Inorganica Chimica Acta, *74* (1983) 15–20

Haloxanthates of Antimony(III) and Bismuth(III): Crystal Structure of $Sb(S_2COEt)_2Br$

ROBERT W. GABLE, BERNARD F. HOSKINS*, ROBYN J. STEEN, EDWARD R. T. TIEKINK and GEORGE WINTER

Department of Inorganic Chemistry, University of Melbourne, Parkville, Vic., Australia, 3052

Received March 28, 1983

The complexes $Sb(S_2COEt)_2X$ *(X = Cl, Br, I) and* $Bi(S_2COEt)_2X$ *(X = Cl, Br) have been isolated as crystalline compounds. From infrared spectra and molecular weight determinations it is concluded that they are polymeric in the solid state but dissociate in solution. An X-ray structure determination of* $Sb(S_2COEt)_2Br$ *shows that the antimony atom is six coordinate, with the bromine atoms forming bridges between pairs of antimony atoms leading to a zigzag chain. The unit cell is monoclinic, space group* $P2_1/c$*, with* a = *10.769(2),* b = *16.462(2),* c = *8.360(2)* Å*, and* β = *110.71(2)°.*

Introduction

Polymeric metal xanthates are usually the result of bridging through the bidentate xanthate moiety (*i.e.* M–S–C–S–M bridges). The tendency for such polymers is particularly pronounced in the zinc, cadmium and mercury triad [1]. In sulphur, selenium and tellurium xanthates however, polymers are formed by relatively weak intermolecular interactions via M–S–M (M = central atom) bridges.

For haloxanthates the possibility of polymer formation through halogen bridges might be expected. In fact, this has been observed in $Te(S_2COEt)Br$, which has a helical structure in the solid state [2, 3]. Our studies have now been extended to antimony and bismuth of group V where the parent trisxanthates show no tendency to associate [1].

Results

The complexes $Bi(S_2COEt)_2X$, (X = Cl, Br) and $Sb(S_2COEt)_2X$ (X = Cl, Br, I) were prepared by the following methods:

$$2M(S_2COEt)_3 + X_2 \longrightarrow 2M(S_2COEt)_2X + (S_2COEt)_2$$

$$4M(S_2COEt)_3 + 2CuX_2 \longrightarrow 4M(S_2COEt)_2X + 2Cu(S_2COEt) + (S_2COEt)_2$$

$$MCl_3 + 2M(S_2COEt)_3 \longrightarrow 3M(S_2COEt)_2Cl$$

$$SbCl_3 + 2K(S_2COEt) \longrightarrow Sb(S_2COEt)_2Cl + 2KCl$$

The complexes are crystalline and thermally stable but susceptible to hydrolysis. Attempts to prepare the corresponding haloxanthates of arsenic were not successful. In this connection it is worth mentioning that for antimony and bismuth, the tetrakisxanthate ions [4, 5] and the mixed xanthate–dithiocarbamates [6, 7] are known, but the corresponding complexes of arsenic are not.

Except for the expected reduction in absorption intensity to approximately two thirds, the electronic spectra (due to transitions within the xanthate ligand) showed no significant differences from those of the corresponding parent trixanthates [4]. However this was not the case with the infrared studies. The CS_2 solution spectra of the haloxanthates closely resembled those of the parent trixanthate compounds whereas the solid state spectra differed markedly. Similar variations between solid and solution infrared spectra were observed for tellurium haloxanthates which exist as halide bridged polymeric compounds in the solid state [2, 3] but as monomers in solution.

A determination of the molecular weight by vapour pressure osmometry in chloroform was 470 (calculated 444) which is consistent with the presence of a monomeric species in solution.

Therefore a crystal structure determination of the complex $Sb(S_2COEt)_2Br$ (abbreviated as $Sb(xan)_2Br$) was initiated to investigate the nature of the compound in the solid state.

---

*Author to whom correspondence should be addressed.

0020-1693/83/$3.00

Crystallography

Crystals of Sb(xan)$_2$Br suitable for X-ray structural analysis were grown by the slow evaporation of a n-heptane solution. The crystals were pale yellow needles, elongated in the *c*-direction and the crystal chosen for structure analysis had approximate dimensions 0.10 mm X 0.10 mm X 0.75 mm.

Oscillation and equi-inclination Weissenberg photographs revealed the crystal to be monoclinic with systematic absences h0l : l = 2n + 1 and 0k0 : k = 2n + 1 unambiguously defining the space group as P2$_1$/c [8(a)].

The crystal was mounted on a Siemens automatic single crystal diffractometer so that its *c*-axis was coincident with the diffractometer ϕ axis. Accurate cell dimensions were obtained by a least squares method [9], using the 2θ values found for eleven well resolved, near axial reflections measured using Cu K_{α_1} radiation (λ = 1.54051 Å).

Intensity data were collected by means of a 'five-values' θ:2θ scan method [10], using Cu $K_{\bar{\alpha}}$ (nickel filtered) radiation (λ: 1.5418 Å) to a maximum Bragg angle of 70°. The intensity of a reference reflection was monitored after every twenty measurements. Due to some decomposition, the intensity data were corrected in accordance with the variation of the check reflection.

Reflections for which $I \leqslant 3\sigma(I)$ were rejected as unobserved. The intensity data were corrected for Lorentz and polarization effects and for absorption (max. and min. transmission coefficients 0.3233 and 0.1130) [8(b), 11]. After equivalent reflections were amalgamated there were 1971 unique reflections, with a R_{amal} of 0.044 where $R_{amal} = [\Sigma(N\Sigma(W(F_{(mean)} - F)^2))/\Sigma((N - 1)\Sigma(WF^2))]^{1/2}$; the inner summations are over N equivalent reflections averaged to give $F_{(mean)}$, the outer summations are over all unique reflections and the weight, W, taken as $(\sigma(F))^{-2}$.

Crystal data

$Sb(S_2COEt)_2Br$ – $C_6H_{10}BrO_2S_4Sb$, M 444.05, monoclinic, a = 10.769(2), b = 16.462(2), c = 8.360(2) Å, β = 110.71(2)°, U = 1386.33 Å^3, D_m = 1.09, Z = 4, D_{calc} = 1.128 Mg m^{-3}, F(000) = 848, space group P2$_1$/c (C_{2h}^5, No. 14), Cu $K_{\bar{\alpha}}$ (nickel filtered) 1.5418 Å, μ = 25.01 mm^{-1}, $0° < \theta < 70°$, absorption corrections applied, oscillation and Weissenberg photographs, Siemens automatic diffractometer.

The solution of the Patterson synthesis was not obvious due to the coincidence of heavy atom vectors. However, using the program EEES in SHEL-76 [11], the coordinates of the antimony atom were chosen. The set of structure factors calculated on the basis of these antimony coordinates gave a conventional R factor of 0.62 where $R = \Sigma\Delta F/\Sigma|F_o|$; $\Delta F = ||F_o| - |F_c||$. Subsequent difference maps enabled the location of all other non-hydrogen atoms. A full matrix least squares refinement that minimized the function $\Sigma w\Delta F^2$ was carried out on the scale factor, atomic coordinates and individual isotropic temperature factors which converged at R = 0.094. Refinement was continued with anisotropic temperature factors which yielded a R value of 0.068. Analysis of the data indicated $w(\Delta F)^2/n$ over a range of F_o was not constant, which did not conform to the criteria suggested by Cruickshank [12]. Hence the weight, w, was modified by the equation, $W = (\sigma^2(F) + |g|F^2)^{-1}$ were g was given a value 0.00005. At convergence R 0.068 and R_w 0.064 where $R_w = \Sigma w^{1/2}\Delta F/\Sigma w^{1/2}|F_o|$. At this stage an attempt was made to locate the positions of the hydrogen atoms but since only eight of the ten hydrogen atoms were revealed in the difference map none was included in the model. A final difference map revealed no peaks with heights greater than 0.67 e Å^{-3}.

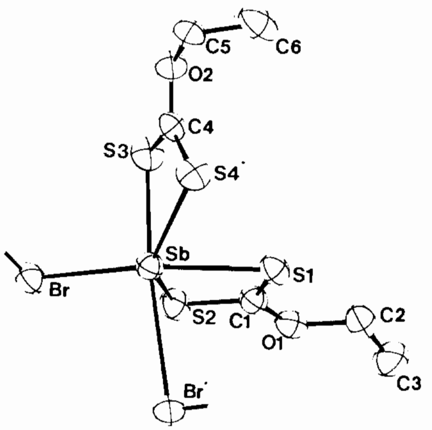

Fig. 1. Diagram showing the immediate coordination of the antimony atom and the numbering scheme used.

The scattering factors for C, O, S and Br were those collected by Sheldrick [11], while the scattering factors for atomic Sb were those given in ref. [8(c)], the value being corrected for both the real and imaginary anomalous dispersion terms, $\Delta f'$ and $\Delta f''$ [8(d)]. Structure determination and refinement were performed using the SHELX-76 program system [11].

The fractional atomic coordinates and their estimated standard deviations are given in Table II and the numbering scheme used is shown in Fig. 1. Listings of anisotropic temperature factors and of the observed and calculated structure factors derived from the final set of parameters have been deposited with the Editors.

Description of Structure

The structure determination confirmed the presence of a polymeric species in the solid state. As for the $Te(S_2COEt)Br$ complex the polymer is

TABLE I. Infrared Absorptions in the C–O and C–S regions (cm^{-1}).

		C–O	C–S
$Sb(S_2COEt)_3$*	solid	1230	1029
	solution	1218	1030
$Sb(S_2COEt)_2Cl$	solid	1278, 1259, 1240, 1215	1030, 1017, 999
	solution	1220	1033
$Sb(S_2COEt)_2Br$	solid	1275, 1256, 1234, 1214	1028, 1016, 998
	solution	1220	1033
$Sb(S_2COEt)_2I$	solid	1275, 1260, 1225	1030, 1017, 995
	solution	1221	1031
$Bi(S_2COEt)_3$*	solid	1210, 1190	1035, 1022
	solution	1210	1032
$Bi(S_2COEt)_2Cl$	solid	1276, 1247, 1230	1023, 1010, 999
	solution	1217	1034
$Bi(S_2COEt)_2Br$	solid	1275, 1245, 1228	1021, 1005, 999
	solution	1217	1033

*Ref. 4.

TABLE II. Fractional Atomic Coordinates. Estimated standard deviations in parentheses.

Atom	x/a	y/b	z/c
Sb	0.1725(1)	0.1939(1)	0.0554(1)
Br	0.3474(2)	0.1913(1)	0.3945(2)
S(1)	0.3262(4)	0.0803(3)	0.0479(5)
S(2)	0.0929(4)	0.1216(2)	–0.2543(5)
S(3)	0.0253(4)	0.1018(3)	0.1458(6)
S(4)	–0.1151(4)	0.2395(3)	–0.0778(6)
O(1)	0.2836(10)	0.0175(6)	–0.2464(14)
O(2)	–0.2175(10)	0.1382(7)	0.0773(14)
C(1)	0.2323(14)	0.0670(9)	–0.1679(20)
C(2)	0.2088(18)	–0.0025(12)	–0.4307(24)
C(3)	0.2953(21)	–0.0519(13)	–0.4967(29)
C(4)	–0.1144(14)	0.1593(9)	0.0481(19)
C(5)	–0.3482(14)	0.1742(11)	0.0044(21)
C(6)	–0.4241(17)	0.1413(11)	–0.1649(23)

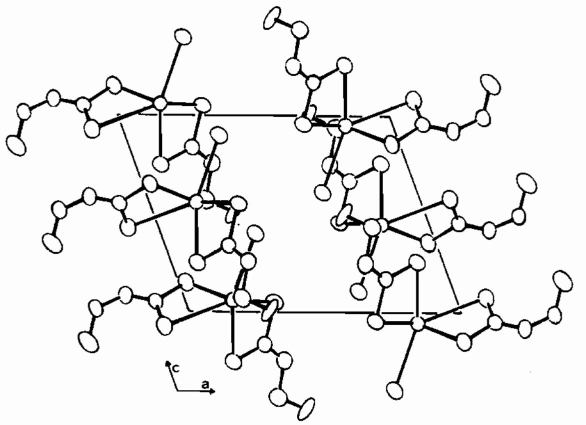

Fig. 2. The unit of cell of $[Sb(S_2COEt)_2Br]_n$ viewed down the [010] direction.

formed by bromine bridges between the metal atoms [2, 3]. However in this compound the polymer, which is generated by a *c*-glide symmetry operation on the asymmetric unit, forms a zigzag chain of antimony atoms bridged by bromine atoms. When the polymer is viewed along the antimony backbone of the chain, it is evident that the bromine atoms lie to one side of the chain and the xanthate groups lie on the other: this allows for the close approach of the antimony and bromine atoms (Fig. 2).

An inspection of Fig. 2 shows that no significant interchain interactions exist. However within a chain, a long Sb to S(2′) interaction is present where S(2′) is related by the symmetry operation $x, \frac{1}{2} - y, \frac{1}{2} + z$. The separation of 4.545(1) Å when compared with the sum of the van der Waals radii for antimony of 4.4 Å [13] indicates that there is no direct metal to metal interaction.

Apart from the polymeric nature of the solid the coordination geometry of the antimony atom is an interesting feature of the compound. The six coordinate atoms form a distorted octahedron about the antimony atom such that the donor atoms consist of two sets each of two sulphur atoms and a bromine atom and which define two approximately parallel triangles of unequal size as shown in Fig. 3.

The smaller triangle is defined by the atoms S(1), S(3) and Br which form the shorter set of bond distances to the antimony atom [2.513(5), 2.493(5) and 2.780(2) Å respectively] than those with the donor set comprising the larger triangle *viz.* S(2), S(4) and Br′ [2.685(4), 2.993(4) and 3.269(2) Å respectively] where Br′ is related by the symmetry operation $x, \frac{1}{2} - y, \frac{1}{2} + z$. This reflects the consider-

TABLE III. Interatomic Distances (Å). Estimated standard deviations are given in parentheses.

Atoms	Distance	Atoms	Distance	Atoms	Distance
Sb–Br	2.780(2)	S(1)–C(1)	1.732(16)	C(4)–O(2)	1.291(18)
Sb–S(1)	2.513(5)	S(2)–C(1)	1.678(15)	O(1)–C(2)	1.493(22)
Sb–S(2)	2.685(4)	S(3)–C(4)	1.719(15)	O(2)–C(5)	1.483(18)
Sb–S(3)	2.493(5)	S(4)–C(4)	1.683(16)	C(2)–C(3)	1.480(28)
Sb–S(4)	2.993(4)	C(1)–O(1)	1.284(18)	C(5)–C(6)	1.458(24)
Sb–Br′	3.269(2)	where Br′ is related by the symmetry operation x, ½ – y, ½ + z.			

TABLE IV. Intramolecular Bond Angles (degrees). Estimated standard deviations are given in parentheses.

Atoms	Angle	Atoms	Angle	Atoms	Angle
Br–Sb–S(1)	78.3(1)	Sb–S(2)–C(1)	83.9(6)	C(1)–O(1)–C(2)	119(1)
Br–Sb–S(2)	146.7(1)	Sb–S(3)–C(4)	93.8(5)	C(4)–O(2)–C(5)	121(1)
Br–Sb–S(3)	87.7(1)	Sb–S(4)–C(4)	78.3(5)	O(1)–C(2)–C(3)	108(1)
Br–Sb–S(4)	128.3(1)	S(1)–C(1)–S(2)	118.8(9)	O(2)–C(5)–C(6)	110(1)
S(1)–Sb–S(2)	68.7(1)	S(3)–C(4)–S(4)	122.4(9)	Br′*–Sb–S(1)	86.6(1)
S(2)–Sb–S(4)	79.6(1)	S(1)–C(1)–O(1)	114(1)	Br′–Sb–S(2)	84.2(1)
S(3)–Sb–S(4)	65.1(1)	S(2)–C(1)–O(1)	127(1)	Br′–Sb–S(3)	173.9(1)
S(1)–Sb–S(3)	92.8(2)	S(3)–C(4)–O(2)	113(1)	Br′–Sb–S(4)	112.0(1)
Sb–S(1)–C(1)	88.4(5)	S(4)–C(4)–O(2)	124(1)		

*Primed atoms related by the symmetry operation x, ½ – y, ½ + z.

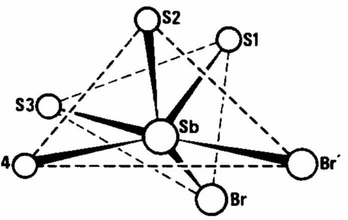

Fig. 3. An idealized view of the octahedral environment of the antimony atom looking down the pseudo three-fold axis.

able difference between the Sb–S distances associated with each xanthate ligand as well as the asymmetric nature of the –Br–Sb–Br′– bridging system. The observation that the bond angles subtended at the antimony atom all differ markedly from the ideal value of 90° is in keeping with the asymmetric nature of the bonding already noted together with the restricted bite distance of the xanthate ligand. All the relevant bond lengths and angles are given in Tables III and IV.

Except for the terminal methyl carbon, the ethyl xanthate ligands are found to be planar. The shortening of the C–O and C–S bonds relative to their normal single bond distances of 1.43 and 1.82 Å respectively [14], combined with the observed planarity suggests there is some delocalization over the ligand. The ligand geometry is consistent with that observed in previously determined ethylxanthate structures.

Whereas the asymmetry of the two C–S bonds is the same for all xanthate moieties in the antimony tris xanthate [15], there is a notable difference in the extent of asymmetry displayed by the two xanthate ligands of the bromo complex (Table III).

Discussion

The distorted octahedral environment described for the antimony atom in the $\mathrm{Sb(xan)_2Br}$ polymer is similar to that which has been noted for the $\mathrm{MX_6E}$ type compounds by Hoskins and Pannan [16]. For example, in the related tris xanthate complex, $\mathrm{Sb(xan)_3}$ [15] three sulfur atoms (one from each ligand) which comprise one of the triangular faces all form short antimony–sulphur bonds, whereas the sulphur atoms of the opposite octahedral face form longer, thus weaker bonds with the antimony atom. The geometry of the $\mathrm{Sb(xan)_2BrBr'}$ system can be considered to be derived from $\mathrm{Sb(xan)_3}$ by replacing one xanthate ligand with two bromine atoms. As might be expected, the two triangular faces of the antimony environment are no longer parallel as in $\mathrm{Sb(xan)_3}$, a result of the presence of the larger bromine atoms and bromine–bromine repulsions. One of the triangular faces has been enlarged which may be explained by the presence of a lone pair of electrons. This overall geometry is consistent with a capped octahedral arrangement of seven electron pairs about the central atom and since the lone pair can be visualised to protrude through one triangular face and thereby enlarging it, the observed elongation of the Sb–S and Sb–Br bonds associated with this face is to be expected.

Experimental

Halobis(O-ethylxanthato)antimonate(III)

Method 1

To antimony trisxanthate (2 g) in 50 ml dichloromethane was added 0.5 mol equivalents bromine, chlorine or iodine dissolved in carbon tetrachloride. After stirring for one hour (for the iodo complex the solution was allowed to stand overnight) the solution was evaporated under reduced pressure to give an oil which solidified on standing. The material was washed with 50 ml light petroleum to remove dixanthogen. The solid was then recrystallized from light petroleum (for the iodo complex chloroform/light petroleum was used).

Analyses for the chloro, bromo and iodo complexes, $Sb(S_2SOEt)_2X$, with calculated values in parentheses, were: C 18.2(18.0), 16.3(16.2), 14.8 (14.7); H 2.7(2.5), 2.3(2.3), 2.1(2.1); S 32.3(32.1), 28.8(28.9), 25.8(26.1); X 9.0(8.9), 18.3(18.0), 25.5% (25.8%).

Method 2

To antimony trisxanthate (2 g) in 50 ml dichloromethane was added 0.5 mol equivalents cupric chloride or cupric bromide. After stirring for 3 hours the mixture was filtered and the filtrate evaporated under reduced pressure, to a given oil which solidified on standing. The material was washed with light petroleum, to remove dixanthogen, and the solid recrystallized from light petroleum. The i.r. spectra of the products were identical to those obtained by method 1.

Method 3

To antimony trichloride (0.5 g) in 50 ml dichloromethane was added antimony trisxanthate (2.1 g) in 30 ml dichloromethane. After stirring for two hours the solution was evaporated under reduced pressure to give an oil which solidified on standing. The material was recrystallized from light petroleum. The i.r. spectrum of the product was identical to that obtained by method 1.

Method 4

To antimony trichloride (1 g) in 50 ml dichloromethane was added 2 mol equivalents potassium ethylxanthate. After stirring for two hours the mixture was filtered and the filtrate evaporated under reduced pressure to give an oil which solidified on standing. The material was recrystallized from light petroleum. The i.r. spectrum of the product was identical to that obtained by method 1.

Halobis(O-ethylxanthato)bismuthate(III)

Method 1

To bismuth trisxanthate (2 g) in 50 ml dichloromethane was added 0.5 mol equivalents chlorine or bromine, dissolved in carbon tetrachloride. After stirring for one hour, the solution was evaporated under reduced pressure to give an oil which solidified on standing. After washing with light petroleum to remove dixanthogen, the solid was then recrystallized from chloroform/light petroleum.

Analyses for the chloro and bromo complexes $Bi(S_2COEt)_2X$, with calculated values in parentheses were: C 14.7(14.8), 13.5(13.6); H 2.0(2.1), 2.0(1.9); S 26.4(26.3), 24.2(24.1); X 7.6(7.3), 15.3% (15.0%).

Method 2

To bismuth trisxanthate (2 g) in 50 ml dichloromethane was added 0.5 mol equivalent of cupric chloride or cupric bromide. After stirring for 3 hours the mixture was filtered and the filtrate evaporated under reduced pressure to give an oil which solidified on standing. The material was washed with light petroleum, to remove dixanthogen, and the solid recrystallized from chloroform/light petroleum. The i.r. spectra of the materials were identical to those obtained by Method 1.

Instrumentation

Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer. For the U.V. spectra a Unicam SP800B ultraviolet spectrophotometer was used.

Analyses

Analyses were performed by the Australian Microanalytical Service.

References

1 G. Winter, *Reviews in Inorganic Chemistry*, *2*, 253 (1980) and references therein.

2 R. W. Gable, B. F. Hoskins, R. J. Steen and G. Winter, *Inorg. Chim. Acta*, *65*, L127 (1982).

3 R. W. Gable, B. F. Hoskins, R. J. Steen and G. Winter, *Inorg. Chim. Acta, 72,* 173 (1983).

4 G. Winter, *Aust. J. Chem., 29,* 559 (1976).

5 D. L. Kepert, C. L. Raston, A. H. White and G. Winter, *Aust. J. Chem., 31,* 757 (1978).

6 F. M. N. Kheiri, C. A. Tsipis and G. E. Manoussakis, *Inorg. Chim. Acta, 25,* 223 (1977).

7 F. M. N. Kheiri, C. A. Tsipis, C. L. Tsiamis and G. E. Manoussakis, *Can. J. Chem., 57,* 767 (1979).

8 International Tables for X-ray Crystallography, (a) Vol. 1; (b) Vol. 4, p, 58; (c) Vol. 4, p. 100; (d) Vol. 4, p. 150, Kynoch Press, Birmingham, 1969, 1974.

9 W. R. Busing, R. D. Ellison, H. A. Levy, S. P. King and R. T. Roseberry, Oak Ridge National Laboratory Rep. ORNL-4143 (1968).

10 W. Hoppe, *Angew. Chem. Int. Ed. Engl., 6,* 508 (1965), 'Automatic Single Crystal Diffractometer AED According to W. Hoppe'; Users Manual for Siemens Automated Diffractometer, Siemens, Karlsruhe, 1967.

11 G. M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, 1976.

12 D. W. J. Cruickshank, 'Computing Methods in Crystallography', J. S. Rollett (Ed.), Pergamon Press, London, 1965.

13 A. Bondi, *J. Phys. Chem., 68,* 441 (1964).

14 L. Pauling, 'The Nature of the Chemical Bond', 3rd Ed., Cornell University Press, New York, 1960.

15 C. Gottardi, *Z. Krist., 115,* 451 (1961).

16 B. F. Hoskins and C. D. Pannan, *Aust. J. Chem., 29,* 2541 (1976).