Crystal and Molecular Structure of Antimony Trifluoride–Terpyridine 1:1 Adduct: a Case of Pseudo-pentagonal-bipyramidal Geometry†

Luigi P. Battaglia,[*,a] **Anna Bonamartini Corradi,**[a] **Giorgio Pelosi,**[a] **Andrea Cantoni,**[a] **Giuseppe Alonzo**[b] **and Nuccio Bertazzi**[c]
[a] *Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Universita' di Parma, Viale Delle Scienze, I-43100 Parma, Italy*
[b] *Dipartimento di Chimica Inorganica, Universita' di Palermo, Via Archirafi 26, I-90123 Palermo, Italy*
[c] *Dipartimento di Chimica e Tecnologie Inorganiche e Metallorganiche, Universita' di Cagliari, via Ospedale 72, I-09124 Cagliari, Italy*

The crystal structure of SbF_3(terpy) (terpy = 2,2′:6′2″-terpyridine) has been determined: monoclinic, space group $P2_1/c$, with a = 12.511(2), b = 14.132(3), c = 17.106(3) Å, β = 105.10(1)°; R = 0.0434. The asymmetric unit contains two independent molecules which show only small differences: each contains a terpy molecule, two fluorines nearly accommodated in a plane and a fluorine at the apical site of a pseudo-pentagonal-bipyramidal arrangement in which the seventh position is occupied by the antimony lone pair.

While a number of crystal structures concerning complexes of antimony(III) fluoride with various anionic ligands, including F^-, have been reported, very little is known about SbF_3 adducts with neutral oligodentate donors. Pure antimony trifluoride consists of primary SbF_3 units interacting *via* asymmetric fluoride bridges providing also three longer Sb $\cdots$ F contacts to each antimony atom.[1] The presence of a stereoactive lone pair of electrons can be inferred both from the ligand disposition about antimony as well as from the relatively large value of its ^{121}Sb Mössbauer quadrupole coupling constant.[2] The tendency of antimony to exhibit secondary bonding interactions through fluorine bridges was expected to be progressively reduced by satisfying the co-ordination demand with other donors and, in the case of adducts with tridentate ligands such as 2,2′:6′,2″-terpyridine (terpy), evidence was obtained for the existence of isolated molecules for which Mössbauer data are still indicating the stereoactivity of the antimony lone pair.[3] The compound SbF_3(terpy) was considered an attractive subject for X-ray structural analysis as it was not immediately evident how the overall geometry could harmonize the expected tendency of the SbF_3 unit to maintain a pyramidal arrangement, the stereochemical requirements of the lone pair, and the planar (*mer*) disposition of the terpy ligand.

Experimental

Crystals suitable for X-ray analysis were obtained from samples previously found[3] after recrystallization from methanol.

Data Collection, Solution and Refinement of the Structure.—A crystal was mounted in a random orientation on a Philips PW1100 four-circle diffractometer. The resulting crystal data and the details concerning data collection and refinements are given in Table 1. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares and anisotropic thermal parameters for non-hydrogen atoms; hydrogen atoms, located from a ΔF map, were introduced in the final structure factor but not refined. Final atomic coordinates of non-hydrogen atoms are in Table 2. The atomic scattering factors used, corrected for anomalous dispersion, were from ref. 4; the calculations were performed on a GOULD 32/77 computer using the SHELX 76,[5] ORTEP[6] and PARST[7] programs.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The asymmetric unit contains two independent complex molecules which show similar co-ordination geometry (Fig. 1): each metal is surrounded by three nitrogens from a terpyridine molecule and two fluorines nearly accommodated in a plane; the apical sites are occupied by the F(3) or the F(6) atoms. This co-ordination can be considered as pseudo-pentagonal bipyramidal in which the lone pair is assumed to occupy the seventh (apical) position. It is seldom encountered in species having 6 + 1 valence electron pairs on the central atom. Some authentic examples are provided by antimony(III) species, as shown by the crystal structures of tris(oxalato)antimonate(III)[8] (in the potassium and ammonium salts), tris(diphenyldithiophosphinato)antimony(III)[9] and (*O*-ethyl dithiocarbonato)bis(quinolin-8-olato)antimony(III).[10] Interestingly, in spite of the expected distortions due to the presence of different donor atoms and constraints inherent to the chelating ligands, the stereochemistry observed in the present compound satisfies, practically in all details, the requirements of the valence shell electron pair repulsion (VSEPR) model. With respect to the N_3F_2 best equatorial planes, atoms Sb(1) and Sb(2) are displaced by 0.281(1) and 0.279(1) Å respectively, in the direction opposite to the apical fluorine. The Sb–N bond distances (Table 3) are considerably longer than the sum of the

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

covalent radii (2.10 Å), which can be seen as the effect of the repulsive forces exerted by the lone pair on these bonds located in the equatorial plane. The observed values compare well with those found in trifluoro(1,10-phenanthroline)(thiourea)antimony(III)[11] [2.556(3), 2.731(3) Å] and difluoro(methoxydi-2-pyridylmethoxo-*N*,*N*′,*O*)antimony(III)[12] [2.580(7) Å], as well as with the longer bonds of the asymmetrically chelated phenanthrolines observed in catecholatofluoro(1,10-phenanthroline)antimony(III)[13] [2.569(9) Å] and catecholatobis(1,10-phenanthroline)antimony(III)[14] [2.592(5), 2.694(5) Å], all the cited cases being considered as examples of Sb–N bonds which are similarly affected by the antimony stereoactive lone pair. An example of a diimineantimony(III) complex showing sensibly shorter Sb–N bonds is given by $SbCl_3$(bipy)[15] (bipy = 2,2′-bipyridine) [2.245(14), 2.317(15) Å]. The examination of the geometrical environment at Sb in the latter molecule (rather distorted and with an additional Sb···Cl longer contact) suggests that the probable location of an active lone pair is just roughly *trans* to the shorter Sb–N bond. Another factor to be considered is possibly the lower steric requirements and higher flexibility of bipy with respect to both terpy and phen ligands. Following the guidelines of the VSEPR model, the Sb–F

Table 1 Experimental data for the crystallographic analysis

Formula	$C_{15}H_{11}F_3N_3Sb$
Crystal symmetry	Monoclinic
Space group	$P2_1/c$
a/Å	12.511(2)
b/Å	14.132(3)
c/Å	17.106(3)
α/°	90.0
β/°	105.10(1)
γ/°	90.0
U/Å^3	2920(1)
Z	8
D_c/g cm^{-3}	1.874
D_m/g cm^{-3}	1.82
No. of reflections for lattice parameters	25 (θ 10.0–15.5°)
Radiation	Mo-Kα (λ 0.7093 Å)
F(000)	1600
T/K	294
Crystal size/mm	0.16 × 0.62 × 0.65
μ/cm^{-1}	19.31
Scan speed/° min^{-1}	3.5–12.0
Scan width/°	1.20 + 0.35tanθ
θ range/°	3.0–23.0
h,k,l ranges	−16 to 16, 0–18, 0–21
Standard reflection	3 5 3
Maximum intensity variation (%)	0.05
Scan mode	ω–2θ
No. of measured reflections	4083
No. of reflections N used in the refinement [$I > 3\sigma(I)$]	2167
Minimum maximum height in final difference map/e Å^{-3}	−0.34, 0.44
No. of refined parameters, p	397
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.0434
$R' = [\Sigma w(\Delta F)^2/\Sigma w F_o^2]^{\frac{1}{2}}$	0.0470
$S = [\Sigma w(\Delta F)^2/(N - P)]^{\frac{1}{2}}$	0.67
k, g in $w = k[\sigma^2(F_o) + gF_0^2]^{-1}$	0.59, 2.475 × 10^{-3}

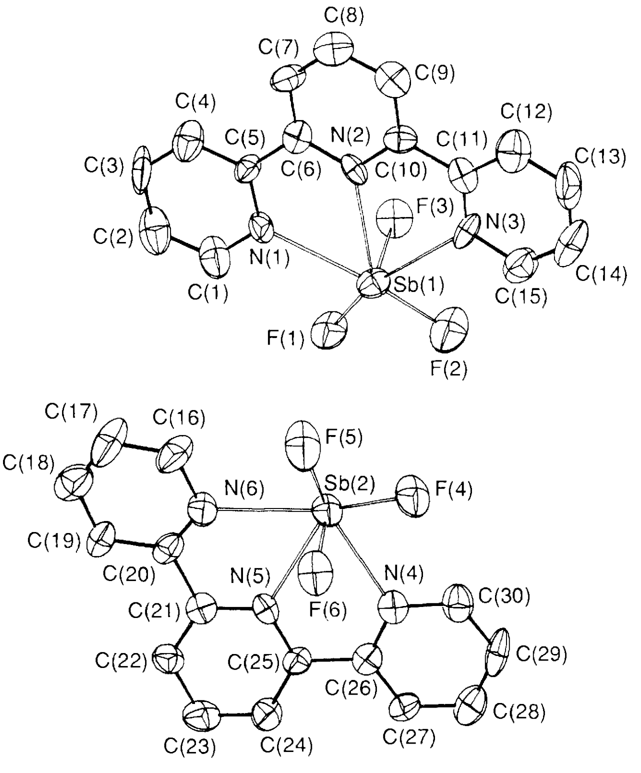

Fig. 1 Perspective view of the complex molecules

Table 2 Atomic coordinates for SbF_3(terpy) with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Sb(1)	0.443 40(7)	0.223 57(6)	0.072 88(5)	C(9)	0.699 4(1)	−0.041 2(9)	0.069 3(9)
Sb(2)	0.054 17(7)	0.294 73(6)	−0.071 19(6)	C(10)	0.633 6(9)	0.039 8(8)	0.055 6(8)
F(1)	0.366 9(7)	0.302 4(5)	0.138 4(5)	C(11)	0.633 2(10)	0.105 6(9)	−0.013 6(8)
F(2)	0.454 7(8)	0.345 0(6)	0.019 3(6)	C(12)	0.696 9(13)	0.086 7(11)	−0.067 9(9)
F(3)	0.579 6(6)	0.259 0(5)	0.147 7(4)	C(13)	0.695 3(14)	0.148 2(14)	−0.129 8(10)
F(4)	0.132 6(7)	0.304 1(5)	−0.156 5(6)	C(14)	0.627 7(17)	0.223 4(12)	−0.139 6(10)
F(5)	0.098 4(8)	0.161 5(6)	−0.071 6(6)	C(15)	0.566 4(12)	0.241 0(11)	−0.083 3(9)
F(6)	−0.073 4(6)	0.259 9(6)	−0.154 1(5)	C(16)	−0.006 6(13)	0.124 3(10)	0.053 4(9)
N(1)	0.431 0(8)	0.116 8(7)	0.195 5(6)	C(17)	−0.040 9(17)	0.081 9(11)	0.116 1(11)
N(2)	0.565 0(7)	0.064 6(7)	0.101 4(6)	C(18)	−0.111 9(12)	0.128 3(11)	0.151 0(9)
N(3)	0.570 3(9)	0.182 2(8)	−0.021 3(6)	C(19)	−0.159 9(12)	0.214 2(8)	0.121 1(8)
N(4)	−0.007 5(9)	0.461 7(7)	−0.133 1(7)	C(20)	−0.121 4(10)	0.252 9(9)	0.057 1(8)
N(5)	−0.115 1(8)	0.385 8(7)	−0.031 1(6)	C(21)	−0.169 0(10)	0.344 0(8)	0.018 0(10)
N(6)	−0.050 8(9)	0.210 2(7)	0.023 4(7)	C(22)	−0.260 2(10)	0.382 5(9)	0.034 7(8)
C(1)	0.360 2(12)	0.138 3(10)	0.237 9(10)	C(23)	−0.305 4(11)	0.467 5(10)	−0.006 5(8)
C(2)	0.350 6(13)	0.090 0(11)	0.305 0(11)	C(24)	−0.248 0(10)	0.508 8(9)	−0.055 6(8)
C(3)	0.415 7(15)	0.011 5(10)	0.328 1(11)	C(25)	−0.154 9(10)	0.465 8(8)	−0.068 2(7)
C(4)	0.483 9(13)	−0.013 3(9)	0.282 2(10)	C(26)	−0.092 1(9)	0.511 2(8)	−0.120 2(7)
C(5)	0.492 7(11)	0.038 2(8)	0.217 2(8)	C(27)	−0.118 7(10)	0.598 3(9)	−0.153 2(8)
C(6)	0.566 0(11)	0.010 1(9)	0.167 7(8)	C(28)	−0.061 7(11)	0.638 7(9)	−0.205 0(8)
C(7)	0.630 0(11)	−0.070 5(10)	0.182 6(8)	C(29)	0.025 1(12)	0.586 4(9)	−0.220 4(8)
C(8)	0.696 1(13)	−0.098 7(9)	0.135 3(9)	C(30)	0.052 4(11)	0.499 8(10)	−0.181 1(9)

Table 3 Relevant bond distances (Å) and angles (°) involving co-ordination polyhedra

Sb(1)–F(1)	1.993(9)	Sb(2)–N(5)	2.715(10)
Sb(1)–F(2)	1.968(9)	Sb(2)–N(6)	2.622(12)
Sb(1)–F(3)	1.912(7)	Sb(2)–F(4)	1.963(10)
Sb(1)–N(1)	2.621(11)	Sb(2)–F(5)	1.963(8)
Sb(1)–N(2)	2.685(9)	Sb(2)–F(6)	1.904(7)
Sb(1)–N(3)	2.606(12)		
Sb(2)–N(4)	2.619(10)		
N(2)–Sb(1)–N(3)	61.1(3)	F(4)–Sb(2)–N(5)	136.8(3)
N(1)–Sb(1)–N(3)	122.5(3)	N(4)–Sb(2)–N(6)	121.2(4)
N(1)–Sb(1)–N(2)	61.5(3)	F(6)–Sb(2)–N(6)	83.4(3)
F(3)–Sb(1)–N(3)	83.8(4)	F(6)–Sb(2)–N(4)	80.2(3)
F(3)–Sb(1)–N(2)	74.5(3)	F(5)–Sb(2)–N(6)	75.7(4)
F(3)–Sb(1)–N(1)	81.0(3)	F(5)–Sb(2)–N(4)	156.4(4)
F(2)–Sb(1)–N(3)	77.2(4)	F(5)–Sb(2)–F(6)	86.1(4)
F(2)–Sb(1)–N(2)	135.1(4)	F(5)–Sb(2)–N(5)	134.0(3)
F(2)–Sb(1)–N(1)	154.3(4)	F(6)–Sb(2)–N(5)	75.7(3)
F(2)–Sb(1)–F(3)	85.6(4)	F(4)–Sb(2)–N(6)	156.5(3)
F(1)–Sb(1)–N(3)	158.8(3)	F(4)–Sb(2)–N(4)	77.9(3)
F(1)–Sb(1)–N(2)	134.3(3)	N(4)–Sb(2)–N(5)	60.5(3)
F(1)–Sb(1)–N(1)	74.6(3)	F(4)–Sb(2)–F(6)	87.0(4)
F(1)–Sb(1)–F(3)	87.3(3)	N(5)–Sb(2)–N(6)	60.7(3)
F(1)–Sb(1)–F(2)	83.0(3)	F(4)–Sb(2)–F(5)	82.3(4)

distances can be considered as belonging to two groups: apical ones with F(3) and F(6) have the shortest values 1.912(7) and 1.904(7) Å respectively, the remaining fluorines belonging to the basal planes all being in the range 1.963(8)–1.993(9) Å. The range of the F–Sb–F angles is 82.3(4)–87.3(3)°. The two sets of values compare well with those reported for apical and equatorial Sb–F bonds, respectively, in pyramidal (pseudo-octahedral) SbX$_5$E species such as, for example, trifluorobis(4-methoxypyridine *N*-oxide)antimony(III) hydrate[16] [1.905(5), apical; 1.968(6) Å, equatorial] and the already cited difluoro-(methoxydi-2-pyridylmethoxo-*N*,*N′*,*O*)antimony(III)[12] [1.967(4) Å, equatorial] and catecholatofluoro(1,10-phenanthroline)antimony(III)[13] [1.965(7) Å].

Bond distances and angles at Sb in both molecules are very similar (Table 3). The most relevant differences concern the terpyridine ligands: each of the six rings is planar, and in the molecule with Sb(1) the three rings are nearly coplanar, while the second terpy molecule deviates more significantly from planarity; the dihedral angles formed by the planes of these rings (numbering the rings according to the numbering of the nitrogens as 4, 5, 6) are 4–5 5.8(3), 4–6 12.6(3) and 5–6 15.1(3)°. These differences in ligand behaviour could be attributed to the packing forces generated by several carbon–carbon intermolecular contacts, some of which may be interpreted as weak hydrogen bonds.

Acknowledgements

The financial support of Ministero dell'Università e della Ricerca Scientifica e Tecnologica is acknowledged.

References

1 A. J. Edwards, *J. Chem. Soc. A*, 1970, 2751.
2 J. G. Ballard, T. Birchall, R. Fourcade and G. Mascherpa, *J. Chem. Soc., Dalton Trans.*, 1976, 2409.
3 G. Alonzo, M. Consiglio, F. Maggio and N. Bertazzi, *Inorg. Chim. Acta*, 1988, **147**, 217.
4 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
5 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.
6 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.
7 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.
8 M. C. Poore and D. R. Russell, *Chem. Commun.*, 1971, 18.
9 M. J. Begley, D. B. Sowerby and I. Haiduc, *J. Chem. Soc., Chem. Commun.*, 1980, 64; *J. Chem. Soc., Dalton Trans.*, 1987, 145.
10 B. F. Hoskins, E. R. T. Tienkink and G. Winter, *Inorg. Chim. Acta*, 1985, **97**, 217.
11 G. Bombieri, G. Bruno, F. Nicolò, G. Alonzo and N. Bertazzi, *J. Chem. Soc., Dalton Trans.*, 1987, 2451.
12 G. Alonzo, N. Bertazzi, G. Bombieri and G. Bruno, *J. Chem. Soc., Dalton Trans.*, 1987, 2337.
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 A. Lipka and H. Wunderlich, *Z. Naturforsch., Teil B*, 1980, **35**, 1548.
16 J. C. Dewan, A. J. Edwards, J. E. Guerchais and F. Petillon, *J. Chem. Soc., Dalton Trans.*, 1975, 2295.

Received 4*th April* 1991; *Paper* 1/01579F