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NOVEL FLUORINE OXIDIZERS

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This reports the results of a three-year program in novel energetic materials. The majority of the results was summarized in 30 manuscripts which are in various stages of publication (in various stages of publication). Major achievements include the synthesis of the ClF_6^- anion, the combination of the $N(CH_3)_4^+$ cation with powerful halogen fluorine anion oxidizers, the synthesis of truly anhydrous $N(CH_3)_4F$ which generated a worldwide renaissance in high coordination number chemistry, the synthesis of XeF_5^- which is the first known example of a pentagonal planar species, the synthesis of OsO_2F_4, the development of a quantitative scale for the strength of oxidizers, and the discovery of a new class of vibrationally stable polynitrogen compound.

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SUMMARY

A three year research program was carried out in the area of novel energetic high energy density materials (HEDM). The program was highly productive and numerous new materials were generated and characterized. For example, the discovery of a process for preparing truly anhydrous $N(CH_3)_4F$ provided a source of free highly soluble fluoride ions which could be used for the syntheses of a host of novel oxidizer anions at the limits of coordination and oxidation. Thus, XeF_5^-, the first example of a pentacoordinate species in which all five ligands and the central atom are arranged in the same plane, was prepared and characterized. Other novel anions prepared from $N(CH_3)_4F$ include IOF_6^-, $TeOF_6^{2-}$, PF_4^-, and ClF_6^-. The combination of an organic cation, such as $N(CH_3)_4^+$, with a powerful incendiary, such as ClF_4^-, in CH_3CN solution to form a salt, $N(CH_3)_4^+ClF_4^-$, which is stable up to 100°C and not shock sensitive, is unprecedented. The resistance of $N(CH_3)_4^+$ toward oxidative fluorination has allowed the preparation and characterization of many new $N(CH_3)_4^+$ salts containing fluoro anions at the limits of coordination and oxidation. This has led to a worldwide renaissance in high coordination number chemistry. Of particular interest in this respect were heptacoordinate species due to their nonrigid pentagonal bipyramidal structures which allow for a rapid dynamic distortion of the equatorial plane. Our studies have led to an understanding of the nature and bonding of heptacoordinated species such as IF_7, XeF_7^+, TeF_7^-, IOF_6^- and $TeOF_6^{2-}$.

In nitrogen chemistry, we have demonstrated by metathetical reactions between NF_4^+ and F^- in CHF_3 solution at -142°C that $NF_4^+F^-$, which is the ionic form of NF_5, is unstable toward decomposition to NF_3 and F_2 even at -142°C. The crystal structure of $N_2F^+AsF_6^-$ was studied and it was shown that N_2F^+ possesses the shortest N-F bond of any known nitrogen fluoride compound. LDF calculations were used to identify a previously reported novel nitrogenoxyfluoride as *cis*-FONO.

In azide chemistry, we have isolated and characterized stable $H_2N_3^+$ salts by protonation of HN_3 in anhydrous HF. It was shown that the structure of $H_2N_3^+$ is analogous to that of cyanamid, i.e. it is unsymmetrical with both protons attached to the same nitrogen. Also, a new synthesis of $N(CH_3)_4N_3$ was discovered and its structure was determined. A new class of polynitrogen compounds derived from azidamines was shown by theoretical calculations to be vibrationally stable.

In high oxidation state chemistry, a new Os (+VIII) compound, OsO_2F_4, was prepared and characterized. A systematic study on oxygen-fluoride exchange reactions was completed, and the results were summarized in a review. It is shown that NO_3^- and SO_4^{2-} are effective, low cost, nontoxic reagents for a controlled, stepwise fluorine-oxygen exchange.

The first quantitative scale for the strength of oxidizers was developed and will be extremely useful for the future synthesis of yet unknown super oxidizers.

Novel compounds prepared and characterized under this contract include the SF_4^- and SF_4O^- radical anions, Br_3^+ and Br_5^+ salts, PF_4^- salts and their hydrolysis products. The structure of IOF_5 was also reanalyzed and it is shown that there is no evidence for the existence of previously postulated secondary relaxation effects.

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INTRODUCTION

This is the final repot of a research program carried out at Rocketdyne between 20 July 1990 and 1 August 1993. The responsible scientist and principal investigator was Dr. Karl Christe, assisted by Dr. William Wilson. The program was administered by Drs. Steve Hurlock and Joseph Flanagan. The purpose of this program was to explore the synthesis and properties of novel high energy density materials (HEDM). Although the program was directed toward basic research, potential applications of the results were continuously considered.

Only completed items of research, which have been summarized in manuscript form, are included in this report. A total of 17 technical papers were published, 5 papers are in press, and 5 more are in the final stages of manuscript preparation. In addition, chapters were contributed to three books, three patents were filed or issued, 10 papers were presented at international and national conferences, and an invited lecture series was given in Berlin, Germany. The technical papers are given as Appendices A through DD. Effects in several other areas, including hotwire reactions and the syntheses of ClF_5O and nitramines, are not complete and will be continued in a follow on program.

PUBLICATIONS AND PATENTS GENERATED UNDER THIS PROGRAM

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2. "Syntheses, Properties, and Structures of Anhydrous Tetramethylammonium Fluoride and its 1:1 Adduct with trans-3-Amino-2-Butene Nitrile," by K.O. Christe, W.W. Wilson, R.D. Wilson, R. Bau, J. Feng, *J. Am. Chem. Soc.*, 112, 7619 (1990).
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10. A Quantitative Scale for the Oxidizing Strength of Oxidative Fluorinators," by K.O. Christe and D.A. Dixon, *J. Am. Chem. Soc.*, 114, 2978 (1992).
11. "Nitrogen Pentafluoride: Covalent NF_5 versus Ionic $NF_4^+F^-$ and Studies on the Instability of the Latter," by K.O. Christe and W.W. Wilson, *J. Am. Chem. Soc.*, 114, 9934 (1992).

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19. "The $TeOF_6^{2-}$ Anion: The First Example of a Divalent, Pentagonal Bipyramidal AX_5YZ Species and the Vibrational Spectra of the $TeOF_5^-$ Anion," by K.O. Christe, D.A. Dixon, J.C.P. Sanders, G.J. Schrobilgen, and W.W. Wilson, *Inorg. Chem.*, in press.

20. "On the Structure of IOF_5," by K.O. Christe, E.C. Curtis, and D.A. Dixon, *J. Am. Chem. Soc.*, in press.

21. "Osmium Tetrafluoride Dioxide, *cis*-OsO_2F_4," by K.O. Christe, D.A. Dixon, H.G. Mack, H. Oberhammer, A. Pagelot, J.C.P. Sanders, an G.J. Schrobilgen, *J. Am. Chem. Soc.*, in press.

22. "The Tetrafluorophophite, PF_4^-, Anion," by K.O. Christe, D.A. Dixon, H.P.A. Mercier, J.C.P. Sanders, G.J. Schrobilgen, and W.W. Wilson, *J. Am. Chem. Soc.*, in press.

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23. "On the Hydrolysis and Methanolysis of PF_4^- and Characterization of the POF_2^- and HPO_2F^- Anions," by K.O. Christe, D.A. Dixon, J.C.P. Sanders, G.J. Schrobilgen, and W.W. Wilson.

24. "The POF_4^- Anion," by K.O. Christe, W.W. Wilson and D.A. Dixon.

25. "On the Structure of the $XeOF_5^-$ Anion," by K.O. Christe, D.A. Dixon, J.C.P. Sanders, G.J. Schrobilgen, S.S. Tsai, and W.W. Wilson.

26. "Mutual Ligand Interactions in Hydrogen Substituted Main Group Hexafluorides. Density Functional Calculations, Vibrational Spectra, and Normal Coordinate Analyses of the Isoelectronic Species HPF_5^- and HSF_5," by K.O. Christe, D.A. Dixon, and W.W. Wilson.

27. "On the Structures and Stabilities of Triazidamine, $N(N_3)_3$, Diazidamine, $HN(N_3)_2$, the Diazidamide Anion, $N(N_3)_2^-$, and the Tetrazidammonium Cation, $N(N_3)_4^+$," by H.H. Michels, J.A. Montgomery, Jr., and K.O. Christe.

BOOKS AND SECTIONS THEREOF PUBLISHED

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30. "Chemical Methods for the Generation of Fluorine," Chapter contributed to Houben Weyl's Handbook of Organic Chemistry, Thieme Verlag, by K.O. Christe.

ISSUED PATENT

31. "Anhydrous, Chloride- and Bifluoride-Free Tetramethylammonium Fluoride," K.O. Christe and W.W. Wilson, Taiwan. Patent 56294 (1992).

FILED PATENTS

32. "Anhydrous, Chloride- and Bifluoride-Free Tetramethylammonium Fluoride," by K.O. Christe and W.W. Wilson, filed in U.S., Canada, Japan, Europe.

33. "Improved Method for the Synthesis of Tetramethylammonium Azide," by K.O. Christe and W.W. Wilson, filed in U.S.

PAPERS PRESENTED AT CONFERENCES

34. "Synthesis and Characterization of Unusual, Highly Coordinated Anions," by K.O. Christe, W.W. Wilson and E.C. Curtis, Tenth Winter Fluorine Conference, St. Petersburg, FL (January 28 - February 2, 1991).

35. "Lewis Acid Behavior of Xenon (II) Cations and the Synthesis of the XeF_5^- Anion; Examples of Novel Xe-N and Xe-F Bonds," by N.T. Arner, K.O. Christe, H.P. Mercier, M. Rokoss, J.C.P. Sanders, G.J. Schrobilgen, and J.S. Thrasher, Tenth Winter Fluorine Conference, St. Petersburg, FL (January 28 - February 2, 1991).

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37. "Lewis Acid Behavior of Xenon (II) Cations and the Synthesis and Characterization of Fluoro- and Oxofluoro-Xenon Anions at the Limits of Coordination," by K.O. Christe, H.P. Mercier. J.C. Sanders, G.J. Schrobilgen, J.S. Thrasher, and W.W. Wilson, 13th International Symposium on Fluorine Chemistry, Bochum, Germany (September 1-6, 1991).

38. "Synthesis and Characterization of the New PF_4^- and HPO_2F^- Anions," by W.W. Wilson and K.O. Christe, 203rd ACS National Meeting, San Francisco, CA (April 5-10, 1992).

39. "From Hepta-Coordination to Fulleronium Salts," by K.O. Christe and W.W. Wilson, 203rd ACS National Meeting, San Francisco, CA (April 5-10, 1992).

40. "Application of Local Density Functional Theory to Fluorinated Systems," by D.A. Dixon and K.O. Christe, 203rd ACS National Meeting, San Francisco, CA (April 5-10, 1992).

41. "Osmium Tetrafluoride Dioxide, OsF_4O_2. A New Osmium (+VIII) Fluoride Oxide," by K.O. Christe, Tenth European Symposium on Fluorine Chemistry, Padua, Italy (September 20-25, 1992).

42. "Experimental and Computational Chemistry. A Marriage Made in Heaven," by K.O. Christe, W.W. Wilson and D.A. Dixon, Eleventh Winter Fluorine Conference, St. Petersburg, FL (January 25-30, 1993).

43. "Computational Studies of Fluorinated Systems," by D.A. Dixon, K.W. Dobbs, and K.O. Christe, Eleventh Winter Fluorine Conference, St. Petersburg, FL (January 25-30, 1993).

INVITED SEMINARS

44. Invited lecture series at the Freie Universität, Berlin, Germany (1990).

RESULTS AND DISCUSSION

Since a vast amount of new data was generated under this program, only some of the major achievements will be highlighted in this section. For more detail, the interested reader is referred to the Appendices.

NEW ANIONS AT THE LIMITS OF OXIDATION AND COORDINATION

The synthesis of truly anhydrous tetramethylammonium fluoride was achieved for the first time (Appendix P), and it was demonstrated that the tetramethylammonium cation is kinetically stable toward very strong oxidizers [Ref. 1]. This discovery provided a source of highly soluble "naked" fluoride ions in the presence of a large, stable cation and allowed the syntheses of many new complex fluoro anions at the limits of oxidation and coordination [Ref. 2]. Since generally these salts are soluble in solvents such as CH_3CN, single crystals can be readily grown for structure determinations by X-ray diffraction. This has resulted in a general, worldwide renaissance of high coordination number chemistry, and exciting work is carried out in this area by numerous research groups. Since the fluoride anion is also an extremely powerful catalyst in reactions such as the polymerization of fluoroolefins, the $N(CH_3)_4F$ has many other potential applications [Ref. 2]. Thus, we have succeeded to combine for the first time an organic cation, i.e. $N(CH_3)_4^+$, with a chlorine fluoride anion, i.e. ClF_4^-. The resulting salt, $N(CH_3)_4^+ClF_4^-$ is stable up to 100°C and is not shocksensitive [Ref. 1]. This reaction chemistry was extended toward the synthesis of the previously unknown ClF_6^- anion (Appendix Q). Although the isolation of a stable ClF_6^- salt was not possible due to consistent explosions, the existence and octahedral structure of the ClF_6^- anion has now been established by low-temperature Raman and NMR spectroscopy. The synthesis of ClF_6^- had been successfully pursued for more than 30 years.

Using our $N(CH_3)_4F$ technology, we have achieved the first syntheses of other novel anions, such as XeF_5^- (Appendix Q), IOF_6^- (Appendix A), $TeOF_6^{2-}$ (Appendix S), PF_4^- (Appendix Y) and the characterization of known ions such as TeF_7^- (Appendix U), BrF_6^- [Ref. 3], IF_6^- [Ref. 3], IF_8^- (Appendix M), and $XeOF_5^-$ (Appendix BB), and XeF_8^{2-}. The XeF_5^- anion is of special significance because it is the first known example of a pentagonal planar AX_5 species (Appendix Q). The IOF_6^- (Appendix A) and $TeOF_6^{2-}$ (Appendix S) anions are the first known examples of pentagonal bipyramidal AX_5YZ species.

PROBLEMS ASSOCIATED WITH COORDINATION NUMBER 7.

In connection with the XeF_5^-, IOF_6^-, and TeF_7- anions, we have successfully solved the problems associated with fivefold symmetry and heptacoordination. The intriguing IF_7 molecule was thoroughly analyzed and the long standing problems and questions concerning its structure, fluxionality, bonding and vibrational spectra were resolved (Appendix C).

DEVELOPMENT OF A QUANTITATIVE OXIDIZER STRENGTH SCALE

Although a major effort of oxidizer chemistry is the development of new oxidizers of increased oxidizer strength, no quantitative methods existed until now to either define, measure or compute the strength of an oxidizer. The only data available were some isolated observations that some oxidizers were capable to fluorinate a given substrate while others were not. However, even these qualitative data were inconsistent because it was impossible to distinguish whether the failure of an attempted oxidative fluorination was due to an insufficient oxidizer strength of poorly chosen reaction conditions or excessively high activation energy barriers.

These problems were now overcome by the development of a quantitative oxidizer strength scale (Appendix J). It was shown from Born-Haber cycles that the oxidizer strength of an oxidative fluorinator is exclusively a function of the F^+ detachment energies. Since the required F^+ detachment energy values are not directly available and are very difficult to compute, we have in collaboration with Dr. Dixon from DuPont determined differences in F^+ detachment energies between given oxidizers by total energy computations using local density functional calculations. The resulting relative oxidizer strength scale was then converted to an absolute scale by defining a zero point for the scale and by anchoring the scale to the zero point by an experimental number. We have chosen F^+ as the zero point and an experimentally known KrF^+ value as the anchor point. The validity of the resulting quantitative scale was tested for XeF^+ and ArF^+ and gave excellent agreement with experimental values.

In this manner, the oxidizing strengths of 27 oxidizers were computed and summarized in Table 1 of Appendix J. The oxidizer strength table was also used to calculate the heats of formation of these oxidizers, thus providing yet another set of valuable information.

The development of a quantitative oxidizer strength scale is a significant advancement in oxidizer chemistry and will be invaluable for future experimental and theoretical work. The F^+ detachment energies (or their negative values which are the F^+ affinities) are the equivalents to the proton affinities in organic chemistry.

NITROGEN FLUORIDE CHEMISTRY

Nitrogen fluorides are the most promising candidates for energetic halogen oxidizers. They offer the best compromise between a high energy content and chemical and thermal stability. During the current program, significant progress was made in the areas of NF_4^+ and NF_5 chemistry, and compounds with unusually short N-F bonds.

The possibility of synthesizing NF_5, either in its covalent form or as ionic $NF_4^+F^-$, was studied. Using metathetical reactions of NF_4^+ and F^- ions in CHF_3 solution, it was demonstrated that $NF_4^+F^-$ is unstable toward decomposition to NF_3 and F_2 at temperatures as low as -142°C (Appendix F).

Another fascinating problem in nitrogen fluoride chemistry was the bonding in the N_2F^+ cation. Our previous spectroscopic studies [Ref. 4] had indicated that N_2F^+ either possesses an unusually short N-F bond [Ref. 5] or was a rare exception to Gordy's rule [Ref. 6] which correlates force constants with bond distances. A crystal structure determination of $N_2F^+AsF_6^-$, carried out in collaboration with Prof. Bau's group as USC, confirmed the extreme shortness of the N-F bond (1.217 Å) in N_2F^+ while also showing a very short (1.098 Å) N-N bond (Appendix L). A theoretical analysis of this problem using local density functional calculations revealed that the shortness of the N-F and the N-N bonds is due to the high s-character of the sigma bonds. This feature had previously been demonstrated only for carbon compounds.

OXYGEN-FLUORINE EXCHANGE REACTIONS

Our systematic study of oxygen-fluorine exchange reactions was completed (Appendix I). Whereas many methods are known for the replacement of oxygen by fluorine, very little work had been done on the opposite reaction, the controlled replacement of fluorine by oxygen. We have shown that 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 oxoanion, the countercations and the mole ratio of the reagents. These reactions appear to be quite general, controllable, safe, and scalable. It was also shown that in IF_7 the PF_3O molecule readily replaces two fluorine ligands for a doubly bonded oxygen, thereby providing a new and convenient synthesis for IF_5O [Ref. 7].

POLYNITROGEN AND AZIDE CHEMISTRY

Protonation of HN_3 in anhydrous HF solution resulted in the isolation of stable SbF_6^-, AsF_6^- and BF_4^- salts of $H_2N_3^+$. These salts are hygroscopic white solids which are stable at room temperature. They were fully characterized and from an X-ray diffraction study at 20°K shown to contain asymmetric $H_2N_3^+$ cations with both hydrogens bonded to the same nitrogen atom (Appendix B).

We have also discovered an improved synthesis of pure $N(CH_3)_4N_3$ from $N(CH_3)_4F$ and $Si(CH_3)_3N_3$ in CH_3CN solution (Appendix K). At the same time, some unexpected reaction chemistry was observed. It was found that even at -80°C, HN_3 displaces F^- from MF with formation of equimolar amounts of MN_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^- (Appendix K).

In the area of polynitrogen compounds, we have demonstrated the stability of a new family of compounds by ab initio calculations. The geometries, vibrational frequencies and heats of formation of $N(N_3)_3$, $HN(N_3)_2$, the $N(N_3)_2^-$ anion and the $N(N_3)_4^+$ cation were determined, and potential methods for their synthesis are proposed (Appendix DD).

+VIII OXIDATION STATES

Osmium is one of the very few elements that can form compounds in the +VIII oxidation state. A report by Bougon [Ref. 8] on the preparation of $OsOF_6$ and apparent discrepancies in his vibrational assignments prompted us to reexamine his work. It was found that his compound actually is *cis*-OsO_2F_4, a new Os(+VIII) oxyfluoride. The compound was identified by electron diffraction, multinuclear NMR and vibrational spectroscopy and theoretical calculations (Appendices H and V).

MISCELLANEOUS

The work under this contract has produced numerous spin-off results. Thus, the novel SF_4^- and SF_4O^- radical anions were prepared and characterized (Appendix D). The ONOF molecule was studied by theoretical calculations (Appendix E), and the Br_3^+ (Appendix N) and Br_5^+ (Appendix G) cations were characterized. The published [Ref. 9] structure of IOF_5 was found to be in error, and the data were reanalyzed (Appendix T). The PF_4^- anion was isolated for the first time and thoroughly characterized (Appendix Y). A study of its reaction chemistry resulted in the first isolation of a stable POF_2^- salt and its characterization (Appendix Z).

CONCLUSIONS

Our work during this contract period has been very fruitful and has resulted in a wealth of new chemistry at the limits of coordination and oxidation. Important achievements include the synthesis of the ClF_6^- anion, the combination of the organic $N(CH_3)_4^+$ cation with powerful oxidizer anions, such as ClF_4^-, in the form of stable salts, the synthesis of truly anhydrous $N(CH_3)_4F$ which resulted in a renaissance of high coordination number chemistry, the synthesis of the XeF_5^- which is the first known example of a pentagonal planar species, the development of a quantitative scale for the strength of oxidizers, and the discovery of a new family of vibrationally stable polynitrogen compounds. The outstanding productivity of this program was made possible by enlisting, at no cost to the program, the support of many outside experts. Among these collaborators are: Dr. Dixon (Du Pont), Prof. Schrobilgen and his group (McMaster University), Prof. Oberhammer (University of Tübingen), Prof. Bau and his group (USC), Prof. Khan (UCLA), Dr Bougon (CEN Saclay), Prof. Seppelt (University of Berlin), Prof. Minkwitz (University of Dortmund), Dr. Michels (UTC), Prof. Williams (University of Tennessee), and Dr Goldberg (Rockwell Science Center). The success of this program demonstrates the benefits which can be gained from well-planned, goal-oriented basic research and program continuity.

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Appendix A

The IOF_6- Anion: The First Example of a Pentagonal Bipyramidal AX_5YZ Species

K.O. Christie, D.A. Dixon, A.R. Mahjoub, H.P.A. Mercier, J.C.P. Sanders,
K. Seppelt, G.J. Schrobilgen, and W.W. Wilson

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 $N(CH_3)_4^+$ 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, *R* = 0.0373 and 0.0291 for 876 [$I > 3\sigma(I)$] reflections, respectively). In addition to two perfectly ordered $N(CH_3)_4^+$ 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 $I-O-F_{ax}$ angle is constrained by symmetry to be 180°, whereas there are no constraints on the positions of the equatorial fluorines. The I-O bond length indicates substantial double bond character, and the axial I-F bond length is significantly shorter than the five equatorial I-F bond lengths. The mean $O-I-F_{eq}$ 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- in its $N(CH_3)_4^+$ 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_5 symmetry type, and the deviations from the ideal equatorial plane are relatively small and decrease with decreasing temperature. Furthermore, the axial I-O bond length decreases and the mean $I-O-F_{eq}$ 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 $N(CH_3)_4^+IOF_6$ 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 intermolecular equatorial-axial ligand exchange on the NMR time scale because of the more repulsive, doubly bonded oxygen. The vibrational spectra of $N(CH_3)_4^+IOF_6^-$ 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_z 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.

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Appendix B

The Aminodiazonium Cation, $H_2N_3^+$

Karl O. Christie, William W. Wilson, David A. Dixon, Saeed I. Khan
Robert Bau, Tobias Metzenthin, and Roy Lu

Abstract

The $H_2N_3^+$ salts of SbF_6^-, and ASF_6^-, and BF_4^- have been prepared and, for the first time, been isolated from HF solutions of HN_3 and the corresponding Lewis acids. They are hygroscopic white solids which are stable at room temperature. The crystal structure of $H_2N_3^+SbF_6^-$ was determined at 20 K. This compound crystallizes in the orthohombic system, space group $Pmc2_1$, with two molecules in a unit cell of dimensions $a = 5.94\ (3)$ Å, $b = 5.113\ (2)$ Å, and $c = 9.919\ (5)$ Å with $R = 0.015$, $R_w = 0.022$. for 587 observed $[I > 3\sigma(I)]$ reflections. In addition to two almost perfectly octahedryl SbF_6^- anions, the unit cell contains two asymmetric $H_2H_3^+$ cations with N(1)–N(2) = 1.295 (5) Å, N(2)–N(3) = 1.101 (6) Å, and N(1)–N(2)–N(3) = 175.3 (5) Å and both hydrogens bonded to the same nitrogen atom, N(1). The infrared and Raman spectra of these salts were also recorded. Local density functional calculations were carried out for $H_2N_3^+$ and isoelectric H_2NCN and used for the assignment of the observed vibrational spectra and the determination of their force fields. The general agreement between the calculated and observed geometries and frequencies is very good. The results from the LDF calculations indicate that the H_2N group in $H_2N_3^+$ is less pyramidal than that in H_2NCN and, therefore, possesses a lower inversion energy barrier.

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Abstract C

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

Karl O. Christe, E.C. Curtis, and David A. Dixon

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 IF_7 are consistent with a highly fluxional, dynamically distorted pentagonal-bipyramidal molecule possessing D_{5h} symmetry in the ground state. The fluxionality of IF_7 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 the 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 sp_z hybrid for the formation of two mainly covalent axial bonds.

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Appendix D

Tetrafluorosulfate(1-) and Tetrafluorooxosulfate(1-) Radical Anions (SF_4^- and SF_4O^-)

K.O. Christe, D.A. Dixon, I.B. Goldberg, C.J. Schack, B.W. Walther,
J.T. Wang, and F. Williams

Abstract

The novel radical anions SF_4^- and *trans*-SF_4O^- were generated by γ-irradiation of $CsSF_5$ and $CsSF_5O$, respectively, at -196°C and characterized by their isotropic EPR spectra at +27°C. The SF_4^- 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*-SF_4O^- 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 SF_4^- and *cis*- and *trans*-SF_4O^- 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 SF_5 radical, the *cis*- and *trans*-PF_4O^{2-} radical anions, and the SF_4, SF_4), and SF_6 molecules were also calculated by this method. These calculations show that the exclusive formation of *trans*-SF_4O^- 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.

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Appendix E

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

David A. Dixon and Karl O. Christe

Abstract

Local density functional (LDF) throery 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*-FONON, *trans*-FONO, and FNO_2. It is shown that FNO_2 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 NO_2 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, $\angle FON = 118.0°$, and $\angle ONO = 135.2°$.

J. Phys Chem. **1992**, *96*, 1018–1021

Appendix F

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

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_4 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 covalent synthesis of truly anhydrous $N(CH_3)_4F$ 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}.

J. Am. Chem. Soc., Vol. 114, No. 25, 1992, 9934-9936

Appendix G

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

K.O. Christe, D.A. Dixon, and R. Minkwitz

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 $Br_5^+MF_6^-$ (M = As, Sb). The small energy difference of 1.2 kcal mol^{-1} between the skew and the trans configurations, combined wth crystal packing effects, can account for the planar trans configuration of Br_5^+ in solid $Br_5MF_6^-$. 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.

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Appendix H

Osmium Tetrafluoride Dioxide, OsF_4O_2: a New Osmium(viii) Oxide Fluoride

Karl O. Christe and Roland Bougon

Abstract

The reaction of OsO_4 with KrF in anhydrous HF produces *cis*-OsF_{42} and not OsF_6 as previously reported.

J. Chem. Soc., Chem. Commun., 1992, 1056

Appendix I

Chapter 2

Controlled Replacement of Fluorine by Oxygen in Fluorides and Oxyfluorides

Karl O. Christe, William W. Wilson, and Carl J. Schack

Synthetic Fluorine Chemistry, edited by George A. Olah, Richard D. Chambers, and G.K. Surya Prakash, John Wiley & Sons, Inc., 1992
ISBN 0-471-54370-5

Appendix J

A Quantitative Scale for the Oxidizing Strength of Oxidative Fluorinators

Karl O. Christe and David A. Dixon

Abstract

A quantitative scale for the oxidizing strength of oxidative fluorinators has been developed for the first time. This scale is based on the 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 oxiding 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.

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Appendix K

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 HF

Karl O. Christe, William W. Wilson, Robert Bau, and Steven W. Bunte

Abstract

Tetramethylammonium azide, $N(CH_3)_4{}^+N_3{}^-$, was obtained in high purity and quantitative yield by the reaction of $N(CH_3)_4{}^+F^-$ with $Si(CH_3)_3N_3$ in CH_3CN solution. This compound is isostructural with $N(CH_3)_4{}^+HF_2{}^-$ and cystallizes in the orthorhombic system: space group, *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 $N(CH_3)_4{}^+$ cation is somewhat distorted from tetrahedral symmetry due to crystal packing effects. The infrared and Raman spectra of $N(CH_3)_4{}^+N_3{}^-$ 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 system [M = Na, K, Rb, Cs, $N(CH_3)_4$] 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 $H–F–N_3{}^-$ or $N_3–H–N_3{}^-$ anions from HN_3 and either MF or MN_3, respectively, were unsuccessful.

J. Am. Chem. Soc., Vol. 114, No. 9, 1992, 3411-3414

Appendix L

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

Abstract

The $N_2F^+AsF_6^-$ 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 $N_2F^+AsF_6^-$ and FNO yields exclusively *cis*–N_2F_2. The Lewis acids BF_3 and PF_5 do not form a stabel 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_3. The crystal structure of $N_2F^+AsF_6^-$ (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, $CH_2{=}{=}CH_3$, $CH{\equiv}CH$ and CF_4, $CF_2{=}{=}CF_2$, $FC{\equiv}N$ series, respectively. 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.

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Appendix M

High-coordination Number Fluoro- and Oxofluoro-anions; IF_6O^-, TeF_6O^{2-}, TeF_7^-, IF_8^- and TeF_8^{2-}

Karl O. Christe, Jeremy C.P. Sanders, Gary J. Schrobilgen and William W. Wilson

Abstract

The novel hypervalent, highly coordinated, high-oxidation state anions IF_6O^-, $TeF_6)^{2-}$, TeF_7^-, IF_8^- and TeF_8^{2-} have been synthesized in anhydrous MeCN using anhydrous $N(Me)_4{}^+F^-$ 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^-, TeF_6O^{2-}), and D_{5h} (TeF_7^-) and D_{4d} (IF_8^-, TeF_8^{2-}).

J. Chem. Soc., Chem. Commun., 1991, 837-840

Appendix N

X-ray Crystal Structure and Raman Spectrum of Tribromine(1+) Hexafluoroarsenate(V), $Br_3^+AsF_6^-$, and Raman Spectrum of Pentabromine(1+) Hexafluoroarsenate(V), $Br_5^+AsF_6^-$

K.O. Christe, R. Bau and D. Zhao

Abstract

A single crystal of $Br_3^-AsF_6^-$ was isolated from a sample of $BrF_2^-AsF_6^-$ which had been stored for 20 years. It was characterized by x-ray diffraction and Raman spectroscopy. It is shown that $Br_3^-AsF_6^-$ (triclinic, a = 7.644(7) Å, b = 5.641(6) Å, c = 9.810(9) Å, χ = 99.16(8)°, β = 86.61(6)°, γ = 100.11(7)°, space group P1 R(F) = 0.0608) is isomorphous with $I_3^+AsF_6^-$. 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 distance of 2.270(5) Å and a bond angle of 102.5(2)°. The trhee fundamental vibrations of Br_3^+ were observed at 297 (ν_3), 293 (ν_1), and 124 cm^{-1} (ν_2). The Raman spectra of $Cl_3^+AsF_6^-$ and $I_3^+AsF_6^-$ were reinvestigated and $\nu_3(B_1)$ 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 $BrF_2^-AsF_6^-$ or $O_2^+AsF_6^-$ produce mixtures of $Br_3^+AsF_6^-$ and $Br_5^+AsF_6^-$. Based on its Raman spectra, the Br_5^+ cation possesses a planar, centrosymmetric structure of C_{2h} symmetry with three semi-ionically bound, colinear, central Br atoms and two more covalently, perpendicularly bound, terminal Br atoms.

Z. anorg. allg. Chem 593 (1991) 46-60 *J.A. Barth, Leipzig*

Appendix O

The Pentafluoroxenate(IV) Anion, XeF_5^-: The First Example of a Pentagonal Planar AX_5 Species

Karl O. Christe, Earl C. Curtis, David A. Dixon, Hélène P. Mercier,
Jeremy C. P. Sanders, and Gary J. Shrobilgen

Abstract

Xenon tetrafluoride forms stable 1:1 adducts with $N(CH_3)_4F$, 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 $N(CH_3)_4^+XeF_5^-$, Raman and infrared spectra, and ^{19}F and ^{129}Xe NMR spectroscopy. The X-ray crystal structure of $N(CH_3)_4^+XeF_5^-$ was determined at -86°C. This compound crystallizes in the orthorhombic system, space group *Pmcm*, 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 for 638 observed $[I > 3\sigma(I)]$ reflections. In addition to four $N(CH_3)_4^+$ cations, the structure contains four pentagonal planar XeF_5^- anions per unit cell with D_{5h} symmetry. The Xe-F distances are 1.9979 (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$1- 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.

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Appendix P

Syntheses, Properties, and Structures of Anhydrous Tetramethylammonium Fluoride and Its 1:1 Adduct with *trans*-3-Amino-2-butenenitrile

Karl O. Christe, William W. Wilson, Richard D. Wilson, Robert Bau
and Jin-an Feng

Abstract

A simple method for the preparation of anhydrous and essentially HF_2^- -free $N(CH_3)_4F$ 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 $N(CH_3)_4^+$ 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 CH_3CN 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 HF_2^- or other secondary reaction products. Its relatively simple synthesis and lower cost, combined with its good solubility and the high chemical inertness of the $N(CH_3)_4^+$ cation, make $N(CH_3)_4F$ an excellent substitute for presently used fluoride ion sources, such as either $[(CH_3)_4]_3S^+F_2Si(CH_3)_3^-$, which is commonly referred to as tris(dimethylamino)sulfonium fluoride, or CsF. The reaction of $N(CH_3)_4F$ with CH_3CN results in the dimerization of CH_3CN and the formation of a 1:1 adduct of $N(CH_3)_4F$ with this dimer, *trans*-3-amino-2-butenenitrile. The crystal structure and vibrational spectra of this adduct are reported.

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Appendix Q

The Hexafluorochlorate(V) Anion, ClF_6^-

Karl O. Christe, William W. Wilson, Raman V. Chirakal, Jeremy C.P. Sanders,
and Gary J. Schrobilgen

Abstract

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.

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Appendix R

Nuclear Magnetic Resonance Spectrum of the Fluoride Anion

Karl O. Christe and William W. Wilson

Summary

The fluorine 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.

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0022-1139/90/$3.50

Appendix S

The $TeOF_6^{2-}$ Anion: The First Example of a Multiply Charged, Pentagonal Bipyramidal, Main-Group Element AX_5YZ Species and the Vibrational Spectra of the $TeOF_5^-$ Anion

Karl O. Christe, David A. Dixon, Jeremy C.P. Sanders, Gary J. Schrobilgen, and William W. Wilson

Abstract

The new $TeOF_6^{2-}$ anion has been isolated in the form of its tetramethylammonium salt from solutions of $N(CH_3)_4F$ and $N(CH_3)_4TeOF_5$ in CH_3CN. It was characterized by vibrational spectroscopy, a normal coordinate analysis and ab initio calculations. It is shown that its structure is analogous to that of the recently discovered, isoelectronic IOF_6^- anion which makes it only the second known representative of a pentagonal bipyramidal, main-group element AX_5YZ species and the first multiply charged example of such a species. The stretching force constant of the TeF_5 part of $TeOF_6^{2-}$ is significantly smaller than that in IOF_6^- indicating the the additional negative charge in $TeOF_6^{2-}$ weakens mainly the equatorial Te–F bonds. The vibrational spectra of $N(CH_3)_4TeOF_5$ are also reported, and the results of ab initio calculations and of a normal coordinate analysis of $TeOF_5^-$ show that six of its fundamental vibrations had previously been assigned incorrectly.

submitted to *Inorganic Chemistry*, in press

Appendix T

On the Structure of IOF_5

Karl O. Christe, Earl C.Curtis and David A. Dixon

Abstract

Ab initio and density functional theory calculations were carried out for IOF_5 and, together with experimental and ab initio data for isoelectronic $TeOF_5^-$, suggest that the axial and the equatorial I-F bonds of IOF_5 are of comparable lengths and that the $O–I–F_{eq}$ bond angle is close to 97.2°. Using these two constraints and the previously published $I^{16}OF_5$ and $I^{18}OF_5$ microwave data, the structure of IOF_5 was determined as: $rI–O = 1.725$ Å, $rI–F_{ax} \equiv rI–F_{eq} = 1.826$ Å, and $\measuredangle\ OIF_{eq} = 97.2°$. The finding that the axial I-F bond length is comparable to the equatorial one, eliminates the needs for invoking for IOF_5 either a "secondary relaxation effect" which lengthens the fluorine bond in trans–position to a doubly bonded oxygen ligand, or a "trans effect" which shortens this bond.

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Appendix U

Heptacoordination: On the Pentagonal Bipyramidal XeF_7^+ and TeF_7^- Ions

Karl O. Christe, David A. Dixon, Jeremy C.P. Sanders, Gary J. Schrobilgen, and
William W. Wilson

Abstract

The TeF_7^- anion was studied experimentally by vibrational and ^{19}F and ^{125}Te NMR spectroscopy. Ab initio calculations employing effective core potentials and density functional theory calculations at the self-consistent nonlocal level with the nonlocal exchange potential of Becke and the nonlocal correlation functional of Perdew were used for the analysis of the isoelectronic series TeF_7^-, IF_7, XeF_7^+. It is shown that XeF_7^+ is a stable structure, that all three members of this series possess a pentagonal bipyramidal equilibrium geometry and that from the two closest lying saddle point geometries only the monocapped trigonal prism, but not the monocapped octahedron is a transition state for the intramolecular axial-equatorial ligand exchange. The results from a normal coordinate analysis reveal the existence of an unusual new effect which counteracts the ligand-ligand repulsion effect and is characterized by axial bond stretching encouraging equatorial bond stretching. While in TeF_7^- the ligand-ligand repulsion effect dominates, in XeF_7^+ the new effect becomes preponderant.

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Appendix V

Osmium Tetrafluoride Dioxide, cis-OsO_2F_4

Karl O. Christe, David A. Dixon, Hans Georg Mack, Heinz Oberhammer, Alain Pagelot,
Jeremy C.P. Sanders, and Gary J. Schrobilgen

Abstract

The new osmium (+VIII) oxofluoride obtained from the reaction of KrF_2 and OsO_4 in anhydrous HF solution and originally identified as $OsOF_6$ is shown by quantitive material balance, electron diffraction, NMR and vibrational spectroscopy, and density functional theory calculations to be *cis*-OsO_2F_4. The combined electron diffraction study and DFT calculations result in the following geometry: $r_{Os=O} = 1.674(4)Å$, $r_{Os-Fe} = 1.883(3)Å$, $r_{Os-Fa} = 1.843(3)Å$, ∡ $O=Os=o = 103.5(25)°$, ∡ $F_e-Os-F_e = 77.3(26)°$, ∡ $F_a-Os-F_a = 172.0(35)°$, ∡ $O=Os-F_a = 92.4(17)°$. In addition to the ^{19}F NMR spectrum, the ^{187}Os chemical shift was measured for *cis*-OsO_2F_4 from its $^{19}F\{^{187}Os\}$ inverse correlation spectrum. The results from the density functional theoretical calculations show that for OsO_2F_4 the *cis*-structure of C_{2v} symmetry is a true minimum and that, in accord with expectations for a d° transition metal complex, the *trans*-D_{4h} structure is not a minimum energy structure and distorts to a C_{2v} structure.

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Appendix W

Chemical Methods for the Generation of Fluorine

K.O. Christe

Generally, the electrochemical production of fluorine which involves only low cost chemicals and electricity in a single step process, is simpler and cheaper than the chemical generation of fluorine and, therefore, is used exclusively when larger amounts of fluorine are needed on a routine basis. However, occasions may arise when commercially sold fluorine gas or electrochemical cells for its production are either not available or not desirable for reasons such as logistics or safety. Under these circumstances, fluorine can be generated by chemical methods.

These methods can be classified into two categories. The first one is a purely chemical synthesis which excludes either techniques such as electrolysis, photolysis, electric discharge, etc. or the use of elemental fluorine for the synthesis of any of the required starting materials. The second category encompasses compounds which have been prepared from fluorine but can be decomposed by either mild heating or displacement reactions to evolve fluorine. Although, from a puristic point of view, this second category is better defined as a chemical storage and regeneration scheme of fluorine, it nevertheless is frequently included in the chemical methods for the generation of fluorine.

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Appendix X

On Heptacoordinated Main-Group Fluorides and Oxofluorides

K.O. Christie, E.C. Curtis, D.A. Dixon, H.P.A. Mercier, J.C.P. Sanders,
G.J. Schrobilgen, and W.W. Wilson

Abstract

The major problems associated with heptacoordination in main-group fluorides and oxofluorides have been resolved. A detailed discussion of the structures of ClF_6^-, BrF_6^-, IF_6^-, XeF_5^-, IF_7^-, IOF_6^- and $TeOF_6^{2-}$ is given. It is shown (i) that the steric activity of a free valence electron pair (E) in XF_6E species depends on the size of X; (ii) that in the XeF_5^- anion, which is the first known example of a pentagonal planar XF_5E_2 species, the two free valence electron pairs are sterically active and occupy the two axial positions; (iii) that the XF_7 and XOF_6 species possess pentagonal bipyramidal structures with five equatorial fluorine ligands which, in free molecules, are highly fluxional and dynamically distorted; (iv) that the dynamic distortion in XF_7 is the result of a rapid puckering motion of the five equatorial fluorines and of a much slower intramolecular, axial-equatorial ligand exchange; (v) that, in the XOF_6 species, this axial-equatorial ligand exchange is precluded by the more repulsive oxygen ligand which resides exclusively in one of the less congested axial positions; (vi) that, in solid $N(CH_3)_4^+IOF_6^-$, the dynamic puckering of the equatorial ligands is frozen out by hydrogen-fluorine bridges; (vii) that the pentagonal bipyramidal structures of these fluorides and oxofluorides cannot be explained by the VSEPR rules of repelling points on a sphere but are governed by the spatial distribution of the valence orbitals of the central atom; and (viii) that the bonding in these heptacoordinated species is best explained by a model involving delocalized $p_{x,y}$ 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_z 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 observed differences in bond lengths.

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Appendix Y

$N(CH_3)_4{}^+PF_4{}^-$: The First Example of a $PF_4{}^-$ Salt

Karl O. Christe, David A. Dixon, Hélène P.A. Mercier, Jeremy C.P. Sanders,
Gary J. Schrobilgen, and William W. Wilson

Abstract

$N(CH_3)_4{}^+PF_4{}^-$, the first example of a $PF_4{}^-$ salt, has been prepared from $N(CH_3)_4F$ and PF_3 using either CH_3Cn, CHF_3 or excess PF_3 as a solvent. The salt is a white, crystalline solid which is thermally stable up to 150°C where it decomposes to $N(CH_3)_3$, CH_3F and PF_3. It crystallizes in the tetragonal system, space group $P\bar{4}2_1m$, with two molecules in a unit cell of dimensions $a = 8.465(3)$Å and $c = 5.674(2)$Å with $R = 0.0564$ for 185 observed $[I \geq 2\sigma(I)]$ reflections. The structure can be derived from a distorted body centered cubic CsCl-type structure with tetrahedral $N(CH_3)_5{}^+$ cations and pseudotrigonal bipyramidal $PF_4{}^-$ anions. These anions possess two axial fluorine ligands and an equatorial plane which contains the remaining two fluorine ligands and one sterically active free valence electron pair. This plane is subject to a three-fold disorder with unequal occupancy factors. Since the disorder involves a free valence electron pair which is shorter and more repulsive than the P-F bonds, the apparent equatorial P-F bond lengths are much too short and the apparent bond angles differ significantly from those predicted by the ab initio calculations for the free $PF_4{}^-$ ion. However, good agreement between the apparent and the calculated geometries can be reached by correction of the calculated geometry for the disorder effects. Therefore, the geometry of the ordered, free $PF_4{}^-$ ion must be very close to the calculated one. The calculated structure of ordered $PF_4{}^-$ is similar to that of isoelectronic SF_4, but differs significantly from those found for the corresponding tetrachlorides or -bromides which are deformed toward ionic X^----MX_3 type structures. The variable temperature ^{31}P and ^{19}P nmr spectra of $PF_4{}^-$ in CH_3CN solution were recorded and represent classic examples for an intramolecular exchange process occurring most likely by the way of a Berry pseudorotation mechanism. The infrared and Raman spectra of $N(CH_3)_4PF_4$ were recorded and assigned with the help of SCF, MP-2, and local density functional calculations and a normal coordinate analysis.

Appendix Z

On the Hydrolysis and Methanolysis of PF_4^- and Characterization of the POF_2^- and HPO_2F^- Anions

Karl O. Christe, David A. Dixon, Jeremy C.P. Sanders, Gary J. Schrobilgen, and
William W. Wilson

Abstract

The hydrolysis and methanolysis of $N(CH_3)_4PF_4$ were studied by their material balances and multilinear NMR and vibrational spectroscopy. With an equimolar amount of water in CH_3CN solution, PF_4- forms HPO_2F^- and HPF_5^- in a 1:1 mole ratio. With an excess of water, HPO_2F^- is the sole product which was also obtained by the hydrolysis of HPF_5^-. In the presence of a large excess of F^-, the hydrolysis of PF_4^- with an equimolar amount of water produces POF_2^- salt. The resulting $N(CH_3)_4POF_4^-$ is the first known example of a stable POF_2^- salt. The geometries and vibrational spectra of POF_2^- and HPO_2F^- were calculated using local density functional theory, and normal coordinate analyses were carried out for POF_2^-, HPO_2F^- and the isoelectronic SOF_2 and HSO_2F molecules. The methanolysis of PF_4^- produces $PF_3(OCH_3)$ and $PF(OCH_3)_2$ as the main products.

Appendix AA

The POF_2^- Anion

K.O. Christe, W.W. Wilson, D.A. Dixon, J.C.P. Sanders, and G.J. Schrobilgen

Abstract

It is shown that the POF_4^- anion is less stable than the recently prepared and closely related PF_4^- anion and, at temperatures as low as −31 °C, rapidly disproportionates to PF_6^- and $PO_2F_2^-$. The geometry, vibrational spectra and the force field of POF_4^- have been calculated using local and nonlocal functional theory and are presented.

Appendix BB

On the Structure of the $XeOF_5^-$ Anion

K.O. Christe, David A. Dixon, Jeremy C.P. Sanders, Gary J. Schrobilgen, Scott S. Tsai, and William W. Wilson

Abstract

A new $XeOF_5^-$ salt, $N(CH_3)_4^+XeOF_5^-$, was prepared. This highly explosive compound was characterized by infrared, Raman, and multinuclear NMR spectroscopy and calculations for $XeOF_5^-$ using local and nonlocal functional theory. It is shown that, contrary to a previous literature report which assumed for $XeOF_5^-$ a distorted octahedral structure similar to those of XeF_6 and IF_6^-, $XeOF_5^-$ has a pseudo-pentagonal bipyramidal structure of C_{5v} symmetry. It possesses five equatorial fluorine ligands, with one oxygen atom and one sterically active free valence electron pair occupying the two axial positions. Its structure is analogous to those of XeF_5^-, IF_7, and IOF_6^-.

Appendix CC

Mutual Ligand Interactions in Hydrogen Substituted Main Group Hexafluorides. Density Functional Calculations, Vibrational Spectra, and Normal Coordinate Analyses of the Isoelectronic Species HPF_5^- and HSF_5

Karl O. Christe, David A. Dixon, and William W. Wilson

Abstract

The new HPF_5^- salt, $N(CH_3)_4^+HPF_5^-$, was prepared and the infrared and Raman spectra of $N(CH_3)_4HPF_5$ and $CsHPF_5$ were recorded. The spectra were assigned with the help of local density functional calculations, and a normal coordinate analysis was carried out. For comparison, the unknown isoelectronic molecule HSF_5 was also calculated and found to be vibrationally stable. The internal stretching force constants of HPF_5 are compared to those of closely related phosphorous and sulfur fluorides and hydrides, providing for the first time experimental data on the mutual ligand interactions in hydrogen substituted main group hexafluorides. The observed substitution effects are explained in terms of a hypervalent bonding scheme and result in a general weakening of all fluorine bonds with the four equatorial *cis* bonds being affected more strongly than the unique axial *trans* bond, i.e., hydrogen substitution results in a *cis*–effect.

Appendix DD

On the Structures and Stabilities of Triazidamine, $N(N_3)_3$, Diazidamine, $HN(N_3)_2$, the Diazidamide Anion, $N(N_3)_2^-$, and the Tetrazidammonium Cation, $N(N_3)_4^+$

H. Harvey Michels, John A. Montgomery, Jr., and Karl O. Christe

Abstract

Ab initio calculations show the azidamines, a new family of polynitrogen compounds, are vibrationally stable at the RHF/6-31G* and MP2/6-31G* levels of theory. The geometries, vibrational frequencies, and heats of formation are predicted for $N(N_3)_3$, $HN(N_2)_2^-$ anion, and the $N(N_3)_4^+$ cation. All these compounds are highly energetic materials with large positive heats of formation. Their calculated activation energy barriers toward N_2 elimination are comparable to that found for the known FN_3 molecule and suggest that these polynitrogen compounds are synthetically accessible; potential methods for their synthesis are proposed.