligand should increase the oxidizing power and decrease the FPD value of an oxidizer, albeit not by as much as that observed for the replacement of one free pair by two fluorine ligands. Inspection of Table I clearly shows that this is not the case. For example, the oxidizing strength of ClF₂O⁺ is 25.9 kcal mol⁻¹ lower than that of ClF₂⁺ while that of ClF₄O⁺ is 23.1 kcal mol⁻¹ higher than that of ClF₄⁺.

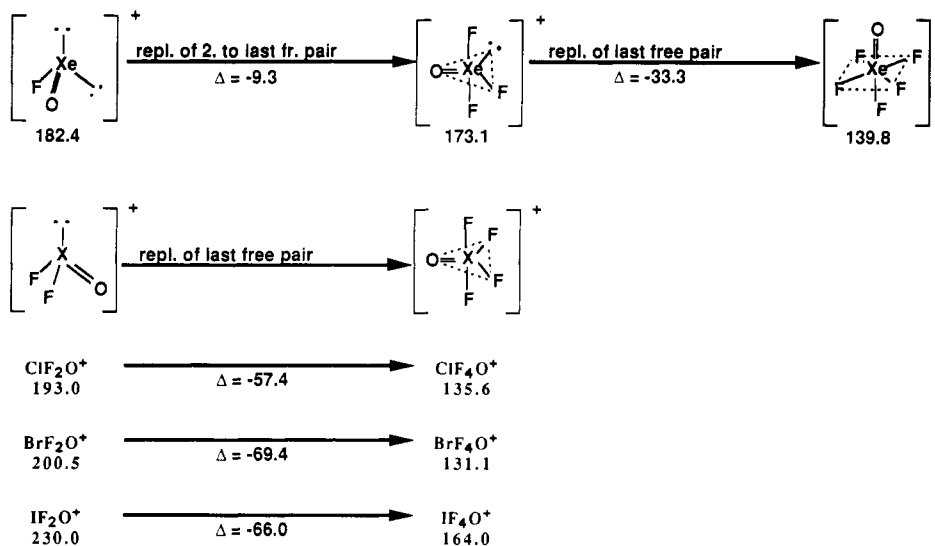
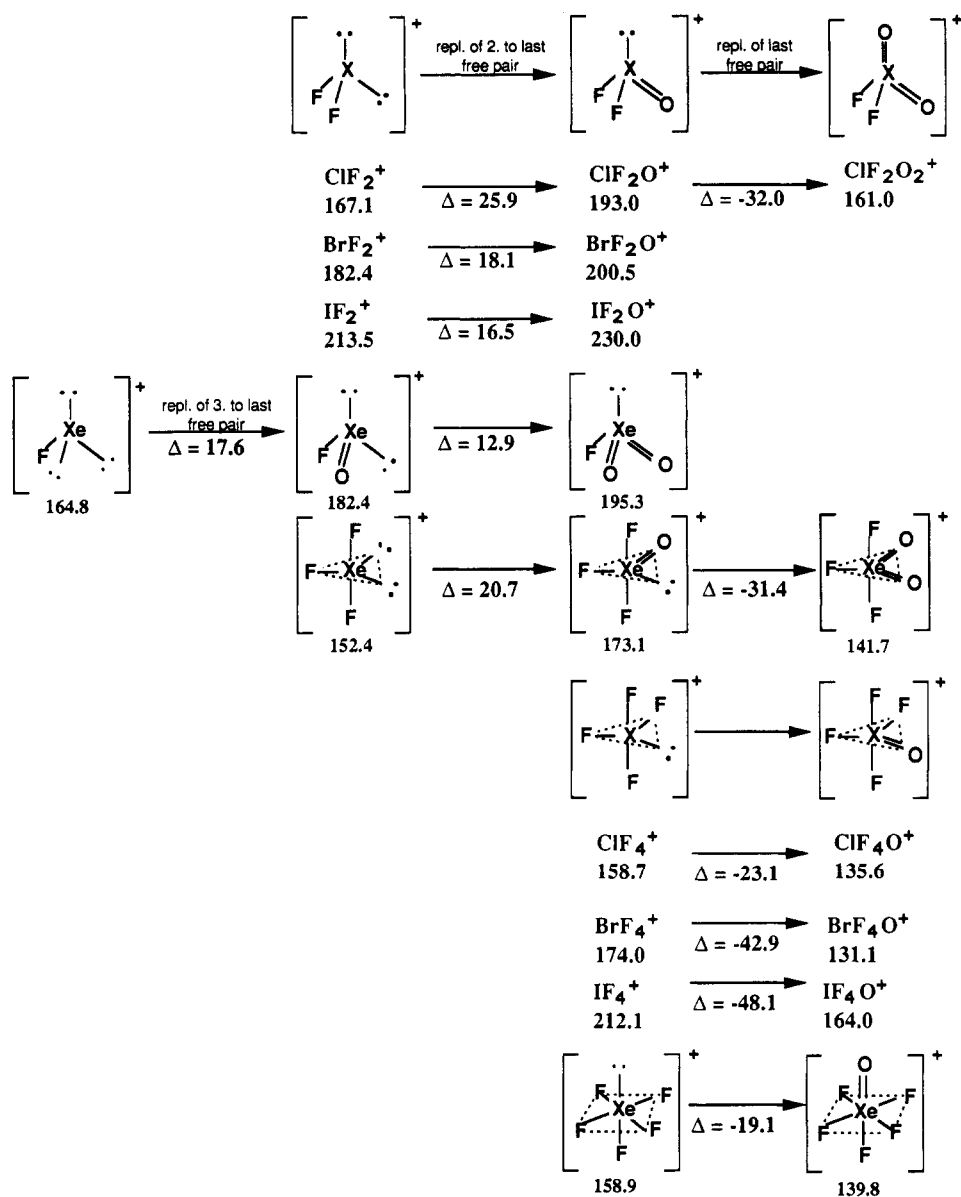
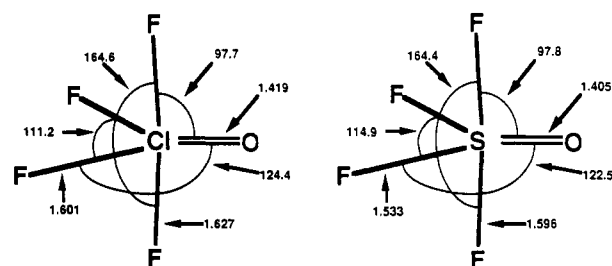
Table V. Relative Oxidizer Strengths (FPD Values) of Oxyfluorides Resulting from the Stepwise Replacement of Free Valence Electron Pairs by Two Fluorine Atoms (i.e., Oxidative Fluorination Reactions)

Table VI. Relative Oxidizer Strengths (FPD Values) of Oxyfluorides Resulting from the Stepwise Replacement of Free Valence Electron Pairs by One Doubly Bonded Oxygen Atom (i.e., Oxidative Oxygenation Reactions)

To verify that these results were not caused by computational problems, the geometry of the ClF_3O molecule was computed and compared to that experimentally determined.³² As can be seen from Figure 3, the agreement between the calculated and experimental geometry was good, particularly when one remembers that the bond lengths calculated by the LDF method are generally about 0.05 Å longer than the observed values for these types of compounds.³³ Similarly, the geometry calculated for ClF_4O^+ is very similar to that previously determined³⁴ for isoelectronic SF_4O (see Figure 4). Therefore, the LDF method results are deemed reliable for this type of compounds.

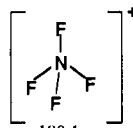
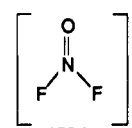
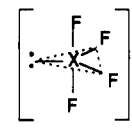
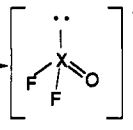
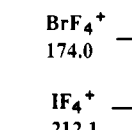
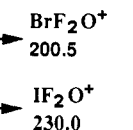
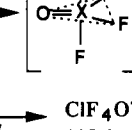
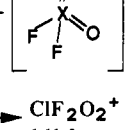
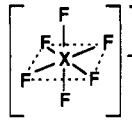
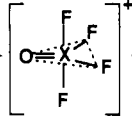
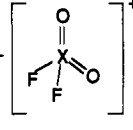
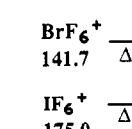
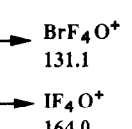
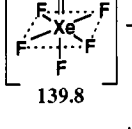
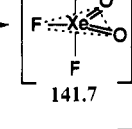
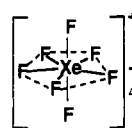
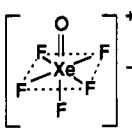
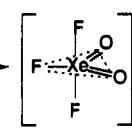
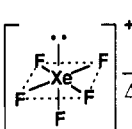
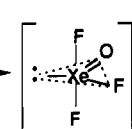
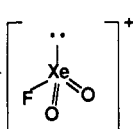
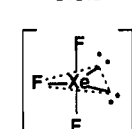
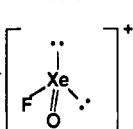
In spite of the seeming lack of an obvious general trend to the FPD values of the oxyfluorides of Table I, a closer inspection reveals that the data are indeed self-consistent and exhibit systematic trends. These become obvious from an analysis of how the FPD values vary with the following three processes.

**Figure 4.** Calculated geometry of ClF_4O^+ compared to that experimentally determined³⁴ for isoelectronic SF_4O .

(i) **Stepwise Replacement of Free Valence Electron Pairs on the Central Atom by Fluorine Ligands (i.e., Oxidative Fluorination Reactions).** When a sterically active free valence electron pair is replaced by two fluorine ligands, the coordination number and the formal oxidation state of the central atom are increased by one and two units, respectively; i.e., we are dealing with an oxidative fluorination reaction. As can be seen from the examples given in Table V, and also from those given for oxidative oxygenation reactions (Table VI), the replacement of the last free valence electron pair results in a much larger increase in the

(32) Oberhammer, H.; Christe, K. O. *Inorg. Chem.* **1982**, *21*, 273.(33) Christe, K. O.; Curtis, E. C.; Dixon, D. A.; Mercier, H. P.; Sanders, J. C. P.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **1991**, *113*, 3351.(34) (a) Gundersen, G.; Hedberg, K. J. *Chem. Phys.* **1969**, *51*, 2500. (b) Hargittai, I. *J. Mol. Struct.* **1979**, *56*, 301. (c) Oberhammer, H.; Boggs, J. E. *J. Mol. Struct.* **1979**, *56*, 107.

Table VII. Relative Oxidizer Strengths (FPD Values) of Oxyfluorides Resulting from the Stepwise Replacement of Two Fluorine Ligands by a Doubly Bonded Oxygen Ligand (i.e., Fluorine–Oxygen Exchange Reactions)

pentagonal bipyramid	octahedron	trigonal bipyramid	tetrahedron	trigonal plane
			 180.1	 175.3
			$\Delta = -4.8$	
		 158.7	 193.0	
		$\Delta = 34.3$		
		 174.0	 200.5	
		$\Delta = 26.5$		
		 212.1	 230.0	
		$\Delta = 17.9$		
		 147.3	 135.6	 161.0
		$\Delta = -11.7$		$\Delta = 25.4$
		 141.7	 131.1	
		$\Delta = -10.6$		
		 175.0	 164.0	
		$\Delta = -11.0$		
		 116.7	 139.8	 141.7
		$\Delta = 23.1$		$\Delta = 1.9$
		 158.9	 173.1	 195.3
		$\Delta = 14.2$		$\Delta = 22.2$
		 152.4	 182.4	
		$\Delta = 30.0$		

oxidizer strength of the product than the replacement of any of the other free pairs. As for the binary fluoride cations (see above), the FPD values increase for isotopic cations with increasing atomic weight of the central atom. Again, the only exception is Br(+VII), which is a slightly stronger oxidizer than Cl(+VII).³¹

(ii) **Stepwise Replacement of Free Valence Electron Pairs on the Central Atom by Oxygen Ligands (i.e., Oxidative Oxygenation Reactions).** Although, in oxidative oxygenation reactions, the replacement of a free valence electron pair by a doubly bonded oxygen ligand increases again the formal oxidation state of the central atom by two, its coordination number remains unchanged. As observed above for the oxidative fluorination reactions, the most salient feature is again the large decrease in the FPD value on replacement of the last free valence electron pair. For the replacement of any of the other pairs, the FPD values of all our examples actually increase; i.e., in these cases oxidative oxygen-

ation results in a weaker oxidizer. This is a highly remarkable and unexpected result. The only previous indication for the existence of such an effect was based on normal coordinate analyses for some of these ions, which showed that, for XF_nO_m -type compounds, frequently the X–F force constants decreased with oxidative oxygenation.³⁵ In these compounds, a weakening of the force constant implies an increase of the $\text{X}^{(\delta+)} - \text{F}^{(\delta-)}$ polarity of the X–F bond which counteracts the F-plus dissociation (FPD), thereby increasing the FPD value and decreasing the oxidizer strength of the species.

(iii) **Stepwise Replacement of Two Fluorine Ligands by a Doubly Bonded Oxygen Ligand (i.e., Fluorine–Oxygen Exchange Reactions).** In fluorine–oxygen exchange reactions, two singly bonded

(35) Christe, K. O.; Schack, C. J. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 331.

Table VIII. Comparison between Intuitively Predicted Qualitative and Calculated Oxidizer Strengths for Fluorides and Oxyfluorides of Chlorine and Xenon

predicted order		calculated order		FPD value (kcal/mol)
oxidation state	species	oxidation state	species	
+VII	ClF_6^+	+VII	ClF_4O^+	135.6
+VII	ClF_4O^+	+VII	ClF_6^+	147.3
+VII, +V	ClF_2O_2^+ , ClF_4^+	+V	ClF_4^+	158.7
+V	ClF_2O_2^+	+VII	ClF_2O_2^+	161.0
+III	ClF_2^+	+III	ClF_2^+	167.1
+I	Cl_2F^+	+I	Cl_2F^+	179.1
		+V	ClF_2O^+	193.0
+VIII	XeF_7^+	+VIII	XeF_7^+	116.7
+VIII	XeF_5O^+	+VIII	XeF_5O^+	139.8
+VIII, +VI	XeF_3O_2^+ , XeF_5^+	+VIII	XeF_3O_2^+	141.7
+VI	XeF_3O^+	+IV	XeF_3^+	152.4
+VI, +IV	XeFO_2^+ , XeF_3^+	+VI	XeF_5^+	158.9
+IV	XeFO^+	+II	XeF^+	164.8
+II	XeF^+	+VI	XeF_3O^+	173.1
		+IV	XeFO^+	182.4
		+VI	XeFO_2^+	195.3

fluorine ligands are replaced by one doubly bonded oxygen ligand. Therefore, the formal oxidation state of the central atom remains the same but its coordination number is decreased by one. Since the formal oxidation state does not change, the number of free valence electron pairs on the central atom also remains constant. Hence, a study of the trends of the FPD values in fluorine-oxygen exchange reactions is ideally suited for the elimination of the strong effect exercised by a change in the number of free valence electron pairs (see above) and for an analysis of the influence caused by a change in the coordination numbers, i.e., of steric effects. In the absence of any steric effects, the oxidizing strength should monotonically decrease (i.e., the FPD values increase) with the stepwise replacement of two fluorines by one oxygen. Inspection of Table VII, however, clearly shows that the FPD values do not change monotonically, and that pseudooctahedral and pseudo-tetrahedral species are considerably weaker oxidizers than pseudo-pentagonal-bipyramidal, pseudo-trigonal-bipyramidal, and pseudo-trigonal-planar species. This effect is most pronounced for the transitions from the HalF_6^+ to the HalF_4O^+ cations. Instead of increasing FPD values, they exhibit a systematic decrease by about 11 kcal mol⁻¹. The surprising implication that HalF_4O^+ cations are significantly stronger oxidizers than the corresponding HalF_6^+ cations is in accord with our past experimental failures to synthesize these HalF_4O^+ cations.

Conclusions

Local density functional calculations are well-suited for the calculation of the geometries and relative energies of oxidative fluorinators. The oxidizing strength of oxidative fluorinators is determined by their F^+ detachment energies. A relative scale of FPD values can be obtained from the LDF calculations and can be converted to an absolute scale by the choice of a suitable zero point (FPD of $\text{F}^+ \equiv 0$) and an experimentally known FPD value (KrF^+ in this study).

An analysis of the oxidizer strengths, calculated in the above manner for 36 oxidative fluorinators, shows that the results are self-consistent and exhibit some expected, but also some highly unexpected features. Obviously, the oxidizing strength is governed to a large extent by the oxidation state and electronegativity of the central atom and the fact that the contribution of one doubly bonded oxygen is less than that of two singly bonded fluorine ligands. Among the less expected features are the following: (i) the presence of one or more free valence electron pairs on the central atom strongly decreases the oxidizing strength of a species, and (ii) the oxidizer strengths of pseudooctahedral and -tetrahedral species are depressed relative to those of pseudopentagonal or -trigonal-bipyramidal and -trigonal-planar ions. Thus, a simplistic picture is inadequate, that is, that the oxidizer strength should be governed exclusively by the oxidation state of the central atom and that, in case of similar values between a binary fluorine and oxyfluorides, the species with the larger number of fluorine ligands will be the stronger oxidizer. This is demonstrated by Table VIII, which shows a comparison between intuitive qualitative predictions and the quantitative results from our calculations for the fluorides and oxyfluorides of chlorine and xenon. For the chlorine compounds, the top placement of ClF_4O^+ and last placement of ClF_2O^+ are highly unexpected. Similarly, the last rank of XeFO_2^+ and the position of XeF_5^+ below XeF_3^+ and the high ranking of XeF^+ are a total surprise, but can be understood on the basis of the above analysis.

The availability of a quantitative oxidizer strength scale is expected to significantly contribute to our understanding of oxidizer chemistry and to the future syntheses of novel and known oxidative fluorinators. It also stresses the importance of employing high activation energy sources such as discharges or plasmas to generate intermediate F^+ cations, if novel oxidizers are desired which are more powerful than KrF^+ .

Acknowledgment. The work at Rocketdyne was financially supported by both the U.S. Army Research Office and the Air Force Phillips Laboratories. K. Dobbs (du Pont) is thanked for help in performing some of the calculations.

A Protective Strategy in Carbene Complex Chemistry. Synthesis of Functionalized Fischer Carbene Complexes via Dianion Formation

Satoshi Aoki, Tsutomu Fujimura, and Eiichi Nakamura*

Contribution from the Department of Chemistry, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan. Received September 12, 1991

Abstract: Anionic derivatives of Fischer-type carbene complexes (A and B) are stable toward strong bases and nucleophiles, and their organic moieties R and R² can be elaborated under strongly basic conditions to provide access to heteroaromatic and aliphatic carbene complexes bearing organic functional groups. The concept of anionic protection has been illustrated by the reactions of dianions **9** and **14** and the preparation of carbene complexes possessing up to four chiral centers. Some attempts to effect ortho lithiation of aromatic carbene complexes are also described.

Despite the importance of Fischer carbene complexes for the development of novel organic transformations,¹ there are still a

very limited number of basic repertoires for the synthesis of complexes possessing elaborate organic functional groups.² This

New Synthesis, Crystal Structure, and Vibrational Spectra of Tetramethylammonium Azide and Reactions of the Fluoride Anion with HN_3 and of the Azide Anion with $\text{HF}^\dagger$

Karl O. Christe,^{*,†} William W. Wilson,[‡] Robert Bau,[§] and Steven W. Bunte[§]

Contribution from Rocketdyne, A Division of Rockwell International Corporation, Canoga Park, California 91303, and The Department of Chemistry, University of Southern California, Los Angeles, California 90007. Received October 15, 1991

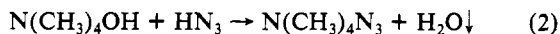
Abstract: Tetramethylammonium azide, $\text{N}(\text{CH}_3)_4^+\text{N}_3^-$, was obtained in high purity and quantitative yield by the reaction of $\text{N}(\text{CH}_3)_4^+\text{F}^-$ with $\text{Si}(\text{CH}_3)_3\text{N}_3$ in CH_3CN solution. This compound is isostructural with $\text{N}(\text{CH}_3)_4^+\text{HF}_2^-$ and crystallizes in the orthorhombic system: space group, $\text{Pmn}2_1$ (No. 31); $a = 6.879$ (5) Å; $b = 5.479$ (4) Å; $c = 8.858$ (7) Å; $Z = 2$; $R(F) = 0.0388$. Its N_3^- anion is symmetric and linear and the $\text{N}(\text{CH}_3)_4^+$ cation is somewhat distorted from tetrahedral symmetry due to crystal packing effects. The infrared and Raman spectra of $\text{N}(\text{CH}_3)_4^+\text{N}_3^-$ were also recorded. The symmetric stretching mode of N_3^- exhibits the pronounced frequency decrease expected for increasing ionicity with increasing cation size. A study of the HN_3 -MF systems [$M = \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{N}(\text{CH}_3)_4$] revealed some unexpected chemistry. Even at -80°C , HN_3 displaces F^- from MF with formation of equimolar amounts of M^+N_3^- and HF. The latter reacts with MF to give M^+HF_2^- . On the other hand, HF quantitatively displaces N_3^- from MN_3 with formation of HN_3 and M^+HF_2^- . This apparent discrepancy can be explained by the vast difference in basicity between F^- and HF_2^- . Attempts to isolate stable $\text{F}-\text{H}-\text{N}_3^-$ or $\text{N}_3-\text{H}-\text{N}_3^-$ anions from HN_3 and either MF or MN_3 , respectively, were unsuccessful.

Introduction

Although tetramethylammonium azide, $\text{N}(\text{CH}_3)_4^+\text{N}_3^-$, had been known¹ since 1918, only very little information has since been reported²⁻⁶ for this interesting compound. According to the previous reports,¹⁻⁶ the compound was prepared by either the reaction of $\text{N}(\text{CH}_3)_4\text{I}$ with AgN_3 (1) in either water¹ or anhydrous



ethanol⁴ or the neutralization^{3,5,6} of $\text{N}(\text{CH}_3)_4\text{OH}$ with aqueous HN_3 (2). Both preparations involve the use of shock-sensitive



starting materials, i.e. AgN_3 and HN_3 , and suffer from solubility and purification problems. No structural or spectroscopic data had previously been reported for $\text{N}(\text{CH}_3)_4\text{N}_3$, except for partial vibrational spectra.⁶ In this paper, we report an improved synthesis for $\text{N}(\text{CH}_3)_4\text{N}_3$ and its crystal structure and vibrational spectra.

Experimental Section

Caution! Hydrazoic acid is shock sensitive when undiluted, and appropriate shielding and safety precautions must be used when working with this compound.

Materials. CH_3CN (Baker, Bio-analyzed, having a water content of 40 ppm) was treated with P_2O_5 and freshly distilled prior to use, thereby reducing its water content to <4 ppm. The synthesis of $\text{N}(\text{CH}_3)_4\text{F}$ has previously been described.⁷ $\text{Si}(\text{CH}_3)_3\text{N}_3$ (Petrarch) was distilled prior to use. Hydrazoic acid was generated from NaN_3 and stearic acid at about 110°C , as previously described.⁸ Dry KF, RbF, and CsF were obtained by fusing these materials in a platinum crucible and transferring the resulting clinkers into a drybox while still hot. The RbF single crystal (Semi-Elements, Inc.), used for the low-temperature infrared study, was freshly cleaved with a razor blade in the drybox and then mounted in a dry N_2 atmosphere into the tip of an Air Products Model DE 202S helium refrigerator equipped with external CsI windows. The HF (Matheson) was dried by storage over BiF_3 .⁹

Apparatus. Volatile materials were handled either in a flamed-out Pyrex vacuum line equipped with Kontes Teflon valves, in a stainless-steel vacuum line equipped with Teflon-FEP U-traps,¹⁰ or in the dry nitrogen atmosphere of a glovebox. Solids were manipulated exclusively in the drybox.

Raman spectra were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer by use of the 488-nm exciting line of an Ar ion or the 647.1-nm line of a Kr ion laser, respectively. Baked-out Pyrex melting point capillaries were used as sample holders. Infrared spectra were recorded as KBr disks on a Perkin-Elmer Model 283

Table I. Summary of Crystal Data and Refinement Results for $\text{N}(\text{CH}_3)_4^+\text{N}_3^-$

space group	$\text{Pmn}2_1$ (No. 31)
a (Å)	6.879 (5)
b (Å)	5.479 (4)
c (Å)	8.858 (7)
V (Å ³)	333.9 (7)
molecules/unit cell	2
formula weight (g/mol)	116.2
crystal dimens (mm)	$0.28 \times 0.34 \times 0.88$
calcd density (g cm ⁻³)	1.156
wavelength (Å) used	0.71069
for data collec	
$\sin(\theta/\lambda)$ limit (Å ⁻¹)	0.6497
total no. of reflcns measured	1469
no. of independent reflcns	762
no. of reflcns used in structural analysis,	427
$I > 3\sigma(I)$	
no. of variable params	77
final agreement factor	$R(F) = 0.0388$
	$R_w(F) = 0.0359$

spectrophotometer. The KBr disks were pressed in a Wilks minipress and left in the press for the recording of the spectra. The spectra obtained in this manner were identical with those obtained for pressed AgCl disks, indicating that no reaction between KBr and $\text{N}(\text{CH}_3)_4\text{N}_3$ had occurred during the pressing operation. The cryostat used for the low-temperature infrared studies has previously been described.¹¹

Synthesis of $\text{N}(\text{CH}_3)_4\text{N}_3$. A solution of $\text{Si}(\text{CH}_3)_3\text{N}_3$ (29.92 mmol) in 15 mL of CH_3CN was slowly added in a dry atmosphere to $\text{N}(\text{CH}_3)_4\text{F}$ (24.10 mmol) dissolved in 29 mL of CH_3CN . In a mildly exothermic reaction, a white precipitate was formed instantaneously. The mixture was agitated for about 10 min, and then all volatile material was pumped off at room temperature. The white solid residue (2.794 g; weight calculated for 24.10 mmol of $\text{N}(\text{CH}_3)_4\text{N}_3 = 2.797$ g, corresponding to a 99.9% yield) was identified by vibrational spectroscopy and a crystal

(1) Friedländer, F. *J. Am. Chem. Soc.* **1918**, *40*, 1945.

(2) Straumanis, M.; Circulis, A. Z. *Anorg. Allg. Chem.* **1943**, *252*, 17.

(3) Gutmann, V.; Hampel, G.; Leitmann, O. *Monatsh. Chem.* **1964**, *95*, 1034.

(4) Weller, F.; Dehnicke, K. *J. Organomet. Chem.* **1972**, *35*, 237.

(5) Bojes, J.; Chivers, T. *Inorg. Chem.* **1978**, *17*, 318.

(6) Glavincevski, B.; Brownstein, S. J. *Inorg. Nucl. Chem.* **1981**, *43*, 1827.

(7) Christe, K. O.; Wilson, W. W.; Wilson, R. D.; Bau, R.; Feng, J. *J. Am. Chem. Soc.* **1990**, *112*, 7619.

(8) Krakow, B.; Lord, R. C.; Neely, G. O. *J. Mol. Spectrosc.* **1968**, *27*, 198.

(9) Christe, K. O.; Wilson, W. W.; Schack, C. J. *J. Fluorine Chem.* **1978**, *11*, 71.

(10) Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Synth.* **1986**, *24*, 3.

(11) Christe, K. O.; Wilson, R. D. *Inorg. Chem.* **1987**, *26*, 920.

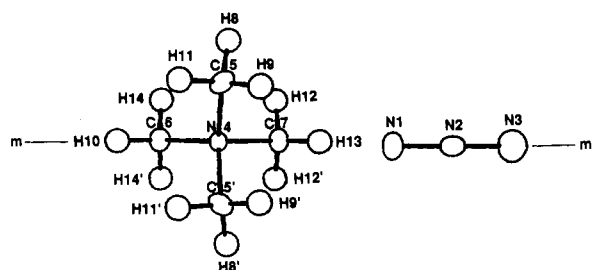
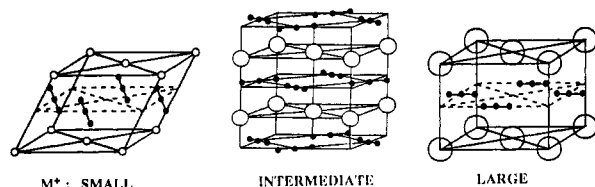
[†] Dedicated to Prof. Alois Haas on the occasion of his 60th birthday.

[‡] Rocketdyne.

[§] University of Southern California.

Table II. Bond Distances (Å) for $\text{N}(\text{CH}_3)_4\text{N}_3^-$

N1-N2	1.155 (5)	C5-H9	0.944 (10)
N2-N3	1.176 (5)	C5-H11	0.961 (10)
N4-C5	1.496 (2)	C6-H10	1.046 (10)
N4-C6	1.470 (7)	C6-H14	0.981 (8)
N4-C7	1.529 (7)	C7-H12	1.001 (8)
C5-H8	1.030 (7)	C7-H13	0.990 (11)

**Figure 1.** View of the molecular $\text{N}(\text{CH}_3)_4\text{N}_3$ unit showing the positions and labeling of the hydrogen atoms and the crystallographic mirror plane.**Figure 2.** Packing in azides and bifluorides as a function of the cation size.

structure determination as $\text{N}(\text{CH}_3)_4\text{N}_3$. Its decomposition point was found to be 255 °C.

Crystal Structure of $\text{N}(\text{CH}_3)_4\text{N}_3$. Single crystals of $\text{N}(\text{CH}_3)_4\text{N}_3$ were grown from a hot CH_3CN solution. A suitable crystal was selected under the microscope and sealed in a glass capillary because the compound diffracts slowly, and intensity data were collected at room temperature on a Nicolet/Syntax P2, automated four circle diffractometer, with Mo $K\alpha$ radiation and a graphite crystal monochromator. The unit cell parameters were determined by least-squares refinement of 15 centered reflections. Data were collected with the ω -scan technique for all reflections such that $4.0^\circ < 2\theta < 55.0^\circ$. Throughout the data collection, three reflections were monitored periodically and no decay was observed. A set of 1469 intensity values, representing a hemisphere of data, was collected and the four equivalent octants were merged to give a total of 427 unique reflections. The R factor for averaging was 1.8%. The positions of the non-hydrogen atoms were obtained by direct methods using the computing package SHELX-86.¹² The hydrogen atoms were later located from a difference Fourier map. The structure was then refined to final agreement factors of $R(F) = 3.88\%$ and $R_w(F) = 3.59\%$, using 427 reflections with $I > 2\sigma(I)$. In the least-squares refinement, the H atoms were also varied and were assigned equal isotropic temperature factors. Details of the data collection parameters and other crystallographic information are given in Table I, and the final atomic coordinates and temperature factors are listed in Tables A and B, respectively, of supplementary material. Interatomic distances and angles are given in Tables II and III, respectively. A view of the molecular $\text{N}(\text{CH}_3)_4\text{N}_3$ unit showing the positions and labeling of the hydrogen atoms is given in Figure 1, and the packing in $\text{N}(\text{CH}_3)_4\text{N}_3$ is shown in Figure 2 for the large cation case.

Reactions of HN_3 with MF ($M = \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{N}(\text{CH}_3)_4$). Samples of these fluorides were exposed at room temperature to about 100 Torr of HN_3 vapor for 12 h. The solid reaction products were weighed and identified by infrared and Raman spectroscopy and showed about equimolar amounts of N_3^- and HF_2^- . No evidence for the formation of any new species, such as $\text{F}-\text{H}-\text{N}_3^-$ or $\text{N}_3-\text{H}-\text{N}_3^-$, was observed.

A sample of HN_3 was condensed at 12 K onto a RbF single crystal window. The temperature of the window was steadily increased, and infrared spectra were periodically recorded. Between 12 and 100 K the spectra showed only solid HN_3 , with increasing temperature causing irreversible band broadening. At 130 K the HN_3 deposit was slowly pumped away. Therefore, the pumping was interrupted and the RbF window, while kept at 190 K, was exposed to an HN_3 -He mixture (1:10

Table III. Bond Angles (deg) for $\text{N}(\text{CH}_3)_4\text{N}_3^-$

N1-N2-N3	179.0 (3)	N4-C7-H12	106.6 (7)
C5-N4-C6	111.8 (4)	N4-C7-H13	108.3 (6)
C5-N4-C7	107.3 (4)	H8-C5-H9	109.6 (9)
C5-N4-C5'	109.1 (3)	H8-C5-H11	109.6 (8)
C6-N4-C7	109.3 (2)	H9-C5-H11	112.0 (7)
N4-C5-H8	109.9 (4)	H10-C6-H14	109.2 (7)
N4-C5-H9	109.2 (6)	H14-C6-H14'	116.8 (8)
N4-C5-H11	106.5 (6)	H12-C7-H13	111.0 (7)
N4-C6-H10	107.9 (6)	H12-C7-H12'	113.1 (9)
N4-C6-H14	106.6 (7)		

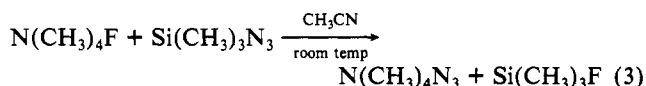
mole ratio) at a total pressure of about 35 Torr. The infrared spectrum, recorded at this temperature, showed only N_3^- and HF_2^- but no unreacted HN_3 . This indicates that, even at 190 K, the reaction of RbF with HN_3 to give RbN_3 and RbHF_2 is fast and complete.

Reactions of HF with MN_3 ($M = \text{Na}, \text{Cs}, \text{N}(\text{CH}_3)_4$). Weighed amounts of MN_3 were exposed to less than stoichiometric amounts of gaseous HF for several hours at room temperature. Essentially all of the HF was consumed, and HN_3 was liberated. The solid reaction products were identified spectroscopically as mixtures of $\text{MF} \cdot n\text{HF}$ and unreacted excess MN_3 .

For NaN_3 , a sample was treated at room temperature with a 31-fold excess of liquid anhydrous HF. After removal of the volatile products, which consisted of a mixture of HF and HN_3 , the solid residue was identified as NaHF_2 .

Results and Discussion

Synthesis and Properties of $\text{N}(\text{CH}_3)_4\text{N}_3$. The ready access to truly anhydrous $\text{N}(\text{CH}_3)_4\text{F}^7$ combined with the commercial availability of $\text{Si}(\text{CH}_3)_3\text{N}_3$ provides a convenient and safe synthesis (3) for $\text{N}(\text{CH}_3)_4\text{N}_3$. Using a slight excess of $\text{Si}(\text{CH}_3)_3\text{N}_3$, $\text{N}(\text{C}-\text{H}_3)_4\text{N}_3$ can be prepared in quantitative yield and excellent purity.



The observed decomposition point of 255 °C is in good agreement with that previously reported⁴ for a sample prepared from AgN_3 and $\text{N}(\text{CH}_3)_4\text{I}$ in $\text{C}_2\text{H}_5\text{OH}$ and recrystallized from 2-propanol but disagrees with that of 125 °C originally reported¹ by Friedländer. The compound is a white, crystalline, nonsensitive, and slightly hygroscopic solid. It has little solubility in cold CH_3CN , moderate solubility in hot CH_3CN , and is highly soluble in alcohol and water.

Crystal Structure of $\text{N}(\text{CH}_3)_4\text{N}_3$. The structure of $\text{N}(\text{CH}_3)_4\text{N}_3$ can be derived from a primitive cubic CsCl lattice which is orthorhombically distorted by the nonspherical N_3^- anions. The packing in $\text{N}(\text{CH}_3)_4\text{N}_3$ is identical to that¹³ found for $\text{N}(\text{C}-\text{H}_3)_4\text{HF}_2$, and the two compounds are isotopic. In both, the M^+HF_2^- and the M^+N_3^- series, the packings are governed by the ionic radii of the M^+ cations. For small M^+ (Li^+ , $r = 0.60$ Å; Na^+ , $r = 0.95$ Å), the anion layers are stacked perpendicular to the M^+ layers; for intermediate M^+ (K^+ , $r = 1.33$ Å; Rb^+ , $r = 1.48$ Å; Cs^+ , $r = 1.69$ Å), the anions are oriented with their axes parallel to the M^+ layers and perpendicular to each other;¹⁴ and for large M^+ ($\text{N}(\text{CH}_3)_4^+$, $r \approx 2.74$ Å), the anions are oriented with their axes parallel both to the M^+ layers and to each other (see Figure 2).

Both the tetramethylammonium cation and the azide anion were found to be situated on crystallographic mirror planes. The cationic mirror plane bisects the angle $\text{C5}-\text{N4}-\text{C5}'$ and passes through atoms N4, C6, C7, H10, and H13, while the anionic mirror plane passes through all three N atoms N1, N2, and N3. The azide ion refined to an essentially linear, symmetrical structure [$\text{N1}-\text{N2} = 1.155$ (5) Å, $\text{N2}-\text{N3} = 1.176$ (5) Å, $\text{N1}-\text{N2}-\text{N3} = 179.0$ (3)°], even though there are no symmetry constraints that require it to be linear and symmetric. Its N-N bond length of 1.16 Å is comparable to those found for other ionic azides.¹⁴ The

(13) Wilson, W. W.; Christe, K. O.; Feng, J.; Bau, R. *Can. J. Chem.* **1989**, *67*, 1898.

(14) Choi, C. S. In *Energetic Materials*; Fair, H. D., Walker, R. F., Eds.; Plenum Press: New York, 1977; Vol. 1, p 97.

(12) Sheldrick, G. M. *SHELX System of Crystallographic Programs*; University of Goettingen: Germany, 1986.

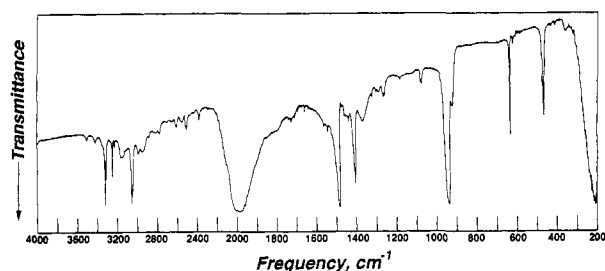


Figure 3. Infrared spectrum of solid $N(CH_3)_4N_3$ pressed in an AgBr disk. The absorption at 250 cm^{-1} is due to the window material.

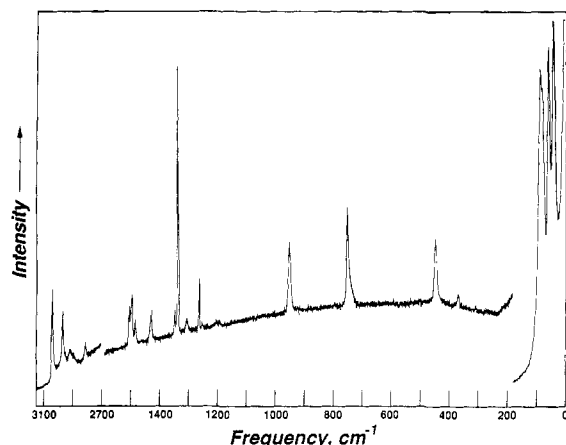


Figure 4. Raman spectrum of solid $N(CH_3)_4N_3$ recorded at ambient temperature. The region $0\text{--}200\text{ cm}^{-1}$ was recorded at a 10 times lower sensitivity.

tetramethylammonium cation is slightly but significantly distorted, with angles around N ranging from 107.3 (4)° to 111.8 (4)° , compared to angles ranging from 108.8 (2)° to 110.3 (2)° in isotopic $N(CH_3)_4HF_2$.¹³ This increased distortion of the $N(CH_3)_4^+$ cations is attributed to packing effects caused by the slightly larger anion size on going from HF_2^- to N_3^- .

Vibrational Spectra. The infrared and Raman spectra of solid $N(CH_3)_4^+N_3^-$ are shown in Figures 3 and 4, respectively. The observed frequencies and their assignments are summarized in Table IV. The assignments and mode descriptions for $N(CH_3)_4^+$ follow those¹⁵ published by Berg. These spectra confirm the findings from the crystal structure determination that the $N(CH_3)_4^+$ cation in $N(CH_3)_4^+N_3^-$ is more distorted from tetrahedral symmetry than that in $N(CH_3)_4^+HF_2^-$. This is manifested by the significant difference in the relative Raman intensities of the two NC_4 deformation modes, $\nu_{19}(F_2)$ and $\nu_8(E)$, in these two compounds. In $N(CH_3)_4HF_2$, the $\nu_8:\nu_{19}$ intensity ratio equals 3.6, whereas in $N(CH_3)_4N_3$ it is only 0.29. It has previously been demonstrated^{16,17} that this ratio decreases with increasing distortion of the $N(CH_3)_4^+$ cation. Additional evidence for the increased cation distortion is the frequency decrease of the antisymmetric CH_3 stretching mode, $\nu_{13}(F_2)$,^{16,17} from 3036 cm^{-1} in $N(CH_3)_4HF_2$ to 3022 cm^{-1} in $N(CH_3)_4N_3$, and the infrared activity of the F_1 modes, which for strict T_d symmetry should be inactive.¹⁵

The bands observed for the N_3^- anion (see Table I) are in excellent agreement with those previously reported for a symmetric linear ion of symmetry $D_{\infty h}$.^{18–20} The frequency of ν_1 follows a trend previously noted²⁰ for the alkali metal azides, i.e. a decrease in ν_1 with increasing ionic radius and ionicity of the cation (Li^+ , 1372 ; Na^+ , 1360 ; K^+ , 1343 ; Rb^+ , 1335 ; Cs^+ , 1328 ; $N(CH_3)_4^+$, 1317 cm^{-1}).

Table IV. Vibrational Spectra of Solid $N(CH_3)_4^+N_3^-$

obsd frequencies, cm^{-1} (rel intens)		assignments (point group)	
IR	R	$N(CH_3)_4 (T_d)$	$N_3^- (D_{\infty h})$
3486vw			
3400vw			
3330sh			
3297ms			
3225mw			$\nu_1 + \nu_3 (\Sigma u^+)$
3201vw			
3130w			
3031ms			
3023sh	3022 (7)	$\nu_{13}(F_2)\nu_{as}CH_3$	
2970w	2953 (5)	$\nu_5(E)\nu_{as}CH_3$	
	2900 (1)	$\nu_{14}(F_2)\nu_{sym}CH_3$	
	2882sh	$\nu_1(A_1)\nu_{sym}CH_3$	
	2802 (1)	+ combin. bands	
2790vw			
2750vw			
2579w			
2529vw			
2480w			
2358w			
1998vs			$\nu_3(\Sigma u^+)\nu_{as}$
1492s		$\nu_{15}(F_2)\delta_{as}CH_3$	
	1480 (3)	$\nu_2(A_1)\delta_{sym}CH_3$	
	1473 (5)	$\nu_6(E)\delta_{as}CH_3$	
	1460 (2)	$\nu_{10}(F_1)\delta_{as}CH_3$	
1439vw			
1414ms	1407 (3)	$\nu_{16}(F_2)\delta_{sym}CH_3$	
1365mw	1327 (2)		
	1317 (30)		$\nu_1(\Sigma g^+)\nu_{sym}$
1299vw			
1288vw	1287 (1)	$\nu_{17}(F_2)CH_3\text{rock}$	
1263w			
1256w	1245 (5)		$2\nu_2(\Sigma g^+)$
1175vw	1180 (0+)	$\nu_7(E)CH_3\text{rock}$	
1077w			
1071w		$\nu_{11}(F_1)CH_3\text{rock}$	
959sh			
950s	947 (8)	$\nu_{18}(F_2)\nu_{as}CN_4$	
922m		$2\nu_{19}(F_2)$	
	756 (11)	$\nu_3(A_1)\nu_sCN_4$	$\nu_2(\pi_u)\delta$
632ms			
614vw			
462ms	459 (7)	$\nu_{19}(F_2)\delta CN_4$	
	383 (2)	$\nu_8(E)\delta CN_4$	
347w		$\nu_{12}(F_1)\tau CH_3$	
	105 (100)		
	78 (75)		
	61 (75)		Lattice Vibrations

A comparison of our spectra with those previously reported⁶ for $N(CH_3)_4N_3$ shows significant discrepancies. Thus, ν_3 of N_3^- differs by more than 60 cm^{-1} from the previous report, and numerous other bands differ in both frequencies and relative intensities. In view of the high purity of our sample, as shown by the crystal structure and correct decomposition point, our spectra should be preferred over those previously reported.⁶

Reactions of HN_3 with the F^- Anion and of HF with the Azide Anion. The N_3 group can be considered as a pseudohalogen²¹ or para-halogen.²² Since other pseudohalides, such as NO_3^- or ClO_4^- , are known to form the bihalide-type anions, $[O_2NO-H-ON-O_2]^-$,^{23–28} $[F-H-ONO_2]^-$,²⁹ and $[O_3ClO-H-OCIO_3]^-$,³⁰ respec-

(15) Berg, R. W. *Spectrochim. Acta, Part A* 1978, 34A, 655.

(16) Kabisch, G.; Klose, M. *J. Raman Spectrosc.* 1978, 7, 311.

(17) Kabisch, G. *J. Raman Spectrosc.* 1980, 9, 285.

(18) Bryant, J. I. *J. Chem. Phys.* 1964, 40, 3195; 1966, 45, 689.

(19) Hathaway, C. E.; Temple, P. A. *Phys. Rev. B* 1971, 3, 3497.

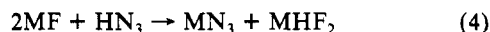
(20) Iqbal, Z.; Prask, H. J.; Trevino, S. F. In *Energetic Materials*; Fair, H. D., Walker, R. F., Eds.; Plenum Press: New York, 1977; Vol. 1, p 131.

(21) Golub, A. M.; Köhler, H.; Skopengo, V. V. Chemistry of Pseudohalides. In *Topics in Inorganic and General Chemistry*; Clark, R. J. H., Ed.; Monograph 21; Elsevier: Amsterdam, 1986; p 28.

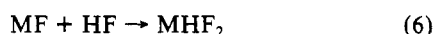
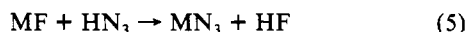
(22) Haas, A. *Adv. Inorg. Chem. Radiochem.* 1984, 28, 167.

(23) Gillard, R. D.; Mitchell, S. H. *Polyhedron* 1987, 6, 1885.

tively, it was interesting to study the interaction of HN_3 with both the N_3^- and the F^- anions. With $\text{N}(\text{CH}_3)_4\text{N}_3$, HN_3 did not form an adduct stable at room temperature. With MF [$\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$, $\text{N}(\text{CH}_3)_4$], gaseous or liquid HN_3 reacted at or below room temperature with the formation of an equimolar mixture of MN_3 and MHF_2 (4). The products of reaction 4 are best



interpreted by the summation of (5) and (6), where step 5 might

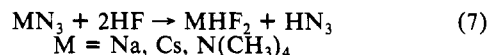


involve an intermediate $\text{F}-\text{H}-\text{N}_3^-$ anion which readily eliminates HF to give the final N_3^- product. Attempts were made to isolate this intermediate anion by reacting HN_3 with a RbF single crystal infrared window at low temperature. Below -100°C , no reaction occurred, and above this temperature, the only new products observable by infrared spectroscopy were RbN_3 and RbHF_2 .

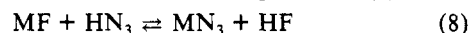
Reaction 5, i.e. the displacement of F^- from M^+F^- by HN_3 , was surprising since, in aqueous solution, HN_3 ($P_k = 4.77$) is a weaker acid than HF ($P_k = 3.18$). Furthermore, molten weak organic acids such as stearic acid also displace N_3^- from NaN_3 .⁸ Since reaction 5 was not carried out in aqueous solution in which the acidity of HF is enhanced by the hydration energy of F^- , but between solid MF and neat gaseous or liquid HN_3 , it should not

be governed by the above P_k values but by the proton affinities of F^- and N_3^- . In view of the proton affinity of F^- (371.5 kcal mol⁻¹) exceeding that of N_3^- (328.6 kcal mol⁻¹) by about 43 kcal mol⁻¹, it is then not surprising that HN_3 can displace F^- from M^+F^- .

On the other hand it was found that HF quantitatively displaces N_3^- from M^+N_3^- (7). This reaction does not require the use of an excess of HF . If less than the stoichiometric amounts of HF are used, the resulting products still are MHF_2 and HN_3 and not MF and HN_3 . Hence, it appears that both reactions 5 and 7 are



irreversible and that the puzzling observations that HN_3 displaces F^- from MF (5) while HF displaces N_3^- from MN_3 (7) are not due to the shifting of a single chemical equilibrium (8).



The observed reaction chemistry can be explained by the vastly different Lewis basicities of F^- and HF_2^- . Thus, the very strong Lewis base F^- is readily displaced by the weak acid HN_3 (5), but the more acidic HF_2^- anion is the final product which, once it has been formed, cannot be displaced anymore by the weak acid HN_3 .

Acknowledgment. We thank C. J. Schack and R. D. Wilson for their help and the U.S. Air Force Phillips Laboratory and the U.S. Army Research Office for financial support of the work carried out at Rocketdyne.

Registry No. Trimethylsilyl azide, 4648-54-8; tetramethylammonium fluoride, 373-68-2; tetramethylammonium azide, 999-77-9; hydrazoic acid, 7782-79-8; sodium fluoride, 7681-49-4; potassium fluoride, 7789-23-3; rubidium fluoride, 13446-74-7; cesium fluoride, 13400-13-0; azide, 14343-69-2; bifluoride, 18130-74-0; fluoride, 16984-48-8; hydrogen fluoride, 7664-39-3.

Supplementary Material Available: Tables of final atomic coordinates and anisotropic thermal parameters (2 pages); tables of calculated and observed structure factor amplitudes (2 pages). Ordering information is given on any current masthead page.

- (24) Al-Zamil, N. S.; Evans, E. H. M.; Gillard, R. D.; James, D. W.; Jenkins, T. E.; Lancashire, R. J.; Williams, P. A. *Polyhedron* 1982, 1, 525.
 (25) Rozière, J.; Lehman, M. S.; Potier, J. *Acta Crystallogr.* 1979, B35, 1099.
 (26) Rozière, J.; Rozière-Bories, M. T.; Williams, J. M. *Inorg. Chem.* 1976, 15, 2490.
 (27) Williams, J. M.; Dowling, N.; Gunde, R.; Hadzi, D.; Orel, B. *J. Am. Chem. Soc.* 1976, 98, 1581.
 (28) Rozière, J.; Berney, C. V. *J. Am. Chem. Soc.* 1976, 98, 1582.
 (29) Al-Zamil, N.; Delf, B. W.; Gillard, R. D. *J. Inorg. Nucl. Chem.* 1980, 42, 1117.
 (30) Karelín, A. I.; Grigorovich, Z. I.; Rosolovskii, V. Ya. *Izv. Akad. Nauk. SSSR, Ser. Khim.* 1974, 1228.

Formation of Fibrous Molecular Assemblies by Amino Acid Surfactants in Water

Toyoko Imae,* Yoshiyuki Takahashi, and Hidetoshi Muramatsu

Contribution from the Department of Chemistry, Faculty of Science, Nagoya University, Nagoya 464, Japan. Received May 9, 1991. Revised Manuscript Received December 9, 1991

Abstract: Gel-like solutions are obtained at medium pH and low temperature for aqueous solutions of *N*-acyl-L-aspartic acids (C_nAsp , $n = 12-18$). Electron microscopic observation reveals that helical, fibrous molecular assemblies are formed in the gel-like solutions. The rheological behavior reflects the formation of swarms or bundles of fibers. The hydrogen bonding of amide groups and the moderate degree of ionization of carboxyl groups are confirmed from the infrared absorption bands, consistent with the pH titration result. The possible models of helical, fibrous assemblies are the double stranded or the superhelical structure of helical bilayer strands or the twisted ribbon of a planar bilayer sheet. While *N*-dodecanoyl-L-glutamic acid (C_{12}Glu) molecules cannot be associated into fibrous assemblies, *N*-dodecanoyl-β-alanine (C_{12}Ala) molecules form cylindrical fibers which have no helical structure.

Biopolymers such as polynucleotides, polypeptides, and polysaccharides can take the helical structure which is very important in the occurrence of biological functions. The formation of similar helical structures has recently been reported for assemblies of some native and artificial amphiphiles.

When mineral oil was used as a dispersion medium, lithium 12-hydroxystearate formed fibers with the structure of a twisted

ribbon or helical rope.¹ Twisted fibrous aggregates were also constructed by *N*-(2-hydroxydodecyl) amino acids in organic solvents.² Helical and cylindrical aggregates in an aqueous

- (1) Tachibana, T.; Kambara, H. *J. Am. Chem. Soc.* 1965, 87, 3015-3016.
 (2) Hidaka, H.; Murata, M.; Onai, T. *J. Chem. Soc., Chem. Commun.* 1984, 562-564.

The N_2F^+ Cation. An Unusual Ion Containing the Shortest Presently Known Nitrogen–Fluorine Bond

Karl O. Christe,^{*,†} Richard D. Wilson,[†] William W. Wilson,[†] Robert Bau,[‡] Sunanda Sukumar,[‡] and David A. Dixon[§]

Contribution from Rocketdyne, A Division of Rockwell International Corporation, Canoga Park, California 91303, the Department of Chemistry, University of Southern California, Los Angeles, California 90007, and the Central Research and Development Department, E.I. du Pont de Nemours and Company, Inc., Experimental Station, Wilmington, Delaware 19880.

Received May 3, 1990

Abstract: The $\text{N}_2\text{F}^+\text{AsF}_6^-$ salt was prepared in high yield from *trans*- N_2F_2 by thermal *trans*–*cis* isomerization in the presence of AsF_5 at 70 °C. A displacement reaction between $\text{N}_2\text{F}^+\text{AsF}_6^-$ and FNO yields exclusively *cis*- N_2F_2 . The Lewis acids BF_3 and PF_5 do not form a stable adduct with *cis*- N_2F_2 at temperatures as low as –78 °C and do not catalyze the N_2F_2 *trans*–*cis* isomerization. A semiempirical molecular orbital model is used to explain the puzzling differences in the reaction chemistry of *cis*- and *trans*- N_2F_2 . The crystal structure of $\text{N}_2\text{F}^+\text{AsF}_6^-$ (monoclinic, $C2/m$, $a = 9.184$ (5) Å, $b = 5.882$ (2) Å, $c = 5.160$ (2) Å, $\beta = 90.47$ (4)°, $Z = 2$) was determined. Alternate space groups (Cm and $C2$) can be rejected on the basis of the observed vibrational spectra. Since in $C2/m$ the N_2F^+ cations are disordered, only the sum of the N–F and N–N bond distances could be determined from the X-ray data. Local density functional calculations were carried out for N_2F^+ and the well-known isoelectronic FCN molecule. The results from these calculations allowed the sum of the N_2F^+ bond lengths to be partitioned into the individual bond distances. The resulting N–F bond length of 1.217 Å is by far the shortest presently known N–F bond, while the N–N bond length of 1.099 Å is comparable to the shortest presently known N–N bond length of 1.0976 (2) Å in N_2 . The surprising shortness of both bonds is attributed to the high s-character (sp hybrid) of the σ -bond orbitals on nitrogen and the formal positive charge on the cation. Thus, the shortening of the N–F bond on going from sp^3 -hybridized NF_4^+ (1.30 Å) to sp -hybridized N_2F^+ (1.22 Å) parallels those found for the C–H and C–F bonds in the CH_4 , $\text{CH}_2=\text{CH}_2$, $\text{CH}\equiv\text{CH}$ and CF_4 , $\text{CF}_2=\text{CF}_2$, $\text{FC}\equiv\text{N}$ series, respectively. The oxidative power of N_2F^+ has also been studied. The N_2F^+ cation oxidized Xe and ClF to XeF^+ and ClF_2^+ , respectively, but did not oxidize ClF_5 , BrF_5 , IF_5 , XeF_4 , NF_3 , or O_2 .

Introduction

The chemistry of N_2F_2 and its derivatives is fascinating and presents many mysteries.¹ Thus, N_2F_2 exists as two planar $\text{FN}=\text{NF}$ isomers, a *cis* and a *trans* form. In spite of only a small enthalpy difference of 3.04 kcal/mol between the two isomers,² their properties and reaction chemistry are very different. For example, only the *cis* isomer reacts with strong Lewis acids to form N_2F^+ salts. Furthermore, some of the synthetic methods for N_2F_2 produce exclusively the *trans* isomer, and its slow and erratic isomerization to the more stable *cis* isomer is poorly understood, as shown by recent *ab initio* calculations.³

The N_2F^+ cation^{4–9} is also of great interest. Force field⁹ and *ab initio* calculations^{10–12} suggested that this cation should possess an unusually short N–F bond. On the basis of the previously published⁹ NF stretching force constant value of 8.16 mdyn/Å and N–F bond length–force constant plots,^{10,13} a value of about 1.23 Å can be extrapolated for the N–F bond in N_2F^+ . This surprisingly short N–F bond length value for N_2F^+ was also supported by *ab initio* calculations^{10–12} which resulted in values of 1.28, 1.24, and 1.23 Å, respectively. Considering that in covalent main group element fluorides the bond length generally decreases with an increase in the formal oxidation state of the central atom and that the shortest previously known N–F bond was 1.30 Å in NF_4^+ (+V),¹⁴ a value of about 1.23 Å for N_2F^+ (+I) would be unique indeed.

On the other hand, if the N–F bond length in N_2F^+ were considerably longer than the value predicted from the force field computations, the N_2F^+ cation would be an ideal test case for “Gordy’s rule”.¹⁵ According to this rule, the bond stretching force constant k is related to the bond distance d by the equation

$$k_{AB} = aN(X_A X_B / d_{AB}^2)^{3/4} + b$$

where X are the Pauling electronegativities, N the bond order, and a and b empirically determined constants. Although no *a priori* reason dictates such a relationship since bond lengths

measure the position of the potential energy minimum whereas force constants indicate its curvature, only one exception to Gordy’s rule has previously been reported.¹⁶ Thus, a knowledge of the N–F bond distance in N_2F^+ was of significant interest since it would either confirm the existence of an unusually short N–F bond or provide a rare example of a species not obeying Gordy’s rule.

Experimental Section

Materials. The following commercial materials were used without further purification: N_2F_4 (Air Products); Xe, O_2 , IF_5 , PF_5 , and BF_3 (Matheson); ClF_5 and NF_3 (Rocketdyne); and ClF (Ozark Mahoning). Literature methods were used for the syntheses of *trans*- N_2F_2 ,¹⁷ $\text{N}_2\text{F}^+\text{AsF}_6^-$,⁴ FNO ,¹⁸ and XeF_4 ,¹⁹ the purification of BrF_5 ,²⁰ and the drying of HF.²¹

- (1) For an exhaustive review of the properties and chemistry of N_2F_2 ; see: *Gmelin Handbook of Inorganic Chemistry, Fluorine*, Springer Verlag; Berlin, 1986; Suppl. Vol. 4, pp 385–403.
- (2) Craig, N. C.; Piper, L. G.; Wheller, V. L. *J. Phys. Chem.* **1971**, *75*, 1453.
- (3) Lee, T. J.; Rice, J. E.; Scuseria, G. E.; Schaefer, H. F., III *Theor. Chim. Acta* **1989**, *75*, 81.
- (4) Moy, D.; Young, A. R. *J. Am. Chem. Soc.* **1965**, *87*, 1889.
- (5) Ruff, J. K. *Inorg. Chem.* **1966**, *5*, 1791.
- (6) Roesky, H. W.; Glemser, O.; Bormann, D. *Chem. Ber.* **1966**, *99*, 1589.
- (7) Pankratov, A. V.; Savenkova, N. I. *Russ. J. Inorg. Chem.* **1968**, *13*, 1345.
- (8) Shamir, J.; Binenboym, J. *J. Mol. Struct.* **1969**, *4*, 100.
- (9) Christe, K. O.; Wilson, R. D.; Sawodny, W. *J. Mol. Struct.* **1971**, *8*, 245.
- (10) Pulay, P.; Ruoff, A.; Sawodny, W. *Mol. Phys.* **1975**, *30*, 1123.
- (11) Peters, N. J. S. *Chem. Phys. Lett.* **1987**, *142*, 76.
- (12) Yakobson, V. V.; Zyubina, T. S.; Charkin, O. P. *Russ. J. Inorg. Chem., Engl.* **1988**, *33*, 1727.
- (13) Christe, K. O. *Spectrochim. Acta, Part A* **1986**, *42A*, 939.
- (14) Christe, K. O.; Lind, M. D.; Thorup, N.; Russell, D. R.; Fawcett, J.; Bau, R. *Inorg. Chem.* **1988**, *27*, 2450.
- (15) Gordy, W. *J. Chem. Phys.* **1946**, *14*, 305.
- (16) Mack, H. G.; Christen, D.; Oberhammer, H. *J. Mol. Struct.* **1988**, *190*, 215.
- (17) Münch, V.; Selig, H. *J. Fluorine Chem.* **1980**, *15*, 235.
- (18) Christe, K. O. *Inorg. Chem.* **1973**, *12*, 1580.
- (19) Bartlett, N.; Sladky, F. O. *J. Am. Chem. Soc.* **1968**, *90*, 5316.
- (20) Wilson, W. W.; Christe, K. O. *Inorg. Chem.* **1987**, *26*, 1573.

[†] Rocketdyne Division, Rockwell International Corp.

[‡] University of Southern California, Los Angeles.

[§] E.I. du Pont de Nemours and Company, Inc.

Table I. Summary of Crystal Data and Refinement Results for $N_2F^+AsF_6^-$

space group	$C2/m$ (No. 12)
<i>a</i> , Å	9.184 (5)
<i>b</i> , Å	5.882 (2)
<i>c</i> , Å	5.160 (2)
β , deg	90.47 (4)
<i>V</i> , Å ³	278.7 (2)
molecules per unit cell	2
formula weight, g	235.9
cryst dimens, mm	$0.32 \times 0.38 \times 1.08$
calcd density, g cm ⁻³	2.82
abs coeff, mm ⁻¹	59.8
range in transmission factor (normalized to unity)	0.61–1.00
wavelength used for data collection, Å	0.71069
$\sin \theta/\lambda$ limit, Å ⁻¹	0.6497
tot no. of reflns measd	1272
no. of independent reflns	364
no. of reflns used in structural analysis $I > 3\sigma(I)$	362
no. of variable params	30
final agreement factor	0.0404

Apparatus. Volatile materials were handled in a well-passivated (with ClF_3) stainless steel Teflon-FEP vacuum line.²² Nonvolatile materials were manipulated under the dry nitrogen atmosphere of a glovebox. Vibrational spectra were recorded as previously described.²⁰

Reaction of $N_2F^+AsF_6^-$ with FNO. A sample of $N_2F^+AsF_6^-$ (1.84 mmol) was placed inside the drybox into a prepassivated $3/4$ in. Teflon-FEP ampule that was closed by a stainless steel valve. On the vacuum line, FNO (4.14 mmol) was added at -196°C , and the resulting mixture was allowed to slowly warm from -196 to -78°C by the use of a liquid N_2 -dry ice slush bath. The mixture was then allowed to slowly warm from -78°C to room temperature over a 12-h period. The ampule was cooled to -196°C , and the volatile material was separated during warm-up of the ampule to 25°C by fractional condensation through traps kept at -126 and -210°C . The -126°C trap contained unreacted FNO (2.29 mmol) and the -210°C trap contained *cis*- N_2F_2 (1.8 mmol). The white solid residue (401 mg, weight calcd for 1.84 mmol of $NO^+AsF_6^- = 403$ mg) was identified by vibrational spectroscopy as $NO^+AsF_6^-$.²³

Oxidation Reactions of $N_2F^+AsF_6^-$. All oxidation reactions of $N_2F^+AsF_6^-$ were carried out in the same manner. About 2 mmol of $N_2F^+AsF_6^-$ was placed in the drybox into a prepassivated 0.5 in. o.d. Teflon-FEP ampule that was closed by a stainless steel valve. On the vacuum line, about 2 mL of liquid anhydrous HF and about 5 mmol of the compound to be oxidized were added, and the resulting mixture was kept at room temperature for 24 h. The ampule was cooled to -196°C and the amount of evolved nitrogen was measured by expansion into the vacuum line. The material volatile at room temperature was separated by fractional condensation through a series of cold traps kept at appropriate temperatures. The contents of these traps were measured by PVT and identified by infrared spectroscopy. The solid residues in the ampule were weighed and identified by infrared and Raman spectroscopy.

Crystal Structure Determination of $N_2F^+AsF_6^-$. Single crystals of $N_2F^+AsF_6^-$ were obtained by slowly cooling a saturated HF solution from 25 to 0°C and separating the resulting crystals from the cold solution by decantation. A suitable crystal was selected under a microscope inside the glovebox and sealed in a quartz capillary.

Diffraction data were collected at room temperature using a Siemens/Nicolet/Syntex P2₁ diffractometer with $Mo\ K\alpha$ radiation up to a 2θ limit of 45° . A total of 1272 intensity values for an entire reflection sphere was collected and the four equivalent quadrants merged to give 364 unique reflections. An empirical ψ -scan absorption correction was applied, based on the variation in intensity of an axial reflection.²⁴

The pattern of systematic absences was consistent with any one of the following centered monoclinic space groups: $C2$ (No. 5), Cm (No. 8), or $C2/m$ (No. 12). The structure was solved for all three space groups. The positions of the atoms were obtained by direct methods with use of

Table II. Final Atomic Coordinates for $N_2F^+AsF_6^-$

atom	<i>x</i>	<i>y</i>	<i>z</i>	no. ^a
As1	0	0	0.5	2
F2	0.1235 (6)	0	0.2574 (9)	4
F3	-0.0948 (5)	0.2027 (9)	0.3406 (9)	8
N4	0	0.5	1	2
X5 ^b	-0.1203 (7)	0.5	0.9313 (11)	4

^a Number of times this atom appears in the unit cell. ^b X is the disordered terminal atom (50% N/50% F) of the $[N_2F]^+$ cation in space group $C2/m$.

the computing package SHELX-86.²⁵ The structures were then refined with use of 362 reflections with $I > 3\sigma(I)$. Details of the data collection parameters and other crystallographic information are given in Table I. The final atomic coordinates, thermal parameters, interatomic distances, and bond angles for the preferred (see Discussion section) $C2/m$ model are given in Tables II–IV, respectively.

Computational Methods. The geometry and vibrational frequencies of N_2F^+ and FCN were calculated in the local density functional approximation²⁶ by using the program system DMol.²⁷ The atomic basis functions are given numerically on an atom-centered, spherical-polar mesh. The radial portion of the grid is obtained from the solution of the atomic LDF equations by numerical methods. The radial functions are stored as sets of cubic spline coefficients so that the radial functions are piecewise analytic, a necessity for the evaluation of gradients. The use of exact spherical atom results offers some advantages. The molecule will dissociate exactly to its atoms within the LDF framework, although this does not guarantee correct dissociation energies. Furthermore, because of the quality of the atomic basis sets, basis set superposition effects should be minimized and correct behavior at the nucleus is obtained.

Since the basis sets are numerical, the various integrals arising from the expression for the energy need to be evaluated over a grid. The integration points are generated in terms of angular functions and spherical harmonics. The number of radial points N_R is given as

$$N_R = 1.2 \times 14(Z - 2)^{1/3}$$

where Z is the atomic number. The maximum distance for any function is 12 au. The angular integration points N_θ are generated at the N_R radial points to form shells around each nucleus. The value of N_θ ranges from 14 to 302 depending on the behavior of the density.²⁸ The Coulomb potential corresponding to the electron repulsion term is determined directly from the electron density by solving Poisson's equation. In DMol, the form for the exchange-correlation energy of the uniform electron gas is that derived by von Barth and Hedin.²⁹

All of the DMol calculations were done with a double numerical basis set augmented by polarization functions. This can be thought of in terms of size as a polarized double- ζ basis set. However, because of the use of exact numerical solutions for the atom, this basis set is of significantly higher quality than a normal molecular orbital double- ζ basis set. The fitting functions have angular momentum numbers one greater than that of the polarization function. Since all of the atoms have d polarization functions, the value of 1 for the fitting function is 3.

Geometries were optimized by using analytic gradient methods. There are two problems with evaluating gradients in the LDF framework which are due to the numerical methods that are used. The first is that the energy minimum does not necessarily correspond exactly to the point with a zero derivative. The second is that the sum of the gradients may not always be zero as required for translational invariance. These tend to introduce errors on the order of 0.001 Å in the calculation of the coordinates if both a reasonable grid and basis set are used. This gives bond lengths and angles with reasonable error limits. The difference of 0.001 Å is about an order of magnitude smaller than the accuracy of the LDF geometries when compared to the experimental ones. The frequencies

(25) Sheldrick, G. M. *SHELX System of Crystallographic Programs*, University of Goettingen, West Germany, 1986.

(26) (a) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989. (b) Salahub, D. R. In *Ab Initio Methods in Quantum Methods in Quantum Chemistry-II*; Lawlwy, K. P., Ed.; J. Wiley & Sons: New York, 1987; p 447. (c) Wimmer, E.; Freeman, A. J.; Fu, C.-L.; Cao, P.-L.; Chou, S.-H.; Delley, B. In *Supercomputer Research in Chemistry and Chemical Engineering*; Jensen, K. F., Truhlar, D. G., Eds.; ACS Symp. Ser.; American Chemical Society: Washington, DC, 1987; p 49. (d) Jones, R. O.; Gunnarsson, O. *Rev. Mod. Phys.* **1989**, *61*, 689.

(27) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508. DMol is available commercially from BIOSYM Technologies, San Diego, CA.

(28) This grid can be obtained by using the FINE parameter in DMol.

(29) von Barth, U.; Hedin, L. *J. Phys. Chem.* **1972**, *5*, 1629.

(21) Christe, K. O.; Wilson, W. W.; Schack, C. J. *J. Fluorine Chem.* **1978**, *11*, 71.

(22) Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Synth.* **1986**, *24*, 3.

(23) Griffiths, J. E.; Sunder, W. A.; Falconer, W. E. *Spectrochim. Acta, Part A* **1975**, *31A*, 1207.

(24) For details on the ψ -scan empirical correction, see: Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 3548.

Table III. Final Temperature Factors for $N_2F^+AsF_6^-$

atom	10^4U_{11}	10^4U_{22}	10^4U_{33}	10^4U_{12}	10^4U_{13}	10^4U_{23}
As1	416 (5)	331 (5)	333 (4)	0 (0)	9 (4)	0 (0)
F2	745 (16)	935 (17)	659 (16)	0 (0)	312 (15)	0 (0)
F3	1220 (16)	1407 (17)	1240 (16)	715 (16)	301 (15)	716 (16)
N4	723 (18)	440 (17)	532 (17)	0 (0)	146 (17)	0 (0)
X5 ^a	655 (17)	750 (17)	809 (17)	0 (0)	7 (16)	0 (0)

^a X is the disordered terminal atom (50% N/50% F) of the $[N_2F]^+$ cation in space group $C2/m$.

Table IV. Bond Distances (Å) and Bond Angles (deg) in $[N_2F]^+[AsF_6]^-$

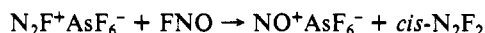
As1-F2	1.696 (4)	F2'-As1-F3	90.8 (2)
As1-F3	1.686 (4)	F3-As1-F3'	180.0 (0)
N4-X5	1.158 (6)	F3-As1-F3''	90.0 (2)
		F3'-As1-F3''	90.0 (2)
F2-As1-F3	89.2 (2)	F3''-As1-F3'''	180.0 (0)
F2-As1-F2'	180.0 (0)	X5-N4-X5'	180.0 (0)

were determined by numerical differentiation of the gradient. A two-point difference formula was used and a displacement of 0.01 au.

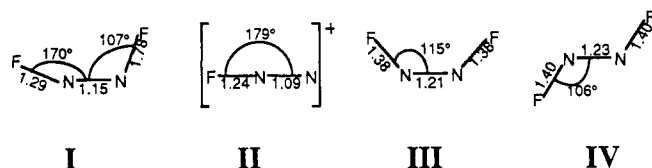
Results and Discussion

Trans-Cis Isomerization of N_2F_2 and the Synthesis of N_2F^+ Salts. Most of the known N_2F_2 syntheses produce exclusively the trans isomer.¹ Since the trans isomer is much less reactive than the cis isomer and, for example, does not form N_2F^+ salts, conversion of the trans to the cis isomer is often required. This trans-cis isomerization is usually quite erratic. Although it proceeds at room temperature in stainless steel, it often exhibits long and irreproducible induction periods and requires numerous months to go to completion. This isomerization can be accelerated by increasing the temperature; however, the yields of *cis*- N_2F_2 sharply decrease at elevated temperature due to decomposition of N_2F_2 to N_2 + F_2 .³⁰ In our study, aimed at the isomerization of N_2F_2 and its subsequent conversion to $N_2F^+AsF_6^-$, it was found advantageous to combine the *trans*- N_2F_2 with an excess of AsF_5 in a prepassivated, small volume stainless steel cylinder and to carry out the isomerization at about 70 °C. In this manner, any *cis*- N_2F_2 formed is immediately removed from the cis-trans equilibrium by complexation and thereby protected against decomposition to N_2 and F_2 . In this manner, yields of $N_2F^+AsF_6^-$ as high as 80% have been obtained from *trans*- N_2F_2 in 3 days at 70 °C.

It was also of interest to study which N_2F_2 isomer is formed in the displacement reactions of $N_2F^+AsF_6^-$ with a strong Lewis base, such as FNO. It was found that exclusively *cis*- N_2F_2 is formed in quantitative yield according to



Recent ab initio calculations³ on the transition-state structure for the N_2F_2 trans-cis isomerization resulted in the proposition of structure I. A similar transition state might be expected for a fluoride abstraction from *cis*- N_2F_2 (III) by a strong Lewis acid leading to the N_2F^+ cation (II).

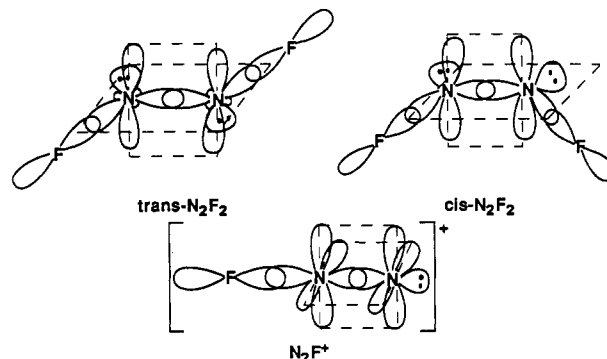


These results suggested that Lewis acids which are capable of forming N_2F^+ salts might also promote the formation of the isomerization transition state and thereby catalyze the N_2F_2 trans-cis isomerization. In order to be an effective isomerization catalyst, the strength of the Lewis acid should be such that it interacts with N_2F_2 but does not form a stable complex at the desired isomerization temperature. To test the validity of this

approach, we have studied the interaction of *cis*- N_2F_2 with BF_3 and PF_5 . It was found that the resulting N_2F_2 adducts are indeed labile enough and exhibit some dissociation pressure at temperatures as low as -78 °C. However, both PF_5 and BF_3 did not catalyze the isomerization of *trans*- N_2F_2 to *cis*- N_2F_2 in the temperature range of -78 to 25 °C.

Thus, the chemistry of N_2F_2 raises numerous puzzling questions for which, to our best knowledge, no satisfactory answers have previously been given.¹ Among these questions are the following: (i) why does only *cis*- N_2F_2 , but not *trans*- N_2F_2 form N_2F^+ salts, (ii) why do Lewis acids not catalyze the N_2F_2 trans-cis isomerization, and (iii) why is the *cis*- N_2F_2 isomer exclusively formed in the displacement reaction between N_2F^+ salts and FNO?

The great difference in reactivity between *cis*- and *trans*- N_2F_2 cannot be due to differences in thermodynamic properties or bond strengths because these values are very similar for both molecules.¹ Therefore, the difference in reactivity should be connected with the different spatial arrangement of the fluorine ligands and the free valence electron pairs on nitrogen. With use of a semi-empirical molecular orbital model, the bonding in N_2F_2 can be described by two sp^2 -hybridized nitrogen atoms resulting in one N-N and two N-F σ -bonds and two sterically active, free valence electron pairs on the two nitrogens. In addition, the remaining p orbitals on the nitrogen atoms form a [p-p] π -bond perpendicular to the plane of the sp^2 hybrids. In linear N_2F^+ , the two nitrogens form a [sp-sp] σ -bond and two perpendicular [p-p] π -bonds.



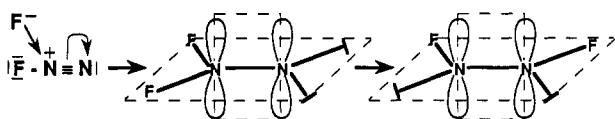
When a Lewis acid, such as AsF_5 , approaches a *cis*- N_2F_2 molecule, one of the fluorine ligands and hereby some electron density is pulled away from the remainder of the molecule. This results in an intermediate similar to the transition state (I) of the N_2F_2 trans-cis isomerization. This removal of electron density from one of the nitrogen atoms should result in the lowering of the electron density in the antibonding orbitals of the two free valence electron pairs on the two nitrogens. This enables them to form a partial triple bond, as demonstrated by the shortening of the N-N bond from 1.21 Å in *cis*- N_2F_2 (III) to 1.15 Å in the postulated trans-cis isomerization transition state (I). Therefore, the energy required for the elongation of one of the N-F bonds in I can be compensated for by the simultaneous formation of a partial $N\equiv N$ triple bond thereby resulting in a very low energy barrier toward N_2F^+ formation. However, the formation of such a partial $N\equiv N$ triple bond should be possible only for *cis*- N_2F_2 , i.e. when the two free valence electron pairs on the nitrogens are on the same side of the molecule and can overlap. In *trans*- N_2F_2 , migration of a nitrogen free valence electron pair from one side of the molecule to the other is blocked in the N_2F_2 plane by the fluorine ligands and in the perpendicular plane by the [p-p] π -bond. Furthermore, the $N=N$ double bond in N_2F_2 does not

(30) Pankratov, A. V.; Sokolov, O. M. *Russ. J. Inorg. Chem.* **1966**, *11*, 943.

permit free rotation around the N–N axis. Therefore, N_2F^+ formation from $\text{trans-N}_2\text{F}_2$ should be a high activation energy process requiring almost complete removal of one fluoride ion from N_2F_2 , before the FNN angle in the remaining FN_2 fragment becomes large enough for the nitrogen free electron pair to tunnel through to the other side and form the second π -bond.

This rationale explains not only why $\text{trans-N}_2\text{F}_2$ does not form N_2F^+ salts but also why Lewis acids do not catalyze the N_2F_2 trans-cis isomerization. As already pointed out above, the structure of the isomerization transition state closely resembles that of an expected intermediate in the N_2F^+ formation. If Lewis acids cannot abstract an F^- anion from $\text{trans-N}_2\text{F}_2$, it is then not surprising at all that they also do not promote the formation of the isomerization transition state.

The third question remaining to be answered was why in the FNO displacement reaction of $\text{N}_2\text{F}^+\text{AsF}_6^-$ exclusively the *cis-N*₂F₂ isomer is formed. In N_2F^+ , the most important resonance structure is $[\text{F}-\text{N}^+\equiv\text{N}]$ and, therefore, the formal positive charge resides mainly on the α -nitrogen atom. Furthermore, the free valence electron pair on the β -nitrogen atom is more diffuse than the N–F bond pair orbitals. Consequently, the attack of F^- on N_2F^+ should occur at the α -nitrogen atom resulting in the formation of an intermediate $\text{F}_2\text{N}=\text{N}$ molecule. The latter could easily undergo an α -fluorine migration to give FNNF.



Since in all these steps a [p–p] π -bond between the two nitrogens is always retained, free rotation around the N–N axis is precluded and the rearrangement of the fluorine atoms and the nitrogen free valence electron pairs must take place in the plane perpendicular to the N–N π -bond. Therefore, the sequence of the fluorine ligands and the nitrogen free electron pairs in $\text{F}_2\text{N}=\text{N}$ (F,F,P,P) must also be retained in FNNF, resulting exclusively in the *cis*-FNNF isomer. The general ease of this type of α -migration could explain the failure to isolate the intermediate $\text{F}_2\text{N}=\text{N}$ isomer.

Structure of the N_2F^+ Cation. The crystal structure of $\text{N}_2\text{F}^+\text{AsF}_6^-$ can be solved either in the non-centrosymmetric space groups Cm or $C2$ with ordered or disordered N_2F^+ cations, respectively, or the centrosymmetric space group $C2/m$ with disordered N_2F^+ cations. All three models resulted in acceptable agreement factors (Cm , $R = 2.96\%$; $C2$, $R = 2.68\%$; $C2/m$, $R = 4.04\%$) which to some extent are influenced by the number of variable parameters (Cm , 53; $C2$, 46; $C2/m$, 30). The Cm model resulted in an ordered almost linear N_2F^+ cation ($r_{\text{NF}} = 1.221$ (13) Å, $r_{\text{NN}} = 1.099$ (13) Å, $\angle\text{NNF} = 177.2$ (8)°) and a strongly distorted AsF_6^- anion with angles deviating by as much as 11.5° from those of an ideal octahedron. The $C2$ model resulted in a disordered bent N_2F^+ cation ($\sum r_{\text{NF}} + r_{\text{NN}} = 2.342$ (22) Å, $\angle\text{NNF} = 163.6$ (12)°) and again a strongly distorted AsF_6^- anion with angles deviating by as much as 13.8° from O_h symmetry. The $C2/m$ model resulted in a disordered linear N_2F^+ cation ($\sum r_{\text{NF}} + r_{\text{NN}} = 2.316$ (12) Å) and an AsF_6^- anion which within experimental error is perfectly octahedral. Since the Raman spectra of $\text{N}_2\text{F}^+\text{AsF}_6^-$ crystals are in perfect agreement with O_h symmetry (only three narrow bands at 689 (ν_1 , A_{1g}), 576 (ν_2 , E_g), and 376 cm^{-1} (ν_3 , F_{2g}) with half widths of 10 cm^{-1} or less at 25 °C), models Cm and $C2$ must be rejected in spite of their lower R factors. This situation closely resembles that in isotopic $\text{NS}_2^+\text{AsF}_6^-$ for which the alternate Cm and $C2$ models could also be rejected on the basis of the observed vibrational spectra.³¹ The packing diagram for $\text{N}_2\text{F}^+\text{AsF}_6^-$ is shown in Figure 1. The AsF_6^- anions occupy the corners of the cell and the centers of the ab faces, while the NX_2 cations occupy the remaining faces of the cell.

As pointed out already in the introduction, a knowledge of the exact N–F and N–N bond distances in N_2F^+ is of great interest.

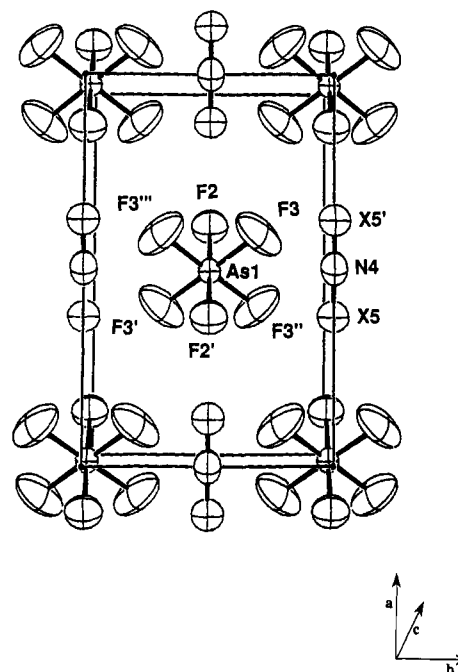


Figure 1. A unit cell plot of $\text{N}_2\text{F}^+\text{AsF}_6^-$ viewed down the c axis. In addition to the mirror plane, 2-fold rotational axes pass through As1 (bisecting the F3–As1–F3'' angle) and N4 (perpendicular to the X5–N4–X5' axis). The N_2F^+ cation is required by symmetry to be disordered, with the terminal X5, X5' positions being occupied equally by N and F atoms. This packing disorder causes the NX_2 cation to be linear and symmetric, and the central nitrogen atoms to be elongated along the molecular axis.

Table V. Calculated and Experimental Bond Distances (Å) and Vibrational Frequencies (cm^{-1}) for FCN

	expt	calcd (LDF)
$r_{\text{C}\equiv\text{N}}$	1.159	1.169
$r_{\text{C}-\text{F}}$	1.262	1.274
$\text{C}\equiv\text{N}$ stretch	2323	2355
$\text{C}-\text{F}$ stretch	1077	1081
$\text{F}-\text{C}\equiv\text{N}$ bend	451	465

Since the above crystal structure determination provides only a value for the sum of the N–F and N–N bond lengths, a reliable method was sought to partition this sum into its individual components. This partitioning was achieved by local density functional (LDF) calculations providing both the geometry and the vibrational frequencies.

The accuracy of the LDF calculations was tested for FCN which is isoelectronic with FNN^+ and for which both the geometry³² and the vibrational frequencies³³ are well-known (see Table V). As expected from a number of studies,³⁴ the LDF method slightly overestimates the bond distances and vibrational frequencies but otherwise excellently reproduces the experimental values (see Table V). Similarly, LDF calculations for the dinitrogen molecule, N_2 , resulted in a bond length value (1.113 Å) only slightly longer than the experimental one (1.098 Å).³⁵

The results of the LDF calculations for N_2F^+ are summarized in Table VI. As expected, the N_2F^+ cation is linear and the bond

(31) Johnson, J. P.; Passmore, J.; White, P. S.; Banister, A. J.; Kendrick, A. G. *Acta Cryst. Part C* **1987**, *C43*, 1651.

(32) Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619, see p 640.

(33) Shimanouchi, T. *J. Phys. Chem. Ref. Data* **1977**, *6*, 993.

(34) (a) Dixon, D. A.; Andzelm, A.; Fitzgerald, Wimmer, E.; Delley, B. Science and Engineering on Cray Supercomputers, Proceedings of the Fifth International Symposium, Cray Research, Minneapolis, MN, 1990. (b) Dixon, D. A.; Andzelm, A.; Fitzgerald, Wimmer, E.; Jasien, P. In *Theory and Applications of Density Functional Approaches to Chemistry*; Labanowski, J., Ed., in press.

(35) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

Table VI. Calculated and Experimental Bond Distances (Å) and Vibrational Frequencies (cm^{-1}) for FNN^+

	expt	calcd (LDF)				
		LDF	LDFS1	LDFS2	SCF 6-31G** ^a	MP-2 6-31G** ^a
$r_{N\equiv N}$	(1.099) ^b	1.121	1.111	1.106	1.072	1.138
r_{N-F}	(1.217) ^b	1.248	1.236	1.225	1.240	1.256
$\sum r_{N-N} + r_{N-F}$	2.316 (12)	2.369	2.347	2.331	2.312	2.394
$N\equiv N$ stretch	2373	2409				
$N-F$ stretch	1059	1100				
$F-N\equiv N$ bend	388	438				

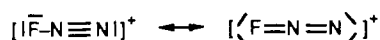
^a Data from ref 11. ^b Values obtained by partitioning the experimentally measured sum of $r_{N-N} + r_{N-F}$ according to their ratio in LDFS2.

lengths are, as for isoelectronic FNC, slightly too long. To obtain better estimates for the actual bond lengths, the LDF values can be scaled in the following manner. Using the scaling factors from the FCN calculations, one obtains the values labeled LDFS1. Using the N_2 results for scaling r_{N-N} and the NF_4^+ results for scaling r_{N-F} (r_{N-F} , LDF = 1.324 Å, ³⁶ experimental = 1.297 Å¹⁴), one obtains the values labeled LDFS2. The sum of r_{N-N} and r_{N-F} of LDFS2 (2.331 Å) is very close to that obtained from the crystal structure determination (2.316 Å). If one partitions the experimentally determined sum of $r_{N-N} + r_{N-F}$ in the same ratio as that in LDFS2, final values of 1.217 and 1.099 Å are obtained for r_{N-F} and r_{N-N} , respectively, in N_2F^+ (see Table VI). The close agreement between these values and those ($r_{NF} = 1.221$ Å, $r_{NN} = 1.099$ Å) obtained by the rejected C_m model with ordered N_2F^+ cations (see above) might be fortuitous.

Of the previously calculated¹⁰⁻¹² N-N and N-F bond lengths for N_2F^+ , the SCF 6-31G* and MP-2 6-31G* values of Peters¹¹ (see Table VI) come the closest to the values from this study but appear to either underestimate or overestimate the r_{N-N} value. When comparing the calculated LDF vibrational frequencies of N_2F^+ with the observed ones (see Table VI), the agreement is very satisfactory, particularly if it is kept in mind that the LDF values are unscaled, harmonic, gas-phase frequencies and the experimental values are anharmonic, solid-state frequencies.

As shown above, the N_2F^+ cation is linear. This result confirms a recent theoretical study¹² which concluded that, contrary to P_2F^+ , for N_2F^+ the linear $C_{\infty v}$ structure is favored by about 50–60 kcal over the symmetric, three-membered-ring structure of symmetry C_{2v} . As already pointed out in the introduction, the most interesting aspect of the N_2F^+ structure is its N-F bond distance. This distance of 1.22 Å is by far the shortest distance found to date for any N-F bond. The previously known range for N-F bonds extended from 1.512 Å in FNO to 1.30 Å in NF_4^+ .^{13,14} The value of 1.22 Å found for N_2F^+ is in good agreement with the value of 1.24 Å estimated from a force field calculation⁹ and force constant–bond distance plot extrapolations.^{11,13} The excellent agreement between our experimental value and the value extrapolated from the stretching force constant demonstrates that N_2F^+ conforms with Gordy's rule.¹⁵

The nitrogen–nitrogen bond distance in N_2F^+ is also of interest. Its value of 1.099 Å is comparable to those of 1.0976 (2) Å²⁶ in N_2 and 1.118 Å in N_2^+ ³⁸ and confirms its triple bond character. Thus the N_2F^+ cation is highly unusual. It possesses by far the shortest known N-F bond while at the same time exhibiting an N-N bond length comparable to the shortest known N-N bond. How can these unusually short bond distances be explained? It is tempting to invoke partial double bond character for the N-F bond by writing the following resonance structures:



If, however, the N-F bond assumes partial double bond character, the $N\equiv N$ bond must lose some of its strength and lengthen accordingly. This is not the case, as evidenced by the short $N\equiv N$ bond of 1.099 Å in N_2F^+ .

Table VII. Influence of Hybridization on Bond Lengths (Å) in Carbon and Nitrogen Compounds

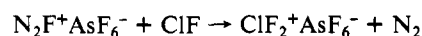
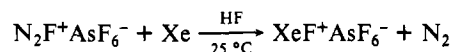
	CH_4 (sp^3)	$H_2C=CH_2$ (sp^2)	$HC\equiv CH$ (sp)
r_{C-H}	1.094 ^a	1.085 ^a	1.061 ^a
	CF_4 (sp^3)	$F_2C=CF_2$ (sp^2)	$FC\equiv N$ (sp)
r_{C-F}	1.323 ^b	1.313 ^b	1.262 ^a
	NF_4^+	$[FN=NF]^+$	$[FN\equiv N]^+$
r_{N-F}	1.30 ^c	?	1.22 ^d

^a Data from ref 32. ^b Data from ref 39. ^c Data from ref 14. ^d This work.

Although a formal positive charge and other highly electronegative ligands generally tend to increase the strength of an X-F bond, this effect alone is insufficient to explain the unusually short N-F and $N\equiv N$ bonds in N_2F^+ . For example, the N-F bond in NF_4^+ still has a value of 1.30 Å,¹⁴ in spite of a formal positive charge and three additional fluorine ligands which should be more electronegative than the nitrogen ligand in $N\equiv NF^+$.

The most plausible explanation for the shortening of the N-F bond in N_2F^+ , compared to NF_4^+ , is the change in hybridization of the nitrogen molecular orbitals. From carbon chemistry it is well-known that the C-H and C-F bond lengths significantly decrease with increasing s-character of the carbon molecular orbital. Therefore, a similar bond shortening should be expected on going from sp^3 -hybridized NF_4^+ to sp -hybridized $N\equiv NF^+$ (see Table VII). To our knowledge, this is the first example of hybridization-induced, dramatic bond shortening outside of carbon chemistry.

The N_2F^+ Cation as an Oxidative Fluorinator. In view of N_2 having a higher ionization potential than Kr, i.e. 15.576 vs 13.999 eV,⁴⁰ and KrF^+ being the most powerful presently known oxidative fluorinator,⁴¹ it was interesting to examine the oxidative power of the N_2F^+ cation. For this purpose, the reactions of $N_2F^+AsF_6^-$, dissolved in anhydrous HF, were studied at 25 °C with the following substrates: ClF_5 , BrF_5 , IF_5 , XeF_4 , Xe , ClF , O_2 , and NF_3 . The KrF^+ cation is capable of oxidizing all of these substrates under comparable reaction conditions. For example, $HalF_5$ is oxidized to $HalF_6^+$ salts, XeF_4 to XeF_5^+ , O_2 to O_2^+ , and NF_3 to NF_4^+ .⁴¹ In the case of N_2F^+ the only substrates oxidized were Xe and ClF according to



The first reaction was briefly mentioned in a previous paper,⁴² but no experimental details were given.

To examine whether fluorination reactions with N_2F^+ might benefit from elevated temperatures, $N_2F^+AsF_6^-$ was heated with a large excess of either ClF_5 or BrF_5 in a small ullage stainless steel cylinder, in the absence of HF, to 70 °C for 3 days. Again, no evidence for the formation of either ClF_6^+ or BrF_6^+ was detected. In the case of ClF_5 , however, a small amount of the N_2F^+ starting material was fluorinated by ClF_5 to $N_2F_3^+$. A detailed

(36) Dixon, D. A.; Christe, K. O. Unpublished work.

(37) Wilkinson, P. G. *J. Astrophys.* **1957**, 126, 1.

(38) Wilkinson, P. G. *Can. J. Phys.* **1956**, 34, 250.

(39) *Tables of Interatomic Distances and Configuration in Molecules and Ions*; The Chemical Society: London, 1958; Special Publication No. 11.

(40) *CRC Handbook of Chemistry and Physics*, 60th ed.; CRC Press: Boca Raton, FL, 1979.

(41) Christe, K. O.; Wilson, W. W.; Wilson, R. D. *Inorg. Chem.* **1984**, 23, 2058.

(42) Stein, L. *Chemistry* **1974**, 47, 15.

analysis of the factors determining the relative strength of an oxidative fluorinator will be given in a separate paper.⁴³

Acknowledgment. The authors thank Dr. Carl Schack for help, Dr. Konrad Seppelt for helpful comments on the crystal structure

disorder problem, and the U.S. Army Research Office and the U.S. Air Force Phillips Laboratory for financial support of the work at Rocketdyne.

Supplementary Material Available: Table SI listing observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

(43) Christe, K. O.; Wilson, W. W.; Dixon, D. A. To be published.

Preparation and Interconversion of Binuclear 2-Ferrazetine and Isomeric Ferrapyrrolinone Complexes

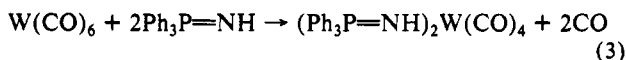
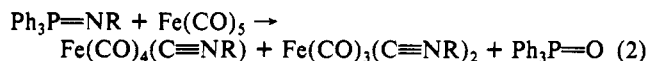
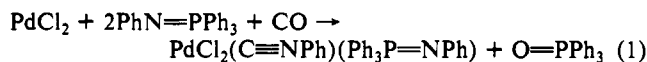
Chad A. Mirkin,[†] Kuang-Lieh Lu,[†] Thomas E. Snead,[†] Bruce A. Young,[†] Gregory L. Geoffroy,^{*,†} Arnold L. Rheingold,[†] and Brian S. Haggerty[†]

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, and Department of Chemistry, University of Delaware, Newark, Delaware 19716. Received September 24, 1990

Abstract: The complex $\text{Fe}_2(\mu\text{-CH}_2)(\text{CO})_8$ reacts with the phosphine imides $\text{R}'_3\text{P}=\text{NR}$ ($\text{R}, \text{R}' = \text{Ph}$; $\text{R} = \text{Bu}^t$, $\text{R}' = \text{Bu}^n$) to form a mixture of the 3-ferra-4-pyrrolin-2-one complexes $\text{Fe}_2(\mu\text{-CH}=\text{CHN}(\text{R})\text{C}(\text{O}))(\text{CO})_6$ and the 2-ferrazetine complexes $\text{Fe}_2(\mu\text{-CH}=\text{CHNR})(\text{CO})_6$. The latter complexes derive from the former by loss of CO, which is accelerated by heating (50 °C, 3 h) or by adding CO-labilizing agents (halides, $[\text{HB}(\text{s-Bu})_3]^+$). This reaction is reversed by photolysis of the 2-ferrazetine complexes under 1 atm of CO. However, when the 2-ferrazetine complexes are allowed to thermally react with CO, the isomeric 2-ferra-4-pyrrolin-3-one complexes $\text{Fe}_2(\mu\text{-C}(\text{O})\text{CH}=\text{CHNR})(\text{CO})_6$ are produced instead. These latter complexes have been found to add electrophiles (HBF_4 and $[\text{Me}_3\text{O}]\text{BF}_4$) to the acyl oxygen to form the cationic complexes $[\text{Fe}_2\{\mu\text{-C}(\text{OR})=\text{CHCH}=\text{NBu}^t\}](\text{CO})_6[\text{BF}_4]$ ($\text{R} = \text{H}, \text{Me}$). The 3-ferra-4-pyrrolin-2-one complexes also react with acid (HBF_4) under 1 atm of CO to form the complexes $[\text{Fe}_2\{\mu\text{-C}(\text{H})(\text{CH}=\text{NHR})\}](\text{CO})_6[\text{BF}_4]$, which possess protonated μ_2, η^1 -azallylidene ligands. The dimethylcarbene complex $\text{Fe}_2(\mu\text{-CMe}_2)(\text{CO})_8$ also reacts with $(\text{Bu}^n)_3\text{P}=\text{NBu}^t$, but this reaction stops at the acyl complex $\text{Fe}_2(\mu\text{-CMe}_2)(\text{CO})_7\text{C}(\text{O})\text{N}(\text{Bu}^t)\text{P}(\text{Bu}^n)_3$ since this species cannot undergo the hydrogen migration needed to give entry to the ferrapyrrolinone and ferrazetine complexes. Mechanisms are proposed for these various transformations, and the following complexes have been crystallographically characterized: $\text{Fe}_2(\mu\text{-CH}=\text{CHNPhC}(\text{O}))(\text{CO})_6$, $\text{Fe}_2(\mu\text{-CH}=\text{CHNBu}^t)(\text{CO})_6$, $\text{Fe}_2(\mu\text{-C}(\text{O})\text{CH}=\text{CHNPh})(\text{CO})_6$, $[\text{Fe}_2(\mu\text{-CHCH}=\text{NBu}^t)(\text{CO})_6][\text{CF}_3\text{SO}_3]$, and $[\text{Fe}_2(\mu\text{-C}(\text{OMe})=\text{CHCH}=\text{NBu}^t)(\text{CO})_6][\text{BF}_4]$.

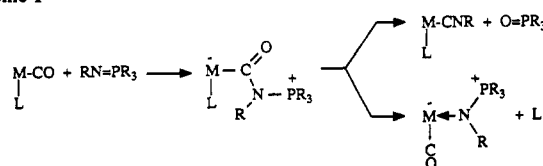
Introduction

Phosphine imides ($\text{R}_3\text{P}=\text{NR}$) are common reagents in the organic chemists repertoire for deoxygenating organic carbonyl compounds to form Schiff bases, reactions that proceed by initial addition of the nucleophilic phosphine imide nitrogen atom to the electropositive carbonyl carbon, followed by elimination of phosphine oxide. In principle, carbonyl ligands attached to transition metals should also be capable of undergoing deoxygenation by phosphine imides to form isocyanide ligands, but only two examples of this reaction have been reported (eqs 1 and 2).¹⁻³



The predominant reaction that occurs upon reaction of carbonyl complexes with phosphine imides is ligand substitution, with the phosphine imide ligand coordinating through the nitrogen atom, e.g., eq 3.⁴ The first step in both processes likely involves initial formation of an acyl intermediate via nucleophilic addition of the phosphine imide nitrogen to a terminal carbonyl ligand. This intermediate can then either eliminate phosphine oxide to form an isocyanide ligand or lose another ligand as the phosphine imide migrates to the metal to yield a substituted complex (Scheme I).⁵

Scheme I



In our continuing studies of complexes containing ketene ligands,⁶ we sought to determine if phosphine imides would deoxygenate a coordinated ketene ($\text{CH}_2=\text{C}=\text{O}$) to form a ketenimine ($\text{CH}_2=\text{C}=\text{NR}$) ligand. The complex $\text{Fe}_2(\mu\text{-CH}_2)(\text{CO})_8$ (1) has been reported to react with nucleophiles to give products that may form via the intermediacy of a μ -ketene complex,⁷ and in an attempt to trap the presumed μ -ketene intermediate, we allowed

(1) (a) Kiji, J.; Matsumura, A.; Haishi, T.; Okazaki, S.; Furukawa, J. *Bull. Chem. Soc. Jpn.* 1977, 40, 2731.

(2) Alper, H.; Partis, R. A. *J. Organomet. Chem.* 1972, 35, C40.

(3) Phosphine imides are well-known to deoxygenate metal oxo complexes to form the corresponding imido compounds. See, for example: (a) Chong, A. O.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* 1977, 99, 3420. (b) Maatta, E. A.; Haymore, B. L.; Wentworth, R. A. D. *Inorg. Chem.* 1980, 19, 1055. (c) Chatt, J.; Dilworth, J. R. *J. Chem. Soc., Chem. Commun.* 1972, 549.

(4) Bock, H.; tom Dieck, H. *Z. Naturforsch.* 1966, 21B, 739.

(5) Abel, E. W.; Muckeljohn, S. A. *Phosphorus Sulfur Relat. Elem.* 1981, 9, 235 and references therein.

(6) (a) Bassner, S. L.; Morrison, E. D.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* 1987, 6, 2207. (b) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* 1986, 106, 4783.

(7) (a) Denise, B.; Navarre, D.; Rudler, H. *J. Organomet. Chem.* 1987, 326, C83. (b) Navarre, D.; Rudler, H.; Daran, J. C. *J. Organomet. Chem.* 1986, 314, C34. (c) Röper, M.; Strutz, H.; Keim, W. *J. Organomet. Chem.* 1981, 219, C5.

[†] The Pennsylvania State University.

[‡] University of Delaware.

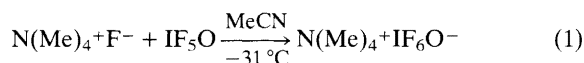
High-coordination Number Fluoro- and Oxofluoro-anions; IF_6O^- , $\text{TeF}_6\text{O}^{2-}$, TeF_7^- , IF_8^- and TeF_8^{2-} Karl O. Christe,^a Jeremy C. P. Sanders,^b Gary J. Schrobilgen^{*b} and William W. Wilson^a^a Rocketdyne, a Division of Rockwell International Corporation, Canoga Park, California 91303, USA^b The Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

The novel hypervalent, highly coordinated, high-oxidation state anions IF_6O^- , $\text{TeF}_6\text{O}^{2-}$, TeF_7^- , IF_8^- and TeF_8^{2-} have been synthesized in anhydrous MeCN using anhydrous $\text{N}(\text{Me})_4^+\text{F}^-$ as the fluoride ion source; the anions have been characterized by NMR and vibrational spectroscopy and represent novel examples of seven and eight-coordinate species having symmetries C_{5v} (IF_6O^- , $\text{TeF}_6\text{O}^{2-}$), D_{5h} (TeF_7^-) and D_{4d} (IF_8^- , TeF_8^{2-}).

The study of fluoro-anions having coordination numbers higher than six and, in particular, those involving free valence electron pairs, have recently received considerable attention.^{1–6} To a large extent, these studies have been greatly facilitated by the development of a convenient preparative scale synthesis of anhydrous $\text{N}(\text{Me})_4^+\text{F}^-$ and the realization that this salt is an excellent reagent for the preparation of novel, high-oxidation state complex fluoro- or oxofluoro-anions. Furthermore, the high solubilities of these $\text{N}(\text{Me})_4^+$ salts in solvents such as MeCN or CHF_3 permit the gathering of valuable structure information through NMR and vibrational studies and the growth of single crystals suitable for X-ray structure determinations.

Our recent success with the preparation of the XeF_5^- anion,⁴ the first known example of a pentagonal planar AX_5E_2 (where E stands for a free valence electron pair) species, prompted us to study some closely related iodine and tellurium compounds. In addition, there are relatively few examples of main-group species which allow the applicability of the valence shell electron pair repulsion (VSEPR) rules to coordination numbers exceeding six to be tested.⁸ In this note, we report on the syntheses and structures of the novel IF_6O^- anion and on the $\text{N}(\text{Me})_4^+$ salts of TeF_7^- , TeF_8^{2-} and IF_8^- .

The salt, $\text{N}(\text{Me})_4^+\text{IF}_6\text{O}^-$, was prepared according to eqn. (1) by the reaction of anhydrous $\text{N}(\text{Me})_4^+\text{F}^-$ with a threefold excess of IF_5O in dry MeCN at -31°C for 30 min.



The solvent and unreacted IF_5O were pumped off at -31°C leaving behind $\text{N}(\text{Me})_4^+\text{IF}_6\text{O}^-$ as a colourless crystalline solid in quantitative yield. According to differential scanning calorimetry (DSC) and pyrolysis data, the compound starts to decompose at about 137°C with formation of CF_4 , COF_2 and IF_4O^- as the major products.

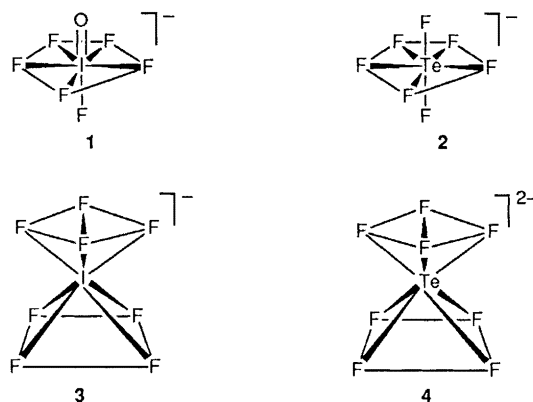
The ^{19}F NMR spectrum of $\text{N}(\text{Me})_4^+\text{IF}_6\text{O}^-$ in MeCN solution recorded at -40°C (Fig. 1) is consistent with the structure predicted by the VSEPR rules, consisting of a pentagonal bipyramidal structure of C_{5v} symmetry (structure 1) in which the oxygen atom occupies an axial position. The spectrum consists of a doublet at δ 166.0, assigned to the

equatorial fluorines, and a 1:5:10:10:5:1 sextet at δ 111.1, assigned to the axial fluorine trans to oxygen. Both resonances are broadened by partially quadrupole-collapsed spin coupling to ^{127}I ($I = 5/2$). The fluorine–fluorine scalar coupling, $^2J(^{19}\text{F}_a\text{--F}_e)$ 205 Hz, is very similar in magnitude to those for IF_5O (271–280 Hz)⁹ and *cis*- IO_2F_4^- (204 Hz in MeCN).¹⁰

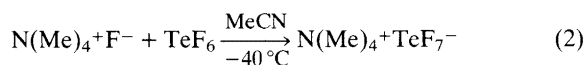
The vibrational spectra of IF_6O^- are also in excellent agreement with symmetry C_{5v} . The assignments were made by comparison with the related IF_7 molecule (see Table 1) and XeF_5^- anion.⁴

The reactions between TeF_6 and alkali metal fluorides have been reported previously, although definitive characterization of the products was never achieved.^{11,12} The reactions of TeF_6 with CsF and RbF suspended in C_6F_6 resulted in products approaching the limiting compositions $\text{CsF}\cdot\text{TeF}_6$ and $2\text{RbF}\cdot\text{TeF}_6$, respectively.¹² Vibrational studies on these materials were tentatively interpreted as indicating D_{5h} and D_{4d} structures for TeF_7^- and TeF_8^{2-} , respectively. However, since both compounds decomposed in solution, a fuller characterization of their nature was precluded.

The preparation of $\text{N}(\text{Me})_4^+\text{TeF}_7^-$ was similar to that for the IF_6O^- salt except that a 5% excess of TeF_6 was allowed to



react with $\text{N}(\text{Me})_4^+\text{F}^-$ according to equation (2). The solvent and an excess of TeF_6 were pumped off at room temperature leaving a white solid in quantitative yield.



The room temperature ^{125}Te NMR spectrum of $\text{N}(\text{Me})_4^+\text{TeF}_7^-$ in MeCN consists of a 1:7:21:35:35:21:7:1 octet centred at δ 327.4 (Fig. 2). The octet fine structure arises from the one-bond spin-spin coupling between the central ^{125}Te and the ^{19}F ligands [$^1J(^{125}\text{Te}-^{19}\text{F})$ 2876 Hz] and is in accord with a TeF_7^- anion structure in which all seven fluorines are rendered equivalent on the NMR time scale by a facile intramolecular exchange process. The ^{19}F NMR spectrum is also consistent with the TeF_7^- anion undergoing a fluxional process in solution, and consists of a single environment (δ 16.1) and natural abundance satellite spectra arising from $^1J(^{123}\text{Te}-^{19}\text{F})$ 2385 and $^1J(^{125}\text{Te}-^{19}\text{F})$ 2876 Hz. Under high resolution at an external field strength of 11.744 T, the central line displays the isotopic shift pattern arising from the natural abundance spinless tellurium isotopes corresponding to the fluorines of the ^{130}Te , ^{128}Te , ^{126}Te , ^{124}Te and ^{122}Te isotopomers, with each isotopomer shifted successively to higher frequency of $^{130}\text{TeF}_7^-$, by 0.004 ppm. Earlier NMR studies have shown that the isoelectronic IF_7 molecule also undergoes rapid intramolecular exchange and gives rise to a single fluorine environment in the room temperature ^{19}F NMR spectrum with partially quadrupole-collapsed fine structure arising from $^1J(^{127}\text{I}-^{19}\text{F})$.¹³

The vibrational spectra of TeF_7^- have been assigned by analogy with those of the isoelectronic IF_7 molecule (Table 1) and are in agreement with a pentagonal bipyramidal structure of D_{5h} symmetry (structure 2). In general, the TeF_7^- frequencies are shifted to lower frequencies relative to those of IF_7 , in accordance with the formal negative charge of TeF_7^- .

The syntheses of Cs^+IF_8^- ,¹⁴ NO^+IF_8^- ,^{14,15} and $\text{NO}_2^+\text{IF}_8^-$ ¹⁵ have previously been reported, and the ionic nature of these salts was established by the observation of the vibrational bands characteristic for NO^+ and NO_2^+ .^{14,15} Although partial Raman¹⁴ and IR spectra¹⁵ had been reported for IF_8^- , no conclusions could be drawn from these data about the exact structure of this interesting octacoordinated anion. To allow a

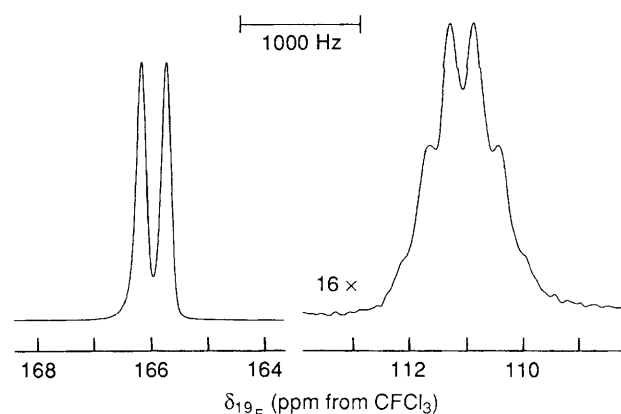


Fig. 1 The ^{19}F NMR spectrum of $\text{N}(\text{Me})_4^+\text{IF}_6\text{O}^-$ recorded at 471.599 MHz in MeCN solvent at -40°C

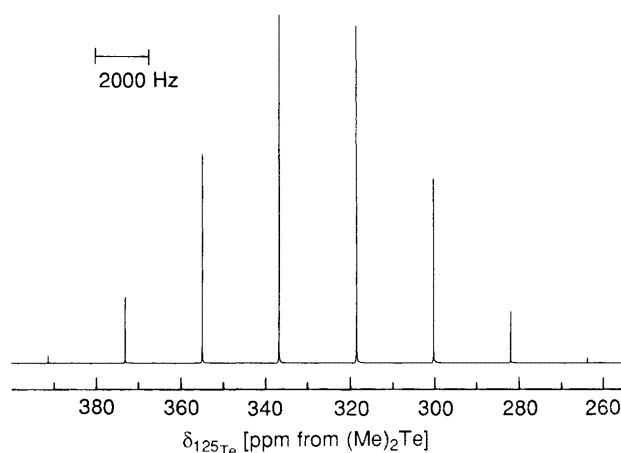


Fig. 2 The ^{125}Te NMR spectrum of $\text{N}(\text{Me})_4^+\text{TeF}_7^-$ recorded at 157.792 MHz in MeCN solvent at 30°C

Table 1 Vibrational frequencies (cm^{-1}) and tentative assignments for IF_6O^- , IF_7 and TeF_7^-

IF ₆ O ⁻ (C _{5v}) ^a				IF ₇ (D _{5h}) ^b			TeF ₇ ⁻ (D _{5h}) ^a	
A ₁	ν ₁	ν I=O	873 [vs, IR; 5.3, R (p)]	A ₁ '	ν ₁	ν sym MF ₂ ax	675 [2.0, R (p)]	597 (2.6, R)
	ν ₂	ν IF ax	649 [s, IR; 8.8 R (p)]		ν ₂	ν sym MF ₅	629 [10, R (p)]	640 (10, R)
	ν ₃	ν sym IF ₅	584 [10, R (p)]	A ₂ ''	ν ₃	ν asym MF ₂ ax	746 (s, IR)	695 (vs, IR)
E ₁	ν ₄	δ umbrella IF ₅	359 (s, IR)	E ₁ '	ν ₄	δ umbrella MF ₅	363 (s, IR)	332 (s, IR)
	ν ₅	ν asym IF ₅	585 (vs, IR)		ν ₅	ν asym MF ₅	672 (vs, IR)	625 (vs, IR)
	ν ₆	δ wag I=O	457 (4.9, R)	E ₁ ''	ν ₆	δ scissoring MF ₂ ax	425 (vs, IR)	384 (vs, IR)
	ν ₇	δ wag IF ax	405 (vs, IR)		ν ₇	δ asym MF ₅ in plane	257 (w, IR)	^c
	ν ₈	δ asym IF ₅ in plane	260 (s, IR; 0.2, R)		ν ₈	δ wag MF ₂ ax	308 (0.6, R)	299 (0.6, R)
	E ₂	ν ₉	ν asym IF ₅	530 (0.4, R)	E ₂ '	ν ₉	ν asym MF ₅	509 (0.9, R)
ν ₁₀		δ scissoring IF ₅ in plane	341 (6.2, R)	E ₂ ''	ν ₁₀	δ scissoring MF ₅ in plane	342 (0.6, R)	326 (0.7, R)
ν ₁₁		δ pucker IF ₅	^d		ν ₁₁	δ pucker MF ₅	^d	^d

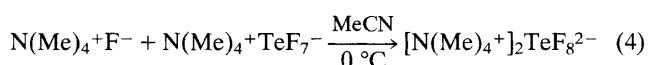
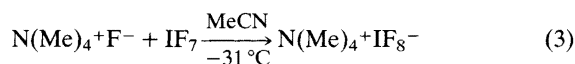
^a Spectra recorded for the $\text{N}(\text{Me})_4^+$ salts at 25°C . ^b Frequencies are taken from H. H. Eysel and K. Seppelt, *J. Chem. Phys.*, 1972, **56**, 5081. A number of modes have been reassigned so that they are consistent with the corresponding assignments for XeF_5^- (ref. 4), which have been confirmed by a force constant analysis and theoretical calculations. ^c Mode not observed. ^d Inactive in both the IR and Raman spectra.

Table 2 Vibrational frequencies (cm^{-1}) and assignments for IF_8^- in $\text{N}(\text{Me})_4^+\text{IF}_8^-$ and TeF_8^{2-} in $[\text{N}(\text{Me})_4^+]_2\text{TeF}_8^{2-}$ in point group D_{4d}

Raman				IR (solid 25 °C)		Assignment in D_{4d}
IF_8^-		TeF_8^{2-}		IF_8^-	TeF_8^-	
Solid		MeCN sol'n				
25 °C	−142 °C					
660 (0+)	660 (0+)			590 vs, br	558 vs	$\nu_{12}(\text{E}_3)$ $\nu_4(\text{B}_2)$ $\nu_6(\text{E}_1)$
	595 (10)					
587 (10)	588 (6.5)	590 (10) p	582 (10)			$\nu_1(\text{A}_1)$
550 (0.3)	550 (0.5)	550 (0+) dp	490 (0.2), br			$\nu_9(\text{E}_2)$
463 (1.8)	463 (1.9)	462 (0.5) p	408 (1.0)	410 s	375 vs	$\nu_2(\text{A}_1)$ $\nu_5(\text{B}_2)$ $\nu_8(\text{E}_1)$
	419 (0.9)					
411 (0.7)	410 (1.4)	410 sh ^a	388 (1.8)			$\nu_{10}(\text{E}_2)$
	380 (0+) ^b		325 (0.3)			
				314 m	265 w	$\nu_{13}(\text{E}_3)$ $\nu_7(\text{E}_1)$

^a Shoulder on strong MeCN solvent band. ^b This band could possibly be due to the $\text{N}(\text{Me})_4^+$ cation.

better characterization of the IF_8^- anion, we have prepared the new $\text{N}(\text{Me})_4^+\text{IF}_8^-$ salt and its isoelectronic tellurium analogue, TeF_8^{2-} , by the reaction of $\text{N}(\text{Me})_4^+\text{F}^-$ with excess IF_7 and a stoichiometric amount of $\text{N}(\text{Me})_4^+\text{TeF}_7^-$, respectively. For reaction (3) the solvent and unreacted IF_7 were pumped off at −22 and 0 °C, respectively, leaving behind colourless $\text{N}(\text{Me})_4^+\text{IF}_8^-$ in quantitative yield. In the case of reaction (4), $[\text{N}(\text{Me})_4^+]_2\text{TeF}_8^{2-}$ was isolated in admixture with ca. 20–30% $\text{N}(\text{Me})_4^+\text{TeF}_7^-$. The $[\text{N}(\text{Me})_4^+]_2\text{TeF}_8^{2-}$ salt



has a strong tendency to dissociate in MeCN, thus far preventing the preparation of a sample containing only the TeF_8^{2-} anion. At room temperature, dissociation of the insoluble TeF_8^{2-} anion into TeF_7^- and F^- results in rapid solvent attack by F^- and formation of HF_2^- anion. Even in the presence of a fivefold excess of $\text{N}(\text{Me})_4^+\text{F}^-$ at −5 °C, significant amounts of TeF_7^- and F^- were observed in the ^{19}F NMR spectrum, but no resonance attributable to TeF_8^{2-} could be observed. The $\text{N}(\text{Me})_4^+\text{IF}_8^-$ salt is a crystalline solid which, according to DSC data, is stable up to ca. 110 °C where it undergoes exothermic decomposition.

The IF_8^- and TeF_8^{2-} anions possess eight fluorine ligands and no free central atom valence electron pair. Their structures could, therefore, be either a cube of symmetry O_h , which is unlikely owing to steric interactions,⁸ a dodecahedron of symmetry D_{2d} or a square antiprism of symmetry D_{4d} (structures 3 and 4).^{17–20} Distinction among these three possibilities was made by vibrational spectroscopy. The dodecahedral structure is expected to give rise to two polarized stretching modes and four deformation modes (two polarized; two depolarized) exclusively in the Raman. The IR bands are mutually non-exclusive and comprise four stretching modes and five deformation modes which are all depolarized in the Raman. All Raman and IR bands observed for IF_8^- and TeF_8^{2-} are mutually exclusive, thereby eliminating D_{2d}

symmetry. For the cubic O_h structure, two stretching modes are expected (one polarized; the other depolarized) and two depolarized deformation modes in the Raman, as well as one stretching and one deformation mode in the infrared. All these modes should be mutually exclusive.¹⁸ For the square antiprismatic D_{4d} structure, one polarized and two depolarized stretching modes are expected as well as one polarized and three depolarized deformation modes in the Raman. In the IR spectrum, two stretching and three deformation modes are expected, which again should be mutually exclusive.^{17,19,20} Although the full number of fundamentals for D_{4d} was not observed (see Table 2), probably because of either low relative intensities or coincidences, the observation of a polarized Raman deformation band at 462 cm^{-1} and of at least two IR active deformation modes at 410 and 314 cm^{-1} , respectively, establish the square antiprismatic D_{4d} structure for IF_8^- . It was not possible to obtain polarization data on TeF_8^{2-} owing to the insolubility of the salt and its tendency to dissociate in MeCN. However, the vibrational spectra of TeF_8^{2-} can be assigned by their close analogy to those of IF_8^- (Table 2) and it may be concluded that TeF_8^{2-} also possesses a square antiprismatic structure.

X-Ray crystal structure determinations on these and other closely related anions are underway both in our laboratories and in an independent effort by Dr K. Seppelt and coworkers at the Freie Universität, Berlin.

Note added in proof: The $\text{TeF}_6\text{O}^{2-}$ anion has also been synthesized by the reaction of equimolar amounts of $\text{N}(\text{Me})_4^+\text{F}^-$ and $\text{N}(\text{Me})_4^+\text{TeF}_5\text{O}^-$ at −9 °C in MeCN. The vibrational assignments (v/cm^{-1}) under C_{5v} establish that $\text{TeF}_6\text{O}^{2-}$ is isostructural with IF_6O^- : ν_1 829 (s, IR; s, R); ν_2 613 (m, IR; vs, R); ν_3 528 (m, R); ν_4 330 (s, IR); ν_5 525 (vs, IR); ν_6 388 (m, R); ν_7 365 (vs, IR); ν_8 245 (not observed, beyond spectrometer limit; w, R); ν_9 not observed; ν_{10} 322 (s, R); ν_{11} (not observed). The ^{19}F NMR spectrum of $\text{N}(\text{Me})_4^+\text{IF}_8^-$ has been obtained at 30 °C (δ 248.6) and is a partially quadrupole collapsed multiplet (saddle-shaped with a 'doublet' separation of 3807 Hz) arising from the ^{127}I – ^{19}F scalar coupling and is consistent with the small electric field gradient at the ^{127}I nucleus that is anticipated for a square antiprismatic AX_8 geometry.

The authors thanks US Air Force Astronautics Laboratory, Edwards AFB, California (K. O. C. and G. J. S.), the US Army Research Office (K. O. C.) and the Natural Sciences and Engineering Research Council of Canada (G. J. S.) for financial support; and Dr K. Seppelt for bringing his X-ray structural studies to our attention.

Received, 21st January 1991; Com. 1/00298H

References

- 1 W. W. Wilson and K. O. Christe, *Inorg. Chem.*, 1989, **28**, 4172.
- 2 K. O. Christe and W. W. Wilson, *Inorg. Chem.*, 1989, **28**, 3275.
- 3 K. O. Christe, W. W. Wilson, R. V. Chirakal, J. C. P. Sanders and G. J. Schrobilgen, *Inorg. Chem.*, 1990, **29**, 3506.
- 4 K. O. Christe, E. C. Curtis, D. A. Dixon, H. P. Mercier, J. C. P. Sanders and G. J. Schrobilgen, *J. Am. Chem. Soc.*, 1991, **113**, 3351.
- 5 A. R. Mahjoub, A. Hoser, J. Fuchs and K. Seppelt, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1526.
- 6 A. R. Mahjoub, B. Nuber and K. Seppelt, personal communication.
- 7 K. O. Christe, W. W. Wilson, R. D. Wilson, R. Bau and J. Feng, *J. Am. Chem. Soc.*, 1990, **112**, 7619.
- 8 R. J. Gillespie and I. Hargittai, *The VSEPR Model of Molecular Geometry*, Allyn and Bacon, Boston, 1991.
- 9 R. J. Gillespie and J. W. Quail, *Proc. Chem. Soc.*, 1963, 278; M. Brownstein, R. J. Gillespie and J. P. Krasznai, *Can. J. Chem.*, 1978, **56**, 2253.
- 10 K. O. Christe, R. D. Wilson and C. J. Schack, *Inorg. Chem.*, 1981, **20**, 2104.
- 11 E. L. Muetterties, *J. Am. Chem. Soc.*, 1957, **79**, 1004.
- 12 H. Selig, S. Sarig and S. Abramowitz, *Inorg. Chem.*, 1974, **13**, 1508.
- 13 R. J. Gillespie and J. W. Quail, *Can. J. Chem.*, 1964, **42**, 2671; E. L. Muetterties and K. J. Packer, *J. Am. Chem. Soc.*, 1964, **86**, 293.
- 14 C. J. Adams, *Inorg. Nucl. Chem. Lett.*, 1974, **10**, 831.
- 15 F. Seel and M. J. Pimpl, *J. Fluorine Chem.*, 1977, **10**, 413.
- 16 K. O. Christe and William W. Wilson, *J. Fluorine Chem.*, 1990, **47**, 117.
- 17 A. Beuter, W. Kuhlmann and A. Sawodny, *J. Fluorine Chem.*, 1975, **6**, 367.
- 18 C. W. F. T. Pistorius, *Bull. Soc. Chim. Belg.*, 1959, **68**, 630.
- 19 H. L. Schläfer and H. F. Wasgestian, *Theoret. Chim. Acta*, 1963, **1**, 369.
- 20 K. O. Hartman and F. A. Miller, *Spectrochim. Acta, Part A*, 1968, **24**, 669.

X-ray Crystal Structure and Raman Spectrum of Tribromine(1+) Hexafluoroarsenate(V), $\text{Br}_3^+\text{AsF}_6^-$, and Raman Spectrum of Pentabromine(1+) Hexafluoroarsenate(V), $\text{Br}_5^+\text{AsF}_6^-$

K. O. CHRISTE*

Canoga Park, CA (USA), Rocketdyne Division, Rockwell International

R. BAU and D. ZHAO

Los Angeles, CA (USA), University of Southern California, Department of Chemistry

Dedicated to Professor Josef Goubeau in memoriam¹⁾

Abstract. A single crystal of $\text{Br}_3^+\text{AsF}_6^-$ was isolated from a sample of $\text{BrF}_2^+\text{AsF}_6^-$ which had been stored for 20 years. It was characterized by x-ray diffraction and Raman spectroscopy. It is shown that $\text{Br}_3^+\text{AsF}_6^-$ (triclinic, $a = 7.644(7) \text{ \AA}$, $b = 5.641(6) \text{ \AA}$, $c = 9.810(9) \text{ \AA}$, $\alpha = 99.16(8)^\circ$, $\beta = 86.61(6)^\circ$, $\gamma = 100.11(7)^\circ$, space group $\text{P}\bar{1}$, $R(\text{F}) = 0.0608$) is isomorphous with $\text{I}_3^+\text{AsF}_6^-$. The structure consists of discrete Br_3^+ and AsF_6^- ions with some cation-anion interaction causing distortion of the AsF_6^- octahedron. The Br_3^+ cation is symmetric with a bond distances of $2.270(5) \text{ \AA}$ and a bond angle of $102.5(2)^\circ$. The three fundamental vibrations of Br_3^+ were observed at $297 (\nu_3)$, $293 (\nu_1)$, and $124 \text{ cm}^{-1} (\nu_2)$. The Raman spectra of $\text{Cl}_3^+\text{AsF}_6^-$ and $\text{I}_3^+\text{AsF}_6^-$ were reinvestigated and $\nu_3(\text{B}_1)$ of I_3^+ was reassigned. General valence force fields are given for the series Cl_3^+ , Br_3^+ , and I_3^+ . Reactions of excess Br_2 with either $\text{BrF}_2^+\text{AsF}_6^-$ or $\text{O}_2^+\text{AsF}_6^-$ produce mixtures of $\text{Br}_3^+\text{AsF}_6^-$ and $\text{Br}_5^+\text{AsF}_6^-$. Based on its Raman spectra, the Br_5^+ cation possesses a planar, centrosymmetric structure of C_{2h} symmetry with three semi-ionically bound, collinear, central Br atoms and two more covalently, perpendicularly bound, terminal Br atoms.

Kristallstruktur und Raman-Spektrum von Tribrom(1+) Hexafluoroarsenat(V), $\text{Br}_3^+\text{AsF}_6^-$, und Raman-Spektrum von Pentabrom(1+) Hexafluoroarsenat(V), $\text{Br}_5^+\text{AsF}_6^-$

Inhaltsübersicht. Ein Einkristall von $\text{Br}_3^+\text{AsF}_6^-$, gebildet während 20jähriger Aufbewahrung einer $\text{BrF}_2^+\text{AsF}_6^-$ Probe, wurde isoliert und mittels Röntgenstrukturanalyse und Raman-Spektren charakterisiert. Es wird gezeigt, daß $\text{Br}_3^+\text{AsF}_6^-$ (triklin, $a = 7,644(7) \text{ \AA}$, $b = 5,641(6) \text{ \AA}$, $c = 9,810(9) \text{ \AA}$, $\alpha = 99,16(8)^\circ$, $\beta = 86,61(6)^\circ$, $\gamma = 100,11(7)^\circ$, Raumgruppe $\text{P}\bar{1}$, $R(\text{F}) = 0,0608$) isomorph mit $\text{I}_3^+\text{AsF}_6^-$ ist. Die Struktur besteht aus diskreten Br_3^+ - und AsF_6^- -Ionen mit schwachen Anion-Kation-Wechselwirkungen, die in einer Verzerrung der AsF_6^- -Oktaeder resultieren. Das Br_3^+ -Kation ist symmetrisch mit einem Bindungsabstand von $2,270(5) \text{ \AA}$ und einem Bindungswinkel von $102,5(2)^\circ$. Die drei Grundschrwingungen von Br_3^+ wurden bei $297 (\nu_3)$, $293 (\nu_1)$ und $124 \text{ cm}^{-1} (\nu_2)$ gefunden.

¹⁾ One of us (KOC) is deeply indebted to Prof. GOUBEAU for the profound influence he has had on his professional and personal career. Prof. GOUBEAU has given him much more than a solid chemical education, he has instilled in him an everlasting love and enjoyment of chemistry.

Raman-Spektren von $\text{Cl}_3^+\text{AsF}_6^-$ und $\text{I}_3^+\text{AsF}_6^-$ wurden neu aufgenommen, und $\nu_3(\text{B}_1)$ von I_3^+ wurde neu zugeordnet. Allgemeine Valenzkraftkonstanten wurden für die Reihe Cl_3^+ , Br_3^+ und I_3^+ berechnet. Umsetzungen von überschüssigem Brom mit $\text{BrF}_2^+\text{AsF}_6^-$ oder $\text{O}_2^+\text{AsF}_6^-$ resultieren in einem Gemisch von $\text{Br}_3^+\text{AsF}_6^-$ und $\text{Br}_5^+\text{AsF}_6^-$. Auf Grund der beobachteten Raman Spektren besitzt das Br_5^+ -Kation eine planare, zentrosymmetrische C_{2h} Struktur mit drei halb-ionisch gebundenen, kollinearen, zentralen Bromatomen und zwei mehr kovalent und rechtwinklig gebundenen, endständigen Bromatomen.

Introduction

Homopolyatomic halogen cations are of considerable interest [1–3] because of their simplicity. They contain only one kind of atom and, contrary to transition metal cluster compounds, the absence of ligands simplifies the bonding aspects. Whereas numerous polyatomic iodine cations are known and I_2^+ [4, 5], I_3^+ [6], I_5^+ [7], I_{15}^{3+} [8], and I_4^{2+} [9] salts have been well characterized, much less is known about the lighter halogen polycations.

For bromine, the Br_2^+ cation has been well characterized in the form of its $\text{Sb}_2\text{F}_{16}^-$ salt [10, 11] and in superacid solutions [5, 12], but for Br_3^+ no structural data and only incomplete vibrational spectra [12–17] had previously been given. Furthermore, some of the vibrational frequencies attributed to Br_3^+ [17] are inconsistent with those observed for isoelectronic SeBr_2 [18] and the I_3^+ [1] and Cl_3^+ [19] cations. The only evidence for the existence of a polybromine cation containing more than three bromine atoms was obtained [14] when $\text{Br}_3^+[\text{Au}(\text{SO}_3\text{F})_4]^-$ was reacted with excess Br_2 at 70°C resulting in a solid of the composition $\text{Br}_5[\text{Au}(\text{SO}_3\text{F})_4]$. Raman bands at 304, 295, 267, and 205 cm^{-1} were tentatively attributed [14] to the cation in this compound but are not consistent with our predictions for a centrosymmetric Hal_5^+ cation of C_{2h} symmetry (see below).

For chlorine, the only known polychlorine cation containing salt is $\text{Cl}_3^+\text{AsF}_6^-$ which is unstable and was characterized by its low-temperature Raman spectrum [19]. The Cl_2^+ ion has been observed only in the gas phase at very low pressures [20, 21]. A claim for the observation of Cl_2^+ by ESR spectroscopy in superacid solutions [22] has subsequently been disputed [2, 19, 23, 24].

In view of the scant information available on the lighter halogen homopolyatomic cations and the accidental isolation of some deeply colored single crystals from a $\text{BrF}_2^+\text{AsF}_6^-$ sample, we have undertaken a study of the bromine homopolyatomic cations.

Experimental

Materials and Apparatus

Literature methods were used for the syntheses of $\text{BrF}_2^+\text{AsF}_6^-$ [25] and $\text{O}_2^+\text{AsF}_6^-$ [26]. The Br_2 and HF were dried by storage over P_2O_5 and BiF_3 [27], respectively. Reactions involving Br_2 were carried out using a flamed out Pyrex-glass vacuum line equipped with grease-free Teflon stopcocks. Anhydrous HF was handled in a stainless steel-Teflon FEP vacuum line [28]. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glove box. Raman spectra were recorded on a

Spex Model 1403 spectrophotometer using either the 647.1-nm exciting line of a Kr ion laser or the 514.5-nm line of an Ar ion laser and a previously described [29] device for obtaining the low-temperature spectra. The ^{19}F NMR spectra were recorded at 84.6 MHz on a Varian Modell EM 390 spectrometer.

Reaction of $\text{BrF}_2^+\text{AsF}_6^-$ with Br_2

A flamed out 100 ml Pyrex flask equipped with a Teflon stopcock was loaded in the dry box with $\text{BrF}_2^+\text{AsF}_6^-$ (3.94 mmol). On the vacuum line, dry Br_2 (13.49 mmol) was added at -196°C and the resulting mixture was kept at 25°C for 2 hr. The flask was cooled to 0°C and volatile products were pumped off at 0°C for 30 min. The chocolate brown solid residue in the flask weighed 2164 mg (weight calculated for 3.94 mmol of $\text{Br}_3^+\text{AsF}_6^- = 1846$ mg and 3.94 mmol of $\text{Br}_5^+\text{AsF}_6^- = 2476$ mg). The brown solid slowly gave off bromine vapors on standing at room temperature. Pumping on the solid at room temperature for 35 min reduced the weight to 1427 mg. The resulting residue still had some dissociation pressure at ambient temperature as evidenced by the slow evolution of Br_2 vapors above the solid. Low-temperature Raman spectroscopy showed this residue to be mainly $\text{Br}_3^+\text{AsF}_6^-$ with some $\text{Br}_5^+\text{AsF}_6^-$ as a by-product.

Reaction of $\text{O}_2^+\text{AsF}_6^-$ with Br_2

$\text{O}_2^+\text{AsF}_6^-$ (5.15 mmol) and Br_2 (13.54 mmol) were combined at -196°C in a 100 ml Pyrex flask. The mixture was warmed to 25°C for 2 hr, then cooled back to -196°C . The evolved oxygen (5.14 mmol) was pumped off at -196°C and excess Br_2 was pumped off at 0°C for 10 min. The resulting brown residue (1871 mg, weight calculated for 5.15 mmol of $\text{Br}_3^+\text{AsF}_6^- = 2414$ mg) was somewhat inhomogeneous showing smaller patches of material ranging in color from carmine red to greyish-green. Again some Br_2 vapor evolved above the solid on standing at room temperature. Low-temperature Raman spectra of the solid taken from different patches showed mainly $\text{Br}_5^+\text{AsF}_6^-$ with varying amounts of $\text{Br}_3^+\text{AsF}_6^-$ as a by-product.

Crystal Structure Determination of $\text{Br}_3^+\text{AsF}_6^-$

During 20 years of storage of a sample of $\text{BrF}_2^+\text{AsF}_6^-$ at room temperature in a Teflon tube closed by a stainless steel fitting several single crystals of $\text{Br}_3^+\text{AsF}_6^-$ had formed. Due to their great difference in color, $\text{BrF}_2^+\text{AsF}_6^-$ is colorless and $\text{Br}_3^+\text{AsF}_6^-$ is dark brown, the crystals were easily separated in the dry box. The diffraction data were collected at room temperature, using a Siemens/Nicolet/Syntex P 2_1 diffractometer with $\text{MoK}\alpha$ radiation up to a 2θ limit of 55° . 1538 intensity

Table 1 Summary of Crystal Data and Refinement Results for $[\text{Br}_3]^+[\text{AsF}_6]^-$

space group	$\text{P}\bar{1}$	absorption coefficient (μ : mm^{-1})	18.6
a ($\text{\AA}$)	7.644(7)	max. & min. transmission factors	0.55–1.66
b ($\text{\AA}$)	5.641(6)	(scaled to an average of unity)	
c ($\text{\AA}$)	9.810(9)	crystal dimensions (mm)	$0.64 \times 0.34 \times 0.33$
α (deg)	99.16(8)	calculated density (g cm^{-3})	3.47
β (deg)	86.61(6)	wavelength ($\text{\AA}$) used for data collection	0.71069
γ (deg)	100.11(7)	$\sin \Theta/\lambda$ limit ($\text{\AA}^{-1}$)	0.6497
V ($\text{\AA}^3$)	411.3(7)	total number of reflections measured	1538
molecules/unit cell	2	number of independent reflections	1387
formula weight (g)	384.0	number of reflections used in structural analysis $1 > 3\sigma(I)$	538
		number of variable parameters	91
		final agreement factors	$R(F) = 0.0608$ $R(wF) = 0.0608$

values for an entire reflection sphere were collected and the two equivalent hemispheres merged to give a total of 546 unique reflections. The R factor for averaging was 2.3%. The positions of the As and three Br atoms were obtained by direct methods using the computing package SHELX-86 [30a]. The rest of the atoms were then located from a difference-Fourier map, and the entire structure was anisotropically refined by SHELX-76 [30b] to a final agreement factor of $R = 6.08\%$, using 538 reflections with $1 > 3\sigma(I)$. At that point it was realized that the unit cell parameters were virtually identical to those of $[\text{I}_3]^+[\text{AsF}_6]^-$ [6], and the coordinates were then transformed accordingly, to be consistent with those reported for the $[\text{I}_3]^+$ analog. Crystal data and refinement results are summarized in Table 1, the final atomic coordinates and temperature factors are given in Table 2, and the bond distances and angles are given in Table 3.

Table 2 Final Atomic Coordinates and Temperature Factors for $[\text{Br}_3]^+[\text{AsF}_6]^-$

Atom	x	y	z	$U_{11} \times 10^3$	$U_{22} \times 10^3$	$U_{33} \times 10^3$	$U_{12} \times 10^3$	$U_{13} \times 10^3$	$U_{23} \times 10^3$
As	0.7857(5)	0.5650(8)	0.7972(4)	46(2)	64(3)	32(2)	19(2)	-3(2)	0(2)
Br1	0.8030(5)	0.8212(8)	0.2097(3)	56(2)	79(3)	30(2)	20(2)	2(2)	5(2)
Br2	0.6162(5)	1.0790(8)	0.1780(4)	58(3)	85(3)	57(3)	20(2)	-10(2)	5(2)
Br3	0.7695(6)	0.8069(9)	0.4394(4)	68(3)	108(4)	32(2)	26(2)	0(2)	3(2)
F1	0.7800(33)	0.7883(45)	0.7066(20)	133(21)	105(20)	32(11)	43(17)	-5(12)	-7(12)
F2	0.8702(32)	0.7820(47)	0.9273(21)	106(18)	102(20)	39(12)	-12(15)	-6(12)	-15(13)
F3	0.9991(34)	0.5559(62)	0.7415(36)	74(18)	172(32)	184(31)	52(19)	52(19)	-12(24)
F4	0.5759(26)	0.5799(60)	0.8601(32)	32(13)	184(30)	169(28)	42(16)	14(15)	59(23)
F5	0.7054(37)	0.3490(52)	0.6663(25)	145(24)	117(24)	71(18)	-23(20)	-37(17)	-38(17)
F6	0.7957(36)	0.3498(56)	0.8913(32)	111(22)	112(24)	147(27)	17(19)	-16(20)	8(21)

Table 3 Bond Distances (Å) and Angles (deg) for $[\text{Br}_3]^+[\text{AsF}_6]^-$

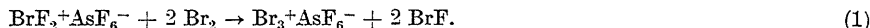
As—F1	1.660(23)	F1—As—F2	87.4(12)
		F1—As—F3	89.9(15)
As—F2	1.693(22)	F2—As—F3	86.6(14)
		F1—As—F4	91.0(13)
As—F3	1.696(22)	F2—As—F4	90.9(15)
		F3—As—F4	177.4(17)
As—F4	1.695(20)	F1—As—F5	92.4(13)
		F2—As—F5	178.9(13)
As—F5	1.686(22)	F3—As—F5	92.3(15)
		F4—As—F5	90.2(15)
As—F6	1.652(31)	F1—As—F6	178.0(14)
		F2—As—F6	90.6(14)
Br1—Br2	2.275(5)	F3—As—F6	89.6(16)
		F4—As—F6	89.5(14)
Br1—Br3	2.266(5)	F5—As—F6	89.5(15)
		Br2—Br1—Br3	102.5(2)

Results and Discussion

Synthesis of $\text{Br}_3^+\text{AsF}_6^-$

Single crystals of $\text{Br}_3^+\text{AsF}_6^-$ were obtained from a sample of $\text{BrF}_2^+\text{AsF}_6^-$ which had been stored for 20 years at room temperature in a Teflon-stainless

steel container. Its formation can be explained by the reduction of a small amount of BrF_2^+ to Br_2 by the container material and a subsequent reaction of Br_2 with BrF_2^+ according to:



The BrF is thermally unstable and disproportionates readily [31] to BrF_3 and Br_2 , with the BrF_3 most likely being reduced by the container material to additional Br_2 , and the Br_2 being consumed according to (1).

To verify reaction (1) and to obtain larger amounts of $\text{Br}_3^+\text{AsF}_6^-$, a sample of $\text{BrF}_2^+\text{AsF}_6^-$ was treated at room temperature with an excess of Br_2 . The colorless $\text{BrF}_2^+\text{AsF}_6^-$ was rapidly converted to a dark brown solid. After pumping off the unreacted Br_2 at 0°C , this brown solid consisted of a mixture of $\text{Br}_3^+\text{AsF}_6^-$ and $\text{Br}_5^+\text{AsF}_6^-$ (see below). Attempts to convert the $\text{Br}_5^+\text{AsF}_6^-$ to $\text{Br}_3^+\text{AsF}_6^-$ by pumping at room temperature was only partially successful and resulted in the loss of both $\text{Br}_3^+\text{AsF}_6^-$ and $\text{Br}_5^+\text{AsF}_6^-$. This is not surprising since, at room temperature, $\text{Br}_3^+\text{AsF}_6^-$ has some dissociation pressure, as evidenced by the build up of Br_2 vapor above the brown solid. This Br_2 vapor can on standing equilibrate with $\text{Br}_3^+\text{AsF}_6^-$ to reform some $\text{Br}_5^+\text{AsF}_6^-$ thus explaining the difficulties encountered with preparing and handling samples of pure $\text{Br}_3^+\text{AsF}_6^-$. The previously reported [13] synthesis of $\text{Br}_3^+\text{AsF}_6^-$ from BrF_5 , Br_2 and AsF_5 is based on the same approach, i. e. conproportionation of a higher bromine fluoride with bromine to BrF and its subsequent reaction with Br_2 and AsF_5 to form $\text{Br}_3^+\text{AsF}_6^-$ (2–4).



In this reaction the formation of $\text{Br}_5^+\text{AsF}_6^-$ can be suppressed by the use of excess BrF_5 and AsF_5 .

We have also repeated the previously reported [13] reaction of $\text{O}_2^+\text{AsF}_6^-$ with excess Br_2 . In this system, O_2 evolution is facile and quantitative, however the formed product appears inhomogenous with varying amounts of $\text{Br}_5^+\text{AsF}_6^-$ and $\text{Br}_3^+\text{AsF}_6^-$ being produced.

Crystal Structure of $\text{Br}_3^+\text{AsF}_6^-$

$\text{Br}_3^+\text{AsF}_6^-$ is isomorphous with $\text{I}_3^+\text{AsF}_6^-$ [6]. Both compounds are triclinic with similar unit cells and packing arrangements (see Figure 1). The structures are predominantly ionic containing discrete Hal_3^+ cations and AsF_6^- anions, with some cation-anion interaction (see Figure 2) resulting in a distortion of the AsF_6^- anion from O_h symmetry. As expected, the Br_3^+ cation is symmetric ($r_{\text{Br}-\text{Br}} = 2.270(5) \text{ \AA}$) and bent ($102.5(2)^\circ$). The $\text{Br}-\text{Br}$ distance in Br_3^+ is similar to that for Br_2 ($2.281 \text{ \AA}$ [32]) and resembles in this respect the I_3^+ ($2.665(4) \text{ \AA}$ [6]) and I_2 ($2.666 \text{ \AA}$ [32]) couple. The fluorine contacts to Br_3^+ are very similar to those found for I_3^+ in $\text{I}_3^+\text{AsF}_6^-$ [6], resulting in an approximately planar network

of two fluorine bridges to the central and of one fluorine bridge to each terminal bromine atom (see Figure 2). A more detailed discussion of these interactions has previously been given for $\text{I}_3^+\text{AsF}_6^-$ [6] and, therefore, does not need reiteration.

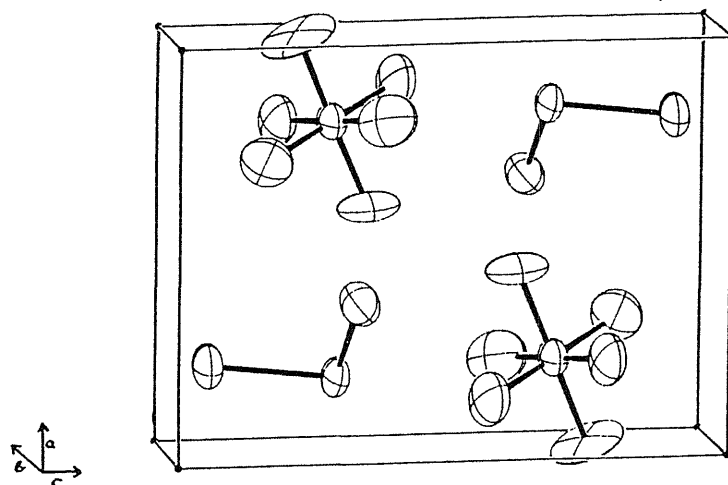


Fig. 1 Unit cell packing diagram for $\text{Br}_3^+\text{AsF}_6^-$, viewed down the *b* axis.

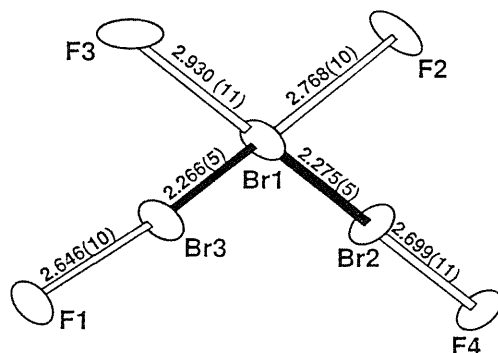


Fig. 2 Br_3^+ cation with closest anion-cation contacts.

^{19}F NMR Spectrum of $\text{Br}_3^+\text{AsF}_6^-$

The ^{19}F NMR spectrum of $\text{Br}_3^+\text{AsF}_6^-$ in anhydrous HF solution was recorded at room temperature. It consisted of a well resolved quartet of equal intensity ($\delta = 65$ ppm, upfield from external CFCl_3 , with $J_{\text{AsF}} = 925$ Hz and a line width of 100 Hz), in excellent agreement with previous reports for octahedral AsF_6^- [33].

Raman Spectra of $\text{Br}_3^+\text{AsF}_6^-$, $\text{Cl}_3^+\text{AsF}_6^-$, and $\text{I}_3^+\text{AsF}_6^-$

Raman spectra of bromine polyatomic cation salts are very difficult to obtain due to the intense colors of the cations. The Raman spectrum of a randomly

oriented single crystal of $\text{Br}_3^+\text{AsF}_6^-$ at -150°C is shown in Figure 3. The observed frequencies and their assignments are summarized in Table 4. The two bands at 173 and 85 cm^{-1} , respectively, are due to a small amount of Br_5^+ formed during the handling of the crystal and recording of the spectrum and are denoted in Figure 3 by an asterisk. The assignments given in Table 4 are clear cut and do not require further discussion. The fact that the observed AsF_6^- bands deviate from the O_h selection rules, i. e. $\nu_3(F_{1u})$ becomes Raman active and $\nu_2(E_g)$ is split into its degenerate components, is not surprising in view of the distortion of the AsF_6^- octahedron by fluorine bridging with the Br_3^+ cations. Raman spectra of powdered samples of $\text{Br}_3^+\text{AsF}_6^-$ were also recorded at 25 and -150°C . They were of lower quality than that of the single crystal material but showed the same main features, i. e. $\nu_{\text{sym}} \text{Br}_3^+$ at 293 cm^{-1} with a shoulder at 297 for $\nu_{\text{asym}} \text{Br}_3^+$, δBr_3^+ at about 120 cm^{-1} , and $\nu_{\text{sym}} \text{AsF}_6^-$ at about 675 cm^{-1} .

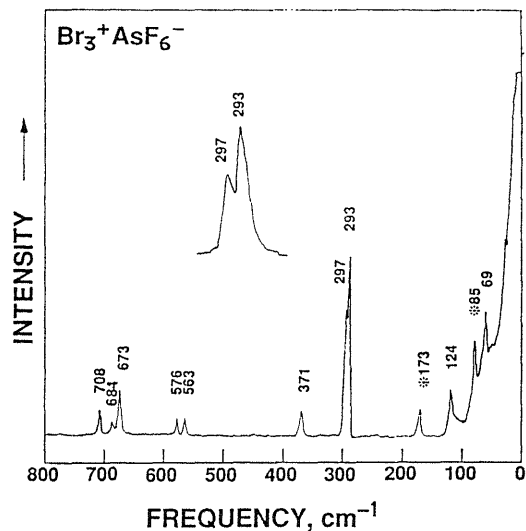


Fig. 3 Raman spectrum of a single crystal of $\text{Br}_3^+\text{AsF}_6^-$ recorded at -150°C with random orientation of the crystal. The insert shows the Br_3^+ stretching bands, recorded with tenfold abscissa expansion.

Previous literature reports on the vibrational spectra of Br_3^+ suggested for $\nu_1(A_1)$ frequencies of 295 cm^{-1} in $\text{Br}_3^+[\text{Pt}(\text{SO}_3\text{F})_6]^-$ [15], 280 cm^{-1} in $\text{Br}_3^+[\text{Au}(\text{SO}_3\text{F})_4]^-$ [14], 290 cm^{-1} in fluorosulfuric acid solutions [12], for $\nu_3(B_1)$ a frequency of 288 cm^{-1} in $\text{Br}_3^+\text{SO}_3\text{F}^-$ [16], and for $\nu_2(A_1)$ a doublet at 227 and 238 cm^{-1} in an $\text{HBr}-\text{NO}_2$ reaction product [17]. Whereas the reported frequencies of the two stretching modes are in fair agreement with our findings for $\text{Br}_3^+\text{AsF}_6^-$, the previously reported [17] deformation mode frequency is much too high for Br_3^+ , as is also obvious from a comparison with the known fundamental vibrations of I_3^+ (see below), Cl_3^+ [19], and isoelectronic SeBr_2 [18] which are summarized in Table 5.

Table 4 Low Temperature Raman Spectrum of a Randomly-Oriented Single Crystal of $\text{Br}_3^+\text{AsF}_6^-$

obsd. freq. (cm^{-1})	assignments (point group) and approximate mode descriptions	
rel. int.	$\text{Br}_3^+ (\text{C}_{2v})$	$\text{AsF}_6^- (\text{O}_h)$
708(15) } 684(4) }		(O_h) $\nu_3(\text{F}_{1u})$, as stretch
673(25)		$\nu_1(\text{A}_{1g})$, sym in phase stretch
576(9) } 563(10) }		$\nu_2(\text{E}_g)$, sym out of phase stretch
371(15)		$\nu_5(\text{F}_{2g})$, sym bend
297(60)	$\nu_3(\text{B}_1)$, asym stretch	
293(100)	$\nu_1(\text{A}_1)$, sym stretch	
124(23)	$\nu_2(\text{A}_1)$, bend	
69(25) } 39 sh } 30 sh }		lattice vibrations

Table 5 Vibrational Frequencies (cm^{-1}) of Br_3^+ Compared to Those of I_3^+ , Cl_3^+ , and SeBr_2

	I_3^+		Br_3^+		Cl_3^+ [19]	SeBr_2 [18]
	this work	previous work [1]	this work	previous work [12-17]		
$\nu_3(\text{B}_1)$	211	233	297	288	508	290
$\nu_1(\text{A}_1)$	205	207	293	280-295	489	266
$\nu_2(\text{A}_1)$	110	114	124	227/238	225	96

The Raman spectra of $\text{Cl}_3^+\text{AsF}_6^-$ [19] and $\text{I}_3^+\text{AsF}_6^-$ [6, 34] were also recorded for comparison. The spectrum of $\text{Cl}_3^+\text{AsF}_6^-$ agreed well with that previously reported [19] with the following exceptions. The unassigned 170 cm^{-1} band was either completely absent or of variable intensity in different samples, and, therefore, does not belong to $\text{Cl}_3^+\text{AsF}_6^-$. Furthermore, two additional bands at 709 and 686 cm^{-1} were observed in the $\nu_3(\text{F}_{1u})$ region of AsF_6^- which resemble those in $\text{Br}_3^+\text{AsF}_6^-$. In the low frequency region, two lattice vibrations were observed at 132 and 101 cm^{-1} , respectively.

The Raman spectrum of $\text{I}_3^+\text{AsF}_6^-$ which was prepared from I_2 and AsF_5 in AsF_3 solution [34], was recorded for both the solid state and in anhydrous HF solutions using either 647.1 , 514.5 , or 488 nm excitation. Due to the intense, dark brown to black color of $\text{I}_3^+\text{AsF}_6^-$ the quality of the obtainable spectra was poor. With 647.1 nm excitation, the spectra were dominated by a very intense resonance Raman spectrum of I_2^+ [2] which was present in the sample as a minor impurity. In addition to the intense 238 cm^{-1} band of I_2^+ [1, 2], a weak band at 206 cm^{-1} was observed for $\nu_1(\text{A}_1)$ of I_3^+ . With 488 nm excitation, only a weak band at 208 cm^{-1} was observed. The best spectrum was obtained with 514.5 nm excitation and is shown in Figure 4. It clearly locates $\nu_1(\text{A}_1)$ and $\nu_2(\text{A}_1)$ of I_3^+ at 205 and 110 cm^{-1} , respectively, in good agreement with the 207 and 114 cm^{-1}

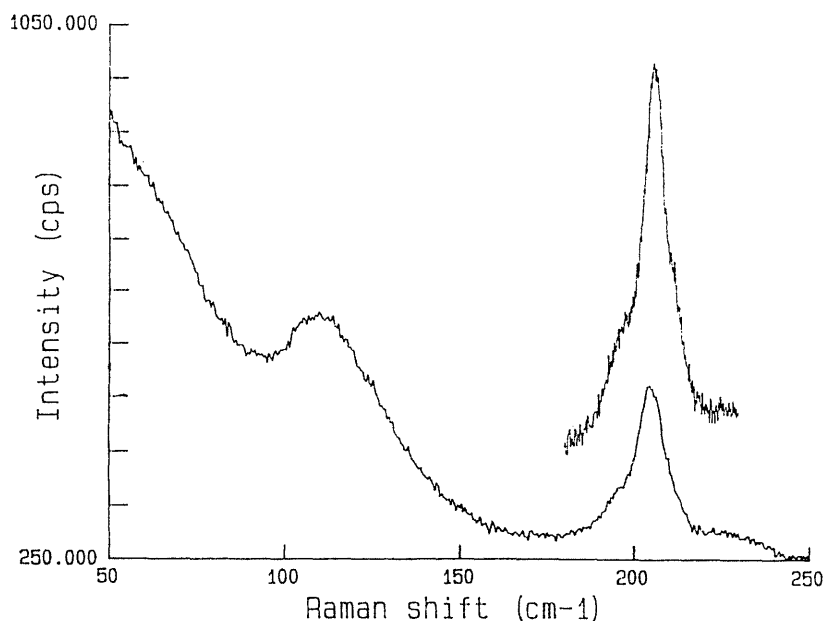


Fig. 4 Raman spectrum of an anhydrous HF solution of $\text{I}_3^+\text{AsF}_6^-$ in a Teflon-FEP tube recorded at 25°C with 514.5-nm excitation. The band shown as an insert was recorded with a smaller slit width of 2 cm^{-1} to resolve the shoulder on the high frequency side.

values previously reported [1]. However, the previously reported [1] 233 cm^{-1} band for $\nu_3(\text{B}_1)$ could not be confirmed. By analogy with Br_3^+ and based on model calculations for the frequency separation of the two stretching modes of an XY_2 group as a function of their bond angle and relative masses [35], $\nu_3(\text{B}_1)$ of I_3^+ should be about 5 cm^{-1} higher than $\nu_1(\text{A}_1)$. As shown by the insert in Figure 4, the 205 cm^{-1} Raman band of I_3^+ indeed exhibits a pronounced shoulder at 210 cm^{-1} which is assigned to $\nu_3(\text{B}_1)$. This reassignment of ν_3 is also supported by our force field calculations (see below). On the low frequency side of the 205 cm^{-1} Raman band of I_3^+ another shoulder was observed. A firm assignment cannot be given for this shoulder at the present time, but based on the arguments given in [35] it cannot represent $\nu_3(\text{B}_1)$ of I_3^+ .

General Valence Force Fields for Cl_3^+ , Br_3^+ , and I_3^+

General valence force fields were calculated for Cl_3^+ , Br_3^+ , and I_3^+ using WILSONS GF method [36]. Since the A_1 block (2 frequencies, 3 force constants) is underdetermined, the complete range of possible solutions was computed using SAWODNYS method [37]. The resulting force constant ellipses are given in Figure 5. To allow a better comparison, the stretch-bend interaction constants F_{12} and bending constants F_{22} have been normalized for distance.

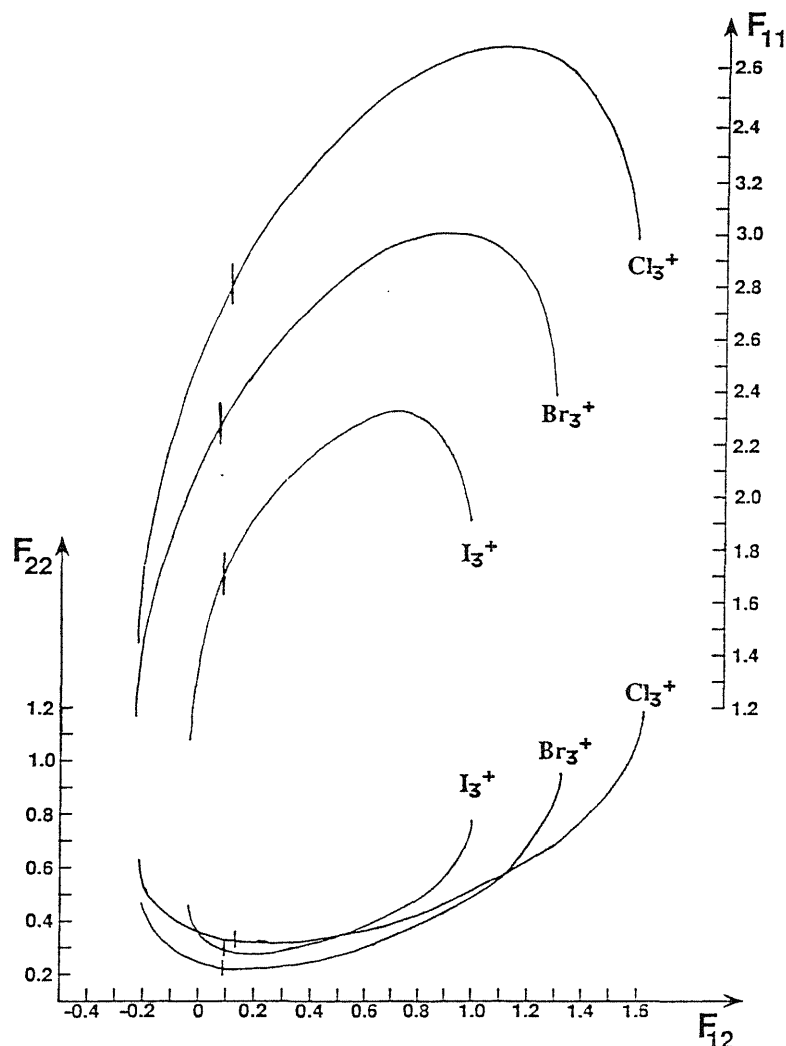


Fig. 5 Range of possible solutions for the A_1 General Valence Force Fields for Cl_3^+ , Br_3^+ , and I_3^+ (all values in $\text{mdyn}/\text{\AA}$). The preferred solutions have been marked by vertical lines.

As can be seen from Figure 5, the values of the stretching force constants F_{11} strongly depend on the choice of F_{12} . In the absence of additional experimental data, assumptions about the values of F_{12} had to be made to select preferred sets of force constants. The method of Thakur {factoring the F_{12} value of the $F_{22} \equiv \text{minimum}$ solution [37] by $G_{12}/\sqrt{(G_{11} \cdot G_{22} + G_{12}^2)}$ } was chosen because it best duplicates the General Valence Force Fields of molecules with similar mass ratios [38]. The internal force constants obtained in this manner for Cl_3^+ , Br_3^+ , and I_3^+ are summarized in Table 6 and compared to those of the related Hal_2 molecules and Hal_2^+ cations.

Table 6 Internal Force Constants (mdyn/Å) and Bond Lengths (Å) and Angles (deg) of the Hal_3^+ , Hal_2 , and Hal_2^+ Series

	Cl_3^+	Cl_2 [1]	Cl_2^+ [1]	Br_3^+	Br_2 [2]	Br_2^+ [1]	I_3^+ [1]	I_3^+ this work	I_2 [1]	I_2^+ [1]
fr	2.607	3.16	4.29	2.063	2.36	3.05	1.923	1.607	1.70	2.12
frr	0.184	—	—	0.192	—	—	0.156	0.097	—	—
$f\alpha$	0.314	—	—	0.216	—	—	0.294	0.273	—	—
$f\alpha$	0.076	—	—	0.052	—	—	0.070	0.065	—	—
r	[1.98] ^a	1.98	1.89	2.268	2.28	2.13	2.665	2.666	2.56	
α	[103] ^a	—	—	102.7	—	—	101.75	—	—	

^a) estimated values

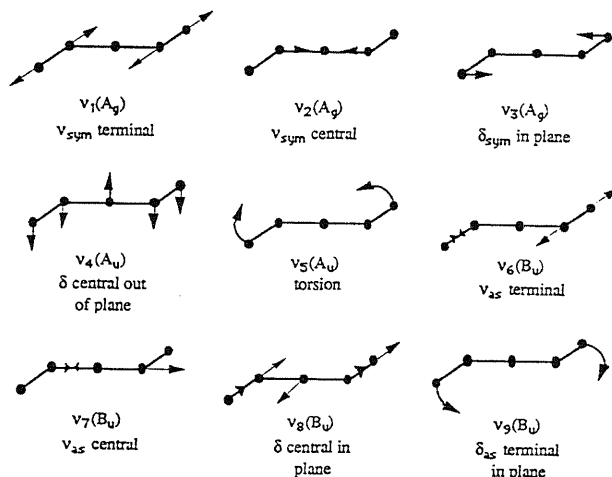
As can be seen from Figure 5 and Table 6, the stretching force constants fr monotonously increase from Cl_3^+ to I_3^+ , in good analogy with those of the Hal_2 molecules and Hal_2^+ cations. The finding that the stretching force constants in Hal_3^+ cations are smaller than those predicted from their bond lengths and the known force constants and bond lengths in the corresponding homonuclear diatomic molecules or ions, is not surprising. From NQR measurements on I_3^+ [39] it is known that in Hal_3^+ cations most of the positive charge resides on the central atom. This results in a significant bond polarity for the Hal_3^+ cations, while the bond polarity in the homonuclear diatomics is zero. Since polar bonding contributes strongly to the bond shortening but not to the stretching force constants, it is not surprising that the stretching force constant of a Hal_3^+ cation should be smaller than that of a Hal_2 molecule or ion possessing the same bond length. A closer inspection of the data of Table 6 reveals that for I_3^+ only our revised assignment for ν_3 results in a plausible value for the stretching force constant fr .

The Raman Spectrum of $\text{Br}_5^+\text{AsF}_6^-$

In the reactions of either $\text{Br}_2^+\text{AsF}_6^-$ or $\text{O}_2^+\text{AsF}_6^-$ with an excess of Br_2 (see above) products were obtained which contained in addition to Br_3^+ a second polybromine cation salt. Its Raman spectrum is shown in Figure 6, and the observed frequencies and their assignments are summarized in Table 7. The most likely candidate for this cation is Br_5^+ . In the literature, only one brief reference was made [14] to Br_5^+ and Raman bands at 304, 295, 267, and 205 cm^{-1} were tentatively attributed to Br_5^+ . Otherwise, the only structural information available for a Hal_5^+ cation is a crystal structure of $\text{I}_5^+\text{AsF}_6^-$ [7]. The latter study showed that I_5^+ has a centrosymmetric, planar structure of C_{2h} symmetry $[\text{I}-\text{I}-\text{I}-\text{I}-\text{I}]^+$. It is therefore reasonable to assume an analogous C_{2h} structure for Br_5^+ .

A Br_5^+ cation of symmetry C_{2h} possesses nine fundamental vibrations which are classified as $\Gamma = 3A_g + 2A_u + 4B_u$. Of these, the A_g modes are only Raman

and the A_u and the B_u modes only infrared active. The following diagram gives an approximate description of these modes.

Table 7 Raman Spectra of $\text{Br}_3^+\text{AsF}_6^-$

obsd. freq. (cm^{-1}), rel. int.		assignments (point group) and approximate made descriptions	
solid, -155°C	HF solution, 25°C	$\text{AsF}_6^- (\text{O}_h)$	$\text{Br}_3^+ (\text{C}_{2h})$
718(0.5)	685(4)	$\nu_3(\text{F}_{1u})$	
681(0.7)		$\nu_1(\text{A}_{1g})$	
670(3.5)			
618(0.4)			
570(0.2)		$\nu_2(\text{E}_g)$	
563(0.3)	309(20) pol	$\nu_4(\text{F}_{1u})$	
487(0.2)		$\nu_5(\text{F}_{2g})$	
399(0.1)			$\nu_1(\text{A}_g)$, sym terminal stretch
366(0.8)			$\nu_7(\text{B}_u)$, asym central stretch
348(1)			$\nu_2(\text{A}_g)$, sym central stretch
309(9)	182(100) pol		$\nu_3(\text{A}_g)$, sym term. in plane def
190 sh			
174(100)			
87(69)			
66(3)	108(68) pol		
37(20)			
27(12)			
		lattice vibrations	

Since in I_3^+ the collinear central I—I bonds ($2.895 \text{ \AA}$) are much longer than the perpendicular terminal ones ($2.645 \text{ \AA}$) [7], the bonding in a Hal_3^+ cation is best described by a semi-ionic, three center-four electron bonding model [40–43], as in the Hal_3^- anions, for the three central halogen atoms and two essentially normal covalent bonds, as in Hal_2 and Hal_3^+ , for the perpendicular terminal bonds.

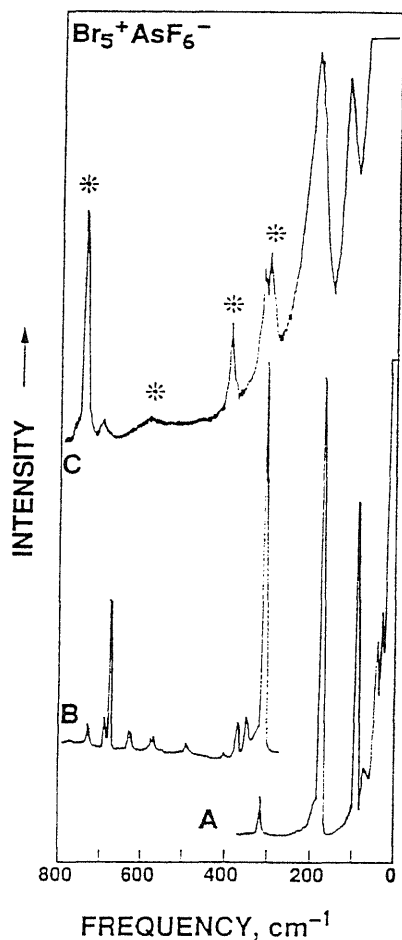


Fig. 6 Raman spectrum of $\text{Br}_5^+\text{AsF}_6^-$. Traces A and B are spectra of the solid recorded at -155°C at two different recorder voltages; trace C is the spectrum of a saturated solution in anhydrous HF at 25°C . Bands marked by an asterisk are due to the Teflon container.

Consequently, the frequencies of the three Raman active modes of Br_5^+ can be predicted as follows: $\nu_1(\text{A}_g)$ should be similar to that in Br_2 (320 cm^{-1} [2]), $\nu_2(\text{A}_g)$ to that of ν_{sym} in Br_3^- (162 cm^{-1} [44]), and $\nu_3(\text{A}_g)$ to that of the bending mode in Br_3^+ (124 cm^{-1} , see above).

The observed spectra (Figure 5, Table 7) are in excellent agreement with the above predictions for a Br_5^+ cation of C_{2h} symmetry. Disregarding the weak lines above 300 cm^{-1} which are due to AsF_6^- and the lattice modes which disappear for the HF solution, we are left with three very intense Raman lines at 309, 174, and 84 cm^{-1} in the solid and at 309, 182, and 108 cm^{-1} in the HF solution which in the solution spectrum are all polarized as expected for A_g modes. The frequency differences between the solid state and solution spectra are attributed to solid

state and solvation effects. The weak shoulder observed at 190 cm^{-1} for the solid is attributed to the antisymmetric central Br_3 stretching mode $\nu_7(\text{B}_u)$, which is activated by solid state effects and occurs for Br_3^- at 193 cm^{-1} [44].

In view of this excellent agreement the observed spectra can be attributed to a Br_5^+ cation of C_{2h} symmetry with bonding conditions similar to those in I_5^+ , i. e. a semi-ionic, three center-4 electron bond for the three collinear central bromine atoms and two mainly covalent bonds for the perpendicular terminal bromine atoms. The occurrence of a semi-ionic, three center-four electron bond in Br_5^+ but not in Br_3^+ is readily understood from a simple consideration of the number of valence electrons in each cation. In Br_3^+ , all three bromine atoms have an electron octet, whereas in Br_5^+ the central bromine atom is hypervalent possessing 10 valence electrons which favors the formation of semi-ionic, three center-four electron bonds [43].



Acknowledgement. One of us (KARL O. CHRISTE) is indebted to Drs. C. J. SCHACK, W. W. WILSON, and R. D. WILSON for their help, to R. SHRODER for the recording of the 514.5-nm Raman spectrum of $\text{I}_3^+\text{AsF}_6^-$, and to the U.S. Army Research Office for financial support.

Note added in proof: After submission of this paper we learned from Prof. Dr. HARTL about an x-ray crystal structure determination for $\text{Br}_5^+\text{AsF}_6^-$ which confirms the above conclusions about the structure of Br_5^+ .

References

- [1] GILLESPIE, R. J.; MORTON, M. J.; SOWA, J. M.: *Adv. Raman Spectrosc.* **1** (1972) 539.
- [2] GILLESPIE, R. J.; PASSMORE, J.: *Adv. Inorg. Chem. Radiochem.* **17** (1975) 49.
- [3] LI, Y.; WANG, X.; JENSEN, F.; HOUK, K. N.; OLAH, G. A.: *J. Amer. Chem. Soc.* **112** (1990) 3922.
- [4] DAVIS, C. G.; GILLESPIE, R. J.; IRELAND, P. R.; SOWA, J. M.: *Canad. J. Chem.* **52** (1974) 2048.
- [5] WILSON, W. W.; THOMPSON, R. C.; AUBKE, F.: *Inorg. Chem.* **19** (1980) 1489.
- [6] PASSMORE, J.; SUTHERLAND, G.; WHITE, P. S.: *Inorg. Chem.* **20** (1981) 2169.
- [7] APBLETT, A.; GREIN, F.; JOHNSON, J. P.; PASSMORE, J.; WHITE, P. S.: *Inorg. Chem.* **25** (1986) 422.
- [8] PASSMORE, J.; TAYLOR, P.; WHIDDEN, T.; WHITE, P. S.: *Canad. J. Chem.* **57** (1979) 968.
- [9] GILLESPIE, R. J.; KAPOOR, R.; FAGGIANI, R.; LOCK, C. J.; MURCHIE, M.; PASSMORE, J.: *J. Chem. Soc. Chem. Commun.* (1983) 8.
- [10] EDWARDS, A. J.; JONES, G. R.; SILLS, R. J. C.: *J. Chem. Soc. Chem. Commun.* (1968) 1527.
- [11] EDWARDS, A. J.; JONES, G. R.: *J. Chem. Soc. A*, (1971) 2318.
- [12] GILLESPIE, R. J.; MORTON, M. J.: *Inorg. Chem.* **11** (1972) 586, and *J. Chem. Soc. Chem. Commun.* (1968) 1565.
- [13] GLEMSE, O.; SMALC, A.: *Angew. Chem., Int. Ed. Engl.* **8** (1969) 517.
- [14] LEE, K. C.; AUBKE, F.: *Inorg. Chem.* **19** (1980) 119.
- [15] LEE, K. C.; AUBKE, F.: *Inorg. Chem.* **23** (1984) 2124.
- [16] WILSON, W. W.; WINFIELD, J.; AUBKE, F.: *J. Fluorine Chem.* **7** (1976) 245.
- [17] CHEN, L. H.; NOUR, E. M.; LAANE, J. M.: *J. Raman Spectrosc.* **14** (1983) 232.

- [18] MILNE, J.: Polyhedron **4** (1985) 65.
[19] GILLESPIE, R. J.; MORTON, M. J.: Inorg. Chem. **9** (1970) 811.
[20] HERZBERG, G.: "Molecular Spectra and Molecular Structure", Vol. 1; Van Nostrand-Reinhold, Princeton, NJ, 1960.
[21] „Gmelins Handbuch der Anorganischen Chemie“, Chlor, Ergänzungsband, Teil A, p. 183; Verlag Chemie, Weinheim, Germany, 1968.
[22] OLAH, G. A.; COMISAROW, M. B.: J. Amer. Chem. Soc. **90** (1968) 5033 and **91** (1969) 2172.
[23] CHRISTE, K. O.; MUIRHEAD, J. S.: J. Amer. Chem. Soc. **91** (1969) 7777.
[24] EACHUS, R. S.; SLEIGHT, T. P.; SYMMONS, M. C. R.: Nature (London) **222** (1969) 769.
[25] CHRISTE, K. O.; SCHACK, C. J.: Inorg. Chem. **9** (1970) 2296.
[26] SHAMIR, J.; BINENBOYM, J.: Inorg. Chim. Acta **2** (1968) 37.
[27] CHRISTE, K. O.; WILSON, W. W.; SCHACK, C. J.: J. Fluorine Chem. **11** (1978) 71.
[28] CHRISTE, K. O.; WILSON, R. D.; SCHACK, C. J.: Inorg. Synth. **24** (1986) 3.
[29] MILLER, F. A.; HARNEY, B. M.: Appl. Spectrosc. **23** (1969) 8.
[30] a) SHELDRIX, G. M.: SHELX-86 System of Crystallographic Computational Programs, University of Göttingen, Germany, 1986.
b) SHELDRIX, G. M.: SHELX-76 System of Crystallographic Computational Programs, University of Cambridge, England, 1976.
[31] NAUMANN, D.: „Fluor und Fluorverbindungen“, Spezielle Anorganische Chemie, Band 2; Steinkopff, Darmstadt, Germany, 1980.
[32] HUBER, K. P.; HERZBERG, G.: "Molecular Spectra and Molecular Structure"; Vol. 4; Van Nostrand-Reinhold, New York, NY, 1979.
[33] MUETTERTIES, E. L.; PHILLIPS, W. D.: J. Amer. Chem. Soc. **81** (1959) 1084, PACKER, K. J.; Muetterties, E. L.: Proc. Chem. Soc., London **1964**, 147.
[34] PASSMORE, J.; TAYLOR, P. J.: Chem. Soc., Dalton Trans. **1976**, 804.
[35] WEIDLEIN, J.; MÜLLER, U.; DEHNICKE, K.: „Schwingungsspektroskopie“; G. Thieme Verlag, Stuttgart, Germany, 1982.
[36] WILSON, E. B.; DECIUS, J. C.; CROSS, P. C.: "Molecular Vibrations. The Theory of Infrared and Raman Vibrational Spectra"; McGraw Hill Book Co., New York, 1955.
[37] SAWODNY, W.: J. Mol. Spectrosc. **30** (1969) 56.
[38] THAKUR, S. N.; RAI, S. M.: J. Mol. Structure **5** (1970) 320.
[39] MERRYMAN, D. J.; CORBETT, J. D.; EDWARDS, P. A.: Inorg. Chem. **14** (1975) 428.
[40] PIMENTEL, G. C.: J. Chem. Phys. **19** (1951) 446.
[41] HACH, R. J.; RUNDLE, R. E.: J. Amer. Chem. Soc. **73** (1951) 4321.
[42] RUNDLE, R. E.: J. Amer. Chem. Soc. **85** (1963) 112.
[43] WIEBENGA, E. H.; HAVINGA, E. E.; BOSWIJK, K. H.: Adv. Inorg. Chem. Radiochem. **3** (1961) 158.
[44] PERSON, W. B.; ANDERSON, G. R.; FORDEWALT, J. N.; STAMMREICH, H.; FORNERIS, R.: J. Chem. Phys. **35** (1961) 908.

Bei der Redaktion eingegangen am 3. September 1990.

Anschr. d. Verf.: Dr. K. O. CHRISTE, Rocketdyne Division, Rockwell International Corporation, Canoga Park, CA 91303, USA

The results of our molecular mechanics calculations on these square-planar isomers are shown in Table V; results from the previous calculations are also included for comparison.²⁶ In contrast to the latter results, the (low-spin) trans-III isomer was calculated to be the lower energy isomer in the present study, a result largely attributable to the presence of the out-of-plane bending term in the force field. That is, our calculations suggest that the trans-III isomer is favored over the trans-I isomer as originally proposed. While it remains difficult to decide on the "correct" order from the present study, the results do illustrate the sensitivity of the method to the nature of the force field employed.⁵⁶ Clearly, in studies of the present type, appropriate

caution should be exercised when using the molecular mechanics procedure for predicting the relative energies of isomeric metal complexes.

Acknowledgment. We thank the Australian Institute of Nuclear Science and Engineering and the Australian Research Council for support.

(56) It needs to be emphasized that the present force field has been optimized only in terms of geometry and that the associated energy terms have not been "calibrated"—especially with respect to those parts of the structures influenced by the central metal.

The Pentafluoroxenate(IV) Anion, XeF_5^- : The First Example of a Pentagonal Planar AX_5 Species

Karl O. Christe,^{*1} Earl C. Curtis,¹ David A. Dixon,² Hélène P. Mercier,³ Jeremy C. P. Sanders,³ and Gary J. Schrobilgen^{*3}

Contribution from Rocketdyne, A Division of Rockwell International, Canoga Park, California 91303, the Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada, and the Central Research and Development Department, E. I. du Pont de Nemours and Company, Inc., Experimental Station, Wilmington, Delaware 19880-0328. Received September 28, 1990

Abstract: Xenon tetrafluoride forms stable 1:1 adducts with $\text{N}(\text{CH}_3)_4\text{F}$, CsF , RbF , KF , and NaF and an unstable 1:1 adduct with FNO . All these adducts are ionic salts containing pentagonal planar XeF_5^- anions as shown by a crystal structure determination of $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$, Raman and infrared spectra, and ^{19}F and ^{129}Xe NMR spectroscopy. The X-ray crystal structure of $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$ was determined at -86°C . This compound crystallizes in the orthorhombic system, space group $Pmcn$, with four molecules in a unit cell of dimensions $a = 6.340$ (2) Å, $b = 10.244$ (3) Å, and $c = 13.896$ (4) Å with $R = 0.0435$ for 638 observed [$I > 3\sigma(I)$] reflections. In addition to four $\text{N}(\text{CH}_3)_4^+$ cations, the structure contains four pentagonal planar XeF_5^- anions per unit cell with D_{5h} symmetry. The Xe-F distances are 1.979 (2)–2.034 (2) Å with F-Xe-F angles of 71.5 (4)–72.3 (4)°. The D_{5h} structure of the XeF_5^- anion is highly unusual and represents the first example of an AX_5E_2 (E = valence electron lone pair) species in which all six atoms are coplanar. The results from the crystal structure determination and a normal coordinate analysis show that the XeF_5 plane of XeF_5^- is considerably more rigid than that in the fluxional IF_7 molecule due to the increased repulsion from the xenon free valence electron pairs. Local density functional calculations were carried out for XeF_5^- and XeF_4 with a double-numerical basis set augmented by polarization functions and confirm the experimentally observed geometries and vibrational spectra. It is shown that the bonding in XeF_5^- closely resembles that in XeF_4 . In a valence bond description, it can be visualized as the two axial positions being occupied by two sp-hybridized free valence electron pairs and the equatorial fluorines being bound by two Xe 5p electron pairs through semiionic multicenter four-electron bonds.

Introduction

Recent work in our laboratories has shown that anhydrous $\text{N}(\text{CH}_3)_4\text{F}^4$ holds great potential for the synthesis and characterization of novel, high oxidation state, complex fluoro anions.⁵⁻⁷ An area of special interest to us is the problem of maximum coordination numbers and their influence on the steric activity of free valence electron pairs. For example, it was shown that nitrogen(V) cannot accommodate five fluorine ligands,⁸ whereas the iodine in IF_6^- , which had long been thought to have a distorted octahedral structure,^{9,10} has recently been confirmed to possess a sterically active lone valence electron pair.¹⁰ In contrast, the

central atom free valence electron pairs in the smaller ClF_6^- and BrF_6^- anions become sterically inactive due to space limitations, as demonstrated in very recent vibrational^{6,10} and single-crystal X-ray structure studies.¹¹

In this context, the likely structures of the XeF_5^- and XeF_6^{2-} anions posed an interesting problem, since both anions contain two free valence electron pairs on the xenon central atom. Therefore, they are representatives of the novel AX_5E_2 and AX_6E_2 geometries, respectively, where E stands for a free valence electron pair. Whereas no reports have been published on the existence or possible structure of XeF_5^- or any other AX_5E_2 species, Kiselev and co-workers¹³⁻¹⁵ recently reported the synthesis of M_2XeF_6 salts ($\text{M} = \text{Cs}, \text{Rb}, \text{K}, \text{Na}$) from XeF_4 and MF . On the basis of vibrational spectra, they surprisingly assigned an octahedral structure to XeF_6^{2-} . However, a closer inspection of their published

- (1) Rockwell International, Rocketdyne Division.
- (2) E. I. du Pont de Nemours and Company, Inc.
- (3) McMaster University.
- (4) Christe, K. O.; Wilson, W. W.; Wilson, R. D.; Bau, R.; Feng, J. J. *Am. Chem. Soc.* **1990**, *112*, 7619.
- (5) Wilson, W. W.; Christe, K. O. *Inorg. Chem.* **1989**, *28*, 4172.
- (6) Christe, K. O.; Wilson, W. W.; Chirakal, R. V.; Sanders, J. C. P.; Schrobilgen, G. J. *Inorg. Chem.* **1990**, *29*, 3506.
- (7) Wilson, W. W.; Christe, K. O.; Feng, J.; Bau, R. *Can. J. Chem.* **1989**, *67*, 1988.
- (8) Christe, K. O.; Wilson, W. W.; Schrobilgen, G. J.; Chirakal, R. V.; Olah, G. A. *Inorg. Chem.* **1988**, *27*, 789.
- (9) Klammer, H.; Meinert, H.; Reich, P.; Witke, P. *Z. Chem.* **1968**, *8*, 469.
- (10) Christe, K. O.; Wilson, W. W. *Inorg. Chem.* **1989**, *28*, 3275 and references cited therein.

- (11) Mahjoub, A. R.; Hoser, A.; Fuchs, J.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1526.
- (12) Reference deleted in proof.
- (13) Spitzin, V. I.; Kiselev, Yu. M.; Fadeeva, N. E.; Popov, A. I.; Tchu-maevsky, N. A. *Z. Anorg. Allg. Chem.* **1988**, *559*, 171.
- (14) Kiselev, Yu. M.; Goryachenkov, S. A.; Martynenko, L. I.; Spitsyn, V. I. *Dokl. Akad. Nauk SSSR* **1984**, *278*, 881.
- (15) Kiselev, Yu. M.; Fadeeva, N. E.; Popov, A. I.; Korobov, M. V.; Nikulin, V. V.; Spitsyn, V. I. *Dokl. Akad. Nauk SSSR* **1987**, *295*, 378.

spectra¹³ revealed that both the frequency separations and relative intensities of the observed bands are incompatible with an octahedral species.¹⁶ Furthermore, it was noted that the Raman spectrum attributed to Cs_2XeF_6 was identical with that previously observed during the laser photolysis of CsXeF_7 and tentatively assigned to Cs_2XeF_8 .¹⁷ In view of these discrepancies we decided to investigate the fluoride-acceptor properties of XeF_4 using $\text{N}(\text{CH}_3)_4\text{F}$ as a fluoride ion source and to reinvestigate the XeF_4 -MF systems.

Experimental Section

Apparatus and Materials. Volatile materials were handled in stainless steel-Teflon and Pyrex glass vacuum lines, as previously described.^{18,19} Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox.

Literature methods were used for the syntheses of anhydrous $\text{N}(\text{C}_2\text{H}_5)_4\text{F}$,⁴ XeF_4 ,²⁰ and FNO ²¹ and the drying of CH_3CN .^{4,22} The LiF (Research Inorganic Chemicals, Research Organic Chemicals), NaF (Matheson), and BaF_2 (Baker and Adamson) were dried under vacuum at 125 °C prior to their use. The KF (Allied), RbF (American Potash), and CsF (KBI) were dried by fusion in a platinum crucible, followed by transfer of the hot clinkers to the dry nitrogen atmosphere of the glovebox where the fluoride samples were ground prior to use.

Syntheses of M^+XeF_5^- ($\text{M} = \text{Cs}, \text{Rb}, \text{K}, \text{Na}$). The dry, finely powdered alkali metal fluorides (2 mmol) and XeF_4 (4–8 mmol) were loaded inside the drybox into prepassivated (with ClF_3), 10-mL, stainless steel Hoke cylinders that were closed by metal valves. The cylinders were evacuated at –78 °C on the vacuum line and then heated in an oven to 190 °C for 14 h. Unreacted XeF_4 was pumped off at 30 °C and collected in a tared Teflon U-trap at –196 °C until the cylinders reached a constant weight. The combining ratios of MF with XeF_4 were obtained from the observed material balances, i.e., the weights of MF, XeF_4 used, XeF_4 recovered, and the products. Under the above conditions, the following combining ratios were observed: $\text{CsF}:\text{XeF}_4 = 1:0.99$, $\text{RbF}:\text{XeF}_4 = 1:0.95$, $\text{KF}:\text{XeF}_4 = 1:0.65$, and $\text{NaF}:\text{XeF}_4 = 1:0.32$. Additional heating of the $\text{KF}-\text{XeF}_4$ and $\text{NaF}-\text{XeF}_4$ adducts with more XeF_4 to 135 °C for 10 days increased the conversion of KF and NaF to the corresponding XeF_5^- salts to 73% and 36%, respectively.

Synthesis of $\text{NO}^+\text{XeF}_5^-$. In the drybox, XeF_4 (1.03 mmol) was loaded into a prepassivated 0.5-in.-o.d. Teflon-FEP ampule that was closed by a stainless steel valve. On the vacuum line, FNO (6.77 mmol) was added to the ampule at –196 °C. The ampule was allowed to warm to 0 °C and was kept at this temperature for 10 min with agitation, and the unreacted FNO was then pumped off at –78 °C. The white solid residue (265 mg, weight calculated for 1.03 mmol of $\text{NO}^+\text{XeF}_5^- = 264$ mg) had a dissociation pressure of 10 Torr at 0 °C.

Synthesis of $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$. In a typical synthesis, $\text{N}(\text{CH}_3)_4\text{F}$ and XeF_4 (2.01 mmol each) were loaded into a Teflon-FEP ampule in a drybox and CH_3CN (3 mL liquid) was vacuum distilled onto the solid at –196 °C. The mixture was warmed to –40 °C for 30 min with agitation and then allowed to warm to room temperature, followed by removal of the solvent in vacuo at this temperature. The white solid residue [605 mg, weight calculated for 2.01 mmol of $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^- = 604$ mg] was identified as $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$ by vibrational and NMR spectroscopy and a crystal structure determination. When isolated from CH_3CN solution, the compound is stable indefinitely at room temperature.

Caution! When solutions of $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$ in CH_3CN are frozen in liquid nitrogen, they may detonate. Similar, but milder, detonations were also found to occur when XeF_4 solutions were frozen at –196 °C. Exposure of solid samples of $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$ to atmospheric moisture for even brief periods has resulted in the violent detonation of bulk samples.

Crystal Structure Determination of $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$. **Crystal Growing.** Single crystals of $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$ suitable for X-ray analysis were grown from CH_3CN solution by vacuum distilling ca. 2.5 mL of dry CH_3CN onto ca. 50 mg of $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$ in a 1/4-in.-o.d. FEP reaction vessel equipped with a Kel-F valve. The mixture was warmed to 65 °C to effect

Table I. Summary of Crystal Data and Refinement Results for $[\text{N}(\text{CH}_3)_4]^+[\text{XeF}_5]^-$ ^a

space group	<i>Pm</i> <i>cn</i> (orthorhombic)
<i>a</i> (Å)	6.340 (2)
<i>b</i> (Å)	10.244 (3)
<i>c</i> (Å)	13.896 (4)
<i>V</i> (Å ³)	902.55
molecules/unit cell	4
molec wt (g mol ^{–1})	300.44
calcd density (g cm ^{–3})	2.153
<i>T</i> (°C)	–86
color	colorless
cryst decay (%)	0.6
μ (cm ^{–1})	35.77
wavelength (Å) used for data collect	0.710 69
$\sin \theta/\lambda$ limit (Å ^{–1})	0.538
total no. of reflns measured	1414
no. of independent reflns	641
no. of reflns used in struct anal. $I > 3\sigma(I)$	638
no. of variable params	83
final agreement factors	$R(F) = 0.0435$ $R(WF) = 0.0435$

^a Unit cell parameters obtained at 23 °C were $a = 6.400$ Å, $b = 10.321$ Å, and $c = 14.029$ Å; volume, 926.71 Å³.

dissolution and allowed to cool slowly to room temperature (ca. 5 °C/h). Colorless crystals up to 5 mm in length, having a needle-like morphology, formed overnight. The mother liquor was syringed off the crystals in a dry nitrogen atmosphere and residual solvent was removed under dynamic vacuum. Several crystals were cleaved perpendicular to their long axes to give fragments measuring ca. 0.2 mm × 0.2–0.3 mm and transferred in a drybox to 0.2-mm-o.d. Lindemann glass capillaries (previously dried under dynamic vacuum at 250 °C for 1 day) and sealed under a dry nitrogen atmosphere. The crystals were shown to be identical with the bulk sample prior to recrystallization by obtaining the single-crystal Raman spectrum at room temperature (see Figure 5b) and were found to be stable at room temperature in glass indefinitely.

Collection and Reduction of X-ray Data. Crystals of $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$ were centered on a Syntex P₃ diffractometer. Accurate cell dimensions were determined at $T = 23$ °C and at $T = -86$ °C from a least-squares refinement of the setting angles (χ , ϕ , and 2θ) obtained from 15 accurately centered reflections (with $22.14^\circ < 2\theta < 28.11^\circ$) chosen from a variety of points in reciprocal space. At $T = 23$ °C, and after several hours in the X-ray beam, the crystal appeared to be totally decomposed, resulting in an opaque white coloration. Integrated diffraction intensities were collected on a new crystal at $T = -86$ °C using a θ – 2θ scan technique (slowest rate 5.0°/min) with $0 \leq h \leq 10$, $0 \leq k \leq 15$, and $-15 \leq l \leq 15$, using molybdenum radiation monochromatized with a graphite crystal ($\lambda = 0.710 69$ Å). Throughout the data collection, two standard reflections were monitored every 48 reflections; a decay of 0.6% was observed; the intensities were adjusted accordingly. A total of 1414 reflections were collected out of which 641 reflections, satisfying the condition $I > 3\sigma(I)$, were chosen for structure solution. The intensities of these reflections were corrected for Lorentz polarization effects.

Solution and Refinement of the Structure. There were two space groups that were consistent with the reflection pattern: the noncentrosymmetric space group *P21cn* (No. 33) and the centrosymmetric space group *Pm**cn* (No. 62). The structure has been solved in both centrosymmetric (*Pm**cn*) and noncentrosymmetric (*P21cn*) space groups. The direct method of structure solution in the computer program SHELX-76²³ was used to locate the positions of the Xe atom and the five F atoms. Successive Fourier synthesis yielded all the remaining non-hydrogen atoms. The structure was refined by using the full-matrix least-squares technique with isotropic thermal parameters for individual atoms. In the case of the *Pm**cn* space group and after full convergence of the isotropic refinement ($R = 0.1265$), the atoms were assigned anisotropic thermal parameters and further refined by the full-matrix least-squares technique ($R = 0.0714$). The positions of the hydrogen atoms were calculated and the fixed hydrogen atoms were given an isotropic temperature factor of 0.05 Å².²⁴ The *R* factor obtained was 0.0652, with the unit weights. There was significant disagreement between the F_o and F_c values of three reflections, 110, 312, and 413, and these values were consequently omitted in a further refinement. This resulted in a global improvement of the structure and a final value for the *R* factor of 0.0435.

(16) Weidlein, J.; Müller, U.; Dehnicke, K. *Schwingungsspektroskopie*; Georg Thieme Verlag: Stuttgart, Germany, 1982.

(17) Christe, K. O.; Wilson, W. W. *Inorg. Chem.* **1982**, *21*, 4113.

(18) Christe, K. O.; Wilson, R. B.; Schack, C. J. *Inorg. Synth.* **1986**, *24*, 3.

(19) Syvret, R. G.; Schrobilgen, G. J. *Inorg. Chem.* **1989**, *28*, 1564.

(20) (a) Bartlett, N.; Sladky, F. O. *J. Am. Chem. Soc.* **1968**, *90*, 5316. (b) Malm, J. G.; Chernick, C. L. *Inorg. Synth.* **1966**, *8*, 254.

(21) Christe, K. O. *Inorg. Chem.* **1972**, *12*, 1580.

(22) Winfield, J. M. *J. Fluorine Chem.* **1984**, *25*, 91.

(23) Sheldrick, G. M. *SHELX-76 Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

(24) Hall, S. R.; Stewart, J. H. *XTAL 2.6 User's Manual*; University of Western Australia and University of Maryland.

Table II. Final Atomic Coordinates for $[\text{N}(\text{CH}_3)_4]^+[\text{XeF}_5]^-$

atom	x	y	z	pop. ^a
Xe1	0.2500	0.1233 (1)	0.0155 (1)	0.5
F1	0.2500	0.1876 (9)	0.1497 (6)	0.5
F2	0.2500	-0.0324 (8)	0.1025 (6)	0.5
F3	0.2500	-0.0399 (8)	-0.0673 (6)	0.5
F4	0.2500	0.1799 (9)	-0.1236 (6)	0.5
F5	0.2500	0.3217 (8)	0.0110 (6)	0.5
N1	0.2500	-0.403 (1)	0.172 (1)	0.5
C1	0.2500	0.628 (2)	0.068 (1)	0.5
C2	0.2500	-0.281 (2)	0.231 (1)	0.5
C3	0.437 (5)	-0.483 (2)	0.196 (1)	1.0

^aThe site occupation factor.

The same procedure was used for the $P2_1cn$ space group, which gave rise to a final R factor of 0.0763. The ratio of agreement factors $R(7.63/4.35) = 1.75$ is sufficient by Hamilton's R factor ratio test⁷ to state that the correct space group is $Pm\bar{c}n$.

An empirical absorption correction was also applied, but no significant improvement in the refinement was observed; in particular there was no change in the anisotropic thermal parameters.

Details of the data collection parameters and other crystallographic information for the $Pm\bar{c}n$ space group are given in Table I, and the final atomic coordinates are summarized in Table II. The following programs were used: XTAL,²⁴ data reduction; SHELX-76,²³ structure refinement; SNOOPI,²⁵ diagrams.

Vibrational Spectroscopy. Raman spectra were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer using a 488-nm exciting line of an Ar ion or the 647.1-nm line of a Kr ion laser, respectively. Baked-out Pyrex melting point capillaries or thin-walled Kel-F tubes were used as sample containers. A previously described²⁶ device was used for recording the low-temperature spectra (at -150°C). Single-crystal spectra of $[\text{N}(\text{CH}_3)_4]^+[\text{XeF}_5]^-$ were recorded at room temperature on a Instruments S.A. Mole S-3000 triple spectrograph system equipped with a microscope for focusing the excitation laser to a one-micrometer spot. The Ar laser line at 514.5 nm was selected for excitation of the sample. Crystals were sealed in Lindemann glass capillaries as described below.

Infrared spectra were recorded by using AgBr disks on a Perkin-Elmer Model 283 spectrophotometer. The finely powdered samples were sandwiched between two thin AgBr disks and pressed together in a Wilks minipress inside the drybox.

Nuclear Magnetic Resonance Spectroscopy. The ^{19}F and ^{129}Xe NMR spectra were recorded unlocked (field drift $< 0.1\text{ Hz h}^{-1}$) with Bruker WM-250 and Bruker AM-500 spectrometers equipped with 5.8719-T and 11.744-T cryomagnets, respectively. Fluorine-19 spectra were obtained by using a 5-mm combination $^1\text{H}/^{19}\text{F}$ probe operating at 235.36 MHz. The spectra were accumulated in 16K memory. Spectral width settings of 5000 and 30000 Hz were employed, yielding data point resolutions of 0.61 and 3.6 Hz/data point and acquisition times of 1.638 and 0.279 s, respectively. No relaxation delays were applied. Typically 300–7000 transients were accumulated. The pulse width corresponding to a bulk magnetization tip angle, θ , of approximately 90° was equal to $1\text{ }\mu\text{s}$. No line broadening parameters were applied in the exponential multiplication of the free induction decays prior to Fourier transformation.

Xenon-129 NMR spectra were obtained by using a broad-band VSP probe tunable over the range 23–202 MHz; spectra were recorded at 139.05 MHz. The spectra were accumulated in a 16K memory. A spectral width setting of 50 kHz was employed, yielding a data point resolution of 6.1 Hz/data point and an acquisition time of 0.164 s. No relaxation delays were applied. Typically 10000 transients were accumulated. The pulse width corresponding to a bulk magnetization tip angle, θ , of approximately 90° was equal to $18\text{ }\mu\text{s}$. Line-broadening parameters of 4 Hz were applied in the exponential multiplication of the free induction decays prior to Fourier transformation.

The ^{19}F and ^{129}Xe NMR spectra were referenced to neat external samples of CFCl_3 and XeOF_4 , respectively, at ambient temperature. The chemical shift convention used is that a positive (negative) sign signifies a chemical shift to high (low) frequency of the reference compound.

The ^{129}Xe NMR samples of saturated solutions of $[\text{N}(\text{CH}_3)_4]^+[\text{XeF}_5]^-$ in CH_3CN were prepared in 25-cm lengths of $3/8$ -in.-o.d., $1/32$ -in. wall FEP plastic tubing that had been reduced to 9-mm o.d. by squeezing in a heated precision brass mold. The FEP tubing was heat sealed at one

end with the open end flared (45° SAE) and joined, by means of compression fittings, to a Kel-F valve. The FEP tubes were heat sealed under dynamic vacuum with their contents frozen at -78°C . The sealed FEP sample tubes were inserted into 10-mm thin-walled precision NMR tubes (Wilmad) in order to run their spectra.

The ^{19}F NMR samples were prepared in precision 5-mm glass NMR tubes (Wilmad). Solid $[\text{N}(\text{CH}_3)_4]^+[\text{XeF}_5]^-$ [or $[\text{N}(\text{CH}_3)_4]^+[\text{XeF}_5]^-$ and $[\text{N}(\text{CH}_3)_4]^+[\text{F}]^-$] was loaded into the NMR tube in the drybox and CH_3CN solvent distilled in vacuo into the tube at -78°C . The tube was flame sealed. On warming to room temperature, a colorless saturated solution resulted containing some solid $[\text{N}(\text{CH}_3)_4]^+[\text{XeF}_5]^-$, which was decanted into the top of the tube prior to obtaining the NMR spectrum.

Computational Method. The calculations described below were done by using the local density functional theory^{27–30} with the program system DMol.³¹ DMol employs numerical functions for the atomic basis sets. The atomic basis functions are given numerically as an atom-centered, spherical, polar mesh. The radial portion of the grid is obtained from the solution of the atomic LDF equations by numerical methods. The radial functions are stored as sets of cubic spline coefficients so that the radial functions are piecewise analytic, a necessity for the evaluation of gradients. The use of exact spherical atom results offers certain advantages. Because of the quality of the atomic basis sets, basis set superposition effects should be minimized, correct behavior at the nucleus is obtained, and radial nodal properties of the wave function are present.

Because the basis sets are numerical, the various integrals arising from the expression for the energy need to be evaluated over a grid. The integration points are generated in terms of angular functions and spherical harmonics. The number of radial points N_R is given as

$$N_R = 1.2 \times 14(Z + 2)^{1/3} \quad (1)$$

where Z is the atomic number. The maximum distance for any function is 12 au. The angular integration points N_θ are generated at the N_R radial points to form shells around each nucleus. The value of N_θ ranges from 14 to 302 depending on the behavior of the density.³² The Coulomb potential corresponding to the electron repulsion term could be solved by evaluation of integrals. However, since the method is based on the density, it was found to be more appropriate to determine the Coulomb potential directly from the electron density by solving Poisson's equation

$$-\nabla^2 V_e(r) = 4\pi e^2 \rho(r) \quad (2)$$

In DMol, the form for the exchange–correlation energy of the uniform electron gas is that derived by von Barth and Hedin.³³

All of the DMol calculations were done with a double-numerical basis set augmented by d polarization functions. This can be thought of in terms of size as a polarized double- ζ basis set. However, because exact numerical solutions are employed for the atom, this basis set is of significantly higher quality than a normal molecular orbital polarized double- ζ basis set. The fitting functions have an angular momentum number one greater than that of the polarization function, resulting in a value of $l = 3$ for the fitting functions.

Geometries were determined by optimization using analytic gradient methods.³⁴ First derivatives in the LDF framework can be calculated efficiently and only take on the order of three to four SCF iterations or 10–25% of an energy evaluation. There are two problems with evaluating gradients in the LDF framework, which are due to the numerical methods that are used. The first is that the energy minimum does not nec-

(27) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(28) Salahub, D. R. In *Ab Initio Methods in Quantum Methods in Quantum Chemistry*, 2nd ed.; Lawley, K. P., Ed.; J. Wiley & Sons: New York, 1987; p 447.

(29) (a) Wimmer, E.; Freeman, A. J.; Fu, C.-L.; Cao, P.-L.; Chou, S.-H.; Delley, B. In *Supercomputer Research in Chemistry and Chemical Engineering*; Jensen, K. F., Truhlar, D. G., Eds.; ACS Symposium Series: American Chemical Society: Washington, DC, 1987; p 49. (b) Dixon, D. A.; Andzelm, J.; Fitzgerald, G.; Wimmer, E.; Delley, B. In *Science and Engineering on Cray Supercomputers. Proceedings of the Fifth International Symposium*; Cray Research: Minneapolis, MN, 1990; p 285.

(30) Jones, R. O.; Gunnarsson, O. *Rev. Mod. Phys.* **1989**, *61*, 689.

(31) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508. DMol is available commercially from BIOSYM Technologies, San Diego, CA.

(32) This grid can be obtained by using the FINE parameter in DMol.

(33) von Barth, U.; Hedin, L. *J. Phys. Chem.* **1972**, *5*, 1629.

(34) (a) Versluis, I.; Ziegler, T. *J. Chem. Phys.* **1988**, *88*, 3322. (b) Andzelm, J.; Wimmer, E.; Salahub, D. R. In *The Challenge of d and f Electrons: Theory and Computation*; Salahub, D. R., Zerner, M. C., Eds.; ACS Symposium Series 394; American Chemical Society: Washington, DC, 1989; p 228. (c) Fournier, R.; Andzelm, J.; Salahub, D. R. *J. Chem. Phys.* **1989**, *90*, 6371.

(35) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

(36) Bondi, A. J. *Phys. Chem.* **1964**, *68*, 441.

(25) Davies, K. *CHEMGRAF Suite: SNOOPI*; Chemical Design Ltd.: Oxford, England, 1983.

(26) Miller, F. A.; Harney, B. M. *Appl. Spectrosc.* **1969**, *23*, 8.

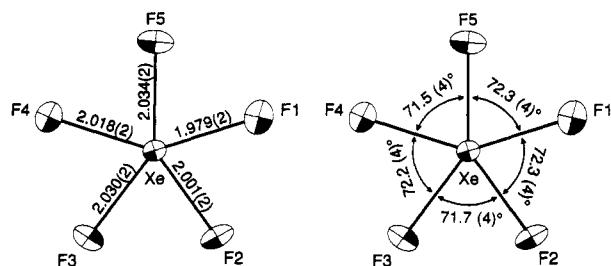


Figure 1. Atom numbering scheme, bond lengths (Å) and angles (deg) for XeF_5^- at -86°C in $[\text{N}(\text{CH}_3)_4]^+[\text{XeF}_5]^-$. Projection of the XeF_5^- anion on (111). Esd's are given in parentheses; thermal ellipsoids are shown at the 50% probability level.

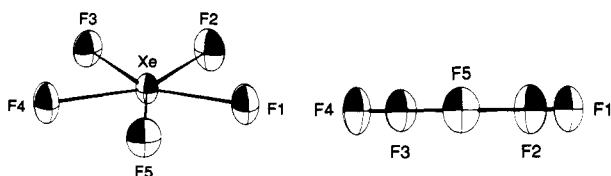


Figure 2. Projections of the XeF_5^- anion on (130) (left) and (010) (right). Thermal ellipsoids are shown at the 50% probability level.

essarily correspond exactly to the point with a zero derivative. The second is that sum of the gradients may not always be zero as required for translational invariance. These tend to introduce errors on the order of $0.001 \text{ \AA}$ in the calculation of the coordinates if both a reasonable grid and basis set are used. This gives bond lengths and angles with reasonable error limits. The difference of $0.001 \text{ \AA}$ is about an order of magnitude smaller than the accuracy of the LDF geometries as compared to experiment.

Results and Discussion

Syntheses and Properties of XeF_5^- Salts. The reactions of the alkali-metal fluorides with XeF_4 were studied under conditions (190°C , 14 h) very similar to those previously reported by Kiselev and co-workers.¹³⁻¹⁵ It was found that XeF_4 combines with either CsF or RbF in a clean 1:1 mole ratio to form the corresponding, previously unidentified XeF_5^- salts. In the case of KF and NaF the same anion was formed; however, the percentage conversion of MF to MXeF_5 decreased with decreasing atomic weight of M (CsF = 99%, RbF = 95%, KF = 65%, and NaF = 32%) and increased reaction times were required for higher conversions.

The interactions of LiF and BaF₂ with XeF_4 were also examined, but in neither case was evidence for the formation of a stable adduct obtained.

The XeF_5^- salts of Cs⁺, Rb⁺, K⁺, and Na⁺ are white, stable solids. Their physical properties, thermal stabilities, etc. are those previously attributed by Kiselev and co-workers to the corresponding M_2XeF_6 salts.¹³⁻¹⁵ As will be shown below, they all contain pentagonal planar XeF_5^- anions.

Attempts to prepare CsXeF₅ from CsF and XeF_4 at room temperature in CH_3CN solutions were unsuccessful because of the very low solubility of CsF in this solvent. However, the highly soluble $\text{N}(\text{CH}_3)_4\text{F}$ readily forms $[\text{N}(\text{CH}_3)_4]^+[\text{XeF}_5]^-$ under these

Table III. Bond Distances (Å) and Bond Angles (deg) in $[\text{N}(\text{CH}_3)_4]^+[\text{XeF}_5]^-$

Bond Lengths			
Xe1-F1	1.979 (2)	N1-C1	1.481 (6)
Xe1-F2	2.001 (2)	N1-C2	1.488 (6)
Xe1-F3	2.030 (2)	N1-C3	1.524 (4)
Xe1-F4	2.018 (2)		
Xe1-F5	2.034 (2)		
Bond Angles			
F2-Xe1-F1	72.3 (4)	C2-N1-C1	110.7 (3)
F3-Xe1-F2	71.7 (4)	C3-N1-C1	108.9 (5)
F4-Xe1-F3	72.2 (4)	C3-N1-C2	109.6 (4)
F5-Xe1-F1	72.3 (4)		
F5-Xe1-F4	71.5 (4)		

conditions. Even with a 2:1 molar ratio of $\text{N}(\text{CH}_3)_4\text{F}:\text{XeF}_4$ in CH_3CN solvent and a large excess of MF in the XeF_4 -MF systems, only XeF_5^- , and no XeF_6^{2-} , was observed, indicating that XeF_5^- is the favored anion. The $[\text{N}(\text{CH}_3)_4]^+[\text{XeF}_5]^-$ salt is a white, stable solid whose structure was established by a crystal structure determination and vibrational and NMR spectroscopy (see below).

The lack of XeF_6^{2-} formation in these systems was further demonstrated by a study of the FNO- XeF_4 system. Even when a large excess of FNO was used, only $\text{NO}^+[\text{XeF}_5]^-$, and no $(\text{NO}^+)_2\text{XeF}_6^{2-}$, was formed at temperatures as low as -78°C . The $\text{NO}^+[\text{XeF}_5]^-$ salt is a white solid having a dissociation pressure of 10 Torr at 0°C . It is ionic, containing NO^+ and XeF_5^- ions as shown by vibrational spectroscopy (see below).

In view of the above results and the structural evidence presented below, it appears quite clear that the salts obtained by the reactions of XeF_4 with fluoride ion sources are XeF_5^- , and not XeF_6^{2-} , salts. The fact that some of the products reported¹³⁻¹⁵ by the Soviet workers gave elemental analyses approaching the M_2XeF_6 composition might be attributed to incomplete conversion of MF to MXeF_5 thus resulting in $\text{MF} + \text{MXeF}_5$. There is also no doubt that the products observed during the laser photolysis of either CsXeF_7 or NF_4XeF_7 were not XeF_6^{2-} but XeF_5^- salts.¹⁷

X-ray Crystal Structure of $[\text{N}(\text{CH}_3)_4]^+[\text{XeF}_5]^-$. The crystal structure consists of well-separated $[\text{N}(\text{CH}_3)_4]^+$ and $[\text{XeF}_5]^-$ ions. The $[\text{N}(\text{CH}_3)_4]^+$ cation is tetrahedral with the expected bond lengths. Different views of the $[\text{XeF}_5]^-$ anion are shown in Figures 1 and 2, while a stereoview of the packing in the unit cell is given in Figure 3 in which the hydrogen atoms have been omitted in the cation. Important bond lengths and angles are listed in Table III. The xenon and five fluorines of the $[\text{XeF}_5]^-$ anion and the nitrogen and two carbons of the cation are located on special positions that are on the mirror plane, resulting in an anion that is planar by crystal symmetry. The closest anion-cation distance occurs between F2 and C2, which lies in the anion plane, at $3.105(5) \text{ \AA}$, whereas the remaining closest F...C distances occur at $3.237(5) \text{ \AA}$ (F5...C1), $3.354(5) \text{ \AA}$ (F3...C2), $3.370(5) \text{ \AA}$ (F1...C3), and $3.651(5) \text{ \AA}$ (F4...C2). The sum of the van der Waals radii of CH_3 ($2.00 \text{ \AA}$)³⁵ and F ($1.35^{35}-1.40^{36} \text{ \AA}$) is $3.35-3.40 \text{ \AA}$. The F2...C2 distance suggests weak hydrogen bonding between the C2 methyl group and F2 and is somewhat shorter than the shortest F...C

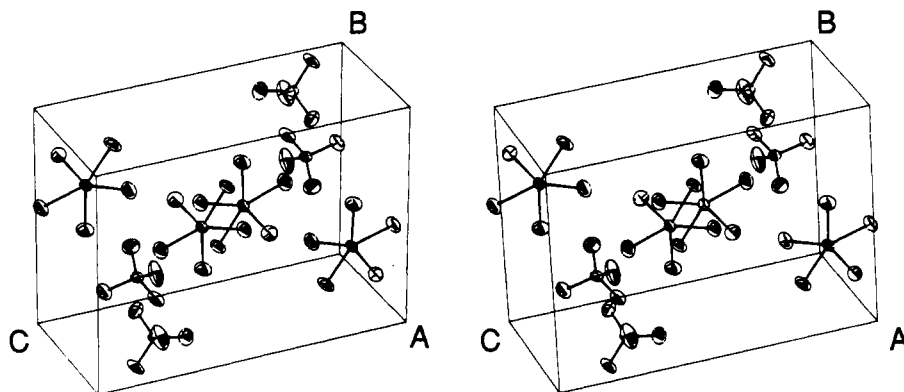


Figure 3. Stereoview [111] of the unit cell of $[\text{N}(\text{CH}_3)_4]^+[\text{XeF}_5]^-$; hydrogen atoms are excluded.

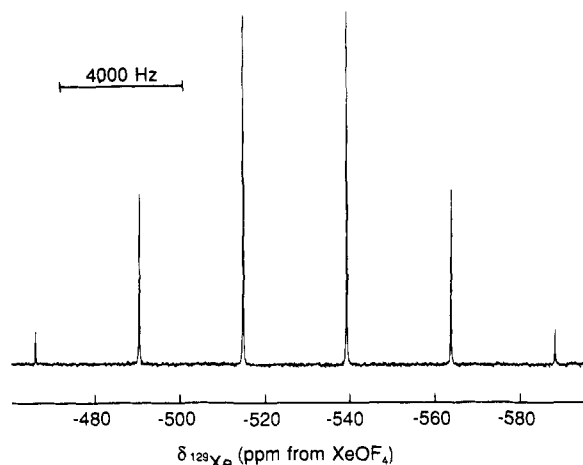


Figure 4. ^{129}Xe NMR spectrum (139.05 MHz) at 24 °C of a saturated solution of $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$ in CH_3CN containing a 1 M excess of $\text{N}(\text{CH}_3)_4^+\text{F}^-$.

distance in $\text{N}(\text{CH}_3)_4^+\text{HF}_2^-$ [3.313 (5) Å],⁷ which appears to be at the limit of the van der Waals distance. The short $\text{F2}\cdots\text{C2}$ distance appears to account for the greater elongation of the thermal ellipsoid of F2 (in the direction of the C_5 -axis of the anion; Figure 2).

Although the site symmetry of the XeF_5^- anion is C_s , the five fluorines are clearly equivalently bonded to the xenon, giving a pentagonal planar structure of D_{5h} symmetry. The average $\text{F}-\text{Xe}-\text{F}$ angle of 72.0 (4)° is essentially the ideal angle of 72°. The average $\text{Xe}-\text{F}$ bond length [2.012 (2) Å] is significantly longer than the average bond length of XeF_4 [1.953 (2) Å]³⁷ and the average equatorial bond length of IF_7 [1.858 (4) Å].³⁸ The nearest-neighbor $\text{F}\cdots\text{F}$ contacts in the XeF_5^- anion are 2.35–2.38 Å and are substantially less than twice the nominal van der Waals radius for fluorine, i.e., 2.70³⁵–2.80³⁸ Å, indicating that the fluorines of the pentagon are significantly congested and are consistent with the long $\text{Xe}-\text{F}$ bond length in XeF_5^- . This contrasts with the shorter $\text{Xe}-\text{F}$ bond length of XeF_4 , where the fluorines in the plane are not contacting, and the intramolecular $\text{F}\cdots\text{F}$ distances (2.76 Å) are at the limit of the sum of the fluorine van der Waals radii. The short $\text{I}-\text{F}$ bond lengths for the equatorial belt of five fluorines in IF_7 relative to the $\text{Xe}-\text{F}$ bond length of XeF_5^- may be attributed to relief of the congestion in the IF_5 belt by means of a 7.5° puckering, which has been deduced from electron diffraction studies³⁸ but not corroborated by an independent study. The fact that XeF_5^- does not relieve its steric congestion by a puckering distortion may be attributed to the presence of the two axial lone pairs of electrons, which exert greater repulsive forces than the two axial fluorines in the IF_7 molecule, thus forcing the XeF_5^- anion to be planar. Moreover, the formal negative charge on XeF_5^- leads to a greater $\text{Xe}-\text{F}$ bond polarity and elongation of the $\text{Xe}-\text{F}$ bond, as is evident from a comparison with the $\text{Xe}-\text{F}$ bond length of XeF_4 , and serves to alleviate some of the steric congestion in the anion plane.

The steric crowding in the XeF_5^- molecular plane is further illustrated by the thermal parameters, which remain essentially unaltered before and after empirical absorption corrections. It is apparent that the principal axes of motion of the fluorine atoms in XeF_5^- and XeF_4 ³⁷ are perpendicular to the bond directions, producing the anticipated polar flattening of the thermal ellipsoids in the $\text{Xe}-\text{F}$ bond directions. However, the thermal ellipsoids in XeF_5^- are elongated in the direction of the C_5 -axis and flattened in the direction perpendicular to the $\text{Xe}-\text{F}$ bonds in the molecular plane. In contrast to the fluorine thermal ellipsoids in XeF_5^- , those of XeF_4 are essentially isotropic in the directions perpendicular to the $\text{Xe}-\text{F}$ bonds and in the molecular plane where the fluorine atoms are apparently not contacting one another to any significant

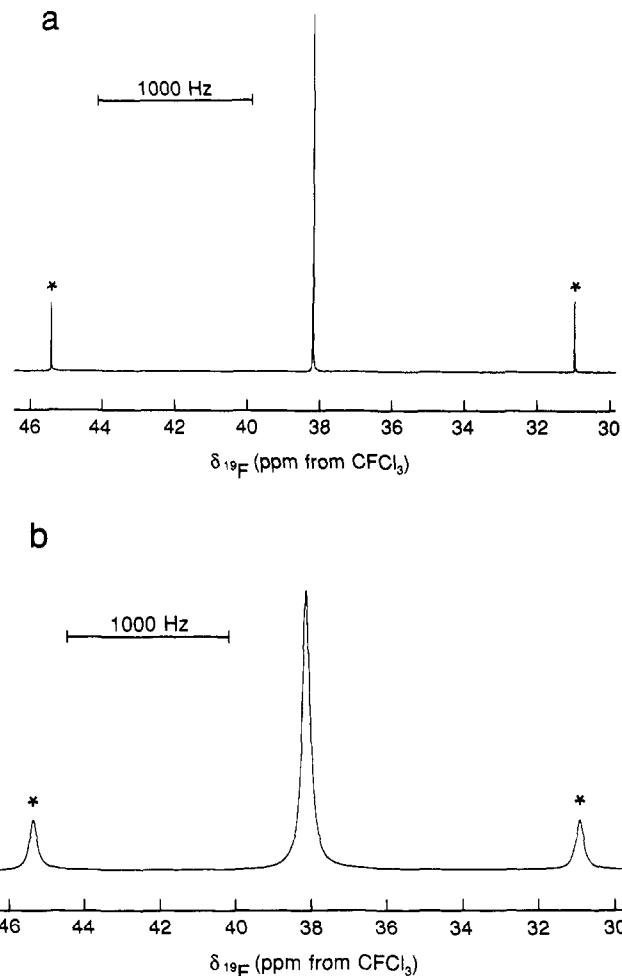


Figure 5. ^{19}F NMR spectrum (235.36 MHz) at 24 °C of (a) a saturated solution of $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$ in CH_3CN containing a 1 M excess of $\text{N}(\text{CH}_3)_4^+\text{F}^-$ and (b) a saturated solution of pure $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$ in CH_3CN . Asterisks (*) denote ^{129}Xe satellites.

extent. Steric congestion in XeF_5^- is additionally supported by vibrational force constant calculations (see below).

^{129}Xe and ^{19}F NMR Spectra of the XeF_5^- Anion. The ^{129}Xe NMR spectrum of $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$ dissolved in CH_3CN containing a 1 M excess of $\text{N}(\text{CH}_3)_4^+\text{F}^-$ at 24 °C (Figure 4) displays a well-resolved binomial sextet ($\Delta\nu_{1/2} = 15$ Hz), consistent with the coupling of the ^{129}Xe nucleus to five chemically equivalent ^{19}F nuclei in the XeF_5^- anion [$\delta(^{129}\text{Xe})$, -527.0 ppm from XeOF_4 ; $^1J(^{129}\text{Xe}-^{19}\text{F})$, 3400 Hz]. The ^{129}Xe chemical shift of XeF_5^- is significantly more shielded (i.e., by -843.9 ppm) than that of XeF_4 in CH_3CN at 24 °C [$\delta(^{129}\text{Xe})$, 316.9 ppm from XeOF_4 ; $^1J(^{129}\text{Xe}-^{19}\text{F})$, 3895 Hz]. This behavior follows the expected trend of increased shielding that accompanies an increase in negative charge.³⁹ The ^{19}F NMR spectrum of a similar sample at 24 °C (Figure 5a) shows a narrow singlet ($\Delta\nu_{1/2} = 2.8$ Hz) flanked by natural abundance (26.44%) ^{129}Xe satellites [$\delta(^{19}\text{F})$, 38.1 ppm from CFC_13 ; $^1J(^{129}\text{Xe}-^{19}\text{F})$, 3398 Hz]. A resonance due to unreacted fluoride was observed at -75 ppm. Interestingly, the ^{19}F chemical shift of XeF_5^- is deshielded by 56.8 ppm with respect to that of XeF_4 in CH_3CN at 24 °C [$\delta(^{19}\text{F})$, -18.7 ppm from CFC_13 ; $^1J(^{129}\text{Xe}-^{19}\text{F})$, 3896 Hz]. This result is somewhat surprising in view of the increased ionic character of the $\text{Xe}-\text{F}$ bonds (i.e., greater bond length and smaller stretching force constant) compared with those in XeF_4 ; the reason for this is not clear but may be related to the congested environment of the fluorine ligands and the rather short nearest-neighbor $\text{F}\cdots\text{F}$ contact distance. The ^{19}F NMR spectrum of a sample prepared from equimolar

(37) Burns, J. H.; Agron, P. A.; Levy, H. A. *Science* **1963**, *139*, 1208.

(38) Adams, W. J.; Thompson, H. B.; Bartell, L. S. *J. Chem. Phys.* **1970**, *53*, 4040.

(39) Jameson, C. J.; Mason, J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; Chapter 3, pp 66–68.

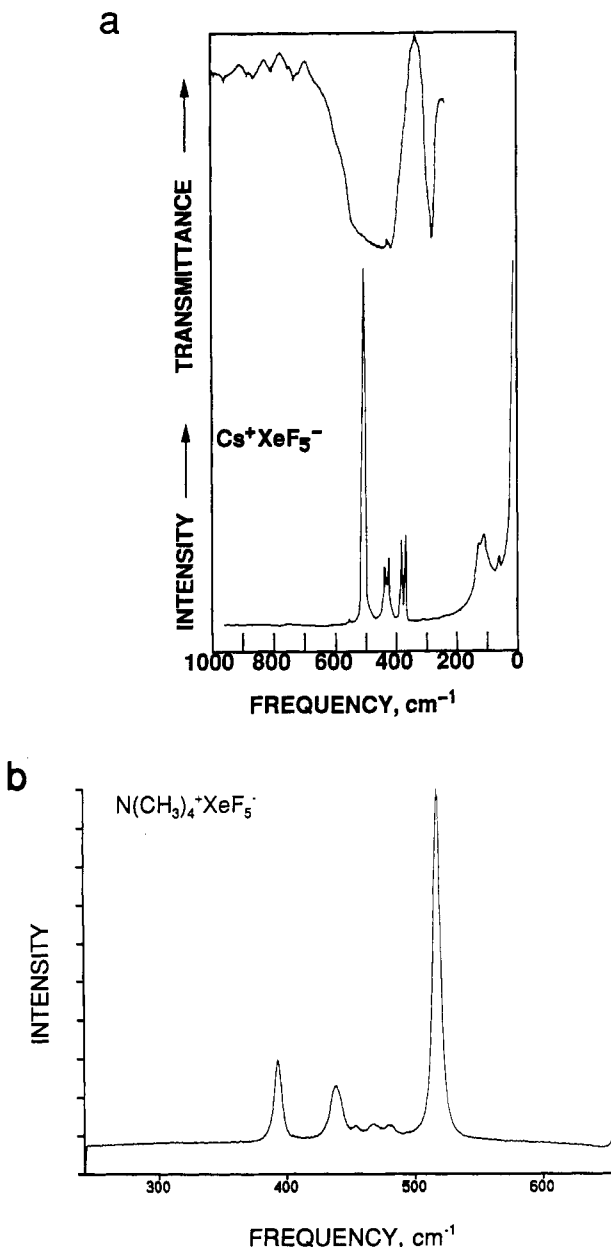


Figure 6. (a) Vibrational spectra of solid $\text{Cs}^+\text{XeF}_5^-$. Upper trace, infrared spectrum recorded at room temperature with an AgBr disk; lower trace; Raman spectrum recorded in a glass capillary at 25 °C with 647.1-nm excitation. (b) Single-crystal Raman spectrum of $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$ recorded in a glass capillary at room temperature with 514.5-nm excitation.

quantities of XeF_4 and $\text{N}(\text{CH}_3)_4^+\text{F}^-$ in CH_3CN showed a similar resonance, with accompanying ^{129}Xe satellites, at 38.1 ppm; however, the linewidth was significantly broader, $\Delta\nu_{1/2} = 53$ Hz (Figure 5b). This indicates that XeF_5^- undergoes dissociative fluorine exchange, which can be suppressed by the presence of excess fluoride. There was no evidence for the formation of XeF_6^{2-} at $\text{XeF}_4:\text{N}(\text{CH}_3)_4^+\text{F}^-$ ratios exceeding 1:1, thus casting further doubt on the previous claims¹³⁻¹⁵ for the existence of stable salts of the XeF_6^{2-} anion.

The magnitude of the one-bond $^{129}\text{Xe}-^{19}\text{F}$ coupling constant drops from 3895 Hz in XeF_4 to 3400 Hz in XeF_5^- under the same conditions (i.e., solvent and temperature) of experimental measurement. If it is assumed that the Fermi-contact mechanism provides the dominant coupling contribution,⁴⁰ then the smaller

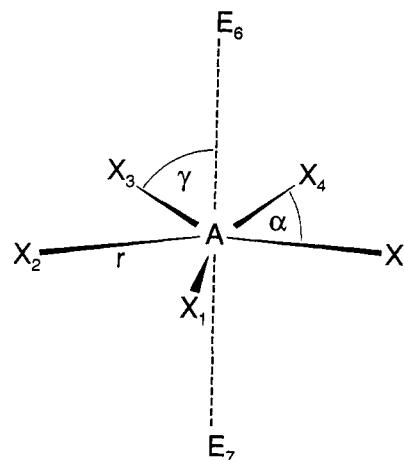


Figure 7. Internal coordinates for pentagonal planar AX_5 .

value of $^1J(^{129}\text{Xe}-^{19}\text{F})$ in XeF_5^- is in accord with the greater ionic character of the Xe-F bonds in the anion.

In the VSEPR notation, XeF_5^- is a seven-coordinate AX_5E_2 system, and is the first example of this geometry.⁴¹ The solution structure proposed for the anion that is consistent with five equivalent fluorines is a pentagonal planar (D_{5h}) structure having five equivalent equatorial fluorines and two axial lone pairs of electrons. The dynamic behavior for related seven-coordinate geometries is well established in the cases of XeF_6 and IF_7 . In contrast to IF_7 and XeF_5^- , the gas-phase structure of XeF_6 (AX_6E) is based upon a distorted octahedral geometry⁴² in which the valence electron lone pair distorts the octahedral geometry to C_{3v} by occupying triangular faces of the octahedron, passing among adjacent faces via a transition state having intermediate C_3 and C_{2v} geometries, with intramolecular exchange dynamics that are distinct from those of IF_7 . The dynamic behavior of IF_7 (AX_7) is also well documented; on the basis of gas-phase electron diffraction measurements it is purported to have a puckered arrangement for the five equatorial fluorines³⁸ in the gas phase and it has been shown by ^{19}F NMR spectroscopy that axial and equatorial fluorine environments of IF_7 undergo rapid intramolecular exchange in solution.⁴³ The single fluorine environment observed in the NMR spectra of XeF_5^- could also be accounted for by assuming that the anion is fluxional. The VSEPR rules postulate that the valence shell lone pairs exert larger repulsive forces on adjacent electron pairs than do bonding pairs, so that, unlike IF_7 , the transition state for exchange of axial lone pair positions with equatorial fluorine positions in XeF_5^- would presumably give rise to prohibitively large repulsive energies when a lone pair or lone pairs occupy an equatorial position, suggesting that XeF_5^- is likely to be rigid in solution.

Vibrational Spectra and Normal Coordinate Analysis of XeF_5^- . The infrared and Raman spectra of CsXeF_5 , RbXeF_5 , KXeF_5 , NaXeF_5 , and $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$ and the Raman spectra of NOXeF_5 have been recorded. The observed frequencies and their assignments are summarized in Table IV. Figure 6 shows, as typical examples, the vibrational spectra of CsXeF_5 and $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$.

As shown above by the NMR data and the crystal structure determination, the XeF_5^- anion is pentagonal planar and, therefore, belongs to point group D_{5h} . After the removal of translational and rotational degrees of freedom, the irreducible representation of the molecule is

$$\Gamma_{\text{vib}} = 1\text{A}_1'(\text{R}) + 1\text{A}_2''(\text{IR}) + 2\text{E}_1'(\text{IR}) + 2\text{E}_2'(\text{R}) + \text{E}_2''(\text{ia})$$

Since XeF_5^- is the first known example of an AX_5 species of symmetry D_{5h} , it is not surprising that a normal coordinate analysis

(41) Gillespie, R. J. *Molecular Geometry*; Van Nostrand Reinhold Co.: London, 1972.

(42) (a) Bartell, L. S.; Gavin, R. M.; Thompson, H. B. *J. Chem. Phys.* **1965**, *43*, 2547. (b) Bartell, L. S.; Gavin, R. M. *J. Chem. Phys.* **1968**, *48*, 2466.

(43) Gillespie, R. J.; Quail, J. W. *Can. J. Chem.* **1964**, *42*, 2671.

(40) (a) Jameson, C. J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; Chapter 4, pp 97-101; Chapter 18. (b) Schrobilgen, G. J. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978; Chapter 14.

Table IV. Vibrational Spectra of the XeF_5^- Anion in Different Salts

observed frequencies, ^a cm ⁻¹											assignments for XeF ₅ ⁻ in point group D _{3h}	
NOXeF ₅ ^b		N(CH ₃) ₄ XeF ₅ ^c		NaXeF ₅		KXeF ₅		RbXeF ₅		CsXeF ₅		
R		R		R		R		R		R		
25 °C	-150 °C		IR		IR		IR		IR			IR
									970 vw		955 vw	ν ₁ + ν ₃ (E ₁ ')
									882 vw		870 sh	ν ₃ + ν ₅ (E ₁ ' + E ₂ ')
							860 vw				850 vw	2ν ₃ (A ₁ ' + E ₁ ' + A ₂ ')
							800 vw		808 vw		795 vw	ν ₅ + ν ₆ (A ₁ ' + E ₁ ' + A ₂ ')
									752 vw		740 sh	2ν ₆ (A ₁ ' + E ₁ ')
							740 vw		728 vw		724 vw	ν ₄ + ν ₅ (E ₁ ' + E ₂ ')
											705 sh	
									668 vw		650 sh	ν ₄ + ν ₆ (E ₁ ' + E ₂ ') 2ν ₂ (A ₁ ') ν ₁ (A ₁ ') ν ₃ (E ₁ ') ν ₅ (E ₂ ') ν ₆ (E ₂ ') ν ₄ (E ₁ ') ν ₂ (A ₂ '')
503 (10)	506 (10)	502 (10)		519 (10)	525 sh	544 (0.1)		550 (0.1)		547 (0.1)		
	498 (1)					505 (10)		509 (10)		504 (10)		
			509 sh			498 sh		489 sh				
482 (0+)			465 vs	473 (0.1)	450 vs, br		480 vs	471 (0.1)	470 vw, br		450 vs, br	
	475 (0.5)		420 sh		415 s		410 s	453 sh	418 s		415 s	
								440 (1.6)				
440 sh	445 (1.8)	423 (2.1)		444 (1.8)		438 (1.4)		437 sh		432 (1.5)		
429 (1.1)	424 (1)			422 (1.3)		424 (1.2)		437 sh		422 (1.6)		
382 sh	384 (1)	377 (3.3)		386 (2.0)		388 (2.4)	379 sh	389 (2.2)	372 w	380 (2.2)		
374 (2.3)	373 (2.5)			383 sh		381 (1.9)		379 (1.6)		369 (2.3)		
290 (0+)	282 (0.5)			293 (0+)		290 (0+)		299 (0+)	288 sh	312 (0+)	288 sh	
240 (0.2)	244 (0.6)		278 s		276 s		275 s	278 (0+)	275 s		274 s	
								169 (0.7)				
								131 (1.1)				
								107 (0.4)				
								91 (1.3)				
								77 (1)				
								59 (1.4)				
								52 sh				
								47 sh				
								35 (0.6)				
135 (1)	144 (1.5)					147 (1.5)						
97 (0.8)	100 (1.5)					113 sh						
75 (1.5)	82 (3.0)	90 (1)		144 (1.4)		102 (0.5)				124 (1.2)		
35 (0.5)	42 (1)					90 (2)				104 (1.5)		
						65 sh				57 (0.3)		
						52 sh						
						42 sh						
												lattice vibrations

^a Values in parentheses denote relative intensities; sh, shoulder; s, strong; w, weak. ^b The NO^+ stretching mode was observed at 2314 cm^{-1} with a relative intensity of 1.0. ^c Only the bands due to the XeF_5^- anion have been listed in the table. In addition to these bands, the following bands due to the $\text{N}(\text{CH}_3)_4^+$ cation were observed. Ra: 3035 (0.2), 2990 (0.1), 2970 (0.1), 2930 (0.2), 2820 (0.1), 1484 (0.1), 1458 (0.3), 1185 (0+), 954 (0.5), 758 (0.9), 480 (0.2), 468 (0.2), 456 (0.1). IR: 3040 m, 2968 w, 1491 s, 1423 w, 954 s, 462 s. For their assignment, see ref 3.

Table V. Symmetry Coordinates and Approximate Mode Descriptions for a Pentagonal Planar XY_5 Molecule

$S_1 = \frac{1}{\sqrt{5}} (\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4 + \Delta r_5)$		symmetric stretch
$S_2 = \frac{1}{\sqrt{10}} [\sum_{i=1}^5 (\Delta \gamma_{i6} - \Delta \gamma_{i7})]$		symmetric out of plane (umbrella) deformation
$S_{3a} = \frac{1}{\sqrt{5}} [\Delta r_1 + \cos \alpha (\Delta r_2 + \Delta r_5) + \cos 2\alpha (\Delta r_3 + \Delta r_4)]$		asymmetric stretch
$S_{3b} = \frac{1}{\sqrt{5}} [\sin \alpha (\Delta r_2 - \Delta r_5) + \sin 2\alpha (\Delta r_3 - \Delta r_4)]$		
$S_{4a} = \frac{1}{\sqrt{5}} [\Delta \alpha_{34} + \cos \alpha (\Delta \alpha_{45} + \Delta \alpha_{23}) + \cos 2\alpha (\Delta \alpha_{15} + \Delta \alpha_{12})]$		asymmetric in plane deformation
$S_{4b} = \frac{1}{\sqrt{5}} [\sin \alpha (\Delta \alpha_{45} - \Delta \alpha_{23}) + \sin 2\alpha (\Delta \alpha_{15} - \Delta \alpha_{12})]$		
$S_{5a} = \frac{1}{\sqrt{5}} [\Delta r_1 + \cos 2\alpha (\Delta r_2 + \Delta r_5) + \cos \alpha (\Delta r_3 + \Delta r_4)]$		asymmetric stretch
$S_{5b} = \frac{1}{\sqrt{5}} [\sin 2\alpha (\Delta r_2 + \Delta r_5) + \sin \alpha (\Delta r_3 + \Delta r_4)]$		
$S_{6a} = \frac{1}{\sqrt{5}} [\Delta \alpha_{34} + \cos 2\alpha (\Delta \alpha_{45} + \Delta \alpha_{23}) + \cos \alpha (\Delta \alpha_{15} + \Delta \alpha_{12})]$		in plane (scissor) deformation
$S_{6b} = \frac{1}{\sqrt{5}} [\sin 2\alpha (\Delta \alpha_{45} - \Delta \alpha_{23}) - \sin \alpha (\Delta \alpha_{15} - \Delta \alpha_{12})]$		
$S_{7a} = \frac{1}{\sqrt{5}} [(\Delta \gamma_{16} - \Delta \gamma_{17}) + \cos 2\alpha (\Delta \gamma_{26} - \Delta \gamma_{27} + \Delta \gamma_{56} - \Delta \gamma_{57}) + \cos \alpha (\Delta \gamma_{36} - \Delta \gamma_{37} + \Delta \gamma_{46} - \Delta \gamma_{47})]$		asymmetric out of plane deformation
$S_{7b} = \frac{1}{\sqrt{5}} [\sin 2\alpha (\Delta \gamma_{26} - \Delta \gamma_{27} + \Delta \gamma_{56} - \Delta \gamma_{57}) - \sin \alpha (\Delta \gamma_{36} - \Delta \gamma_{37} + \Delta \gamma_{46} - \Delta \gamma_{47})]$		

Table VI. G Matrix^a for Pentagonal Planar XeF_5^- of Symmetry D_{5h}

A_1'	$G_{11} = \mu_y = 5.2637 \times 10^{-2}$
A_2''	$G_{22} = (2/r^2)(\mu_y + 5\mu_x) = 4.4802 \times 10^{-2}$
E_1'	$G_{33} = \mu_y + 5\mu_x/2 = 7.1677 \times 10^{-2}$
	$G_{34} = 5(5^{1/2})\mu_x/(4r \sin \alpha) = 1.1123 \times 10^{-2}$
	$G_{44} = (1/r^2)(5\mu_y \sin^2 2\alpha + \mu_x) = 2.4333 \times 10^{-2}$
E_2'	$G_{55} = \mu_y = 5.2637 \times 10^{-2}$
	$G_{56} = 0$
	$G_{66} = (1/r^2)(4\mu_y \sin^2 \alpha) = 4.7026 \times 10^{-2}$
E_2''	$G_{77} = 2\mu_y/r^2 = 2.5995 \times 10^{-2}$

^a The following geometry was used for the calculation of the G matrix: $r = 2.0124 \text{ \AA}$ and $\alpha = 72^\circ$.

had not previously been carried out for such a species. Force constants were calculated by the Wilson FG matrix method.⁴⁴ Figure 7 shows our choice of internal coordinates to describe the vibrations of such a molecule. Two imaginary ligands, E_6 and E_7 , have been placed in the axial positions to define the angles γ , required for the definition of the out-of-plane deformation modes. The symmetry coordinates and approximate mode descriptions are given in Table V and are derived from those previously reported for the IF_7 molecule after correction for two apparent typographical errors.⁴⁵ The analytical G and F matrices, together with the computed numerical values, are given in Tables VI and VII, respectively. The correctness of our G matrix was verified by an independent calculation of the numerical G matrix by using a computational method that gave identical values.

Vibrational Assignments. In agreement with the above predictions for XeF_5^- of symmetry D_{5h} , three mutually exclusive Raman and two infrared bands were observed in the 200–700- cm^{-1} region expected for the fundamental vibrations. The $\text{N}(\text{CH}_3)_4^+$ salt, containing the largest cation and, hence, the best isolated XeF_5^- anion, shows three narrow Raman lines at 502, 423, and 377 cm^{-1} . On the basis of their relative intensities and frequencies, which are similar to those of the three closely related Raman-active modes of octahedral molecules, the 502-, 423-, and 377- cm^{-1} bands are assigned to the symmetric stretch, $\nu_1(A_1')$, the antisymmetric stretch, $\nu_5(E_2')$, and the symmetric in-plane deformation, $\nu_6(E_2')$, respectively. The rigorous adherence of the observed Raman spectrum to the vibrational selection rules for symmetry D_{5h} and the failure to observe further splittings of the vibrational bands serve to underscore that the vibrational modes of the XeF_5^- anion

Table VII. F Matrix and Force Field for Pentagonal Planar XeF_5^- of Symmetry D_{5h}

assignment	freq, cm^{-1}	symmetry force constants ^a
A_1'	ν_1 502	$F_{11} = f_r + 2f_{rr} + 2f_{rr'} = 2.820$
A_2''	ν_2 274	$F_{22} = r^2(f_\gamma + 2f_{\gamma\gamma} \cos \alpha + 2f_{\gamma\gamma'} \cos 2\alpha) = 0.996$
E_1'	ν_3 465	$F_{33} = f_r + 2f_{rr} \cos \alpha + 2f_{rr'} \cos 2\alpha = 1.830$
		$F_{34} = r(f_{ra} + 2f_{ra'} \cos \alpha + 2f_{ra''} \cos 2\alpha) = -0.342$
	ν_4 290	$F_{44} = r^2(f_\alpha + 2f_{\alpha\alpha} \cos \alpha + 2f_{\alpha\alpha'} \cos 2\alpha) = 2.212$
E_2'	ν_5 423	$F_{55} = f_r + 2f_{rr} \cos 2\alpha + 2f_{rr'} \cos \alpha = 2.003$
		$F_{56} = r(f_{ra} + 2f_{ra'} \cos 2\alpha + 2f_{ra''} \cos \alpha) = 0$
	ν_6 377	$F_{66} = r^2(f_\alpha + 2f_{\alpha\alpha} \cos 2\alpha + 2f_{\alpha\alpha'} \cos \alpha) = 1.797$
E_2''	ν_7 79 ^b	$F_{77} = r^2(f_\gamma + 2f_{\gamma\gamma} \cos 2\alpha + 2f_{\gamma\gamma'} \cos \alpha) = 0.143$

^a Stretching constants in $\text{mdyn/\AA}$, deformation constants in $\text{mdyn \AA/rad}^2$, and stretch-bend interaction constants in mdyn/rad . ^b Value taken from the ab initio calculation.

in its $\text{N}(\text{CH}_3)_4^+$ salt are only very weakly coupled.⁴⁶ It also justifies the use of the assumed free anion symmetry in the subsequent vibrational analysis and force field calculations.

In the salts with smaller cations, stronger coupling of the XeF_5^- motions or slight distortions of the anions can occur, resulting in a splitting of the two E_2' modes into their doubly degenerate components. As expected, the anion-cation interaction is strongest for the NO^+ salt, causing some of the infrared-active modes, such as $\nu_3(E_1')$ and $\nu_4(E_1')$, also to become weakly active in the Raman spectrum.

In the infrared spectra two strong anion bands were observed above 250 cm^{-1} . The first one was a very intense broad band extending from 400 to 550 cm^{-1} , which must be due to the antisymmetric stretching mode $\nu_3(E_1')$. The second one is an intense band at 274 cm^{-1} , which, on the basis of its frequency and relative intensity, must be the symmetric out-of-plane (umbrella) deformation, $\nu_2(A_2'')$.

The third predicted infrared-active mode is the antisymmetric in-plane deformation, $\nu_4(E_1')$. Assuming the F_{66} and F_{44} symmetry force constants to be identical (both modes involve f_α and different combinations of $f_{\alpha\alpha}$ and $f_{\alpha\alpha'}$, with the latter being small due to the large mass of the xenon central atom), a frequency of 274 cm^{-1} was calculated for $\nu_4(E_1')$. Therefore, $\nu_4(E_1')$, which should be of medium infrared intensity, might either be hidden underneath the intense $\nu_2(A_2'')$ band at 274 cm^{-1} or occur just below the 250- cm^{-1} cutoff frequency of the AgBr windows used for our study. A frequency range 240–290 cm^{-1} for $\nu_4(E_1')$ is also supported by the Raman spectrum of $\text{NO}^+\text{XeF}_5^-$ (see Table IV). In this compound, where the anion-cation interaction is the strongest and the infrared-active modes become also weakly Raman active, two weak Raman bands were observed at 244 and 282 cm^{-1} , respectively. Furthermore, the infrared spectra of RbXeF_5 and CsXeF_5 exhibit a 288- cm^{-1} shoulder on the strong 275- cm^{-1} band, and the Raman spectra of all the alkali-metal XeF_5^- salts show an extremely weak band at about 290 cm^{-1} . Consequently, a frequency of 290 cm^{-1} was chosen by us for $\nu_4(E_1')$ and used for the force field computations. Our choice of 290 cm^{-1} for ν_4 is also supported by ab initio calculations for XeF_5^- (see below) and IF_7 .⁴⁷ Assuming the frequency differences between calculated and observed frequencies to be the same for the two in-plane deformation modes in XeF_5^- , a value of 291 cm^{-1} is predicted for ν_4 . Similarly, the

(46) A factor-group analysis of the vibrational modes of the unit cell was carried out by use of the correlation chart method (Carter, R. L. *J. Chem. Educ.* 1971, 48, 297 and references therein). The free anion symmetry (D_{5h}) was correlated to the site symmetry of the anion (C_2), which, in turn, was correlated to the crystal symmetry (D_{2h}). Assuming complete vibrational coupling occurs in the unit cell of $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$, all the vibrational modes of the XeF_5^- anion are found to be Raman- and infrared-active under the crystal symmetry. Moreover, ν_3 , ν_4 , ν_5 , ν_6 , and ν_7 will be split into four and three components in their Raman (A_g , B_{1g} , B_{2g} , B_{3g}) and infrared (B_{1u} , B_{2u} , B_{3u}) spectra, respectively; ν_1 will be split into two components in both the Raman (A_g , B_{3g}) and infrared (B_{1u} , B_{2u}) spectra and ν_2 will not be split in the infrared (B_{3u}) but will be split into two components in the Raman (B_{1g} , B_{2g}) spectrum.

(47) Bartell, L. S.; Rothman, M. J.; Gavezotti, A. *J. Chem. Phys.* 1982, 76, 4136 and references cited therein.

(44) Wilson, E. B. *J. Chem. Phys.* 1941, 9, 76.

(45) Khanna, R. K. *J. Mol. Spectrosc.* 1962, 8, 134.

Table VIII. Internal Force Constants (mdyn/Å) and Bond Length (Å) of XeF_5^- Compared with Those of XeF_2 , XeF_4 , and IF_4^-

force const	XeF_2^a	XeF_4^b	$\text{IF}_4^-^b$	$\text{XeF}_5^-^c$
f_r	2.83	3.055	2.221	2.096
f_{rr}	0.14	0.120	0.183	0.143
$f_{rr'}$		0.007	0.466	0.219
$f_a (-f_{aa'})$	0.20	0.193	0.182	0.458
$f (-f')$		0.299	0.257	0.072
$f_{aa} - f_{aa'}$				0.045
$f_a - f_{aa'}$				0.413
$f - f'$				0.093
$f - f'$				-0.021
r	1.98	1.953		2.012

^a Data from ref 53. ^b Data from ref 50. The f values in ref 49 have not been properly normalized and must be divided by two to correspond to the values from this work. ^c This work.

transfer of the computed frequency difference of 102 cm^{-1} for the two in-plane deformation modes from IF_7 to XeF_5^- results in a ν_4 value of 275 cm^{-1} for XeF_5^- .

The only missing fundamental vibration is the ring puckering mode, $\nu_7(\text{E}_2'')$, which ideally is inactive in both the infrared and Raman spectra. Since no experimental frequency is available for this mode, the frequency of 79 cm^{-1} obtained by the ab initio calculation (see below) was used.

In addition to the fundamental vibrations, numerous Raman bands were observed in the low-frequency region, which are attributed to lattice vibrations. The infrared spectra exhibit some weak bands above 600 cm^{-1} , which can be readily assigned to different overtones or combination bands of XeF_5^- (see Table IV).

In $\text{NO}^+\text{XeF}_5^-$ and $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$, cation bands were also observed (see Table IV) with frequency values that are in excellent agreement with previous literature data.^{4,5,7,48}

Force Constants. The symmetry force constants of XeF_5^- are shown in Table VII. Except for the E_1' and E_2' blocks, all of the symmetry force constants are one-dimensional and well determined. In the two-dimensional E_2' block, G_{56} equals zero (see Table VI), resulting in F_{56} also becoming zero. Therefore, the only remaining underdetermined problem is the two-dimensional E_1' block. The range of possible solutions for this block was computed by using the extremal conditions reported by Sawodny.⁴⁹ It has previously been pointed out⁴⁹⁻⁵² that in weakly coupled (heavy central atom) systems the values of the general valence force field tend to fall within the range given by $F_{34} = 0$ as the lower and $F_{34} = \frac{1}{2}[F_{34}(\text{max}) - F_{34}(\text{min})]$ as the upper limit with $F_{44} = \text{min}$ being an excellent choice. The latter choice results in an F_{33} value of 1.830 mdyn/Å with an error limit of about 0.14 mdyn/Å and, therefore, F_{33} can be considered to be reasonably well determined.

The most important internal force constants of XeF_5^- , together with the known bond length, are given in Table VIII and are compared with those of the closely related XeF_2 ,⁵³ and XeF_4 ,⁵⁰ molecules and the IF_4^- anion.⁵⁰ As can be seen from Table VIII, the force constants well reflect our expectations. Compared with XeF_2 and XeF_4 , the increased $\delta^+\text{Xe}-\text{F}^-$ polarity of the Xe-F bond in XeF_5^- , combined with the crowding effect in the equatorial plane, should decrease the Xe-F stretching (f_r), increase the in-plane deformation (f_a), and decrease the out-of-plane deformation (f_{rr}) force constants. Furthermore, ($f_{aa} - f_{aa'}$) and ($f_{rr} - f_{rr'}$) should exhibit positive signs as expected for adjacent angles interacting more strongly than nonadjacent angles. The excellent agreement between these expectations and the experimental values from Table VIII lends strong support to the above assignments for XeF_5^- .

Table IX. Calculated and Experimental Vibrational Frequencies (cm^{-1}) of XeF_4

assignment	calcd freq	obsd freq ^a	approx mode descriptn
$\text{A}_{1g} \nu_1$	532	543	ν_{sym} (in phase)
$\text{A}_{2u} \nu_2$	271	291	δ_{sym} (out of plane)
$\text{B}_{1g} \nu_3$	498	502	ν_{sym} (out of phase)
$\text{B}_{2g} \nu_4$	182	235	δ_{sym} (in plane)
$\text{B}_{2u} \nu_5$	156	inactive	δ_{asym} (out of plane)
$\text{E}_u \nu_6$	591	586	ν_{asym}
$\text{E}_u \nu_7$	143	123	δ_{asym} (in plane)

^a Data from ref 55.

Table X. Calculated and Experimental Vibrational Frequencies (cm^{-1}) for XeF_5^-

assignment	calcd freq			obsd freq	approx mode descriptn
	a	b	c		
$\text{A}_1' \nu_1$	467	537	551	502	ν_{sym} (in plane)
$\text{A}_2'' \nu_2$	270	274	275	274	δ_{sym} (out of plane)
$\text{E}_1' \nu_3$	502	574	585	400-550	ν_{asym}
$\text{E}_1' \nu_4$	248	255	254	290	δ_{asym} (in plane)
$\text{E}_2' \nu_5$	413	477	489	423	ν_{asym}
$\text{E}_2' \nu_6$	335	356	361	377	δ_{sym} (in plane)
$\text{E}_2'' \nu_7$	79	21	28i		δ_{asym} (out of plane)

^a With the calculated Xe-F bond length of 2.077 Å. ^b With an assumed Xe-F bond length of 2.022 Å. ^c With the observed Xe-F bond length of 2.012 Å.

The data in Table VIII demonstrate that the stretching force constants f_r are mainly influenced by the polarity of the Xe-F bonds, with increasing polarity decreasing the force constant. On the other hand, steric crowding has a strong impact on the deformation constants. If this crowding is anisotropic, as in the case of XeF_5^- where the crowding is concentrated in the equatorial plane, the deformation constants in the congested plane increase while the deformation constants out of the congested plane decrease significantly. The low value of the out-of-plane deformation constant f_{rr} , in combination with a comparable $f_{rr'}$ value, implies a low energy barrier toward puckering of the equatorial plane. When the f_{rr} value approaches zero or becomes negative, spontaneous puckering should occur.

Computational Results. For a better understanding of the molecular structure of XeF_5^- , local density functional calculations were carried out for this ion and for XeF_4 . The quality of these calculations for relatively large and heavy molecules was first tested for the well-characterized^{54,55} and closely related XeF_4 molecule. The well-known square-planar (D_{4h}) symmetry and a Xe-F bond length of 1.998 Å (0.045 Å longer than that observed for the solid⁵⁴) were obtained. The calculated vibrational frequencies are in excellent agreement with the experimental values⁵⁵ (Table IX), except for the in-plane deformation modes, where the agreement is only fair.

For XeF_5^- , the computations confirmed that the pentagonal planar D_{5h} structure is indeed a minimum. Again, the computed bond length (2.077 Å) is slightly longer (0.065 Å) than the observed one (2.012 Å). A comparison between the observed and calculated spectra is given in Table X. As for XeF_4 , the agreement between computed and observed frequencies for XeF_5^- is quite good, with the largest discrepancies again being found for the in-plane deformation modes. These results confirm the assignments made above for XeF_5^- .

The influence of the bond length on the vibrational spectrum of XeF_5^- was also examined by computing the spectra for two shorter Xe-F bond distances, one at the experimental bond length and one 0.01 Å longer (Table X). As expected, the stretching frequencies are the most sensitive to changes in the bond length except for the equatorial ring puckering mode, ν_7 , which is also

(48) Christie, K. O.; Wilson, W. W.; Bougon, R. A. *Inorg. Chem.* **1986**, *25*, 2163.

(49) Sawodny, W. *J. Mol. Spectrosc.* **1969**, *30*, 56.

(50) Christie, K. O.; Naumann, D. *Inorg. Chem.* **1973**, *12*, 59.

(51) Pfeiffer, M. *J. Mol. Spectrosc.* **1969**, *21*, 181.

(52) Thakur, S. N.; Rai, S. N. *J. Mol. Struct.* **1970**, *5*, 320.

(53) Siebert, H. *Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie*; Anorganische und Allgemeine Chemie in Einzeldarstellung, VII; Springer Verlag: Berlin, Germany, 1966.

(54) Burns, J. H.; Agron, P. A.; Levy, H. A. *Science* **1963**, *139*, 1208. Templeton, D. H.; Zalkin, A.; Forrester, J. D.; Williamson, S. M. *J. Am. Chem. Soc.* **1963**, *85*, 242. Ibers, J. A.; Hamilton, W. C. *Science* **1963**, *139*, 106.

(55) Claassen, H. H.; Chernick, C. L.; Malm, J. G. *J. Am. Chem. Soc.* **1963**, *85*, 1927.

Table XI. Valence Molecular Orbitals for XeF_5^-

symmetry	orbital ^a	energy, eV
A_2'	p_y anti on F	3.00
A_2''	p_z anti 0.67 Xe, 0.40 F	3.15
E_1'	p_y on F	3.71
A_1'	0.43 p_x on F, 0.57 s on Xe, anti	4.00
E_2''	p_z on F	4.06
E_1''	p_z on F some Xe d	4.69
E_2'	p_{xy} on F	4.78
E_2'	p_{xy} on F	5.72
A_2''	0.77 p_z Xe, 0.21 p_z F	7.38
E_1'	0.56 p_x , p_y Xe, 0.40 p_x on F	9.01
A_1'	0.89 Xe s	16.02

^a x = Xe-F bond axis, y = orthogonal to Xe-F axis in plane, z = orthogonal to Xe-F axis out of plane.

very sensitive to shortening of the bond length. At the experimental distance, the degenerate deformation frequency becomes imaginary, showing that the molecule would assume a nonplanar structure. As discussed above, increasing congestion in the equatorial ring will result in spontaneous puckering and an imaginary frequency for ν_7 . The calculations at the experimental geometry are far enough from the theoretical minimum that the calculated frequencies should be employed only to show the expected trends, as they do not refer to the minimum energy structure. The data in Table X also indicate that the frequency order of the Xe-F stretching modes is essentially independent of the Xe-F bond length. It should be noted that all the calculated frequencies are harmonic values and were not scaled to include anharmonicity effects, which are usually on the order of 5%.

The Mulliken charges for XeF_5^- are +1.48e for the Xe atom and -0.50e for the F atoms. This differs from the nominal assignments of -1.0e for each F and +4.0e for the Xe. The molecular orbitals (Table XI) provide some insight into the bonding in this molecule. If we consider only the valence p orbitals on F since the 2s orbitals are quite low in energy, the remaining orbitals can be qualitatively summed up as follows: There are 10 electrons in the $2p_y$ lone pairs on F orthogonal to the Xe-F bond. There are roughly 10 electrons in the $2p_z$ orbitals on F, which are orthogonal to the molecular plane. The totally symmetric group of these orbitals interacts with the out-of-plane $5p_z$ orbital on Xe in a symmetric and antisymmetric way. The $2p_x$ orbitals on fluorine along the Xe-F bond have about 10e in them. These mix with the $5p_x$ and $5p_y$ orbitals on Xe. Although the Xe 5s orbital does mix to some extent with the 2p orbitals on F, it is predominantly a lone pair. The basic description is thus a Xe with a $5s^2 5p_z^2$ occupancy surrounded by five F⁻ atoms. Delocalization of fluorine electron density into the Xe $5p_{xy}$ orbitals with only a small participation of the d orbitals on Xe then reduces the charges on the F atoms. The HOMO is the antibonding combination of the in-plane lone pairs on the F atom orthogonal to the Xe-F axis. The NHOMO is almost degenerate in energy with the HOMO and is the antibonding out-of-plane combination of the F $2p_z$ and the Xe $5p_z$ orbitals (Figure 8).

Both the orbitals and the bonding in XeF_5^- are quite similar to those of XeF_4 , which were calculated for comparison. In XeF_4 , the Mulliken charges on Xe and F are +1.65e and -0.41e, respectively. The Xe 5s orbital participates in two orbitals, with most of its density in the orbital at 22.02 eV just as in XeF_5^- . The $5p_z$ orbital of Xe and the out-of-plane $2p_z$ orbitals on the fluorines interact to give bonding and antibonding molecular orbitals. The orbital configuration at Xe is thus dominated by the $5s^2 5p_z^2$ configuration just as in the anion. The HOMO in XeF_4 is at 9.15 eV and is the $5p_y$ antibonding orbital as found in XeF_5^- . Its significantly higher value, compared with that of XeF_5^- , is in agreement with our expectations for an anion and its parent molecule.

It is important to note that the calculations provide a molecular orbital description of the bonding in XeF_5^- and XeF_4 . The orbitals reported above are the canonical orbitals with molecular symmetry. Because of the molecular symmetry, the 5s and $5p_z$ orbitals cannot mix and thus give separate s^2 and p^2 occupancies. In contrast,

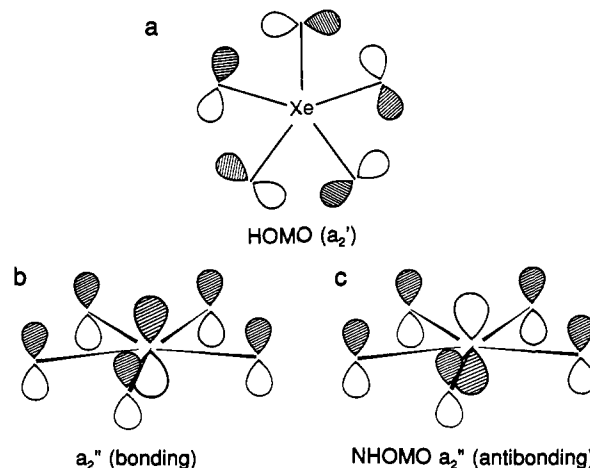


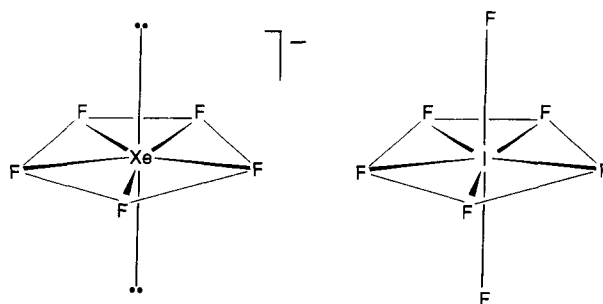
Figure 8. Selected molecular orbitals for XeF_5^- . (a) HOMO, antibonding combination of in-plane p_y 's on F; (b) bonding out-of-plane orbital combination between Xe $5p_z$ and p_z 's on F; (c) antibonding out-of-plane orbital combination between Xe $5p_z$ and p_z 's on F.

in the VSEPR model used elsewhere in this work, the valence electron lone pairs may be described as two doubly occupied sp hybrids above and below the plane, but this is not required by the VSEPR model. The two models are equivalent, as the VSEPR model is derived from a localized orbital approach, whereas the calculations are based on a molecular orbital approach. The sum and difference of the $5s^2$ and $5p_z^2$ orbitals will lead to the two sp hybrid lone pairs. However, the total electron density, which is the invariant quantity, is independent of the choice of models used to describe it. (In a formal sense, the wave function is invariant to a unitary transformation.)

Conclusions

Xenon tetrafluoride indeed forms stable adducts with strong Lewis bases, such as tetramethylammonium fluoride and the heavier alkali-metal fluorides. However, contrary to previous reports,¹³⁻¹⁵ these salts do not contain the XeF_6^{2-} dianion, but the XeF_5^- anion.

The XeF_5^- anion has a highly unusual pentagonal planar structure for which no other examples were previously known. It can be derived from that of a pentagonal bipyramid, such as IF_7 ,³⁸ in which the two axial fluorine ligands have been replaced by two sterically active free valence electron pairs. Compared with IF_7 ,



which is a fluxional molecule undergoing with relative ease a dynamic ring-puckering pseudorotation,^{38,47} the equatorial XeF_5 plane of XeF_5^- appears to be considerably more rigid. The increased rigidity of the XF_5 plane in XeF_5^- is attributed to the stabilizing effect of the two free valence electron pairs on xenon. These free pairs are more diffuse and hence more repulsive than the axial I-F bond pairs in IF_7 , thereby offering more resistance toward the puckering of the equatorial XeF_5 plane.

Acknowledgment. We thank C. J. Schack, W. W. Wilson, R. D. Wilson, and S. S. Tsai for their help; F. Adar, Instruments S.A.; Edison, NJ, for recording the single-crystal Raman spectrum of $\text{N}(\text{CH}_3)_4^+\text{XeF}_5^-$; the U.S. Air Force Astronautics Laboratory, Edwards AFB (K.O.C. and G.J.S.); the U.S. Army Research Office (K.O.C.) and the Natural Sciences and Engineering Re-

search Council of Canada (G.J.S.) for financial support; Ministry of Foreign Affairs, France, for a Lavoisier Fellowship (H.P.M.); and C.N.R.S. Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques, Montpellier, France, for granting a leave of absence to H.P.M.

Supplementary Material Available: Tables of anisotropic thermal parameters (Table 1) and hydrogen atomic coordinates (Table 2) (2 pages); tabulation of calculated and observed structure factor amplitudes (Table 3) (13 pages). Ordering information is given on any current masthead page.

Thermodynamics and Kinetics of Carbon Dioxide Binding to Two Stereoisomers of a Cobalt(I) Macrocycle in Aqueous Solution

Carol Creutz,* Harold A. Schwarz,* James F. Wishart, Etsuko Fujita, and Norman Sutin

Contribution from the Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973. Received October 1, 1991

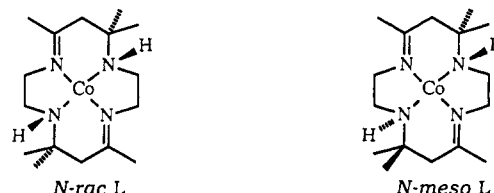
Abstract: The thermodynamics and kinetics of binding of CO_2 , CO , and H^+ to *N*-racemic and *N*-meso stereoisomers of the cobalt(I) macrocycle CoL^+ ($\text{L} = 5,7,7,12,14,14$ -hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) have been determined in aqueous media with use of the pulse radiolysis technique and transient ultraviolet–visible spectroscopy. *N*-rac- or *N*-meso- CoL^+ was produced by the hydrated electron reduction of *N*-rac- or *N*-meso- CoL^{2+} , with *tert*-butyl alcohol generally added to scavenge hydroxyl radicals. Reactions of both *N*-rac- and *N*-meso CoL^+ are readily followed by the disappearance of intense ($\epsilon = 1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) absorption bands at 630 and 635 nm, respectively. The product absorptions are much less intense ($\epsilon = 200\text{--}500 \text{ M}^{-1} \text{ cm}^{-1}$) and shifted to higher energy (400–500 nm). Carbon dioxide adducts were also produced via the reactions of *N*-rac- or *N*-meso- CoL^{2+} with formate radical $^{\bullet}\text{CO}_2^-$ in solutions containing sodium formate and CO_2 and hydrogen ion adducts (hydrides) by the reactions with $^{\bullet}\text{H}$ atom in acid solution. The known stereochemistry of the methyl radical additions to *N*-rac- and *N*-meso- CoL^{2+} was used to assign the different isomers of the adducts. Thus, reaction of $^{\bullet}\text{H}$ and $^{\bullet}\text{CO}_2^-$ with *N*-rac- CoL^{2+} yields *sec*-*N*-rac- $\text{CoL}(\text{H})^{2+}$ and *sec*-*N*-rac- $\text{CoL}(\text{CO}_2)^+$, respectively, and the reaction of *N*-rac- CoL^+ with H^+ and CO_2 yields *prim*-*N*-rac- $\text{CoL}(\text{H})^{2+}$ and *prim*-*N*-rac- $\text{CoL}(\text{CO}_2)^+$, respectively. As expected, only *N*-meso adducts are obtained from either *N*-meso- CoL^+ or *N*-meso- CoL^{2+} . Formation constants for the complexes (determined by analysis of equilibrium absorptions or equilibration kinetics) at 25 °C are $\text{CoL}(\text{CO}_2)^+$, $2.5 \times 10^8 \text{ M}^{-1}$ (*prim*-*N*-rac), $6.0 \times 10^6 \text{ M}^{-1}$ (*N*-meso); $\text{CoL}(\text{CO})^+$, $1.6 \times 10^8 \text{ M}^{-1}$ (*prim*-*N*-rac), $0.8 \times 10^8 \text{ M}^{-1}$ (*N*-meso); $\text{CoL}(\text{H})^{2+}$, $2.5 \times 10^{11} \text{ M}^{-1}$ (*prim*-*N*-rac), $\geq 7.9 \times 10^{13} \text{ M}^{-1}$ (*N*-meso). The rate constants are large and generally parallel the stability of the adduct. The following are values of k ($\text{M}^{-1} \text{ s}^{-1}$) for addition at 25 °C: CO_2 , 1.7×10^8 (*prim*-*N*-rac), 1.5×10^7 (*N*-meso); CO , 5.0×10^8 (*prim*-*N*-rac), 8.3×10^8 (*N*-meso); H^+ , 3.0×10^9 (*prim*-*N*-rac), 2.3×10^9 (*N*-meso).

Introduction

Cobalt complexes have attracted attention as potential catalysts for photo- and electroreduction of water to H_2 and of carbon dioxide to CO and HCO_2^- .^{1–5} The cobalt(I) complexes, which are accessible through photo- or electroinduced one-electron reduction of the cobalt(II) complexes, may bind hydrogen ion or carbon dioxide and, in some cases, facilitate their reduction. A particularly attractive family for systematic studies is the tetraazacyclotetradecyl macrocycle series,⁶ in which the cobalt(II)/(I) potential ranges from -0.34 to -1.65 V (versus SCE) in acetonitrile.⁷ In such a series, the relationships between metal reduction potentials, ligand steric factors, etc. and the reactivity of the complex toward both the binding and reduction of small molecules may be explored. Indeed, this problem is currently being studied by several groups.^{7–10}

Of the above series, the macrocycle $\text{L} = 5,7,7,12,14,14$ -(CH_3)₆-1,4,8,11-tetraazacyclotetradeca-4,11-diene has received the most intensive study to date. For this ligand, the Co(III)/(II)

and Co(II)/(I) reduction potentials are ca. -0.2 and -1.34 V , respectively, vs SCE in acetonitrile.⁷ The cobalt(III) complexes are six-coordinate, the low-spin d^7 cobalt(II) complexes appear to be five- or six-coordinate, and the low-spin d^8 cobalt(I) complexes are four- or five-coordinate.^{11,12} Stereoisomers of the complexes arise through the chirality of the saturated nitrogen atoms.¹³ Although *cis*- Co(III)LB ($\text{B} = \text{bidentate ligand}$) is known, most complexes of this series are trans, with the four nitrogen atoms of the macrocycle occupying the equatorial plane of the complex. At minimum, two trans isomers (*N*-meso and *N*-racemic) are possible. In aqueous solutions of the five- or



six-coordinate CoL^{2+} (the coordination sphere of the cobalt(II) being completed by solvent molecule(s)), the *N*-rac isomer is favored at equilibrium but the *N*-meso isomer can also be studied in $\text{pH} < 7$ solutions.¹² The low-spin $d^8 \text{ CoL}^+$ can also exist as either isomer, as will be seen. When the axial positions of the complex are asymmetrically substituted (CoLXY , X and Y different ligands), three isomers are possible—*N*-meso, primary *N*-rac, and

- (1) Brown, G. M.; Brunschwig, B. S.; Creutz, C.; Endicott, J. F.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 1298–1300.
- (2) Fisher, B.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7363–7366.
- (3) Pearce, D. J.; Pletcher, D. *J. Electroanal. Chem.* **1986**, *197*, 317.
- (4) Simpson, T. C.; Durand, R. R. *Electrochim. Acta* **1988**, *33*, 581.
- (5) Tinnemans, A. H. A.; Koster, T. P. M.; Thewissen, D. M. W. H.; Mackor, A. **1984**, *103*, 288.
- (6) Tait, A. M.; Lovaglio, F. V.; Busch, D. H. *Inorg. Chem.* **1977**, *16*, 2206.
- (7) Fujita, E.; Creutz, C.; Sutin, N.; Szalda, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 343–353.
- (8) Gangi, D. A.; Durand, R. R. *Chem. Soc., Chem. Commun.* **1986**, 697.
- (9) Creutz, C.; Schwarz, H. A.; Wishart, J. F.; Fujita, E.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 1153–4.
- (10) Schmidt, M. H.; Miskelly, G. M.; Lewis, N. S. *J. Am. Chem. Soc.* **1990**, *112*, 3420–3426.

- (11) Szalda, D. J.; Fujita, E.; Creutz, C. *Inorg. Chem.* **1989**, *28*, 1446–50.
- (12) Szalda, D. J.; Schwarz, C. L.; Endicott, J. F.; Fujita, E.; Creutz, C. *Inorg. Chem.* **1989**, *28*, 3214–19.
- (13) Warner, L. G.; Rose, N. J.; Busch, D. H. *J. Am. Chem. Soc.* **1968**, *90*, 6938–6946.

Syntheses, Properties, and Structures of Anhydrous Tetramethylammonium Fluoride and Its 1:1 Adduct with *trans*-3-Amino-2-butenitrile

Karl O. Christe,^{*,†} William W. Wilson,[†] Richard D. Wilson,[†] Robert Bau,[†] and Jin-an Feng[†]

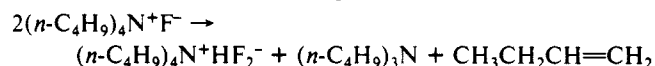
Contribution from Rocketdyne, A Division of Rockwell International, Canoga Park, California 91303, and the Department of Chemistry, University of Southern California, Los Angeles, California 90007. Received February 26, 1990

Abstract: A simple method for the preparation of anhydrous and essentially HF₂[−]-free N(CH₃)₄F is described. The compound was characterized by X-ray diffraction, NMR, infrared, and Raman spectroscopy. It crystallizes in the hexagonal system with a hexagonal closest packing of the N(CH₃)₄⁺ cations. It is shown that the free F[−] anion is a very strong Lewis base and chemically reacts with most of the solvents, such as CH₃CN or chlorinated hydrocarbons, previously used for studies of the fluoride anion. As a result, some of the properties previously reported for F[−] were due to HF₂[−] or other secondary reaction products. Its relatively simple synthesis and lower cost, combined with its good solubility and the high chemical inertness of the N(CH₃)₄⁺ cation, make N(CH₃)₄F an excellent substitute for presently used fluoride ion sources, such as either [(CH₃)₂N]₃S⁺F₂Si(CH₃)₃[−], which is commonly referred to as tris(dimethylamino)sulfonium fluoride, or CsF. The reaction of N(CH₃)₄F with CH₃CN results in the dimerization of CH₃CN and the formation of a 1:1 adduct of N(CH₃)₄F with this dimer, *trans*-3-amino-2-butenitrile. The crystal structure and vibrational spectra of this adduct are reported.

Introduction

The free fluoride anion is a very strong base and plays an important role in many organic and inorganic reactions.¹ Although alkali-metal fluorides are readily available, their low solubilities in most of the common solvents have rendered them of very limited practical use. Since the solubility of an ionic fluoride generally increases with increasing size of its counteranion, the solubility limitations of the alkali-metal fluorides could be overcome by the use of a larger counteranion. However, this large counteranion must be chemically inert toward the fluoride anion, solvents, and other reagents, and its fluoride salt must be readily accessible to make it of practical use.

Although tetraalkylammonium fluorides would appear to be ideally suited for this purpose, they have not been developed into widely used reagents because of the great experimental difficulties encountered with their syntheses in anhydrous form. Thus, the tetraalkylammonium fluorides are generally available only as hydrates that, upon attempted water removal, undergo an E₂ elimination reaction with the formation of bifluoride and an olefin. The observation of the following reaction



has prompted Sharma and Fry to conclude² that "it is very unlikely that pure, anhydrous tetraalkylammonium fluoride salts have ever, in fact, been produced in the case of ammonium ions susceptible to E₂ elimination; rather, reactions which have been reported to proceed in the presence of naked fluoride ion generated from such sources have probably actually been caused either by hydrated fluoride ion or by bifluoride ion". Although tetramethylammonium fluoride does not contain any carbon-carbon bond and, therefore, cannot undergo an E₂-type elimination reaction, Sharma and Fry's conclusion has also been applied to this compound, as evidenced by a recent statement^{3a} that N(CH₃)₄F "has never been obtained anhydrous and that removal of water results in decomposition". Similarly, Rieux and co-workers recently concluded^{3b} that "the naked fluoride is still a myth and not yet a reality". In view of these reports, it is not surprising that N(CH₃)₄F has not been exploited as a readily accessible, chemically inert, and highly soluble form of naked fluoride and that costly alternatives, such as tris(dimethylamino)sulfonium difluorotrimethylsilicate,⁴

[(CH₃)₂N]₃S⁺F₂Si(CH₃)₃[−], have been developed. Although the latter compound does not contain a free fluoride ion per se, the F₂Si(CH₃)₃[−] anion serves as an excellent fluoride ion donor toward stronger Lewis acids.

Recent work in our laboratory on the synthesis of the ClF₆[−] anion⁵ required a counteranion that was larger and more soluble than cesium and at the same time resisted chemical attack by ClF₅. Since ClF₅ reacts violently with H₂O and is a much weaker Lewis acid than HF, incapable of displacing it from HF₂[−], we needed H₂O- and HF₂[−]-free N(CH₃)₄F.

Numerous reports^{6–12} on the synthesis of tetramethylammonium fluoride can be found in the literature. They are based on two approaches. The first one dates back to 1888 and involves the neutralization of N(CH₃)₄OH with HF in aqueous solution, followed by water removal in vacuo at temperatures up to 160 °C.⁶ If the water is removed at various temperatures, intermediate N(CH₃)₄F·*n*H₂O-type hydrates can be isolated with *n* ranging from 1 to 5.¹³ The difficulty with this process is the removal of the last amounts of water from the N(CH₃)₄F, because at 160 °C the removal rate is still slow while the N(CH₃)₄F already begins to undergo a very slow decomposition.⁶ Thus, the products obtained by this method have been reported to contain significant amounts of impurities, attributed to either HF₂[−]⁹ or the monohydrate.¹⁰ In a minor modification⁸ of this method, the bulk of the water was removed from the aqueous N(CH₃)₄F solution in vacuo on a rotating evaporator. The resulting syrupy oils were converted to an N(CH₃)₄F·CH₃OH solvate by repeated treatment

(1) Young, J. A. *Fluorine Chem. Rev.* **1967**, *1*, 359.

(2) Sharma, R. K.; Fry, J. L. *J. Org. Chem.* **1983**, *48*, 2112.

(3) (a) Emsley, J. *Polyhedron* **1985**, *4*, 489. (b) Rieux, C.; Langlois, B.; Gallo, R. C. *R. Acad. Sci., Ser. 2*, **1990**, *310*, 25.

(4) (a) Middleton, W. J. U.S. Patent 3940402, Feb 1976. (b) Middleton, W. J. *Org. Synth.* **1985**, *64*, 221.

(5) Christe, K. O.; Wilson, W. W.; Schrobilgen, G. J.; Chirakal, R. *Inorg. Chem.*, in press.

(6) Lawson, A. T.; Collie, N. *J. Chem. Soc.* **1888**, *53*, 624.

(7) Musker, W. K. *J. Org. Chem.* **1967**, *32*, 3189.

(8) Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1968**, *7*, 155.

(9) Tunder, R.; Siegel, B. *J. Inorg. Nucl. Chem.* **1963**, *25*, 1097.

(10) Harmon, K. M.; Gennick, I.; Madeira, S. L. *J. Phys. Chem.* **1974**, *78*, 2585.

(11) Urban, G.; Dötzer, R. German Patent 1 191 813, May 1965.

(12) Cunico, R. F.; Han, Y. K. *J. Organomet. Chem.* **1978**, *162*, 1.

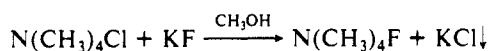
(13) Gennick, I.; Harmon, K. M.; Hartwig, J. *Inorg. Chem.* **1977**, *16*, 2241.

[†] Rocketdyne.

[†] University of Southern California.

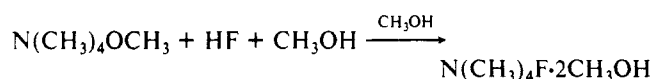
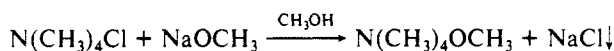
with CH₃OH and drying in vacuo at 100 °C.

The second approach utilizes metathetical reactions,⁹⁻¹² such as

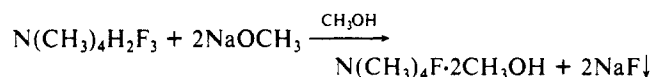
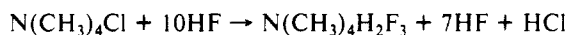


The resulting crude N(CH₃)₄F was purified by recrystallization from isopropyl alcohol.⁹ This synthetic method has frequently been used but, according to Klanberg and Muetterties,⁸ the N(CH₃)₄F prepared in this manner always contained at least 1–2% of chloride, while commercially available N(CH₃)₄F had an even higher Cl[−] content of 6.6%.

Another metathesis that has been described in a German patent¹¹ is based on the reaction of N(CH₃)₄Cl with HF and NaOCH₃ in CH₃OH to give N(CH₃)₄F·2CH₃OH. This solvate is then converted to N(CH₃)₄F by vacuum pyrolysis at 150 °C. The reaction of N(CH₃)₄Cl with HF and NaOCH₃ must be carried out in two separate steps. Reacting the N(CH₃)₄Cl first with NaOCH₃ according to



results in a more efficient use of the starting materials than the reverse sequence



According to Klanberg and Muetterties⁸ these NaOCH₃–HF-based processes suffer from the same drawback, i.e., Cl[−] impurities, as the N(CH₃)₄Cl + KF metathesis and the use of excess HF will generate HF₂[−] impurities.

Although some of the above chemistry dates back for more than 100 years,⁶ reliable analytical data, such as water analyses, detailed spectroscopic or structural data, and physical and chemical properties have not been reported for “anhydrous” N(CH₃)₄F. Therefore, it was also highly desirable to better characterize this important compound.

Experimental Section

Materials. The CH₃CN (Baker, Bio-analyzed, having a water content of 40 ppm) was treated with P₂O₅ and freshly distilled prior to use, thereby reducing its water content to <4 ppm. The N(CH₃)₄OH (Baker, analyzed, 10% aqueous solution), HF (Baker, analyzed, 50% aqueous solution), CH₃OH (Baker, absolute, 0.003% H₂O), and (CH₃)₂CHOH (Mallinckrodt, A.R., 0.03% H₂O) were used as received.

Apparatus. Volatile materials were handled either in a flamed-out Pyrex vacuum line equipped with Kontes Teflon valves or in the dry nitrogen atmosphere of a glovebox. Solids were manipulated exclusively in the drybox.

Raman spectra were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer by use of the 488-nm exciting line of an Ar ion or the 647.1-nm line of a Kr ion laser, respectively. Baked-out Pyrex melting point capillaries were used as sample holders. Infrared spectra were recorded as KBr disks on a Perkin-Elmer Model 283 spectrophotometer. For the exclusion of moisture, only KBr that had been fused and finely ground in the drybox was used. The KBr disks were pressed in a Wilks minipress inside the drybox, with the sample in a powdered KBr matrix being sandwiched between two prepressed layers of neat KBr, and the resulting sandwiches were left in the press for the recording of the spectra. The spectra obtained in this manner were identical with those obtained for pressed AgCl disks, indicating that no reaction between KBr and N(CH₃)₄F had occurred during the pressing operation.

The ¹⁹F and ¹H NMR spectra were measured at 84.6 and 90 MHz, respectively, on a Varian Model EM390 spectrometer, with 5-mm Teflon-FEP tubes (Wilmad Glass Co.) as sample containers and CFCI₃ and TMS, respectively, as internal standards, with negative shifts being upfield from the standards. A Perkin-Elmer differential scanning calorimeter, Model DSC-1B, was used to determine the thermal stability and to check for phase transitions. The samples were crimp-sealed in aluminum pans, and a heating rate of 10 °C/min in N₂ was used. The

Table I. Summary of Crystal Data and Refinement Results for the Tetramethylammonium Fluoride–3-Amino-2-butenenitrile Adduct

space group	P2 ₁ /C (monoclinic)
<i>a</i> (Å)	10.252 (3)
<i>b</i> (Å)	8.579 (2)
<i>c</i> (Å)	13.324 (3)
β (deg)	111.65 (2)
<i>V</i> (Å ³)	1089.2 (5)
molecules/unit cell	4
molecular weight	174.99
crystal dimensions (mm)	0.5 × 2.0 × 1.2
calculated density (g cm ^{−3})	1.071
wavelength (Å) used for data collection	0.71069
(sin θ)/λ limit (Å ^{−1})	0.539
total number of reflections measured	1493
number of independent reflections	1492
number of reflections used in structural analysis	1141
<i>I</i> > 3σ(<i>I</i>)	
number of variable parameters	181
final agreement factors	<i>R</i> (<i>F</i>) = 0.0387 <i>R</i> _w (<i>F</i>) = 0.0529

Table II. Bond Distances in the Tetramethylammonium Fluoride–3-Amino-2-butenenitrile Adduct

C2···N1	1.486 (2)	C3'···C2'	1.489 (2)
C3···N1	1.485 (2)	C4'···C2'	1.357 (1)
C4···N1	1.491 (2)	C5'···C4'	1.408 (2)
C5···N1	1.503 (2)	N6'···C5'	1.150 (2)
C2'···N1'	1.337 (2)		

Table III. Bond Angles (deg) in the Tetramethylammonium Fluoride–3-Amino-2-butenenitrile Adduct

C3–N1–C2	110.4 (1)	C3'–C2'–N1'	115.9 (1)
C4–N1–C2	109.3 (1)	C4'–C2'–N1'	122.6 (1)
C4–N1–C3	111.5 (1)	C4'–C2'–C3'	121.5 (1)
C5–N1–C2	108.1 (1)	C5'–C4'–C2'	121.8 (1)
C5–N1–C3	109.1 (1)	N6'–C5'–C4'	179.6 (1)
C5–N1–C4	108.3 (1)		

instrument was calibrated with the known melting points of *n*-octane and indium. Water contents were measured by the Karl Fischer method¹⁴ on a Photovolt Model Aquatest IV, with Teflon ampules as sample containers and plastic syringes for the sample injection.

X-ray diffraction patterns of powdered samples in sealed 0.5-mm quartz capillaries were obtained by using a General Electric Model XRD-6 diffractometer, Ni-filtered Cu Kα radiation, and a 114.6-mm-diameter Philips camera.

Crystal Structure of N(CH₃)₄F–*trans*-NH₂C(CH₃)=CHCN. Single crystals of N(CH₃)₄F–*trans*-NH₂C(CH₃)=CHCN were grown by allowing *n*-hexane vapors to diffuse slowly into a saturated solution of N(CH₃)₄F in CH₃CN. A rocklike crystal was mounted in a quartz capillary in the glovebox. A Nicolet/Syntex P2₁ automated four-circle diffractometer, with Mo Kα radiation and a graphite crystal monochromator, was used for the intensity data collection. The unit cell parameters were determined by least-squares refinement of 15 centered reflections. Data were collected with the ω-scan technique for all reflections such that 4.0° < 2θ < 45.0°. Throughout the data collection, three reflections were monitored periodically and no decay was observed. Of 1493 reflections collected, 1141 reflections with *I* > 3σ(*I*) were retained for the ensuing structure analysis.

The structure was solved by direct methods with the SHELXS86 system¹⁵ of crystallographic programs. The positions of all atoms were revealed after direct method analysis of the data. Subsequent least-squares refinements of the atomic coordinates, including positions of the hydrogen atoms, and thermal parameters resulted in final agreement values of *R* = 3.87% and *R*_w = 5.29%. Details of the data collection parameters and other crystallographic information are given in Table I, and the final atomic coordinates are listed in Table A (supplementary material). Interatomic distances and angles are given in Tables II and III, respectively. Figures 1 and 2 show a packing diagram for the N(CH₃)₄F adduct and the interactions of the fluorine atoms, respectively.

(14) Scholz, E. *Karl Fischer Titration, Methoden zur Wasserbestimmung*; Springer Verlag: Berlin, 1984.

(15) Sheldrick, G. M. *SHELX System of Crystallographic Programs*; University of Goettingen: West Germany, 1986.

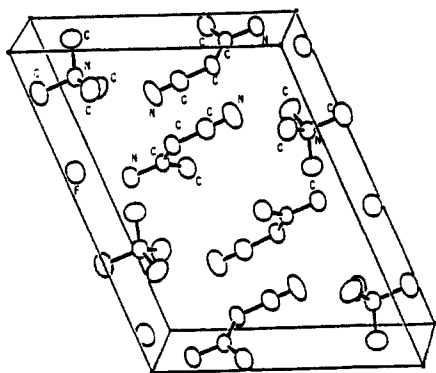


Figure 1. Packing diagram of $\text{N}(\text{CH}_3)_4\text{F}\text{-trans-H}_2\text{NC}(\text{CH}_3)\text{CHCN}$ viewed along the b axis.

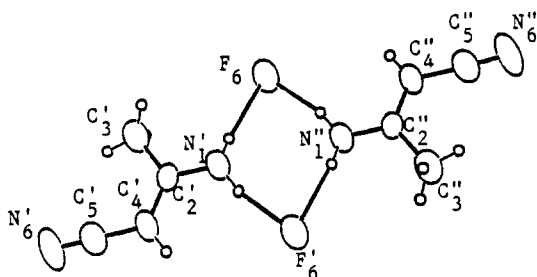


Figure 2. View of the molecular $\text{N}(\text{CH}_3)_4\text{F}\text{-H}_2\text{NC}(\text{CH}_3)\text{CHCN}$ unit showing the interactions of the fluorine atoms.

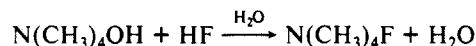
Synthesis of $\text{N}(\text{CH}_3)_4\text{F}$. The following generalized procedure was found to yield the purest samples of $\text{N}(\text{CH}_3)_4\text{F}$. Inside a glovebag purged by nitrogen or CO_2 -free air, a measured amount of a 10% aqueous $\text{N}(\text{CH}_3)_4\text{OH}$ solution was placed into a polyethylene beaker. With a pH electrode as an indicator and a Teflon-coated magnetic stirring bar for mixing, the $\text{N}(\text{CH}_3)_4\text{OH}$ solution was titrated with 50% aqueous HF to the exact equivalence point. Plasticware was used exclusively for the handling of the HF solution. The last few percent of the required HF was added slowly with a more dilute HF solution to avoid overshooting the end point. The resulting $\text{N}(\text{CH}_3)_4\text{F}$ solution was transferred into a round-bottom Pyrex flask, and the water was pumped off with a rotary film evaporator while the temperature was slowly raised toward 150°C . After most of the water had been removed at 150°C , the solid white residue was finely ground in a porcelain mortar in the dry N_2 atmosphere of a glovebox and then further pumped on at 150°C for several days until the weight became essentially constant, and the infrared absorption bands of $\text{N}(\text{CH}_3)_4\text{F}\cdot\text{H}_2\text{O}^{16}$ at 822 and 895 cm^{-1} showed an intensity comparable to or less than that of the weak $\text{N}(\text{CH}_3)_4^+$ band at 1203 cm^{-1} (see later text). The other main impurities present at this stage were small amounts of HF_2^- and, if glass equipment had been used, SiF_6^{2-} , which were readily monitored by their characteristic infrared absorptions^{17,18} at 1256 and at 708 and 728 cm^{-1} , respectively. In the drybox, the crude $\text{N}(\text{CH}_3)_4\text{F}$ was recrystallized by dissolving it in dry isopropyl alcohol and pumping off enough of the solvent to precipitate most of the $\text{N}(\text{CH}_3)_4\text{F}$, in the form of its alcoholate, out of the solution. The $\text{N}(\text{C}-\text{H}_3)_4\text{HF}_2$ and $[\text{N}(\text{CH}_3)_4]_2\text{SiF}_6$ impurities were enriched in the mother liquor, and the solvated isopropyl alcohol was removed from the recrystallized material in a dynamic vacuum at 80°C . The yield of purified $\text{N}(\text{CH}_3)_4\text{F}$ was about 80%, and material with a water content $\leq 0.06\text{ wt } \%$ and a trace of HF_2^- as the only detectable impurity was obtained in this manner. The quality of the product was checked for H_2O , isopropyl alcohol, HF_2^- , and SiF_6^{2-} contamination by Karl Fischer titration and infrared, Raman, and ^{19}F and ^1H NMR spectroscopy.

Thermal Decomposition of $\text{N}(\text{CH}_3)_4\text{F}$. Anhydrous $\text{N}(\text{CH}_3)_4\text{F}$ (7.08 mmol) was placed inside the glovebox into a flamed-out Pyrex vessel equipped with a Teflon valve. The vessel was connected to a Pyrex vacuum line and gradually heated in a dynamic vacuum to 230°C . The volatile products were separated by passage through two cold traps kept at -126 and -196°C . After 4 h, the pyrolysis was essentially complete. The Pyrex vessel contained 18 mg (0.06 mmol) of a white solid residue

that was identified by its infrared spectrum as $[\text{N}(\text{CH}_3)_4]_2\text{SiF}_6$. The -126°C trap contained $\text{N}(\text{CH}_3)_3$ (7.01 mmol), and the -196°C trap contained CH_3F (7.03 mmol).

Results and Discussion

Synthesis of Anhydrous $\text{N}(\text{CH}_3)_4\text{F}$. Our synthesis of anhydrous $\text{N}(\text{CH}_3)_4\text{F}$ is based on the method of Lawson and Collie from 1888, but incorporates the following improvements: (i) the neutralization step



is carried out in a CO_2 -free atmosphere to avoid the formation of carbonate or bicarbonate impurities; (ii) a pH electrode is used as an indicator to titrate exactly to the equivalence point of aqueous $\text{N}(\text{CH}_3)_4\text{F}$; (iii) only plastic (polyethylene or Teflon) equipment is used for the handling of the HF solution to avoid SiF_6^{2-} formation; (iv) the water is removed in a dynamic vacuum with a rotary film evaporator; (v) the bath temperature is precisely controlled to 150°C for the final water removal that is periodically monitored by the weight loss of the sample and by infrared spectroscopy; (vi) the crude product is azeotroped with isopropyl alcohol for additional water removal; and (vii) the azeotroped product is purified by recrystallization from dry isopropyl alcohol.

This process is capable of producing $\text{N}(\text{CH}_3)_4\text{F}$ in very high yield. The only significant loss of material is that retained in the mother liquor during the final recrystallization step. Water contents, based on Karl Fischer titrations of methanol solutions, as low as 0.06 wt % were obtained, with no detectable SiF_6^{2-} and only a trace of HF_2^- as an impurity. Since the process does not involve any chlorine-containing reagents, chloride contamination is precluded. The process is also readily scalable and was carried out on a 100-g scale without any complications.

Recrystallizations of the crude $\text{N}(\text{CH}_3)_4\text{F}$ from either CH_3CN or CH_3OH were also studied, but are inferior to that using isopropyl alcohol. Methanol does not form an azeotrope with H_2O , and its solvate with $\text{N}(\text{CH}_3)_4\text{F}$ is considerably more stable than that of isopropyl alcohol, thus rendering the CH_3OH removal more difficult. Acetonitrile reacts with the free fluoride ion (see later text), resulting in significant material losses and the formation of $\text{N}(\text{CH}_3)_4\text{HF}_2$ and $\text{N}(\text{CH}_3)_4\text{F}\text{-NH}_2\text{C}(\text{CH}_3)=\text{CHCN}$ as potential contaminants.

Properties of $\text{N}(\text{CH}_3)_4\text{F}$. The compound is a white, crystalline, hygroscopic solid that starts to decompose slowly in a dynamic vacuum at about 170°C . The previously postulated⁶ decomposition path



was confirmed by a quantitative vacuum pyrolysis at $210\text{--}230^\circ\text{C}$. The only byproduct obtained in the pyrolysis was a trace of $[\text{N}(\text{CH}_3)_4]_2\text{SiF}_6$ that had been formed by handling of the material in glass. The $\text{N}(\text{CH}_3)_4\text{F}$ is highly soluble in water and alcohols with which it tends to form solvates, in partially chlorinated hydrocarbons with which it undergoes a ready chlorine-fluorine exchange,¹⁹ and in CH_3CN from which it readily abstracts a proton resulting in the formation of CH_2CN^- , $\text{NH}_2\text{C}(\text{CH}_3)=\text{CHCN}$, and HF_2^- .²⁰ It is also soluble in formamide; however, the ^{19}F NMR signal in this solvent is very broad (about 200 Hz at 25°C), indicating strong interaction with the solvent. Furthermore, $\text{N}(\text{CH}_3)_4\text{F}$ dissolves exothermically in acetone, exhibiting originally a signal at about -103.6 ppm that rapidly decays giving rise to a new signal at about -103.0 ppm . It dissolves also in nitromethane with a faint yellow color showing a ^{19}F signal at -150 ppm . It thus appears that in most solvents in which $\text{N}(\text{C}-\text{H}_3)_4\text{F}$ is soluble, strong interactions with the solvent occur. The most inert solvent found to date is CHF_3 (bp -84.4°C , mp -160°C). At -80°C , CHF_3 dissolves 4.4 wt % of $\text{N}(\text{CH}_3)_4\text{F}$ and the only ^{19}F signal observed in addition to the solvent peak is a singlet with a line width of about 7 Hz at -107 ppm for the fluoride ion. There was no evidence for hydrogen abstraction and HF_2^- for-

(16) Harmon, K. M.; Gennick, I. *Inorg. Chem.* **1975**, *14*, 1840.

(17) Wilson, W. W.; Christe, K. O.; Feng, J.; Bau, R. *Can. J. Chem.* **1989**, *67*, 1898.

(18) Siebert, H. *Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie*; Springer Verlag: Berlin, 1966.

(19) Christe, K. O.; Wilson, W. W. *J. Fluorine Chem.* **1990**, *46*, 339.

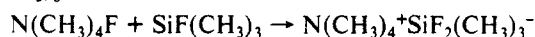
(20) Christe, K. O.; Wilson, W. W. *J. Fluorine Chem.* **1990**, *47*, 117.

Table IV. ^{19}F NMR Shifts (ppm Upfield from CFCl_3) of Tetramethylammonium Fluoride in Various Solvents

$(\text{CH}_3)_2\text{SO}$	-73	CH_3COCH_3	-103	$(\text{CH}_3)_2\text{CHOH}$	-122
CH_3CN	-74	CHF_3	-107	$\text{C}_2\text{H}_5\text{OH}$	-137
H_2NCHO	-96	CHCl_3	-113	CH_3OH	-148
CH_2Cl_2	-97	H_2O	-119	CH_3NO_2	-150

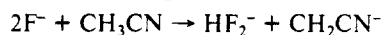
mation under these conditions. When the CHF_3 solvent is pumped off from the $\text{N}(\text{CH}_3)_4\text{F}$ at -78°C , a CHF_3 adduct of approximately a 1:1 composition was obtained that dissociates at a higher temperature reversibly to $\text{N}(\text{CH}_3)_4\text{F}$ and CHF_3 . Low-temperature Raman spectra of this adduct showed only minor frequency shifts compared to the starting materials, indicating weak interaction. In some other solvents such as hexane, dimethoxyethane, ethyl acetate, propylene carbonate, dimethylformamide, benzene, 1,2-difluorobenzene, tetrahydrofuran, dioxane, trichlorofluoromethane, sulfonyl chloride fluoride, sulfolane, or carbon disulfide, however, little or no solubility of $\text{N}(\text{CH}_3)_4\text{F}$ was observed by ^{19}F NMR spectroscopy. Whereas the proton resonance of the $\text{N}(\text{CH}_3)_4^+$ cation exhibits the expected chemical shift and coupling constant ($\delta = 3.1$, $J_{\text{H}^{14}\text{N}} = 0.6$ Hz),²⁰ the observed ^{19}F NMR shifts of the fluoride anion are highly solvent dependent,²⁰ as can be seen in Table IV, and strongly deviate from those previously reported.²¹ The trend in chemical shifts for $^{19}\text{F}^-$ in different solvents relative to those of $^{35}\text{Cl}^-$ ions in the same solvents is similar to that observed for ^{129}Xe relative to Cl^- . Therefore, this solvent dependency cannot be attributed to varying degrees of hydrogen bonding between F^- and protons of the solvents.²²

Chemically, the free fluoride anion in $\text{N}(\text{CH}_3)_4\text{F}$ acts, as expected, as a very strong Lewis base and readily complexes with suitable Lewis acids, such as BF_3 ,²³ PF_5 ,²³ SbF_5 ,²⁴ HF ,¹⁷ SiF_4 , SF_4 ,⁹ etc., forming the corresponding complex fluoro anions. In the absence of good fluoride acceptor molecules, it can abstract even relatively firmly bound protons from compounds such as CH_3CN .¹⁹ The $\text{N}(\text{CH}_3)_4^+$ cation is coordinatively saturated and, due to the relatively high strength of the carbon–nitrogen bond, possesses a high activation energy toward chemical reactions. Compared to the tris(dimethylamino)sulfonium cation, TAS^+ ,⁴ the $\text{N}(\text{CH}_3)_4^+$ cation is chemically much more inert as shown, for example, by its ability to form a stable ClF_4^- salt.²⁵ On the other hand, TAS^+ salts are more soluble and are also thermally more stable. This was shown by complexing $\text{N}(\text{CH}_3)_4\text{F}$ with $\text{SiF}(\text{CH}_3)_3$.



The resulting $\text{N}(\text{CH}_3)_4^+\text{SiF}_2(\text{CH}_3)_3^-$ salt was found to be of only marginal stability at room temperature, whereas $\text{TAS}^+\text{SiF}_2(\text{CH}_3)_3^-$ is stable up to its melting point of $98\text{--}101^\circ\text{C}$.⁴ Thus, the main advantages of $\text{N}(\text{CH}_3)_4^+$ over $[(\text{CH}_3)_2\text{N}]_3\text{S}^+$ are its lower cost and increased chemical inertness.

Crystal Structure of Tetramethylammonium Fluoride. Although the crystal structures of $\text{N}(\text{CH}_3)_4\text{Cl}$, $\text{N}(\text{CH}_3)_4\text{Br}$, and $\text{N}(\text{CH}_3)_4\text{I}$ are well-known^{26–29} and exhibit interesting polymorphism, no crystal data were previously available for $\text{N}(\text{CH}_3)_4\text{F}$. Our attempts failed to grow single crystals of pure $\text{N}(\text{CH}_3)_4\text{F}$ that were suitable for an X-ray diffraction study. With CH_3CN , hydrogen abstraction occurs¹⁹ resulting in the formation of CH_2CN^-



(21) Hudlicky, M. *J. Fluorine Chem.* **1985**, 28, 461.

(22) Carmona, C.; Eaton, G.; Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* **1987**, 873.

(23) Köksal, F.; Celik, F.; Cakir, O. *Radiat. Phys. Chem.* **1989**, 33, 135 and references cited therein.

(24) Heyns, A. M.; De Beer, W. H. *Spectrochim. Acta, Part A* **1983**, 39A, 601.

(25) Wilson, W. W.; Christe, K. O. *Inorg. Chem.* **1989**, 28, 4172.

(26) Cheban, Yu. M.; Dvorkin, A. A.; Rotaru, V. K.; Malinovsky, T. I. *Sov. Phys.-Crystallogr.* **1987**, 32, 604.

(27) Pistorius, C. W. F. T.; Gibson, A. A. V. *J. Solid State Chem.* **1973**, 8, 126.

(28) Dufourcq, J.; Haget-Bouillaud, Y.; Chanh, N. B.; Lamanceau, B. *Acta Crystallogr., Sect. B* **1972**, B28, 1305.

(29) Wyckoff, R. W. G. *Crystal Structures*, 2nd ed.; John Wiley & Sons: New York, **1962**, Vol. 1.

Table V. X-ray Powder Data^a for $\text{N}(\text{CH}_3)_4\text{F}$

$d(\text{obsd})$, Å	$d(\text{calcd})$, Å	intens	h	k	l
5.35	5.356	vs	1	0	0
4.57	4.577	s	1	0	1
4.40	4.406	ms	0	0	2
3.398	3.403	mw	1	0	2
3.092	3.092	m	1	1	0
2.677	2.678	m	2	0	0
2.565	2.562	ms	2	0	1
2.530	2.531	ms	1	1	2
2.290	2.289	mw	2	0	2
2.202	2.203	w	0	0	4
1.979	1.979	m	2	0	3
1.838	1.839	mw	2	1	2
1.794	1.794	w	1	1	4
1.751	1.750	w	3	0	1
1.667	1.667	mw	2	1	3

^a Hexagonal; $a = 6.185$ Å, $c = 8.812$ Å; Cu K α radiation, Ni filter.

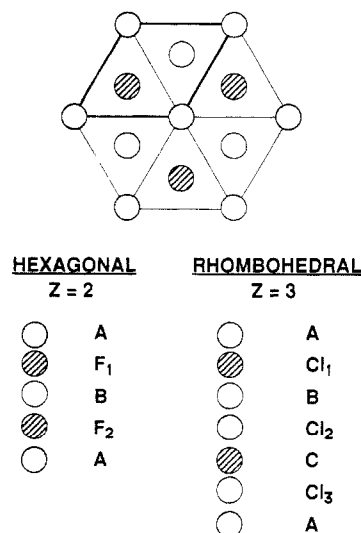
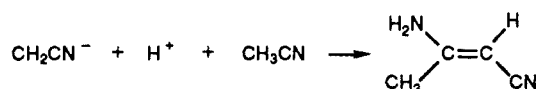


Figure 3. Packing arrangements for the hexagonal anion and cation layers in hexagonal $\text{N}(\text{CH}_3)_4\text{F}$ and rhombohedral $\text{N}(\text{CH}_3)_4\text{Cl}$, viewed along the c axis. The actual unit cell is marked by a heavier line.

followed by its reaction with CH_3CN to give *trans*-3-amino-2-butenitrile³⁰



which forms a 1:1 adduct with $\text{N}(\text{CH}_3)_4\text{F}$ (see later text). Thus, all the single crystals obtained during this study from CH_3CN solutions were either the tetramethylammonium bifluoride¹⁷ or the 1:1 adduct of $\text{N}(\text{CH}_3)_4\text{F}$ with *trans*-3-amino-2-butenitrile (see later text). In chlorinated solvents, rapid halogen exchange was observed,²⁰ while from alcoholic solutions only solvates of $\text{N}(\text{CH}_3)_4\text{F}$ were obtained. Therefore, our structure determination of $\text{N}(\text{CH}_3)_4\text{F}$ was limited to powder data.

The observed powder pattern is given in Table V. It can be indexed for a hexagonal unit cell with $a = 6.185$, $c = 8.812$ Å, $Z = 2$, and a calculated density of 1.058 g cm^{-3} . The hkl indices show no restrictions indicating a primitive lattice, and the presence of two molecules per unit cell precludes the possibility of a rhombohedral unit cell. Since the observed c/a value of 1.42 strongly deviates from 1.63, a zincite-type structure is highly unlikely^{29,31} and $\text{N}(\text{CH}_3)_4\text{F}$ most likely possesses an *anti*-NiAs-type structure. In the latter, the $\text{N}(\text{CH}_3)_4^+$ cation would be surrounded by six fluoride anions located at the corners of a trigonal prism, while the fluoride anion would be surrounded by six $\text{N}(\text{CH}_3)_4^+$

(30) Krüger, C. *J. Organomet. Chem.* **1967**, 9, 125.

(31) Krebs, H. *Grundzüge, der Anorganischen Kristallchemie*; Ferdinand Enke Verlag: Stuttgart, **1968**; p 122.

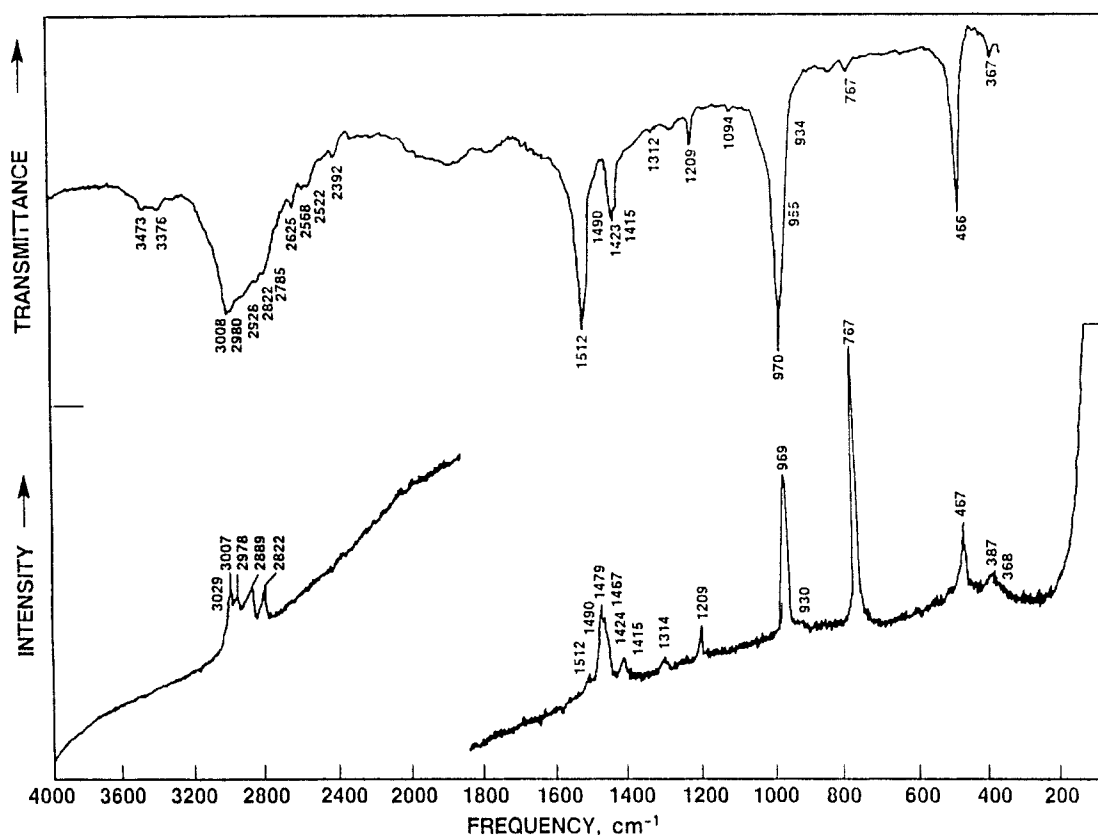


Figure 4. Infrared and Raman spectra of solid $\text{N}(\text{CH}_3)_4\text{F}$.

cations and two other fluoride anions.^{29,31}

It is interesting to compare the structure of $\text{N}(\text{CH}_3)_4\text{F}$ with that of $\text{N}(\text{CH}_3)_4\text{Cl}$. The latter exhibits five phases: two low-temperature phases and a tetragonal room-temperature phase that is irreversibly transformed at 140 °C to a room-temperature stable, rhombohedral phase, which in turn reversibly changes at 263 °C to a face-centered cubic high-temperature phase.²⁷ The tetragonal room-temperature phase is a hydrated phase that exists only in the presence of a small amount of water.²⁸

The main difference between the rhombohedral $\text{N}(\text{CH}_3)_4\text{Cl}$ and the hexagonal $\text{N}(\text{CH}_3)_4\text{F}$ phases consists of the stacking arrangements of the hexagonal anion and cation layers. In $\text{N}(\text{CH}_3)_4\text{F}$, the cations are arranged in a hexagonal closest packing with $Z = 2$ and alternating AB layers, while in rhombohedral $\text{N}(\text{CH}_3)_4\text{Cl}$ they are stacked in a cubic closest packing with $Z = 3$ and alternating ABC layers³¹ (see Figure 3). In $\text{N}(\text{CH}_3)_4\text{F}$, the two fluoride anions are located above each other within the unit cell, while in $\text{N}(\text{CH}_3)_4\text{Cl}$ the three chloride anions occupy all three possible positions. This difference can be explained by the larger radius and space requirement of Cl^- versus F^- .

No evidence was found by DSC measurements between 30 and 330 °C for a phase transition from the hexagonal to a higher temperature phase. The only observed effect was the onset of endothermic decomposition at about 210 °C.

Vibrational Spectra of $\text{N}(\text{CH}_3)_4\text{F}$. The infrared and Raman spectra of solid $\text{N}(\text{CH}_3)_4\text{F}$ are shown in Figure 4. The observed frequencies and their assignments^{17,32–35} are summarized in Tables VI and G (supplementary material).

The previous literature data on the vibrational spectra of $\text{N}(\text{CH}_3)_4\text{F}$ had been limited to incomplete infrared spectra of Nujol and Fluorolube mulls in the NaCl region.^{10,16} Whereas the antisymmetric NC_4 stretching and the CH_3 deformation modes had been properly assigned,¹⁰ the CH_3 rocking mode, $\nu_{17}(\text{F}_2)$, had been incorrectly attributed to an HF_2^- impurity band at 1263 cm^{-1} .

Table VI. Vibrational Spectra of Solid $\text{N}(\text{CH}_3)_4\text{F}$ and Their Assignment

obsd freq, cm^{-1} (rel intens)		assgnt in pt gp T_d
IR	Raman	
3473 w, br		$\nu_{\text{CH}_3} + \nu_{19}$
3376 w, br		$\nu_{\text{CH}_3} + \nu_8$
3030 sh	3029 sh	ν_{CH_3} and binary bands
3008	3007 (2)	
2980	2978 (1.3)	
2928	2889 (1.9)	
2822	2822 (1.4)	
2785		
2625 w		$\nu_7 + \nu_{16}, 2\nu_{17}$
2568 w		$\nu_3 + \nu_8 + \nu_{16}$
2522 w		$\nu_7 + \nu_{17}$
2392 w		$\nu_{16} + \nu_{18}$
1880 w, vbr		$\nu_8 + \nu_{15}$
1770 w, br		$\nu_{17} + \nu_{19}$
1512 s	1512 (0.4)	ν_{15}
1490 sh	1490 sh	
	1479 (2.9)	ν_6
	1467 sh	ν_2
1423 m	1424 (0.7)	ν_{16}
1415 sh	1415 sh	
1312 vw	1314 (0.4)	ν_{17}
1209 w	1209 (1.3)	ν_7
1094 vw		3×367 or ν_{11}
970 vs	969 (5.8)	ν_{18}
955 sh		
934 sh	930 (0.2)	$2\nu_{19}$
767 vw	767 (10)	ν_3
466 ms	467 (2.4)	ν_{19}
	387 (0.4)	ν_8
	368 (0.3)	ν_8 or ν_{12}
367 w		

As shown by our study, this mode occurs at 1312 cm^{-1} , in excellent agreement with the values of 1293, 1297, and 1299 cm^{-1} observed for the corresponding iodide, bromide, and chloride salts.³³

Furthermore, the previous predictions made from these partial IR data, that $\text{N}(\text{CH}_3)_4\text{F}$ should be tetragonal,¹⁰ were ill founded,

(32) Berg, R. W. *Spectrochim. Acta, Part A* 1978, 34A, 655.

(33) Bottger, G. L.; Geddes, A. L. *Spectrochim. Acta* 1965, 21, 1708.

(34) Kabisch, G.; Klose, M. *J. Raman Spectrosc.* 1978, 7, 312.

(35) Kabisch, G. *J. Raman Spectrosc.* 1980, 9, 279.

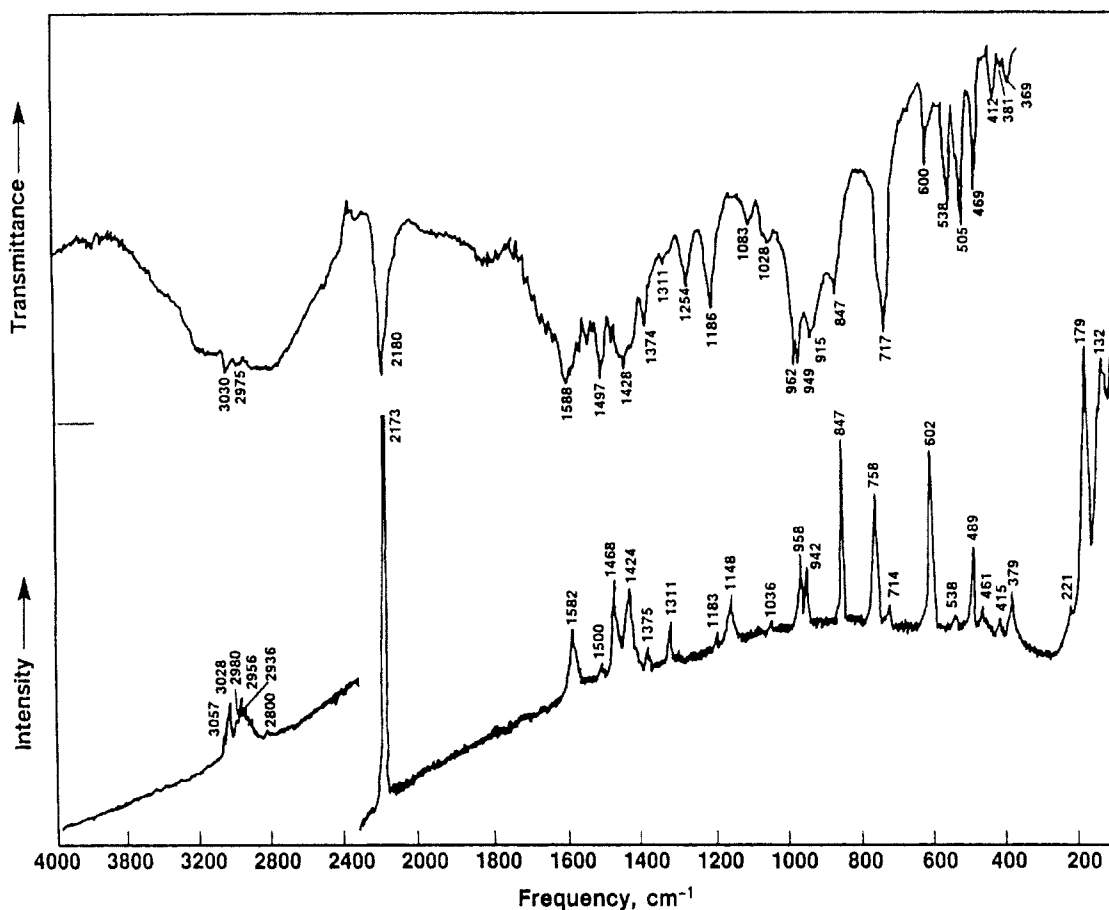


Figure 5. Infrared and Raman spectra of solid $\text{N}(\text{CH}_3)_4\text{F} \cdot \text{H}_2\text{NC}(\text{CH}_3)\text{CHCN}$.

as demonstrated by the above X-ray diffraction data showing the compound to be hexagonal.

The assignments for $\text{N}(\text{CH}_3)_4\text{F}$ can be derived from those of the free $\text{N}(\text{CH}_3)_4^+$ cation. As a free ion, $\text{N}(\text{CH}_3)_4^+$ belongs to the point group T_d and has 19 fundamental vibrations that are classified as $3A_1 + A_2 + 4E + 4F_1 + 7F_2$. Of these, only the F_2 modes are infrared and the A_1 , E , and F_2 modes Raman active.³² In the solid state, the number of fundamentals can increase and the selection rules be violated due to effects, such as distortion of the $\text{N}(\text{CH}_3)_4^+$ tetrahedron, site symmetries lower than T_d , and factor group splittings. Thus, the deviations of the observed spectra from the T_d selection rules, coupled with crystallographic information, can be used to judge the degree of deformation of the $\text{N}(\text{CH}_3)_4^+$ from tetrahedral symmetry.³⁵ On the basis of a comparison of the Raman spectrum of the free $\text{N}(\text{CH}_3)_4^+$ ion with those of cubic $[\text{N}(\text{CH}_3)_4]_2\text{SnCl}_6$, hexagonal $\text{N}(\text{CH}_3)_4\text{CdCl}_3$, monoclinic $\text{N}(\text{CH}_3)_4\text{HgCl}_3$, and tetragonal $\text{N}(\text{CH}_3)_4\text{ClO}_4$, $\text{N}(\text{C}_2\text{H}_5)_4\text{NO}_3$, $\text{N}(\text{CH}_3)_4\text{Cl}$, $\text{N}(\text{CH}_3)_4\text{Br}$, and $\text{N}(\text{CH}_3)_4\text{I}$, Kabisch has derived empirical rules for estimating, from the vibrational spectra, the degree of distortion of the $\text{N}(\text{CH}_3)_4^+$ cation.³⁵

A comparison of our $\text{N}(\text{CH}_3)_4\text{F}$ spectra (see Figure 4 and Table VI) with the data³⁵ of Kabisch shows that the spectrum of the $\text{N}(\text{CH}_3)_4^+$ cation in solid $\text{N}(\text{CH}_3)_4\text{F}$ is very similar to those of the free $\text{N}(\text{CH}_3)_4^+$ cation and of the very weakly distorted $\text{N}(\text{CH}_3)_4^+$ cation in $[\text{N}(\text{CH}_3)_4]_2\text{SnCl}_6$. Therefore, it can be concluded that in $\text{N}(\text{CH}_3)_4\text{F}$ the distortion of the $\text{N}(\text{CH}_3)_4^+$ cation from tetrahedral symmetry must also be minimal. This finding is not unexpected since Kabisch has also shown that within the $\text{N}(\text{CH}_3)_4\text{I}$, $\text{N}(\text{CH}_3)_4\text{Br}$, and $\text{N}(\text{CH}_3)_4\text{Cl}$ series the cation distortion decreases with decreasing anion size.³⁵ Therefore, repulsion effects are more important than electrostatic effects, and fluoride should be the least distorting.

On the basis of the broadness of the CH_3 stretching bands in its infrared spectrum, $\text{CH} \cdots \text{F}$ hydrogen bonding has previously been postulated for $\text{N}(\text{CH}_3)_4\text{F}$.¹⁰ This postulate requires further substantiation since the CH_3 deformation modes show no evidence

for similar broadenings and the widths of the CH_3 stretching infrared bands can be readily explained by the Fermi resonance bands also observed in the Raman spectra of the free $\text{N}(\text{CH}_3)_4^+$ ion.^{32,34,35}

Since infrared spectroscopy is a very useful technique to analyze $\text{N}(\text{CH}_3)_4\text{F}$ for impurities, we have scrutinized all the weak infrared features. In our opinion, essentially all of the weak bands shown in Figure 4 belong to $\text{N}(\text{CH}_3)_4\text{F}$. The most common impurities in $\text{N}(\text{CH}_3)_4\text{F}$ are HF_2^- , SiF_6^{2-} , $\text{F}^- \cdot n\text{H}_2\text{O}$, and different solvates. All of these are readily detected by their characteristic absorptions, most of which are given in the Experimental Section.

$\text{N}(\text{CH}_3)_4\text{F} \cdot \text{trans-H}_2\text{NC}(\text{CH}_3)=\text{CHCN}$ Adduct. As already mentioned, the fluoride anion can abstract a proton from CH_3CN , and the resulting CH_2CN^- anion can react with a second CH_3CN molecule and a proton to give the rearranged acetonitrile dimer, 3-amino-2-butenitrile. During attempts to grow single crystals of $\text{N}(\text{CH}_3)_4\text{F}$ by allowing *n*-hexane to slowly diffuse into a saturated CH_3CN solution, large single crystals were obtained that were characterized by X-ray diffraction and vibrational spectroscopy as a 1:1 adduct between $\text{N}(\text{CH}_3)_4\text{F}$ and *trans*-3-amino-2-butenitrile (I).

The crystal structure of I is shown in Figures 1 and 2, and the pertinent crystallographic data are summarized in Tables I–III and A–F. The monoclinic unit cell of I consists of layers of $\text{N}(\text{CH}_3)_4\text{F}$ that are separated by four molecules of the aminobutenitrile. To maximize the packing density, the four aminobutenitrile molecules are arranged in four different orientations, with the linear $\text{C} \equiv \text{C} \equiv \text{N}$ groups pointing alternately to the left and to the right and the



groups forward and backward (see Figure 1). The F^- anion forms two weak bridges to two hydrogen atoms from two different $-\text{NH}_2$ groups at 1.808 and 1.856 Å, respectively, with the remaining

distances to other hydrogens being considerably longer than the sum of the van der Waals radii. As a result, the tetramethylammonium cation shows little distortion and is essentially tetrahedral.

The bond distances and angles found for the $\text{H}_2\text{N}-\text{C}(\text{C}-\text{H}_3)=\text{CH}-\text{CN}$ part of the adduct agree well with those predicted from the known structures of the similar molecules, CH_3CN , $\text{NC}-\text{CN}$, $\text{CH}_2=\text{CH}_2$, CH_3CHO , H_2NCHO , and CH_3COCN .³⁶

The infrared and Raman spectra of the $\text{N}(\text{CH}_3)_4\text{F}-\text{H}_2\text{NC}(\text{C}-\text{H}_3)\text{CHCN}$ adduct are given in Figure 5. The sizes of the molecules involved, the low crystal symmetry, and the large unit cell make detailed assignments difficult. However, the following vibrations can be readily assigned: $\nu(\text{C}\equiv\text{N})$, 2173; $\nu(\text{C}=\text{C})$, 1582; $\nu_{\text{as}}(\text{NC}_4)$, 958, 942; $\nu_{\text{s}}(\text{NC}_4)$, 758; $\delta_{\text{as}}(\text{NC}_4)$, 469 cm^{-1} . The intense and narrow $\text{C}\equiv\text{N}$ stretching vibration at 2173–2180 cm^{-1} is very useful for checking for the presence of the nitrile adduct in $\text{N}(\text{CH}_3)_4\text{F}$ that has been handled in CH_3CN .

Conclusion

Contrary to the general belief that $\text{N}(\text{CH}_3)_4\text{F}$ cannot be obtained anhydrous and that removal of water results in decomposition,³ it was shown in this study that $\text{N}(\text{CH}_3)_4\text{F}$ with a water content of ≤ 0.06 wt % can be prepared with relative ease. This synthesis of anhydrous $\text{N}(\text{CH}_3)_4\text{F}$ provides a relatively cheap source of highly soluble fluoride containing a chemically very inert

counteranion. Thus, anhydrous $\text{N}(\text{CH}_3)_4\text{F}$ might become an attractive substitute for the more expensive and less inert fluoride ion source, $(\text{TAS})\text{F}$, $[(\text{CH}_3)_2\text{N}]_3\text{S}^+\text{F}_2\text{Si}(\text{CH}_3)_3^-$. A characterization of anhydrous $\text{N}(\text{CH}_3)_4\text{F}$ also revealed that the properties of the "naked" fluoride ion in solution are poorly understood and that some of the properties previously attributed to the fluoride ion are due to other anions, such as HF_2^- . Furthermore, it was shown that certain solvents, such as CH_3CN or partially chlorinated hydrocarbons, which in the past have been preferred for fluoride ion reactions,^{37,38} undergo chemical reactions with F^- . Finally, a novel 1:1 adduct of $\text{N}(\text{CH}_3)_4\text{F}$ with a dimer of CH_3CN was isolated from CH_3CN solution, and its crystal structure was determined.

Acknowledgment. We thank Dr. Carl Schack for helpful discussions and the preparation of a sample of $\text{SiF}(\text{CH}_3)_3$. The work at Rocketdyne was financially supported by the Air Force Astronautics Laboratory and the Army Research Office.

Supplementary Material Available: Tables A–G listing final atomic coordinates, hydrogen atom positions, N–H and C–H bond distances, hydrogen bond distances, final temperature factors, and mode descriptions for the $\text{N}(\text{CH}_3)_4^+$ cation, respectively (6 pages); observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

(36) Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* 1979, 8, 619.

(37) Miller, W. T.; Fried, J. H.; Goldwhite, H. *J. Am. Chem. Soc.* 1960, 82, 3091.

(38) Fawcett, F. S.; Tullock, C. W.; Coffman, D. D. *J. Am. Chem. Soc.* 1962, 84, 4275.

[3 + 3]-Carbocyclizations of Nitroallylic Esters and Enamines with Stereoselective Formation of up to Six New Stereogenic Centers

Dieter Seebach,* Martin Missbach,¹ Giorgio Calderari,² and Martin Eberle²

Contribution from the Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, ETH-Zentrum, Universitätsstr. 16, CH-8092 Zürich, Switzerland.

Received December 15, 1989

Abstract: Enamines (**1**) from open-chain and cyclic ketones react with 2-nitro-2-propen-1-yl acetates and pivalates (nitroallylic esters **2**) to give, after aqueous workup, 4-nitrocyclohexanones (Schemes I–IV; products **3–18**). Monocyclic as well as bicyclic [4.3.1], [3.3.1], and [3.2.1] systems may be prepared. With appropriate substitution of the educt structures, up to five stereogenic centers are formed in this [3 + 3]-carbocyclization. One diastereoisomer usually prevails (60% to >95% selectivity). With enamines from (*S*)-2-(methoxymethyl)pyrrolidine (prolinol methyl ether) and cyclic ketones, enantiomerically pure compounds are obtained (see **8** and **15–18** in Scheme VI). The configuration and conformation of the products are assigned by extensive use of NMR spectroscopy. An additional stereogenic center may be formed by stereoselective borohydride reduction of the keto group in the nitrocyclohexanones, and Baeyer–Villiger oxidation introduces another functional group (see the hydroxydimethylnitrocyclooctanecarboxylic acid derivatives **23** in Scheme VII). The mechanism of the complex sequence of reactions, leading to the observed products, is discussed (Schemes VIII, X, XI). The structures of the products and intermediates, which can be trapped under certain conditions (Scheme IX), as well as previous investigations of single steps of the in situ reaction sequence involved in the carbocyclization are used to arrive at a tentative proposal for the steric course of these steps: (i) intermolecular coupling of the trigonal centers of enamine and nitroolefin with preferred relative topology like, (ii) intramolecular coupling of the trigonal centers in an intermediate olefinic enamine, (iii) protonation of a nitronate anion moiety, and (iv) protonation of an enamine (in the case of the monocyclic products).

(A) Introduction

Due to their special reactivity³ and ease of functional-group interchange,⁴ aliphatic nitrocompounds have acquired an important

position as intermediates in organic synthesis. Among the most commonly encountered reactions are the nitroaldol addition and condensation⁵ and the Michael addition of either nitroalkanes to enones or of nucleophiles to nitroolefins.⁶ Also Diels–Alder

(1) Most of the results described here are taken from the dissertation of M. Missbach, ETH-Nr. 9152, Eidgenössische Technische Hochschule, 1990.

(2) Part of the dissertations of G. Calderari, ETH-Nr. 7841, 1985, and M. Eberle, ETH-Nr. 8394, Eidgenössische Technische Hochschule, 1987; we thank Louis Odermann for carrying out some of the experiments in the course of his Master's Thesis work, 1984.

(3) Seebach, D.; Colvin, E. W.; Lehr, F.; Weller, T. *Chimia* 1979, 33, 1.

(4) Schickh, O. V.; Apel, G.; Padeken, H. G.; Schwarz, H.; Segnitz, A. In *Houben-Weyl-Müller: Methoden der Organischen Chemie*; Vol. X/1, Thieme-Verlag: Stuttgart, 1971; Vol. X/1. Patai, S., Ed. *The Chemistry of Amino, Nitroso and Nitro Compounds and Their derivatives*; Wiley-Interscience: New York, 1982; Supplement F, Part 1 and 2.

(5) Seebach, D.; Beck, A. K.; Mukhopadhyay, T.; Thomas, E. *Helv. Chim. Acta* 1982, 65, 1101 and references therein.

hydride and stored over molecular sieves. Ethanol was dried over P_2O_5 and stored over molecular sieves. $CDCl_3$ and Me_4Si were purchased from MSD and Aldrich, respectively, and stored over molecular sieves. $AsCl_3$, Pr^iMgCl , (vinyl) $MgCl$, and $PhMgCl$ were obtained from Strem Chemical Co. Et_3Al , Pr^i_3Al , Bu^i_3Al , and Bu^i_3Al , and Bu^i_3Al were purchased from Ethyl Corp. and used as obtained.

Pr^i_2Zn and Bu^i_2Zn were synthesized by the slow, room-temperature addition of the stoichiometric amount of the appropriate trialkylalane to a suspension of anhydrous $Zn(C_2H_3O_2)_2$ (obtained from the commercial dihydrate with boiling acetic anhydride) in *n*-hexane. After the addition was complete, the reaction mixture was refluxed for 7 h, the solvent was distilled, and the dialkylzinc compound was purified by distillation on a spinning-band column: Pr^i_2Zn (77 °C (56 Torr), 86% yield) and Bu^i_2Zn (61 °C (4 Torr), 92% yield). The ^1H ($Pr^i_2Zn^{59}$ and $Bu^i_2Zn^{60}$) and ^{13}C NMR ($Bu^i_2Zn^{60}$) spectral data agreed with those previously reported. The ^{13}C spectral data (δ_c , ppm) for Pr^i_2Zn are as follows: 19.27, ($C-H_3CH_2CH_2As$); 19.78, ($CH_3CH_2CH_2As$); 21.12, ($CH_3CH_2CH_2As$).

OCH_2CH_2OAsCl and $OCMe_2CMe_2OAsCl$ were synthesized by using a slight modification of the previously described procedure.⁶¹ The use of Et_3N , in place of pyridine, provided a better yield (62%). OCH_2CH_2OPCl was synthesized from the reaction of PCl_3 with ethylene glycol.⁶²

General Synthesis of R_3As by the Reactions of $RMgX$ ($X = Cl, Br$) and RLi with OCH_2CH_2OAsCl . In a typical synthesis, 0.06 mol of OCH_2CH_2OAsCl was added to 400 mL of Et_2O (*n*-hexane for the RLi reactions) in a 1-L three-necked, round-bottom flask fitted with a reflux condenser, a mechanical stirrer, and a pressure-equalizing addition fun-

nel. A solution of 0.18 mol of the appropriate alkylating reagent was added slowly over a period of 2 h to the vigorously stirred chloroarsolane solution that was maintained at 0 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. [In the case of (mesityl) $_3As$, the mixture was refluxed for 12 h. The RLi reactions were refluxed for 24 h.] Unreacted alkylating agent was then hydrolyzed with a degassed, saturated NH_4Cl solution. After the organic solvent layer, which contained the arsine, was isolated, the aqueous layer was extracted three times with 75 mL of Et_2O or *n*-hexane and the extracts were added to the initial solvent layer. The arsine-containing solution was dried over anhydrous Na_2SO_4 . Following distillation of the solvent, the liquid tertiary arsines were purified by distillation on a spinning-band column. In the case of the solid tertiary arsines, the pure compounds were obtained from the residue by recrystallization from hot ethanol. Yield data are given in Table I.

General Synthesis of R_3As from the Reactions of R_2Zn and R_3Al with OCH_2CH_2OAsCl . In a 1-L, three-necked, round-bottom flask equipped with a reflux condenser, mechanical stirrer, and pressure-equalizing addition funnel, 0.06 mol of OCH_2CH_2OAsCl was added to 400 mL of *n*-hexane. Then, 0.12 mol of the appropriate alkylating agent in 100 mL of hexane was added slowly with vigorous stirring at room temperature. The reaction mixture was then refluxed for 24 h. After the reaction was cooled to room temperature, any unreacted metal alkyl was hydrolyzed by using 200 mL of a degassed, saturated NH_4Cl solution. The mixture was filtered to remove the solid hydrolysis products. The hexane layer of the filtrate was separated, the three 50-mL hexane extracts of the aqueous layer were combined with the initial hexane layer, and the hexane solution of the arsine was dried over anhydrous Na_2SO_4 . After distillation of the hexane, the arsine was distilled on a spinning-band column. Yield data are given in Table I.

The purity of all synthesized arsines was checked by melting point; boiling point; IR spectroscopy; ^1H , ^{13}C , and/or ^{29}Si NMR spectroscopy; and EI mass spectrometry. A satisfactory elemental analysis for Bu^i_3As was obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY. Anal. Calcd: C, 58.52; H, 11.05. Found: C, 58.36; H, 11.02.

Supplementary Material Available: Tables of mass spectral data and IR data (2 pages). Ordering information is given on any current masthead page.

- (59) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 4558.
 (60) Hofstee, H. K.; Boersma, J.; van der Meulen, J. D.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1978**, *153*, 245.
 (61) Kama, G. K.; Khisamova, Z. L. *J. Gen. Chem. USSR (Engl. Transl.)* **1954**, *23*, 1387.
 (62) Lucas, H. J.; Mitchell, F. W., Jr.; Scully, C. N. *J. Am. Chem. Soc.* **1950**, *72*, 5491.
 (63) Abel, E. W.; Farrow, G. W. *J. Chem. Res., Synop.* **1979**, 278.
 (64) Rieker, A.; Kessler, H. *Tetrahedron Lett.* **1969**, 1227.
 (65) Hellwinkel, D.; Kiltzau, G. *Chem. Ber.* **1968**, *101*, 121.

Contribution from Rocketdyne, A Division of Rockwell International Corporation, Canoga Park, California 91303, Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada, and Department of Nuclear Medicine, Chedoke-McMaster Hospitals, Hamilton, Ontario L8N 3Z5, Canada

The Hexafluorochlorate(V) Anion, ClF_6^-

Karl O. Christe,^{*,1a} William W. Wilson,^{1a} Raman V. Chirakal,^{1b,c} Jeremy C. P. Sanders,^{1b} and Gary J. Schrobilgen^{*,1b}

Received February 12, 1990

The low-temperature reactions of either $N(CH_3)_4F$ or CsF with ClF_5 in CH_3CN solutions produce white solids, which on the basis of material balances and low-temperature Raman spectra, contain the ClF_6^- anion. The similarity of the Raman spectrum of ClF_6^- to that of the octahedral BrF_6^- ion indicates that ClF_6^- is also octahedral and that the free valence electron pair on chlorine is sterically inactive. The existence of the ClF_6^- anion was further supported by an ^{18}F exchange experiment between ClF_5 and ^{18}F -labeled FNO that showed complete randomization of the ^{18}F isotope among the two molecules. A high-field ^{19}F NMR study of neat ClF_5 and ClF_5 in anhydrous HF solution in the presence and absence of excess CsF has provided accurate measurements of the ClF_5 NMR parameters including, for the first time, both $^{37/35}Cl$ secondary isotopic ^{19}F NMR shifts. Moreover, the NMR study also supports the existence of ClF_6^- , showing that ClF_5 undergoes slow chemical exchange with excess CsF in anhydrous HF at room temperature.

Introduction

The hexafluorochlorate(V) anions belong to the interesting class of AX_6E compounds,² which possess six X ligands and a free valence electron pair E. Depending on the size of the central atom A, the free valence electron pair E can be either sterically active

or inactive. Thus, a recent study has shown that in IF_6^- the free valence electron pair is sterically active, while in BrF_6^- it is not.³ Whereas the ClF_5 molecule was discovered 27 years ago,⁴ and the BrF_6^- and IF_6^- anions have been known for about as long,^{5,6}

- (1) (a) Rocketdyne. (b) McMaster University. (c) Chedoke-McMaster Hospitals.
 (2) Gillespie, R. J. *Molecular Geometry*; Van Nostrand Reinhold Co.: London, 1972.

- (3) Christe, K. O.; Wilson, W. W. *Inorg. Chem.* **1989**, *28*, 3275.
 (4) Maya, W.; Bauer, H. F. U.S. Pat. 3,354,646, 1967.
 (5) Emeleus, H. J.; Sharpe, A. G. *J. Chem. Soc.* **1949**, 2206.
 (6) Whitney, E. D.; MacLaren, R. O.; Fogle, C. E.; Hurley, T. J. *J. Am. Chem. Soc.* **1964**, *86*, 2583.

the ClF_6^- anion has so far proven elusive. For example, ClF_5 does not form any stable adducts with alkali-metal fluorides and the only reaction observed is a catalytic decomposition of ClF_5 to ClF_3 and F_2 .⁷ Furthermore, a ^{18}F radiotracer study of the $\text{CsF}-\text{ClF}_5$ system did not provide any evidence for fluorine exchange and, thereby, for the formation of a ClF_6^- intermediate.⁸ The well-established existence of the ClF_6^+ cation⁹⁻¹² and of the $\text{ClF}_6^\bullet$ radical,¹³ combined with the recent finding that in BrF_6^- the bromine free valence electron pair is sterically inactive,³ indicated that the weak Lewis acidity of ClF_5 and the low solubilities of CsF and CsClF_6 in ClF_5 are the most likely reasons for the previous failures^{7,8} to isolate the ClF_6^- anion. Our recent success¹⁴ with handling ClF_3 in CH_3CN solution and the surprisingly high thermal stability of $\text{N}(\text{CH}_3)_4\text{ClF}_4$, combined with its high solubility in CH_3CN , suggested that similar reaction conditions, i.e., the use of $\text{N}(\text{CH}_3)_4^+$ as a large, stabilizing counterion, of CH_3CN as a solvent, and of low temperature, might provide the long sought after ClF_6^- anion.

Experimental Section

Caution! Mixtures of ClF_5 or ClF_6^- salts with organic materials, such as CH_3CN or $[\text{N}(\text{CH}_3)_4]^+$ salts, are highly explosive and must be handled on a small scale with appropriate safety precautions, such as barricades, face shields, heavy leather gloves, and protective clothing.

Materials. The CH_3CN (Baker, Bio-analyzed, having a water content of 40 ppm) was treated with P_2O_5 and freshly distilled in a flamed-out Pyrex vacuum system prior to use, thereby reducing its water content to ≤ 4 ppm. The CsF (KBI) was dried by fusion in a platinum crucible and ground in the drybox. The ClF_5 (Rocketdyne) was purified by fractional condensation prior to its use. The synthesis of HF_2^- - and H_2O -free $\text{N}(\text{CH}_3)_4\text{F}$ is described elsewhere.¹⁵

Apparatus. All reactions were carried out in well-passivated (with ClF_3) Teflon-FEP or Kel-F ampules that were closed by stainless steel valves. The ClF_5 was handled in a stainless steel-Teflon-FEP vacuum line,¹⁶ and the CH_3CN was transferred on a baked-out Pyrex vacuum line equipped with Teflon stopcocks. Nonvolatile materials were handled in the dry N_2 atmosphere of a glovebox.

Fluorine-18 Exchange Reaction between FNO and ClF_5 . A 50-mL nickel can was heated to red heat four times with 2 atm of H_2 , followed by pumping each time. The procedure was repeated four times with F_2 , followed by treatment with 3 atm of FNO at room temperature for 1 day and pumping for 4 h. Nitric oxide (0.62 mmol) was combined at -196°C in the can with a $\text{Ne}/^{18}\text{F}$ -labeled F_2 mixture, which was accelerator produced under conditions previously described.¹⁷ The Ne was pumped off at -196°C , and F_2 (0.31 mmol) was added to the can. The can was briefly warmed to 20°C , and the resulting ^{18}F -labeled FNO was condensed, for the removal of any HF , at -196°C into a U-tube containing 0.5 g of NaF , followed by warming to -78°C . It was then combined at -196°C in a $1/4$ in. o.d. Teflon-FEP ampule with ClF_5 (0.62 mmol). The resulting mixture was warmed to 20°C for several minutes and then vacuum-distilled through two U-traps kept at -120 and -196°C . The -120°C trap contained the ClF_5 , and the -196°C one, the FNO. Individual activity measurements were corrected for the elapsed time by correcting to zero time of the experiment. At the end of the experiment, the -120°C trap, containing ClF_5 , showed a zero time activity of 71.6 mCi (84.9%), whereas that in the -196°C trap, containing the FNO, was 12.7 mCi (15.1%).

Synthesis of $\text{N}(\text{CH}_3)_4\text{ClF}_6^-$. In a typical experiment, $\text{N}(\text{CH}_3)_4\text{F}$ (150.9 mg, 1.62 mmol) was transferred in the drybox into a prepassivated Teflon-FEP ampule that was closed by a stainless steel valve. Dry CH_3CN (5.96 mL, 4.702 g) was added at -196°C on the Pyrex vacuum line, and the mixture was warmed to room temperature. ClF_5 (1.62

mmol) was added at -196°C on the stainless steel vacuum line, and the mixture was kept at -31°C for 3 h with occasional very careful agitation. All material volatile at -31°C was pumped off and trapped in a -196°C trap and consisted of 4.70 g of CH_3CN . The white solid residue was highly shock sensitive and consistently exploded when either exposed to a laser beam at low temperature or warmed to room temperature.

When the above experiment was repeated at room temperature, gas evolution set in at about 0°C , and after solvent removal at 20°C , a stable white solid was obtained, which, on the basis of its weight and vibrational spectrum, was identified as $\text{N}(\text{CH}_3)_4\text{ClF}_4$.¹⁴

When CsF was substituted for $\text{N}(\text{CH}_3)_4\text{F}$ in the reaction with ClF_5 in CH_3CN at -31°C , the volatile materials at -31°C consisted of the CH_3CN and ClF_5 starting materials, and the nonvolatile residue was unreacted CsF .

For the recording of the low-temperature Raman spectrum of CsClF_6 , a solution of ClF_5 in CH_3CN was kept in contact with excess CsF for several hours at -40°C and then slowly cooled to -110°C . The Raman spectrum of the product in the bottom of the tube was recorded at -110°C and indicated the presence of CsClF_6 (see below) and solid CH_3CN .

Nuclear Magnetic Resonance Spectroscopy. The ^{19}F NMR spectra were recorded unlocked (field drift $< 0.1\text{ Hz h}^{-1}$) by using a Bruker WM-250 or AM-500 spectrometer equipped with a 5.8719 or 11.744 T cryomagnet, respectively. On both instruments, spectra were obtained by using 5-mm combination $^1\text{H}/^{19}\text{F}$ probes operating at 235.361 MHz (WM-250) or 470.599 MHz (AM-500).

The 5.8719-T ^{19}F spectra were typically accumulated in a 16K memory. Spectral width settings of 5 and 10 kHz were employed, yielding data point resolutions of 0.62 and 1.22 Hz and acquisition times of 1.638 and 0.819 s, respectively. No relaxation delays were applied. The number of free-induction decays accumulated was typically between 2000 and 10000 transients.

The 11.744-T ^{19}F spectra were accumulated in a 16K memory. Spectral width settings of 5 and 30 kHz were employed, yielding data point resolutions of 0.61 and 3.59 Hz and acquisition times of 1.638 and 0.278 s, respectively. No relaxation delays were applied. Typically 80–1000 transients were accumulated.

On both instruments the pulse width corresponding to a bulk magnetization tip angle, θ , of approximately 90° was equal to 1 μs . No line-broadening parameters were applied in the exponential multiplication of the free-induction decays prior to Fourier transformation.

The spectra were referenced to neat CFCl_3 . The chemical shift convention used is that a positive (negative) sign signifies a chemical shift to high (low) frequency of the reference compound.

Low-temperature studies were carried out by using Bruker temperature controllers. The temperature was measured with a copper-constantan thermocouple inserted directly into the sample region of the probe and was considered accurate to $\pm 1^\circ\text{C}$.

Fluorine-19 NMR samples were prepared in 25-cm lengths of AWG 9 (ca. 4-mm o.d., 0.8-mm wall) FEP plastic tubing heat sealed at one end with the open end flared (45° SAE) and joined, by means of a compression fitting, to a Kel-F valve. The assembly was seasoned overnight with ca. 1 atm of F_2 gas, evacuated, and weighed. A weighed amount of CsF was transferred into a sample tube in a drybox. Both ClF_5 and HF were distilled into NMR tubes through a metal line fitted with a pressure transducer that had been previously seasoned overnight with ca. 1 atm of ClF_5 vapor. The ClF_5 pressure was measured ($\pm 0.5\%$ accuracy) in a calibrated portion of the metal vacuum line with a pressure transducer (0–1000 Torr range), whose wetted surfaces were Inconel, and condensed at -196°C into the FEP NMR sample tube. The amount of HF solvent used was determined by direct weighing of the tube assembly. The FEP tube was heat sealed under dynamic vacuum with its contents frozen at -196°C . The FEP sample tubes were placed in 5-mm thin-walled precision NMR tubes (Wilmad) in order to run their spectra.

Raman Spectroscopy. Low-temperature Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 488-nm exciting line of an Ar ion laser.

Results and Discussion

Synthesis of ClF_6^- Salts. It was found that the activation energy for the $\text{ClF}_5-\text{CH}_3\text{CN}$ reaction is sufficiently high to permit the judicious handling of ClF_5 in a large excess of dry CH_3CN . Although ClF_5 is a more powerful oxidizer than ClF_3 , its pseudooctahedral structure with five fluorine ligands and one free valence electron pair renders it less reactive than the pseudotrigonal-bipyramidal ClF_3 .

To take advantage of the high activation energy of the $\text{ClF}_5-\text{CH}_3\text{CN}$ reaction, $\text{N}(\text{CH}_3)_4\text{F}$ was carefully combined with ClF_5 in this solvent at -31°C . Removal of the solvent at -31°C resulted in a white, highly sensitive solid that violently exploded

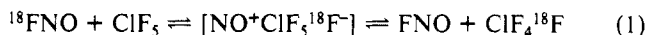
- (7) Christe, K. O.; Wilson, W. W.; Wilson, R. D. *Inorg. Chem.* **1989**, *28*, 675.
- (8) Bougon, R. *Bull. Inf. Sci. Tech., Commis. Energ. At. (Fr.)* **1971**, *161*, 9.
- (9) Christe, K. O. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 741.
- (10) Roberto, F. Q. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 737.
- (11) Christe, K. O. *Inorg. Chem.* **1973**, *12*, 1580.
- (12) Christe, K. O.; Wilson, W. W. *Inorg. Chem.* **1983**, *22*, 1950.
- (13) Boate, A. R.; Morton, J. R.; Preston, K. R. *Inorg. Chem.* **1975**, *14*, 3127.
- (14) Wilson, W. W.; Christe, K. O. *Inorg. Chem.* **1989**, *28*, 4172.
- (15) Wilson, W. W.; Christe, K. O.; Feng, J.; Bau, R. To be published.
- (16) Christe, K. O.; Wilson, R. D.; Shack, C. J. *Inorg. Synth.* **1986**, *24*, 3.
- (17) Chirakal, R.; Firnaui, G.; Schrobilgen, G. J.; McKay, J.; Garnett, E. S. *Int. J. Appl. Radiat. Isot.* **1984**, *35*, 401.
- (18) Bougon, R.; Charpin, P.; Soriano, J. C. R. *Hebd. Seances Acad. Sci., Ser. C* **1971**, *272*, 565.

either on exposure to a laser beam at low temperature or on warming to room temperature, thereby preventing its direct identification. It was shown, however, by quantitative material balances that most of the ClF_5 starting material had been retained by the $\text{N}(\text{CH}_3)_4\text{F}$ at -31°C .

When the reaction between $\text{N}(\text{CH}_3)_4\text{F}$ and ClF_5 was carried out at temperatures above -31°C , gas evolution was observed at about 0°C and, after solvent removal at 20°C , a stable, white solid was isolated, which was identified by vibrational spectroscopy as $\text{N}(\text{CH}_3)_4\text{ClF}_4$.¹⁴ Since the latter compound is stable up to 100°C and is not shock sensitive,¹⁴ the explosive material from the -31°C reaction could not have been $\text{N}(\text{CH}_3)_4\text{ClF}_4$ but most likely was $\text{N}(\text{CH}_3)_4\text{ClF}_6$.

To overcome the experimental difficulties associated with the characterization of $\text{N}(\text{CH}_3)_4\text{ClF}_6$, the $\text{N}(\text{CH}_3)_4\text{F}$ starting material in the $\text{N}(\text{CH}_3)_4\text{F}-\text{ClF}_5-\text{CH}_3\text{CN}$ system was substituted by CsF . It was hoped that CsClF_6 would be stable at -31°C , the lowest temperature at which the CH_3CN solvent could be pumped off at a reasonable rate. However, it was found that CsClF_6 is thermally unstable even at -31°C , and all the ClF_5 was pumped off at -31°C , together with the CH_3CN solvent. Since CH_3CN is a much weaker Raman scatterer than the chlorine fluorides,¹⁴ it was possible to record the low-temperature Raman spectrum of CsClF_6 without removal of the CH_3CN and, thereby, to identify the ClF_6^- anion. A detailed discussion of the observed spectrum will be given below.

¹⁸F Radiotracer Study. Further evidence for the formation of the ClF_6^- anion was obtained by an ¹⁸F radiotracer study of the ClF_5 -¹⁸FNO system. It was found that ClF_5 undergoes rapid fluorine exchange with ¹⁸FNO (eq 1). Within several minutes



at room temperature, complete randomization of the ¹⁸F isotope had occurred. The measured values of 84.9% for the radioactivity in ClF_5 and 15.1% in FNO are in excellent agreement with the values 83.3 and 16.7% predicted for a random distribution of ¹⁸F involving an unstable $\text{NO}^+\text{ClF}_5^-$ intermediate. The rapid fluorine exchange in the $\text{FNO}-\text{ClF}_5$ system is in marked contrast to the results from the previous study of the $\text{CsF}-\text{ClF}_5$ system for which no evidence of exchange was reported.⁸ The lack of exchange in the $\text{CsF}-\text{ClF}_5$ system is probably due to the very low solubility of CsF in ClF_5 and not to the lack of ClF_6^- formation (see below).

¹⁹F NMR Study of Chemical Exchange Behavior between F^- and ClF_5 . Chlorine pentafluoride has previously been shown in two ¹⁹F NMR studies to possess a square-pyramidal (C_{4v}) AX_5E structure in the liquid state^{19,20} as predicted by the VSEPR model.² Alexandre and Rigny²⁰ demonstrated that, unlike the equatorial X_4 part of the ¹⁹F NMR spectrum, which showed a secondary isotopic shift arising from ¹⁹F bonded to ³⁵Cl and ³⁷Cl, the axial A part of the spectrum was broadened significantly and showed no evidence for an isotopic shift.²⁰ This study concluded that chemical exchange between the axial (F_{ax}) and equatorial (F_{eq}) fluorines could be disregarded and that the line broadening of F_{ax} arises from partially quadrupole-collapsed scalar couplings between ¹⁹F_{ax} and the spin- $3/2$ quadrupolar nuclei ³⁵Cl and ³⁷Cl, $^1J_{\text{F}_{\text{ax}}-^{35/37}\text{Cl}}$, which are significantly larger than $^1J_{\text{F}_{\text{eq}}-^{35/37}\text{Cl}}$. Nuclear relaxation time measurements in the same study have confirmed this and have provided estimates of the magnitudes of the scalar couplings ($^1J_{\text{F}_{\text{ax}}-^{35}\text{Cl}} = 192$ and $^1J_{\text{F}_{\text{eq}}-^{35}\text{Cl}} \leq 20$ Hz). The larger value for $^1J_{\text{F}_{\text{ax}}-^{35}\text{Cl}}$ is in accord with the shorter $\text{F}_{\text{ax}}-\text{Cl}$ bond observed in this molecule.²¹ The temperature behavior of the ¹⁹F NMR spectrum of liquid ClF_5 was investigated in the previous study, but it does not report any variations of line widths as a function of temperature. We have recorded the ¹⁹F NMR spectra of neat ClF_5 at 25, -56 , and -90°C (Figure 1). While there is little effect upon the line width of the F_{eq} resonance

on lowering the temperature, a significant narrowing of the F_{ax} resonance line width is observed together with partial resolution of its chlorine isotopic shift. The observed line narrowing for the F_{ax} resonance is attributable to the increased quadrupolar relaxation rates of ³⁵Cl and ³⁷Cl at low temperatures where the isotropic molecular tumbling correlation time (τ_c) for ClF_5 is greater.²² This behavior is consistent with the dominant contribution of scalar relaxation of the second kind, via $^1J_{\text{F}_{\text{ax}}-^{35/37}\text{Cl}}$, to the spin-spin relaxation time (T_2) of the F_{ax} nuclei, as found in the previous study.²⁰

The ¹⁹F NMR spectra of a solution of ClF_5 (0.536 m) in anhydrous HF and a solution of ClF_5 (0.619 m) in anhydrous HF containing CsF (5.60 m) were investigated. The ¹⁹F NMR spectrum of ClF_5 recorded in HF solvent at 25°C consists of two well-resolved doublets corresponding to equatorial fluorines on ³⁵Cl and ³⁷Cl spin coupled to the axial fluorine environment (Figure 2). The latter environment, as in the neat sample of ClF_5 at 24.4°C , is broadened significantly owing to partial quadrupole collapse of the $^1J_{\text{F}_{\text{ax}}-^{35/37}\text{Cl}}$ scalar couplings so that resolution of the isotopically shifted quintets (Figure 2; also cf. Figure 1) is precluded. The line broadening on the quintets is again dominated by scalar coupling and not by fluorine exchange, as has been established for neat ClF_5 in the present and earlier studies.²⁰ The addition of F^- to HF solutions of ClF_5 results in pronounced broadening of the doublet resonances at 25°C , preventing resolution of the isotope shift, whereas the appearance of the axial fluorine resonance remains essentially unchanged (Figure 3). The line broadening is consistent with slow intermolecular ¹⁹F exchange arising from equilibrium 2 and the intermediacy of ClF_6^- in the



exchange process. Cooling of the ClF_5-F^- sample to -56°C slowed ¹⁹F chemical exchange sufficiently to allow resolution of the equatorial fluorine doublets (Figure 3) and the axial fluorine quintets. This is the first time the two quintet patterns arising from the ³⁵Cl-³⁷Cl secondary isotope effect have been observed in ClF_5 . The sharpening of the axial fluorine resonance is not, however, attributed to slowing of the ¹⁹F chemical exchange process but is primarily attributed to the dominant effect of the increased quadrupole relaxation rates of the ³⁵Cl and ³⁷Cl nuclei on $^1J_{\text{F}_{\text{ax}}-^{35/37}\text{Cl}}$ at low temperatures where τ_c for ClF_5 is greater. The addition of CsF presumably increases the viscosity of the solvent medium owing to $\text{F}(\text{HF})_x^-$ formation and hence increases τ_c for ClF_5 , leading to collapse of the $^1J_{\text{F}_{\text{ax}}-^{35/37}\text{Cl}}$ couplings. In contrast, the ¹⁹F resonances associated with ClF_5 dissolved in HF do not sharpen as significantly, although the quintet pattern clearly possesses a narrower line width than at 25°C (Figure 2). The broader lines can be attributed to the low viscosity of the HF solvent medium, even at -56°C , allowing the partially collapsed $^1J_{\text{F}_{\text{ax}}-^{35/37}\text{Cl}}$ couplings to persist in the slow chemical exchange limit.

The secondary isotope shifts, $^1\Delta^{19}\text{F}_{\text{ax}}(^{37/35}\text{Cl}) = -0.189$ ppm and $^1\Delta^{19}\text{F}_{\text{eq}}(^{37/35}\text{Cl}) = -0.085$ ppm for ClF_5/CsF in HF at -56°C (Figure 3), follow the usual trend and are negative; i.e., the observed NMR nucleus bonded to the heavier of two isotopes has its NMR resonance to lower frequency.²³ They are comparable in magnitude to those for closely related species in the same row of the periodic table; i.e., for ClF_6^+ , $^1\Delta^{19}\text{F}_{\text{ax}}(^{37/35}\text{Cl}) = -0.15$ ppm,²⁴ for SF_6 , $^1\Delta^{19}\text{F}_{\text{ax}}(^{34/32}\text{S}) = -0.0552$ ppm,²⁵ and for SF_4 , $^1\Delta^{19}\text{F}_{\text{ax}}(^{34/32}\text{S}) = -0.0690$ ppm and $^1\Delta^{19}\text{F}_{\text{eq}}(^{34/32}\text{S}) = -0.0330$ ppm²⁵ with the ¹⁹F bonded to the heavier isotope occurring at lower frequency. The relative sizes of isotopic shifts are known to be larger for shorter bonds,²⁶ and this is also true for the secondary isotopic shifts of ClF_5 [$r(\text{Cl}-\text{F}_{\text{ax}}) = 1.58$, $r(\text{Cl}-\text{F}_{\text{eq}}) = 1.67$ Å²¹ and $f_{\text{Rax}} = 3.01$, $f_{\text{Req}} = 2.57$ mdyn Å⁻¹]²⁷ and BrF_5 [$r(\text{Br}-\text{F}_{\text{ax}}) = 1.689$,

(19) Pilipovich, D.; Maya, W.; Lawton, E. A.; Bauer, H. F.; Sheehan, D. F.; Ogimachi, N. N.; Wilson, R. D.; Gunderloy, F. C.; Bedwell, V. E. *Inorg. Chem.* **1967**, *6*, 1918.

(20) Alexandre, M.; Rigny, P. *Can. J. Chem.* **1974**, *52*, 3676.

(21) Goulet, P.; Jurek, R.; Chanutot, J. *J. Phys.* **1976**, *37*, 495.

(22) Boeré, R. T.; Kidd, R. G. *Annu. Rep. NMR Spectrosc.* **1982**, *13*, 320.

(23) Jameson, C. J.; Osten, H. J. *J. Am. Chem. Soc.* **1985**, *107*, 4158.

(24) Christe, K. O.; Hon, J. F.; Pilipovich, D. *Inorg. Chem.* **1973**, *12*, 84.

(25) Gombler, W. Z. *Naturforsch.* **1985**, *40b*, 782.

(26) Jameson, C. J. *J. Chem. Phys.* **1977**, *66*, 4983.

(27) Begun, G. M.; Fletcher, W. H.; Smith, D. F. *J. Chem. Phys.* **1965**, *42*, 2236.

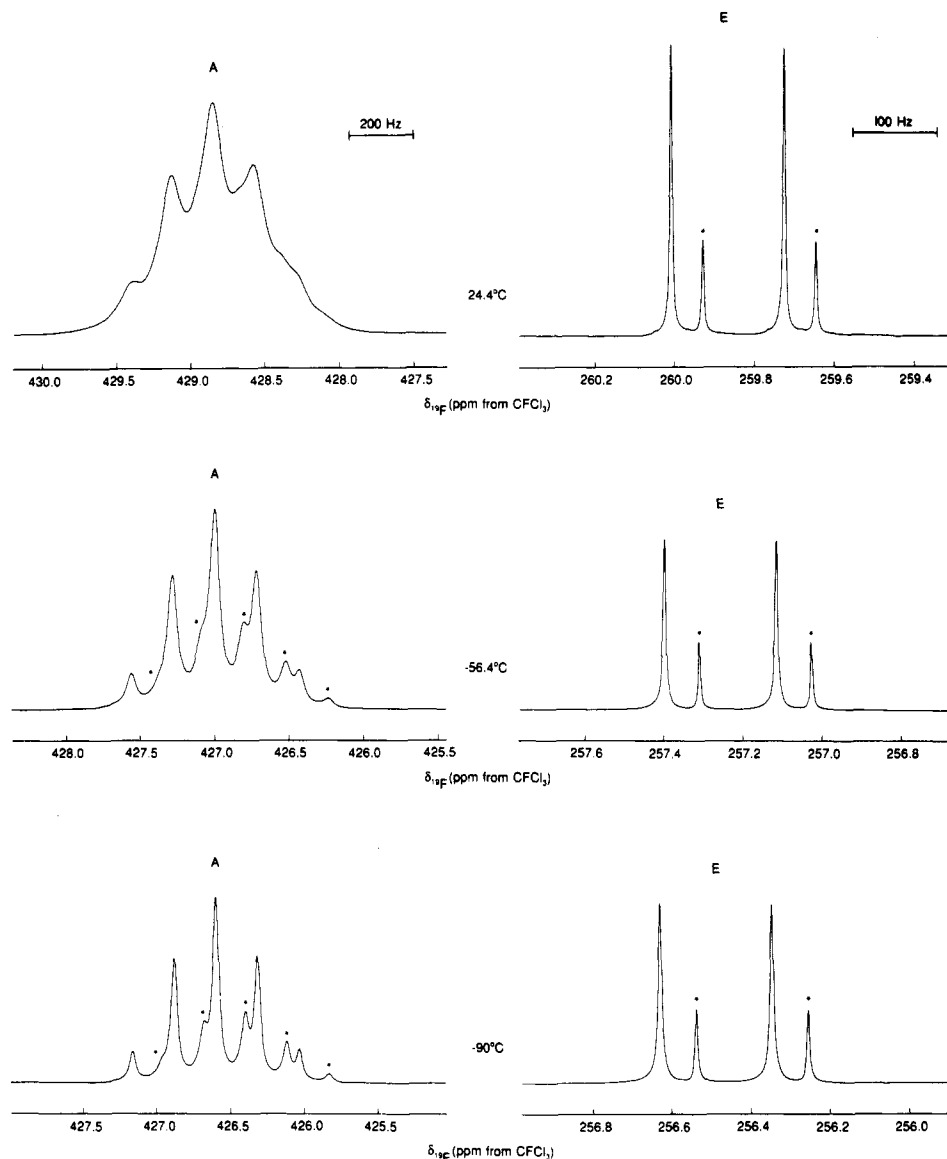


Figure 1. Variable-temperature ^{19}F NMR spectra (470.599 MHz) of neat ClF_5 . A and E denote resonances for the axial and equatorial fluorine environments, respectively; asterisks denote resonances arising from the ^{37}Cl isotopomer.

Table I. ^{19}F NMR Data for Neat ClF_5 and $\text{ClF}_5\text{-HF}$ and $\text{ClF}_5\text{-CsF-HF}$ Solutions

sample compn	T, °C	chem shift δ , ppm ^a		$^2J(\text{F}_{\text{ax}}\text{-F}_{\text{eq}})$, Hz	line width, Hz		secondary isotopic shift ^b $^1\Delta^{19}\text{F}(^{37}/^{35}\text{Cl})$, ppm	
		F_{eq}	F_{ax}		F_{eq}	F_{ax}	F_{eq}	F_{ax}
neat ClF_5	24.4	259.8	428.8	133	3.5	~110	-0.079	<i>e</i>
	-56.4	257.2	426.9	133	4.0	44	-0.088	-0.1977
	-90.0	256.4	426.6	133	5.2	26	-0.091	-0.199
ClF_5 in HF solv ^c	25	256.4	424.6	130	5.7	~140	-0.078	<i>e</i>
	-56.3	253.9	422.6	130	2.5	71	-0.087	<i>e</i>
ClF_5/CsF in HF solv ^d	25	253.6	420.9	123	28	~100	<i>e</i>	<i>e</i>
	-56.3	250.8	418.8	124	6.9	18	-0.085	-0.189

^aSpectra were referenced with respect to external CFCl_3 at 25 °C. ^b $^1\Delta^{19}\text{F}(^{37}/^{35}\text{Cl})/\text{ppm} = \delta(\text{F}(^{37}\text{Cl})) - \delta(\text{F}(^{35}\text{Cl}))$. ^cConcentration of $\text{ClF}_5 = 0.536$ m. ^dConcentration of $\text{ClF}_5 = 0.619$ m, and that of $\text{CsF} = 5.60$ m. ^eIsotopic shift not resolved.

$r(\text{Br-F}_{\text{eq}}) = 1.774 \text{ \AA}^{28}$ and $f_{\text{Rax}} = 4.07$, $f_{\text{Req}} = 3.19 \text{ mdyn \AA}^{-1}$,²⁷ where $^1\Delta^{19}\text{F}_{\text{ax}}(^{81}/^{79}\text{Br}) = -0.030$ and $^1\Delta^{19}\text{F}_{\text{eq}}(^{81}/^{79}\text{Br}) = -0.015$ ppm.²⁹ Moreover, the ratio $^1\Delta^{19}\text{F}_{\text{ax}}(^{37}/^{35}\text{Cl})/^1\Delta^{19}\text{F}_{\text{eq}}(^{37}/^{35}\text{Cl}) = 2.22$ is remarkably similar to those found for the axial and equatorial secondary isotopic shifts of SF_4 , $^1\Delta^{19}\text{F}_{\text{ax}}(^{34}/^{32}\text{S})/^1\Delta^{19}\text{F}_{\text{eq}}(^{34}/^{32}\text{S}) = 2.09$, and BrF_5 , $^1\Delta^{19}\text{F}_{\text{ax}}(^{81}/^{79}\text{Br})/^1\Delta^{19}\text{F}_{\text{eq}}(^{81}/^{79}\text{Br})$

$= 2.0$.²⁹ NMR data are summarized in Table I.

Raman Spectrum of CsClF_6 . The Raman spectrum of the product from the low-temperature reaction of CsF with ClF_5 in CH_3CN solution was recorded at -110 °C in frozen CH_3CN . In the region of the Cl-F fundamental vibrations, three bands were observed at 525, 384, and 289 cm^{-1} (Figure 4, trace A, which, under the influence of the laser beam, rapidly decayed giving rise to new bands at 507, 418, and 290 cm^{-1} (Figure 4, trace B). These new bands are due to the ClF_4^- anion, as shown by the Raman spectrum of $\text{N}(\text{CH}_3)_4\text{ClF}_4$ in CH_3CN recorded under identical

(28) Robiette, A. G.; Bradley, R. H.; Brier, P. N. *J. Chem. Soc., Chem. Commun.* **1971**, 1567.

(29) Sanders, J. C. P.; Schrobilgen, G. J. Unpublished results.

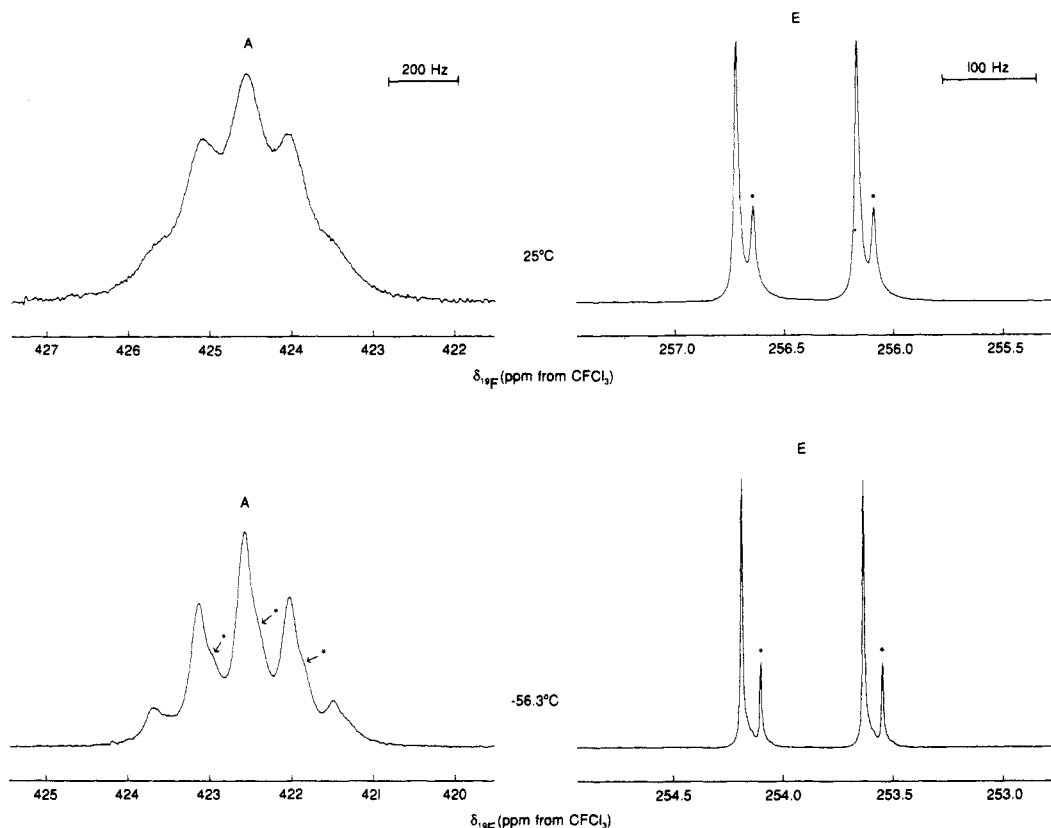


Figure 2. Variable-temperature ^{19}F NMR spectra (235.361 MHz) of ClF_5 (0.536 m) in HF solution. A and E denote resonances for the axial and equatorial fluorine environments, respectively; asterisks denote resonances arising from the ^{37}Cl isotopomer.

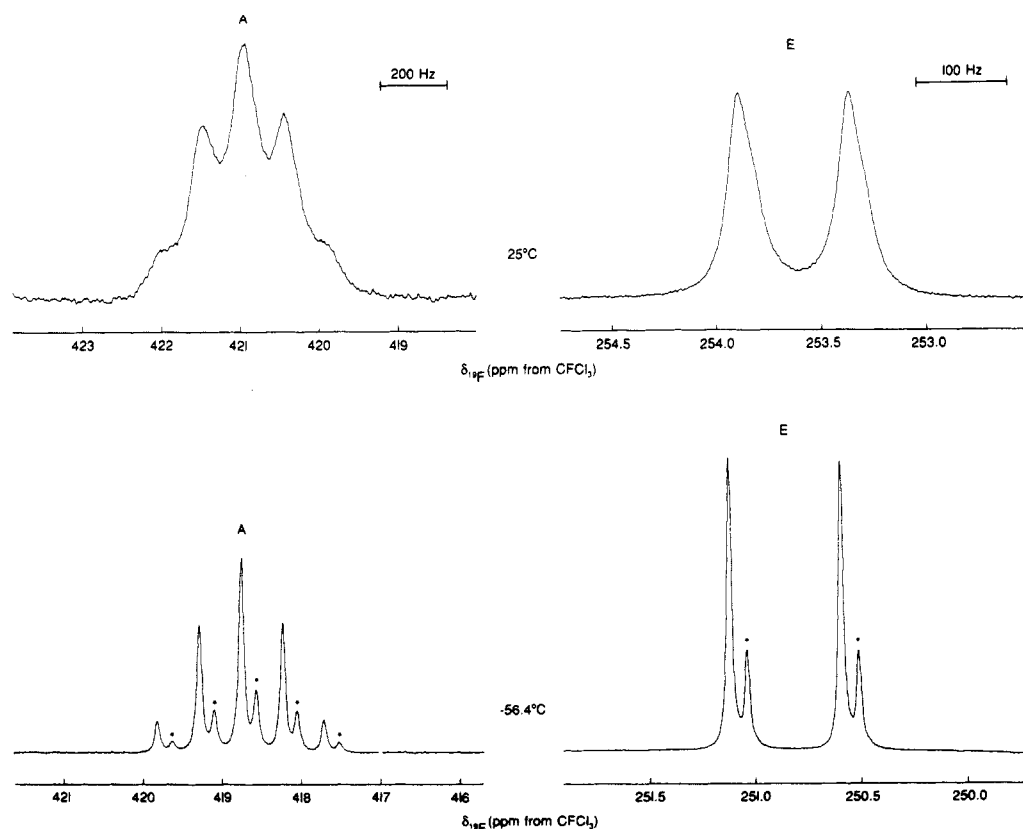


Figure 3. Variable-temperature ^{19}F NMR spectra (235.361 MHz) of ClF_5 (0.619 m)- CsF (5.60 m) in HF solution. A and E denote resonances for the axial and equatorial fluorine environments, respectively; asterisks denote resonances arising from the ^{37}Cl isotopomer.

conditions (Figure 4, trace C). The new set of bands at 525, 384, and 289 cm^{-1} are attributable to ClF_6^- for the following reasons: (i) the bands cannot be assigned to either CH_3CN , ClF_3 , or ClF_4^- , (ii) they must be due to a species that on photolysis can produce

ClF_4^- , (iii) the relative intensities of these Raman bands are very similar to those observed for solid $\text{Cs}^+\text{BrF}_6^-$,¹⁸ and (iv) the observed frequencies are in excellent agreement with our expectations for ClF_6^- .

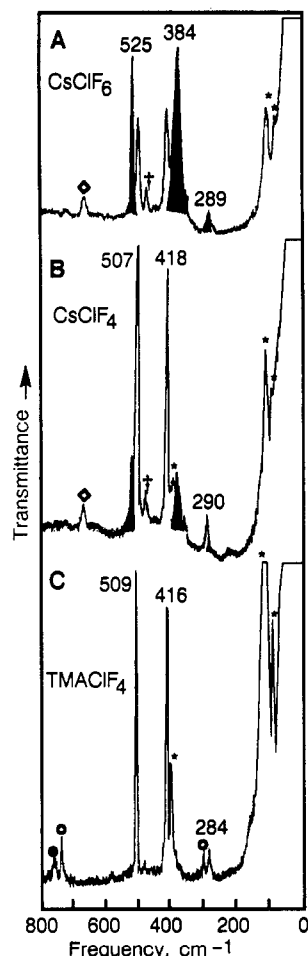


Figure 4. Raman spectra of CsClF_6 (trace A), CsClF_4 (trace B), and $\text{N}(\text{CH}_3)_4\text{ClF}_4$ (trace C) recorded at -110°C for the solids in frozen CH_3CN . The bands assigned to the anions of the title compounds are marked by their frequency values. Bands due to ClF_5 , CH_3CN , Kel-F, Teflon-FEP, and the $\text{N}(\text{CH}_3)_4^+$ cation have been marked by daggers, stars, diamonds, hollow circles, and full circles, respectively. Traces A and B are the first and second scan of the same sample and demonstrate the rapid decay of ClF_6^- (solid peaks) to ClF_4^- (hollow peaks) under the influence of the laser beam.

The last point needs some amplification. By analogy with octahedral BrF_6^- ,³ the ClF_6^- anion, which possesses a smaller central atom than BrF_6^- , should also be octahedral; i.e., the free valence electron pair on chlorine should be sterically inactive. Octahedral ClF_6^- should possess six fundamental vibrations of which only the $\nu_1(\text{A}_{1g})$, $\nu_2(\text{E}_g)$, and $\nu_3(\text{F}_{2g})$ modes would be Raman active. Since in all the Raman active modes the central Cl atom is at rest, the observed frequencies should depend only on the force constants and should be independent of the mass of the central atom. Furthermore, the F -matrix expressions of these modes contain the same elements as the corresponding modes of the closely related octahedral HalF_6^+ cations and the pseudooctahedral HalF_5 molecules and HalF_4^- anions. Therefore, a plot of the frequencies of the modes should be mass independent and should exhibit smooth trends, with the frequencies decreasing with decreasing oxidation state of the central atom and increasing negative charge on the species. Plots of the sums of the frequencies of the symmetric in-phase and symmetric out-of-phase stretching modes and of those of the scissoring deformation mode for the series BrF_4^- ,³⁰ BrF_6^- ,³ BrF_5 ,^{26,31} and BrF_6^+ ,^{32,33} and ClF_4^- ,³⁴ ClF_6^- ,

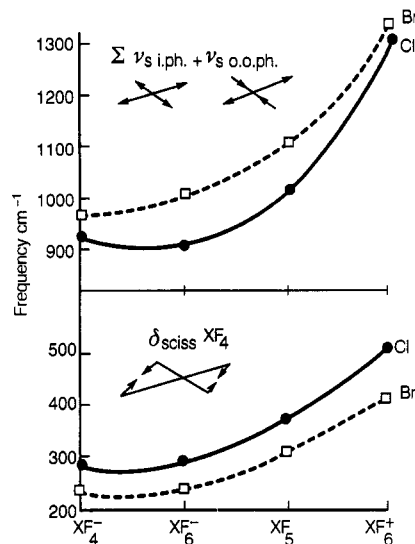


Figure 5. Plots of the sums of the frequencies of the two symmetric stretching modes and of those of the scissoring deformation mode for the different octahedral and pseudooctahedral halogen fluoride ions and molecules. The symmetry coordinates of each mode are depicted by the arrow diagrams.

ClF_5 ,^{21,26,35} and ClF_6^+ ³⁶ are shown in Figure 5. With the exception of the ClF_6^- values, all the other frequencies had previously been established experimentally. As can be seen from Figure 5, the frequencies observed in this study for ClF_6^- perfectly fit the expected trends and strongly support their assignment to an octahedral ClF_6^- anion.

Conclusion. The results from this study, i.e., Raman spectroscopy and the ^{18}F radiotracer study, provide strong evidence for the existence of the ClF_6^- anion and its octahedral structure. As previously suggested, the past failures^{7,8} to isolate the ClF_6^- anion are due to its thermal and photolytic instability, combined with the low solubility of CsF and CsClF_6 in liquid ClF_5 . These problems were overcome by the use of the larger counterion $\text{N}(\text{CH}_3)_4^+$, which helps to stabilize the ClF_6^- anion and increases the solubility of the resulting salt, the use of CH_3CN as a more effective solvent, and the use of low-temperature spectroscopic techniques. The obvious limitations of this approach are the horrendous incompatibility problems encountered when one works with one of the most powerful known oxidizers in an organic solvent with an organic counterion. In view of our previous work³ on the structure of BrF_6^- , the steric inactivity of the free valence electron pair on the chlorine atom of ClF_6^- is not surprising and is at variance with the conclusions reached from a theoretical study, which examined the Laplacian of the calculated electronic charge distribution of gaseous ClF_6^- and predicted a fluxional structure having a distorted octahedral (C_{3v}) equilibrium geometry.³⁷

Acknowledgment. We thank Dr. C. J. Schack and Mr. R. D. Wilson for their help, the U.S. Air Force Astronautics Laboratory, Edwards AFB (K.O.C. and G.J.S.), the U.S. Army Research Office (K.O.C.), and the Natural Sciences and Engineering Research Council of Canada (G.J.S.) for financial support, and Dr. E. S. Garnett for the use of the facilities of the Nuclear Medicine Department, Chedoke-McMaster Hospitals.

(30) Christe, K. O.; Schack, C. J. *Inorg. Chem.* **1970**, *9*, 1852.

(31) Selig, H.; Holzman, H. *Isr. J. Chem.* **1969**, *7*, 417.
 (32) Gillespie, R. J.; Schrobilgen, G. J. *Inorg. Chem.* **1974**, *13*, 1230.
 (33) Christe, K. O.; Wilson, R. D. *Inorg. Chem.* **1975**, *14*, 694.
 (34) Christe, K. O.; Sawodny, W. Z. *Anorg. Allg. Chem.* **1968**, *357*, 127.
 (35) Christe, K. O. *Spectrochim. Acta, Part A* **1971**, *27a*, 631.
 (36) Christe, K. O. *Inorg. Chem.* **1973**, *12*, 1580.
 (37) MacDougall, P. J. *Inorg. Chem.* **1986**, *25*, 4400.

Received March 20, 1989; accepted June 28, 1989

NUCLEAR MAGNETIC RESONANCE SPECTRUM OF THE FLUORIDE ANION

KARL O. CHRISTE* and WILLIAM W. WILSON

Rocketdyne, a Division of Rockwell International Corporation, Canoga Park, California 91303 (USA)

SUMMARY

The fluorine NMR shift of the fluoride anion in CH_3CN solution has been recorded. The observed shift of -74 ppm significantly differs from the value of -150.6 ppm recently reported. The previously observed signal is attributed to the HF_2^- anion. It is also shown that the previously reported and unexplained satellite at about -131 ppm is due to the SiF_6^{2-} anion. The chemical shifts of F^- in isopropanol, ethanol and CH_2Cl_2 have also been recorded and suggest that the F^- shifts are strongly solvent dependent.

INTRODUCTION

During a recent ^{19}F NMR study of the tetramethylammonium salts of the ClF_4^- , BrF_4^- and BrF_6^- anions in CH_3CN solution [1], we have also measured the chemical shift of the fluoride anion in this solvent. To our surprise, the observed shift dramatically deviated from the values given in a recent paper [2]. Furthermore, in that same paper a mysterious satellite had been reported for F^- which could not be explained. The purpose of this note is to explain these inconsistencies.

RESULTS AND DISCUSSION

The ^{19}F NMR chemical shifts of the F^- , HF_2^- , and SiF_6^{2-} anions were measured at 84.6 MHz on a Varian Model EM390 spectrometer using either 5 mm glass or Teflon-FEP tubes (Wilmad Glass Co.) and CFCl_3 as an external standard with negative shifts being upfield from the standard. The observed chemical shifts are summarized in the Table.

TABLE

^{19}F NMR Data for HF and $[\text{N}(\text{CH}_3)_4]^+$ or Na^+ Salts of F^- , HF_2^- and SiF_6^{2-} in either dry CH_3CN , $(\text{CH}_3)_2\text{CHOH}$, $\text{CH}_3\text{CH}_2\text{OH}$, CH_2Cl_2 or H_2O at Ambient Temperature

Solute	Solvent	Chemical Shift (ppm)*	Multiplicity of Peak and line width (ppm) at half height	Coupling Constant (Hz)
$[\text{N}(\text{CH}_3)_4]\text{F}$	CH_3CN	-73.2	singlet (2)	--
	$(\text{CH}_3)_2\text{CHOH}$	-122.4	singlet (4)	--
	$\text{CH}_3\text{CH}_2\text{OH}$	-136.7	singlet (4)	--
	CH_2Cl_2	-97.0	singlet (2)	--
$[\text{N}(\text{CH}_3)_4]\text{HF}_2$	CH_3CN	-145.6	doublet (3)	$J_{\text{HF}} = 122$
HF	CH_3CN	-184	singlet (4)	--
NaF	H_2O	-119.2	singlet (30)	--
NaHF_2	H_2O	-146.0	singlet (80)	--
NaF/NaHF_2	H_2O	-119 to -146**	singlet (80)	--
HF	H_2O	-160 to -170***	singlet	--
Na_2SiF_6	H_2O	-130	singlet (5) with ^{29}Si satellites	$J_{^{29}\text{SiF}} = 110$

* All chemical shifts are relative to the external standard CFCl_3 with negative values being upfield from the standard.

** Shifts depend on the mole ratio of NaF to NaHF_2 .

*** Data from ref. 2; shifts depend on the concentration of the HF.

As can be seen from the Table, the fluoride anion in a saturated solution of $[\text{N}(\text{CH}_3)_4]\text{F}$ (prepared in our laboratory) in CH_3CN (Baker, Bioanalyzed, having an initial H_2O content of 40 ppm which was reduced to 4 ppm by distillation from P_2O_5) exhibits a chemical shift of -73 ppm. This value deviates greatly from the value of -150.6 ppm, recently reported [2]. Furthermore, it is far outside the range of -121 to -166 ppm, given in the same paper for the fluoride anion of other salts in CH_3CN . Since the previously reported values were measured for aqueous CH_3CN solutions (the water content of the CH_3CN was unfortunately not specified), we have added 10% water to our solution of $[\text{N}(\text{CH}_3)_4]\text{F}$ in CH_3CN . Two immiscible layers formed, and only the aqueous layer exhibited a ^{19}F NMR signal. Its chemical shift value (-118 ppm) is in excellent agreement with previous reports for aqueous fluoride solutions [3-6] and our own observation for an aqueous NaF solution. It appears that the large upfield shifts observed in [2] for NaF (-146.5), AgF (-166.3) and $[\text{N}(\text{C}_2\text{H}_5)_4]\text{F}$ (-150.6) are probably due to the presence of HF_2^- , HF or a combination of the two. The HF_2^- anion has a chemical shift of about -146 ppm, both in CH_3CN and aqueous solution. Whereas for the HF_2^- and F^- anions well separated signals with an H-F spin-spin coupling for HF_2^- are observed in CH_3CN solution (see the Table and [7]), a single peak with a line width of about 80 Hz results for HF_2^- , F^- and HF in aqueous solution due to rapid exchange. The chemical shift of this peak depends on the mole ratios of the three species and, therefore, can vary from -118 to -170 ppm.

We have also measured the chemical shifts of F^- for solutions of $\text{N}(\text{CH}_3)_4\text{F}$ in anhydrous isopropanol ($\delta = -122.6$), ethanol ($\delta = -136.7$) and CH_2Cl_2 ($\delta = -97.0$). Our data show that the chemical shifts of the F^- anion are strongly solvent dependent and span a chemical shift range of at least -73 to -137 ppm. This is also supported by a previously published [8] plot of $^{19}\text{F}^-$ shifts versus those of $^{35}\text{Cl}^-$ in various solvents. Based on this plot, a chemical shift range from about -75 to -150 ppm can be deduced for the F^- anion.

Another mystery in [2] was the observation of a satellite peak at about -131 ppm in the spectra of the HF_2^- salts and those fluorides which, based on their unusually high chemical shifts, probably also were bifluorides. In our study, a similar signal was observed for all samples containing either HF_2^- or HF , but only when recorded in glass tubes and in aqueous solvents. These observations strongly suggested that this signal might be generated by attack on the glass by HF . Therefore, the most likely candidate for this signal was the SiF_6^{2-} anion. The identity of the -131 ppm signal as SiF_6^{2-} was confirmed by comparison with the spectrum of Na_2SiF_6 in H_2O (see the Table) and the observation of ^{29}Si satellite peaks with a coupling constant $J^{29}\text{Si-F} = 110\text{ Hz}$, which are characteristic for SiF_6^{2-} [9].

In conclusion, the chemical shifts previously reported in [2] for the F^- anion have been flawed by the presence of HF_2^- , HF or both in some of the samples. Furthermore, our measurements show that the chemical shift range of F^- extends over a much wider range than previously reported [2], and that the unexplained satellite at about -131 ppm is due to SiF_6^{2-} .

ACKNOWLEDGMENT

The authors are grateful to the Air Force Astronautics Laboratory for financial support of this work and to Dr. C. J. Schack and Mr. R. D. Wilson for their help.

REFERENCES

- 1 W. W. Wilson and K. O. Christe, *Inorg. Chem.* in press.
- 2 M. Hudlicky, *J. Fluorine Chem.*, 28 (1985) 461.
- 3 H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, 19 (1951) 1259.
- 4 R. E. Connick and R. E. Poulson, *J. Chem. Phys.*, 63 (1959) 568.
- 5 C. Deverell and K. Schaumburg, *Anal. Chem.*, 39 (1967) 1879.
- 6 K. Schaumburg and C. Deverell, *J. Am. Chem. Soc.*, 90 (1968) 2495.
- 7 J. S. Martin and F. Fujiwara, *Can. J. Chem.*, 49 (1971) 3071.
- 8 C. Carmona, G. Eaton, and M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, (1987) 873.
- 9 P. A. W. Dean and D. F. Evans, *J. Chem. Soc. (A)*, (1970) 2569.