3066 *Inorg. Chem.* **1999,** *38,* 3066−3069

Trifluorosulfite Anion, SOF_3^-

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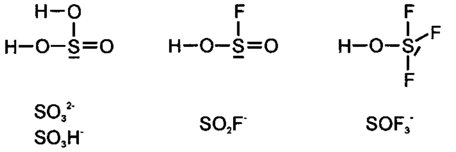
Received July 28, 1998

$Me_4N^+SOF_3^-$, the first example of a SOF_3^- salt, has been prepared from Me_4NF and SOF_2. The colorless, microcrystalline solid was characterized by its Raman and infrared spectra, and in acetonitrile solution by ^{19}F NMR. The structure of the SOF_3^- anion is predicted by ab initio calculations to possess a pseudo trigonal bipyramidal structure with two remarkably long sulfur−fluorine bonds in the axial position. One fluorine, the oxygen atom, and a sterically active lone pair of electrons occupy the equatorial plane.

Introduction

Sulfurous acid is present in small amounts in aqueous solutions of SO_2, and a wide range of its salts are well-known and belong partly to basic chemicals in industrial processes.[1] Far less is known about its fluoroderivates.



Fluorosulfurous acid has been assumed to be present in HF/SO_2 mixtures,[2] but later Sommer et al. showed by NMR spectroscopy that such mixtures do not contain considerable amounts of HSO_2F molecules.[3] Salts of fluorosulfurous acid have been known since Seel's investigations of the lead chamber process in 1953.[4,5] They are readily formed by the reaction of sulfur dioxide with alkali metal and ammonium fluorides as well as with fluorides with appropriate bulky organic countercations.[5−9]

To our knowledge, no evidence for the existence of trifluorosulfurous acid has been reported in the literature. The free trifluorosulfite anion has been observed in ion cyclotron resonance experiments and identified as a transient short-lived species formed in a discharge of moist SF_6.[10−12] Garber and Ault reported in 1983 the isolation of a $Cs^+SOF_3^-$ ion pair by co-deposition of CsF vapor and SOF_2 in an argon matrix.[13] Their evidence for the formation of such an ion pair is weak since only four infrared bands were observed, and their frequencies do not correspond well to those found in this study. There is no further mention in the literature of an isolated SOF_3^- salt formed through fluoride ion addition to SOF_2. In prior studies trifluorosulfites were assumed to play a role as intermediates in reactions of SOF_2 involving alkali metal fluorides as catalysts.[14] More recently, Winfield et al. ruled out this assumption on the basis of radiotracer experiments with $SOF^{18}F$ on CsF and KF supported on fluorinated γ-alumina, since they did not find an $^{18}F/^{19}F$ exchange in CsF and KF treated with $SOF^{18}F$.[15]

During this decade the syntheses of several missing fluoroanions such as FCO_2^-, IOF_6^-, and PF_4^- have been achieved using "naked fluoride" (Me_4NF) as the fluoride ion source.[16−18] Tetramethylammonium fluoride possesses higher reactivity than CsF and enables reactions with molecules of low fluoride affinity. Trends in the tendency to form yet unknown anionic species by fluoride addition can be predicted on the basis of F^- affinities available from ion cyclotron measurements. Considering a simple thermochemical cycle, the uncertainty of such general predictions lies in the change of the lattice energy between the fluorinating and the resulting salt which can be estimated only roughly.[5,10] Thus, especially if the F^- affinity exceeds small values the uncertainty of the latter term becomes dominant and the predictions are vague.

The fluoride affinity of SOF_2 in the gas phase (37.4 kcal/mol)[10] is comparatively small, and a reaction with CsF does

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10.1021/ic9809005 CCC: $18.00 © 1999 American Chemical Society
Published on Web 05/29/1999

not take place. Therefore it was interesting to us whether SOF_3^- salts could be prepared using "naked fluoride".

Experimental Section

Apparatus and Materials. All synthetic work and sample handling were performed by standard Schlenk techniques on a standard vacuum line. The Me_4NF was obtained by the literature method.[19] The preparation of SOF_2 from $SOCl_2$ and NaF is described elsewhere.[20] ***(Caution:** SOF_2 is poisonous due to formation of HF on hydrolysis!)*

The Raman spectra were recorded with a T64000 (ISA) spectrometer using an argon ion laser (Spectra Physics) at 514.5 nm. The infrared spectrometer and the sample preparation have been described previously.[21] The ^{19}F NMR spectra were recorded on a Bruker DPX-300 spectrometer. The spectra were referenced to external samples of neat $CFCl_3$. The IUPAC chemical shift convention was used.

Preparation of Me_4NSOF_3. Dry Me_4NF (190 mg; 2.04 mmol) was placed into a dried quartz ampule, and 2.15 g (25 mmol) of SOF_2 was condensed in at −196 °C. The sealed ampule was warmed to room temperature. The reaction proceeds in a few hours in an ultrasonic bath. The excess of SOF_2 was pumped off at dry ice temperature. The weight (360 mg, calcd: 369 mg) of the colorless solid indicated almost quantitative yield of Me_4NSOF_3. Further characterization of the obtained compound was carried out by vibrational and ^{19}F NMR spectroscopies. The trifluorosulfite salt is extremely sensitive to moisture. The salt decomposes at ca. 135 °C under formation of trimethylamine, methyl fluoride, thionyl fluoride and traces of other unidentified products.

Computational Methods. The ab initio calculations for SO_2F^- and SOF_2 were performed at the restricted Hartree−Fock level of theory using the Gaussian 94 program.[22] All calculations were carried out at the 6-31+G* basis level, which augments the standard double-ζ plus polarization treatment (6−31-G*) with a diffuse set of s,p functions (+) on each heavy atom, and is known to describe anionic systems in an appropriate way. Harmonic vibrational frequencies were computed for the minimum energy structures and scaled by the empirical factor 0.90 to maximize their fit with the experimentally observed frequencies.[23,24]

Results and Discussion

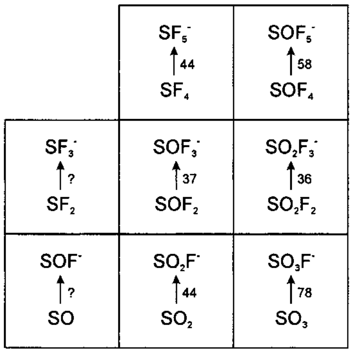
Synthesis and Properties of Me_4NSOF_3. The salt is formed slowly by reacting an excess of SOF_2 with "naked fluoride" (Me_4NF) according to eq 1. The reaction proceeds faster using

$$Me_4NF + SOF_2 \rightarrow Me_4NSOF_3 \qquad (1)$$

acetonitrile as a solvent or employing an ultrasonic bath.

The trifluorosulfite salt is a colorless microcrystalline solid which rapidly hydrolyzes on contact with moisture according to eq 2. An excess of water leads to further hydrolysis of the Me_4NSO_2F according to eq 3.[5]

Scheme 1. Fluoride Affinities (kcal/mol) of Sulfur Fluorides, Oxides, and Oxofluorides; Data from Ref 10



$$3Me_4N^+SOF_3^- + H_2O \rightarrow 2Me_4N^+HF_2^- + Me_4N^+SO_2F^- + 2\ SOF_2 \qquad (2)$$

$$4Me_4N^+SO_2F^- + H_2O \rightarrow 2Me_4N^+HF_2^- + (Me_4N)_2S_2O_5 + 2\ SO_2 \qquad (3)$$

The trifluorosulfite salt is insoluble in nonpolar solvents and slightly soluble in polar solvents such as CH_3CN. In acetonitrile solutions a slow decomposition of the SOF_3^- anion was observed. Sulfur dioxide cannot be used as a solvent because it reacts with Me_4NSOF_3 according to eq 4.

$$Me_4N^+SOF_3^- + SO_2 \rightarrow Me_4N^+SO_2F^- + SOF_2 \qquad (4)$$

Attempts to obtain single crystals for X-ray diffraction were not successful due to the absence of a suitable solvent. Also, the ultrasonic method for crystal growing, used for Me_4NHPF_5, failed in this case.[25]

As mentioned in the Introduction, SOF_2 has a comparatively low fluoride affinity, and a reaction with CsF does not take place. Scheme 1 shows a summary of the simplest sulfur oxides, oxofluorides, and fluorides, and their fluoride affinities in the gas phase as far as known in the literature (sulfur hexafluoride has not been considered for further discussion). Sulfur monoxide and sulfur difluoride are both unstable molecules, and to our knowledge, no successful synthesis of the corresponding fluoride anions is reported in the literature. Among the sulfur(IV) and sulfur(VI) compounds in Scheme 1, SOF_2 and SO_2F_2 have the lowest fluoride affinities and do not react with alkali metal fluorides, whereas the other molecules form corresponding anions. Therefore the successful synthesis of the SOF_3^- anion (as well as the $SO_2F_3^-$ anion which will be reported in another paper)[26] can be ascribed to the high reactivity of "naked fluoride".

^{19}F NMR Spectra. The ^{19}F NMR spectrum of a freshly prepared sample of Me_4NSOF_3 in acetonitrile at room temperature shows a broad singlet at $\delta = 67.7$ ppm and in addition a small singlet at 102.3 ppm and a doublet at −147.6 ppm ($J =$ 122 Hz). The latter two resonances are attributable to SO_2F^- [$\delta = 103.3$ ppm for $(Me_2N)_3S^+SO_2F^-$][6] and HF_2^- ($\delta = -145$ to -148 ppm, $J_{HF} = 121$ Hz for $Me_4N^+HF_2^-$ in acetonitrile).[27] Both anions have arisen from the hydrolysis of the SOF_3^- anion during synthesis or sample preparation. The lack of the expected fine structure for a rigid pseudo-pentacoordinated anion comprising a doublet and a triplet for the axial and equatorial fluorine

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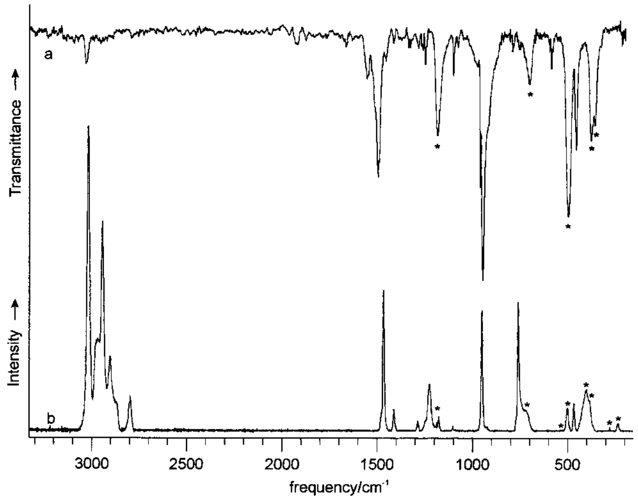

Figure 1. Infrared (a) and Raman Spectra (b) of Me_4NSOF_3. Vibrations of the SOF_3^- anion are marked with an asterisk (*).

Table 1. Vibrational Frequencies (cm^{-1}) of Tetramethylammonium Trifluorosulfite

		assignment	
IR	Raman	SOF_3^-	Me_4N^+
3039 (w)	3040 (100)		$\nu(CH_3)$
	2991 (30)		
	2964 (70)		
	2925 (24)		
	2817 (9)		
1939 (vw)			$2\delta(CH_3)$
1492 (s)			$\delta_{as}(CH_3)$
	1470 (46)		
1428 (w)	1417 (7)		$\delta_s(CH_3)$
1268 (w)			$\delta_{rock}(CH_3)$
	1288 (3)		
	1229 (15)		
1189 (s)	1180 (5)	$\nu(SO)$	
1105 (m)	1104 (1)	$[\nu_1(SO_2F^-)]^a$	
949 (vs)	949 (39)		$\nu_{as}(C_4N)$
758 (w)	756 (40)		$\nu_s(C_4N)$
725 (w)	725 (6)	$\nu(SF_{eq})$	
652 (w)			
593 (w)		$[\nu_2(SO_2F^-)]^a$	
504 (vs)	526 (0.2)	$\nu_{as}(SF_{ax})$	
	496 (5)	$\nu_s(SF_{ax})$	
462 (s)	463 (6)		$\delta_{as}(C_4N)$
403 (s)	400 (13)	$\delta_{sciss}(OSF_{eq})$	
	394 (12)		$\delta_s(C_4N)$
383 (s)	380 (11)	$\delta_{rock}(OSF_{eq})$	
	273 (0.1)	$\delta_{wag}(OSF_{eq})$	
	229 (1)	$\delta_s(SF_{ax})$	

[a] Hydrolysis product SO_2F^-.

atoms, respectively, indicates that the SOF_3^- anion undergoes a fast inter- or intramolecular ligand exchange. To suppress a possible intermolecular exchange, a sample with an excess (ca. 80%) of Me_4NF was measured, but no significant changes occur for the singlet at $\delta = 67.7$ ppm. Also spectra measured above the melting point of acetonitrile (−40 °C) did not show the expected fine structure.

Vibrational Spectra. The Raman and infrared spectra of Me_4NSOF_3 are shown in Figure 1, and the observed frequencies are summarized in Table 1. The assignments for SOF_3^- were made by comparison with the isoelectronic compounds shown in Figure 2.[18,28−31] An ab initio investigation, which is discussed later, gives the expected structure of symmetry C_s, in accordance to the isoelectronic $ClOF_3$ molecule. Consequently, nine fundamentals ($6A' + 3A''$) that should all be active in both the infrared and the Raman spectra are expected for SOF_3^-. The assignments for the Me_4N^+ cation were made according to well-known literature data.[17−19]

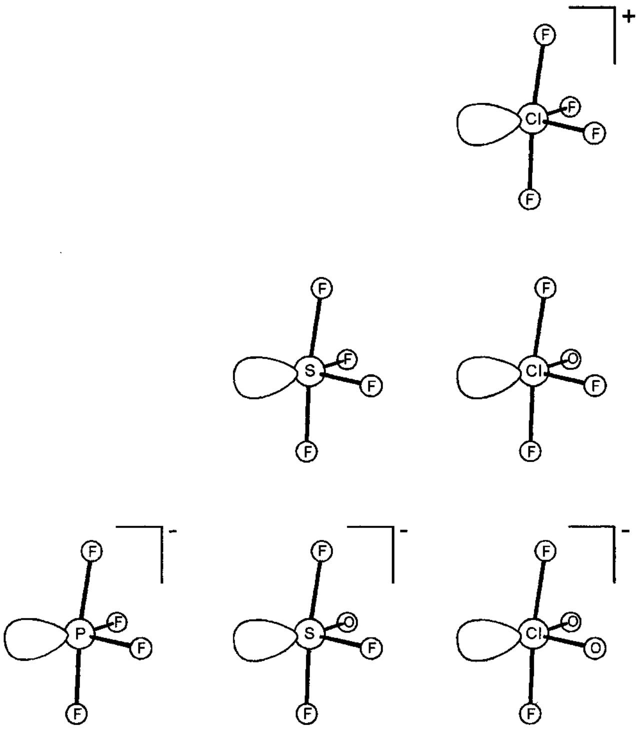

Figure 2. Trifluorosulfite and its isoelectronic ions and molecules.

The oxygen−sulfur stretching mode of the SOF_3^- anion is observed at 1185 cm^{-1} in a region typical for S−O bonds. The three sulfur−fluorine stretching modes occur in the region above 500 cm^{-1}. In accordance with a trigonal bipyramidal arrangement of the ligands and the electron lone pair, the $\nu(S{-}F_{eq})$ is observed at 725 cm^{-1}, whereas the $S{-}F_{ax}$ stretching modes appear at lower frequencies (515 and 496 cm^{-1}).

The five deformation modes occur below 500 cm^{-1}. The mode descriptions, listed in Table 2, were made by consideration of the calculated displacement coordinates. Overall, the SOF_3^- deformation modes show the expected trend appearing at somewhat lower frequencies than those of the isoelectronic $ClOF_3$ molecule.

The frequencies for a $Cs^+SOF_3^-$ ion pair found by Garber and Ault in matrixes of CsF co-deposited with SOF_2 do not correspond well to those found in this study. Similar discrepancies were noted by Christe et al. between $Me_4N^+PF_4^-$ and a reported $Cs^+PF_4^-$ ion pair isolated in an argon matrix.[18,32] The differences between the frequencies for both ion pairs isolated in matrixes and the calculated gas-phase frequencies cannot be explained in terms of regular matrix effects only. It seems more likely that the structures of the anions in the ion pairs are strongly affected by the adjacent cation. Also covalent bonding between cations and anions might exist in the alledged ion pairs, as is known for alkali metal halides trapped in matrixes.[33] To get a deeper insight into the nature of these ion pairs, more thorough matrix experiments together with theoretical calculations are required.

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Table 2. Comparison of Observed and Calculated Frequencies (cm^{-1}) of SOF_3^- with Isoelectronic Molecules and Ions

C_S						C_{2V}					
SOF_3^-			$ClOF_3$	assignment		$ClO_2F_2^-$	PF_4^-	SF_4	ClF_4^+	assignment	
obsd[a]	calcd[b]	matrix[c]	expt[d]			expt[a,f]	expt[g]	expt[h]	expt[i]		
1185	1187	1264	1223	ν_1 (A′)	ν(XO)[e]	1212	795	892	800	ν_1 (A_1)	ν_s(XY)[j]
725	753	695	694	ν_2 (A′)	$\nu(XF_{eq})$	1066	746	867	829	ν_8 (B_2)	ν_{as}(XY)
515	527	667	652	ν_7 (A″)	$\nu_{as}(XF_{ax})$	510	523	729	795	ν_6 (B_1)	$\nu_{as}(XF_{ax})$
496	499		482	ν_3 (A′)	$\nu_s(XF_{ax})$	480	446	558	571	ν_2 (A_1)	$\nu_s(XF_{ax})$
402	395		490	ν_4 (A′)	$\delta_{sciss}(OXF_{eq})$	559	464	533	510	ν_3 (A_1)	$\delta_{sciss}(YXF_{eq})$
382	388	623	500	ν_8 (A″)	$\delta_{rock}(OXF_{eq})$	363	416	474	475	ν_5 (A_2)	$\delta_{rock}(YXF_{eq})$
−	347		414	ν_9 (A″)	$\delta_s(XF_{ax})$	337	(392)	350	385	ν_7 (B_1)	$\delta_s(XF_{ax})$
273	286		319	ν_5 (A′)	$\delta_{wag}(OXF_{eq})$	337	293	356	537	ν_9 (B_2)	δ_{wag}(YXY)
229	222		227	ν_6 (A′)	$\delta_s(XF_{ax})$	198	201	226	237	ν_4 (A_1)	$\delta_s(XF_{ax})$

[a] Average values from infrared and Raman spectra. [b] RHF/6-31+G*; frequencies scaled by an empirical factor of 0.9. [c] From ref 13. [d] From ref 28. [e] X = central arom. [f] From ref 29. [g] From ref 18. [h] From ref 30. [i] From ref 31. [j] Y = O, F_{eq}.

Table 3. Geometry of SOF_3^- (Calcd) Compared to Those of Isoelectronic Ions and Molecules

	SOF_3^- calcd[b]	$ClOF_3$ expt[c]	PF_4^- expt[d]	PF_4^- calcd[d]	SF_4 expt[e]	ClF_4^+ expt[f]
$r(X-F_{ax})$[a] (pm)	179.1	171.3	171.6	174.1	164.6	161.7
$r(X-F_{eq})$ (pm)	160.0	160.3	152.2/138.6	160.4	154.5	153.0
$r(X-O)$ (pm)	143.3	140.5				
$\angle(F_{ax}\text{-}X-F_{ax})$ (deg)	166.5	170.5	178.0	168.3	173.1	173.9
$\angle(O-X\text{-}F_{eq})$ (deg)	106.7	108.9				
$\angle(F_{eq}\text{-}X-F_{eq})$ (deg)			108.0	99.9	101.6	103.1
$\angle(F_{ax}\text{-}X-F_{eq})$ (deg)	85.1	87.9	89.0/90.3	86.2		
$\angle(F_{ax}\text{-}X-O)$ (deg)	95.8	94.7				

[a] X = S, Cl, P. [b] RHF/6-31+G*. [c] From ref 34. [d] From ref 18. [e] From ref 35. [f] From ref 38.

Ab Initio Calculation. The ab initio RHF/6-31+G* calculated harmonic frequencies for the SOF_3^- anion are given in Table 2 and compared with the observed frequencies. We find reasonable agreement for all vibrational modes. The calculated geometry for SOF_3^- and the experimental data for the isoelectronic $ClOF_3$, PF_4^-, and SF_4 are presented in Table 3.[18,34,35]

The pseudotrigonal bipyramidal SOF_3^- anion of symmetry C_s has bond angles similar to those of the isoelectronic $ClOF_3$.[34] The sterically active electron lone pair causes a bending of the $F_{ax}-S-F_{ax}$ bonds (166.5°) and a compression of the $F_{eq}-S-O$ angle (106.7°). The S−O bond length of 143.3 pm is in the range of regular sulfur−oxygen bonds in similar anions, such as SO_2F^- (calcd: 145.8 pm)[5] and SO_3F^- (expt: 142.4(4); 145.5(6) pm).[36]

The calculated S−F bond lengths of 179.1 and 160.0 pm reveal the different kinds of bonds in the ion, which can be rationalized in terms of semi-ionic three-center four-electron bonding for the axial fluorine ligands and a mainly covalent $S-F_{eq}$ bond, respectively. In molecules, such as SF_4, differences between $S-F_{eq}$ and $S-F_{ax}$ of up to 12 pm have been observed. Only in the case of SF_5^- salts differences of up to 17 pm occur and the S−F bond length exceeds 178.9 pm.[37] Obviously, the formal negative charges in these anions enhance the formation of semi-ionic, three-center four-electron bonds, thereby causing their unusual lengths.

Conclusion

The first example of a SOF_3^- salt has been prepared from Me_4NF and SOF_2. The successful synthesis of the SOF_3^- anion can be ascribed to the high reactivity of "naked fluoride", since prior studies had shown that alkali metal fluorides do not react with SOF_2. The vibrational spectra agree well with ab initio calculations, which predict a pseudotrigonal bipyramidal structure of symmetry C_s.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft.

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