



Investigations on the reactivity of arylantimony halides with N,O-donor ligands

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Abstract. The reactions of organoantimony(V) halides with N,O-donor ligands in presence of a base were investigated. The synthesis and crystal structure of three novel organoantimony(V) compounds (Ph₂Sb)₂(Q)₂(O)₂ **1**, (Ph₃Sb)(PM)Cl **2** and (Ph₂Sb)(TEA) **3** [where Q = 8-hydroxyquinoline, PM = 2-pyridinemethanol and TEA = triethanolamine] are reported herein. **1** crystallizes as a dimer resulting in the formation of a four-membered Sb₂O₂ ring while **2** and **3** are monomeric in the solid state. Interestingly, compound **3** crystallizes in orthorhombic chiral space group *P*2₁2₁2₁ and is a rare example of spontaneous chirality exhibited in organoantimony(V) compounds.

Keywords. Organoantimony(V) compounds; N,O-donor ligands; Sb₂O₂ ring; structural elucidation; spontaneous chirality.

1. Introduction

Since organoantimony(V) compounds have potential applications in the fields like catalysis¹ and biology,² there has been continued interest in the synthesis and structural characterization of novel organoantimony(V) compounds. Generally, these compounds have been synthesized by the reaction of tri/di-organantimony(V) halides with protic ligands like carboxylates, phosphinates and alkoxides in the presence of a base resulting in the formation of diphenyl antimony(V) oxo/chloro carboxylates and phosphinates whose nuclearity vary from *mono*, *di*, *tetra*, *octa* and *nona*-nuclear forms.^{3–9} Organoantimony compounds, particularly with antimony in the oxidation state of +5, can exist in coordination numbers as high as seven or eight due to its hypervalent nature.^{10–15} Very recently, the chemistry of mono-organantimony compounds have started gaining interest since the ability of organostibonic acids to act as inorganic cryptand incorporating d⁵ and d¹⁰ metal ions in their cavity was reported.¹⁶ Further, the isolation

of the first molecular arylstibonic acids and subsequently the use of mixed arylstibonate/phosphonate clusters as *proligands* for the assembly of multinuclear cobalt clusters have increased the interest in organoantimony compounds in general.¹⁷ A careful investigation of the literature reports of organoantimony(V) compounds revealed that mostly protic ligands with oxo donors have been used as ligands to generate novel organoantimony(V) compounds.^{18–24} Hence, we investigated the reactions of organoantimony(V) halides with N,O-donor ligands in presence of a base with the aim of isolating new structural forms. Synthesis and crystal structure of three novel organoantimony(V) compounds (Ph₂Sb)₂(Q)₂(O)₂ **1**, (Ph₃Sb)(PM)Cl **2** and (Ph₂Sb)(TEA) **3** are reported herein.

2. Experimental

2.1 Materials and measurements

8-Hydroxyquinoline, 2-pyridinemethanol, triethanolamine, solvents and other common reagents were used as purchased

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from commercial sources. Ph_2SbCl_3 and Ph_3SbCl_2 were synthesized using literature procedures.^{25,26} Infrared spectra were recorded on a JASCO-5300 FT-IR spectrometer as KBr pellets. The ^1H and ^{13}C solution NMR spectra were recorded on a Bruker DRX 400 instrument. Elemental analysis was performed on a Flash EA Series 1112 CHNS analyzer.

2.2 Synthesis of complexes (1–3)

For compounds **1** and **3**, general synthetic method used is as follows. Organoantimony starting material (Ph_2SbCl_3) and respective ligands [8-hydroxyquinoline (for **1**), triethanolamine (for **3**)] were dissolved separately in toluene. The ligand was deprotonated by adding triethylamine and the deprotonated ligand was added to organoantimony halide in toluene. The solution was then stirred for 6 h, filtered and evaporated to afford a gelly material. Crystals [pale yellow (**1**) and colorless (**3**)] suitable for single-crystal X-ray studies were grown from dichloromethane/hexane or toluene in 5 days. Compound **2** was also prepared in a way similar to **1** and **3** except that both antimony compound (Ph_3SbCl_2) and the ligand 2-pyridinemethanol were taken in toluene followed by slow addition of the base. Colorless crystals suitable for single crystal X-ray studies were grown from toluene in a week.

2.3 Synthesis of $(\text{Ph}_2\text{Sb})_2(\text{Q})_2(\text{O})_2$ (**1**)

Ph_2SbCl_3 (0.20 g, 0.523 mmol), 8-hydroxyquinoline (0.22 g, 1.56 mmol) and Et_3N (0.15 g, 1.56 mmol). Yield: 0.08 g (35.08%, based on the weight of antimony). M.p.: 272 °C. Anal. Calcd. for $\text{C}_{42}\text{H}_{32}\text{Sb}_2\text{O}_4\text{N}_2$: C, 57.8; H, 3.69; N, 3.20%. Found: C, 57.65; H, 3.61; N, 3.28%. IR (cm^{-1} , KBr pellet): 3045 w, 1601 m, 1574 m, 1498 s, 1462 s, 1429 m, 1375 m, 1323 m, 1273 m, 1107 s, 1062 m, 821 w, 781 w, 731 s, 696 s, 538 m, 453 w. ^1H NMR in CDCl_3 : δ 8.91–8.54 (m, 4H), 7.81–7.60 (m, 6H), 7.50–7.39 (m, 12H), 7.36–7.27 (m, 8H), 7.02–6.86 (m, 2H). ^{13}C NMR in CDCl_3 : δ 152.23, 142.36, 136.12, 133.11, 132.88, 129.81, 128.53, 128.29, 127.76, 121.86, 117.90, 110.00 ppm.

2.4 Synthesis of $(\text{Ph}_3\text{Sb})(\text{PM})\text{Cl}$ (**2**)

Ph_3SbCl_2 (0.30 g, 0.707 mmol), 2-pyridinemethanol (0.15 g, 1.41 mmol) and Et_3N (0.14 g, 1.41 mmol). Yield: 0.13 g (37.03%, based on the weight of antimony). M.p.: 134 °C. IR (cm^{-1} , KBr pellet): 3053 w, 1601 m, 1572 m, 1477 s, 1462 s, 1431 s, 1363 m, 1288 m, 1076 s, 1045 m, 761 w, 733 s, 690 s, 466 m.

2.5 Synthesis of $(\text{Ph}_2\text{Sb})(\text{TEA})$ (**3**)

Ph_2SbCl_3 (0.30 g, 0.784 mmol), triethanolamine (0.11 g, 0.784 mmol) and Et_3N (0.15 g, 2.35 mmol). Yield: 0.12 g (30.8%, based on the weight of antimony). M.p.: 232 °C. Anal. Calcd. for $\text{C}_{18}\text{H}_{22}\text{SbO}_3\text{N}$: C, 51.2; H, 5.25; N, 3.31%.

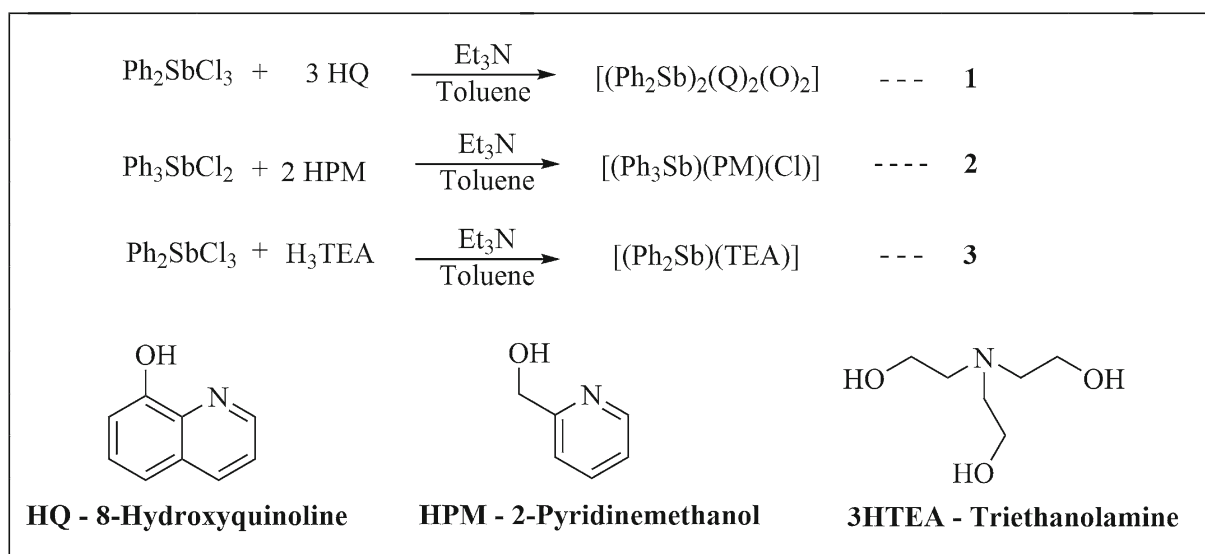
Found: C, 51.36; H, 5.18; N, 3.41%. IR (cm^{-1} , KBr pellet): 3045 w, 2918 w, 2879 m, 2847 s, 1462 s, 1431 m, 1304 m, 1267 m, 1153 m, 1105 s, 1076 m, 881 s, 754 m, 736 m, 700 s, 594 m, 516 s, 470 w. ^1H NMR in CDCl_3 : δ 7.99–7.64 (m, 6H), 7.43–7.35 (m, 4H), 4.41–3.76 (m, 6H), 3.13–2.62 (m, 6H). ^{13}C NMR in CDCl_3 : δ 135.04, 134.61, 134.06, 128.77, 128.65, 128.25, 58.66, 56.92, ppm.

2.6 Single crystal X-ray structure determination

Single crystal X-ray data collection (for **1**, **2** and **3**) was carried out at 100(2) K on a Bruker Smart Apex CCD area detector system ($\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$), with a graphite monochromator. The data were reduced using SAINT PLUS,²⁷ and the structures were solved using SHELXS-97²⁸ and refined using SHELXL-97. All non-hydrogen atoms were refined anisotropically. Selected crystal parameters for **1–3** are given in Table S1 (in Supplementary Information). CCDC 864363, 864364 and 864365 contain the supplementary crystallographic data for compounds **1**, **2** and **3** respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

3. Results and Discussion

The methodology used for synthesizing **1** is as follows. 8-Hydroxyquinoline was dissolved in toluene and deprotonated by adding an equimolar ratio of triethylamine. Diphenylantimony trichloride was separately dissolved in toluene to which was added the solution of deprotonated 8-hydroxyquinoline and the mixture was stirred for 6 h at room temperature. The solution was then filtered to remove the triethylamine hydrochloride formed and the filtrate evaporated under high vacuum to yield a gelly material which was dissolved in dichloromethane, layered with hexane and left undisturbed. After 5 days, pale yellow crystals of **1**, suitable for single-crystal X-ray characterization were isolated in good yields. For the synthesis of **2** and **3**, a similar synthetic procedure was followed except that the reagents used were different (Scheme 1). For the synthesis of **2**, triphenylantimony dichloride and 2-pyridinemethanol were reacted in presence of base triethylamine and in the case of **3**, diphenylantimony trichloride was reacted with triethanolamine in presence of triethylamine. In the case of **2**, crystals were grown from toluene whereas in **3** crystals suitable for single crystal X-ray characterization were obtained by dichloromethane/hexane layering method in a week's time. Compounds **1** and **3** were subjected to standard spectroscopic and analytical techniques. The detailed experimental methods with the exact molar ratios of the reagents used along with



Scheme 1. Synthesis of organoantimony(V) complexes (1–3).

complete spectroscopic and analytical data are given in the experimental section.

3.1 Crystallographic Analysis

Single crystal X-ray elucidation reveals the formation of an oxo-bridged dimer in **1** (Figure 1). Compound **1** crystallizes in orthorhombic space group *Pbcn* along with a molecule of dichloromethane as a solvent of crystallization. The coordination geometry around Sb is octahedral. The deprotonated ligand 8-hydroxyquinoline chelates to the metal ion through its N and O atom accounting for two coordination sites around the metal center. Two more coordination arises out of the phenyl carbons and the fifth and the sixth coordination are accounted for from the μ^2 -bridging oxygen atoms satisfying the coordination sphere around the metal atom. This bridging μ^2 -oxygen which connects the two metal atoms leads to the formation of a four-membered Sb_2O_2 ring. Such Sb_2O_2 four-membered rings are common structural motifs in organoantimony compounds.⁶ Ph_2SbCl_3 is a weak Lewis acid which readily forms 1:1 adduct compounds with solvent molecules like water ($\text{Ph}_2\text{SbCl}_3 \cdot \text{H}_2\text{O}$). We anticipate that a little excess Et_3N base used in the reaction deprotonates the coordinated water molecule from the $\text{Ph}_2\text{SbCl}_3 \cdot \text{H}_2\text{O}$ and thereby stabilizes the oxo-bridged dimer(**1**). The Sb–O, Sb–N bond distances and other metric parameters are given in Table S2 (in Supplementary Information). These bond parameters fall in the range as reported in literature.¹⁵

Compound **2** crystallizes in monoclinic space group *P2₁/c* (Figure 2). As in compound **1**, the geometry around the central metal atom antimony is octahedral. The deprotonated 2-pyridinemethanol ligand chelates

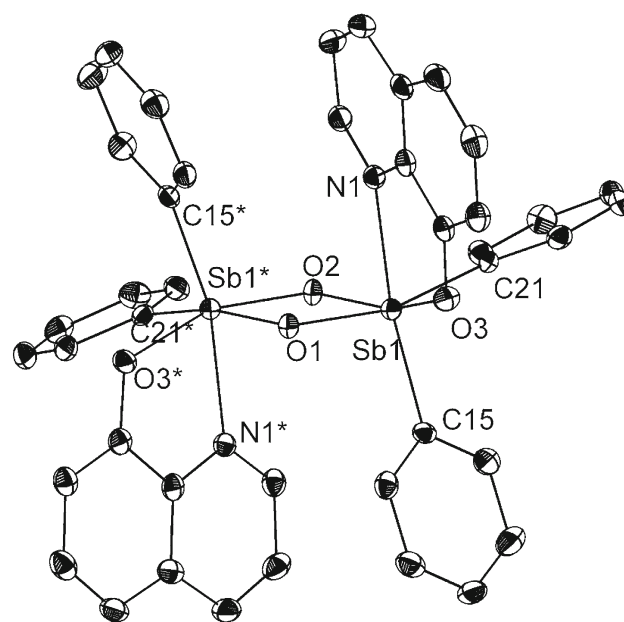


Figure 1. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure **1**. For the sake of clarity, all hydrogen atoms have been omitted.

to the metal atom by replacing a chloride atom from triphenylantimony dichloride while the other chlorine remains attached to the metal ion. In organoantimony(V) chemistry, instances where a chloride ion present can bridge to the metal atom of another molecule leading to the formation of halogen bridged dimers are common.^{29,30} This kind of halogen bridging is also generally accompanied by increasing the coordination numbers to seven or even eight due to hypervalent nature of antimony in +5 state of oxidation. But, probably the bulky nature of the ligand has led to the isolation of a monomeric organoantimony compound. It has

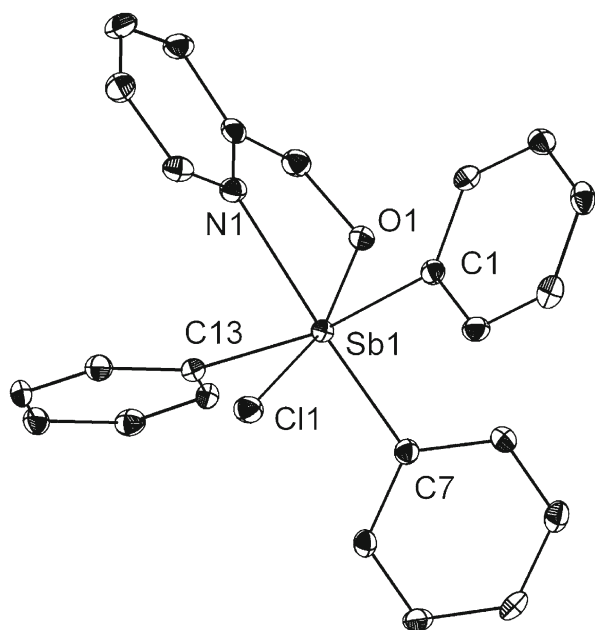


Figure 2. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure **2**. For the sake of clarity, all hydrogen atoms have been omitted.

to be mentioned here that aggregation is not the only way to reach higher coordination numbers around the metal ion in organoantimony compounds as there is a literature report of a hypervalent seven coordinate monomeric organoantimony compound.¹⁰ Hence, the steric, as well as electronic properties of the ligand in addition to the organic groups bound to the antimony starting material, might play a role in deciding whether

or not one can achieve higher coordination number than six in organoantimony compounds. Important metric parameters of **2** are given in Table S2. It has to be mentioned here that **2** could not be obtained in pure form as small amounts of free ligand always precipitated with **2**. Hence, elemental analysis and NMR data for **2** are not included in the experimental section. Fortunately, small amounts of crystals of **2** (free of ligand) could be isolated to elucidate the solid-state structure of **2** by single crystal X-ray crystallographic technique.

Compound **3** crystallizes in orthorhombic chiral space group $P2_12_12_1$ (Figure 3). The coordination geometry around the central metal atom is octahedral. The deprotonated triethanolamine ligand coordinates to the metal atom through its oxygen and nitrogen atoms accounting for four coordination sites while the other two coordination is accounted for by the phenyl carbons. Important metric parameters are given in Table S2. Probably due to the steric nature of the ligand used, aggregation leading to the formation of larger clusters has been prevented. It is of interest to mention here that this compound is an example of spontaneous chirality as although both the starting materials are achiral, the end product has crystallized in a chiral space group and hence chiral. The flak parameter also reflects the chirality present in the molecule. When triethanolamine has been used as a ligand in certain transition metal complexes, it has been reported to lead to spontaneous chirality resulting in the crystallization of these transition metal compounds in chiral space group.^{31,32} But, to our knowledge, such reports are uncommon in

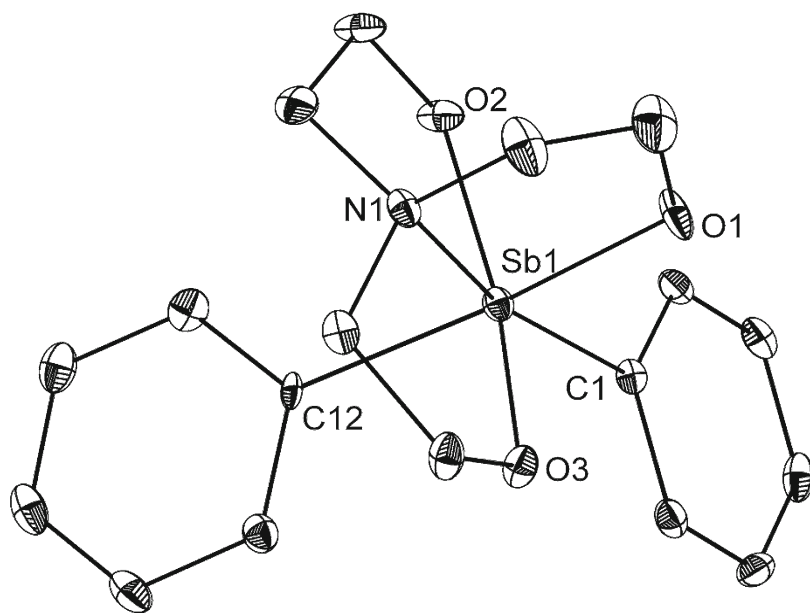


Figure 3. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure **3**. For the sake of clarity, all hydrogen atoms have been omitted.

organoantimony literature. Hence, this observation of spontaneous chirality is quite unprecedented.

4. Conclusions

Investigation of the reactions of di/tri-organoantimony halides with N,O-donor ligands has afforded an oxo-bridged dimer and two monomeric organoantimony compounds (**1–3**). When triethanolamine was used as ligand, a monomeric organoantimony compound which crystallizes in chiral space group has been isolated. To our knowledge, this is the first observation of spontaneous chirality in such organoantimony systems. Hydrolytic cleavages of Sb–C bonds in **1–3** under mildly acidic conditions are being currently investigated in our laboratory.

Supplementary Information (SI)

Crystallographic data, structural refinement and selected bond lengths/angles for complexes **1–3**, NMR spectra of complex **1** and complex **3** are given in Tables S1 and S2. Supplementary Information is available at www.ias.ac.in/chemsci.

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