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Solid state and gas phase structure of *cis*-sulfanuric fluoride $(NS(O)F)_3$

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Abstract

The molecular structure of *cis*-sulfanuric fluoride was determined in the solid state by low temperature X-ray crystallography and in the gas-phase by electron diffraction. The results of both structure investigations are in close agreement. The six-membered sulfur–nitrogen ring is slightly puckered with NSNS dihedral angles of 34.5(10)° (crystal) and 24.5(48)° (gas) and S–N bond lengths of 1.553(3) Å (crystal) and 1.551(6) Å (gas). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Solid state; X-ray crystallography; *cis*-Sulfanuric fluoride; Gas phase

1. Introduction

Due to its high stability sulfanuric fluoride (1,3,5-trifluoro-1,3,5-trioxo-1λ^6,3λ^6,5λ^6-trithia-2,4,6-triazine), $(NS(O)F)_3$ **1** is the best characterized member among the cyclic sulfur–nitrogen–fluorine compounds, which contain only sulfur and nitrogen in the ring. Preparation of the fluoride is via the chloride which was synthesized by Kirsanov [1,2] (Eq. (1)). Metatheses with 'active' KF, KSO_2F [3,4] and with SbF_3 [5,6] have been reported (Eq. (2)).

$$3ClSO_2NPCl_3 \xrightarrow{\Delta} \underset{\mathbf{2}}{(NS(O)Cl)_3} + 3POCl_3 \qquad (1)$$

$$\mathbf{2} + 3KF(KSO_2F,SbF_3) \rightarrow \underset{\mathbf{1}}{(NS(O)F)_3} + 3KCl(KCl + 3SO_2,SbCl_3) \qquad (2)$$

$$\begin{tikzcd} NSF_3 + Me_3SnOSnMe_3 \arrow[r] & \{NSF_2OSnMe_3\} + Me_3SnF \arrow[d, "\sim"'] \\ & Me_3SnNS(O)F_2 \longrightarrow 1/3\ \mathbf{1} + Me_3SnF \end{tikzcd} \qquad (3)$$

The fluoride **1** can also be obtained directly from NSF_3 which was described for the first time by Glemser and Schröder [7]. An excellent alternative synthesis of the latter compound was developed by Clifford and Thompson [8] by fluorination of $FC(O)NSF_2$ with AgF_2.

$Me_3SnNS(O)F_2$ is formed from the reaction of NSF_3 with hexamethyl distannanoxane after rearrangement of the primary product. Its decomposition gives $(NS(O)F)_3$ in quantitative yield (Eq. (3)) [9]. **1** has been used as a starting material in numerous nucleophilic substitution reactions [10–12]. So far, structural investigations have been reported only for the phenyl derivative $(PhS(O)N)(FS(O)N)_2$ [13]. For discussion of the influence of various substituents on the structure and bonding properties of this ring a structure determination of the parent compound **1** is required.

Fluorine compounds possess in most cases a much lower melting point and a higher volatility than chlorine or otherwise substituted derivatives. For this reason many of these compounds are not suitable for X-ray crystallographic studies. On the other hand their physical properties make them highly suitable for structure determination in the gas phase, using electron diffraction (GED). So far, very little is known about the differences in structural parameters which are derived from the solid and gaseous state. Recently, we published such a structure determination in both phases for $(NSF)_3$ [14] and in the present paper we report the structure of *cis*-$(NS(O)F)_3$ in the crystal and in the gas phase.

2. Crystal structure of *cis*-$(NS(O)F)_3$ (1)

Suitable single crystals for X-ray crystallography were obtained by sublimation. Transfer of the crystals from the sublimation vessel under cooling and in an inert gas atmosphere is necessary because the melting point of **1** is slightly

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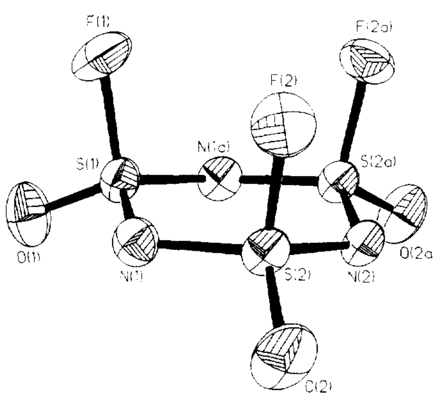

Fig. 1. X-ray molecular structure of (**1**) showing thermal ellipsoids at 50% probability. Bond length [Å] and angles [°]: S(1)–O(1) 1.394(4), S(1)–F(1) 1.537(3), S(1)–N(1) 1.548(3), S(2)–O(2) 1.398(2), S(2)–F(2) 1.538(2), S(2)–N(1) 1.554(3), S(2)–N(2) 1.557(2), O(1)–S(1)–F(1) 107.6(2), O(1)–S(1)–N(1) 112.98(14), F(1)–S(1)–N(1) 103.90(14), N(1)–S(1)–N(1a) 114.3(2), O(2)–S(2)–F(2) 107.1(2), O(2)–S(2)–N(1) 113.6(2), O(2)–S(2)–N(2) 113.2(2), F(2)–S(2)–N(1) 103.9(2), F(2)–S(2)–N(2) 104.0(2), N(1)–S(2)–N(2) 113.9(2), S(1)–N(1)–S(2) 122.1(2), S(2a)–N(2)–S(2) 121.8(2).

below room temperature (17.4°C) and because **1** is sensitive towards hydrolysis. The crystal for the structure determination was selected under a polarization microscope in cooled Nujol and the measurements were performed at −120°C. Details of the structure analysis are given below and in Fig. 1 with bond lengths and bond angles. The atoms S(1), N(2), F(1) and O(1) lie on a mirror plane of the space group. For this reason there are only two independent SF and SO and three independent SN distances.

Crystal data: $F_3N_3O_3S_3$, $M = 243.21$, orthorhombic, space group *Pnma*; $a = 6.817(2)$, $b = 11.2140(10)$, $c = 9.139(3)$ Å; $V = 698.6(3)$ Å^3; $Z = 4$; $D_x = 2.312$ Mg m^{-3}; λ(Mo K$_\alpha$) = 0.71073 Å; $\mu = 1.092$ mm^{-1}. Data were collected to $2\theta_{max} = 52°$ on a Siemens P4 diffractometer. Of 2678 collected data, 738 were unique ($R_{int} = 0.048$). The structure was solved by direct methods and refined anisotropically on F^2 (structure solution and graphics: Siemens SHELXTL-Plus: G.M. Sheldrick, Release 4.0 for Siemens R3 Crystallographic Research Systems, Siemens Analytical X-ray Instruments, Madison, WI, USA, 1989; structure refinement: SHELXL-93, G.M. Sheldrick, University of Göttingen). The final $wR2$ was 0.0952 for all 738 unique reflections and 61 parameters, conventional $R1$ was 0.0361. Final atomic coordinates are presented in Table 1.

3. Gas phase structure of *cis*-(NS(O)F)$_3$ (1)

The electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2 [15] at two nozzle-to-plate distances (50 and 25 cm) with an accelerating voltage of 60 kV. The electron wavelength was determined from ZnO powder diffraction patterns. The sample reservoir was warmed to 30°C, the inlet system and gas nozzle to 40°C. The photographic plates (Kodak Electron Image 13×18 cm) were analyzed by the usual procedures [16] and averaged molecular intensities in the s-ranges ($s = (4\pi)/(\lambda)\ \sin(\theta)/(2)$, λ electron wavelength, θ scattering angle) 2–18 and 8–35 Å^{-1} in intervals of $\Delta s = 0.2$ Å^{-1} are presented in Fig. 2.

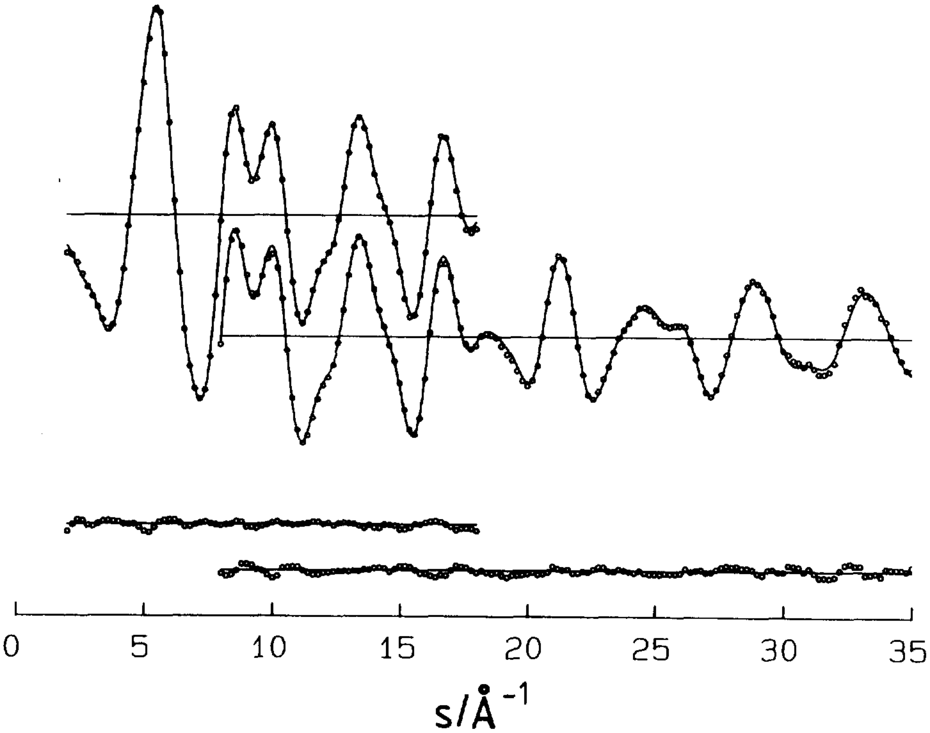

Fig. 2. Experimental (dots) and calculated (full line) molecular intensities and differences for (NS(O)F)$_3$.

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for compound (1)

	x	y	z	U (equivalent)
S(1)	−796(2)	2500	4725(1)	28(1)
S(2)	2250(1)	3713(1)	5927(1)	26(1)
N(1)	108(4)	3660(2)	5348(3)	30(1)
N(2)	3027(6)	2500	6519(4)	27(1)
F(1)	−157(5)	2500	3111(3)	47(1)
F(2)	3482(3)	3935(2)	4543(2)	42(1)
O(1)	−2840(5)	2500	4756(5)	48(1)
O(2)	2597(4)	4667(2)	6877(3)	46(1)

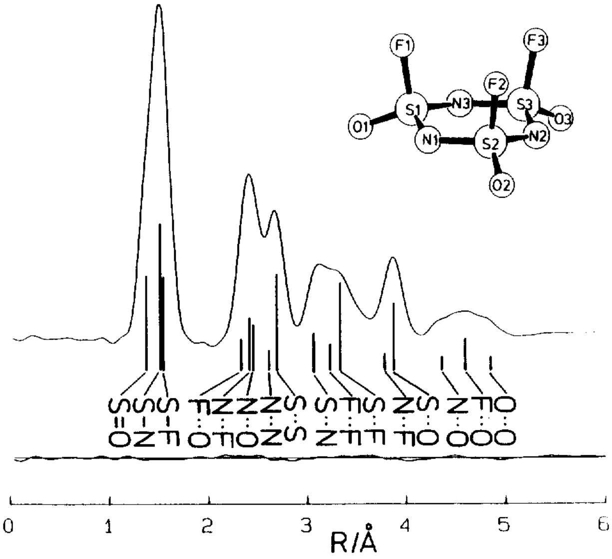

Fig. 3. Experimental radial distribution function and difference curve for $(NS(O)F)_3$. The positions of important interatomic distances are indicated by vertical bars.

The radial distribution function (RDF) was calculated by Fourier Transform of the molecular intensities and is shown in Fig. 3. A preliminary analysis of the RDF demonstrates that all three fluorine atoms are on the same side of the six-membered ring (*cis*-conformation). All SN bonds possess equal or nearly equal length and the ring is slightly puckered. In the least squares refinement the molecular intensities were multiplied by a diagonal weight matrix and known complex scattering factors were used [17]. The overall symmetry was constrained to C_{3v}. Since S–N and S–F bond lengths are very similar, a mean value $(S\text{–}N, S\text{–}F)_{mean}$ and the difference $\Delta = (S\text{–}F) - (S\text{–}N)$ were refined in the least squares analysis. The ring structure was described by the S–N bond length and the nonbonded S···S and N···N distances. The vibrational amplitudes for the S–N and S–F bonds were assumed to be equal and some nonbonded amplitudes were collected in groups according to their distances (see Table 2). With these constraints seven geometric parameters p_i and 12 vibrational amplitudes l_k were refined simultaneously. The following correlation coefficients had values larger than $|0.6|$: $p_3/p_5 = -0.80$, $p_3/l_6 = -0.63$, $p_5/l_4 = 0.66$, $p_6/l_7 = -0.62$, $p_7/l_3 = 0.80$ and $l_{11}/l_{12} = 0.64$. The final results of the GED analysis are listed in Table 2.

Table 2
Results of gas electron diffraction experiment for $(NS(O)F)_3$[a]

Geometric Parameters

	Distance			Angle	
S = O	1.390 (3)	p_1	NSN	115.2 (11)	
$(S\text{-}N,S\text{-}F)_{mean}$	1.553 (2)	p_2	SNS	121.6 (9)	
$\Delta = (S\text{-}F\text{-}S\text{-}N)$	0.006 (12)	p_3	NSF	103.0 (5)	p_6
S-N	1.551 (6)		FSO	105.0 (7)	p_7
S-F	1.557 (9)		NSO	114.2 (5)	
S···S	2.708 (5)	p_4	SNSN	24.5 (48)	
N···N	2.619 (12)	p_5	NSNS		

Interatomic Distances and Vibrational Amplitudes

	Distance	Amplitude	
S = O	1.39	0.040 (3)	ℓ_1
S-N	1.55	0.048 (1)	ℓ_2
S-F	1.56		
F1···O1	2.34	0.047 (6)	ℓ_3
N1···F1	2.43		
N1···O1	2.47		
N1···N2	2.62	0.065 (4)	ℓ_4
S1···S2	2.71		
S1···N2	3.08	0.059 (9)	ℓ_5
F1···F2	3.24	0.113 (30)	ℓ_6
S1···F2	3.35	0.160 (13)	ℓ_7
N1···F3	3.80	0.189 (68)	ℓ_8
S1···O2	3.89	0.071 (5)	ℓ_9
N1···O3	4.37	0.072 (25)	ℓ_{10}
F1···O2	4.61	0.117 (19)	ℓ_{11}
O1···O2	4.87	0.085 (30)	ℓ_{12}

[a] r_a-values in [Å] and [°], uncertainties are 3σ values. For atom numbering see Fig. 3.

4. Discussion

It is well known that $(NS(O)Cl)_3$ (**2**) as well as $(NS(O)F)_3$ (**1**) exist in two isomeric forms. X-ray crystallography for 'α-$(NS(O)Cl)_3$' demonstrates [18] that all chlorine atoms are axial and in *cis* positions, and all oxygens point in equatorial directions. The six-membered SN ring deviates slightly from planarity and possesses chair conformation. The recently reported structure of 'β-$(NS(O)Cl)_3$' [19] justifies this compound to be called '*trans*-$(NS(O)Cl)_3$'. Again all oxygens point in equatorial directions and all chlorines in axial directions, one chlorine, however, is *trans* with respect to the two other chlorines. The ring adopts a boat conformation. The terminology *cis*/*trans* has been suggested much earlier for the two isomers of the fluoride, on the basis of ^{19}F-NMR spectra (A_3 and A_2B spectra, respectively). The results of the present structure deter-

Table 3
Gas-phase and crystal structures of $(NS(O)F)_3$ and $(NSF)_3$ and crystal structures of $(NS(O)Cl)_3$ and $(NSCl)_3$[a]

	$(NSOF)_3$ gas[c]	$(NSOF)_3$ crystal[c]	$(NSF)_3$ gas[d]	$(NSF)_3$ crystal[d]	$(NSOCl)_3$ crystal[e]	$(NSCl)_3$ crystal[f]
S–N	1.551(6)	1.553(3)	1.582(4)	1.593(3)	1.571(4)	1.605(5)
S–X[b]	1.557(9)	1.538(3)	1.624(7)	1.610(3)	2.003(3)	2.128(4)
S=O	1.390(3)	1.397(3)	–	–	1.407(7)	–
NSN	115.2(11)	114.0(2)	112.7(12)	112.6(2)	112.8(4)	113.4(4)
SNS	121.6(9)	122.0(2)	124.3(6)	123.2(1)	122.0(4)	124.0(4)
NSX	103.0(5)	103.9(2)	100.9(9)	101.5(2)	106.3(3)	113.7(3)
NSO	114.2(5)	113.3(2)	–	–	111.9(4)	–
XSO	105.0(7)	107.3(2)	–	–	107.9(4)	–
NSNS	24.5(48)	34.5(10)	24.2(43)	28.5(8)	37.6(19)	16.7(19)

[a] Values in [Å] and [°]. Uncertainties are 3σ values for gas-phase structures and σ values for crystal structures. Mean values are given for crystal structures.
[b] X = F or Cl.
[c] This work.
[d] Ref. [14].
[e] Ref. [18].
[f] Ref. [20].

minations for '*cis*-$(NS(O)F)_3$' confirm the interpretation of the NMR spectra. So far, we did not succeed to measure single crystals of '*trans*-$(NS(O)F)_3$' but from the results discussed above we expect that the conformation of this compound is similar to that of 'β-$(NS(O)Cl)_3$' and that the bond lengths are very similar to those of '*cis*-$(NS(O)F)_3$'.

As in the case of α-$(NS(O)Cl)_3$, *cis*-$(NS(O)F)_3$ possesses a chair conformation. Table 3 compares the geometric parameters of **1** derived for the gas phase and for the solid phase (average values) with those of $(NSF)_3$ and with the crystal structures of the analogous chlorides. As shown by the NSNS dihedral angles, the degree of puckering of **1** is slightly larger in the solid state than in the gas-phase. This difference can be due to packing effects or due to vibrational effects. Considering systematic differences between geometric parameters determined in the gaseous and solid phase, the results of the two structure analyzes for **1** are in very good agreement. The differences in exocyclic S–F and S=O bond lengths are most likely due to vibrational effects. Bending vibrations have different effects on bond lengths in the solid and gaseous phase, resulting in differences of up to 0.03 Å. Comparison of structural parameters of $(NSF)_3$ with those of $(NS(O)F)_3$ demonstrates that increasing the sulfur oxidation number from IV to VI, leads to shortening of both S–N and S–F bond lengths by 0.03–0.04 Å and by ca. 0.07 Å, respectively. On the other hand, the degree of puckering of the fluorinated SN ring depends very little on the sulfur oxidation number. In the analogous chlorinated derivatives, which were studied only in the solid state, the S–N bonds are slightly longer by 0.01–0.02 Å. The SN ring of $(NSCl)_3$ is less puckered than that of the other compounds.

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