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Pentagonal Planar AX_5 Species: Synthesis and Characterization of the Iodine (III) Pentafluoride Dianion, IF_5^{2-}[♥]

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Abstract: The new IF_5^{2-} dianion, which is only the second known example of a pentagonal planar AX_5 species, was prepared as its $N(CH_3)_4^+$ salt from $N(CH_3)_4IF_4$ and $N(CH_3)_4F$ in CH_3CN solution. Its structure was established by infrared and Raman spectroscopy, *ab initio* calculations and a comparison to isoelectronic XeF_5^-. Furthermore, vibrational spectroscopy and x-ray powder diffraction data show that the previously reported composition "Cs_3IF_6" is actually a mixture of Cs_2IF_5 and CsF. Ab inito calculations also show that the most probable geometries for IF_6^{3-} are vibrationally unstable and undergo spontaneous F^- ion loss with formation of either pentagonal planar IF_5^{2-} or square planar IF_4^-. The synthesis and some properties of the new $N(CH_3)_4IF_4$ salt and a revised normal coordinate analysis of XeF_5^- are also presented.

Introduction

In 1991, the synthesis and characterization of the XeF_5^- anion was reported.[1] This anion is highly unusual as it is the only known example of a pentagonal planar AX_5 species. In our search for additional representatives of this class, it was noted that the Raman spectrum of a sample[2] having the analytical composition Cs_3IF_6 closely resembled that of $CsXeF_5$. As the unknown IF_5^{2-} is isoelectronic with XeF_5^- and is likely to be isostructural, we suspected that the previously reported "Cs_3IF_6" composition might actually be a mixture of CsF and Cs_2IF_5. Fortunately, the original sample of "Cs_3IF_6" had been preserved in our laboratory for 25 years and showed no signs of deterioration. Therefore, this sample was reinvestigated as it could possibly contain a pentagonal planar IF_5^{2-} dianion. Unfortunately, both CsF and the cesium salt of the multiply charged anion present in the "Cs_3IF_6" sample were found to be insoluble in all available chemically inert solvents, thus preempting either their separation by extraction methods or the identification of the multiply charged anion by methods such as multinuclear NMR spectroscopy or growing of a single crystal for x-ray diffraction. It was therefore interesting to synthesize soluble IF_4^- and F^- salts containing a common cation, which would allow the determination of the true combining ratio of IF_4^- with F^-. A comparison of the vibrational spectra of the resulting product with those of "Cs_3IF_6" should then also permit a positive indentification of the anion present in "Cs_3IF_6".

Experimental

The original [2] Cs_3IF_6 sample, prepared by the combination of CsF and IF_3 in a 3:1 mol ratio in a $CFCl_3$ suspension at -78°C, [3,4] was used in this study. The preparation of IF_3,[3] anhydrous $N(CH_3)_4F$[5] and XeF_2[6] have previously been described. The purity of the IF_3 was checked by its low temperature Raman spectum which was in excellent agreement with a previous report.[7] The $N(CH_3)_4I$ (K & K Labortories, Inc.) was used as received. The CH_3CN (J.T. Baker, bioanalyzed, low water) was dried over P_2O_5 prior to its use. The volatile fluorine compounds were handled in a stainless-steel Teflon-FEP vacuum line, similar to one previously described.[8] The CH_3CN was handled in a flamed out Pyrex glass vacuum line equipped with Kontes Teflon valves and a Heise pressure gauge.

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer using AgCl disks prepared by pressing the finely powdered sample between two thin AgCl plates in a Barnes Engineering minipress inside the glove box. An AgCl blank was placed into the reference beam to compensate for the absorption of the window material. Raman spectra were recorded on either a Cary Model 83GT, a Spex Model 1403 or a Bruker Equinox 55 spectrophotometer using the 488 nm exciting line of an Ar ion laser, the 647.1 nm line of a Kr ion laser or the 1064 nm line of a neodymium yag laser, respectively. ^{19}F NMR spectra were recorded at 84.24 MHz on a Jeol FX902 multinuclear instrument between +30 and -30 °C, using CH_3CN as a solvent and d6-

acetone/$CFCl_3$ as an external lock substance and standard. The DSC data were recorded using a DuPont Model 910 DSC. A DuPont Model 2000 Thermal Analyst was used for recording and analyzing the data. The samples were crimp sealed in aluminum pans inside the drybox and heated at a rate of 2 °C/min.

Synthesis of $N(CH_3)_4IF_4$. Inside the dry box, $N(CH_3)_4I$ (2.163 mmol) and XeF_2(4.327 mmol) were combined in a prepassivated (with ClF_3) Teflon FEP, 0.75 inch o.d. Teflon FEP U-tube which was closed with two stainless steel valves. On the glass vacuum line, CH_3CN (10 mL liquid) was added at -196 °C, and the mixture was warmed to -31 °C. After 8 hr, all gas evolution had ceased, and the amount of gas volatile at -78 °C (2.1 mmol of Xe) was measured. A white solid had formed in the bottom of the tube which was identified as $N(CH_3)_4IF_2$.[9] Upon warming of the mixture to room temperature, the yellowish CH_3CN solution turned more orange and additional gas evolved. After 1.5 hr at 20 °C, the gas evolution (2.13 mmol of Xe) was complete, resulting in a white solid and clear orange-yellow solution. All volatile material was pumped off at room temperature leaving behind 602 mg of a white solid (weight calcd for 2.163 mmol of $N(CH_3)_4IF_4$ = 599.4 mg) which was identified by vibrational and NMR spectroscopy as $N(CH_3)_4IF_4$.

$N(CH_3)_4IF_4$ was also prepared by the reaction of stoichiometric amounts of $N(CH_3)_4F$ and IF_3 in CH_3CN solution of -31 °C. However, this synthesis is inferior to the one described above.

Synthesis of $[N(CH_3)_4]_2IF_5$. Inside the dry box, $N(CH_3)_4IF_4$ (0.58 mmol) and $N(CH_3)_4F$ (0.72 mmol) were loaded into a prepassivated, 0.75 inch o.d., Teflon-FEP ampoule which contained a Teflon coated magnetic stirring bar and was closed by a stainless steel valve. On the glass line, dry CH_3CN (7.2 mL) was added at -196 °C and the mixture was stirred for 18 hr at -31 °C. The solvent was pumped off for 14 hr, first at -31 °C and during the last stages at room temperature, resulting in a white dry solid (227 mg, weight calcd for 0.58 mmol

$[N(CH_3)_4]_2IF_5$ plus 0.14 mmol $N(CH_3)_4F$ = 228 mg) which was shown by vibrational spectroscopy to consist mainly of $[N(CH_3)_4]_2IF_5$, containing a small amount of unreacted $N(CH_3)_4IF_4$ and the excess of $N(CH_3)_4F$ used in the reaction.

Theoretical Calculations. Electronic structure calculations were done at the local density functional theory (LDFT) level[10,11] with a polarized valence double zeta basis set (DZVP)[12], and at the Hartree-Fock (HF) level[13] with an effective core potential (ECP)[14] on I for the core electrons and with a polarized double zeta basis set for the valence electrons, and with an all electron polarized double zeta valence set on F.[15] Geometries were optimized using analytical methods.[16] Analytic second derivatives were calculated at the optimized LDFT geometries.[17] Numerical second derivatives were calculated at the Hartree-Fock level by using a two-point differencing scheme. The LDF calculations were done with DGauss[18], and the HF calculations were done with Gaussian 94.[19] The calculated Hessian matrices (second derivatives of the energy with respect to Cartesian coordinates) were converted to symmetry-adapted internal coordinates for further analysis using the program systems GAMESS[20] and Bmtrx.[21]

Results and Discussion

Synthesis and Properties of $N(CH_3)_4IF_4$. As already pointed out in the Introduction, the determination of the combining ratio of IF_4^- with F^- required the availability of soluble salts of these two anions with a common counterion. Since $N(CH_3)_4F$[5] and $N(CH_3)_4XF_4$ (x = Br or Cl)[22] were known to have good solubility in CH_3CN, the $N(CH_3)_4IF_4$ salt appeared to be an ideal candidate for our reactions. Our first attempts to prepare this salt from $N(CH_3)_4F$ and IF_3 in CH_3CN solution at -31 °C produced only impure products. Subsequently, the following improved synthesis (1) gave very pure $N(CH_3)_4IF_4$, eliminated the need for the thermally unstable IF_3, which is difficult to purify,[3,4] and utilized only commercially available starting materials. It is

$$N(CH_3)_4I + 2XeF_2 \xrightarrow[-31 \text{ to } 20\,^\circ C]{CH_3CN} N(CH_3)_4IF_4 + 2Xe \qquad (1)$$

similar to the one previously reported[23] for 1,1,3,3,5,5 hexamethylpiperidinium $(pip^+)IF_4^-$ from pip^+F^-, iodine and XeF_2, but offers the advantages of avoiding a 7 step, 14% yield synthesis of pip^+F^- and the handling of volatile elemental iodine.

$N(CH_3)_4IF_4$ is a white crystallinic solid which, based on DSC data and vibrational spectra, undergoes a reversible endothermic phase change of 21.8 J/g at 73.8 °C and irreversible exothermic decomposition at 284 °C. The surprisingly high thermal stability of this compound is in marked contrast to that of $pip^+IF_4^-$ which was reported[23] to be unstable above 0 °C.

The ^{19}F NMR spectra of $N(CH_3)_4IF_4$ in CH_3CN solution were recorded at -30 and 30 °C and consisted of broad singlets at $\delta = -106.5$ with half widths of 385 and 1061 Hz, respectively. The observed chemical shift is in excellent agreement with the value of -106 ppm, previously reported[23] for $pip^+IF_4^-$ in CH_3CN at -20 °C. The chemical shift of IF_4^- fits nicely the trends observed for other halogen fluoride anions,[25,26] i.e., the shielding of the fluorine ligands decreases with increasing oxidation state and electronegativity of the central atom (see Table 1). Pronounced line broadening with increasing temperature was also observed for BrF_4^- and ClF_4^-.[26]

The infrared and Raman spectra of $N(CH_3)_4IF_4$ are summarized in Table 2. The bands observed for the IF_4^- part of $N(CH_3)_4IF_4$ agree well with those previously reported for $CsIF_4$,[2] but not with those (Ra: 573.5, 461 and 213 cm^{-1}) previously listed[23] for $pip^+IF_4^-$. Particularly, the value of 573.5 cm^{-1}, reported for $\nu_1(A_{1g})$ of $pip^+IF_4^-$, is outside the expected (see Computional Results below) range and is likely incorrect. The bands due to the $N(CH_3)_4^+$ cation have been summarized in a footnote of Table 2. They are in excellent agreement with those previously reported for other $N(CH_3)_4^+$ salts[1,5,9] and, therefore, do not require further discussion.

Synthesis and Properties of $[N(CH_3)_4]_2IF_5$. The combination of $N(CH_3)_4IF_4$ with a slight excess of $N(CH_3)_4F$ in CH_3CN solution at -31 °C produced the desired $[N(CH_3)_4]_2IF_5$ (2).

$$N(CH_3)_4IF_4 + N(CH_3)_4F \xrightarrow[-31\ ^{\circ}C]{CH_3CN} [N(CH_3)_4]_2IF_5 \qquad (2)$$

Prolonged reaction times (about 20 hr) and stirring resulted in an almost quantitative conversion of IF_4^- to IF_5^{2-} thus establishing the 1:1 combining ratio between IF_4^- and F^-. In the presence of a large excess of F^- ions, no further fluoride ion uptake and, hence, no formation of IF_6^{3-} were observed. Attempts to carry out reaction (2) in CHF_3 solution at -78 °C were unsuccessful and only unreacted $N(CH_3)_4IF_4$ was recovered.

The $[N(CH_3)_4]_2IF_5$ salt is a white solid which is stable at room temperature. It has very little solubility in solvents, such as CH_3CN, which precluded its characterization by NMR spectroscopy and the growing of single crystals for a crystal structure determination. Infrared and Raman spectra of the solid were used for its characterization. They are given in Figure 1 and Table 3, and their assigments are discussed below in more detail.

Characterization of Cs_2IF_5. In the original report[2] on "Cs_3IF_6", the true combining ratio of IF_3 with CsF had not been established. An arbitrary 1:3 ratio of the starting materials had been used and, since both, CsF and Cs_2IF_5, are insoluble, the products could not be separated and, therefore, by necessity had the analytical composition Cs_3IF_6.

In the reaction of IF_4^- with an excess of fluoride ions, the logical first step is the addition of one fluoride ion with formation of IF_5^{2-}. The addition of a second fluoride ion with formation of an IF_6^{3-} trianion becomes less likely since the Lewis acidity of the parent anion decreases with the addition of each F^- ion. Although, based on these arguments, the formation of IF_5^{2-} is clearly favored over that of IF_6^{3-}, it previously had not been given much consideration due to the absence of any other AX_5E_2 species containing two free valence electron pairs (E) on A. This picture, however, has changed recently with the synthesis of surprisingly stable XeF_5^- salts.[1]

Our reinvestigation of the original[2] "Cs_3IF_6" sample, which had been preserved in our laboratory for 25 years without noticeable decomposition, showed that is it is indeed a mixture of Cs_2IF_5 and CsF, based on the following evidence:

(i) X-ray powder data: The previously published powder pattern of "Cs_3IF_6" (Table II of reference 2) shows all the lines characteristic[27] for CsF (d(Å), intens: 3.4 ms, 3.03 mw, 2.106 mw, 1.801 mw, 1.735 vw, 1.496 w, 1.370w, 1.336 mw, 1.223 w, 1.153w) and leaves no doubt that "Cs_3IF_6" contains a very significant amount of free CsF.

(ii) Infrared spectrum: The infrared spectrum of "Cs_3IF_6" was rerecorded and compared to that of CsF taken under the same conditions. It was found that the major absorption in both spectra was a very intense and broad band at 298 cm^{-1} due to CsF which in the "Cs_3IF_6" case confirms the presence of free CsF but obscures the less intense IF_5^{2-} bands.

(iii) Raman spectrum: A higher quality Raman spectrum, which did not suffer from fluorescence,[2] was obtained by means of 1064 nm excitation with a neodymium yag laser and is shown in Figure 2. The dominant Raman bands at 478, 396, 339 and 325 cm^{-1} are in excellent agreement with those of IF_5^{2-} in $[N(CH_3)_4]_2IF_5$ (see Table 3) and leave no doubt that the dominant anion in "Cs_3IF_6" is IF_5^{2-}. For a hypothetical IF_6^{3-} anion, the additional fluoride ligand and extra formal negative charge should cause a different band pattern and significant shifts to lower frequencies. In addition to the intense IF_5^{2-} bands, the "Cs_3IF_6" spectrum showed several very weak bands which can be assigned to likely impurities, such as IF_7^{2-} (556 and 454 cm^{-1}) or IOF_5^{2-} (865 cm^{-1})[28] and lattice vibrations (140 and 110 cm^{-1}). The formation of IF_7^{2-} and IOF_5^{2-} can be easily rationalized. Iodine trifluoride has a tendency to disproportionate to I_2 and IF_5,[3] and IF_5 is known[28] to react with excess F^- to give IF_7^{2-}. Similarly, a trace of moisture will result in partial hydrolysis of IF_6^- to give IOF_4^-, which in turn is known to give with excess F^- the IOF_5^{2-} dianion.[28] These impurities had been formed already during the original preparation[4] and were not generated during sample storage.

Vibrational Spectra and Electronic Structure Calculations. The vibrational spectra of IF_5^{2-} are summarized in Table 3 and were assigned by analogy with those established for the isoelectronic XeF_5^- anion.[1,29] The only difference is the reversal of the identity of ν_5 amd ν_6 in the E_2' block, based on the results of the potential energy distribution (see below). The spectra of IF_5^{2-} and

XeF_5^- are very similar. They exhibit the expected frequency decreases for IF_5^{2-} due to the additional negative charge which enhances the X(δ+)-F(δ-) polarity of the bonds. Analogous general frequency and bond weaking effects are also observed on going from IF_4^-(see Table 2) to IF_5^{2-} (see Table 3).

The geometry and the vibrational spectra of IF_5^{2-} and XeF_5^- were studied by electronic structure calculations at the HF and LDFT levels. To evaluate the reliability of our computational methods, the well know IF_4^- geometry[23] and spectra[2] were calculated first. As can be seen from Tables 2 and 4, the HF/ECP/DZP method gave the better results. For IF_4^-, the bond length, calculated at the HF/EDP/DZP level is only 0.013 Å shorter than the observed one.[23] For IF_5^{2-}, the minimun energy structure at both the HF and LDFT levels was pentagonal planar with D_{5h} symmetry. Assuming a similar correction as for IF_4^-, the bond length of IF_5^{2-} is predicted to be 2.11 Å. This bond length increase of 0.09 Å relative to IF_4^- can be explained by the increased polarity of the bonds (see above) and increased ligand-ligand repulsion due to a decrease of the F-I-F bond angle from 90 ° in IF_4^- to 72 ° in IF_5^{2-}.

The symmetry force constants and potential energy distributions (PED) were calculated for IF_5^{2-} and XeF_5^- using the scaled HF/ECP/DZP frequencies (see Table 5). Since we were unable to duplicate with our computer calculations the previously published, hand calculated, out of plane deformation force constants,[1,29] the originally given[1] G matrix was reexamined and found to contain incorrect multiplicity factors for G_{22} and G_{77}. The corrected G matrix for XeF_5^- is given in Table 6 and was verified by the machine methods. A typographical error for a sign in one of the originally published[1] symmetry coordinates, i.e., (S_{5b}) should read $(2/5)^{1/2}$ $[\sin 2\alpha(\Delta r_2-\Delta r_5) - \sin\alpha(\Delta r_3-\Delta r_4)]$ has already been corrected elsewhere.[29] The revised force constant, F_{22} = 0.480 mdyn Å/rad², for the symmetric out of plane deformation of XeF_5^- is now in much better agreement with our expectation. The deformations out of the highly crowded pentagonal plane should possess significantly smaller force constants than the corresponding in plane deformations.

As can be seen from Tables 3 and 5, the results from the normal coordinate analyses confirm the identities of these pentagonal planar anions. The general fit between the calculated and observed frequencies is very good. The only remaining minor ambiguities in the normal coordinate analyses are: (i) for XeF_5^-, the exact location of the infrared active, in plane deformation mode, ν_4, is somewhat uncertain. Based on the calculations, its frequency is similar to, but its infrared intensity is much lower than those of the out of plane umbrella deformation mode, ν_2. Therefore, we assume that ν_4 is hidden under the ν_2 band; (ii) for IF_5^{2-}, the location of the infrared active, out of plane umbrella deformation mode was obscured. In the Cs_2IF_5 spectrum, the strong absorption due to free CsF obscured this region, and in the $[N(CH_3)_4]_2IF_5$ spectrum, the presence of an IF_4^- impurity and the broadness of the ν_3 mode of IF_5^{2-} interferred. In the Raman spectrum of Cs_2IF_5, one of the two E_2' bands exhibits a splitting, similar to those observed for these modes in XeF_5^-. In Table 3, this splitting was tentatively assigned to ν_5 because this requires a smaller splitting . However, if one assumes ν_6 to be split intead of ν_5, the average of the 396 and 339 cm^{-1} components would result in much better agreement with the calculated frequency of 366 cm^{-1} and the $[N(CH_3)_4]_2IF_5$ spectrum, in which ν_6 of IF_5^{2-} probably coincides with a cation band at 366 cm^{-1}.

An inspection of the potential energy distributions for IF_5^{2-} and XeF_5^- (see Table 5) shows that the E modes of XeF_5^- are considerably more characteristic than those of IF_5^{2-}. This is due to the increased bond polarity in IF_5^{2-}, which lowers preferably the stretching force constant and makes its value more similar to those of the deformation constants. This enhances the mixing of the normal modes in IF_5^{2-} and, in its E_2' block, results in the higher frequency mode becoming mainly the bending motion. A further consequence of the larger bond polarity in IF_5^{2-} is the increased coupling of the stretching motions involving opposite bonds (frr' = 0.42 mdyn / Å). This large frr' value is responsible for the low frequency of the antisymmetric stretching mode , $\nu_3(E_1')$, which respresents the reaction coordinate for the loss of an F^- ion. This finding is in accord with the observation that IF_5^{2-} readily loses an F^- ion to give IF_4^-.

The stability of the hypothetical IF_6^{3-} anion was also examined by ab initio methods. The four most likely geometries of IF_6^{3-} are shown in Figure 3. Like IF_5^{2-}, this anion contains two free valence electron pairs on iodine. If both electron pairs are sterically active, the most likely structure is the one with D_{3d} symmetry, in which the two more repulsive free pairs avoid each other as much as possible by occupying the axial trans positions of a bicapped octahedron. If, on the other hand, one of the two free valence electron pairs on iodine is sterically inactive, i.e., occupies an A_{1g} or *s*-orbital, only *p* and *d*-orbitals of iodine are involved in the bonding and, therefore, the resulting structures are governed by repulsion effects, and , as in transition metal heptafluorides,[30] the energetically most favored structures become the monocapped octahedron of C_{3v} symmetry and the monocapped trigonal prism of C_{2v} symmetry. The pentagonal bipyramid of C_{5v} symmetry is slightly higher in energy, but was also considered.[31-33]

The structures of all four geometries of IF_6^{3-} were calculated at the restricted Hartree-Fock (RHF) self-consistent field level, using effective core potentials[34] and the corresponding valence basis sets of Stevens, Basch, Krauss, and Jasien.[35] The basis set was augmented with a diffuse s+p shell[36] and a d polarization function[37] on each atom. All calculations were performed using the GAMESS quantum chemistry package.[20] Since the HOMO of the D_{3d} and C_{3v} structures is a half-filled degenerate orbital pair, Jahn-Teller distortion to lower symmetry is anticipated. Therefore, the initial geometries of these conformations were distorted to C_s symmetry by slight elongation of one pair of trans fluorine ligands. For each of the four conformations, geometry optimization led to the dissociative loss of one or two fluoride ligands. Specifically, optimization of the C_{2v} conformation and the distorted D_{3d} and C_{3v} structures led to formation of square planar $[IF_4]^-$ and 2 fluoride anions, whereas optimization of the C_{5v} structure led to formation of pentagonal planar $[IF_5]^{2-}$ and one fluoride anion. Thus, none of the four conformations were found to be a local minimum. Although more extensive calculations are desirable to definitively rule out the stability of the $[IF_6]^{3-}$, the present results strongly indicate that this anion is not a stable species.

Conclusions

The successful synthesis of a second example of a pentagonal planar AX_5 species demonstrates that XeF_5^- is not a unique case, and that other examples of AX_5 molecules of D_{5h} symmetry, such as TeF_5^{3-}, AuF_5^{2-} or PtF_5^{3-}, might also exist. Although IF_5^{2-} had been prepared 30 years ago,[3] its nature had not been recognized until now. The greatly delayed recognition of this unusual anion parallels the discovery[1] of XeF_5^- which had originally been mistaken for octahedral XeF_6^{2-}.[38-40]

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References

♥ Dedicated to Professor Neil Bartlett on the occasion of his 65th birthday

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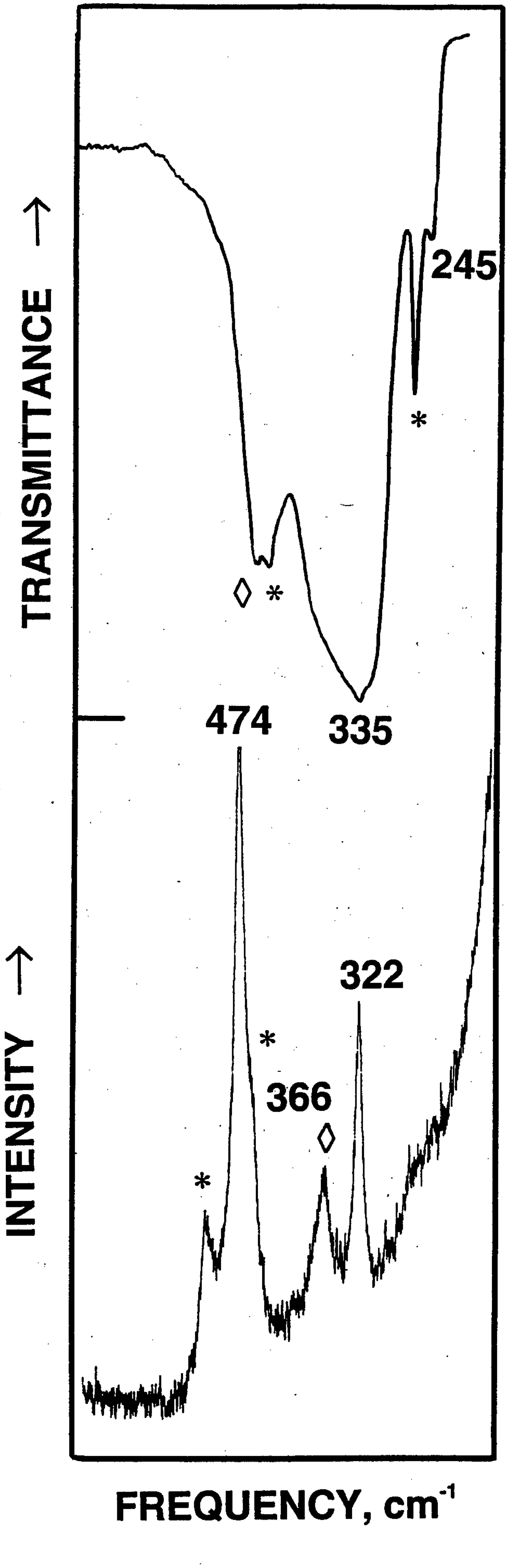
Diagram Captions

Figure 1	Infrared and Raman spectra of solid $[N(CH_3)_4]_2\ IF_5$. The bands masked by asterisks and diamonds are due to IF_4^- and $N(CH_3)_4^+$, respectively, while those marked by frequency values belong to IF_5^{2-}.
Figure 2	Raman spectrum of Cs_2IF_5.
Figure 3	Most likely geometries of the IF_6^{3-} trianion and their spontaneous decomposition modes.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474
335
INTENSITY →
322
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366
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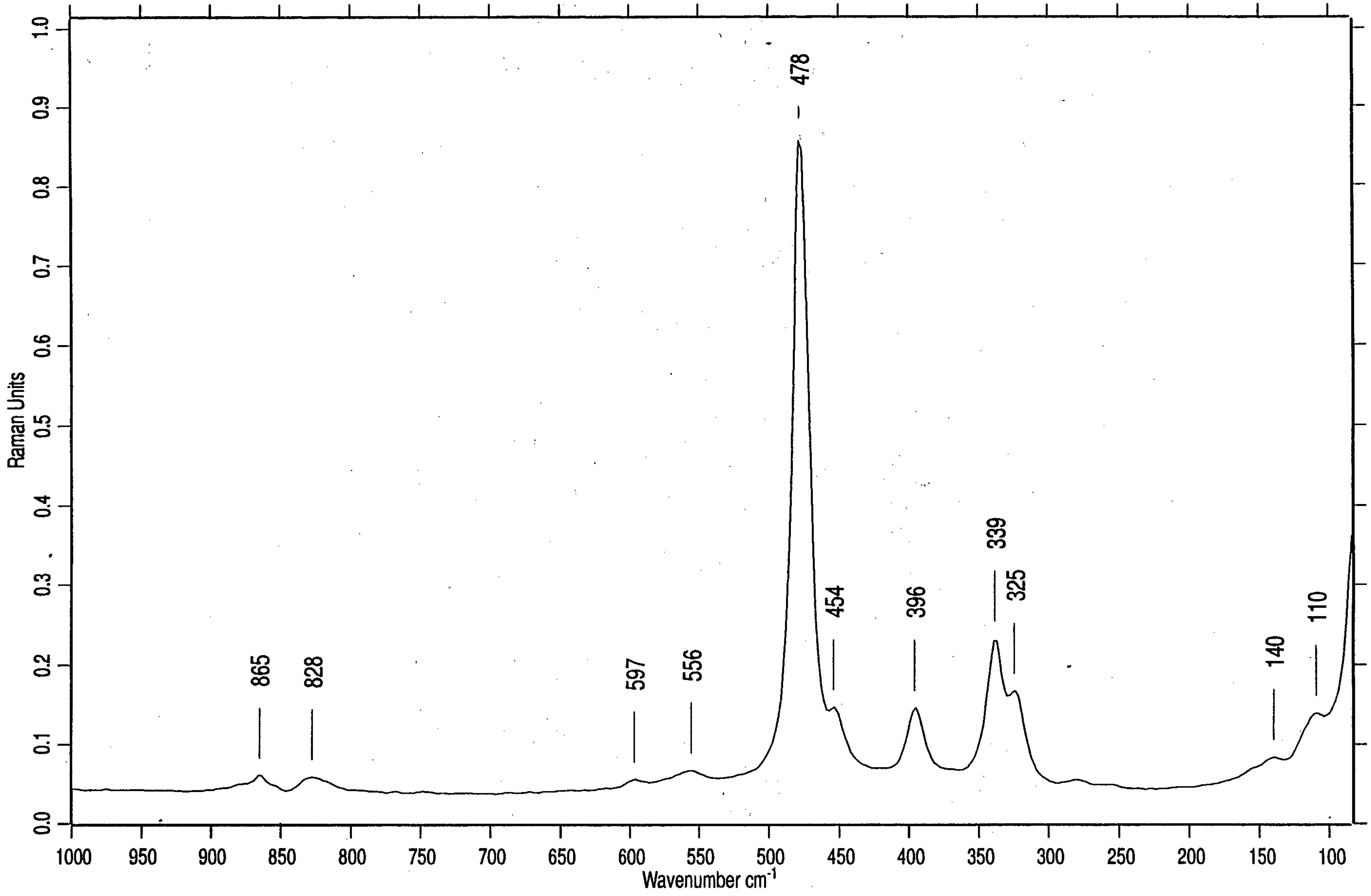
FREQUENCY, cm^{-1}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454
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339
325
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828
597
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Raman Units
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800
750
700
650
600
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300
250
200
150
100
Wavenumber cm^{-1}

Two sterically active free valence electron pairs

One sterically active and one sterically inactive free valence electron pair

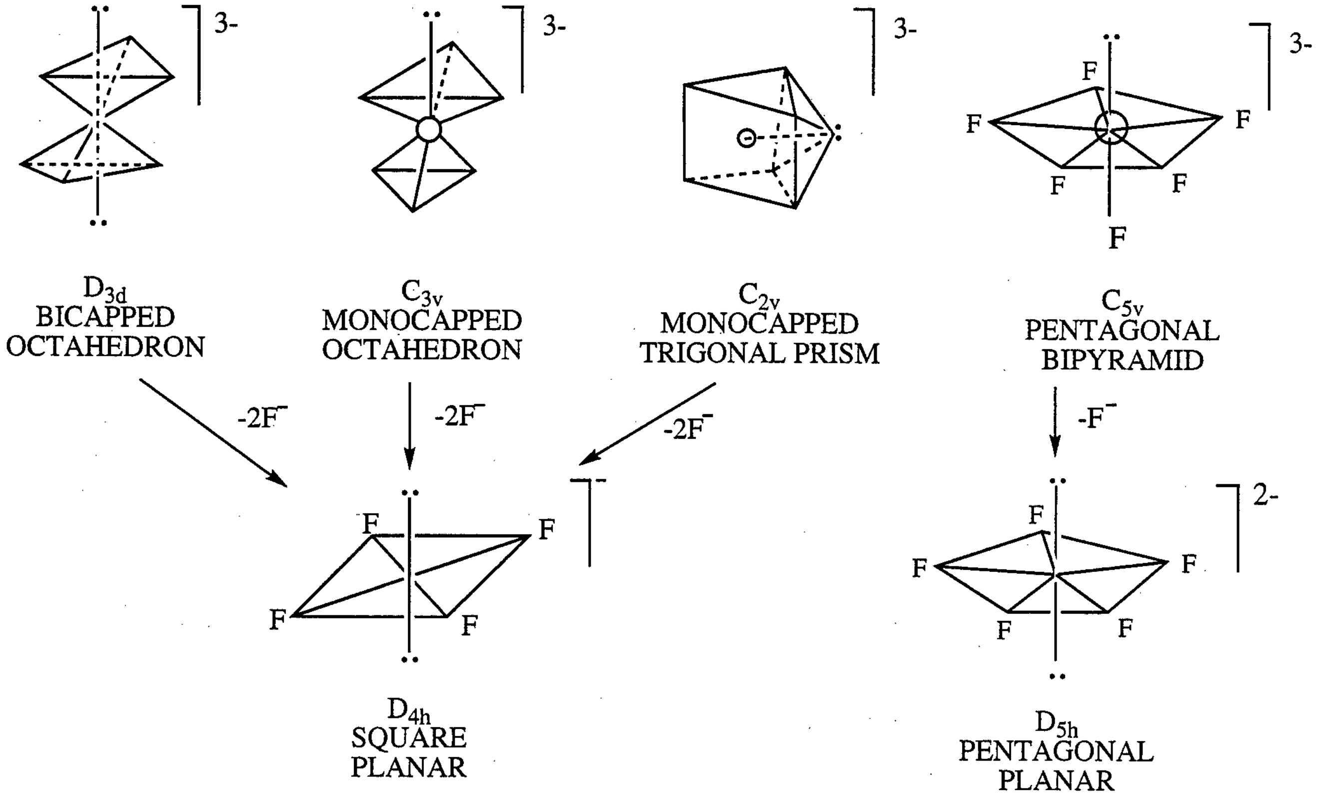

Table 1. ^{19}F Chemical Shifts for Binary Halogen Fluoride Anions

oxidation state of central atom			
+I	IF_2^- -282[a]		
+III	IF_4^- -106[b]	BrF_4^- -37[e]	ClF_4^- 67[e]
+V	IF_6^- 13[c]	BrF_6^- 94[e]	
+VII	IF_8^- 249[d]		

[a]. ref 9. [b] this work and ref 23. [c] ref 25. [d] ref 26. [e] ref 22.

Table 2. Observed and Calculated Vibrational Spectra of IF_4^-

assgnts and approx mode descriptions in point group D_{4h}				obsd freq, cm^{-1} (rel int)[a]				calcd freq, cm^{-1} (IR int)[b]		
				$CsIF_4$		$N(CH_3)_4IF_4$[d]		HF/ECP/DZP		LDFT/DZVP
				IR	RA	IR	RA	unscaled	scaled	unscaled
Ra	A_{1g}	ν_1	ν sym in phase	—	522(10)	—	515(10)	559(0)	520	495(0)
IR	A_{2u}	ν_2	δ umbrella	271ms	—	267ms	—	326(78)	277	255(40)
Ra	B_{1g}	ν_3	ν sym out of phase	—	455(7.2)	—	457(5.6)	493(0)	458	449(0)
Ra	B_{2g}	ν_4	δ scissor	—	195(0+)	—	197(0.5)	225(0)	191	167(0)
—	B_{2u}	ν_5	δ pucker	—	—	—	—	185(0)	157	140(0)
IR	E_u	ν_6	ν asym	448vs	—	449 vs	—	481(951)	447	501(544)
		ν_7	δ asym	n. obsd	—	n. obsd	—	139(3)	118	115(3)

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[a] Data for $CsIF_4$ from ref 2, for $N(CH_3)_4$ IF_4 from this study. [b] Infrared intensities in km/mol. [c] Empirical scaling factors of 0.9294 and 0.8490 for the stretching and deformation modes, respectively, were used to maximize the fit between the observed and calculated frequencies. [d] In addition to the above listed IF_4^- bands, the following bands due to $N(CH_3)_4^+$ were observed: IR: 3118sh, 3040w, 2969vw, 1490 mw, 1444w, 1416mw, 1287w, 952m, 922w, 462m; Ra: 3021(0.7), 2969(0.2), 2942(0.4), 2907(0.1), 2800(0.1), 1471(0.6), 1461(0.7), 1413(0.3), 1284(0.1), 1175(0.15), 1168(0.1), 947(1.5), 754(1.5), 450 sh on the intense 457 IF_4^- band, 369(0.2).

Table 3. Observed and Calculated Vibrational Spectra of IF_5^{2-} Compared to Those Observed for XeF_5^-

assgnts and approx mode descriptions in point group D_{5h}				IF_5^{2-} obsd freq, cm^{-1} (rel int) Cs_2IF_5	IF_5^{2-} obsd freq, cm^{-1} (rel int) $[N(CH_3)_4]_2IF_5$[b]		IF_5^{2-} calcd freq, cm^{-1} (IR int)[f] HF/ECP/DZP		XeF_5^-[a] obsd freq, cm^{-1} (rel int) $CsXeF_5$		XeF_5^-[a] obsd freq, cm^{-1} (rel int) $N(CH_3)_4XeF_5$	
				RA	IR	RA	unscaled	scaled[e]	IR	Ra	IR	Ra
Ra	A_1'	ν_1	ν sym	478(10)		474(10)	487(0)	468		504(10)		502(10)
IR	A_2''	ν_2	δ umbrella		(—)[c]		320(97)	307	274s		278s	
IR	E_1'	ν_3	ν asym		335vs,br		356(588)	342	450vs 415s		509sh 465vs 420sh	
		ν_4	δ asym in plane		245w		259(14)	249	288sh			
Ra	E_2'	ν_5	ν asym	339(2)		322(3.8)	349(0)	335		432(1.5)		423(2.1)
				325(1.6)						422(1.6)		
		ν_6	δ asym in plane	396(0.9)		(366)[d]	381(0)	366		380(2.2) 369(2.3)		377(3.3)
Ra	E_2''	ν_7	δ pucker				104(0)	100				

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[a] Data from ref 1. [b] In addition to the above listed IF_5^{2-} bands, the following bands due to $N(CH_3)_4^+$ were observed: IR: 3034ms, 1507ms, 1415w, 1255m, 963s, 467m; Ra: 3010(1.3), 2943(0.8), 2810(0.4), 1478(1.8), 952(1.8), 751(3.0), 460(sh), 366(1.0). [c] This band is masked by the very intense broad band at 335 cm^{-1}. [d] This band is obscured by the relatively intense 366 cm^{-1} $N(CH_3)_4^+$ band. [e] An empirical scaling factor of 0.9606 was used to maximize the fit between observed and calculated frequencies. [f] Ir intensities in km/mol.

Table 4. Calculated, Observed and Predicted Bond Lenghts for IF_4^- and IF_5^{2-}

	bond distances (Å)			
	observed	calculated		predicted
		HF/ECP/DZP	LDFT/DZVP	
$IF_4^-(D_{4h})$	2.007[a]	1.994	2.069	—
$IF_5^{2-}(D_{5h})$	—	2.094	2.163	2.11

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[a] Ref. 23.

Table 5. Symmetry Force Constants and Potential Energy Distribution of D_{5h} IF_5^{2-} and XeF_5^- Calculated from the Scaled HF/ECP/DZP Second Derivatives

	IF_5^{2-} [a]				XeF_5^- [b]			
	freq, cm^{-1}		sym force consts[c]	PED (%)	freq, cm^{-1}		sym force consts[c]	PED (%)
	obsd	calcd			obsd	calcd		
A_1'	474	468	$F_{11} = 2.445$	100(1)	502	503	$F_{11} = 2.835$	100(1)
A_2''		307	$F_{22} = 0.529$	100(2)	278	305	$F_{22} = 0.480$	100(2)
E_1'	335	342	$F_{33} = 0.867$	70(3),20(4)	455	454	$F_{33} = 1.707$	98(3),2(4)
			$F_{34} = -0.030$				$F_{34} = -0.181$	
	245	249	$F_{44} = 1.886$	80(4),20(3)	278	276	$F_{44} = 1.952$	98(4),2(3)
E_2'	322/339	335	$F_{55} = 1.735$	74 (5),26(6)	423	425	$F_{55} = 1.982$	92(5),8(6)
			$F_{56} = 0.115$				$F_{56} = 0.122$	
	366/396	366	$F_{66} = 1.316$	74(6),26(5)	377	378	$F_{66} = 1.794$	92(6),8(5)
E_2''		100	$F_{77} = 0.260$	100(7)		107	$F_{77} = 0.266$	100(7)

internal force constants

	IF_5^{2-}	XeF_5^-
fr	1.529	2.043
frr	0.035	0.137
frr′	0.423	0.260

---

[a] Empirical scaling factors of 0.9606 and $(0.9606)^2$ were used for the frequencies and force constants, respectively. [b] Scaling factors: 0.87322 and $(0.87322)^2$. [c] Stretching constants in mdyn/Å, deformation constants in mdyn Å/rad^2, and stretch-bend interaction constants in mdyn/rad.

Table 6. 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''	$G_{22} = (5/r^2)(\mu_y + 5\mu_x) = 1.1201 \times 10^{-1}$
E_1'	$G_{33} = \mu_y + 5u_x/2 = 7.1679 \times 10^{-2}$
	$G_{34} = (5^{3/2}\mu_x)/(4r\sin\alpha) = 1.1123 \times 10^{-2}$
	$G_{44} = (1/r^2)(5\mu_y\sin^2 2\alpha + \mu_x) = 2.4334 \times 10^{-2}$
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''	$G_{77} = (3-5^{1/2})(5/2r^2)\mu_y = 2.4823 \times 10^{-2}$

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[a] The following geometry and masses were used for the calculation of the G matrix: $r = 2.0124$ Å and $\alpha = 72°$; $m_x = 131.292$; $m_y = 18.998$.