A moderately strong antiferromagnetic interaction ($2J = -72$ cm^{-1}) has been found for a compound (**3**) with an estimated Cu···Cu separation of ≈7.6 Å, and definitely, this is not the limit for the intramolecular magnetic interaction between two Cu(II) ions, provided the Cu(II) ions and the bridging ligand have the proper geometry.[16f] The mixed-valence species Cu^{II}Cu^{III}Cu^{II} obtained by electrochemical oxidation seems to be stable on the voltammetric time scale, and hence, the chemical preparation of the oxidation products should be feasible.

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Supplementary Material Available: Listings of intraligand bond distances and angles (Tables SI and SII), hydrogen atom coordinates (Table SIII), anisotropic thermal parameters (Table SIV), and crystal data (7 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Preparation of the Nitryl Salts $ON(Cl)F^+AsF_6^-$, $ON(CF_3)F^+AsF_6^-$, and $HON(CH_2)CF_3^+SbF_6^-$ and Crystal Structure of $HON(CH_2)CF_3^+AsF_6^-$

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The $ON(Cl)F^+AsF_6^-$ and $ON(CF_3)F^+AsF_6^-$ salts are prepared by oxidative fluorination of ONCl and ONCF$_3$ with $N_2F^+AsF_6^-$. Methylation of ONCF$_3$ with CH$_3$F and AsF$_5$ gives $ON(CH_3)CF_3^+AsF_6^-$, which in the solid state exists as the enol tautomer hydroxylimmonium salt $HON(CH_2)CF_3^+AsF_6^-$, triclinic, of space group $P\bar{1}$ with $a = 5.063$ (1) Å, $b = 7.757$ (3) Å, $c = 10.429$ (2) Å, $\alpha = 86.75$ (2)°, $\beta = 89.34$ (2)°, and $\gamma = 74.12$ (2)°. The framework of the cation is planar, with C–N bond lengths of 147.7 (5) and 127.3 (5) pm and an N–O distance of 137.2 (4) pm. The cation and anion have a short H···F contact of 166 (6) pm. An alternative method for the preparation of $ONF_2^+MF_6^-$ (M = As, Sb) was found involving the oxidative fluorination of ONF with $XeF^+MF_6^-$.

Introduction

Presently, only two nitryl cations exist: $ONCl_2^+$ and ONF_2^+. Their synthesis is specifically linked to the desired cation. The latter, ONF_2^+, is obtained from trifluoroamine oxide, ONF$_3$, and strong Lewis acids such as AsF$_5$ or SbF$_5$.[1,2] $ONCl_2^+$, which is isoelectronic with phosgene, OCCl$_2$, is formed in very poor yields as a $SbCl_6^-$ salt according to eq 1.[3] The salt is thermally stable up to 145 °C.[3]

$$NCl_3 + OSCl_2 + SbCl_5 \rightarrow ONCl_2^+SbCl_6^- + SCl_2 \qquad (1)$$

In contrast, oxidative chlorination of ONCl by Cl$_2$/AsF$_5$ mixtures at −76 °C (eq 2) gives high yields of $ONCl_2^+AsF_6^-$, but

$$2ONCl + Cl_2 + 3AsF_5 \rightarrow 2ONCl_2^+AsF_6^- + AsF_3 \qquad (2)$$

this compound is stable only below −78 °C. $ONCl_2^+SbF_6^-$, prepared in a similar manner, is also unstable.[4]

Attempts to prepare $ON(CF_3)_2^+SbF_6^-$ are reported in the literature.[5] One-electron transfer with $O_2^+SbF_6^-$ and PtF$_6$ should create the salt from the ON(CF$_3$)$_2$ radical. The high oxidation potentials of these systems, however, cause fission of the N–C bond, giving $NO^+SbF_6^-$ and byproducts.[5]

Although ab initio calculations show potential minima for NF$_5$ and even NF_6^-, assuming unusually long N–F bond distances,[6] neither thermolysis of $NF_4^+HF_2^-$ nor reaction of NF_4^+ salts with alkali-metal fluoride gives pentafluoroazoran. The reactions proceeded according to eqs 3 and 4.[7]

$$NF_4^+HF_2^- \rightarrow NF_3 + F_2 + HF \qquad (3)$$

$$NF_4^+PF_6^- + CsHF_2 \rightarrow NF_4^+HF_2^- + CsPF_6 \qquad (4)$$

$NCl_4^+AsF_6^-$, which has been synthesized by us recently,[8] decomposes similarly:

$$NCl_4^+AsF_6^- \xrightarrow[\text{IR matrix}]{\Delta} NCl_3 + AsF_5 + ClF \qquad (5)$$

The thermal decomposition reaction of $ONF_2^+MF_6^-$ (M = As, Sb) proceeds differently. On heating, trifluoroamine oxide is formed, which attracts high interest with respect to bond theories.[6,9,10]

$$ONF_2^+MF_6^- \rightarrow ONF_3 + MF_5 \qquad M = As, Sb \qquad (6)$$

Since to date neither mixed haloamine oxides nor their cations are known, we became interested in their syntheses.

Experimental Section

Materials and Apparatus. Volatile substances were handled in a high-vacuum line with greaseless stopcocks (Young). Solids were manipulated by Schlenk techniques. Experiments in anhydrous HF were conducted in KEL-F reactors with stainless steel valves (Hoke). Solvents SO$_2$ and CCl$_3$F were stored over CaH$_2$. AsF$_5$ and SbF$_5$ (Merck) were distilled repeatedly before use. (HF)$_x$ was dried in a stainless steel bomb under 1.5 bar of F$_2$. CF$_3$NO was prepared according to the literature[11] and, after repeated distillation, stored in the dark in glass ampules. $N_2F^+AsF_6^-$ was prepared according to the literature[12] and stored under dry N$_2$.

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Table I. Crystallographic Data for $HON(CH_2)CF_3^+AsF_6^-$

$CH_2CF_3NOH^+AsF_6^-$	fw 302.96
$a = 5.063$ (1) Å	space group $P\bar{1}$ (No. 2)
$b = 7.757$ (3) Å	$T = -100$ °C
$c = 10.429$ (2) Å	$\lambda = 0.71073$ Å
$\alpha = 86.75$ (2)°	$\rho_{calcd} = 2.5581$ g cm^{-3}
$\beta = 89.34$ (2)°	$\mu = 4.44$ mm^{-1}
$\gamma = 74.12$ (2)°	no abs cor
$V = 393.3$ (2) Å^3	$R(F_o) = 0.043$
$Z = 2$	$R_w(F_o) = 0.046$

IR spectra were recorded in a low-temperature cuvette,[13] with the use of NaCl windows between 4000 and 600 cm^{-1} and polyethylene windows below 600 cm^{-1} on a Bruker IFS 113v FT-IR instrument, with a resolution 0.5 cm^{-1}. For matrix isolation at 10 K a helium kryostat with CsI windows was used, the matrix gas was nitrogen, and the measurements were made on a Perkin-Elmer 580 B instrument, with a resolution of 0.8 cm^{-1}.

Raman spectra were recorded on a Coderg T 800 instrument, with a resolution of 0.5 cm^{-1} and stimulation by a Spectra Physics Ar$^+$ laser with $\lambda = 514.5$ nm.

NMR spectra were recorded on a Bruker AM 300 FT-NMR spectrometer (^{13}C, 75.5 MHz; ^{1}H, 300.0 MHz; ^{19}F, 282.5 MHz), with a pulse number of ca. 800 for ^{13}C and ^{19}F spectra between +220 and −10 ppm relative to TMS and between +400 and −200 ppm relative to CCl_3F, respectively. ^{1}H NMR spectra were recorded with ca. 20 pulses between +20 and −1 ppm relative to TMS. An upfield shift means a negative chemical shift.

Registration of mass spectra on a Varian CH5 instrument was begun at −196 °C, and the temperature was slowly raised until signals could be detected.

Single-crystal structure data were collected on a Nicolet R3m/V instrument with LT-1 low-temperature equipment, using Mo Kα radiation ($\lambda = 71.073$ nm). The crystal structure was obtained via a Patterson synthesis, a difference Fourier synthesis, and least-squares refinements with anisotropic displacement parameters for all non-hydrogen atoms and a common isotropic temperature factor for all hydrogen atoms.

Crystallographic data and values for the structure determinations are listed in Table I.

Preparation of $HON(CH_2)CF_3^+AsF_6^-$. Equimolar amounts of CH_3F and AsF_5 were condensed on 150 mg (1 mmol) of CF_3NO. The mixture was covered with 2 mL of SO_2 and slowly warmed to −40 °C. The reaction could be followed by the slow fading of the blue color of CF_3NO. After ca. 6 h, the solvent was removed in vacuo. The $HON(CH_2)CF_3^+AsF_6^-$ formed was colorless and stable below 0 °C for a longer time. NMR: ^{19}F −68.4 ppm (s); ^{13}C 62.3 (quart.), 134.4 ppm (quart.); ^{1}H 4.3 (s), 10.9 ppm (s).

Preparation of $ON(CF_3)F^+AsF_6^-$. A 221-mg (1-mmol) sample of $N_2F^+AsF_6^-$ and 100 mg (1 mmol) of CF_3NO were condensed together and dissolved in 1 mL of CCl_3F. After 3 days at −35 °C, the solution was discolored. The solvent was removed in vacuo at −78 °C. The residual colorless $ON(CF_3)F^+AsF_6^-$ was stable below −10 °C. NMR: ^{19}F −63.2 (s), 289.4 ppm (s); ^{13}C 136.7 ppm (quart.).

Preparation of $ONClF^+AsF_6^-$. A 165-mg (0.75-mmol) sample of $N_2F^+AsF_6^-$ and 195 mg (3 mmol) of ClNO were dissolved in 0.5 mL of CCl_3F. After 12 h at −78 °C, no further N_2 was evolved. Excess ClNO and CCl_3F were removed in vacuo, leaving colorless $ONClF^+AsF_6^-$ as the residue. The product was extremely sensitive to moisture and for several days stable below −78 °C. In CCl_3F solution at −78 °C, decay to $NO^+AsF_6^-$ and ClF occurred, with ClF reacting with the glass vessel and formation of SiF_4.

Preparation of $ONF_2^+SbF_6^-$. A KEL-F reactor with a stainless steel valve was charged with 650 mg (10 mmol) of ClNO and 2 mL of anhydrous $(HF)_x$ and kept at −40 °C, while HCl was pumped off. After freezing at −196 °C, the reactor was opened under inert gas flow and $XeF^+SbF_6^-$ (0.5 mmol) was added. At −50 °C, $ONF_2^+SbF_6^-$ was formed within 12 h. The NMR (^{19}F at 330 ppm) and vibrational spectroscopic data were consistent with literature values.[1,2]

Reaction of CF_3NO and Cl_2/AsF_5. CF_3NO (2.0 mmol), Cl_2 (2.5 mmol), and AsF_5 (7.5 mmol) were dissolved in 3 mL of SO_2 at −78 °C. It was not possible to isolate a solid after 24 h. In the volatile products only CF_3NO could be identified (^{19}F NMR −90.4 ppm). When the temperature was raised to −30 °C, $AsCl_4^+AsF_6^-$ was formed (vibrational spectra).

Thermolysis of $ONClF^+AsF_6^-$. A 150-mg amount of $ONClF^+AsF_6^-$ in a KEL-F vessel was connected to the gas inlet of a cryostat. When the temperature was raised from −78 °C to −30 °C, the salt volatilized. Matrix IR spectroscopy identified AsF_5, ONF (1895 (vs), 646 (m), 433 cm^{-1} (s, br)), and ClF (762 cm^{-1} (w)). Mass spectra (EI = 70 eV) identified the fragments of AsF_5 (AsF_4^+, 12%; AsF_3^+, 63%; AsF_2^+, 100%; AsF^+, 18%; As^+, 17%) and ONF (NO^+, 78%; NF^+, 6%). ClF was not detected.

Preparation of Single Crystals of $HON(CH_2)CF_3^+AsF_6^-$. A 500-mg sample of $ON(CH_2)CF_3^+AsF_6^-$ was dissolved in 3 mL of SO_2 in a V-shaped tube. The solution was concentrated at −40 °C within 4 days to saturation by pumping off solvent repeatedly. After the mixture was cooled to −50 °C, crystallization started. The supernatant liquid was decanted and the remaining solvent pumped off. The crystals were transferred to Mark tubes at −110 °C and X-rays measured at the same temperature.

Results and Discussion

Formation. We have shown repeatedly that monofluoro cations of non-metals are easily obtainable by oxidative fluorination with $XeF^+MF_6^-$ (M = As, Sb) in anhydrous $(HF)_x$.[14-16] This method also converts ONF into $ONF_2^+MF_6^-$

$$\begin{gathered} ONF + XeF^+MF_6^- \rightarrow ONF_2^+MF_6^- + Xe \\ M = As, Sb \end{gathered} \tag{7}$$

giving an alternate synthesis for this nitryl salt.

We already mentioned the existence of $ONCl_2^+MF_6^-$.[4] So the intermediate $ONClF^+MF_6^-$ should also be accessible. The previously mentioned synthesis, however, does not work, since ONCl reacts with HF, giving ONF and HCl.

The monofluorodiazinium cation N_2F^+ should be a similar fluorinating reagent, but its potential for synthesis has not yet been used systematically.[17,18]

The reaction

$$ONCl + N_2F^+AsF_6^- \rightarrow ONClF^+AsF_6^- + N_2 \tag{8}$$

is conducted in a heterogeneous system at −78 °C. At this temperature, $N_2F^+AsF_6^-$ does not attack the solvent CCl_3F. Only at room temperature after several days are the higher fluorinated chlorofluorocarbons CF_2Cl_2 and $CClF_3$ formed in NMR-traceable yields.

In a similar way CF_3NO can react, giving $ON(CF_3)F^+AsF_6^-$

$$ONCF_3 + N_2F^+AsF_6^- \rightarrow ON(CF_3)F^+AsF_6^- + N_2 \tag{9}$$

Although Cl_2 and AsF_5 react with NCl_3 in liquid SO_2 according to eq 10, oxidation of CF_3NO to give $ON(CF_3)Cl^+AsF_6^-$ in a

$$2NCl_3 + Cl_2 + 3AsF_5 \rightarrow 2NCl_4^+AsF_6^- + AsF_3 \tag{10}$$

similar manner is not possible, with $AsCl_4^+AsF_6^-$ being formed.[20] However, methylation of CF_3NO by CH_3F and AsF_5 or SbF_5 at low temperatures is possible (eq 11). This reaction depends on

$$\begin{gathered} CF_3NO + CH_3F + MF_5 \rightarrow ON(CH_3)CF_3^+MF_6^- \\ M = As, Sb \end{gathered} \tag{11}$$

SO_2 as a solvent and the methylating agent is $CH_3OSO^+MF_6^-$, according to Gillespie.[21] Whereas the isoelectronic carbonyl compound $CF_3C(O)CH_3$ only exists in the keto form,[22] ON-

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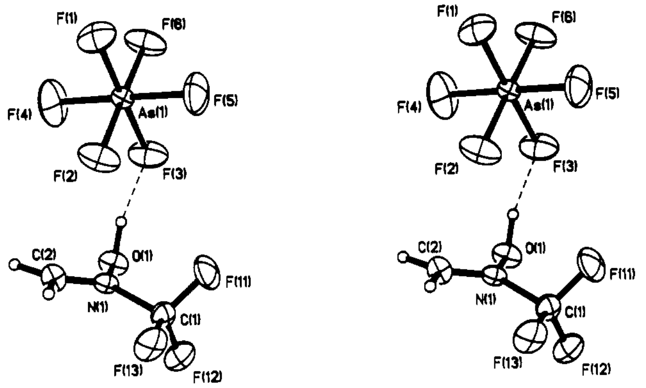

Figure 1. Stereoscopic representation of a formula unit of $HON(CH_2)CF_3^+AsF_6^-$ (all atoms indicated).

Table II. Fractional Coordinates of Atoms and Isotropic or Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^4$) of $HON(CH_2)CF_3^+AsF_6^-$ [a]

	x	y	z	U_{eq}/U
As(1)	0.21343 (6)	0.26503 (4)	0.32473 (3)	197
F(1)	0.4303 (6)	0.3540 (4)	0.4056 (3)	473
F(2)	0.4595 (5)	0.0631 (4)	0.3197 (3)	476
F(3)	−0.0086 (6)	0.1773 (4)	0.2406 (3)	510
F(4)	0.0957 (7)	0.1903 (5)	0.4639 (3)	674
F(5)	0.3320 (7)	0.3379 (5)	0.1842 (3)	596
F(6)	−0.0337 (5)	0.4650 (3)	0.3270 (3)	499
C(1)	0.3133 (8)	−0.2501 (5)	0.0931 (4)	301
F(11)	0.2950 (6)	−0.0919 (3)	0.0401 (2)	487
F(12)	0.1614 (6)	−0.3291 (4)	0.0309 (2)	449
F(13)	0.5674 (5)	−0.3487 (4)	0.0965 (3)	432
N(1)	0.2133 (6)	−0.2286 (4)	0.2265 (3)	222
O(1)	−0.0642 (5)	−0.1502 (4)	0.2320 (3)	308
H(1)	−0.023 (11)	−0.034 (8)	0.246 (5)	572
C(2)	0.3569 (8)	−0.2828 (5)	0.3278 (4)	298
H(21)	0.262 (10)	−0.289 (6)	0.418 (5)	474
H(22)	0.557 (9)	−0.337 (5)	0.319 (4)	256

[a] $U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$.

Table III. Bond Distances (Å) and Bond Angles (deg) in $HON(CH_2)CF_3^+AsF_6^-$ [a]

As(1)–F(1)	1.702 (2)	N(1)–O(1)	1.372 (4)
As(1)–F(2)	1.717 (2)	N(1)–C(2)	1.273 (5)
As(1)–F(3)	1.734 (3)	O(1)–H(1)	1.00 (6)
As(1)–F(4)	1.695 (3)	C(2)–H(21)	1.05 (5)
As(1)–F(5)	1.703 (3)	C(2)–H(22)	0.99 (4)
As(1)–F(6)	1.707 (2)	F(3)···H(1)	1.66 (6)
C(1)–F(11)	1.297 (5)	F(4)···H(21a)	2.16 (5)
C(1)–F(12)	1.305 (6)	F(6)···H(22b)	2.22 (4)
C(1)–F(13)	1.304 (4)	F(1)–H(21c)	2.37 (5)
C(1)–N(1)	1.477 (5)		

F(5)–As(1)–F(6)	89.1 (2)	F(11)–C(1)–N(1)	108.2 (3)
F(4)–As(1)–F(6)	91.3 (2)	F(11)–C(1)–F(13)	111.1 (3)
F(4)–As(1)–F(5)	179.4 (2)	F(11)–C(1)–F(12)	110.2 (3)
F(3)–As(1)–F(6)	89.6 (1)	C(1)–N(1)–C(2)	126.0 (3)
F(3)–As(1)–F(5)	90.4 (2)	C(1)–N(1)–O(1)	112.3 (3)
F(3)–As(1)–F(4)	89.2 (2)	O(1)–N(1)–C(2)	121.6 (3)
F(2)–As(1)–F(6)	178.9 (1)	N(1)–O(1)–H(1)	88 (3)
F(2)–As(1)–F(5)	90.4 (2)	N(1)–C(2)–H(22)	119 (2)
F(2)–As(1)–F(4)	89.2 (2)	N(1)–C(2)–H(21)	121 (3)
F(2)–As(1)–F(3)	89.4 (1)	H(21)–C(2)–H(22)	120 (4)
F(1)–As(1)–F(6)	89.8 (1)	As(1)–F(3)···H(1)	127 (2)
F(1)–As(1)–F(5)	88.9 (2)	F(3)···H(1)–O(1)	166 (5)
F(1)–As(1)–F(4)	91.5 (2)	As(1)–F(4)···H(21a)	134 (1)
F(1)–As(1)–F(3)	179.1 (1)	F(4)···H(21a)–C(2a)	147 (4)
F(1)–As(1)–F(2)	91.1 (1)	As(1)–F(6)···H(22b)	160 (1)
F(13)–C(1)–N(1)	108.3 (3)	F(6)···H(22b)–C(2b)	161 (3)
F(12)–C(1)–N(1)	109.0 (3)	As(1)–F(1)···H(21c)	141 (1)
F(12)–C(1)–F(13)	110.0 (3)	F(1)···H(21c)–C(2c)	114 (4)

F(13)–C(1)–N(1)–O(1)	−170.6 (3)
F(12)–C(1)–N(1)–O(1)	−51.0 (4)
F(11)–C(1)–N(1)–O(1)	68.9 (4)
F(13)–C(1)–N(1)–C(2)	5.8 (5)
F(12)–C(1)–N(1)–C(2)	125.5 (4)
F(11)–C(1)–N(1)–C(2)	−114.6 (4)
C(1)–N(1)–C(2)–H(21)	−166 (3)
C(1)–N(1)–C(2)–H(22)	5 (3)
C(1)–N(1)–O(1)–H(1)	−100 (3)
O(1)–N(1)–C(2)–H(21)	10 (3)
O(1)–N(1)–C(2)–H(22)	−179 (3)
C(2)–N(1)–O(1)–H(1)	84 (3)

[a] Symmetry codes: (a) $-x, -y, 1 - z$; (b) $x - 1, 1 + y, z$; (c) $1 - x, -y, 1 - z$.

$(CH_3)CF_3^+$ is enolized in the solid state and the keto form is formed only in solution of SO_2. Evidently H···F bridging in the solid state between anion and cation is the driving force for this enolization.

Thermolysis. Neither IR nor mass spectroscopy shows trihaloamine oxides during thermolysis of $ONClF^+AsF_6^-$.

We observe decay to ONF, ClF, and AsF_5. This illustrates the extreme bonding situation in ONF_3.[10] Substitution of one fluorine by chlorine already causes destabilization. $ONClF^+AsF_6^-$ is stable only for a short time at −78 °C. Its thermolysis gives ClF, as the similar thermolysis of $ONCl_2^+SbCl_6^-$ gives ONCl and Cl_2 and not $ONCl_3$.[3]

Crystal Structure of $HON(CH_2)CF_3^+AsF_6^-$. The anion and cation of $HON(CH_2)CF_3^+AsF_6^-$ with the numbering scheme are shown in Figure 1. Positional parameters and the equivalent isotropic or isotropic displacement parameters are given in Table II. Bond lengths, bond angles, and short interionic distances are given in Table III.

The structural C(1)–N(1)–O(1)–C(2) fragment of the cation is planar. The CF_3 group, with a mean C–F distance of 130.2 (5) pm and F–C–F bond angles between 110.0 (3) and 111.0 (3)°, shows no irregularities and is similar to the CF_3 group of the cation $CF_3SCl_2^+$ (128.8 (4) pm, 111.8 (4)°[23]). The C(1)–N(1) bond length (147.7 (5) pm) indicates a C–N single bond as in $(CH_3)_2NF{\cdot}BCl_3$ (148.0 (2) pm[24]) and in $(CH_3)_2NCl$ (147.0 (2) pm[25]). The C(2)–N(1) distance (127.3 (5) pm) indicates a C=N bond as in $(CF_3)_2NCFNHCF_3^+AsF_6^-$ (128.0 (1) pm[26]) and in ClNCO (121.8 pm[27]). The N(1)–O(1) bond (137.2 (4) pm) is longer than the double bond between oxygen and nitrogen that was found in CH_3NO (122.0 pm[28]). In comparison with the N–O distance of 145.3 pm in hydroxylamine,[29] it has more the character of an N–O single bond although it shows a shortening of 8.1 pm. The structural analysis shows the existence of tautomerism in the cation such as keto–enol tautomerism in organic carbonyl compounds, with a double-bonded CH_2 group and an O–H group bonded to the nitrogen atom. The hydrogen atom H(1) could be located at a distance of 100 (6) pm from the oxygen atom O(1). This distance does not deviate significantly from the distance of 95.7 pm in H_2O found by microwave studies.[30] The hydrogen atom H(1) and the fluorine atom F(3) of the AsF_6^- octahedron have a short interionic contact of 166 (6) pm. This distance is even shorter than the calculated bond distances of the H_2F^+ cation (173.3–193.5 pm[31]) and is markedly shorter than the H···F distance found in $H_3O^+AsF_6^-$ (183.0 pm[32]). The cation and anion are connected by a bridge bond via the hydrogen atom H(1). This bridge could be responsible for the slightly lengthened As–F(3) bond distance of 173.4 (5) pm. The N(1)–O(1)–H(1) angle is

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Table IV. Vibrational Frequencies of the Series $ONF_nCl_{2-n}^+MF_6^-$ (n = 0, 1, 2; M = As, Sb), Compared to Isoelectronic Carbon Compounds

OCF_2[2]	$ONF_2^+SbF_6^-$[2]		$OCClF$[36]	$ONClF^+SbF_6^-$		$ONClF^+AsF_6^-$	$OCCl_2$[35]	$ONCl_2^+SbF_6^-$	
IR	Raman	IR	Raman	Raman	IR	Raman	IR	Raman	assgnt[a]
1982 ms	1859 (8)	1862 ms	1876	*b*	1698 s	1695 (5)	1827 vs	1684 (5)	$\nu(X{=}O)$
1249 vs	1163 (12)	1163 s							$\nu_{as}(X{-}F)$
965 s	895 (12)	897 ms	1095	802 (15)	810 s	801 (10)			$\nu_s(X{-}F)$
							849 vs	736 (10)	$\nu_{as}(X{-}Cl)$
			667	571 (73)	570 m	570 (78)	569 w	636 (50)	$\nu_s(X{-}Cl)$
774 ms	711 (25)	715 m	776	695 (39)	693 m	696 (41)	580 m	420 (30)	γ
626 m	645 (28)	647 m	501	420 (22)	423 m	420 (27)			$\delta(O{-}X{-}F)$
			415	231 (16)	230 m	233 (18)	440 w	220 (10)	$\delta(O{-}X{-}Cl)$
584 m	565 (13)	569 mw					285 w	137 (20)	$\delta(X{-}Hal_2)$
	645 (100)			648 (100)		685 (100)		668 (100)	$\nu_1(MF_6^-)$
	587 (25)			586 (21)		573 (30)		558 (20)	$\nu_2(MF_6^-)$
		673 vs			669 vs				$\nu_3(MF_6^-)$
					349 s				$\nu_4(MF_6^-)$
	286 (43)			285 (42)		374 (65)		294 (40)	$\nu_5(MF_6^-)$

[a] X = C, N; Hal = F, Cl; M = As, Sb. [b] Not observed.

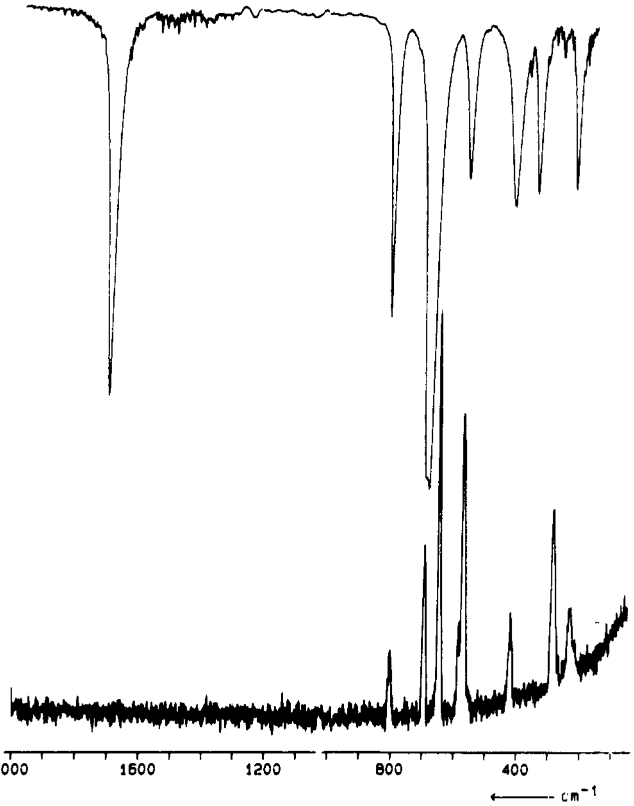

Figure 2. IR and Raman spectra of $ONClF^+SbF_6^-$ at −78 °C.

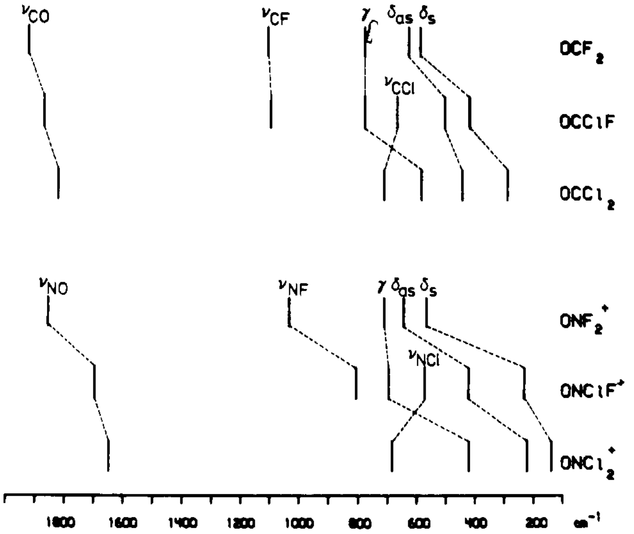

Figure 3. Correlation diagram for the series of the cations ONF_2^+, $ONClF^+$, and $ONCl_2^+$ compared with isoelectronic carbon compounds.

found to be 88.3 (33)°, and the O(1)–H(1)–F(3) angle has a value of 165.9 (50)°.

The AsF_6^- anion is nearly an ideal octahedron with bond angles of 89.0 (2)–91.5 (2) and 178.9 (2)–179.4 (2)°, which are close to the ideal values of 90 and 180°. The As–F distances are in the range 169.5 (3)–173.4 (3) pm.

NMR Spectra. Starting with NOF ($\delta(^{19}F)$ = 479.0 ppm[33]), the ^{19}F NMR spectra of ONF_2^+ (330.0 ppm), $ONFCl^+$ (327.2 ppm), and CF_3FNO^+ (289.4 ppm) show increasing high-field shifts. Coupling with other N ligands is not observed. In contrast, the signal of the CF_3 group shows a low-field shift from −63.2 to −68.4 ppm for $CF_3CH_3NO^+$ and CF_3FNO^+, respectively, depending on the increasing −*I* effect of the other N-bonded ligands. Similar observations are made on methyl(trifluoromethyl)halosulfonium salts $CH_3CF_3SX^+$ (X = F, Cl, Br, I).[34]

The ^{13}C NMR spectrum of $CF_3CH_3NO^+$ shows two quartets at 134.4 ppm ($^1J(^{13}C{-}^{19}F)$ = 327.4 Hz) and 62.3 ppm ($^1J(^1H{-}^{13}C)$ = 149.7 Hz) and a ^1H singlet at 4.3 ppm. This is in contrast to X-ray structural analysis and indicates the presence of the keto tautomer. The enol tautomer should show a triplet of the CH_2 group in the ^{13}C and an additional signal for the proton of the hydroxyl group in the ^1H NMR spectrum. Evidently, in solution the keto tautomer prevails, and on crystallization the enol is formed.

Vibrational Spectra. Table IV lists and compares the frequencies observed for dihalonitryl cations and their isoelectronic phosgene derivatives.

The spectrum of $ONClF^+SbF_6^-$ is shown in Figure 2. The cation should show six IR- and Raman-active modes. They are all found in the IR spectrum, whereas in the Raman spectrum only ν(NO) has too low an intensity to be observed. The Raman spectrum of $ONClF^+AsF_6^-$ shows this vibration with low intensity at 1695 cm⁻¹.

Thus, the new cation $ONClF^+$ fits well in the spectroscopic series of nitryl cations, shown in Figure 3. With decreasing number of F atoms, $\nu(N{=}O)$ decreases from 1859 to 1698 and 1684 cm⁻¹, respectively. The mean N–F frequency also is lowered from 1029 cm⁻¹ for ONF_2^+ to 802 cm⁻¹ for $ONClF^+$. The N–Cl frequency increases from 570 cm⁻¹ for $ONClF^+$ to 686 cm⁻¹ for $ONCl_2^+$. This behavior is similar to that of $OCCl_2$ and OCClF, as shown in Figure 3.[35,36]

The vibrational spectrum of solid $HON(CH_2)CF_3^+AsF_6^-$ is shown in Figure 4, and the data are given in Table V. The H–O

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Table V. Vibrational Frequencies of $ON(CF_3)F^+MF_6^-$ and $HON(CH_2)CF_3^+MF_6^-$, Compared to CF_3CH_3CO and CF_3FCO

CF_3FCO[43]	$ON(CF_3)F^+AsF_6^-$		$HON(CH_2)CF_3^+AsF_6^-$		CH_3CF_3CO[39]	
IR	IR	Raman	IR	Raman	IR	assgnt[a]
			3653 vs	*b*		$\nu(\mathrm{O{-}H})$
			3163 s	3164 (9)	3028 w	$\nu_{as}(CH_3/CH_2)$
			3024 m	3026 (41)	2945 vs	$\nu_s(CH_3/CH_2)$
1899 s					1769 m	$\nu(\mathrm{C{=}O})$
	1673 s	*b*	1663 vs	1665 (24)		$\nu(\mathrm{N{=}O})$
			1453 m	1453 (12)	1428 w	$\delta_{as}(CH_3/CH_2)$
			1352 m	1356 (21)	1371 vw	$\delta_s(CH_3/CH_2)$
			1248 s	1241 (14)	1319 w	$\nu_{as}(COC/CNO)$
1340 m	1204 vs	1202 (6)	1196 s	*b*	1216 vw	$\nu_{as}(CF_3)$
1254 vs	1178 vs	*b*	1121 s	1120 (6)	1157 vw	$\nu_s(CF_3)$
			1103 s	1107 (5)	1112 vw	$\nu_s(CF_3)$
				1089 (21)		$\nu(NO)$
			1038 m	1039 (7)		$\delta(NOH)$
					969 w	$\delta(CH_3)$
	972 m	972 (52)	813 w	807 (63)	766 s	$\nu_s(COC/CNO)$
	845 s	843 (13)				$\nu(NF)$
692 s	756 m	755 (35)	639 m	643 (21)	617 w	$\delta_s(CF_3)$
595 w	565 s	563 (11)	561 m	558 (19)	564 w	$\delta_{as}(CF_3)$
			522 w	525 (5)	498 vw	$\delta_{as}(CF_3)$
	354 m	362 (30)	396 m	401 (11)	423 w	$\delta(COC/CNO)$
	329 m	320 (12)	351 s	347 (16)	370 w	oop
228 m	314 m	312 (14)	241 m	245 (10)	236 vw	$\rho(CF_3)$
		121 (7)			121 vw	$\tau(CH_3)$
		688 (100)		684 (100)		$\nu_1(MF_6^-)$
		581 (26)		574 (22)		$\nu_2(MF_6^-)$
	692 vs		691 vs			$\nu_3(MF_6^-)$
	369 s		392 s			$\nu_4(MF_6^-)$
		373 (43)		379 (46)		$\nu_5(MF_6^-)$

[a] M = As, Sb. [b] Not observed.

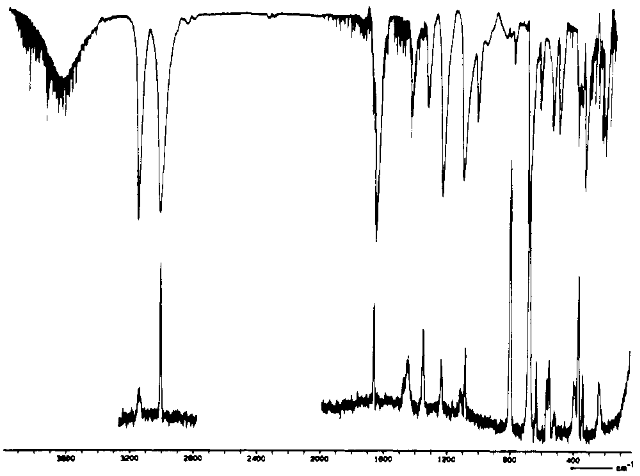

Figure 4. IR and Raman spectra of $HON(CH_2)CF_3^+AsF_6^-$ at −78 °C.

mode is shown with high intensity at 3653 cm^{-1} in the IR spectrum only, and the H–O–N deformation is found at 1038 cm^{-1}. ν(N═O) occurs with high intensity at 1663 cm^{-1}, as compared to that for $F_3CN{=}CF_2$ (1623 cm^{-1} [37]), showing the influence of the positive charge on the nitrogen atom.[38] The reduction in coordination number 4 in $CF_3C(O)CH_3$ to 3 in $HON(CH_2)CF_3^+AsF_6$ is consistent with the increase of ν(C–H) from 3000.3 to 3093.5 cm^{-1},[39] respectively. $HON(CH_2)CF_3^+$ shows an unusual short N–O distance of 137.2 (4) pm, and this corresponds with a high ν(N–O) of 1089 cm^{-1} (H_2NOH: ν(N–O) 895 cm^{-1} [40]).

Conclusion

The preparation of $ONF_2^+MF_6^-$ from ONF and $XeF^+MF_6^-$ is the first example where an atom with less than two lone electron pairs has been fluorinated by XeF^+. In contrast to sulfanes and oxygen compounds,[14-16] nitrogen compounds such as nitriles formed stable adducts with XeF^+.[41] The strongly basic methylhaloamines also could not be fluorinated by $XeF^+MF_6^-$.

In anhydrous HF the nitrogen atom is protonated and the lone electron pair protected against attack by XeF^+.[42] We could show an alternative route to prepare ONF_2^+ salts and ONF_3. The new nitryl cations show properties that are in accordance with those of already known species and isoelectronic carbon compounds.

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Supplementary Material Available: For $HON(CH_2)CF_3^+AsF_6^-$, Tables SI and SII, listing crystallographic data, experimental details, and thermal parameters, and Figure S1, representing the stereoscopic view of the unit cell (3 pages); a table of calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page. Further information concerning the crystal structure investigations can be obtained through the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, by giving No. CSD-54463, the names of the authors, and the reference.

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