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Heterocyclic Compounds Containing Antimony
1. Synthesis, Physicochemical Properties, Crystal and Molecular Structure of 2-(β-Hydroxyethylthio) 1,3,2-Oxathiastibolane

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Abstract

The compound $(HOCH_2CH_2S)\overline{Sb(SCH_2CH_2O)}$ (1) has been prepared by the reaction of antimony(III) isopropoxide and 2-mercaptoethanol in a 1:2 molar ratio. Reaction of 1 with $MOCH_3$ (where M = Li, Na and K) yields bimetallic products of the type, $M[(OCH_2CH_2S)\overline{Sb(SCH_2CH_2O)}]$. All these derivatives have been characterized by elemental analysis, IR, NMR (^1H and ^{13}C) spectra and molar conductivity measurements. Crystals of 1 are triclinic, space group $P\bar{1}$, with $a = 6.449(2)$, $b = 10.285(2)$, $c = 13.494(1)$ Å, $\alpha = 78.08(1)$, $\beta = 75.99(1)$, $\gamma = 71.54(2)°$, $V = 815.48$ Å^3, $Z = 4$, $D_{calc} = 2.239$ g cm^{-3}, (Mo Kα) $\lambda = 0.7107$ Å, $\mu = 3.55$ mm^{-1}, $F(000) = 528$, $T = 295$ K, final $R = 0.0189$ for 2344 reflections. One of the two mercaptoethanol moieties in 1 forms a five-membered chelate ring with antimony, Sb(1)–O(11) = 2.023(2) Å and Sb(1)–S(11) = 2.434(1) Å, while the other is bonded through the S atom only, Sb(1)–S(12) = 2.434(1) Å. The angles between these primary bonds with a mean value of 90.2° suggest a basically pyramidal, or pseudo tetrahedral structure if the stereochemically active lone pair is included in the coordination sphere. Two molecules are linked by intermolecular hydrogen bridges. The presence of weak intermolecular secondary bonding, Sb(1)–O(12) = 2.567(3) Å, in the complex indicates that the overall coordination polyhedron is best described in terms of a distorted trigonal bipyramidal arrangement.

Introduction

X-ray crystallographic investigations are providing ever increasing examples of the importance of 'secondary bonding' in structures of a variety of derivatives, particularly in carboxylates [1–7] and thiocarboxylates [1] of antimony(III). In view of this, it appears appropriate to elucidate the structures of unknown heterocyclic compounds $H[Sb(SCH_2CH_2S)_2]$ and $H[Sb(SCH_2CH_2O)_2]$. The structure of only one similar compound, $H[Sb(SCH_2COO)_2]$ [8], has been reported so far in which the presence of symmetric hydrogen bridges linking molecules into an endless chain has been suggested.

When an attempt was made to synthesize $H[Sb(SCH_2CH_2S)_2]$ by the reaction of $Sb(OPr^i)_3$ with ethylene dithiol in a 1:2 molar ratio in benzene, only the disproportionated product, $Sb_2[S_2(CH_2)_2]_3$, could be isolated, which was characterized by X-ray crystal structure analysis. The constitution of this compound could be best represented as having two bridged five-membered rings with different conformations: envelope and half chair; a literature search, however indicated that the structure of the compound had been reported recently [9].

In sharp contrast to the above, the reaction of $Sb(OPr^i)_3$ with 2-mercaptoethanol in a 1:2 molar ratio in benzene yields the product $H[\overline{Sb(SCH_2CH_2O})_2]$ (1). The synthesis and structure of 1 and its alkali metal derivatives are reported here.

Experimental

Moisture is carefully excluded throughout experimental manipulations. Antimony isopropoxide was prepared by the method of Brill and Campbell [10]. 2-Mercaptoethanol (Fluka, boiling point (b.p.) = 157 °C) and antimony trichloride (Sisco Chem Ind., b.p. = 78.80 °C, 10 mm) were distilled before use. Solvents (benzene, isopropanol, dichloromethane, hexane, acetonitrile, dimethyl sulfoxide, dimethylformamide and methanol) were dried by standard methods [11].

Antimony was estimated iodometrically [12] after converting it to antimony(V); sulphur was

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estimated gravimetrically as barium sulphate [13]. Isopropanol was estimated by the oxiditimetric method using standard chromic acid [14]. IR spectra were recorded as nujol mulls using KBr and CsI plates in the range of 4000–200 cm^{-1} on a Perkin-Elmer spectrophotometer model 577 and NMR spectra were recorded on a 90 MHz Jeol FX 90Q spectrometer in DMSO-d_6 solutions using TMS as an internal standard. The X-ray crystal structure determination was carried out on an Enraf Nonius CAD4 X-ray machine.

Reaction of Antimony Isopropoxide and 2-Mercaptoethanol in 1:2 Molar Ratio

The reaction of antimony isopropoxide (4.55 g, 15.22 mmol) with 2-mercaptoethanol (2.40 g, 30.71 mmol) in a 1:2 molar ratio in refluxing benzene for about 7 h (completion of the reaction was checked by estimating the isopropanol collected azeotropically with benzene) yielded a white solid product, after removal of solvent under vacuum. The product was further purified by crystallization from acetonitrile. Analytical details are summarized in Table 1.

Reaction of 2-(β-Hydroxyethylthio) 1,3,2-Oxathiastibolane and Lithium Methoxide in 1:1 Molar Ratio

A methanol solution of lithium methoxide (prepared by dissolution of 0.028 g lithium, 4.03 mmol in excess methanol) was added to a suspension of 2-(β-hydroxyethylthio) 1,3,2-oxathiastibolane (1.11 g, 4.05 mmol). The mixture was refluxed for ~1 h until a clear solution was obtained. Excess methanol was removed under vacuum, giving a yellow coloured solid and the resultant product was washed with dichloromethane. The other alkali metal derivatives were also prepared using a similar procedure and the details are summarized in Table 1.

Results and Discussion

2-(β-Hydroxyethylthio) 1,3,2-oxathiastibolane (**1**) has been prepared by the reaction of antimony isopropoxide with 2-mercaptoethanol in a 1:2 molar ratio in refluxing benzene.

$$Sb(OPr^i)_3 + 2HOCH_2CH_2SH \xrightarrow{C_6H_6} H[\overline{Sb(SCH_2CH_2O})_2] + 3Pr^iOH$$

The above reaction is quite facile and two moles of isopropanol could be collected easily. However, the removal of the third mole of isopropanol could be accomplished only after prolonged refluxing for 7–8 h in benzene. Progress of the above reaction is followed by estimating the liberated isopropanol azeotropically. The above complex **1** is soluble only in DMF, DMSO and CH_3CN. Reactions of **1** in a 1:1 molar ratio with alkali metal methoxide in

TABLE 1. Physical characteristics and analytical data of 2-(β-hydroxyethylthio) 1,3,2-oxathiastibolane and its alkali metal derivatives

No.	Reactants (g)	Molar ratio	Product	Yield found (calc.) (g)	Yield (%)	Physical state and colour	Melting point (°C)	Analyses: found (calc). (%)		Conductivity (ohm^{-1} cm^2 mol^{-1})
								Antimony	Sulfur	
1	$Sb(OPr^1)_3$ + $HOCH_2–CH_2–SH$ (4.55) (2.40)	1:2	$H[\overline{Sb(SCH_2CH_2O})_2]$	4.011 (4.088)	97.91	White solid	156(D)	44.20 (44.28)	23.29 (23.32)	13.91
			$3Pr^iOH$	2.654 (2.745)						
2	$H[\overline{Sb(SCH_2CH_2O})_2]$ + LiOMe (1.14) (0.028)	1:1	$Li[\overline{Sb(SCH_2CH_2O})_2]$	1.176 (1.186)	99.57	Yellow solid	100	43.11 (43.34)	22.32 (22.83)	22.53
3	$H[\overline{Sb(SCH_2CH_2O})_2]$ + NaOMe (5.08) (0.42)	1:1	$Na[\overline{Sb(SCH_2CH_2O})_2]$	5.399 (5.481)	98.52	Yellow solid	124	38.39 (38.89)	20.18 (20.48)	28.84
4	$H[\overline{Sb(SCH_2CH_2O})_2]$ + KOMe (2.89) (0.41)	1:1	$K[\overline{Sb(SCH_2CH_2O})_2]$	3.255 (3.288)	99.56	Yellow solid	125	40.90 (41.00)	21.50 (21.59)	24.57

D = decomposed.

TABLE 2. IR and NMR (^1H and ^{13}C) of 2-(β-hydroxyethylthio) 1,3,2-oxathiastibolane and its alkali metal complexes

Products	1	2	3	4	5^a
IR bands (cm^{-1})					
νOH	3100br				3050br, 2600 (νSH)
νC–S	1270m	1260m	1270m	1270m	1250m
νC–O	1030m	1030m	1030m	1030m	1050br
νSb–OC stretching	540m	560m	560m	550m	
νSb–OC bending	340w	330w	320w	335w	
νSb–SC bending	270w	280w	270w	270w	
νSb–SC stretching	465m	455m	470m	465m	
^1H NMR chemical shifts (δ ppm)					
$-H_2C-O$	2.9t	2.5t	2.5t	2.8t	3.8t($CDCl_3$)/3.5t(DMSO d_6)
$-H_2C-S-$(ring)	2.9t	2.5t	2.5t	2.8t	
$-H_2C-S-$(open chain)	3.7br	3.8t	3.4t	3.3t	2.8dt($CDCl_3$/2.5t(DMSO d_6)
$-H_2C-OM$		3.9t	4.0t	3.7t	
–OH	6.4s				3.8t($CDCl_3$)/4.8s(DMSO d_6)
–SH					1.5t($CDCl_3$)/1.75g(DMSO d_6)
^{13}C NMR chemical shift (δ ppm)					
$-CH_2-O-$	66.91s	67.49s	66.05s	65.99s	64.06s(DMSO d_6)
$-CH_2-S-$	31.92s	34.19s	32.89s	32.89s	27.50s(DMSO d_6)

br = broad, m = medium, s = sharp, w = weak, vw = very weak, s = singlet, dt = double triplet, t = triplet. ^{a} = 2-Mercapto-ethanol ($HSCH_2CH_2OH$).

methanol are quite facile and yield products of the type $M[\overline{Sb(SCH_2CH_2O})_2]$ (2–4) which are also soluble in methanol.

$$H[\overline{Sb(SCH_2CH_2O})_2] + MOCH_3 \xrightarrow{CH_3OH} M[\overline{Sb(SCH_2CH_2O})_2]$$

(M = Li (2), Na (3), K (4))

To ensure completion of the above reactions, the contents were refluxed for about 1 h. All the above 2-mercaptoethanol derivatives are white or light yellow solids which are soluble in CH_3OH, DMSO and DMF solvents but are insoluble in C_6H_6, $CHCl_3$ and CH_2Cl_2. The molar conductance values of these complexes in 0.001 M DMF solutions are summarized in Table 1, which as expected suggest considerable ionic character for all these complexes [15].

Important bands in the IR spectra of all the above derivatives as well as of the ligand are summarized in Table 2. These assignments have been made on the basis of relevant literature on derivatives of the type $Sb(YR)_3$ (where Y = O or S and R = alkyl or aryl) [10] and on the free 2-mercaptoethanol ligand [16]. A perusal of Table 2 indicates that bands due to –SH and –OH groups in the regions 3000–3200 and 2700–2100 cm^{-1} respectively, present in the free ligand are absent in complexes 2 to 4. However, complex 1 shows the presence of a broad band at 3100 cm^{-1} due to νOH. The bands at 1250 and 1050 cm^{-1} present in the free ligand have been assigned to νC–S and νC–O respectively. These bands have also been observed in the IR spectra of all the above complexes. The weak intensity bands in the regions 560–540, 340–320, 470–455 and 280–270 cm^{-1} in all these complexes may be assigned to Sb–OC stretching and bending, Sb–SC stretching and bending vibrations respectively.

A comparison of ^1H NMR spectra of 2-mercapto-ethanol (in $CDCl_3$[16] and DMSO-d_6) with the spectra of the above complexes (Table 2) reveals many interesting features:

(i) The number of ^1H NMR signals and their integration correspond to the formula suggested for these derivatives.

(ii) In the ^1H NMR spectrum of 2-mercaptoethanol in DMSO-d_6, the appearance of two singlets at δ 1.75 and δ 4.8 ppm and two triplets at δ 2.5 and δ 3.5 ppm could be assigned to –SH, –OH, $-H_2C-S-$ and $-H_2C-O-$ protons respectively [16]. However in the spectrum of complex 1 in DMSO-d_6, only two triplets at δ 2.9 and δ 3.7 ppm and a singlet at δ 6.4 ppm were observed which may be assigned to ring protons, methylene protons ($-S-CH_2-CH_2-OH$) of the open chain ligand moiety and –OH protons respectively. Absence of a signal due to –SH protons around δ 1.75 ppm in the spectrum suggests the formation of Sb–S bonds in the above complex. In the case of complexes 2, 3 and 4, the spectra exhibit three triplets at δ 2.5–2.8, δ 3.3–3.8 and δ 3.7–4.0 ppm, which may be due to methylene protons of the heterocyclic ring, and $-CH_2-S-Sb\!<$ and $-CH_2-O-M$ protons respectively. The

^{1}H NMR spectra of these complexes do not show signals due to free –SH or –OH protons around δ 1.75 and δ 4.8 ppm indicating the formation of these derivatives.

(iii) ^{13}C NMR spectra of these derivatives exhibit the expected number of signals at 65.99–67.49 and 31.92–34.19 ppm which may be due to $-H_2C-O$ and $-H_2C-S$ groups respectively. The above studies appear to suggest that complex **1** has a coordination number three while complexes 2, 3 and 4 have tetra-coordination around antimony.

Crystal Structure of $H[\overline{Sb(SCH_2CH_2O})_2]$

Crystal data

M = 278.64, triclinic, space group $P\bar{1}$, a = 6.449(2), b = 10.285(2), c = 13.494(1) Å, α = 78.08(1), β = 75.99(1), γ = 71.54(2)°, V = 815.48 Å^3, Z = 4, D_{calc} = 2.239 g cm^{-3}, (Mo Kα) λ = 0.7107 Å, μ = 3.55 mm^{-1}, F(000) = 528, T = 295 K; final R = 0.0189 for 2344 reflections.

The structure was solved by direct methods using MULTAN-84 MAIN GERMAIN, WOOLFSON 1984 and refined by the least-squares methods based on F values using SHELX-76, Sheldrick-1976. The atomic scattering factors for Sb are taken from the International Tables for X-ray Crystallography (1974) and those of other atoms from SHELX-76. All the non-H atoms were refined with anisotropic thermal parameters and H atoms, located from difference Fourier maps, were refined isotropically. A total of 235 parameters was refined by using 2344 observed reflections with $|F_o| \geqslant 5\sigma|F_o|$. Final R = 0.0189 and R_w = 0.0249 where $\omega = [k/\sigma^2(F_o) + g(F_o)^2]$ with k = 0.5424 and g = 0.004. In the final difference Fourier map, ΔP_{max} = 0.505 and ΔP_{min} = -0.459 Å^3, $(\Delta/\sigma)_{max}$ = 0.258, CYBER-180 was used for all the computations.

TABLE 3. Atomic coordinates (×10^4, ×10^5 for Sb) and equivalent temperature factors U_{eq} (Å^2 × 10^3) for non-H atoms with e.s.d.s in parentheses

Atom	x	y	z	U_{eq}^{a}
Molecule 1				
Sb(1)	52364(4)	29652(2)	11186(4)	28(1)
S(11)	6863(1)	3336(1)	9294(1)	36(1)
S(12)	5813(2)	475(1)	11329(1)	41(1)
O(11)	2422(4)	3175(3)	10615(2)	37(2)
O(12)	9239(4)	1921(3)	11437(2)	43(2)
C(11)	4587(7)	3050(5)	8885(3)	48(2)
C(12)	2439(5)	3642(4)	9548(3)	43(2)
C(13)	10042(5)	451(4)	11453(3)	42(2)
C(14)	8135(6)	−138(4)	11992(3)	41(2)
Molecule 2				
Sb(2)	93164(4)	20334(2)	38839(2)	29(1)
S(21)	9491(2)	1667(1)	15706(1)	37(1)
S(22)	7611(1)	4524(1)	13668(1)	42(1)
O(21)	6200(4)	1838(3)	14401(2)	40(2)
O(22)	12588(4)	3081(3)	13561(2)	41(2)
C(21)	6523(6)	1972(5)	16115(3)	51(2)
C(22)	5616(5)	1356(4)	15468(4)	48(2)
C(23)	10001(6)	5140(4)	13009(3)	44(2)
C(24)	11927(5)	4557(4)	13537(3)	42(2)

$^aU_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j(\mathbf{a}\cdot\mathbf{a}_j)$.

TABLE 4. Bond distances (Å) and bond angles (°) with e.s.d.s in parentheses

Molecule 1		Molecule 2	
S(11)–Sb(1)	2.434(1)	S(21)–Sb(2)	2.435(1)
S(12)–Sb(1)	2.434(1)	S(22)–Sb(2)	2.433(1)
O(11)–Sb(1)	2.023(2)	O(21)–Sb(2)	2.021(2)
C(11)–S(11)	1.810(4)	C(21)–S(21)	1.802(4)
C(14)–S(12)	1.805(3)	C(23)–S(22)	1.814(3)
C(12)–O(11)	1.419(5)	C(22)–O(21)	1.422(5)
C(13)–O(12)	1.432(5)	C(24)–O(22)	1.437(5)
C(12)–C(11)	1.477(6)	C(22)–C(21)	1.488(6)
C(14)–C(13)	1.505(5)	C(24)–C(23)	1.481(5)
O(12)–Sb(1)	2.567(3)	O(22)–Sb(2)	2.569(2)
S(12)–Sb(1)–S(11)	98.9(1)	S(22)–Sb(2)–S(21)	99.0(1)
O(11)–Sb(1)–S(11)	84.8(1)	O(21)–Sb(2)–S(21)	84.6(1)
O(11)–Sb(1)–S(12)	86.9(1)	O(21)–Sb(2)–S(22)	86.8(1)
C(11)–S(11)–Sb(1)	93.5(1)	C(21)–S(21)–Sb(2)	93.3(1)
C(14)–S(12)–Sb(1)	100.6(1)	C(23)–S(22)–Sb(2)	100.9(1)
C(12)–O(11)–Sb(1)	116.6(2)	C(22)–O(21)–Sb(2)	117.0(2)
C(12)–C(11)–S(11)	110.8(3)	C(22)–C(21)–S(21)	111.1(3)
C(11)–C(12)–O(11)	113.2(3)	C(21)–C(22)–O(21)	111.5(3)
C(14)–C(13)–O(12)	107.3(3)	C(24)–C(23)–S(22)	113.2(3)
C(13)–C(14)–S(12)	113.0(3)	C(23)–C(24)–O(22)	107.5(3)

TABLE 5. Anisotropic thermal parameters for non-hydrogen atoms with respective e.s.d.s given below

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Molecule 1						
Sb(1)	0.0253	0.0297	0.0297	−0.0005	−0.0043	−0.0110
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
S(11)	0.0309	0.0388	0.0351	−0.0006	−0.0007	−0.0139
	0.0004	0.0005	0.0005	0.0004	0.0003	0.0004
S(12)	0.0380	0.0320	0.0593	0.0057	−0.0200	−0.0190
	0.0004	0.0005	0.0006	0.0004	0.0004	0.0004
O(11)	0.0274	0.0398	0.0418	0.0062	−0.0075	−0.0143
	0.0008	0.0009	0.0009	0.0008	0.0008	0.0008
O(12)	0.0310	0.0481	0.0543	0.0014	−0.0103	−0.0228
	0.0008	0.0009	0.0010	0.0009	0.0008	0.0008
C(11)	0.0595	0.0608	0.0359	−0.0039	−0.0166	−0.0301
	0.0011	0.0011	0.0010	0.0010	0.0010	0.0010
C(12)	0.0306	0.0502	0.0530	0.0062	−0.0206	−0.0170
	0.0010	0.0011	0.0011	0.0010	0.0009	0.0009
C(13)	0.0242	0.0475	0.0551	−0.0113	−0.0083	−0.0092
	0.0009	0.0011	0.0011	0.0010	0.0009	0.0009
C(14)	0.0452	0.0323	0.0489	0.0070	−0.0242	−0.0109
	0.0010	0.0010	0.0010	0.0010	0.0009	0.0009
Molecule 2						
Sb(2)	0.0258	0.0306	0.0305	−0.0007	−0.0091	−0.0080
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
S(21)	0.0364	0.0407	0.0353	−0.0002	−0.0148	−0.0118
	0.0004	0.0005	0.0005	0.0004	0.0005	0.0004
S(22)	0.0250	0.0327	0.0600	0.0053	−0.0094	−0.0050
	0.0004	0.0005	0.0006	0.0004	0.0004	0.0003
O(21)	0.0272	0.0489	0.0473	0.0030	−0.0135	−0.0174
	0.0008	0.0009	0.0009	0.0009	0.0008	0.0008
O(22)	0.0245	0.0467	0.0520	0.0039	−0.0142	−0.0134
	0.0008	0.0009	0.0010	0.0009	0.0008	0.0008
C(21)	0.0392	0.0569	0.0397	−0.0074	0.0011	0.0036
	0.0010	0.0011	0.0011	0.0010	0.0010	0.0010
C(22)	0.0247	0.0487	0.0649	0.0108	−0.0077	−0.0157
	0.0010	0.0011	0.0011	0.0010	0.0010	0.0009
C(23)	0.0346	0.0400	0.0535	0.0053	−0.0025	−0.0167
	0.0010	0.0010	0.0011	0.0010	0.0010	0.0009
C(24)	0.0259	0.0467	0.0593	−0.0077	−0.0059	−0.0182
	0.0009	0.0010	0.0011	0.0010	0.0009	0.0009

Discussion of the structure

For the complex $H[\overline{Sb(SCH_2CH_2O)}_2]$ the atomic coordinates and equivalent temperature factors for non-hydrogen atoms with estimated standard deviations (e.s.d.s) in parentheses have been summarized in Table 3, while bond distances and angles are given in Table 4. Anisotropic thermal parameters for the non-hydrogen atoms with respective e.s.d.s are given in Table 5, and atomic coordinates and isotropic factors (Å^2) for H atoms with respective e.s.d.s in Table 6. The numbering of the atoms in two molecules is shown in Fig. 1.

In complex **1**, antimony is surrounded by two sulfur atoms and one oxygen atom as its nearest neighbours. The two Sb–S bonds are closely similar with mean distance of 2.434 Å, which is quite comparable with the reported values of Sb–S distances of 2.487, 2.469 and 2.43 Å in antimony(III) diethyldithiocarbamate [17], thioacetate [1] and hydrogen bis(thioglycolate) [8], respectively. The difference in two Sb–O distances, Sb(1)–O(11) = 2.023(2) Å and Sb(1)–O(12) = 2.567(3) Å is quite significant. The former 2.023(2) Å is comparable to that in $[Sb(O_2CMe)_3]$ [1] (2.059 Å) and $[Sb(O_2CCF_3)_3]$ [6] (2.043 Å), but significantly shorter than that in $[Ph_2Sb(O_2CMe)]$ [4] (2.137 Å), which might be ascribed to the inductive effect of two phenyl groups attached directly to antimony in the last derivative. Thus, the Sb(1)–S(11) and Sb(1)–O(11) distances of 2.434(1) and 2.023(2) Å suggest the formation of a five-membered chelate ring in complex **1**. However, the larger Sb(1)–O(12) distance of 2.567(3) Å in-

TABLE 6. Atomic coordinates and isotropic temperature factors (Å^2) for H atoms with respective e.s.d.s given below

Atom	x	y	z	U_{iso}	Atom	x	y	z	U_{iso}
Molecule 1					Molecule 2				
H(1)	0.0375	0.2316	1.1150	0.0401	H(2)	0.3883	0.2811	1.3772	0.0441
	0.0012	0.0012	0.0011	0.0012		0.0012	0.0012	0.0011	0.0012
H(111)	0.4654	0.3514	0.0199	0.0394	H(211)	−0.4241	0.2953	1.6112	0.0407
	0.0012	0.0012	0.0011	0.0012		0.0012	0.0012	0.0011	0.0012
H(112)	0.4650	0.2177	0.8903	0.0413	H(212)	−0.3681	0.1350	1.6800	0.0943
	0.0012	0.0012	0.0011	0.0012		0.0012	0.0012	0.0012	0.0012
H(121)	0.1257	0.3425	0.9469	0.0404	H(221)	0.4304	0.1533	1.5616	0.0604
	0.0012	0.0012	0.0011	0.0012		0.0012	0.0012	0.0011	0.0012
H(122)	0.2072	0.4657	0.9394	0.0442	H(222)	−0.3912	0.0314	1.5614	0.0949
	0.0012	0.0012	0.0011	0.0012		0.0012	0.0012	0.0012	0.0012
H(131)	1.0562	0.0182	1.0795	0.0507	H(231)	0.9517	0.6078	1.3145	0.0379
	0.0012	0.0012	0.0011	0.0012		0.0012	0.0012	0.0011	0.0012
H(132)	1.1201	0.0178	1.1968	0.0648	H(232)	1.0241	0.5019	1.2292	0.0709
	0.0012	0.0012	0.0011	0.0012		0.0017	0.0012	0.0012	0.0012
H(141)	0.7593	−0.0015	1.2876	0.0732	H(241)	1.3346	0.4828	1.3136	0.0409
	0.0012	0.0012	0.0012	0.0012		0.0012	0.0012	0.0011	0.0012
H(142)	0.8660	−0.1056	1.1985	0.0380	H(242)	1.1597	0.4650	1.4245	0.0663
	0.0012	0.0012	0.0011	0.0012		0.0012	0.0012	0.0012	0.0012

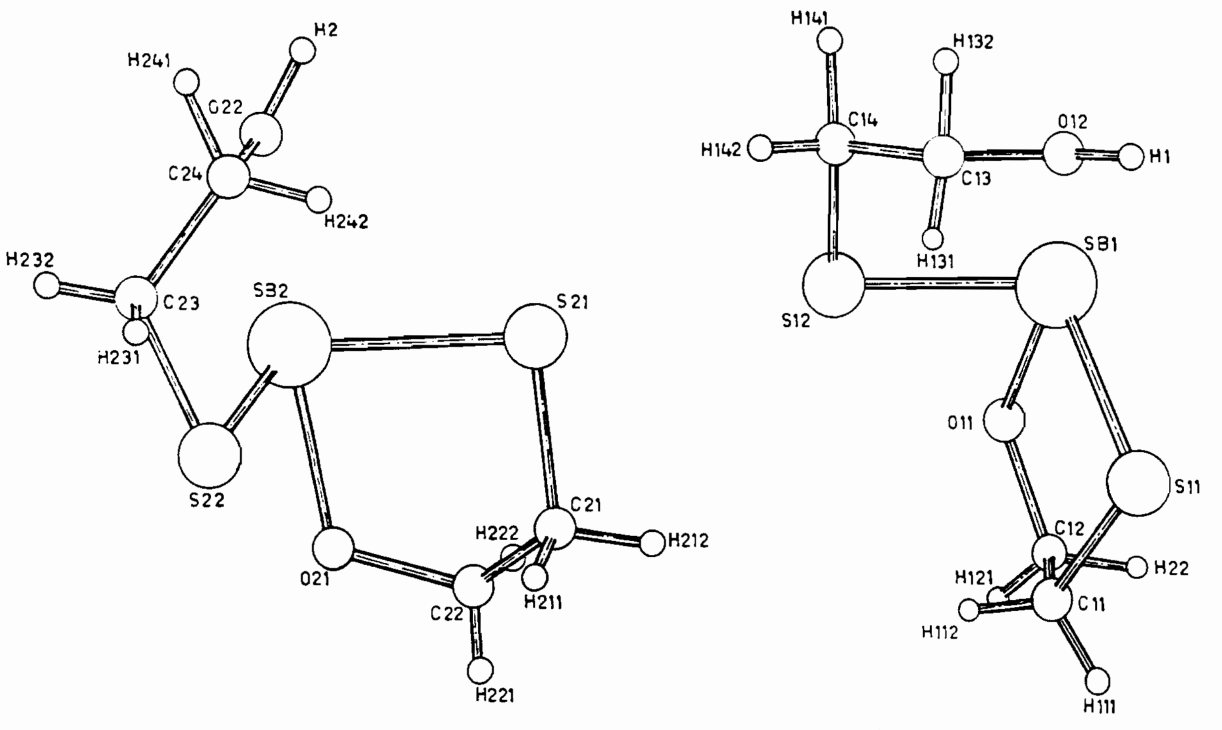

Fig. 1. Molecular structures and numbering of the atoms in two molecules of $H[\overline{Sb(SCH_2CH_2O)_2}]$.

dicates the presence of secondary bonding in it. (It has been reported [1] that secondary bonding involves donation of some electron density from oxygen to antimony with distances ranging between 2.60 and 3.04 Å.) This value, however, is considerably shorter than the reported values of 2.81 Å in $[Sb(SOCMe)_3]$ [1] and 2.67 Å in $[Sb(O_2CMe)_3]$ [1] which indicates stronger 'secondary' antimony–oxygen interaction although the chelate ring remains unsymmetrical.

The X-ray crystal structure of complex 1 also shows the presence of intermolecular hydrogen bonding (Fig. 2). Here the hydrogen bonding is limited to between two molecules, whereas in the

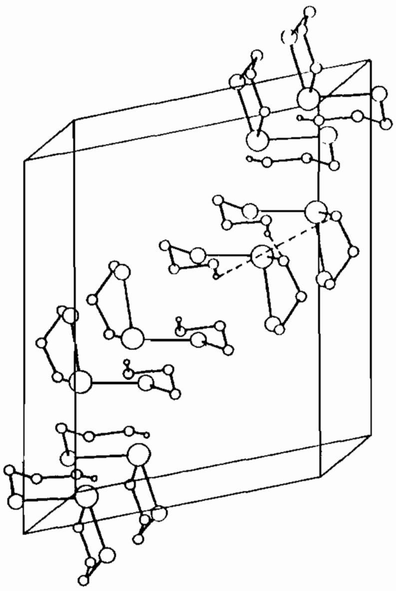

Fig. 2. Unit cell contents for $H[\overline{Sb(SCH_2CH_2O})_2]$.

case of the complex $H[Sb(SCH_2COO)]$ [8] hydrogen bonding links the molecules into endless chains. The angles between the three primary bonds (two Sb–S and one Sb–O) in complex **1**, with a mean value of 90.2°, which is quite comparable to the reported mean values of 83.9 and 90.4° in the complexes $[Sb(O_2CMe)_3]$ [1] and $[Sb(OSCMe)_3$ [1], respectively, suggest a basically pyramidal structure, pseudo tetrahedral if the stereochemically active lone pair is also included in the coordination sphere of complex **1**.

The overall coordination polyhedron in the above complex **1**, which includes secondary bonding as well as the stereochemically active lone pair, may be best described as a distorted trigonal bipyramid, which in general is the most common geometry for antimony(III) complexes having an effective coordination number of five around it [18].

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