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Synthesis and characterization of adducts of ethane-1,2-dithiolato-antimony(III) chloride. X-ray structure of the 1,10-phenanthroline derivative

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Abstract

In the metallacycle 1-chloro-2,5-dithiastibolane, $[Sb(SCH_2)_2Cl]$, antimony(III) conserves a residual coordination ability. Adducts with monodentate (dimethyl sulfoxide) and chelating (2,2′-bipyridine and 1,10-phenanthroline) ligands were obtained and characterized by IR spectra. The X-ray crystal structure of chloro(1,10-phenanthroline)(ethane-1,2-dithiolato[2−]−*S,S′*)antimony(III) has shown that two independent molecules are contained in asymmetric units. The coordination geometry about the antimony is distorted rectangular pyramidal without any intermolecular association.

Introduction

In antimony(III) complexes with thiolate anions, $Sb(SR)_3$ (R = organic group), three-coordinate in a pyramidal geometry, [1], or with S-donor neutral ligands, $Sb(SR)_nX_3$ ($n = 1,2$; X = halogen), essentially trigonal bipyramidal, the metal centre is able to expand the coordination number up to five and six. X-ray structures of xanthates, $Sb(S_2COR)_3$ [2–4], and pyridine-2-thiolates, $Sb(2\text{-}SC_5H_3N\text{-}3\text{-}R)_3$ (R = H, $Si(CH_3)_3$) [5, 6], show three intramolecular secondary bonds, Sb···S and Sb···N, respectively, in a distorted octahedral geometry. Even in the cyclic 1-chloro-4,5-dimethyl-4,5-didehydro-2-thiastibolane two intermolecular Sb···S contacts have been observed and the geometry about the antimony atom was described as square pyramidal [7]. Moreover intermolecular Sb···Cl contacts have been observed to accomplish the hexacoordination in trichloro[1,3-dimethyl-2-(3*H*)-imidazolethione]antimony(III) [8] and have been hypothesized on the basis of IR results for several sulfur donor heterocycles [9]. On the contrary, the structure of the 1-chloro-2,5-dithiastibolane, $[Sb(SCH_2)_2Cl]$, consists of discrete molecules with no significant intermolecular contacts [10], and for this compound complexes with Lewis bases have not been described. Analogous phenylene-1,2-diolato-antimonates(III), $C_6H_4O_2SbX$ (X = halogen) form penta- and hexacoordinate 1,10-phenanthroline complexes, whose structures have been studied [11–13]. Thus, in the course of our study on the coordination of metal- and organometal-thiolates [14, 15], we have synthesized several adducts of 1-chloro-2,5-dithiastibolane with O- and N-donor ligands and determined the crystal structure of the 1,10-phenanthroline derivative, chloro(1,10-phenanthroline)(ethane-1,2-dithiolato[2−]−*S,S′*)antimony(III).

Experimental

Reagents and solvents were commercial products used without further purification. Chloro(ethane-1,2-dithiolato[2−])antimony(III), $[Sb(SCH_2)_2Cl]$ (**I**), was obtained by mixing a water solution of antimony(III) chloride with ethanedithiol in ethanol as previously described [16].

Chloro(1,10-phenanthroline)(ethane-1,2-dithiolato[2−]-S,S′)antimony(III) (II) and chloro(2,2′-bipyridine)(ethane-1,2-dithiolato[2−]-S,S′)antimony(III) (III)

A methanol–benzene solution of the ligand was added to a refluxing benzene solution of **I**. A yellow solid formed immediately and the addition of the ligand was continued to reach the molar ratio 1:1. Suitable crystals

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for X-ray diffraction studies of the phenanthroline derivative were grown by slow evaporation of a methanolic solution. m.p. **II** 206–209 °C (with decomposition); **III** 204–207 °C (with decomposition). *Anal.* **II** Calc. for $C_{14}H_{12}ClN_2S_2Sb$: C, 39.14; H, 2.81; N, 6.52. Found: C, 38.9; H, 2.7; N, 6.3%. **III** Calc. for $C_{12}H_{12}ClN_2S_2Sb$: C, 35.54; H, 2.98; N, 6.91. Found: C, 35.7; H, 3.1, N, 7.0%.

Chloro(dimethyl sulfoxide)(ethane-1,2-dithiolato[2 –]-S,S')antimony(III) (IV)

This complex was prepared on cooling a hot almost saturated solution of **I**. The white solid was filtered and dried under reduced pressure. m.p. 94 °C. *Anal.* Calc. for $C_4H_{10}ClOS_3Sb$: C, 14.67; H, 3.08. Found: C, 14.8; H, 3.1%.

Oxo-bis(ethane-1,2-dithiolato[2 –]-S,S')antimony(III) (V)

A white amorphous solid formed on addition of water to a pyridine solution of **I**. The same solid was also recovered when pyridine was added to a suspension of **I** in ethanol and the mixture stirred for several hours. Decomposes at about 180 °C. *Anal.* for $C_4H_8S_4Sb_2O$: C, 10.82; H, 1.81. Found: C, 11.0; H, 1.9%.

The IR and far-IR spectra of the compounds dispersed in Nujol were recorded on a Nicolet 5SXC and a FAR 20F vacuum spectrometer, respectively. The relevant frequencies are reported in Table 1.

Crystallography

Yellow, transparent, needle shaped crystals of dimensions *c.* 0.15×0.2×0.5 mm were selected.

Crystal data

$C_{14}H_{12}ClN_2S_2Sb$, $M = 429.6$, triclinic, $a = 7.563(1)$, $b = 9.210(2)$, $c = 22.678(4)$ Å, $\alpha = 98.87(2)$, $\beta = 92.25(2)$, $\gamma = 100.62(2)°$, $U = 1533.3(5)$ Å^3, $F(000) = 840$, $Z = 4$, $D_c = 1.86$ g cm^{-3}, space group $P\bar{1}$, μ (Mo Kα) = 2.24 mm^{-1}. Intensity data were recorded at room temperature on an automatic Nicolet Siemens R3m/V diffractometer with graphite filtered Mo Kα radiation ($\lambda = 0.71073$ Å), using the ω–2θ scan procedure. A total of 7030 reflections was measured up to $2\theta = 55°$; of these 5329 were considered observed [$|F_o| > 3\sigma(F_o)$] and were used for the structure analysis. The integrated intensities were corrected for Lorentz and polarization effects and for absorption via a series of Ψ-scans at $\chi \simeq 90°$. The structure was solved by the heavy-atom method. The hydrogens were included in calculated positions with a common, variable isotropic thermal factor. Full-matrix least-squares refinement with anisotropic temperature factors to each non-hydrogen atom converged with agreement factors $R = 0.040$ and $R_w = 0.051$ (*GOF*:1.04; variables: 362). The quantity minimized was $\Sigma w(\Delta F)^2$, with $w = [\sigma^2(F) + 0.0018\,F^2]^{-1}$ and the largest peaks on a final difference map were of 1.1 e Å^{-3}, 0.8 Å away from Sb and Sb' atoms.

TABLE 1. Relevant IR frequencies (cm^{-1})

	I[a]	**II**	**III**	**IV**	**V**
Ligand absorptions					
H o.o.p. def.		727(vs)	760(s)		
		715(s)	730(m)		
o.o.p. ring def.		412(m)	408(s)		
ν(S=O)					925(s)
Sb–X absorptions					
ν_s(Sb–S)	360(s)	351(s)	348(s)	360(s)	380(m)
ν_{as}(Sb–S)	323(s)	301(s)	298(s)	335(m)	334(m)
ν_{as}(Sb–O)					380(vs)
ν_s(Sb–O)					334(vs)
ν(Sb–Cl)	260(vs)	215(s)	212(s)	214(s,br)	

[a] From ref. 21.

Final atomic positional coordinates, with e.s.d.s in parentheses, are listed in Table 2, while selected bond distances and angles are reported in Table 3. For additional data see 'Supplementary material'. Structure determination and refinement were performed with the SHELXTL-PLUS program system [17].

Results and discussion

The compound $[Sb(SCH_2)_2Cl]$ (**I**) is quite stable at room conditions. When freshly prepared, it completely dissolves in hot benzene or acetonitrile and better in Lewis bases. This fact and the preparation of tetra- and penta-coordinate complexes here described demonstrate its potential acceptor ability. Opalescent solutions are obtained if the product is not fresh, probably because of partial hydrolysis with consequent formation of the corresponding oxide. In fact the amorphous white solid obtained by adding water to a pyridine solution or an ethanolic suspension of **I** was identified as $[Sb(SCH_2)_2]_2O$ (**V**). The complexes of **I** with the chelating 1,10-phenanthroline (**II**) and 2,2'-bipyridine (**III**) were readily obtained as yellow solids by mixing the solutions of the substrate and the ligand. The monodentate dimethyl sulfoxide, used as solvent, gives the 1:1 adduct (**IV**). In the IR spectra (see Table 1) typical absorptions of the ligands can be easily identified referring to similar complexes [11–13, 18–20]. In particular the splitting upon coordination of the bipyridine (756 cm^{-1}) and phenanthroline (734 cm^{-1}) out of plane H deformation vibration bands is observed. For the adduct **IV** the dimethyl sulfoxide S=O stretching falls more

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U^a
Sb	9268(1)	6592(1)	3430(1)	38(1)
Cl	11571(2)	8720(2)	3149(1)	86(1)
S(1)	7282(2)	8272(1)	3743(1)	46(1)
S(2)	7598(2)	6055(2)	2439(1)	55(1)
N(1)	7043(5)	4453(4)	3782(2)	38(1)
N(2)	8937(5)	6698(5)	4644(2)	42(1)
C(1)	6577(8)	8623(6)	3016(3)	57(2)
C(2)	5888(8)	7189(7)	2588(3)	62(2)
C(3)	6112(7)	3371(5)	3381(2)	45(2)
C(4)	5077(7)	2076(6)	3515(3)	54(2)
C(5)	5009(7)	1893(6)	4097(3)	56(2)
C(6)	5946(6)	3015(6)	4547(2)	45(2)
C(7)	5861(7)	2937(7)	5171(3)	58(2)
C(8)	6718(7)	4057(7)	5589(2)	60(2)
C(9)	7788(6)	5378(6)	5436(2)	46(2)
C(10)	8671(8)	6568(7)	5853(2)	59(2)
C(11)	9661(8)	7793(8)	5670(3)	64(2)
C(12)	9782(7)	7810(6)	5063(3)	53(2)
C(13)	7936(6)	5490(5)	4821(2)	38(1)
C(14)	6976(6)	4300(5)	4373(2)	37(1)
Sb′	3449(1)	3048(1)	1578(1)	38(1)
Cl′	4802(2)	874(2)	1887(1)	59(1)
S(1′)	625(2)	1382(1)	1248(1)	41(1)
S(2′)	2078(2)	3752(2)	2523(1)	52(1)
N(1′)	2323(5)	5083(4)	1115(2)	41(1)
N(2′)	3118(6)	2668(5)	369(2)	47(1)
C(1′)	−150(7)	1122(6)	1977(2)	52(2)
C(2′)	−148(7)	2583(7)	2375(3)	57(2)
C(3′)	1938(7)	6255(6)	1465(3)	52(2)
C(4′)	1601(8)	7519(6)	1255(3)	64(2)
C(5′)	1619(8)	7561(6)	662(3)	65(2)
C(6′)	2017(7)	6358(6)	271(3)	52(2)
C(7′)	2086(8)	6324(8)	−361(3)	69(2)
C(8′)	2441(8)	5167(8)	−725(3)	72(2)
C(9′)	2806(7)	3880(7)	−495(2)	56(2)
C(10′)	3185(8)	2600(9)	−849(3)	74(2)
C(11′)	3483(7)	1416(8)	−607(3)	72(2)
C(12′)	3451(8)	1496(7)	8(3)	62(2)
C(13′)	2779(6)	3859(6)	128(2)	41(2)
C(14′)	2383(6)	5124(5)	519(2)	41(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Relevant bond lengths (Å) and bond angles (°)

	A	B
Sb–Cl	2.548(2)	2.585(2)
Sb–S(1)	2.399(2)	2.406(1)
Sb–S(2)	2.468(1)	2.467(1)
Sb–N(1)	2.593(4)	2.543(4)
Sb–N(2)	2.593(4)	2.706(5)
S(1)–C(1)	1.808(6)	1.811(6)
S(2)–C(2)	1.816(7)	1.812(5)
C(1)–C(2)	1.506(8)	1.500(8)
N(1)–C(3)	1.314(6)	1.322(7)
N(1)–C(14)	1.370(6)	1.360(6)
N(2)–C(12)	1.330(6)	1.320(7)
N(2)–C(13)	1.351(6)	1.358(7)
Cl–Sb–S(1)	91.3(1)	91.1(1)
Cl–Sb–S(2)	93.4(1)	97.4(1)
Cl–Sb–N(1)	176.3(1)	170.9(1)
Cl–Sb–N(2)	114.8(1)	108.3(1)
S(1)–Sb–S(2)	87.5(1)	87.0(1)
S(1)–Sb–N(1)	89.1(1)	89.2(1)
S(1)–Sb–N(2)	71.7(2)	72.2(2)
S(2)–Sb–N(1)	90.3(1)	91.6(1)
S(2)–Sb–N(2)	144.6(2)	146.8(2)
N(1)–Sb–N(2)	61.8(2)	63.2(2)
Sb–S(1)–C(1)	98.6(2)	98.0(2)
S(1)–C(1)–C(2)	111.8(4)	112.2(4)
S(2)–C(2)–C(1)	112.9(4)	112.9(4)
Sb–S(2)–C(2)	99.9(2)	100.8(2)
Sb–N(1)–C(14)	122.1(2)	121.2(3)
Sb–N(2)–C(13)	117.2(2)	116.1(2)

than 100 cm^{-1} lower than in the free ligand and is indicative of a coordination via oxygen [20]. The metal–sulfur stretching frequencies do not much shift from the values found for **I** [21] and are also close to those found for the pyridine-2-thiolates [6]. The Sb–Cl stretching is expected at values lower than 260 cm^{-1} found for **I** [21] and may be confidently attributed to the strong and broad band around 215 cm^{-1}, which is present in the spectra of the adducts **II**, **III** and **IV** but not **I** and **V**. The Sb–O and Sb–N are much more difficult to attribute: by comparison of the spectra of **I** and **V** we tentatively assign to the Sb–O stretching modes of the oxide **V** the strong bands centered at 321 and 265 cm^{-1}, whereas the Sb–N absorption is probably to be expected around or below 200 cm^{-1} [19], that is in a region with many and poorly defined bands.

The structure of chloro(1,10-phenanthroline)(ethane-1,2-dithiolato[2−]-*S*,*S*′)antimony(III) (**II**) consists of asymmetric units containing two independent molecules A and B. These have almost identical geometries (Fig. 1) and are roughly superimposable, r.m.s. deviation being 0.08 Å, when the coordination sphere is fitted (maximum deviation of 0.12 Å by N(2′)) (Fig. 2). The coordination geometry about the antimony is a distorted rectangular pyramid: the dithiolato ligand occupies an equatorial and an axial position, while the chlorine and the nitrogen donors of the phenanthroline ligand occupy the remaining equatorial sites. In this description N(1), N(2), S(2) and Cl atoms form the basis, S(1) being in the apical position (Fig. 3). The measure of the structural distortion from an idealized geometry is represented by the dihedral angle between normals to the trigonal bipyramidal faces (N(1) S(2) N(2) and S(2) N(2) Cl [22, 23]. In our case the dihedral angle has a value of 24.1°, to be compared to 53.1° for an idealized trigonal bipyramid and 0° for a square pyramid. With respect to the N_2SCl best basal planes, atoms Sb and Sb′ are displaced by 0.22 and 0.21 Å, respectively, in the direction opposite to the apical S(1) and S(1′) atoms. But what is more striking is the large deviation from

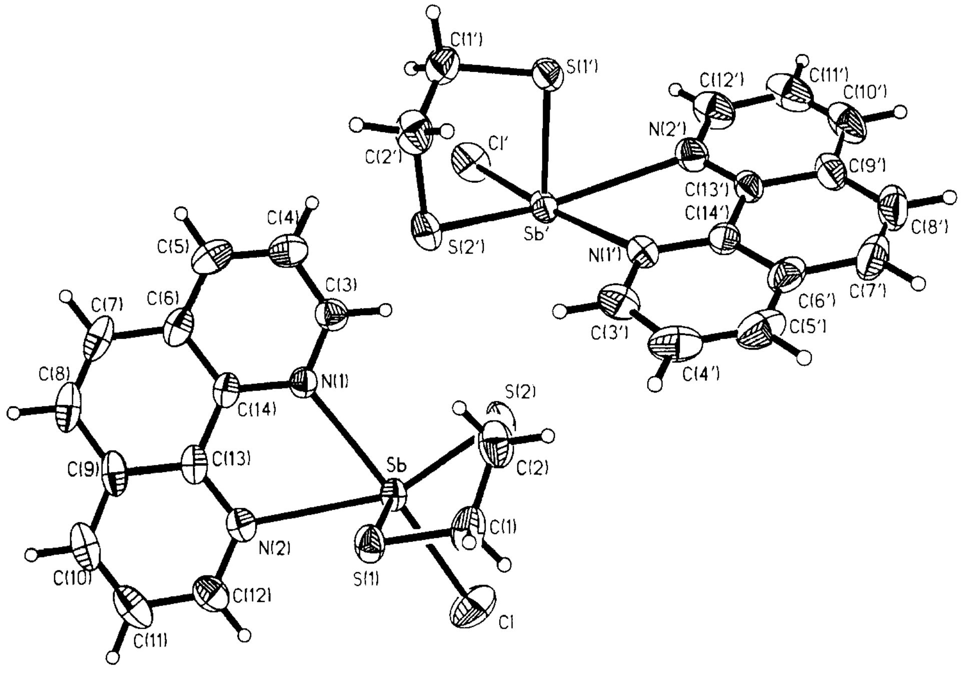

Fig. 1. ORTEP view of the asymmetric unit, showing the atom numbering and the thermal ellipsoid at the 40% probability level.

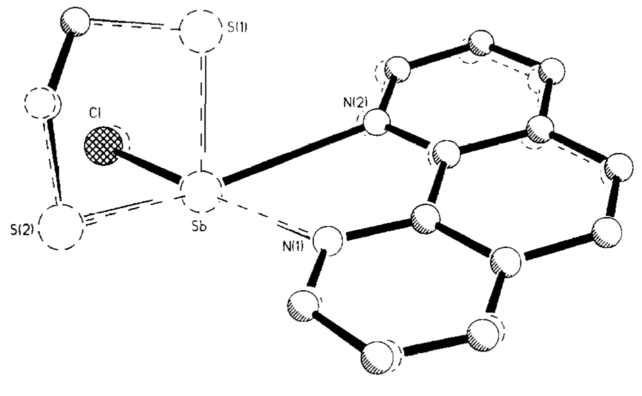

Fig. 2. Superimposition of A (——) with B (– – –).

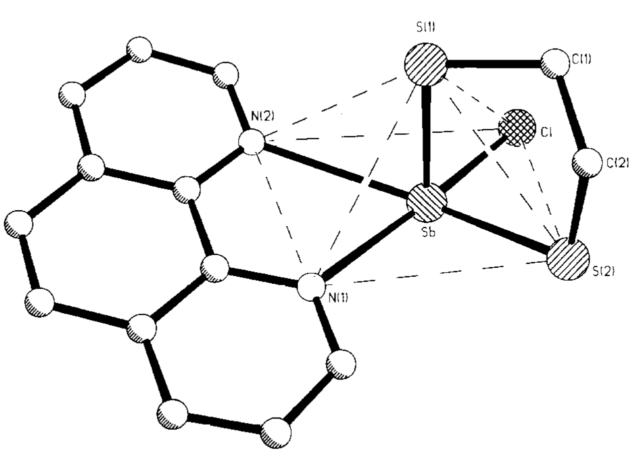

Fig. 3. Rectangular pyramidal geometry around Sb.

the ideal 90° angle observed for S(1)–Sb–N(2) angle (71.7 and 72.2° in A and B, respectively). The five-membered SbS_2C_2 rings adopt an envelope (C_s) conformation and form dihedral angles of 75.9 and 72.8° with the strictly planar phenanthroline ligands. The Sb–Cl bond (2.46 Å in **I**) is appreciably lengthened upon coordination (2.548(2) and 2.585(2) Å in A and B, respectively). Correspondingly a sensible lowering of the stretching vibration frequency is observed in the IR spectrum. The Sb–S(1) bond, *trans* to the gap locating the lone pair, is significantly shorter (2.399(2) and 2.406(1) Å in A and B, respectively) than Sb–S(2) (2.468(1) and 2.467(1) Å in A and B, respectively). These values recall that found in the parent compound **I** (2.41 Å) [10], the former being shorter and the latter longer. Similarly a shorter Sb–O bond *trans* to the assumed site of the lone pair has been found in fluoro(1,10-phenanthroline)(pyrocatecholato)antimony(III) [12]. On the other hand a lengthening upon coordination of the metal–sulfur bond has been observed in the corresponding five-membered rings SnS_2C_2 of the spirocyclic bis(ethane-1,2-dithiolato[2 –]-*S*,*S*′)-tin(IV) [15]. The Sb–N distances (2.593(4), 2.593(4) and 2.543(4), 2.706(5) Å in A and B are appreciably longer than the sum of the covalent radii (about 2.15 Å) and are in the range observed for other Sb(III)–phenanthroline complexes, e.g. fluoro(1,10-phenanthroline)(pyrocatecholato)antimony(III) (2.448(9) and 2.569(9) Å) [12], trifluoro(1,10-phenanthroline)-(thiourea)antimony(III) (2.556(3) and 2.731(3) Å) [24] and [catecholatobis(1,10-phenanthroline)anti-

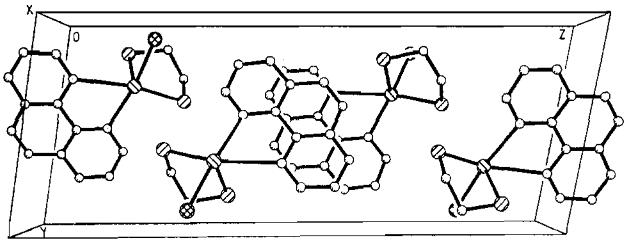

Fig. 4. Packing diagram

mony(III)]$^+$ (2.423(7), 2.592(5) and 2.467(7), 2.694(5) Å) [13]. The only notable difference in the molecules A and B is the chelating mode of the phenanthroline ligand: in A it chelates in a symmetrical way (both Sb–N distances of 2.593 Å), while in B in a very asymmetrical way. The lack of Sb–N distance equivalence in B is thought likely to be a result of packing effects, even if no intermolecular associations outside of the van der Waals type appear in the solid state (Fig. 4), whereas in the structure of the analogous trichloro(2,2′-bipyridine)antimony(III) intermolecular Sb···Cl contacts have been observed to accomplish a distorted octahedral geometry [25]. In conclusion it appears that in the heterocyclic dithiolate structure the antimony centre conserves a residual coordination ability with less tendency to the formation of secondary contacts than the corresponding acyclic thiolates or halides.

Supplementary material

Additional data, including anisotropic thermal parameters (Table A), hydrogen atoms coordinates (Table B), listing of bond lengths (Table C) and angles (Table D) and observed/calculated structure factors (Table E) are available from the authors.

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