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PHILIP A. KESSEL Date
Technical Advisor
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POLYNITROGEN CHEMISTRY AND THE PURSUIT OF NEW HIGH ENERGY DENSITY MATERIALS

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The goal of this AFOSR program is the synthesis of novel polynitrogen-derived HEDM compounds, exploiting the synergism between theory and synthesis.

Under combined DARPA, AFOSR and NSF sponsorship, we have discovered in 1999 the novel polynitrogen compound, $N_5^+AsF_6^-$. The N_5^+ cation is only the third known, homoleptic polynitrogen species that can be prepared and isolated in bulk, the other two being N_2 and the azide anion. $N_5^+AsF_6^-$ was found to be only marginally stable. During the past year, the N_5^+ cation has successfully been tamed by preparing the stable fluoroantimonate salts, $N_5^+SbF_6^-$ and $N_5^+Sb_2F_{11}^-$. The former is surprisingly stable (up to 70 °C) and, according to drop weight tests, is essentially insensitive. The crystal structure of $N_5^+Sb_2F_{11}^-$ was determined, and the geometry of N_5^+ was found to be in excellent agreement with that predicted by our theoretical calculations. A considerable amount of effort was spent on improving the syntheses of the precursors for the N_5^+ salts. This work resulted in the discovery of a new *cis-trans* isomerization process for N_2F_2, a disproportionation reaction of N_2F_2 to give $NF_4^+Sb_3F_{16}^-$ under mild conditions, and several new crystal structures for salts that contain nitrogen fluoride cations. Also, a safer method for producing N_5^+ salts was developed to overcome a series of explosions, encountered in the N_5SbF_6 synthesis. Metathetical reactions were carried out in SO_2 and anhydrous HF solutions between $N_5^+SbF_6^-$ and alkali metal azides, perchlorates, and nitrates, in pursuit of N_5N_3, N_5ClO_4, and N_5NO_3, respectively. It was also found that the N_3^- anion reacts with SO_2 under formation of the novel $SO_2N_5^-$ anion that was characterized by its crystal structure, vibrational spectroscopy, and theoretical calculations. Furthermore, reactions of $N_2F_3^+$ and N_2F_2 with HN_3 were studied in efforts to prepare the N_{11}^+ cation. The $N_2F_3^+$ cation was initially reduced by HN_3 to N_2F^+ that then proceeded to react with HN_3 to give the known N_5^+ cation.

While carrying out structural studies of the NF_2O^+ cation, which is another potential precursor for polynitrogen compounds, a new method for solving oxygen/fluorine positionally disordered crystal structures was discovered. This method was also successfully demonstrated for the SO_2F^- anion. In both cases, it was shown that the crystal structures obtained from disordered data sets with our method were in excellent agreement with those predicted by the theoretical calculations for the free gaseous ions.

In pursuit of novel powerful oxidizers that might be stronger than any presently known oxidizer, the following new concept was developed and tested. Cations are stronger oxidizers than their neutral parent molecules, which in turn are stronger oxidizers than their anions. Therefore, transition metal fluoride anions were prepared in their highest oxidation states by high temperature / high pressure fluorinations with elemental fluorine and then converted to the corresponding cations by acidification with strong Lewis acids. The resulting, thermally unstable cations are indeed very powerful oxidizers. This was successfully demonstrated for the NiF_3^+ system, which was shown to be capable of oxidizing ClF_5 and BrF_5 to ClF_6^+ and BrF_6^+, respectively. However, attempts to use this system for the preparation of the new OF_3^+ or XeF_7^+ cations were not successful. In a quest for finding the strongest possible oxidizer, the oxidizing strength of numerous transition metal fluoride cations that can be prepared in this manner, are presently being calculated by ab initio methods in collaboration with Dave Dixon. In connection with this work, the crystal structures of ClF_6^+, BrF_6^+, and IF_6^+ were determined in collaboration with McMaster University and their force fields were calculated by ab initio methods.

The study of the ClF_4^+ cation, which was started last year, was completed, and extensive theoretical modeling of the influence of strong intermolecular fluorine bridging on the structure and the vibrational spectra was carried out. A simple method for simulating infinite chains by capping with HF was devised and shown to give excellent results. Results from a theoretical study of the closely related BrF_4^+ and IF_4^+ cations strongly disagreed with the previously reported crystal structures and prompted their reinvestigation. It was shown that the previously reported structures were indeed in error and that the correct structures are in excellent agreement with the theoretical predictions. In the case of $IF_4^+SbF_6^-$ a very interesting 9-coordinated environment was found for IF_4^+. In collaboration with Arkady Ellern, the crystal structure of solid ClF_3O was also determined and shown to consist of unusual tetrameric units.

Attempts to prepare and characterize the yet unknown PO_2^- cation, the analogue to the well-known NO_2^+ cation, resulted in a surprise. Acidification of $PO_2F_2^-$ salts with SbF_5 did not produce the expected $PO_2^+SbF_6^-$ salt, but a tetrameric ring structure with P-O-Sb bridges and terminal P-F bonds.