converged to 0·25 with this refinement. This result corresponds to the electronic state $(t_{2g})^{4\cdot75}(e_g)^{2\cdot25}$, and the low-spin model is unequivocally excluded. In fact, the difference Fourier maps after the refinement with the low-spin model (Fig. 3) gave very high positive and very deep negative peaks. The distance of 0·24 Å from the Co nucleus to the new positive peaks in Fig. 2 is, however, much shorter than the distance to the negative peaks in Fig. 1. Therefore, there may be other possibilities to be considered. One is the anharmonic vibration of the Co^{2+} ion, which seems to have an effect at the closer point to the nucleus (Tanaka & Marumo, 1981).

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Crystal Structures of Thionitrosyl Hexafluoroantimonate(V) and Thionitrosyl Undecafluorodiantimonate(V) at 293 K and of Thionitrosyl Undecafluorodiantimonate(V) at 121·5 K: the Effect of Thermal Motion on the Apparent NS Bond Length

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Abstract

$NS^+.SbF_6^-$, M_r = 281·8, orthorhombic, *Pbca*, a = 13·999 (6), b = 8·363 (4), c = 10·468 (4) Å, U = 1225·5 Å^3, Z = 8, D_x = 3·055 Mg m^{-3}, μ(Mo $K\alpha$) = 4·76 mm^{-1} at 293 (2) K. The structure was refined to R = 0·032 for 2025 independent reflexions. $NS^+.Sb_2F_{11}^-$, M_r = 498·3, monoclinic, $P2_1/c$, a = 8·374 (2), b = 11·792 (3), c = 10·108 (3) Å, β = 91·89 (4)°, U = 997·6 Å^3, Z = 4, D_x = 3·328 Mg m^{-3}, μ(Mo $K\alpha$) = 5·79 mm^{-1} at 293 (2) K; a = 8·191 (8), b = 11·760 (8), c = 9·935 (7) Å, β = 92·88 (2)°, U = 955·8 Å^3, Z = 4, D_x = 3·474 Mg m^{-3}, μ(Mo $K\alpha$) = 6·04 mm^{-1} at 121·5 (2·0) K. The structure was refined to R = 0·036 for 2873 independent reflexions at room temperature and 0·037 for 1691 independent reflexions at low temperature. The structures may be described as ionic, with each S atom surrounded by five F atoms at distances of 2·6–2·8 Å. The apparent NS bond length shows a pronounced temperature dependence; a librational analysis of the three structures led to the corrected value r(NS) = 1·42 (1) Å.

Introduction

Glemser & Koch (1971) showed that NSF reacts with SbF_5 to give a crystalline product which they formulated on the basis of the IR and Raman spectra as $NS^+.SbF_6^-$. The transient existence of NS^+ in the gas

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phase was implied in the study of the photoelectron spectrum of NS by Dyke, Morris & Trickle (1977), who estimated $r(\mathrm{NS}^+) = 1{\cdot}44\,(1)$ Å. An independent demonstration of the existence of the NS^+ ion in a crystal environment was the motivation of the X-ray investigations reported here. In the course of the analysis of $\mathrm{NS}^+.\mathrm{SbF}_6^-$ it became clear that the small size of the NS^+ ion gave rise to a large and uncertain librational effect on the observed bond length. Attempts to overcome this problem by collecting low-temperature data were thwarted by a phase change which turned the crystals to powder. We thus prepared the new derivative $\mathrm{NS}^+.\mathrm{Sb}_2\mathrm{F}_{11}^-$, and were successful in collecting X-ray data at 293 and 121·5 (2·0) K, which allowed a detailed analysis of the effect of thermal motion on the apparent NS bond length.

Experimental

$\mathrm{NS}^+.\mathrm{SbF}_6^-$ was prepared by the reaction of NSF with SbF_5 in liquid SO_2 (Mews, 1976). $\mathrm{NS}^+.\mathrm{Sb}_2\mathrm{F}_{11}^-$ was synthesized from $\mathrm{NS}^+.\mathrm{SbF}_6^-$ and SbF_5 in liquid $\mathrm{SO}_2\mathrm{ClF}$. Crystals grown in the course of the preparations were sealed in Lindemann-glass capillary tubes. The compounds are extremely moisture sensitive, so all operations were performed under dry nitrogen.

The room-temperature data for $\mathrm{NS}^+.\mathrm{SbF}_6^-$ and the low-temperature data for $\mathrm{NS}^+.\mathrm{Sb}_2\mathrm{F}_{11}^-$ were measured on a Stoe STADI-2 equi-inclination diffractometer (layers *hk*0–14 and *hk*0–9 respectively). Cell dimensions were determined by least squares from ω measurements of reflexions from different layers (Clegg & Sheldrick, 1979). Room-temperature data for $\mathrm{NS}^+.\mathrm{Sb}_2\mathrm{F}_{11}^-$ were collected on a Stoe–Siemens four-circle diffractometer with the control program written by Clegg (1981). Lp and empirical absorption corrections were applied in all cases. Crystal data are given in the *Abstract* and in Table 1. Both crystals of $\mathrm{NS}^+.\mathrm{Sb}_2\mathrm{F}_{11}^-$ exhibited significant Renninger reflexions, which correlates with the relatively large extinction coefficients obtained in the least-squares refinement.

Table 1. *Crystal data*

	$\mathrm{NS}^+.\mathrm{SbF}_6^-$	$\mathrm{NS}^+.\mathrm{Sb}_2\mathrm{F}_{11}^-$	$\mathrm{NS}^+.\mathrm{Sb}_2\mathrm{F}_{11}^-$
T (K)	293 (2)	293 (2)	121·5 (2·0)
Crystal size (mm)	0·3 × 0·3 × 0·7	0·6 × 0·6 × 0·6	0·3 × 0·3 × 0·3
$2\theta_{\max}$ (°)	60	60	50
Reflexions measured	8073	11692	2889
Unique $F > 4\sigma(F)$	2025	2873	1691
$R = \sum\Delta/\sum\lvert F_o\rvert$	0·032	0·036	0·037
$R' = \sum w^{1/2}\Delta/\sum w^{1/2}\lvert F_o\rvert$	0·044	0·035	0·032
Extinction coefficient x (× 10^{+7})	0·8 (1)	3·11 (5)	2·07 (7)

Structure solution and refinement

The structures were solved by direct and Fourier methods and refined with the weighting scheme $w =$

Table 2. *Atomic coordinates* (× 10^4) *and isotropic thermal parameters* (Å^2 × 10^3) *for* $[\mathrm{NS}]^+[\mathrm{SbF}_6]^-$

$U_{\mathrm{eq}} = \frac{1}{3}$(trace of orthogonalized U_{ij} matrix).

	x	y	z	U_{eq}
Sb	3762 (1)	2273 (1)	5143 (1)	40 (1)
S	3797 (1)	6889 (2)	7546 (1)	49 (1)
F(1)	4927 (2)	2749 (4)	4358 (3)	75 (1)
F(2)	4433 (2)	1135 (3)	6403 (3)	81 (1)
F(3)	2604 (2)	1772 (4)	5932 (3)	89 (1)
F(4)	3095 (2)	3375 (4)	3903 (3)	87 (1)
F(5)	3667 (2)	406 (5)	4177 (5)	92 (1)
F(6)	3876 (2)	4085 (4)	6156 (4)	93 (2)
N	3769 (3)	8398 (6)	8031 (8)	96 (3)

Table 3. *Atomic coordinates* (× 10^4) *and isotropic thermal parameters* (Å^2 × 10^3) *for* $[\mathrm{NS}]^+[\mathrm{Sb}_2\mathrm{F}_{11}]^-$

$U_{\mathrm{eq}} = \frac{1}{3}$(trace of orthogonalized U_{ij} matrix).

	$T = 293$ K				$T = 121{\cdot}5$ K			
	x	y	z	U_{eq}	x	y	z	U_{eq}
S(1)	7910 (2)	4417 (1)	2393 (2)	74 (1)	7906 (2)	4419 (1)	2351 (2)	20 (1)
N(1)	7522 (7)	3937 (5)	1209 (5)	98 (2)	7399 (9)	3874 (5)	1145 (6)	29 (2)
Sb(1)	1803 (1)	2782 (1)	4615 (1)	46 (1)	1824 (1)	2736 (1)	4635 (1)	11 (1)
Sb(2)	3170 (1)	5518 (1)	2754 (1)	50 (1)	3173 (1)	5502 (1)	2766 (1)	12 (1)
F(1)	2844 (3)	3913 (2)	3413 (3)	60 (1)	2865 (5)	3883 (3)	3417 (4)	18 (1)
F(2)	−46 (3)	3107 (3)	3611 (3)	69 (1)	−77 (5)	3018 (3)	3568 (4)	21 (1)
F(3)	2330 (4)	1709 (2)	3367 (3)	70 (1)	2405 (5)	1657 (3)	3378 (4)	20 (1)
F(4)	3776 (4)	2612 (3)	5437 (3)	78 (1)	3855 (5)	2602 (3)	5511 (4)	21 (1)
F(5)	1353 (4)	4018 (3)	5666 (3)	69 (1)	1289 (5)	3978 (3)	5678 (3)	20 (1)
F(6)	785 (4)	1761 (3)	5663 (3)	80 (1)	787 (5)	1701 (3)	5688 (4)	22 (1)
F(7)	3680 (4)	4841 (3)	1181 (3)	75 (1)	3717 (5)	4822 (3)	1168 (3)	20 (1)
F(8)	5263 (4)	5274 (3)	3320 (4)	75 (1)	5325 (5)	5265 (3)	3397 (4)	21 (1)
F(9)	3481 (4)	6965 (2)	2150 (4)	85 (1)	3474 (6)	6965 (3)	2147 (4)	25 (1)
F(10)	2667 (4)	6003 (3)	4415 (3)	79 (1)	2631 (5)	5972 (3)	4462 (4)	22 (1)
F(11)	1024 (4)	5472 (3)	2279 (4)	82 (1)	957 (5)	5439 (3)	2227 (4)	23 (1)

$[\sigma^2(F) + gF^2]^{-1}$ ($g = 0{\cdot}001$ for SbF_6^-, 0·0 for both $Sb_2F_{11}^-$ data sets), complex neutral-atom scattering factors being taken from *International Tables for X-ray Crystallography* (1974). In the final cycles anisotropic temperature factors were employed for all atoms, and an approximate isotropic extinction parameter x was refined such that $F_c^* = kF_c(1 - x|F_c|^2/\sin\theta)$, where k is the overall scale factor and the quantity minimized was $\sum w(|F_o| - |F_c^*|)^2$. Calculations and production of diagrams were performed with the *SHELXTL* system on an Eclipse S250 computer, which also controlled the four-circle data collection. Final R indices and values of x are quoted in Table 1. Final positional parameters are presented in Tables 2 and 3.†

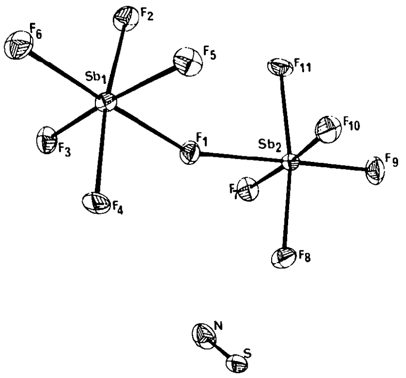

Fig. 3. 50% probability thermal ellipsoids for $NS^+.Sb_2F_{11}^-$ at 121·5 K.

Effect of thermal motion on apparent r(NS)

Figs. 1–3 illustrate the thermal motion of the ions; the motion of N and F perpendicular to the N–S and F–Sb bonds is apparent, as is the considerable reduction in the thermal amplitudes on cooling. As shown in Table 4, the observed NS distance is 1·361 (6) and 1·354 (6) Å at 293 K, but 1·404 (6) Å at 121·5 K. The r.m.s. amplitude is a maximum for motion of the N atom perpendicular to the N–S vector, indicating that libration is responsible for the difference. Unfortunately the N and S anisotropic temperature factors alone do not suffice for a full description of the librational motion and hence calculation of the appropriate bond-length corrections, *e.g.* by the method of Schomaker & Trueblood (1968): it is necessary to make an assumption about the centre of rotation. From the formulae summarized by Johnson (1970) we have calculated the librationally corrected bond length subject to the assumptions (*a*) that the S atom is subject only to translation, and that N in addition rotates about S (a riding model: r_2 in Table 4), and (*b*) that the ion rotates about its centre of mass (r_3 in Table 4). As a result of electrostatic interactions between S and F (see below) which will tend to anchor the S atom, the true centre of rotation is likely to be between the S position and the centre of mass: we thus consider r_2 and r_3 to be lower and upper limits respectively. In Table 4 it can be seen that r_2 and r_3 converge at low temperature, and that a corrected bond length of 1·42 (1) Å is consistent with all data presented. It is this value which should be compared with spectroscopic and theoretical estimates.

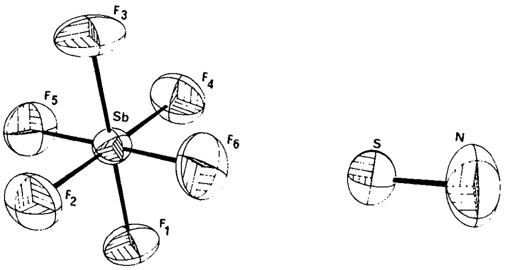

Fig. 1. 50% probability thermal ellipsoids for $NS^+.SbF_6^-$ at 293 K.

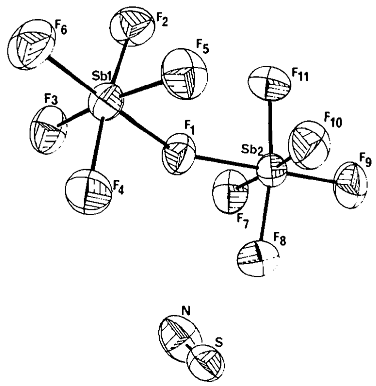

Fig. 2. 50% probability thermal ellipsoids for $NS^+.Sb_2F_{11}^-$ at 293 K.

A value $r_e(NS^+) = 1{\cdot}44\,(1)$ Å was deduced by Dyke, Morris & Trickle (1977) from the vibrational fine structure of the gas-phase photoelectron spectrum of NS. This value is in accord with current theoretical views, *e.g.* Karpfen, Schuster, Petkov & Lischka (1978). A value of 1·429 Å has been proposed by Schnepel (1980) on the basis of empirical force-constant correlations. Although the gas-phase value is longer than the value obtained here by only the sum of the two e.s.d.'s, we should mention two arguments for expecting it to be slightly longer:

(*a*) The X-ray method measures the distance between the two centres of electron density, not the

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† Lists of structure factors and anisotropic thermal parameters for the three analyses have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35840 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Librational analysis of* $r(\mathrm{NS}^+)$

Parallel and perpendicular r.m.s. amplitudes (Å) with $r(\mathrm{NS}^+)$ (Å) corrected according to the models: r_1 no correction, r_2 N rides on S, and r_3 the NS^+ ion rotates about its centre of mass.

Sample	*T* (K)	$u(\mathrm{S})_{\mathrm{par}}$	$u(\mathrm{N})_{\mathrm{par}}$	$u(\mathrm{S})_{\mathrm{per}}$	$u(\mathrm{S})_{\mathrm{per}}$	r_1	r_2	r_3
$\mathrm{NS}^+.\mathrm{SbF}_6^-$	293	0·214	0·239	0·227	0·339	1·361 (6)	1·408	1·526
$\mathrm{NS}^+.\mathrm{Sb}_2\mathrm{F}_{11}^-$	293	0·264	0·298	0·276	0·320	1·354 (6)	1·373	1·423
$\mathrm{NS}^+.\mathrm{Sb}_2\mathrm{F}_{11}^-$	121·5	0·140	0·166	0·143	0·172	1·404 (6)	1·410	1·428

internuclear separation. Although the difference is normally experimentally detectable only for bonds involving H, it is possible that it is also significant for the NS^+ ion, the triple bond and positive charge causing the electron distribution of the N to be displaced slightly towards the S atom. By high-angle refinements on the low-temperature data we estimate that a correction of +0·007 (3) Å should be added to the X-ray result quoted above.

(*b*) The NS^+ ion can be described in terms of the resonance extremes $\mathrm{N{\equiv}S^+}$ and $\mathrm{^+N{=}S}$. Ionic interactions between S and F (see below) in the crystal will tend to stabilize the first of these relative to the gas phase, thereby increasing the bond order and shortening the bond in the crystal.

Anion geometry and interatomic interactions

The structures consist of discrete ions. In both structures, the S atom is surrounded by five F atoms at distances in the range 2·6 to 2·8 Å; the N atom does not exhibit any short interionic interactions, suggesting that the positive charge mainly resides on S. The coordination of Sb by F is octahedral, with angles of 151·5 (2) (293 K) and 151·2 (2)° (121·5 K) at the bridging F atom. The bridging Sb—F bonds are both about 0·08 Å longer than the terminal bonds. Riding-model and rigid-body librational corrections to the Sb—F distances give very similar results. Correlations of Sb—F and S···F distances are presented in Tables 5 and 6; in both structures, the five short S···F interactions are associated with the five longest Sb—F bonds; the interaction with S lengthens the Sb—F bonds by about 0·02 Å. Fig. 4 illustrates the environment of S in $\mathrm{NS}^+.\mathrm{Sb}_2\mathrm{F}_{11}^-$.

Table 5. *Correlation of* Sb—F *and* F···S *distances* (Å) *for* $\mathrm{NS}^+.\mathrm{SbF}_6^-$ *at* 293 K

r = uncorrected, r' = F rides on Sb, r'' = rigid-body libration.

	r(Sb—F)	r'(Sb—F)	r''(Sb—F)	r(F···S)
F(5)	1·865 (4)	1·905	1·904	2·575
F(3)	1·867 (3)	1·905	1·898	2·591
F(1)	1·869 (2)	1·896	1·901	2·693
F(6)	1·857 (3)	1·899	1·895	2·762
F(2)	1·879 (3)	1·911	1·913	2·783
F(4)	1·846 (3)	1·881	1·880	–

Table 6. *Correlation of* Sb—F *and* F···S *distances* (Å) *for* $\mathrm{NS}^+.\mathrm{Sb}_2\mathrm{F}_{11}^-$

r = uncorrected, r' = F rides on Sb. N = 293 K, L = 121·5 K, b = bridge, c = *cis* (to bridge), t = *trans*.

	r_N(Sb—F)	r_L(Sb—F)	r'_N(Sb—F)	r'_L(Sb—F)	r_L(F···S)
F(1)*b*	2·021 (3)	2·028 (4)	2·030	2·033	–
F(1)*b*	2·028 (3)	2·032 (4)	2·035	2·035	
F(2)*c*	1·863 (3)	1·869 (4)	1·881	1·875	2·589
F(8)*c*	1·848 (3)	1·862 (4)	1·867	1·867	2·600
F(3)*c*	1·850 (3)	1·859 (4)	1·870	1·860	2·738
F(5)*c*	1·849 (3)	1·857 (4)	1·868	1·864	2·773
F(11)*c*	1·845 (3)	1·868 (4)	1·871	1·876	2·780
F(4)*c*	1·836 (3)	1·845 (4)	1·862	1·847	–
F(7)*c*	1·842 (3)	1·852 (4)	1·861	1·853	–
F(10)*c*	1·836 (3)	1·849 (4)	1·859	1·851	–
F(6)*t*	1·832 (3)	1·840 (4)	1·860	1·849	–
F(9)*t*	1·834 (3)	1·847 (4)	1·863	1·857	–

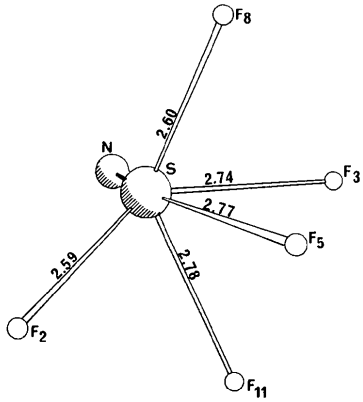

Fig. 4. The environment of the NS^+ ion in $\mathrm{NS}^+.\mathrm{Sb}_2\mathrm{F}_{11}^-$ at 121·5 K. The F atoms are in four different anions. (Distances in Å.)

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