or -carbon atoms whereas the second line corresponds to the methylene-hydrogen or -carbon atoms. It is interesting that the methylene proton resonance shifts to higher field as the molecular association increases from dimer to trimer. These data would suggest that the methylene protons have more negative charge due to the inductive effects in a nominally trianionic species compared to a dianionic species. However, further comparisons with $Ga(CH_2SiMe_3)_3$ in order to determine the effects of oxidation state on NMR chemical shift would not be valid because the coordination number around gallium has changed significantly. In the potassium dimer gallium has an apparent coordination number of 5 whereas in the sodium trimer it is 6, and in $Ga(CH_2SiMe_3)_3$ it is only 3. Similarly, direct comparisons of infrared frequencies assigned to the gallium–carbon stretching modes for the various ((trimethylsilyl)methyl)gallium compounds are also unwarranted.

The behavior of $[NaGa(CH_2SiMe_3)_2]_3$ and $[KGa(CH_2SiMe_3)_2]_2$ as Lewis acids toward the Lewis bases diethyl ether, dimethoxyethane, tetrahydrofuran, acetonitrile, and trimethylamine was investigated in order to determine the relative strength and primary site of reaction, the alkali-metal ion or the gallium(I) atom. Our data suggest that $[NaGa(CH_2SiMe_3)_2]_3$ is the stronger acid and the base reacts primarily with the alkali metal ion. These conclusions are based on the range of bases which form stable 1:1 adducts at room temperature with a given acid and the relative ^1H NMR chemical shift data. The potassium derivative formed a stable adduct with only dimethoxyethane whereas the sodium compound formed adducts with dimethoxyethane, tetrahydrofuran, and trimethylamine. Similarly, the dimethoxyethane protons exhibit larger changes in NMR chemical shifts upon coordination to the sodium compound than those of the potassium compound. However, it is interesting to note that for the bases studied the protons in tetrahydrofuran exhibit the largest change in chemical shift upon coordination, but the magnitude is still small (0.25 ppm downfield) in comparison with the effects of the stronger Lewis acid[13] $[Ga(CH_2SiMe_3)_2Br]_2$ (0.47 ppm). It is also noteworthy that the chemical shift of the methyl (N) protons for free $N(CH_3)_3$ and $NaGa(CH_2SiMe_3)_2{\cdot}N(CH_3)_3$ are identical. All of these data suggest that the base coordinates with the alkali metal ion. If the base had coordinated to the gallium(I), the change in alkali-metal ion should have had a minor effect on the Lewis acidity of the low oxidation state compound. Furthermore, ethers are stronger bases than amines toward the alkali-metal ions whereas amines are usually stronger bases to gallium.[2] The anionic character of the $Ga(CH_2SiMe_3)_2^-$ moiety is probably responsible for the weak Lewis acidic behavior. An X-ray structural study[23] of $[NaBe(C_2H_5)_2H{\cdot}O(C_2H_5)_2]_2$ has shown the ether to be bound exclusively to the sodium ions rather than the beryllium atoms. Reactions of the gallium(I) anions as Lewis bases will be the subject of future publications.

The dimethoxyethane adduct $NaGa(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$ was further characterized by cryoscopic molecular weight measurements in benzene solution. The apparent molecular weight depends upon the concentration of the solution. At higher concentrations, a molecular weight corresponding to the timer was observed. At the lowest concentration, the degree of association was 1.69. These data would suggest either that an equilibrium between monomer, dimer, and trimer exists in solution or, alternatively, the $[NaGa(CH_2SiMe_3)_2]_3$ trimer remains intact but has various numbers of bound dimethoxyethane molecules. The lithium derivative $LiGa(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$ was also prepared, but it was not sufficiently soluble in benzene for molecular weight measurements. Therefore, a structural hypothesis is not warranted at this time.

The successful synthesis of a low oxidation state organometallic anion of gallium opens a new area of chemistry. Periodic trends can be used to predict that analogous compounds might exist for indium and possibly aluminum. Similarly, the available electron pair on the main-group metal atom in the low oxidation state also implies the potential for nucleophilic reaction chemistry. Such aspects of the chemistry of these metal-based anions are being actively pursued.

Acknowledgment. This work was supported in part by the Office of Naval Research. The Varian XL-100 NMR spectrometer was obtained with the aid of a grant from the National Science Foundation. The authors also wish to acknowledge the support of a Samuel B. Silbert Memorial Fellowship to R.G.S.

Registry No. $[NaGa(CH_2SiMe_3)_2]_3$, 74096-67-6; $[KGa(CH_2SiMe_3)_2]_2$, 74112-96-2; $[NaGa(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe]_3$, 74081-90-6; $LiGa(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe$, 74081-92-8; $[NaGa(CH_2SiMe_3)_2{\cdot}O(CH_2)_4]_3$, 74081-93-9; $[NaGa(CH_2SiMe_3)_2{\cdot}N(CH_3)_3]_3$, 74096-69-8; $[KGa(CH_2SiMe_3)_2{\cdot}MeOC_2H_4OMe]_2$, 74081-95-1; $Ga(CH_2SiMe_3)_3$, 72708-53-3; NaH, 7646-69-7; LiH, 7580-67-8; KH, 7693-26-7.

---

[23] Adamson, G. W.; Shearer, H. M. M. *Chem. Commun.* **1965**, 240.

Contribution from Rocketdyne, A Division of Rockwell International Corporation,
Canoga Park, California 91304

Synthesis and Properties of $NF_4^+SO_3F^-$

KARL O. CHRISTE,* RICHARD D. WILSON, and CARL J. SCHACK

Received February 5, 1980

The novel salt $NF_4^+SO_3F^-$ was prepared by metathesis between NF_4SbF_6 and $CsSO_3F$ in anhydrous HF solution at −78 °C. In HF solution, it is stable at room temperature. Removal of the solvent produces a white solid which is stable at 0 °C but slowly decomposes at +10 °C to produce $FOSO_2F$ and NF_3 in high yield. The ionic nature of the compound, both in the solid state and in HF solution, was established by Raman and ^{19}F NMR spectroscopy. Cesium sulfate was found to react with anhydrous HF, producing $CsSO_3F$ as the major product. Similarly, $CsPO_2F_2$, the Raman spectrum of which is reported, was found to react with HF to give $CsPF_6$ in quantitative yield.

Introduction

Among oxidizers, the NF_4^+ cation is unique. In spite of being one of the most powerful oxidizers known, it possesses high kinetic stability,[1] thereby permitting its combination with a surprisingly large number of anions to form stable or metastable salts. Anions capable of NF_4^+ salt formation include

---

[1] Christe, K. O.; Wilson, R. D.; Goldberg, I. B. *Inorg. Chem.* **1979**, *18*, 2572.

BF_4^-,[2-9] XF_5^- (X = Ge, Ti, Sn),[9-11] XF_6^- (X = P, As, Sb, Bi),[6,7,9,12-19] XF_6^{2-} (X = Ge, Sn, Ti, Ni, Mn),[9-11,20,21] ClO_4^-,[22] HF_2^-,[22] and several perfluoro polyanions.[6,10,11,19] Recent studies have shown that NF_4^+ salts of oxygen-containing anions are of particular interest because hypofluorites such as OIF_4OF[23] or $FOClO_3$[22] can be formed during their thermal decomposition.

In this paper we report results on the possible synthesis of salts derived from sulfur or phosphorus oxyfluorides. We are aware of only one unpublished study[3] in this area, in which the evolution of some $FOSO_2F$ from either an NF_4SbF_6–$HOSO_2F$ solution at −78 °C or a supposedly dry mixture of NF_4SbF_6 and $LiSO_3F$ at room temperature was interpreted[3] as evidence that NF_4SO_3F, if it exists, is unstable even at −78 °C. In view of the relative stability of NF_4ClO_4[22] and the similarity between ClO_4^- and isoelectronic SO_3F^- and $PO_2F_2^-$, the isolation of NF_4SO_3F and $NF_4PO_2F_2$ seemed possible.

Experimental Section

Materials and Apparatus. The equipment, handling techniques, and spectrometers used in this study have previously been described.[22] Literature methods were used for the synthesis of NF_4SbF_6,[6] $ClOSO_2F$,[24] and $HOPOF_2$.[25] The $CsPO_2F_2$ was prepared by the addition of Cs_2CO_3 to a 10% excess of $HOPOF_2$ frozen at −196 °C. The mixture was allowed to react at room temperature with agitation, and the volatile products and excess $HOPOF_2$ were pumped off at 40 °C for 12 h. On the basis of observed material balance and vibrational spectra, the solid residue consisted of $CsPO_2F_2$ of high purity. The Cs_2SO_4 was obtained from aqueous Cs_2CO_3 and H_2SO_4 by using a pH electrode for end point (pH 3.86) detection. The solution was taken to dryness and dried in an oven at 100 °C for 24 h. The $CsSO_3F$ was prepared by allowing CsCl (10.3 mmol) and $ClOSO_2F$ (15.5 mmol) to react in a 10-mL stainless-steel cylinder at ambient temperature for several days. All volatile material was removed from the cylinder, and the solid product was pumped on overnight. The weight of the solid (2.43 g vs. 2.40 g theoretical) together with its infrared and Raman spectra confirmed the completeness of the reaction and the identity of the product.

Preparation and Properties of $NF_4^+SO_3F^-$. The compatibility of the SO_3F^- anion with HF was established by dissolving $CsSO_3F$ in dry HF and recording the Raman spectra of the starting material, of the HF solution, and of the solid residue recovered after removal of the solvent. All spectra showed the bands characteristic[26] for SO_3F^-. The ^{19}F NMR spectrum of the HF solution was also recorded and consisted of a singlet at ϕ −33.8 (downfield from external $CFCl_3$) for SO_3F^- and a relatively narrow HF solvent peak at ϕ 191.

In a typical preparation of NF_4SO_3F, NF_4SbF_6 (3.145 mmol), and $CsSO_3F$ (3.146 mmol) were combined in a previously described[22] Teflon metathesis apparatus. Dry HF[22] (3 mL of liquid) was added, and the resulting mixture was stirred at ambient temperature for 3 h with a magnetic stirring bar, followed by cooling to −78 °C and

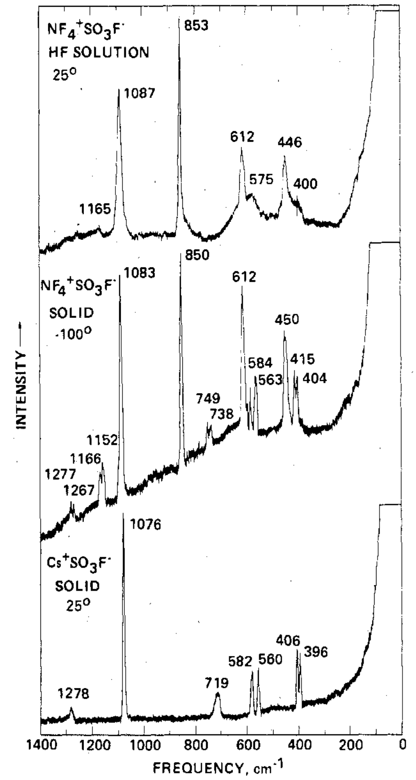

Figure 1. Raman spectra of $NF_4^+SO_3F^-$: upper trace, HF solution at 25 °C; middle trace, neat solid at −100 °C. (Weak bands due to the sample tubes and small amounts of $CsSbF_6$ were substracted from the spectra.); bottom trace, solid $CsSO_3F$ at 25 °C. The spectra were recorded with spectral slit widths of 8, 6, and 4 cm^{-1}, respectively.

Table I. Raman Spectra of NF_4SO_3F and $CsSO_3F$

obsd freq, cm^{-1} (rel intens[a])			assign	
NF_4SO_3F				
HF soln	solid	$CsSO_3F$ solid	NF_4^+ (T_d)	SO_3F^- (C_{3v})
	1277 (0.7)	1278 (0.7)		ν_4(E)
	1267 (0.4)			
1165 (0.4)	1166 (1.3)		ν_3(F_2)	
	1152 (1.8)			
1087 (6.7) p	1083 (10)	1076 (10)		ν_1(A_1)
853 (10) p	850 (9.5)		ν_1(A_1)	
	749 (1.1)	719 (1.2)		ν_2(A_1)
	738 (0.8)			
612 (3)	612 (6)		ν_4(F_2)	
575 (1.2)	584 (1.7)	582 (2)		ν_5(E)
	563 (2.5)	560 (2.2)		ν_3(A_1)
446 (2.8)	450 (4)		ν_2(E)	
400 (1)	415 (2.5)	406 (3.8)		ν_6(E)
	404 (2.3)	396 (3.5)		

[a] Uncorrected Raman intensities.

---

(2) Goetschel, C. T.; Campanile, V. A.; Curtis, R. M.; Loos, K. R.; Wagner, C. D.; Wilson, J. N. *Inorg. Chem.* **1972**, *11*, 1696.
(3) Tolberg, W. E.; Rewick, R. T.; Zeilenga, G. R.; Dolder, M. P.; Hill, M. E., private communication.
(4) Sinel'nikov, S. M.; Rosolovskii, V. Ya. *Dokl. Akad. Nauk SSSR* **1970**, *194*, 1341.
(5) Rosolovskii, V. Ya.; Nefedov, V. I.; Sinel'nikov, S. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1973**, *7*, 1445.
(6) Christe, K. O.; Schack, C. J.; Wilson, R. D. *J. Fluorine Chem.* **1976**, *8*, 541.
(7) Christe, K. O.; Wilson, R. D.; Axworthy, A. E. *Inorg. Chem.* **1973**, *12*, 2478.
(8) Mishra, S. P.; Symons, M. C. R.; Christe, K. O.; Wilson, R. D.; Wagner, R. I. *Inorg. Chem.* **1975**, *14*, 1103.
(9) Christe, K. O.; Schack, C. J.; Wilson, R. D. *Inorg. Chem.* **1976**, *15*, 1275.
(10) Christe, K. O.; Schack, C. J. *Inorg. Chem.* **1977**, *16*, 353.
(11) Christe, K. O.; Schack, C. J.; Wilson, R. D. *Inorg. Chem.* **1977**, *16*, 849.
(12) Christe, K. O.; Guertin, J. P.; Pavlath, A. E. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 83.
(13) Tolberg, W. E.; Rewick, R. T.; Stringham, R. S.; Hill, M. E. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 79.
(14) Guertin, J. P.; Christe, K. O.; Pavlath, A. E. *Inorg. Chem.* **1966**, *5*, 1921.
(15) Tolberg, W. E.; Rewick, R. T.; Stringham, R. S.; Hill, M. E. *Inorg. Chem.* **1967**, *6*, 1156.
(16) Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Chem.* **1977**, *16*, 937.
(17) Christe, K. O.; Guertin, J. P.; Pavlath, A. E.; Sawodny, W. *Inorg. Chem.* **1967**, *6*, 533.
(18) Christe, K. O.; Pilipovich, D. *Inorg. Chem.* **1971**, *10*, 2803.
(19) Christe, K. O.; Wilson, W. W.; Schack, C. J. *J. Fluorine Chem.* **1978**, *11*, 71.
(20) Christe, K. O. *Inorg. Chem.*, **1977**, *16*, 2238.
(21) Christe, K. O.; Wilson, W. W., unpublished results.
(22) Christe, K. O.; Wilson, W. W.; Wilson, R. D. *Inorg. Chem.* **1980**, *19*, 1494.
(23) Christe, K. O.; Wilson, R. D. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 375.
(24) Schack, C. J.; Wilson, R. D. *Inorg. Chem.* **1970**, *9*, 311.
(25) Bernstein, P. A.; Hohorst, F. A.; Eisenberg, M.; DesMarteau, D. D. *Inorg. Chem.* **1971**, *10*, 1549.
(26) Ruoff, A.; Milne, J. B.; Kaufmann, G.; Leroy, M. *Z. Anorg. Allg. Chem.* **1970**, *372*, 119.
(27) Franz, G.; Neumayr F. *Inorg. Chem.* **1964**, *3*, 921.

Table II. Vibrational Spectra of Solid $CsPO_2F_2$ and Their Assignments Compared to Those of SO_2F_2

obsd freq, cm^{-1} (rel intens)					
$CsPO_2F_2$[a]		SO_2F_2[b]			
Raman	IR	Raman	IR	assign (C_{2v})	approx descriptn of mode
1143 (10)	1142 vs	1270 vs	1270 vs	A_1 ν_1	sym PO_2 str
813 (3.7)	825 vs	848 vs	848 vs	ν_2	sym PF_2 str
512 (6)	520 sh	552 m	553 s	ν_3	δ scissoring PO_2
370 sh	370 mw	384 m	384 vw	ν_4	δ scissoring PF_2
353 (5.7)	351 mw				
		[384 ± 15][c]		A_2 ν_5	τ
1318 (0+)	1325 vs	1504 w	1503 vs	B_1 ν_6	asym PO_2 str
501 (2)	494 s	539 m	540 s	ν_7	δ rock PF_2
851 (0.7)	850 sh	888 w	886 vs	B_2 ν_8	asym PF_2 str[d]
830 (1.2)	825 vs				
501 (2)	508 s	544 m	544 s	ν_9	δ rock PO_2

[a] Data from this study; uncorrected Raman intensities; since ν_7 and ν_9 have very similar frequencies and intensities, their assignments are tentative. [b] Data from ref 36–38. [c] From microwave data.[37] [d] In Fermi resonance with $\nu_4 + \nu_9(B_2) = 854\ cm^{-1}$.

filtration at this temperature. The HF solvent was pumped off from the filtrate at −30 °C for 3 h, leaving behind a white solid residue. The thermal stability of this residue was established by incremental warm-up of the solid in a dynamic vacuum and by trapping, measuring (*PVT*), and identifying (infrared spectroscopy) the volatile decomposition products. Up to 0 °C, only HF and small amounts of NF_3 were collected, indicating the possible presence of small amounts of unstable $NF_4HF_2 \cdot HF$[22] in the product. At temperatures of 9 °C or higher, significant decomposition of the solid was observed, producing equimolar amounts of NF_3 and $FOSO_2F$. When we allow for about 20% of the product solution to be retained, as generally seems to be the case with similar metathetical reactions,[22] by the filter cake and to be lost during solvent pump-off, the yield of NF_3 and $FOSO_2F$ was essentially quantitative. The filter cake (1.0 g, weight calculated for 3.15 mmol of $CsSbF_6$ = 1.16 g) was shown by vibrational spectroscopy to be $CsSbF_6$[28] and did not show any detectable impurities.

Caution! $FOSO_2F$ has been reported[29,30] to have explosive properties. The compound should therefore be handled with appropriate safety precautions.

For the spectroscopic identification of NF_4SO_3F, reactions were carried out on a 1-mmol scale in a previously described[22] manner. The ^{19}F NMR spectrum of a solution of $NF_4^+SO_3F^-$ in HF at −30 °C showed the signals characteristic for NF_4^+ (triplet of equal intensity at ϕ −215 with J_{NF} = 226 Hz and a line width of less than 3 Hz),[9] SO_3F^- (singlet at ϕ −33.5), and HF (broad singlet at ϕ 193). No evidence for the presence of $FOSO_2F$[27] was observed. The Raman spectra of the HF solution at 25 °C and of solid NF_4SO_3F at −100 °C were also recorded and are shown in Figure 1. The spectra showed the presence of only small amounts of $CsSbF_6$,[28] indicating a purity of NF_4SO_3F in excess of 90 wt %, in agreement with the observed material balance. Raman and ^{19}F NMR spectra of HF solutions of NF_4SO_3F, which were kept at 25 °C for several days, showed no evidence of $FOSO_2F$ formation.

Reaction of Cs_2SO_4 with HF. The Cs_2SO_4 salt was found to be highly soluble in HF. Raman spectra of these solutions and of the solid residue obtained after the solvent removal showed the complete absence of the SO_4^{2-} anion[28] and the presence of the SO_3F^- anion.[26] The presence of the SO_3F^- anion in the HF solution was confirmed by ^{19}F NMR spectroscopy which showed a strong singlet at ϕ −33.8, characteristic for SO_3F^-.

Reaction of $CsPO_2F_2$ with HF. A sample of $CsPO_2F_2$ (2.1 mmol) was treated with anhydrous HF (3 mL of liquid) for 12 h at 25 °C. The white solid residue, left behind after removal of the solvent, was identified by its infrared and Raman spectrum as $CsPF_6$[28] (2.1 mmol) and did not contain detectable amounts of $PO_2F_2^-$.[31-33]

Results and Discussion

The novel salt $NF_4^+SO_3F^-$ was prepared from NF_4SbF_6 and $CsSO_3F$ by low-temperature metathesis in anhydrous HF solution according to eq 1. The NF_4SO_3F salt can be isolated

$$NF_4SbF_6 + CsSO_3F \xrightarrow[-78\ °C]{HF} CsSbF_6\downarrow + NF_4SO_3F \qquad (1)$$

as a white solid which is stable at 0 °C but slowly decomposes at +10° to produce NF_3 and $FOSO_2F$ in high yield according to eq 2. Its HF solution appears to be stable at ambient

$$NF_4SO_3F \rightarrow NF_3 + FOSO_2F \qquad (2)$$

temperature. The thermal stability of NF_4SO_3F is very similar to that[22] of NF_4ClO_4. This is not surprising since SO_3F^- and ClO_4^- are isoelectronic and chemically very similar. This chemical similarity is also demonstrated by their decomposition modes, which in both cases produce the corresponding hypofluorites in high yield.

The decomposition of $NF_4^+SO_3F^-$ represents a new, high-yield, convenient synthesis of $FOSO_2F$. The previously reported methods for the preparation of $FOSO_2F$ involved either the fluorination of SO_3[34,35] or $S_2O_6F_2$.[36] NF_4SO_3F is the third known example of an NF_4^+ salt of an oxyanion producing on thermal decomposition the corresponding hypofluorite. The other two known examples are NF_4ClO_4[22] and $NF_4IF_4O_2$.[23] This indicates that the thermal decomposition of unstable NF_4^+ salts of oxyanions may be a general method for the synthesis of hypofluorites.

The ionic nature of NF_4SO_3F, both in the solid state and in HF solution, was verified by Raman and ^{19}F NMR spectroscopy. The Raman spectra are shown in Figure 1 and demonstrate the presence of the bands characteristic for NF_4^+[9,22] and SO_3F^-.[26] The observed frequencies and their assignments are summarized in Table I. The SO_3F^- bands in NF_4SO_3F are very similar to those observed for $CsSO_3F$ (see Figure 1). The minor frequency shift observed for the SF stretching mode is not surprising in view of a previous infrared study of the alkali metal salts which showed that the frequency of this fundamental strongly depends on the nature of the cation and varied from 812 cm^{-1} in $LiSO_3F$ to 715 cm^{-1} in $CsSO_3F$.[26] The observed splitting of some of the modes of both the NF_4^+ cation and the SO_3F^- anion into their degenerate components is easily explained by solid-state effects and has also been observed for $NF_4^+ClO_4^-$.[22]

The ^{19}F NMR spectrum of $NF_4^+SO_3F^-$ in HF solution showed a triplet of equal intensity at ϕ −215 with J_{NF} = 226 Hz and a line width of less than 3 Hz, characteristic[9] for NF_4^+, a singlet at ϕ −33.5, characteristic for SO_3F^-, and the char-

---

(28) Siebert, H. "Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie"; Springer-Verlag: Berlin, 1966; Vol. VII.
(29) Lustig, M.; Shreeve, J. M. *Adv. Fluorine Chem.* **1973**, *7*, 175.
(30) Cady, G. H., *Intra-Sci. Chem. Rep.* **1971**, *5*, 1.
(31) Thompson, R. C.; Reed, W. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 581.
(32) Buehler, K.; Bues, W. *Z. Anorg. Allg. Chem.* **1961**, *308*, 62.
(33) Addou, A.; Vast, P. *J. Fluorine Chem.* **1979**, *14*, 163.
(34) Dudley, F. B.; Cady, G. H.; Eggers, D. F. *J. Am. Chem. Soc.* **1956**, *78*, 290. Dudley, J. E.; Cady, G. H. *ibid.* **1959**, *81*, 4166.
(35) Reference 78, cited by: Lustig, M.; Shreeve, J. M. *Adv. Fluorine Chem.* **1973**, *7*, 175.
(36) Roberts, J. E.; Cady, G. H. *J. Am. Chem. Soc.* **1959**, *81*, 4166.

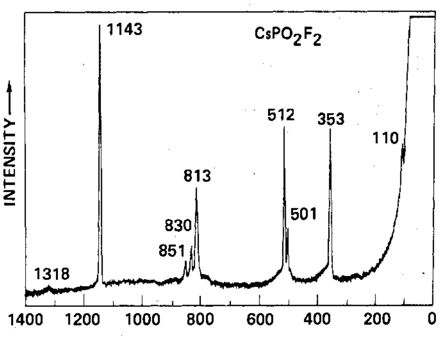

Figure 2. Raman spectrum of solid $CsPO_2F_2$ recorded at 25 °C with a spectral slit width of 5 cm^{-1}.

acteristic HF signal at ϕ 193. The assignment of the ϕ −33 signal to SO_3F^- was verified by recording the spectrum of $CsSO_3F$ in HF under the same conditions.

In view of the above-mentioned usefulness of NF_4^+ salts of oxyanions for the preparation of novel hypofluorites, it appeared interesting to attempt the syntheses of $(NF_4)_2SO_4$ and $NF_4PO_2F_2$. The thermal decomposition of these two hypothetical salts would offer an opportunity to prepare the yet unknown hypofluorites $SO_2(OF)_2$ and $POF_2(OF)$. However, both the SO_4^{2-} and $PO_2F_2^-$ anions were found to interact with anhydrous HF according to eq 3 and 4. Attempts to prepare

$$SO_4^{2-} + 3HF \rightarrow SO_3F^- + H_2O + HF_2^- \qquad (3)$$

$$PO_2F_2^- + 4HF \rightarrow PF_6^- + 2H_2O \qquad (4)$$

$POF_2(OF)$ by fluorination of $HOPOF_2$ with atomic fluorine, generated by the controlled decomposition of $NF_4HF_2{\cdot}nHF$,[22] were also unsuccessful. The main products were NF_4PF_6[9] and an unidentified nonvolatile phosphorus oxyfluoride.

Although vibrational spectra have been reported[31-33] for the $PO_2F_2^-$ anion, the previous assignment of several fundamentals is open to question. Figure 2 and Table II summarize the vibrational spectra of $CsPO_2F_2$, obtained in our study. The given assignment was made by analogy with that of isoelectronic SO_2F_2 which is well established.[37-39] Whereas, the splitting of $\nu_8(B_2)$ can easily be explained by Fermi resonance with $(\nu_4 + \nu_9)(B_2)$, the reason for the observed splitting of ν_4 is less obvious. The possibility of one of the components assigned to ν_4 actually being due to the $\nu_5(A_2)$ torsional mode cannot be ruled out but is unlikely due to the facts that this mode should be infrared inactive under C_{2v} selection rules and usually is of such low intensity in the Raman spectra that it is very difficult to observe.

In summary, the present study shows that within the isoelectronic series ClO_4^-, SO_3F^-, $PO_2F_2^-$, SO_4^{2-}, the first two anions are capable of forming NF_4^+ salts of moderate stability which can decompose to NF_3 and the corresponding hypofluorites. The syntheses of $NF_4PO_2F_2$ and $(NF_4)_2SO_4$ by metathesis in HF were prevented by the reaction of $PO_2F_2^-$ and SO_4^- with the solvent to yield PF_6^- and SO_3F^-, respectively.

Acknowledgment. The authors thank Drs. L. R. Grant and W. W. Wilson for helpful discussions and the Office of Naval Research, Power Branch, and the Army Research Office for financial support of this work.

Registry No. $NF_4^+SO_3F^-$, 74096-76-7; $CsSO_3F$, 13530-70-6; $CsPO_2F_2$, 17117-59-8; NF_4SbF_6, 16871-76-4; NF_3, 7783-54-2; $FOSO_2F$, 13536-85-1; Cs_2SO_4, 10294-54-9; $CsPF_6$, 16893-41-7.

---

(37) Lide, D. R.; Mann, D. E.; Comeford, J. J. *Spectrochim. Acta* **1965**, *21*, 497 and references cited therein.

(38) Sportouch, S.; Clark, R. J. H.; Gaufres, R. *J. Raman Spectrosc.* **1974**, *2*, 153.

(39) Nolin, C.; Tremblay, J.; Savoie, R. *J. Raman Spectrosc.* **1974**, *2*, 71.

Contribution from the Department of Chemistry,
College of William and Mary, Williamsburg, Virginia 23185

Peroxo- and Hydroxolanthanide(III) Complexes of the EDTA Family

CIRILA DJORDJEVIC* and NIKOLA VULETIC

Received August 7, 1979

Three series of crystalline heteroligand lanthanide complexes with EDTA are reported. The new compounds have been characterized by infrared and proton NMR spectra, conductivity in aqueous solution, and powder X-ray photographs. Two of the series contain peroxides. The complexes of the type $KLnEDTA{\cdot}xH_2O_2{\cdot}yH_2O$ ($x = 0.5$, $y = 4$ for Ln = Y; $x = 0.5$, $y = 6$ for Ln = Eu, Gd; $x = 2$, $y = 5$ for Ln = La, Nd) are obtained from neutral or weakly acid solutions. Some of them are considered to be peroxo hydrates because of the easy release of peroxo oxygen. The complexes of the second type, obtained from alkaline solutions, $K_3Ln(O_2)EDTA{\cdot}yH_2O$ ($y = 3$ for Ln = Y; $y = 6$ for Ln = La, Nd) and $K_3Ln(O_2)$-$EDTA{\cdot}xH_2O_2{\cdot}yH_2O$ ($x = 1$, $y = 5$ for Ln = Eu, Gd), contain one peroxo group which is retained on prolonged heating in vacuo, implying the presence of a coordinated peroxo ligand. The infrared spectra support this evidence by showing an additional band between 840 and 825 cm^{-1}, expected for the stretching of a coordinated peroxo group. These monoperoxo–EDTA complexes represent the first crystalline stoichiometric peroxo compounds of rare earths. Molar conductivity of these salts in water indicates the presence of 1/1 and 3/1 electrolytes, respectively, and powder photographs reveal isomorphous pairs dependent upon the degree of hydration. The third series of complexes $K_2Ln(OH)EDTA{\cdot}4H_2O$ is obtained from alkaline solutions. Molar conductivity of these salts implies the presence of 2/1 electrolytes. The proton NMR spectra show a more complex resonance pattern than the spectra of peroxo–EDTA complexes. According to powder X-ray patterns the Ln = Y, La, Eu, and Gd complexes are isomorphous.

Introduction

The peroxo derivatives of lanthanides reported to exist in the solid state so far are poorly characterized oxohydroxolanthanum(III) hydrates, containing Ln/peroxide ratios of 1/1 and 1/2. They are stable at lower temperature only, cannot be dehydrated without loss of oxygen, and decompose at room temperature.[1,2] Some spectrophotometric solution studies do

---

(1) Y. A. Connor and E. A. V. Ebsworth, *Adv. Inorg. Chem. Radiochem.*, 6, 279 (1964).