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Form Approved
OMB No. 0704-0188

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1. REPORT DATE (DD-MM-YYYY) 24-02-1998	2. REPORT TYPE Paper	3. DATES COVERED (From - To)
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4. TITLE AND SUBTITLE Theory and Synthesis of New HEDM Related Materials	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S) K. Christe ¹ ; W. Wilson ¹ ; G. Drake ² ; M. Petrie; J. Sheehy ² ; J. Boatz ²	5d. PROJECT NUMBER 2303
	5e. TASK NUMBER M2C8
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) AND ADDRESS(ES) ¹ Hughes STX Phillips Laboratory Edwards AFB CA 93524	8. PERFORMING ORGANIZATION REPORT ² Air Force Research Laboratory (AFMC) AFRL/PRSP 5 Pollux Drive Edwards AFB CA 93524-7048
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9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR-ED-TP-1998-047

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

20020115 076

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT A	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON P. Carrick
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) (661) 275-4481

THEORY AND SYNTHESIS OF NEW HEDM RELATED MATERIALS

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This paper describes some of the work carried out during the past year by both the HEDM Synthesis Group at the Phillips Laboratory and the ~~associated~~ program at USC, which is partially supported by the Air Force. It exemplifies the benefits and synergism which can be derived from the successful combination of theory and synthesis.

In the area of novel anions, our study of the novel and elusive POF_4^- anion was completed. This anion, which is stable only at -140°C , was characterized, in collaboration with Prof. Schrobilgen from McMaster University, by multinuclear NMR spectroscopy. In collaboration with Dr. Dixon from Pacific Northwest Laboratories, the geometry, NMR shifts, activation barriers for the Berry inversion, vibrational spectra, force field and thermodynamic data were calculated. In the course of our efforts to rationalize the very different dismutation behavior of POF_4^- and isoelectronic SOF_4 , (POF_4^- dismutates at -140°C to PO_2F_2^- and PF_6^- , whereas SOF_4 does not dismutate at all to SO_2F_2 and SF_6), it was shown by our ab initio calculations that the thermodynamic data published for several phosphorus and sulfur oxofluorides are in error by as much as 60 kcal/mol. It was shown that the different dismutation behavior of POF_4^- and SOF_4 is due to mechanistic and not thermodynamic reasons. The results were published in the Journal of the American Chemical Society, **1997**, 119,3918.

In the area of high coordination number chemistry, we have succeeded to prepare and characterize a number of new heptacoordinated anions. Among these are IF_5^{2-} , IF_5O^{2-} , $\text{IF}_5\text{O}_2^{2-}$, IF_7^{2-} , SbF_7^{2-} , and BiF_7^{2-} . Since all these ions possess very little solubility and therefore are not amenable to crystal growing or NMR studies, they were characterized by infrared and Raman spectroscopy. Ab initio calculations, carried out by Dr. Dixon, were used to confirm their identities, structures and vibrational assignments. The IF_5^{2-} anion contains two and IOF_5^{2-} contains one sterically active free valence electron pairs

on the iodine central atom. They are only the second known examples of pentagonal planar and pentagonal pyramidal AX_5E_2 and AX_5OE species, respectively. The $IF_5O_2^{2-}$ ion is the first known example of an AX_5O_2 species and contains two axial oxygen atoms in trans positions. The IF_7^{2-} anion possesses one free valence electron pair on the iodine central atom, but this pair is sterically inactive. The resulting structure is that of a monocapped octahedron which normally is found only for heptacoordinated transition metal compounds. The SbF_7^{2-} and BiF_7^{2-} anions represent the first known examples of heptacoordinate AX_7 pnictogen species and are very remarkable because SbF_6^- and BiF_6^- had been known for a long time. More details on this work are given in the poster abstract by Dr. Drake.

In the process of synthesizing $[N(CH_3)_4]_2IF_5O_2$ from $N(CH_3)_4IF_4O_2$ and F_2 , it became necessary to better characterize this salt. This shock sensitive material, which also explodes on heating, exhibits very interesting polymorphism, phase transitions and rotational disorder. The crystal structures and Raman spectra of its low temperature and room temperature phases were studied and demonstrate that the phase transitions in this molecule are due to the onset of free ion rotation, rather than positional disorder of the rotational oscillation axes. This finding confirms a proposal, made in 1930 by Linus Pauling and repeatedly criticized since then. These results were summarized in manuscript form for publication in *Inorganic Chemistry*.

Attempts were made to synthesize NF_2 -substituted fullerenes by reacting C_{60} with NF_2 radicals, which were generated by uv-photolysis of N_2F_4 . However, no NF_2 -substituted fullerenes could be obtained under these conditions. The only product obtained were fluorinated fullerenes and dinitrogen.

In collaboration with Dr. Korkin and Prof. Bartlett from the University of Florida, the feasibility of preparing NO_4^+ , a bicyclic spiro compound of D_{2d} symmetry, was studied by ab initio calculations. It was found that this cation is vibrationally stable, having a heat of formation of 370 kcal/mol and an N-O bond length of 1.349 Å, but that its barrier towards decomposition to NO_2^+ and groundstate dioxygen is less than 20 kcal/mol due to potential energy surface crossings. Therefore, no experimental efforts were undertaken to synthesize this molecule. In collaboration with the USC team (Drs. Wagner, Rasul, Prakash and Olah), the novel trimethylperoxonium cation was prepared

by methylation of dimethylperoxide with methylfluoride and SbF_5 in SO_2 solution and was characterized by multinuclear NMR spectroscopy. The identity and chemical NMR shifts were confirmed by ab initio calculations. A manuscript has been written and submitted to JACS for publication.

Several extremely energetic, but also extremely shock sensitive, triazidocarbenium salts have been prepared and characterized. These include $\text{C}(\text{N}_3)_3^+\text{N}(\text{NO}_2)_2^-$; $\text{C}(\text{N}_3)_3^+\text{ClO}_4^-$ and $\text{C}(\text{N}_3)_3^+\text{BF}_4^-$. They were characterized by vibrational and NMR spectroscopy and the data were confirmed by ab initio calculations. Their heats of formation were calculated as 252, 218 and -128 kcal/mol, respectively, and show that their energy densities approach that of hydrazoic acid. Theoretical calculations and synthesis efforts on the protonation of the $\text{C}(\text{N}_3)_3^+$ cation were also carried out and show that protonation should occur on the alpha nitrogen atom and that the protonated dication should be vibrationally stable. The results were summarized in manuscript form and submitted to JACS for publication.

Structural studies of three new monopropellant candidates, $\text{H}_3\text{NO}\cdot\text{H}_3\text{NOH}^+\text{C}(\text{NO}_2)_3^-$, $\text{K}^+\text{O}_2\text{N}-\text{N}-\text{CN}^-$, and $\text{H}_2\text{NO}-\text{CH}_2-\text{ONH}_3^+\text{C}(\text{NO}_2)_3^-$ were carried out, using single crystal x-ray diffraction, vibrational spectroscopy and ab initio calculations. More details on this work are given in Dr. Petrie's poster abstract.

In collaboration with Dr. Zhang from USC, the crystal structures of a number of highly energetic cations, including ClF_6^+ , BrF_6^+ , KrF^+ , $\text{FN}-\text{NF}_2^+$ and ONF_2^+ , will be studied. For this purpose, most of these salts have been synthesized, and a special low-temperature device for the handling and mounting of unstable and air-sensitive materials has been designed and built.

In collaboration with Dr. Hoge from USC, the synthesis of ClF_5O is being pursued. This compound would be the highest performing, earth-storable liquid oxidizer with an I_{sp} which is about 10 sec higher than ClF_5 . The potential of HOF to act as a powerful oxygenating agent will be explored, and construction of the necessary hardware for this program has been about 60% completed.