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Inorganic Cations

Synthesis and Characterization of (*Z*)-$[N_3NFO]^+$ and (*E*)-$[N_3NFO]^+$**

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Dedicated to Professor Dieter Naumann on the occasion of his 65th birthday

Only three well-characterized stable nitrogen fluoride oxide molecules, FNO, FNO_2, and NF_3O, and one ion, $[NF_2O]^+$, are known in which the fluorine and oxygen atoms are directly bonded to the same nitrogen atom.[1] Herein, we report the synthesis and characterization of $[N_3NFO]^+$, a novel stable nitrogen fluoride oxide cation which can exist in the form of two different configurational isomers.

Our recent synthesis[2] of the N_5^+ ion [Eq. (1)] prompted us to explore the reactions of similar cations with HN_3. A logical candidate for this type of chemistry was the $[NF_2O]^+$ ion.[3–5] When $[NF_2O][SbF_6]$ was combined with a stoichiometric amount of HN_3 in anhydrous HF solution between −45 °C and room temperature, one of the fluorine ligands was replaced by an azide group [Eq. (2)].

$$[N_2F]^+ + HN_3 \rightarrow N_5^+ + HF \quad (1)$$

$$[NF_2O][SbF_6] + HN_3 \rightarrow [N_3NFO][SbF_6] + HF \quad (2)$$

The use of excess HN_3 under these conditions led to the formation of $N_5^+[SbF_6]^-$ and N_2O [Eq. (3)].

$$[N_3NFO][SbF_6] + HN_3 \rightarrow N_5^+[SbF_6]^- + N_2O + HF \quad (3)$$

The mechanism of Equation (3) was studied experimentally by ^{15}N isotopic substitution and theoretical calculations and involves the intermediate formation of the $[N_7O]^+$ ion. The chemistry taking place in the $[NF_2O]^+/HN_3$ system, however, is considerably more complex than that given by Equations (2) and (3) and will be reported in a separate publication.

The $[N_3NFO][SbF_6]$ salt is a white solid which is stable at room temperature and is highly soluble in anhydrous HF. It does not detonate when either struck with a hammer or scraped with a metal spatula, and deflagrates when heated in an open flame. It ignites ethanol, reacts violently with water, and oxidizes bromide to bromine. Its general properties somewhat resemble those of $N_5^+[SbF_6]^-$.[2] When heated to 50–60 °C, it decomposes mainly to $[NO][SbF_6]$ with evolution of N_2 and NF_3 [Eq. (4)].

$$3\,[N_3NFO][SbF_6] \rightarrow 3\,[NO][SbF_6] + 4\,N_2 + NF_3 \quad (4)$$

Reaction (4) was studied in solution by nitrogen NMR spectroscopy using $[N_3NFO]^+$ that was labeled in the α and γ positions with ^{15}N, resulting in the formation of ^{15}N-labeled N_2 and unlabeled $[NO]^+$. It was also investigated by vacuum pyrolysis of the solid. The Raman spectrum of the solid residue showed $[NO][SbF_6]$; the infrared spectrum of the volatile products, trapped at −196 °C, contained NF_3. Reaction (4) most likely involves an intramolecular attack of the fluorine ligand of $[N_3NFO]^+$ on the electron-rich N_α atom of the azido group, accompanied by extrusion of the $[NO]^+$ ion. The intermediately formed FN_3 molecule can decompose under these conditions to N_2 and NF_3 [Eq. (5)].[6]

$$3\,FN_3 \rightarrow NF_3 + 4\,N_2 \quad (5)$$

In the $^{14/15}N$ and ^{19}F NMR and the Raman spectra of $[N_3NFO][SbF_6]$, two sets of peaks were observed, suggesting the presence of two stereoisomers. This interpretation was confirmed by theoretical calculations at the B3LYP, MP2, and CCSD(T) levels of theory showing two catenated minimum-energy structures of very similar energies ($\Delta E \leq 0.6$ kcal mol^{-1} at all levels of theory, with either one or the other isomer being favored, depending on the level of calculation and basis set used). A third minimum-energy structure was also found, derived from a five-membered N_4O ring[7] with the fluorine atom attached to a nitrogen atom in the α position to the oxygen atom. However, its energy was 39.4 kcal mol^{-1} higher than that of the catenated *Z* isomer at the B3LYP/6-311G(2df) level of theory. The geometries, obtained for the catenated *Z* and *E* isomers at the CCSD(T)/6-311(2df) level, the highest level used in this study, are shown in Figure 1. At this level, the *Z* isomer is favored by 0.6 kcal mol^{-1}. Both structures are planar (C_s symmetry) and differ mainly in the relative positions of the F and O atoms, with the remaining bond lengths and angles being very similar. In the *Z* isomer, the azido and the fluorine ligands are *cis* to each other, while in the *E* isomer they are *trans* to each other.

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

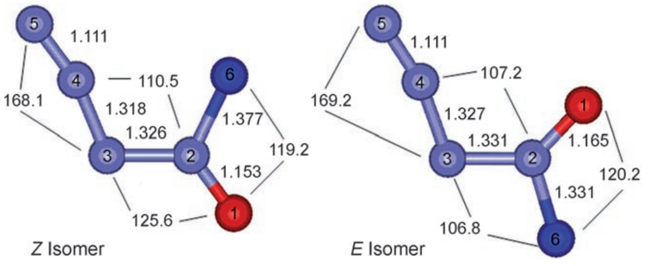

Figure 1. Stuctures of (*Z*)-$[N_3NFO]^+$ and (*E*)-$[N_3NFO]^+$ calculated at the CCSD(T)/6-311G(2df) level of theory (bond lengths in Å, bond angles in degrees; N blue, O red, F dark blue).

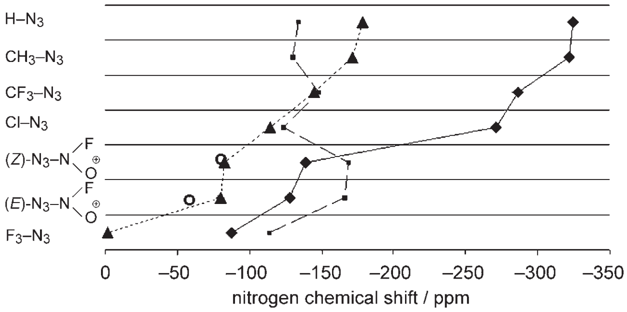

Figure 3. Plot of the nitrogen chemical shifts of (*Z*)-$[N_3NFO]^+$, (*E*)-$[N_3NFO]^+$ and related XN_3-type covalent azides arranged according to increasing electronegativity of the X group; ◆ N_α, ■ N_β, ▲ N_γ, ○ N_1.

The NMR chemical shifts and coupling constants observed for both isomers in HF solution at −30 °C are summarized in Figure 2. As can be seen, the isomeric splitting is very large for the fluorine atoms ($\Delta\delta(^{19}F) = 98$ ppm) and decreases along the nitrogen chain with increasing distance from the fluorine atom ($\Delta\delta(N1) = 22$, $\Delta\delta(N_\alpha) = 11$, $\Delta\delta(N_\beta) = 3$, $\Delta\delta(N_\gamma) = 2$ ppm). The assignments to the two isomers were facilitated by the fact that they were present in a different ratio of 1:1.45 for the *Z* and *E* isomer, by the observed coupling constants, theoretical calculations (the values calculated at the PBE1BPE/6-311+G(2df) level of theory are given in brackets in Figure 2), and by analogy to those known for similar covalent azides.[8,9] For N_α and N_γ, the nitrogen chemical shifts result in smooth trends when plotted against the electron-withdrawing power of the X group of XN_3, while the chemical shifts of N_β are randomly scattered around a value of $\delta = 141 \pm 28$ ppm (Figure 3). The agreement between the observed and calculated trends in the nitrogen shifts is good, particularly if it is kept in mind that the accurate calculation of chemical shifts for nitrogen atoms containing free valence electron pairs is difficult, unless extensive electron-correlation treatment, such as that provided by the CCSD(T) method, is used.[2] The fact that in HF solution at −30 °C the *E* isomer is slightly favored over the *Z* isomer, is in contrast to our highest-level prediction for the free gaseous ion at 0 K and can be attributed to either shortcomings of the computations and/or solvation or temperature effects.

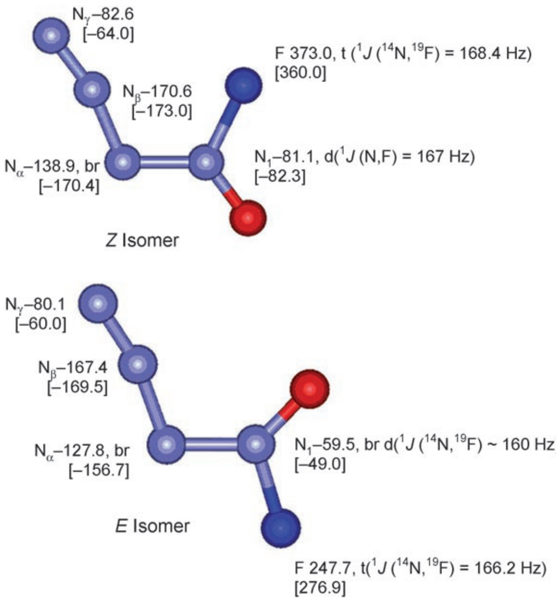

Figure 2. Multinuclear NMR parameters of (*Z*)-$[N_3NFO]^+$ and (*E*)-$[N_3NFO]^+$ (chemical shifts in ppm). The values predicted at the PBE1BPE/6-311+G(2df) level of theory are shown in square brackets.

The presence of an NFO group in each isomer is established by: 1) the ^{19}F NMR spectrum, which shows two triplets of equal intensity with $^1J(^{19}F,^{14}N)$ constants of 166.2 and 168.4 Hz and chemical shifts of $\delta = 274.7$ and 373.0 ppm, respectively, which are reasonable when compared to the $[NF_2O]^+$ signal, observed in this study under the same conditions at $\delta = 325.2$ ppm with $^1J(^{14}N,^{19}F) = 259$ Hz; and 2) the ^{14}N NMR spectrum which shows two broad doublets at $\delta = -59.5$ and −81.1 ppm, respectively, with $^1J(^{14}N,^{19}F) \approx 167$ Hz, resulting from coupling with one fluorine atom. These values are again in good agreement with the nitrogen shift of $\delta = -97.7$ ppm observed for the $[NF_2O]^+$ ion.

Of the three nitrogen atoms of the azido group, only the N_β atoms were observable in the ^{14}N NMR spectra at $\delta = -167.4$ and −170.6 ppm for the *E* isomer and the *Z* isomer, respectively. For the observation of N_α ($\delta = -127.8$ ppm for the *E* isomer, $\delta = -138.9$ ppm for the *Z* isomer) and N_γ ($\delta = -80.1$ ppm for the *E* isomer, $\delta = -82.6$ ppm for the *Z* isomer), ^{15}N substitution was required. The observed nitrogen chemical shifts are consistent with the presence of a covalent azido group attached to a highly electronegative ligand (see Figure 3) and a nitrogen atom attached to a fluorine atom and an oxygen atom.

The second method of identification used for $[N_3NFO]^+$ was vibrational spectroscopy. The observed Raman and infrared spectra (see Tables 1 and 2) are in good agreement with the spectra calculated for the two isomers at the B3LYP, MP2, and CCSD(T) levels of theory. As expected, the CCSD(T) calculations resulted in the best fit with the observed spectra and, therefore, only these data have been included in the tables.

As one might expect, the frequencies of the bands characteristic of the azido groups are similar to those observed in other covalent azides,[2,8] and are also similar for the two isomers. However, three of the modes (ν_2, ν_5, and

Table 1: Observed and unscaled calculated vibrational frequencies [cm^{-1}] and intensities for (*Z*)-$[N_3NFO]^+$.[a]

Mode	Obsd frequency [rel int] Ra, HF soln, 20 °C	Ra, solid, 20 °C	IR,[c] solid, 20 °C	$\Delta\nu$ $^{14}N/^{15}N$[d]	Calcd frequency (IR)[Ra][b] CCSD(T)/6-31G(d) ^{14}N[d]	$\Delta\nu$ $^{14}N/^{15}N$[d,e]
a′ ν_1	2253 [10]	2252 [10]	–[f]	32	2246 (27) [114]	33.2
ν_2	1771 [1.1]	1771 [0.8]	1765 s	0	1810 (387) [6.2]	0
ν_3	1159 [1.7]	1162 [1.8]	1156 vs	12–20[g]	1201 (285) [49]	20.5
ν_4	979 [1]	980 sh, vw	994 ms		991 (71) [0.40]	13.3
ν_5	–[h]	733 [0.8]	732 m		750 (58) [8.3]	4.4
ν_6	680 sh	683 [1]	–[i]		669 (1.7) [9.3]	0.7
ν_7	546 [1.3]	548 [0.6]	545 w		538 (6.7) [5.6]	1.3
ν_8	443 [0.6]	447 [0+]			436 (0.7) [0.87]	0.6
ν_9	204 [4.4]	210 [1.5]			191 (1.1) [2.9]	2.4
a″ ν_{10}	–[k]	683 [1]	–[i]		656 (9.3) [0.77]	3.0
ν_{11}	461 [0.4]	465 [0.3]			451 (3.8) [0.59]	0
ν_{12}	140 sh	140 sh			142(0.37) [0.24]	0.8

[a] The spectra were recorded for a mixture of the *Z* and *E* isomers; therefore, some of the observed relative intensities contain contributions from the other isomer, whenever their frequencies coincide; the Raman spectra were recorded over a temperature range of −110 to 20 °C; because the observed frequencies changed within the temperature range by less than 2 cm^{-1} for all bands, only the data at 20 °C are listed; in addition to the bands from the cations, the following bands were observed for $[SbF_6]^-$: Ra (HF): ν_1, 654, vs; ν_2, 571, w; ν_5, 284, m; Ra (solid): 658, 567, 285 cm^{-1}; IR (solid): ν_3, 651 cm^{-1}. [b] Calculated IR (in parenthesis) and Raman intensities (in square brackets) are given in km mol^{-1} and Å^4 amu^{-1}, respectively; the Raman intensities were calculated at the MP2/cc-pvtz level. [c] The IR spectrum was recorded as a pressed AgCl disk. [d] Frequency differences between the isotopomer containing ^{15}N in the N_α position and that containing ^{15}N in the N_γ position. [e] The calculated isotopic shifts were obtained at the B3LYP/aug-cc-pvdz level and scaled by the same factor by which the calculated frequencies deviated from the observed ones. [f] A strong band was observed at 2241 cm^{-1} with a shoulder on its high-frequency side; decomposition studies showed that this band did not decay together with the other $[N_3NFO]^+$ bands and, therefore, is attributed to an unknown impurity; the high-frequency shoulder probably represents ν_1 of the cation. [g] Based on the line width of a poorly resolved band. [h] Obscured by a strong line from the teflon-FEP sample tube. [i] Obscured by ν_3 of $[SbF_6]^-$. [k] Obscured by ν_4 of $[SbF_6]^-$.

Table 2: Observed and unscaled calculated vibrational frequencies [cm^{-1}] and intensities for (*E*)-$[N_3NFO]^+$.[a]

Mode	Obsd frequency [rel int] Ra, HF soln, 20 °C	Ra, solid, 20 °C	IR,[c] solid, 20 °C	$\Delta\nu$ $^{14}N/^{15}N$[d]	Calcd frequency (IR)[Ra][b] CCSD(T)/6-31G(d) ^{14}N[d]	$\Delta\nu$ $^{14}N/^{15}N$[d,e]
a′ ν_1	2253 [10]	2252 [10]	–[f]	32	2249 (16) [126]	33.4
ν_2	1705 [0.7]	1704 [0.6]	1704 ms	0	1739 (273) [8.9]	0.5
ν_3	1159 [1.7]	1162 [1.8]	1156 vs	12–20[g]	1210 (413) [44]	12.0
ν_4	991 [0.9]	995 [1.3]	994 ms	10	1009 (12) [5.6]	9.8
ν_5	–[h]	901 [0.4]	903 m	18.7	885 (24) [7.2]	18.5
ν_6	668 [1]	672 [0+]	–[i]		658 (14) [6.6]	0.8
ν_7	516 (0.7)	519 [0.6]	518 w		504 (5.3) [3.9]	1.8
ν_8	465 [0+]	465 [0.4]	463 w		451 (1.7) [0.95]	0.9
ν_9	180 sh	193 sh			177 (1.1) [4.2]	2.0
a″ ν_{10}	–[k]		–[i]		675 (10) [0.86]	1.5
ν_{11}		480 [0+]	477 vw		473 (1.5) [0.39]	0.4
ν_{12}	140 sh	140 sh			159 (0.00) [0.39]	0.8

[a]–[k] See footnotes [a]–[k] of Table 1.

ν_7), which involve mainly motions of the FNO group, differ significantly and, in the two isomers, are separated by 47, 160, and 31 cm^{-1}, respectively, in HF solution and by 67, 174, and 26 cm^{-1}, respectively, in the solid state. Additional support for the predicted structures comes from the good agreement between observed and calculated isotopic shifts in $[^{15}N\text{-}N\text{-}N\text{-}NFO]^+$ and $[N\text{-}N\text{-}^{15}N\text{-}NFO]^+$ (Tables 1 and 2).

The assignment of the vibrational spectra was tricky because of the presence of two isomers which could not be separated, as well as some starting materials, such as $[NF_2O]^+$[3] or $[H_2N_3]^+$,[10] and some decomposition products, such as N_5^+,[2] $[NO]^+$,[11] and $[NO_2]^+$.[11] A large number of spectra were recorded, and the assignments to the two $[N_3NFO]^+$ isomers were based on the observed growth and decay patterns. A typical Raman spectrum, in which $[NF_2O]^+$ and $[NO_2]^+$ were present as impurities, is shown in Figure 4. Whereas the 1407 cm^{-1} band of $[NO_2]^+$ and the 1869 and 1158 cm^{-1} bands of $[NF_2O]^+$ presented no problem, the 900 cm^{-1} band of $[NF_2O]^+$ fell right on top of the relatively weak ν_5 band of the *E* isomer. The identity and relative intensity of the latter were confirmed by ^{15}N substitution in either the N_γ or N_α positions of the azido group, resulting in a 50:50 mix of the two isotopomers, $[^{15}N\text{-}N\text{-}N\text{-}NFO]^+$ and $[N\text{-}N\text{-}^{15}N\text{-}NFO]^+$. Both isotopomers shifted away from the unsubstituted $[NF_2O]^+$ peak and resulted in two well-resolved Raman bands of equal intensity with a frequency separation of 18.7 cm^{-1} (calculated value 18.5 cm^{-1}).

Because the identity of the vibrations in the 500 to 1200 cm^{-1} region was not obvious, normal coordinate analyses were carried out for both isomers. The results are summarized in Tables S1 and S2 in the Supporting Information, and show that most of the normal modes are complex mixtures of the corresponding symmetry coordinates. For example, the N–F stretching motion in the *E* isomer is distributed over several modes, with the highest contribution to a single mode (in this case ν_4) being only 29 %. Therefore, the assignment of characteristic modes, such as N–F stretching, to single frequencies and the comparison of such frequencies for the two isomers is unwarranted. Owing to the large size of the A′ blocks and the strong coupling, the determination of explicit F matrices and internal force constants were not feasible.

In conclusion, the new nitrogen fluoride oxide cation $[N_3NFO]^+$ was prepared from $[NF_2O]^+$ and HN_3 and charac-

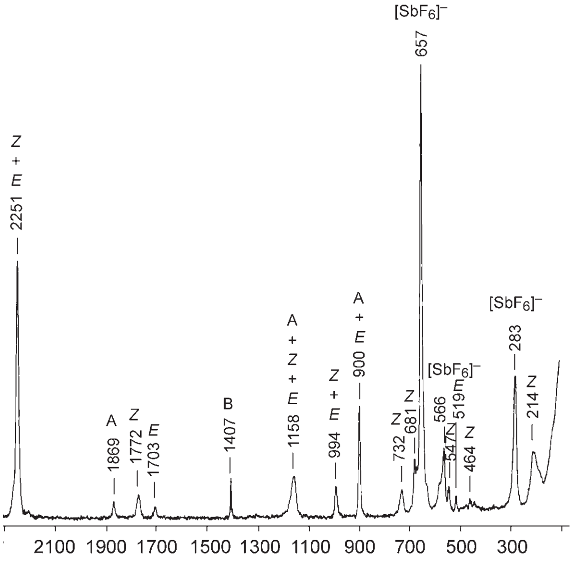

Figure 4. Typical Raman spectrum of a mixture of solid (*Z*)-[N_3NFO][SbF_6] and (*E*)-[N_3NFO][SbF_6] (denoted on the spectrum as *Z* and *E*, respectively), containing some [NF_2O][SbF_6] (A) and [NO_2][SbF_6] (B) as impurities.

terized by vibrational and multinuclear NMR spectroscopy and electronic-structure calculations. The cation is planar and can exist in the form of two stereoisomers, depending on whether the azido group and the fluorine ligand are *cis* (*Z* isomer) or *trans* (*E* isomer) with respect to each other. Although the azido groups in the two isomers are similar, the bond lengths and the ^{19}F NMR chemical shifts of the N−F bonds in the two isomers differ significantly, with the *Z* isomer exhibiting the longer bond (by 0.05 Å).

Experimental Section

Caution! *Neat HN_3 is highly explosive and should, whenever possible, be handled only in solution. Anhydrous HF can cause severe burns and contact with the skin must be avoided.*

Materials and apparatus: All reactions were carried out in teflon-FEP or Kel-F ampules that were closed by stainless-steel valves. Volatile materials were handled in a stainless-steel/teflon-FEP vacuum line.[12] All reaction vessels were passivated with ClF_3 prior to use. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glove box. Raman spectra were recorded directly in the teflon or Kel-F reactors in the range 4000–80 cm^{-1} on a Bruker Equinox 55 FT-RA spectrophotometer by using a Nd-YAG laser at 1064 nm. The infrared spectra were recorded on a Midac, M Series, FT-IR spectrometer using AgCl pellets. The pellets were prepared inside the glove box by using an Econo minipress (Barnes Engineering Co). The starting materials [NF_2O][SbF_6][3] and HN_3[2] were prepared by literature methods. HF was dried by storage over BiF_5.[13]

[N_3NFO][SbF_6]: In a typical experiment, [NF_2O][SbF_6] (0.3 mmol) was added to a prepassivated, thin-walled, 5-mm o.d. Kel-F ampule, which was closed by a stainless-steel valve. On the vacuum line, anhydrous HF (270 mg) was condensed in at −196 °C and the [NF_2O][SbF_6] was dissolved in the HF at room temperature. The ampule was cooled back to −196 °C, and a mixture of HN_3 (0.3 mmol) and HF (750 mg) was condensed in. The resulting mixture was warmed to temperatures between −45 and −20 °C, producing the desired [N_3NFO][SbF_6] salt in HF solution. If the neat solid was desired, all volatile material was removed under reduced pressure at −30 °C. The product was characterized by multinuclear NMR and vibrational spectroscopy.

Theoretical methods: The molecular structures, harmonic vibrational frequencies, and infrared and Raman vibrational intensities were calculated by using second-order perturbation theory (MP2, also known as MBPT(2)[14]) or single- and double-excitation coupled cluster methods,[15] including a noniterative treatment of connected triple excitations,[16] and also at the DFT level by using the B3LYP hybrid functional,[17] which included the VWN5 correlation functional.[18] Hessians (energy second derivatives) were calculated for the final equilibrium structures to verify them as local minima, that is, as having a positive definite Hessian. The calculations were performed by using the electronic structure codes GAMESS,[19] Gaussian 98,[20] and ACES II.[21] The second derivatives were analyzed by using the program BMATRIX.[22]

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[1] *Gmelin Handbook of Inorganic Chemistry, F-Suppl. Vol. 5*, Springer, Berlin, **1987**, pp. 76–214, and references therein.

[2] a) K. O. Christe, W. W. Wilson, J. A. Sheehy, J. A. Boatz, *Angew. Chem.* **1999**, *111*, 2112; *Angew. Chem. Int. Ed.* **1999**, *38*, 2004; b) A. Vij, W. W. Wilson, V. Vij, F. S. Tham, J. A. Sheehy, K. O. Christe, *J. Am. Chem. Soc.* **2001**, *123*, 6308.

[3] a) W. B. Fox, J. S. MacKenzie, N. Vanderkooi, B. Sukornik, C. A. Wamser, J. R. Holmes, R. E. Eibeck, B. B. Stewart, *J. Am. Chem. Soc.* **1966**, *88*, 2604; b) K. O. Christe, W. Maya, *Inorg. Chem.* **1969**, *8*, 1253; c) C. A. Wamser, W. B. Fox, B. Sukornik, J. R. Holmes, B. B. Stewart, R. Juurick, N. Vanderkooi, D. Gould, *Inorg. Chem.* **1969**, *8*, 1249.

[4] a) K. O. Christe, J. F. Hon, D. Pilipovich, *Inorg. Chem.* **1973**, *12*, 84; b) J. Mason, K. O. Christe, *Inorg. Chem.* **1983**, *22*, 1849.

[5] A. Vij, X. Zhang, K. O. Christe, *Inorg. Chem.* **2001**, *40*, 416.

[6] a) J. F. Haller, PhD Thesis, Cornell University, **1942**; b) T. M. Klapoetke, I. C. Tornieporth-Oetting, *Nichtmetallchemie*, VCH, Weinheim, **1994**.

[7] a) A. Schulz, I. C. Torniepoth-Oetting, T. M. Klapoetke, *Angew. Chem.* **1993**, *105*, 1697; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1610; b) N. El-Bakali Kassimi, R. J. Doerksen, A. J. Thakkar, *J. Phys. Chem.* **1996**, *100*, 8752; c) G. P. Bean, *J. Org. Chem.* **1998**, *63*, 2497.

[8] G. Schatte, H. Willner, M. Willert-Porada, *Magn. Reson. Chem.* **1992**, *30*, 118, and references therein.

[9] S. Berger, S. Braun, H. O. Kalinowski, *NMR Spectroscopy of the Non-Metallic Elements*, Wiley, Chichester, **1997**.

[10] K. O. Christe, W. W. Wilson, D. A. Dixon, S. I. Khan, R. Bau, T. Metzenthin, R. Lu, *J. Am. Chem. Soc.* **1993**, *115*, 1836.

[11] J. Weidlein, U. Mueller, K. Dehnicke, *Schwingungsspektroskopie*, Georg Thieme, Stuttgart, **1982**.

[12] K. O. Christe, W. W. Wilson, C. J. Schack, R. D. Wilson, *Inorg. Synth.* **1986**, *24*, 39.

[13] K. O. Christe, W. W. Wilson, C. J. Schack, *J. Fluorine Chem.* **1978**, *11*, 71.

[14] C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618; J. A. Pople, J. S. Binkley, R. Seeger, *Int. J. Quantum Chem.* **1976**, *S10*, 1; M. J. Frisch, M. Head-Gordon, J. A. Pople, *Chem. Phys. Lett.* **1990**, *166*, 275; J. Bartlett, D. M. Silver, *Int. J. Quantum Chem. Symp.* **1975**, *9*, 1927.

[15] G. D. Purvis III, R. J. Bartlett, *J. Chem. Phys.* **1982**, *76*, 1910.

[16] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479.

[17] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; P. J. Stephens, F. J. Devlin, C. F. Chablowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623; R. H. Hertwig, W. Koch, *Chem. Phys. Lett.* **1997**, *268*, 345.

[18] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200.

[19] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.* **1993**, *14*, 1347.

[20] Gaussian 98 (Revision A.6), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.

[21] J. F.Stanton, J. Gauss, J. D. Watts, M. Nooijen, N. Oliphant, S. A. Perera, P. G. Szalay, W. J. Lauderdale, S. R. Gwaltney, S. Beck, A. Balkova, D. E. Bernholdt, K. K. Baeck, P. Rozyczko, H. Sekino, C. Hober, R. J. Bartlett, ACES II, Quantum Theory Project, University of Florida: integral packages included are VMOL (J. Almlof, P. R. Taylor), BPROPS (P. R. Taylor), and ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jorgensen, J. Olsen, P. R. Taylor).

[22] A. Komornicki, BMATRIX Version 2.0, Polyatomics Research Institute, Palo Alto, CA, **1996**.