Preparation, Crystal and Molecular Structure, and Antimony-121 Mössbauer Spectrum of Trifluoro(1,10-phenanthroline)(thiourea)antimony(III)†

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The mixed (1 : 1 : 1) adduct between SbF_3, 1,10-phenanthroline, and thiourea has been prepared. The compound has been characterized *via* Mössbauer spectroscopy and *X*-ray analysis on a single crystal. It crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.736(1)$, $b = 10.443(1)$, $c = 10.509(1)$ Å, $\alpha = 92.3(1)$, $\beta = 108.9(1)$, $\gamma = 111.1(1)°$, and $Z = 2$. The structure was solved by Patterson and Fourier methods; full-matrix least-squares refinement based on 3 340 observed reflections gave a final $R = 0.026$ ($R' = 0.030$). The distorted octahedral co-ordination polyhedron is characterized by very asymmetrical bonds to the central ion [Sb–F(1) 1.938(2), Sb–F(2) 1.997(2), Sb–F(3) 1.948(2), Sb–N(1) 2.556(3), Sb–N(2) 2.731(3) Å] and by a relatively short Sb • • • S interaction of 3.061(3) Å. The whole structure is held together by intermolecular hydrogen bonds.

The acceptor ability of the SbF_3 moiety towards neutral ligands has been previously investigated. Adducts with bi- and tridentate nitrogen donors such as 1,10-phenanthroline (phen)[1] and 2,2′:6′,2″-terpyridine[2] have been obtained. Adducts with unidentate ligands have been reported also and among these the crystal and molecular structures of SbF_3(u) (u = urea),[3] SbF_3(tu) (tu = thiourea),[4] and SbF_3(mopyo) (mopyo = 4-methoxypyridine *N*-oxide)[5] have been solved. An examination of the known structures containing the SbF_3 unit reveals that Sb^{III} tends to extend its co-ordination number to reach seven or even eight pseudo-co-ordination. In several cases this is achieved through halogen bridges or 'secondary bonds'. Also, in the case of the adduct SbF_3(phen),[1] of which no suitable crystal for *X*-ray studies could be obtained, i.r. data indicate the presence of fluorine bridges. In order to investigate the residual ability of Sb^{III} in SbF_3(phen) further to co-ordinate a unidentate ligand, the urea and thiourea molecules have been considered. Whereas the adduct with thiourea could be isolated by simple mixing of the reagents, attempts to obtain the urea adduct under similar conditions were unsuccessful. Here we report on the crystal and molecular structure of SbF_3(phen)(tu) and its spectroscopic characterization.

Experimental

Preparation of SbF_3(phen)(tu).—Equimolar quantities (2 mmol) of SbF_3, phen, and tu were dissolved in methanol (50 cm^3) at room temperature. On cooling overnight, well formed yellow crystals were obtained, m.p. 178 °C. The i.r. spectra (4 000—180 cm^{-1}) were recorded as Nujol or hexachlorobutadiene mulls between CsI plates using a Perkin-Elmer 580 spectrophotometer: ν(Sb–F) 405s, 478s, 530s; ν(Sb–S) 292s; ν(SbN) 238ms, 220 (sh) cm^{-1}. The Mössbauer spectrum was obtained, cooling both the source [0.5 mCi (*ca* 1.85×10^7 Bq) $Ca^{121m}SnO_3$] and the absorber (12 mg Sb cm^{-2}) at liquid-nitrogen temperature by using the apparatus and procedure previously described.[6]

Table 1. Crystal data

Formula	$C_{13}H_{12}F_3N_4SSb$
M	435.07
Space group	$P1$ or $P\bar{1}$*
Crystal system	Triclinic
a/Å	7.736(1)
b/Å	10.443(1)
c/Å	10.509(1)
α/°	92.3(1)
β/°	108.9(1)
γ/°	111.1(1)
U/Å^3	737.2(9)
Z	2
D_c/Mg m^{-3}	1.96
$F(000)$	424
λ(Mo-K_α)/Å	0.710 69
Reflections measured	5 700
Scan method	ω/θ
Scan speed (° min^{-1})	1.20
Scan width (°)	1.20
Background counts per s of counting time	10
$2\theta_{max.}$/°	50
Unique observed reflections [$I \geqslant 3\sigma(I)$]	3 340
Weighting scheme, *w*	$[\sigma^2(F_o) + 0.002\,062(F_o)^2]^{-1}$
$R = (\Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert)$	0.026
$R' = \left[\dfrac{\Sigma w[\lvert F_o\rvert - \lvert F_c\rvert]^2}{\Sigma w\lvert F_o\rvert^2}\right]^{\frac{1}{2}}$	0.030
μ(Mo-K_α)/cm^{-1}	20.5

* Space group $P\bar{1}$ was confirmed after successful structure refinement.

X-Ray Structure Determination.—The crystal and refinement data are summarized in Table 1. The adduct SbF_3(phen)(tu) is

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 2. Atomic co-ordinates ($\times 10^3$ for hydrogens, $\times 10^4$ for other atoms)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb	2 150.3(3)	1 814.7(2)	1 377.7(2)
S	9 309(1)	2 813(1)	−688(1)
F(1)	3 728(3)	3 558(2)	988(2)
F(2)	2 347(4)	911(2)	−253(2)
F(3)	4 778(3)	1 808(3)	2 287(2)
N(11)	7 143(5)	3 723(3)	10 282(4)
H(11)	616(9)	365(6)	1 058(6)
H(12)	756(7)	436(5)	998(5)
N(22)	6 885(5)	1 534(3)	10 543(4)
H(22)	595(7)	153(5)	1 097(5)
H(23)	729(8)	83(6)	1 038(5)
C(1)	7 665(5)	2 675(3)	10 096(3)
N(1)	2 466(4)	3 584(3)	3 280(3)
N(2)	2 438(4)	1 074(3)	3 877(3)
C(2)	2 427(6)	4 795(4)	2 998(4)
H(2)	239(6)	496(4)	218(4)
C(3)	2 399(7)	5 778(4)	3 901(4)
H(3)	243(7)	665(5)	355(5)
C(4)	2 403(6)	5 497(4)	5 144(4)
H(4)	255(9)	621(6)	573(6)
C(5)	2 420(7)	3 856(5)	6 781(4)
H(5)	236(8)	446(6)	738(6)
C(6)	2 523(6)	2 653(5)	7 105(4)
H(6)	249(7)	243(5)	794(5)
C(7)	2 646(7)	399(5)	6 419(5)
H(7)	259(9)	15(6)	724(7)
C(8)	2 642(7)	−488(5)	5 454(5)
H(8)	247(7)	−148(5)	556(5)
C(9)	2 514(7)	−131(4)	4 173(5)
H(9)	261(7)	−67(5)	359(5)
C(10)	2 477(4)	1 971(3)	4 839(3)
C(11)	2 438(4)	3 282(3)	4 523(3)
C(12)	2 426(5)	4 219(3)	5 496(3)
C(13)	2 555(5)	1 684(4)	6 147(3)

in the form of air-stable pale yellow transparent prisms. The *X*-ray intensity data were collected on a four-circle Siemens-Stoe automated diffractomer with graphite-monochromated Mo-K_α radiation. The unit-cell parameters were determined on the basis of 25 strong reflections found by mounting the crystal at random, varying the orientation angles φ and χ over a range of 120° each with the detector position varying between $2\theta = 12$ and $2\theta = 20°$. For the determination of precise lattice parameters 20 strong reflections with $10 < \theta < 15°$ were considered. The intensities of three standard reflections, $-4\ -3\ -4$, $-1\ -5\ -4$, and $-2\ -4\ -2$, monitored at intervals of 100 min, showed no greater fluctuation than those expected from Poisson statistics. The intensity data were corrected for Lorentz and polarization effects.

The structure was solved using three-dimensional Patterson and Fourier techniques and refined by full-matrix least-squares methods with anisotropic thermal parameters assigned to all non-hydrogen atoms. Hydrogen atoms were introduced at the positions indicated by difference-Fourier syntheses and included in the refinement with individual isotropic thermal parameters. In the refinement, the weighting scheme used showed reasonable consistency in a test of $w\Delta^2$ for data sectioned with respect both to F_o and to $\sin\theta/\lambda$. The anomalous dispersion terms[7] for Sb and S were taken into account in the refinement. Atomic scattering factors were from ref. 7.

Data processing and computation were carried out using the SHELX 76 program package.[8] Final positional parameters are presented in Table 2.

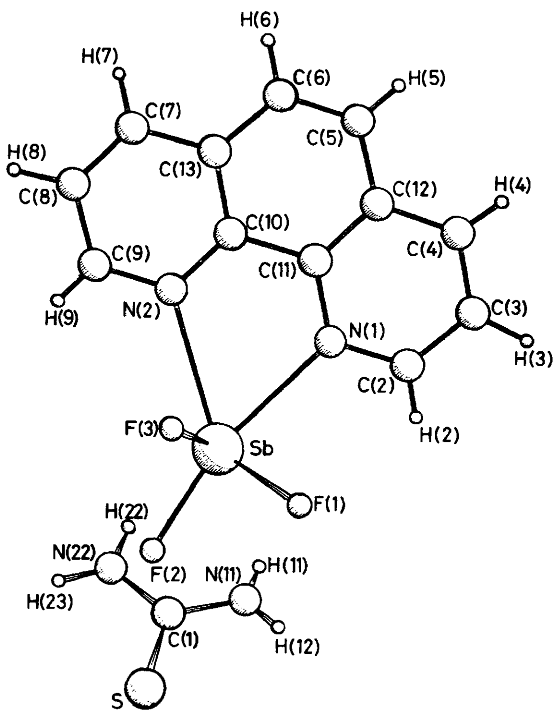

Figure 1. View of the asymmetric unit down *a*

Discussion

The structure consists of molecules of trifluoro(1,10-phenanthroline)antimony(III) and thiourea as shown in Figure 1 together with the atom numbering scheme used. Relevant bond distances and angles are given in Table 3. The molecules are connected together through a S $\cdots$ Sb contact of 3.061(3) Å, which is less than the sum of the van der Waals radii (Sb, 2.2; S, 1.85 Å).[9] The Sb $\cdots$ S separation is very close to that found for the adduct SbF_3(tu) (Sb $\cdots$ S 3.02, Sb $\cdots$ S′ 3.12 Å)[4] but significantly larger than that observed in $SbCl_3$(tmtu) (tmtu = tetramethylthiourea) [2.505(2) Å].[10] A comparison can be also made with the three long (secondary) Sb $\cdots$ S distances found in $Sb[S_2P(OMe)_2]_3$ and $Sb[S_2P(OPr^i)_2]_3$ [Sb $\cdots$ S in the range 3.000(2)—3.031(5) Å in both compounds]; the short (primary) Sb–S distances are 2.522(1)—2.535(2) Å.[11]

Examination of the packing of the molecules in the cell, Figure 2, shows additional interactions between the thiourea molecule and the SbF_3(phen) moiety with intermolecular contacts H(11) $\cdots$ F(1′) 2.03 and H(22) $\cdots$ F(3′) 1.95 Å. In this respect, the thiourea molecule contributes to the cohesion of the structure as in SbF_3(tu).[4] In the present structure we also note that the adjacent phen ligands are parallel to each other with short intermolecular contacts (< 3.5 Å) involving centrosymmetrically related units [N(1) $\cdots$ C(4″) 3.51(1), N(1) $\cdots$ C(12″) 3.53(1), C(2) $\cdots$ C(12″) 3.50(1), and C(11) $\cdots$ C(3″) 3.50(1) Å; double primes denote atoms at $1 - x$, $1 - y$, $1 - z$]. These possible graphitic type interactions presumably further contribute to the packing in the structure.

The SbF_3 moiety appears normal in that only small changes can be noticed if we consider the average of the three short Sb–F bond distances and the related F–Sb–F bond angles in SbF_3[12] and in the previously quoted adducts.[3–5] However, it is worth noting that the two shortest Sb–F bonds are those with F(1) and F(3) which are involved in hydrogen bonds. In Sb^{III} structures, a shortening of the bond with a particular ligand has been ascribed to its position *trans* to that of the non-bonding pair of

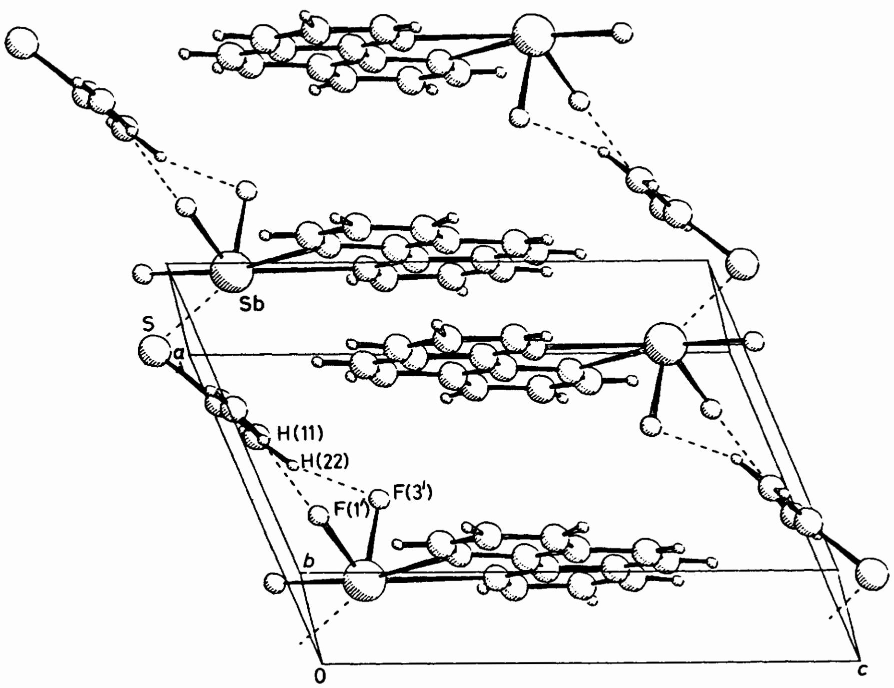

Figure 2. Packing diagram

Table 3. Bond distances (Å) and angles (°)*

Sb • • • S	3.061(3)	N(22)–H(22)	0.96(5)	C(3)–C(4)	1.349(6)	C(7)–C(13)	1.405(6)
Sb–F(1)	1.938(2)	N(22)–H(23)	0.92(5)	C(4)–H(4)	0.89(6)	C(8)–H(8)	1.01(5)
Sb–F(2)	1.997(2)	C(1)–S	1.696(3)	C(4)–C(12)	1.404(5)	C(8)–C(9)	1.393(6)
Sb–F(3)	1.948(2)	N(1)–C(2)	1.318(4)	C(5)–H(5)	0.90(5)	C(9)–H(9)	0.86(5)
Sb–N(1)	2.556(3)	N(1)–C(11)	1.361(4)	C(5)–C(6)	1.338(7)	C(10)–C(11)	1.431(4)
Sb–N(2)	2.731(3)	N(2)–C(9)	1.325(4)	C(5)–C(12)	1.418(5)	C(10)–C(13)	1.405(4)
N(11)–H(11)	0.89(6)	N(2)–C(10)	1.335(4)	C(6)–H(6)	0.92(5)	C(11)–C(12)	1.391(4)
N(11)–H(12)	0.76(5)	C(2)–H(2)	0.88(4)	C(6)–C(13)	1.411(6)	H(11)–F(1′)	2.03(8)
N(11)–C(1)	1.322(4)	C(2)–C(3)	1.380(5)	C(7)–H(7)	0.92(7)	H(22)–F(3′)	1.95(6)
N(22)–C(1)	1.310(4)	C(3)–H(3)	0.990(5)	C(7)–C(8)	1.345(7)		
N(1)–Sb–N(2)	61.7(1)	F(1)–Sb–N(1)	78.4(2)	S–Sb–F(1)	72.0(2)	Sb–N(2)–C(10)	117.8(2)
F(3)–Sb–N(2)	70.6(2)	F(1)–Sb–F(3)	81.3(2)	N(11)–C(1)–S	120.8(3)	Sb–N(2)–C(9)	123.4(2)
F(3)–Sb–N(1)	94.9(1)	F(1)–Sb–F(2)	85.6(2)	N(22)–C(1)–S	121.0(2)	C(9)–N(2)–C(10)	118.8(2)
F(2)–Sb–N(2)	131.0(2)	S–Sb–N(2)	134.4(2)	N(11)–C(1)–N(22)	118.1(4)	N(1)–C(2)–C(3)	123.6(2)
F(2)–Sb–N(1)	164.0(3)	S–Sb–N(1)	89.3(2)	Sb–N(1)–C(11)	123.2(3)	N(2)–C(10)–C(11)	118.5(2)
F(2)–Sb–F(3)	82.8(2)	S–Sb–F(3)	151.6(2)	Sb–N(1)–C(2)	118.5(2)	C(12)–C(11)–N(1)	122.1(3)
F(1)–Sb–N(2)	127.7(2)	S–Sb–F(2)	85.6(1)	C(2)–N(1)–C(11)	117.9(4)		

* (′) = $-1 + x, y, z$.

electrons.[5,13-15] In this case, it seems that the lone pair has equal *trans*-influences on F(1) and F(3).

The phenanthroline ligand chelates in very asymmetrical way to the Sb atom with relatively long bond distances [Sb–N(1) 2.556(3) and Sb–N(2) 2.731(3) Å] as has been found for $SbF(phen)(O_2C_6H_4)$ [2.448(9), 2.569(9) Å][13] and for $[Sb(phen)_2(O_2C_6H_4)]^+$ [2.423(7), 2.592(5) and 2.467(7), 2.694(5) Å, respectively].[14]

In the light of the discussed bond distances and angles at antimony, the overall picture of the present molecule is that of an octahedral co-ordination which is severely distorted by a stereoactive lone pair giving pseudo-seven-co-ordination. This is consistent with the lone pair being located *trans* to F(1) and F(3) and pushing away the Sb–S and Sb–N(2) bonds. These bonds would be expected to make the smallest angles with the supposed direction of the lone pair and they are in fact the longest in the co-ordination sphere.

The low-frequency i.r. spectral data (see Experimental section) are in agreement with the molecular structure. The presence of three Sb–F stretchings indicates a lowering of the C_{3v} local symmetry for the SbF_3 unit. The lowest ν(Sb–F) bands appear at relatively low frequencies[1] which is ascribed to the presence of H • • • F hydrogen bonds. The lengthening of the Sb–N bonds is reflected in the lowering of the ν(Sb–N) absorptions by *ca.* 20 cm^{-1} with respect to previously assigned Sb–N(phen) stretchings.[1,13,14] The strong band, appearing at 292 cm^{-1} has been assigned as ν(Sb–S). Although, as far as we know, a direct comparison with species containing similarly co-ordinated sulphur donor atoms is impossible because of lack of literature data, its value appears lower than those observed

(350—400 cm^{-1}) for compounds containing anionic sulphur donors (see, for example, refs. 16—18).

The Mössbauer spectrum of SbF_3(phen)(tu) shows (relative to the source) $\delta = 15.3$ mm s^{-1}, $eQV_{zz} = 14.3$ mm s^{-1}, $\eta < 0.2$. These values can be instructively compared with those reported for SbF_3 ($\delta = -14.8$ mm s^{-1}, $eQV_{zz} = 19.1$ mm s^{-1})[19] and SbF_3(phen) ($\delta = -13.97$ mm s^{-1}, $eQV_{zz} = 16.8$ mm s^{-1}).[1] We observed a decrease of the quadrupole coupling constant which should mainly reflect a decrease in the stereochemical activity (*i.e.* the *p* character) of the non-bonding pair of electrons, since the latter is considered to provide the main contribution to the total electric-field gradient (e.f.g.) at Sb. The more negative value observed for the isomer shift is in accordance with the above observation, as it corresponds to an increased *s*-electron density at the Mössbauer nucleus. On the other hand, a concomitant factor in reducing the V_{zz} (absolute) value may well come from the sulphur–antimony bond electron density. The latter possibly provides the second largest contribution to the total e.f.g.,[20] but its effect is effectively subtractive in determining V_{zz} since it lies roughly perpendicular to the (supposed) direction of the lone pair.

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References

1 N. Bertazzi, G. Alonzo, and T. C. Gibb, *Inorg. Chim. Acta*, 1983, **73**, 121 and refs therein.
2 G. Alonzo and N. Bertazzi, unpublished work.
3 M. Bourgault, R. Fourcade, B. Ducourant, and G. Mascherpa, *Rev. Chim. Miner.*, 1979, **16**, 155.
4 M. Bourgault, R. Fourcade, and G. Mascherpa, *Rev. Chim. Miner.*, 1978, **15**, 233.
5 J. C. Dewan, A. J. Edwards, J. E. Guerchais, and F. Petillon, *J. Chem. Soc., Dalton Trans.*, 1975, 2223.
6 G. Alonzo, N. Bertazzi, and F. Huber, *Can. J. Spectrosc.*, 1985, **30**, 21.
7 'International Tables for *X*-Ray Crystallography,' 2nd edn., Kynoch Press, Birmingham, 1974, vol. 4, p. 101.
8 G. M. Sheldrick, SHELX 76, program for the solution of *X*-ray crystal structures, University of Cambridge, 1976.
9 L. Pauling, 'The Nature of the Chemical Bond,' 14th edn., Cornell University Press, Ithaca, New York, 1960, p. 260.
10 E. Hough and D. G. Nicholson, *J. Chem. Soc., Dalton Trans.*, 1981, 2083.
11 D. B. Sowerby, J. Haiduc, A. Barbul-Rusu, and R. Salajan, *Inorg. Chim. Acta*, 1983, **68**, 87.
12 A. J. Edwards, *J. Chem. Soc. A*, 1970, 2751.
13 H. Preut, F. Huber, G. Alonzo, and N. Bertazzi, *Acta Crystallogr., Sect. B*, 1982, **38**, 935.
14 F. Huber, H. Preut, G. Alonzo, and N. Bertazzi, *Inorg. Chim. Acta*, 1985, **102**, 181.
15 G. Alonzo, N. Bertazzi, G. Bombieri, and G. Bruno, *J Chem. Soc., Dalton Trans.*, 1987, 2337.
16 G. Alonzo, *Inorg. Chim. Acta*, 1983, **73**, 141.
17 R. A. Mowie, D. W. Grant, and J. L. Wardell, *Inorg. Chim. Acta*, 1978, **30**, 238.
18 M. Hall and D. B. Sowerby, *J. Chem. Soc., Dalton Trans.*, 1980, 1292.
19 J. G. Ballard, T. Birchall, R. Fourcade, and G. Mascherpa, *J. Chem. Soc., Dalton Trans.*, 1976, 2409.
20 F. Di Bianca, N. Bertazzi, G. Alonzo, G. Ruisi, and T. C. Gibb, *Inorg. Chim. Acta*, 1981, **50**, 235.

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