

Heterocyclic compounds containing antimony: Part 3— Synthesis and spectral studies of $(Pr^iO)Sb[O(CH_2)_2X(CH_2)_2O]$ and $[EO(CH_2)_2X(CH_2)_2O]Sb[O(CH_2)_2X(CH_2)_2O]$ (E = H, Li, Na or K; and X = O or S)

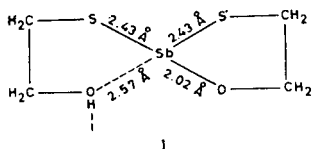
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Reactions of antimony isopropoxide with $HO(CH_2)_2S(CH_2)OH$ or $OH(CH_2)_2O(CH_2)_2OH$ in 1:1 and 1:2 molar ratios in benzene yield compounds of the type $(Pr^iO)Sb[O(CH_2)_2X(CH_2)_2O]$ and $[HO(CH_2)_2X(CH_2)_2O]Sb[O(CH_2)_2X(CH_2)_2O]$, respectively which are soluble in DMSO and DMF. The latter react with alkali metal methoxide in 1:1 molar ratio in methanol to form monomeric complexes $[EO(CH_2)_2X(CH_2)_2O]Sb[O(CH_2)_2X(CH_2)_2O]$ (where E = Li, Na or K and X = O or S). These compounds are highly soluble in methanol but less soluble in DMSO and DMF. All these derivatives have been characterized by elemental analyses, IR, 1H and ^{13}C NMR spectral studies. The studies suggest that these derivatives have six-coordinated Sb(III) atoms with ψ -monocapped octahedral geometry.

Importance of secondary bonding has recently been demonstrated by X-ray crystallographic investigations on the structures of a variety of antimony(III) derivatives, particularly carboxylates and thio-carboxylates¹. More recently, we have also reported² the crystal structure of (I), in which importance of secondary bonding has been highlighted.



We have now extended these studies on heterocyclic compounds of Sb(III) containing eight-membered chelate rings. We report herein the synthesis and properties of heterocyclic compounds of Sb(III) of the type $(Pr^iO)Sb[O(CH_2)_2X(CH_2)_2O]$, $[HO(CH_2)_2X(CH_2)_2O]Sb[O(CH_2)_2X(CH_2)_2O]$ and $[EO(CH_2)_2X(CH_2)_2O]Sb[O(CH_2)_2X(CH_2)_2O]$, (where X = O or S and E = Li, Na or K).

Materials and Methods

Antimony(III) isopropoxide, prepared by the method described by Brill and Campbell³, 2,2'-thiodiethanol (Sisco Chem, b.p. 164-66°/20 mm) and 2,2'-oxydiethanol (Sisco Chem, b.p. 119-20°/7 mm) were used after distillation. All the reactions were carried out under strictly anhydrous conditions. Solvents were dried by reported methods⁴. Antimony

was estimated iodometrically⁶ after conversion into antimony(V) and sulphur was estimated gravimetrically⁵ as barium sulphate. Isopropanol was estimated by the chromate oxidimetric methods⁷.

IR spectra were recorded as nujol mulls using CsI plates in the range of 4000-200 cm^{-1} on a 677 Perkin-Elmer spectrophotometer, 1H NMR spectra in DMSO- d_6 using TMS as an internal standard and ^{13}C NMR spectra in methanol on a 90 MHz Jeol FX-90Q spectrometer using D_2O locks. Molecular weights were determined by Knauer vapour pressure osmometer in methanol solution at 45°C. Molar conductances were measured with the help of a Systronic conductivity bridge.

Reaction of antimony(III) isopropoxide and 2,2'-thiodiethanol in a 1:1 molar ratio

Reaction of antimony isopropoxide (2.82 g, 9.43 mmole) with 2,2'-thiodiethanol (1.17 g, 9.58 mmole) in refluxing benzene (~70 ml) for 4 hr (completion of reaction was checked by estimating the isopropanol collected azeotropically) yielded a white crystalline solid product, which analysed for $(Pr^iO)Sb[O(CH_2)_2S(CH_2)_2O]$ (1). The above product was purified by recrystallization from DMSO-benzene.

Reaction of antimony(III) isopropoxide and 2,2'-thiodiethanol in a 1:2 molar ratio

A benzene solution (~20 ml) of 2,2'-thiodiethanol (3.33 g, 27.25 mmole) was added to a solution of antimony isopropoxide (4.11 g, 13.75 mmole) in

benzene (50 ml). The mixture was refluxed for 7 hr and the completion of the reaction was checked by estimating isopropanol collected azeotropically. Removal of excess of benzene under reduced pressure afforded a white solid product which analysed for $[\text{HO}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{O}] \text{Sb}[\text{O}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{O}]$ (3). The above product was also purified by recrystallization from a mixture of DMSO and benzene.

Reaction of 3 with lithium methoxide in a 1:1 molar ratio

A solution of lithium (0.04 g, 5.76 mmole) in methanol (30 ml) was added to a suspension of 3 (2.04 g, 562 mmole) in methanol (30 ml) and the mixture refluxed for 1 hr till a clear solution was obtained. On removing the solvent under reduced pressure a light yellow solid product, $[\text{LiO}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{O}]\text{Sb}[\text{O}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{O}]$ (5) was obtained.

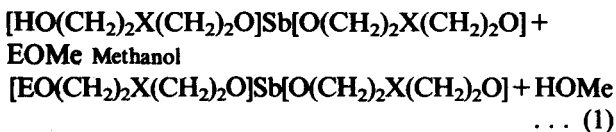
Likewise, the reactions of antimony isopropoxide with 2, 2'-oxydiethanol in 1:1 and 1:2 molar ratios in benzene and of $[\text{HO}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}]\text{Sb}[\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}]$ (3) with lithium, sodium or potassium methoxide in 1:1 molar ratio in methanol were carried out.

Results and Discussions

The analytical results for all these complexes are given in Table 1. All these products were purified by recrystallization from a mixture of DMSO and benzene.

All the reactions described under Materials and Methods appear to be quite facile and two moles of isopropanol could be collected easily. However, removal of the third mole of isopropanol could be accomplished only after prolonged refluxing for 7-8 hr in benzene.

Reaction of $[\text{HO}(\text{CH}_2)_2\text{X}(\text{CH}_2)_2\text{O}]\text{Sb}[\text{O}(\text{CH}_2)_2\text{X}(\text{CH}_2)_2\text{O}]$ with EOMe (where E = Li, Na or K) yields bimetallic heterocycles of the following type



(where E = Li (5), Na (6) or K (7) when X = S; E = Li (8), Na (9) or K (10) when X = O)

To ensure completion of the above reactions, the contents were refluxed for about 1 hr. All these derivatives are light yellow solids, which are highly soluble in MeOH and less soluble in DMSO and DMF. Molecular weight measurements in methanol and molar conductances in DMF (0.001 M) of these bimetallic heterocyclic derivatives indicate that they

are monomeric in nature and have considerable ionic character⁸. The molar conductance values increase in the order $\text{H} < \text{Li} < \text{Na} < \text{K}$.

IR spectra

These assignments of characteristic IR bands of the complexes have been made on comparison with the IR spectra of 2, 2'-thiodiethanol, 2, 2'-oxydiethanol ligands and $\text{Sb}(\text{YR})_3$ (where Y = O or S and R = alkyl or aryl)³.

The νOH of the free ligands $\text{HO}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{OH}$ and $\text{HO}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OH}$ appearing at 3350 and 3400 cm^{-1} respectively are absent in all the complexes except in 3 and 4. In complexes 3 and 4 the presence of broad bands at 3150 and 3240 cm^{-1} respectively can be ascribed to OH coordinated to antimony. The medium intensity bands observed at 1260 and 1050 cm^{-1} in the free ligand $\text{HO}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{OH}$ have been assigned to $\nu\text{C}-\text{S}$ and $\nu\text{C}-\text{O}$ respectively. In the complexes 1, 3, 5, 6 and 7 these bands appear in the regions of 1100-1150 and 1020-1040 cm^{-1} respectively. Weak intensity bands in the regions of 490-550 and 300-380 cm^{-1} in the above complexes may be assigned to $\nu\text{Sb}-\text{OC}$ and $\delta\text{Sb}-\text{OC}$ modes and the presence of medium intensity bands at 235 cm^{-1} in these complexes may be assigned to $\nu\text{Sb}\dots\text{S}$ (transannular) modes⁹. Similarly in the case of ligand $\text{HO}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OH}$, a band at 1040 cm^{-1} has been assigned to $\nu\text{C}-\text{O}$. In the case of complexes 2, 4, 8, 9 and 10 the $\nu\text{C}-\text{O}$ group band appears at 1020-1070 cm^{-1} . Not very intense bands in the above complexes in the regions of 520-560 and 320-380 cm^{-1} may be ascribed to $\nu\text{Sb}-\text{OC}$ and $\delta\text{Sb}-\text{OC}$ modes respectively. The medium intensity bands at 225 cm^{-1} in the complexes 2, 4 and 8-10 may be assigned to $\nu\text{Sb}\dots\text{O}$ (transannular) modes⁹. These conclusions are similar to those enunciated¹⁰ in the cases of $\text{R}_2\text{Sn}[\text{SCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{S}]$ and $\text{R}_2\text{Sn}[\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{O}]$.

The presence of broad -OH group bands in IR spectra of the complexes 3 and 4 indicates considerable intermolecular H-bonding in them.

NMR spectra

A comparison of ¹H NMR spectra of 2, 2'-thiodiethanol and 2, 2'-oxydiethanol in DMSO-d₆ with those of their antimony complexes 1-10 (Table 2) shows many interesting features.

The signal due to OH protons at $\delta 4.8$ ppm or at $\delta 4.6$ ppm in the spectra of the free 2, 2'-thiodiethanol or 2, 2'-oxydiethanol ligands, respectively disappear in all the complexes except 3 and 4, indicating the formation of Sb-O bonds by deprotonation. In the complexes 3 and 4, the -OH signals appear at $\delta 5.0$ ppm and $\delta 4.3$

Table I—Physical and analytical data of 2, 2'-thiodiethanol and 2, 2'-oxydiethanol derivatives of antimony(III)

Sl. No.	Reactants (g)	Molar ratio	Pr ³⁺ OH (g) found (calc.)	Product, colour and physical state and m.p. (°C)	Yield %	Pr ³⁺ O	Sb	S	C	H	Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)	Mol. wt found (calc.)
Sb ₂ (OPr ³⁺) ₃ TDE*												
1.	2.82	1:1	1.03 (1.13)	1 White solid, 140	95	19.20 (19.64)	40.32 (40.46)	10.61 (10.66)	28.24 (27.94)	4.15 (5.03)	—	—
ODE**												
2.	2.35	1:1	0.93 (0.95)	2 Colourless liquid	97	20.35 (0.74)	41.94 (42.73)	—	—	—	—	—
TDE												
3.	4.11	1:2	2.35 (2.48)	3 White solid, 270	98	—	33.58 (33.53)	17.35 (17.66)	26.01 (26.46)	4.12 (4.72)	15.62	—
ODE												
4.	1.87	1:2	1.02 (1.13)	4 Colourless Mobile liquid	95	—	36.96 (36.79)	—	—	—	—	—
3 LiOMe												
5.	2.04	1:1	—	5 Light yellow solid, 180	98	—	33.17 (32.99)	17.21 (17.38)	26.32 (26.04)	4.19 (4.38)	26.84 (369)	362 (369)
NaOMe												
6.	2.59	1:1	—	6 Light yellow solid, 190	97	—	31.96 (31.62)	16.10 (16.66)	24.52 (24.95)	4.59 (4.19)	28.38	381 (385)
KOME												
7.	4.96	1:1	—	7 Light yellow solid, 194	99	—	30.32 (30.36)	15.93 (15.99)	24.01 (23.96)	4.18 (4.02)	36.94	389 (401)
4 LiOMe												
8.	2.60	1:1	—	8 Light yellow solid, 210	99	—	36.22 (36.13)	—	28.81 (28.51)	4.01 (4.79)	21.81	341 (337)
NaOMe												
9.	3.35	1:1	—	9 Yellow solid, 250	99	—	34.51 (34.49)	—	27.10 (27.22)	4.11 (4.57)	28.81	360 (353)
KOME												
10.	3.85	1:1	—	10 Yellow solid, 235	98	—	33.12 (33.00)	—	26.09 (26.04)	4.23 (4.37)	39.01	376 (369)

* HO(CH₂)₂S (CH₂)₂OH** HO(CH₂)₂O(CH₂)₂OH1 = (Pr³⁺O)₂Sb{O(CH₂)₂O(CH₂)₂O}·3, 2 = (Pr³⁺O)₂Sb{O(CH₂)₂S(CH₂)₂O}·3, 3 = [HO(CH₂)₂S(CH₂)₂O]·4 = [HO(CH₂)₂O(CH₂)₂O]·4 = [EO(CH₂)₂S(CH₂)₂O]·4 = [EO(CH₂)₂O(CH₂)₂O]·45, 6 and 7 = [EO(CH₂)₂S(CH₂)₂O]·8, 9 and 10 = [EO(CH₂)₂O(CH₂)₂O]·8, 9 and 10 = [EO(CH₂)₂O(CH₂)₂O]·8 (where E = Li, Na or K).

Table 2—¹H and ¹³C NMR spectral data of 2, 2'-thiodiethanol and 2, 2'-oxydiethanol derivatives of antimony(III)

Product	¹ H NMR chemical shifts in δ ppm				¹³ C NMR chemical shifts in δ ppm	
	-OH	-H ₂ C-O	-H ₂ C-S	CH ₃ , CH*	-CH ₂ -O	-CH ₂ -S
Ligand ^a	4.8s**	3.7t	2.6t	—	—	—
Ligand ^b	4.6s**	3.7t	—	—	—	—
1	—	3.2t	2.9t	1.0d 3.9br*	—	—
2	—	3.7t	—	1.2d 4.8br*	—	—
3	5.0s**	3.6t	2.8t	—	—	—
4	4.3s**	3.8t	—	—	—	—
5	—	3.6t	2.8t	—	74.42	61.96
6	—	3.7t	2.7t	—	72.85	61.64
7	—	3.8t	2.9t	—	72.34	61.96
8	—	4.0t	—	—	73.53	—
9	—	4.2t	—	—	72.64	—
10	—	4.2t	—	—	73.43	—

^a ligand = HO(CH₂)₂S(CH₂)₂OH; ^b HO(CH₂)₂O(CH₂)₂OH

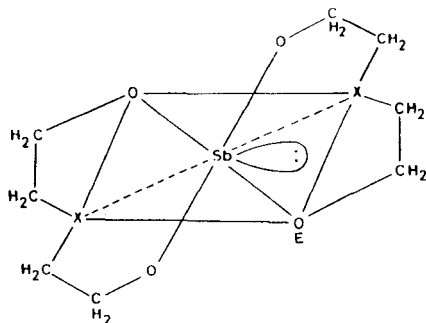


Fig. 1—Tentative structure of [EO(CH₂)₂X(CH₂)₂O]Sb[O(CH₂)₂X(CH₂)₂O] (where E=H, Li, Na or K and X=O or S)

ppm, respectively with a slight shift (0.2 ppm and 0.3 ppm).

In the PMR spectra of all these derivatives 1-10 only one type of methylene protons appear without any appreciable shift, suggesting the equivalence of all methylene protons at room temperature. The ¹³C NMR spectra show expected peak patterns (Table 2).

Since the crystal structure determination of analogous compounds (SCH₂CH₂OCH₂CH₂S)BiPh¹¹ and (SCH₂CH₂SCH₂CH₂S)SbPh⁹ show the presence of transannular Bi...O and Sb...S interactions respectively, therefore, in the above derivatives, [EO(CH₂)₂X(CH₂)₂O]Sb[O(CH₂)₂X(CH₂)₂O] (where E=H, Li, Na or K and X=O or S), one can assume the presence of transannular Sb...O or Sb...S coordination.

Although it is quite difficult to comment on the molecular structures of these complexes in the absence

of X-ray crystal structure analyses, the results presented herein indicate that the primary coordination of Sb(III) in complexes of the type [EO(CH₂)₂X(CH₂)₂O]Sb[O(CH₂)₂X(CH₂)₂O] may be six in solution. If the stereochemically active lone pair is also included in the coordination sphere, then an overall ψ-monocapped octahedral geometry around antimony(III) may be anticipated in these complexes (see Fig. 1).

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