REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 074-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
Nov 05, 2006

3. REPORT TYPE AND DATES COVERED
Final Report, May 15, 2002 – Oct 31, 2006

4. TITLE AND SUBTITLE
High Energy Density Material Chemistry

5. FUNDING NUMBERS
F 49620-[redacted] 02-1-0229

6. AUTHOR(S)
Karl O. Christe

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Loker Research Institute and Department
of Chemistry
University of Southern California
Los Angeles CA 90089-1661

8. PERFORMING ORGANIZATION REPORT NUMBER
USC-AFOSR-USC -2006

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Office of Scientific Research
875 N Randolph St
Suite 325, Room 3112
Arlington VA 22203
Dr Michael Berman/NL

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

AFRL-SR-AR-TR-07-0063

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Distribution Unlimited

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT ***(Maximum 200 Words)***

The overall objectives of this research are the syntheses and characterization of polynitrogen, high-nitrogen and high-oxygen energetic materials, useful as propellants or explosives ingredients. Excellent results were obtained in all areas and are summarized in 38 pubications and 2 patents. The chemistry of N_5^+ was developed and 13 new N_5^+ salts were prepared and characterized. It was demonstrated that N_5^+ cations can be combined with doubly charged anions, thereby doubling the N_5^+ content of a salt. Furthermore, it was shown that N_5^+ can be combined with highly energetic counter-ions, such as $[B(N_3)_4]^-$ and $[P(N_3)_6]^-$. Another novel polynitrogen ion, discovered under this program by electrospray ion mass spectroscopy, is the cyclo-N_5^- anion. Two other novel polynitrogen species, the N_3NOF^+ and N_7O^+ cations, were prepared and characterized. The possible syntheses of compounds, such as $N_5^+N_3^-$ and $N_5^+N_5^-$, were studied. A new method for the processing of nitrogen NMR data with greatly improved signal to noise ratios was developed and successfully applied to N_5^+. A large number of novel polyazides were prepared and characterized, including: $As(N_3)_3$, $Sb(N_3)_3$, $As(N_3)_4^-$, $As(N_3)_5$, $Sb(N_3)_5$, $Sb(N_3)_6^-$, $P(N_3)_6^-$, $B(N_3)_4^-$, $Te(N_3)_4$, $Te(N_3)_5^-$, $Te(N_3)_6^{2-}$, $Ti(N_3)_4$, $Ti(N_3)_5^-$, $Ti(N_3)_6^{2-}$, $W(N_3)_6$, $W(N_3)_7^-$, $OW(N_3)_4$, $OW(N_3)_4 \cdot CH_3CN$, $OW(N_3)_5^-$, $Mo(N_3)_6$, $OMo(N_3)_4^-$, $Ta(N_3)_5$, $Ta(N_3)_6^-$, $Nb(N_3)_5$, $Nb(N_3)_6^-$, $Nb(N_3)_5 \cdot NCCH_3$, $Te(N_3)_4$, $Te(N_3)_5^-$, $Te(N_3)_6^{2-}$, $U(N_3)_6$, $[\textit{trans}\text{-}UO_2(N_3)_4]^{2-}$, $Mn(N_3)_4$, $[Mn(N_3)_6]^{2-}$, $[N{\equiv}W(N_3)_4]^-$, $[ONb(N_3)_5]^{2-}$, $[OMo(N_3)_5]^{2-}$, $[\textit{cis}\text{-}O_2Mo(N_3)_4]^2$, $[\textit{cis}\text{-}O_2W(N_3)_4]^{2-}$, $[Ti(N_3)_5OSi(CH_3)_3]^{2-}$, $V(N_3)_4$, $V(N_3)_6^-$, $[V(N_3)_6]^{2-}$, $[Nb(N_3)_7]^{2-}$, $[Ta(N_3)_7]^{2-}$, $[Pd(N_3)_4]^{2-}$, $[N_5]^+[B(N_3)_4]^-$, and $[N_5]^+[P(N_3)_6]^-$. A new concept for liquid monopropellants, based on oxygen-balanced energetic ionic liquids, was developed and successfully demonstrated. A new stable reagent, $NaSO_3NF_2$, for the introduction of *gem*-bis NF_2 groups was developed. An new solid-gas process, which avoids liquid phase quenching, was invented for generating singlet delta oxygen for the COIL laser.

14. SUBJECT TERMS
Polynitrogen, Polyazides, oxidizer-balanced energetic ionic liquid monopropellants, COIL laser,

15. NUMBER OF PAGES
16

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT

High Energy Density Material Chemistry

(F49620-02-1-0229)

Final Report

May 15, 2002 through October 31, 2006

Karl O. Christe
Loker Hydrocarbon Research Institute
and Department of Chemistry
University of Southern California
Los Angeles, CA 90089
kchriste@usc.edu
(213) 740-3552, fax (213) 740-6679

Objectives

The overall objectives of this research are the syntheses and characterization of polynitrogen, high-nitrogen and high-oxygen energetic materials that are useful as propellants or explosives ingredients.

Status of Effort

Excellent results were obtained, and significant progress was made towards our objectives, particularly, in the areas of polyazido and polynitrogen chemistry and high-oxygen carriers. Because fluorine compounds play an important role as starting materials in many reactions, some work was also carried out in this area. Completed pieces of work were summarized in manuscript form for publication and are listed under publications. Work in these areas continues at USC under two STTR programs funded by AFOSR.

Accomplishments

Numerous major breakthroughs were achieved in different areas during this program. The major results in each area are summarized in the following sections.

A. N_5^+ Chemistry

Following our earlier syntheses of $N_5^+AsF_6^-$ and $N_5^+SbF_6^-$, the scope of N_5^+ chemistry was greatly expanded by synthesizing 13 new N_5^+ salts using metathetical approaches [Pubs. 13 and 22] . In connection with this work, we observed that in SO_2 solution, SO_2 interacts with the azide anion. It was found that N_3^- forms a marginally stable 1:1 adduct with SO_2 and a 1:2 adduct that is stable at lower temperatures [Pubs. 5 and 12]. We have also developed an improved synthesis for pure CsN_3 that is based on its adduct formation with SO_2 [Pub. 2], and a general method for the preparation of anhydrous cesium salts [Pub. 1].

In efforts to synthesize N_5^+ salts having a higher energy content than $N_5^+SbF_6^-$, we demonstrated that the energy content can be doubled by doubling the number of N_5^+ cations per anion. This was achieved by the successful synthesis of $[N_5^+]_2[SnF_6]^{2-}$ [Publ. 13]. This salt decomposes to $N_5^+SnF_5^-$ and one equivalent of FN_5. Because our experimental efforts to trap FN_5 were unsuccessful, a theoretical study of the stability of FN_5 was carried out. It was found that the predicted life time of FN_5 is so short that it precludes its observation [Publ. 15]. As a next step, we studied, both experimentally and computationally, the possibility of combining the N_5^+ cation with highly energetic anions, such as NO_3^-, ClO_4^-, N_3^- or N_5^-. It was found that all these anions cannot form stable salts with N_5^+ [Publ. 18]. However, we have succeeded to isolate and characterize with $[N_5]^+[B(N_3)_4]^-$ and $[N_5]^+[P(N_3)_6]^-$ two extremely energetic salts [Publ. 22]. Although these salts are much too sensitive for practical use and explode violently upon warm up to room temperature, they nevertheless demonstrate the principle that N_5^+ can indeed be combined with highly energetic anions.

We have also developed a more powerful ^{15}N NMR method for the characterization of polynitrogen compounds which does not require time consuming and expensive enrichment procedures. This new technique was demonstrated for N_5^+ and allowed us to observe all its NMR parameters in natural abundance [Publ. 31].

B. N_5^- Chemistry

Another important discovery was the experimental detection of the pentazolate anion, *cyclo*-N_5^- by electrospray ion mass spectroscopy. It was published as a hot paper in Angewandte Chemie [Publ. 6] and highlighted in Chemical & Engineering News.

In pursuit of a bulk synthesis for N_5^-, the possibility of preparing trialkylsilyldiazonium salts was explored because their Si-N bonds might be cleaved readily by strong nucleophiles. Numerous reactions were investigated, but were unsuccessful. Theoretical calculations on the stability of trialkylsilyldiazonium salts confirmed that, in accord with our experimental findings, these compounds spontaneously loose N_2. These calculations also showed that replacement of the trialkyl groups by perfluorotrialkyl groups could lead to stable products.

During our search for alkyl diazonium salts, a potential starting material, the new compound $(C_6H_5)_3CNSO$, was prepared and characterized [Publ. 7]. Also, dimethylamino substituted arylpentazole was prepared and its decomposition in different solvents was studied, but no selective cleavage of the *ipso*-C-N bond was observed with conservation of the N_5 ring.

In a paper following our original report on N_5^- [Publ. 6], Butler from Ireland reported, based on NMR observations, a bulk synthesis for this ion. Because we had strong reservations about the validity of his claim, we have repeated his work using isotopic substitution experiments. We were able to show conclusively that Butler had misinterpreted his results and that the resonance attributed by him to N_5^- is actually due to the NO_3^- anion [Publ. 26].

C. Polyazides

In the area of polyazido compounds, impressive progress was made. The following novel compounds were prepared and characterized by vibrational spectroscopy, theoretical calculations, and in many cases by their crystal structures: $As(N_3)_3$, $Sb(N_3)_3$, $As(N_3)_4^-$, $As(N_3)_5$, $Sb(N_3)_5$, $Sb(N_3)_6^-$, $P(N_3)_6^-$, $B(N_3)_4^-$, $Te(N_3)_4$, $Te(N_3)_5^-$, $Te(N_3)_6^{2-}$, $Ti(N_3)_4$, $Ti(N_3)_5^-$, $Ti(N_3)_6^{2-}$, $W(N_3)_6$, $W(N_3)_7^-$, $OW(N_3)_4$, $OW(N_3)_4 \cdot CH_3CN$, $OW(N_3)_5^-$, $Mo(N_3)_6$, $OMo(N_3)_4^-$, $Ta(N_3)_5$, $Ta(N_3)_6^-$, $Nb(N_3)_5$, $Nb(N_3)_6^-$, $Nb(N_3)_5 \cdot NCCH_3$, $Te(N_3)_4$, $Te(N_3)_5^-$, $Te(N_3)_6^{2-}$, $U(N_3)_6$, $[trans\text{-}UO_2(N_3)_4]^{2-}$, $Mn(N_3)_4$, $[Mn(N_3)_6]^{2-}$, $[N{\equiv}W(N_3)_4]^-$, $[ONb(N_3)_5]^{2-}$, $[OMo(N_3)_5]^{2-}$, $[cis\text{-}O_2Mo(N_3)_4]^2$, [*cis*-

$O_2W(N_3)_4]^{2-}$, $[Ti(N_3)_5OSi(CH_3)_3]^{2-}$, $V(N_3)_4$, $V(N_3)_6^-$, $[V(N_3)_6]^{2-}$, $[Nb(N_3)_7]^{2-}$, $[Ta(N_3)_7]^{2-}$, $[Pd(N_3)_4]^{2-}$, $[N_5]^+[B(N_3)_4]^-$, and $[N_5]^+[P(N_3)_6]^-$. Most of these compounds are very powerful explosives, and in many instances, previous investigators have not been able to either handle or characterize these compounds. Only a small portion of this work has been published so far [Publs. 19, 20, 24, 25, 28, 32, 37], and numerous manuscripts still need to be written in this area. Several of our publications in this area have received wide public attention. Two papers on tellurium azides and titanium azides, which were published in Angewandte Chemie, were highlighted in Chemical and Engineering News. Our paper on arsenic and antimony triazides made the cover page of Chemistry – A European Journal. $Nb(N_3)_5 \cdot NCCH_3$ is also of special interest because it represents the first example of a compound with a linear metal-N-N bond. Also, the transition from ionic to covalent azides with increasing coordination number of the central atom within the same group of the periodic system was demonstrated for the MPh_4N_3 series, PPh_4N_3, $AsPh_4N_3$, and $SbPh_4N_3$ [Publ. 29].

D. Azidamines

We were also actively studying the conversion of nitrogen chlorides into nitrogen azides as a potential synthesis for novel polynitrogens, such as $N(N_3)_2^-$ or $N(N_3)_3$. To this end, we have synthesized some novel and some previously reported but ill characterized R_3SiNCl_2 compounds. [Publ. 38]. However, these compounds were highly unreactive toward azide ion and did not yield any azidamines. Some forty years ago, Bock and Kompa reported the synthesis of $(CH_3)_2N\text{-}N_3$, however the compound was not properly characterized. We have repeated this synthesis under similar conditions and found that this reaction is much more complex than previously reported. Particularly, there is a competing side reaction between azide ion and the CH_2Cl_2 solvent going on that yields covalent azidomethanes which was not recognized by Bock and Kompa. The

$(Me_3Si)_2NCl$ molecule also did not undergo Cl – azide ligand exchange, but with HF, the novel NH_3Cl^+ cation was obtained and characterized [Publ. 23].

E. Novel Polynitrogens

We have continued to pursue the synthesis of the N_3^+ cation by studying the possibility of abstracting a fluoride anion from FN_3 using a strong Lewis acid, such as SbF_5. Because no convenient synthesis for the highly shock-sensitive FN_3 was known, we first had to develop a convenient, high-yield synthesis of pure FN_3. This was achieved by using either HN_3 or $(CH_3)_3SiN_3$ and elemental fluorine in a suitable solvent. We then studied the reaction of FN_3 with SbF_5 in these solutions and characterized the resulting product. It was shown that FN_3 and SbF_5 form indeed a 1:1 adduct, however, this adduct involves an N-Sb bridge and not an F-Sb bridge. This result was also confirmed by theoretical calculations which showed that the alpha nitrogen atom of FN_3 is a better electron density donor than fluorine. Decomposition of this 1:1 adduct in HF resulted in the formation of the $NH_2F_2^+$ cation and allowed us to determine its crystal structure,

We have also pursued the syntheses of the N_3NOF^+ and N_7O^+ cations. It was found that ONF_2^+ salts react with either HN_3 or $(CH_3)_3SiN_3$ to give the novel N_3NOF^+ cation. This cation was isolated in the form of its SbF_6^- salt and characterized by vibrational and multinuclear NMR spectroscopy and theoretical calculations. It is formed either as a *z*- or *e*-isomer depending on whether the N_3 ligand is *cis* or *trans* with respect to the fluorine ligand.

The replacement of the second fluorine ligand of ONF_2^+ by azide resulted in the formation of the N_7O^+ cation. However, this cation readily loses one mol of N_2O giving N_5^+ salts.

F. Fluorine Chemistry

Fluorine compounds play an important role not only as energetic materials, but also as highly reactive starting materials and reagents. For example, our studies were successful to find a stable, storable and readily preparable HNF_2 source for the synthesis of *gem*-bis-NF_2 substituted high energy propellants and explosives, such as the gem-bis(difluoramine) substituted cyclic nitramines, HNFX and TNFX. It was shown that the direct fluorination of the $Na^+SO_3NH_2^-$ anion with F_2 produces $Na^+SO_3NF_2^-$ in high yield. This salt was characterized by spectroscopy and its crystal structure and, when reacted with carbonyl groups in conc. sulfuric acid, it can replace the oxygen atom by two NF_2 groups [Publ. 33].

We have also solved a long-standing problem in NF_4^+ chemistry. The reported vibrational and NMR spectra suggested the presence of perfectly tetrahedral ions while a crystal structure showed two kind of strongly distorted ions. It was shown that the previous crystal structure was flawed by disorder and that the NF_4^+ cations are indeed tetrahedral [Publ. 34].

ClF_3O is the highest performing earth-storable liquid oxidizer for rocket propulsion. We have written up the results of a previous Rocketdyne study on the kinetics of the ClF_3O formation for publication in a memorial issue for the 100th birthday of Prof. Schuhmacher who has pioneered this area of research [Publ. 30].

We have also published papers on the structures of BrF_4^+ and ClF_4^+ [Publ. 8], ClF_3O [Publ. 11], $IO_2F_5^{2-}$ [Publ. 14], ClF_6^+ [Publ. 21] and XeF_6 [Publ. 27], and on the nakedness of the fluoride anion [Publ. 16 and 17].

G. Chemical Oxygen Iodine Laser

In support of the chemical oxygen iodine laser program of the Air Force, we have developed a new gas-solid method for the generation of singlet delta oxygen which avoids the liquid phase quenching problems encountered with the wet basic hydrogen peroxide chlorine process [Publ.9 and Pat. 1].

H. High-Oxygen Carriers and Ionic Liquid Based Liquid Monopropellants

The presently used state of the art monopropellant is hydrazine. Its performance is poor and it is a carcinogen possessing relatively high vapor toxicity. This problem was overcome by developing a new concept [Pat. 2] of using oxidizer balanced, energetic, ionic liquids. The major problem was to provide sufficient oxygen for complete oxidation of the relatively large organic cations. Using large complex inorganic cations, such as tetranitrato borates or aluminates, and more energetic cations, such as tetrazolium salts, high performing liquid nontoxic monopropellants were prepared [Publ. 36].

Personnel Supported

Prof. Karl O. Christe, PI
Dr. Ross Wagner, Senior Research Associate
Dr. William Wilson, Senior Research Associate
Dr. Thorsten Schroer, Senior Research Associate
Dr. Stefan Schneider, Senior Research Associate
Dr. Michael Gerken, Postdoctoral Fellow
Dr. Ralf Haiges, Senior Research Associate
CJ Bigler-Jones, Graduate Student

Publications

(1) "An Improved Method for Product Separation in Metathetical Reactions and its Demonstration for the Synthesis of Anhydrous Cesium Salts," Z. Anorg. Allg. Chem., 628, 1717 (2002), R.Haiges and K. O. Christe.

(2) "Improved Synthesis of CsN_3," Z. Anorg. Allg. Chem., 628, 909 (2002), M. Gerken, S. Schneider, T. Schroer, R. Haiges, and K. O. Christe.

(3) "The ^{19}F NMR Shifts are not a Measure for the Nakedness of the Fluoride Anion," J. Fluor. Chem., 116, 49 (2002), M. Gerken, J. A. Boatz, A. Kornath, R. Haiges, S. Schneider, T. Schroer, and K. O. Christe.

(4) "Triphenylmethyldifluoramine: A Stable Reagent for the Synthesis of *gem*-Bis(difluoramines)," J. Chem. Soc. Chem. Comm., 1712 (2002), G. K. Surya Prakash, M. Etzkorn, G. A. Olah, K. O. Christe, S. Schneider, and A. Vij.

(5) "Synthesis and Characterization of the $SO_2N_3^-$, $(SO_2)_2N_3^-$, and $SO_3N_3^-$ Anions," Inorg. Chem., 41, 4275 (2002), K. O. Christe, J. A. Boatz, M. Gerken, R. Haiges, S. Schneider, T. Schroer, F. S. Tham, A. Vij, V. Vij, R. I. Wagner, and W. W. Wilson.

(6) "Experimental Detection of the Pentaazacyclopentadienide (Pentazolate) Anion, *cyclo*-N_5^-," Angew. Chem. Int. Ed., 41, 3051 (2002), A. Vij, J. G. Pavlovich, W. W. Wilson, V. Vij, and K. O. Christe.

(7) "Tritylsulfinylamine: A New Member in the Family of Sulfinylamines," Solid State Sciences, 4, 1529 (2002), K. O. Christe, M. Gerken, R. Haiges, S. Schneider, T. Schroer, F. S. Tham, and A. Vij.

(8) "Structures of the BrF_4^+ and IF_4^+ Cations," Inorg. Chem., 41, 6397 (2002), A. Vij, F. S. Tham, V. Vij, W. W. Wilson, and K. O. Christe.

(9) "Singlet Delta Oxygen Production from a Gas-Solid Reaction," Angew. Chem. Int. Ed., 41, 3252 (2002), A. J. Alfano and K. O. Christe.

(10) "A Gas-Solid Singlet Delta Oxygen Generator for the Chemical Oxygen-Iodine Laser," AFRL Technology Horizons, Sept 2002, 34, A. Alfano, K. Christe, and R. Corley,

(11) "The Crystal Structures of ClF_3O, BrF_3O, and $[NO]^+[BrF_4O]^-$," Z. Anorg. Allg. Chem., 628, 1991 (2002), A. Ellern, J. A. Boatz, K. O. Christe, T. Drews, and K. Seppelt.

(12) "The $(SO_2)_2N_3^-$ Anion," Inorg. Chem., 42, 419 (2003), K. O. Christe, M. Gerken, R. Haiges, S. Schneider, T. Schroer, I.Tsyba, and R. Bau.

(13) "Polynitrogen Chemistry: Preparation and Characterization of $(N_5)_2SnF_6$, N_5SnF_5, and $N_5B(CF_3)_4$," Chemistry – A European Journal, 9, 2840 (2003), W. W. Wilson, A. Vij, V. Vij, E. Bernhardt, and K. O. Christe.

(14) "Synthesis, Characterization, and Computational Study of the *trans*-$IO_2F_5^{2-}$ Anion," Inorg. Chem., 42, 5282 (2003), J. A. Boatz, K. O. Christe, D. A. Dixon, B. A. Fir, M. Gerken, R. Z. Gnann, H. P. A. Mercier, and G. J. Schrobilgen.

(15) "On the Existence of FN_5, a Theoretical and Experimental Study," J. Phys. Chem. A, 107, 6638 (2003), H. M. Netzloff, M. S. Gordon, K. O. Christe, W. W. Wilson, A. Vij, V. Vij, and J. A. Boatz.

(16) "Quantitative Measure for the Nakedness of Fluoride Ion Sources," J. Am. Chem. Soc., 125, 9457 (2003), K. O. Christe and H. D. B. Jenkins.

(17) "Quantitative Measure for the Nakedness of Fluoride Ion Sources," J. Am. Chem. Soc., 125, 14210 (2003), K. O. Christe and H. D. B. Jenkins.

(18) "Enthalpies of Formation of Gas Phase N_3, N_3^-, N_5^+, and N_5^- from *Ab Initio* Molecular Orbital Theory, Stability Predictions for $N_5^+N_3^-$ and $N_5^+N_5^-$, and Experimental Evidence for the Instability of $N_5^+N_3^-$," J. Am. Chem. Soc., 126, 834 (2004), D. A. Dixon, D. Feller, K. O. Christe, W. W. Wilson, A. Vij, V. Vij, H. D. B. Jenkins, R. M. Olson, and M. S. Gordon.

(19) "Polyazide Chemistry. Preparation and Characterization of $Te(N_3)_4$ and $[P(C_6H_5)_4]_2[Te(N_3)_6]$," Angew. Chem. Int. Ed. Engl., 42, 5847 (2003), R. Haiges, J. A. Boatz, M. Gerken, S. Schneider, T. Schroer, and K. O. Christe.

(20) "First Structural Characterization of Binary As(III) and Sb(III) Azides," Chemistry – A European Journal, 10, 508 (2004), R. Haiges, A. Vij, J. A. Boatz, S. Schneider, T. Schroer, M. Gerken, and K. O. Christe.

(21) "X-ray Crystal Structures of $[XF_6][Sb_2F_{11}]$ (X = Cl, Br, I); $^{35,37}Cl$, $^{79,81}Br$ and ^{127}I NMR Studies and Electron Structure Calculations of the XF_6^+ Cations," Inorg. Chem., 43, 6905 (2004), J. F. Lehmann, G. J. Schrobilgen, K. O. Christe, A. Kornath, and R. Suontamo.

(22) "New High Energy Density Materials. Synthesis and Characterization of $N_5^+P(N_3)_6^-$, $N_5^+B(N_3)_4^-$, $N_5^+HF_2^- \cdot nHF$, $N_5^+BF_4^-$, $N_5^+PF_6^-$, and $N_5^+SO_3F^-$," Angew. Chem. Int. Ed., 43, 4919 (2004), R. Haiges, S. Schneider, T. Schroer, and K. O. Christe.

(23) "The NH_3Cl^+ Cation," Angew. Chem. Int. Ed., 43, 5213 (2004), S. Schneider, R. Haiges, T. Schroer, J. Boatz, and K. O. Christe.

(24) "Polyazide Chemistry. Preparation and Characterization of $As(N_3)_5$, $Sb(N_3)_5$, and $[P(C_6H_5)_4][Sb(N_3)_6]$," Angew. Chem. Int. Ed., 43, 6676 (2004), R. Haiges, J. A. Boatz, A. Vij, V. Vij, M. Gerken, S. Schneider, M. Yousufuddin, and K. O. Christe.

(25) "The Binary Group 4 Azides $[Ti(N_3)_4]$, $[P(C_6H_5)_4][Ti(N_3)_5]$, and $[P(C_6H_5)_4]_2[Ti(N_3)_6]$ and on Linear Ti-N-NN Coordination," Angew. Chem. Int. Ed., 43, 3148 (2004), R. Haiges, J. A. Boatz, A. Vij, V. Vij, M. Gerken, S. Schneider, M. Yousufuddin, and K. O. Christe.

(26) "The race for the first generation of the pentazolate anion in solution is far from over," Chem. Commun., 1607 (2005), T. Schroer, R. Haiges, S. Schneider, and K. O. Christe.

(27) "Heats of Formation of Xenon Fluorides and the Fluxionality of XeF_6 from High Level Electronic Structure Calculations," J. Am. Chem. Soc., 127, 8627 (2005), D. A. Dixon, W. A. de Jong, K. A. Petersen, K. O. Christe, and G. J. Schrobilgen.

(28) "Polyazide Chemistry: The first Binary Group 6 Azides, $Mo(N_3)_6$, $W(N_3)_6$, $[Mo(N_3)_7]^-$, and $[W(N_3)_7]^-$ and the $[NW(N_3)_4]^-$ and $[NMo(N_3)_4]^-$ Ions," Angew. Chem. Int. Ed., 44, 1860 (2005), R. Haiges, J. A. Boatz, R. Bau, S. Schneider, T. Schroer, M. Yousufuddin, and K. O. Christe.

(29) "The Syntheses and Structures of Ph_4N_3 (E = P, As, Sb), an Example for the Transition from Ionic to Covalent Azides within the Same Main Group," Z. Anorg. Allg. Chem., 631, 2691 (2005), R. Haiges, T. Schroer, M. Yousufuddin, and K. O. Christe.

(30) "Photochemistry of Interhalogen Compounds," J. Argent. Chem. Soc., 93, 1 (2005), R. D. Wilson, A. E. Axworthy, and K. O. Christe.

(31) "New Signal Processing Method for the Faster Observation of Natural Abundance ^{15}N NMR Spectra and its Application to N_5^+," Inorg. Chem., 45, 437 (2006), S. D. Kunikeev, H. S. Taylor, T. Schroer, R. Haiges, CJ Bigler Jones, and K. O. Christe.

(32) "Experimental Evidence for Linear Metal-Azide Bonds. The Binary Group 5 Azides $Nb(N_3)_5$, $Ta(N_3)_5$, $[Nb(N_3)_6]^-$ and $[Ta(N_3)_6]^-$, and 1:1 Adducts of $Nb(N_3)_5$ and $Ta(N_3)_5$ with

CH_3CN," Angew. Chem. Int. Ed., 45, 4830 (2006), R. Haiges, J. A. Boatz, T. Schroer, M. Yousufuddin, and K. O. Christe.

(33) "Preparation, Characterization, and Crystal Structures of the SO_3NHF^- and $SO_3NF_2^-$ Anions," Angew. Chem. Int. Ed., 45, 5179 (2006), R. Haiges, R. Wagner, J. A. Boatz, M.Yousufuddin, M. Etzkorn, G. K. Surya Prakash, K. O. Christe, R. D. Chapman, M. F. Welker, and C. B. Kreutzberger.

(34) "Are the NF_4^+ Cations in NF_4BF_4 Really Nontetrahedral?," Inorg. Chem., 45, 7981 (2006), R. Haiges, M. Gerken, A. Iuga, R. Bau, and K. O. Christe.

(35) "Following in the Footsteps of Henri Moissan," L'Actualite Chimique, Oct/Nov Issue, 2006, K. O. Christe.

(36) "Oxygen Balanced Energetic Ionic Liquid," Angew. Chem. Int. Ed., 45, 4830 (2006), C. J. Bigler Jones, R. Haiges, T. Schroer, and K. O. Christe.

(37) "Polyazide Chemistry: Synthesis and Properties of $[Nb(N_3)_7]^{2-}$ and $[Ta(N_3)_7]^{2-}$," Angew. Chem. Int. Ed., in press, R. Haiges, J. A. Boatz, M. Yousufuddin, and K. O. Christe.

(38) "Synthesis and Characterization of Silyldichloramines, their Reactions with F^- Ions, Stability of N_2Cl_2 and NCl_2^-, and Formation of NCl_3," Inorg. Chem., in press, S. Schneider, M. Gerken, R. Haiges, T. Schroer, J. A. Boatz, and K. O. Christe.

Interactions/Transitions

Presentations:

52 invited lectures were presented on results obtained under this program at international and national conferences and universities.

2002 AFOSR Molecular Dynamics Conference, Waltham, MA

2002 Gordon Research Conference on Energetic Materials, Tilton, NH

2002 ACS National Meeting, Boston, MA

Invited Seminars at Harvard University / MIT / USC

2002 Geoffrey Coates Lecture, University of Wyoming, Larramie, WY

2002 HEDM/NANO Conference, Washington, DC

2002 Advanced Energetics Technology Exchange Meeting, Livermore, CA

2003 ACS Winter Fluorine Conference, St. Pete Beach, FL (2 papers)

2003 National ACS Meeting, New Orleans, LA (7 papers)

Invited Seminars, UC San Diego and McMaster University, Hamilton, Ontario

2003 Samuel M. McElvain Lecture, University of Wisconsin, Madison,

2003 ACS Inorganic Chemistry Award Lecture, Northwestern University

2003 AFOSR Molecular Dynamics Conference, San Diego, CA

2003 National ACS Meeting, New York, NY

2003 Advanced Energetics Technology Exchange Meeting, Aberdeen, NJ

2004 National ACS Meeting, Anaheim, CA

2004 Science Advisory Board, Wright Patterson AFB, Dayton, OH

2004 European Symposium on Fluorine Chemistry, Poznan, Poland (2 papers)

Invited Seminar, University of Alberta, Edmonton, AL, Canada

10th Olah Nobel Prize Symposium, University of Southern California, Los Angeles, CA

2004 Molecular Dynamics Conference, Newport, RI

2004 Winter Symposium, University of Helsinki, Finland

2005 ACS Winter Fluorine Conference, St. Pete Beach, FL, (2 papers)

2005 Energetic Materials Technology Exchange, Washington, DC

2005 National ACS Meeting, San Diego, CA

2005 Molecular Dynamics Conference, Monterey, CA

2005 International Fluorine Symposium, Shanghai, China

Invited Seminar, Lawrence Livermore National Laboratory, Livermore, CA

2005 Pacific Basin Countries Conference, Honolulu, HI (3 papers)

2006 AFOSR Workshop on Ionic Liquids, University of Alabama, Tuscaloosa

2006 Molecular Dynamics Conference, Arlington, VA

Invited Seminars, Los Alamos National Laboratory, Los Alamos, NM, and University of Lethbridge, Lethbridge, Canada

2006 National ACS Meeting, Atlanta, GA

2006 Pyrotechnics Workshop, Fort Collins, CO

2006 International Fluorine Symposium, Bremen, Germany (2 papers)

2006 AFOSR Workshop on Polynitrogen Chemistry, Los Angeles, CA

2006 William Weber Symposium, USC, Los Angeles, CA

Joint projects

Joint projects were carried out with the following groups and colleagues:

Dr. Boatz, AFRL Edwards

Prof. Schrobilgen, McMaster University, Canada

Prof. Dixon, University of Alabama, Tuscaloosa

Dr. Feller, Pacific Northwest National Laboratory

Prof. Gordon, Iowa State University

Prof. Klapoetke, University of Munich, Germany

Prof. Jenkins, University of Warwick, UK

Profs. Prakash and Olah, University of Southern California

Dr. Hemley, Carnegie Institution

Prof. Bau, University of Southern California

Dr. Jurek Krzystek, National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL

Prof. Joshua Telser, Roosevelt University, ILL

Dr. Robert Chapman, Naval Research Laboratory, China Lake, CA

Prof. Howard Taylor, University of Southern California

Prof. Konrad Seppelt, Free University, Berlin, Germany

Consulting activities

Consultations were provided to the US Enrichment Corporation of Piketon, OH, in support of their efforts to safely decommission the old gaseous diffusion plants in the US, the Merck GMBH in Darmstadt Germany, the Edwards AFB, and Science and Application Technologies in Moorpark, CA.

Patents

(1) "Process for the Chemical Generation of Singlet Delta Oxygen," U.S._6,623,718 (2002), K. O. Christe and A. Alfano.

(2) "Novel Liquid Monopropellants," U. S. Patent pending, K. O. Christe and G. Drake.

Honors / Awards

2002 Geoffrey Coates Lecturer, University of Wyoming, Larramie

2003 ACS Award in Inorganic Chemistry

2003 Samuel M. McElvain Lecturer, University of Wisconsin, Madison

2003 ACS Inorganic Chemistry Award Lecturer, Northwestern University

2006 Alfred Stock Memorial Prize from the German Chemical Society

Prior Major Awards

1969 NASA Apollo Achievement Award

1986 ACS Award for Creative Work in Fluorine Chemistry

2000 Prix Moissan

The full text of all publications has been attached as a separate file.