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Multidentate aryloxide and oxo-aryloxide complexes of antimony: synthesis and structural characterization of $[\eta^4\text{-}N(o\text{-}C_6H_4O)_3]Sb(OSMe_2)$, $\{\{[\eta^3\text{-}N(o\text{-}C_6H_4OH)\text{-}(o\text{-}C_6H_4O)_2]Sb\}_2(\mu_2\text{-}O)\}_2$ and $\{[\eta^3\text{-}PhN(o\text{-}C_6H_4O)_2]Sb\}_4(\mu_3\text{-}O)_2$†

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Antimony compounds that feature multidentate aryloxide ligands, namely $[\eta^4\text{–}N(o\text{-}C_6H_4O)_3]Sb(OSMe_2)$, $\{\{[\eta^3\text{-}N(o\text{-}C_6H_4OH)(o\text{-}C_6H_4O)_2]Sb\}_2(\mu_2\text{-}O)\}_2$, and $\{[\eta^3\text{-}PhN(o\text{-}C_6H_4O)_2]Sb\}_4(\mu_3\text{-}O)_2$ have been synthesized from $N(o\text{-}C_6H_4OH)_3$ and $PhN(o\text{-}C_6H_4OH)_2$ and structurally characterized by X-ray diffraction. While $[\eta^4\text{-}N(o\text{-}C_6H_4O)_3]Sb(OSMe_2)$ exists as a discrete mononuclear species, the oxo complexes $\{\{[\eta^3\text{-}N(o\text{-}C_6H_4OH)(o\text{-}C_6H_4O)_2]Sb\}_2(\mu_2\text{-}O)\}_2$ and $\{[\eta^3\text{-}PhN(o\text{-}C_6H_4O)_2]Sb\}_4(\mu_3\text{-}O)_2$ are multinuclear. Specifically, the dinuclear fragment $\{[\eta^3\text{-}N(o\text{-}C_6H_4OH)(o\text{-}C_6H_4O)_2]Sb\}_2(\mu_2\text{-}O)\}$ exists in a dimeric form due to the bridging oxo ligand participating in an intermolecular hydrogen bonding interaction, while the dinuclear fragment $\{[\eta^3\text{-}PhN(o\text{-}C_6H_4O)_2]Sb\}_2(\mu\text{-}O)$ exists in a dimeric form due to the bridging oxo ligand serving as a donor to the antimony of a second fragment. The structures of $\{\{[\eta^3\text{-}N(o\text{-}C_6H_4OH)(o\text{-}C_6H_4O)_2]Sb\}_2(\mu_2\text{-}O)\}_2$ and $\{[\eta^3\text{-}PhN(o\text{-}C_6H_4O)_2]Sb\}_4(\mu_3\text{-}O)_2$, therefore, indicate that an oxo ligand bridging two Sb^{III} centers is sufficiently electron rich to serve as both an effective hydrogen bond acceptor and as a ligand for an additional Sb^{III} center.

Introduction

Antimony compounds are widely used as catalysts for the synthesis of poly(ethyleneterephthalate), as manufactured under a variety of brand names, including Dacron®, Mylar® and Terylene®.[1,2] While the most common catalyst for the synthesis of poly(ethyleneterephthalate) by polycondensation of bis(hydroxyethyl)terephthalate is Sb_2O_3, other catalysts include alkoxide derivatives, *e.g.* $[Sb_2(OCH_2CH_2O)_3]_n$,[3] $[Sb(OCH_2CH_2O)(OAc)]_n$,[4] and $Sb(OAr)_3$.[5] Antimony alkoxides, *e.g.* $Sb(OR)_3$ (R = Et, Bu^n), have also been employed as precursors for the deposition of thin films of Sb_2O_3 and Sb_6O_{13}.[6] In this paper, we describe the use of multidentate aryloxide ligands derived from $PhN(o\text{-}C_6H_4OH)_2$ and $N(o\text{-}C_6H_4OH)_3$ to prepare a series of antimony aryloxide compounds.

† Dedicated to the memory of Ian P. Rothwell, a true pioneer in the area of aryloxide chemistry.

Results and discussion

As part of an effort to determine the nature of the antimony catalysts used for the synthesis of poly(ethyleneterephthalate), we have recently reported the structures of a series of ethylene glycolate and related catecholate derivatives, namely $[Sb_2(OCH_2CH_2O)_3]_n$, $[Sb(OCH_2CH_2O)(OAc)]_n$, $[pySb(1,2\text{-}O_2C_6H_4)]_2O$ and $[pyH][Sb(1,2\text{-}O_2C_6H_4)_2]$.[7] This investigation demonstrated that the coordination chemistry of Sb^{III} with alkoxide ligands is very complex, with a variety of structural motifs being observed. For example, both $[Sb_2(OCH_2CH_2O)_3]_n$ and $[Sb(OCH_2CH_2O)(OAc)]_n$ exhibit extended structures, as illustrated in Fig. 1. The existence of these extended ethylene glycolate structures is not surprising given the fact that simple alkoxides also exhibit polynuclear structures. For example, $[Sb(OMe)_3]_n$ exhibits a layer structure with octahedral Sb^{III} centers,[8] while $[Sb(OPr^i)_3]_2$[9] and $[Sb(OSiMe_3)_3]_2$[10] are dinuclear with two bridging alkoxide ligands.[11] In fact,

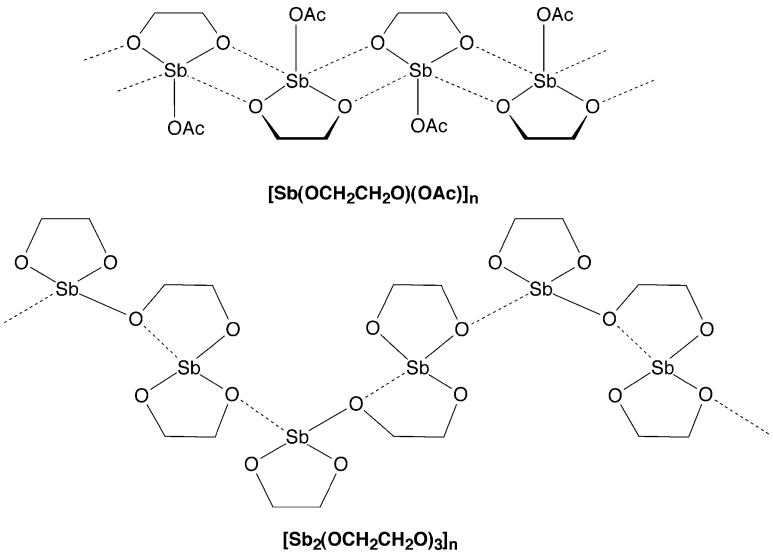

Fig. 1 Oligomeric structures of $[Sb(OCH_2CH_2O)(OAc)]_n$ and $[Sb_2(OCH_2CH_2O)_3]_n$.

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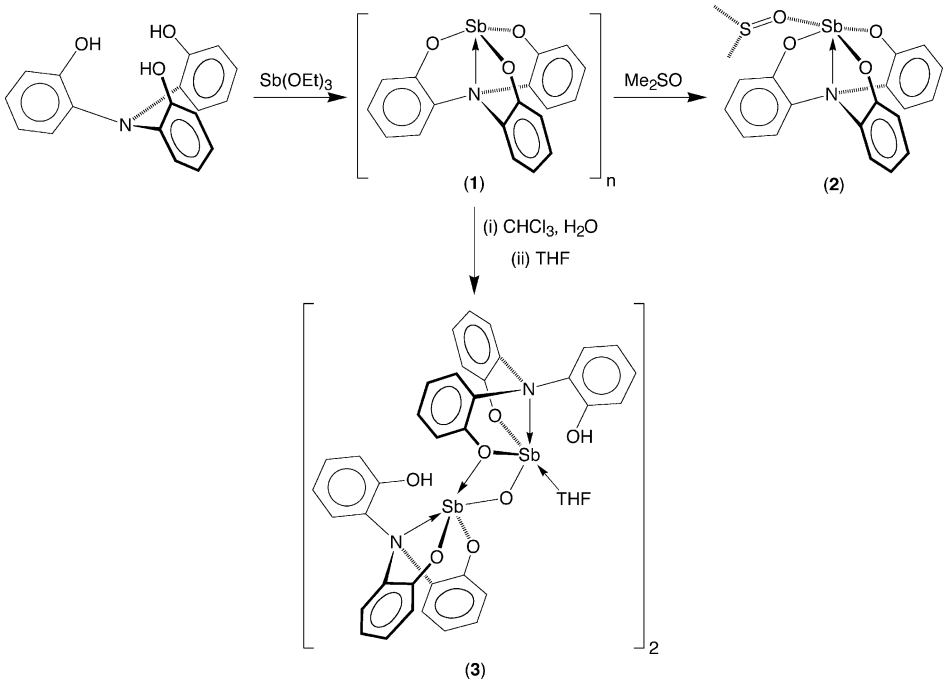


Scheme 1

the first structurally characterized monomeric Sb^{III} aryloxide, namely $Sb(OC_6H_3\text{-}2,6\text{-}Me_2)_3$, has only recently been reported.[12,13] Prompted by this observation, we sought to utilize tetradentate *tris*(2-hydroxyphenyl)amine (also called 2,2′,2″-nitrilotriphenol), $N(o\text{-}C_6H_4OH)_3$,[14] to prepare monomeric antimony aryloxide complexes.[15]

Synthesis and structural characterization of $[\eta^4\text{-}N(o\text{-}C_6H_4O)_3]Sb(OSMe_2)$

Treatment of $Sb(OEt)_3$ with $N(o\text{-}C_6H_4OH)_3$ in chloroform results in the precipitation of a white complex with composition $[N(o\text{-}C_6H_4O)_3]Sb$ (**1**), as illustrated in Scheme 1. Although the reaction does not yield single crystals suitable for X-ray diffraction, appropriate crystals of composition $[\eta^4\text{-}N(o\text{-}C_6H_4O)_3]Sb(OSMe_2)$ (**2**) may be obtained by crystallization from warm dimethylsulfoxide solution. The molecular structure of $[\eta^4\text{-}N(o\text{-}C_6H_4O)_3]Sb(OSMe_2)$ (**2**) has been determined by X-ray diffraction, as illustrated in Fig. 2. Comparison of the Sb–X distances indicates that while the primary interaction between the $[N(o\text{-}C_6H_4O)_3]$ ligand and antimony is with the three aryloxide groups (with Sb–O bond lengths in the range 2.07–2.11 Å),[16] a secondary dative interaction is observed with the nitrogen atom [d(Sb–N) = 2.433(2) Å].[17] As such, $[\eta^4\text{-}N(o\text{-}C_6H_4O)_3]Sb(OSMe_2)$ (**2**) is appropriately classified as possessing an "atrane" rather than "pro-atrane" structure (Fig. 3).[18]

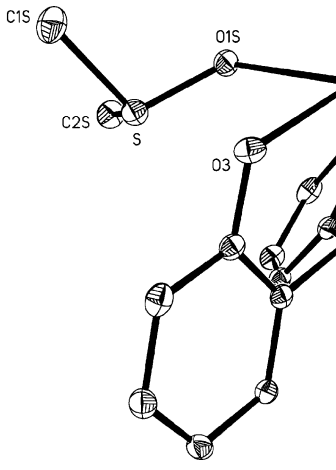


Fig. 2 Molecular structure of $[\eta^4\text{-}N(o\text{-}C_6H_4O)_3]Sb(OSMe_2)$ (**2**). Selected bond lengths (Å): Sb–O1 2.072(2), Sb–O2 2.114(2), Sb–O3 2.066(2), Sb–O1S 2.305(2), Sb–N 2.433(2). Selected bond angles (°): O1–Sb–O2 94.5(1), O2–Sb–O1S 79.3(1), O1S–Sb–O3 80.65(9), O3–Sb–O1 92.8(1), O1–Sb–N 74.26(9), O2–Sb–N 69.67(9), O3–Sb–N 74.16(9), O1S–Sb–N 86.08(9), C11–N–C21 111.6(2), C21–N–C31 118.6(2), C11–N–C31 110.3(2) (the structure illustrated is inverted from that corresponding to the atomic coordinates provided in the CIF file).

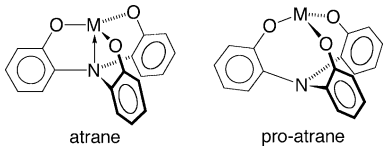


Fig. 3 Atrane and pro-atrane structures.

$[N(o\text{-}C_6H_4O)_3]$ has not been widely studied as a ligand with respect to main group metal chemistry, although aluminium,[19] germanium,[20] and tin[21] derivatives have been reported. With respect to group 15 elements, however, only the phosphorus complexes $[\eta^3\text{-}N(o\text{-}C_6H_4O)_3]P$ and $[\eta^3\text{-}N(o\text{-}C_6H_4O)_3]PO$ have been reported, and these possess "pro-atrane" structures that are devoid of N–P interactions.[22] Thus, $[\eta^4\text{-}N(o\text{-}C_6H_4O)_3]Sb(OSMe_2)$ (**2**) is the first example of a structurally characterized atrane $[N(o\text{-}C_6H_4O)_3]$-complex of the group 15 elements. The observation that $[\eta^4\text{-}N(o\text{-}C_6H_4O)_3]Sb(OSMe_2)$ possesses an atrane geometry, while the phosphorus counterpart does not, is undoubtedly linked to the fact that antimony is larger and more metallic in nature than phosphorus.

As a consequence of the atrane nature of $[\eta^4\text{-}N(o\text{-}C_6H_4O)_3]Sb(OSMe_2)$ (**2**), the antimony is five-coordinate and the geometry is based on a square pyramid; the lone pair is, therefore, stereochemically active and occupies the coordination site *trans* to the axial nitrogen donor.[23] It is also noteworthy that the antimony is displaced from the square plane such that the N–Sb–O angles are less than 90° (69.7–86.1°). Displacement of this type is precedented for isoelectronic species. For example, the F_{ax}–I–F_{eq} bond angle in IF_5 is 81.9°.[24]

The Me_2SO ligand can be viewed as modeling the coordination of bis(hydroxyethyl)terephthalate to antimony in the polyesterifcation catalytic cycle and, in this regard, it is pertinent to note that the Sb–$OSMe_2$ bond length [2.305(2) Å] is notably longer than the three Sb-aryloxide bond lengths

[2.07–2.11 Å]. With respect to the geometry at nitrogen in [η^4-N(*o*-$C_6H_4O)_3$]Sb($OSMe_2$) (**2**), the three C–N–C bond angles [118.6(2)°, 110.3(2)°, and 111.6(2)°] sum to 340.5° indicating that it is significantly more pyramidal than that in the free ligand, N(*o*-$C_6H_4OH)_3$, with $\Sigma_{C\text{-}N\text{-}C} = 348.3°$.[25]

Synthesis and structural characterization of the oxo complex {{[η^3-N(*o*-C_6H_4OH)(*o*-$C_6H_4O)_2$]Sb}$_2$(μ_2-O)}$_2$

In addition to the role of antimony(III) alkoxides and aryloxides as polycondensation catalysts, these species are also of interest with respect to their use in the preparation of thin films of antimony oxides *via* chemical vapor deposition.[6] Furthermore, antimony alkoxides may also be used to prepare oxide materials *via* the sol–gel process,[26] including the synthesis of mixed metal oxides.[27] For example $Sb(OR)_3$ and $Sn(OR')_4$ have been used to prepare antimony-doped tin oxide,[28] a material that has been widely studied because of its semiconductor properties and its application as a gas sensor.[29–31] Oxo-alkoxides are key intermediates of the sol–gel process[32] and it is therefore noteworthy that we have isolated a discrete oxo complex *via* controlled hydrolysis of {[N(*o*-$C_6H_4O)_3$]Sb}$_n$. Thus, addition of H_2O to {[N(*o*-$C_6H_4O)_3$]Sb}$_n$, generated *in situ via* treatment of $Sb(OEt)_3$ with N(*o*-$C_6H_4OH)_3$, yields the oxo bridged complex {{[η^3-N(*o*-C_6H_4OH)(*o*-$C_6H_4O)_2$]Sb}$_2$(μ_2-O)}$_2$ (**3**), in which the generation of the oxo bridge is accompanied by the formation of a phenolic group. The molecular structure of {{[η^3-N(*o*-C_6H_4OH)(*o*-$C_6H_4O)_2$]Sb}$_2$(μ_2-O)}$_2$ (**3**) has been determined by X-ray diffraction (Figs. 4 and 5), thereby demonstrating the multinuclear nature of the oxo complex. There are several noteworthy features pertaining to the structure of {{[η^3-N(*o*-C_6H_4OH)(*o*-$C_6H_4O)_2$]Sb}$_2$(μ_2-O)}$_2$ (**3**). Firstly, while the primary coordination geometries of the two antimony centers are similar, comprising one oxide, one amine, and two aryloxide interactions, the two centers of the discrete {[η^3-N(*o*-C_6H_4OH)(*o*-$C_6H_4O)_2$]Sb}$_2$(μ_2-O)} unit differ by virtue of the fact that an aryloxide group attached to one of the antimony centers interacts weakly with the other antimony, with an Sb···O distance of 2.91 Å,[33] while the other antimony interacts with a THF molecule, with an Sb···O distance of 2.80 Å (Figs. 4 and 5). Secondly, the bridging oxo ligand participates in an intermolecular hydrogen bonding interaction with the OH group of another molecule, with an O···O distance of 2.63 Å,[34] thereby resulting in the formation of a tetranuclear species (Fig. 5). For comparison, the other OH group is involved in a hydrogen bonding interaction with a THF molecule, with

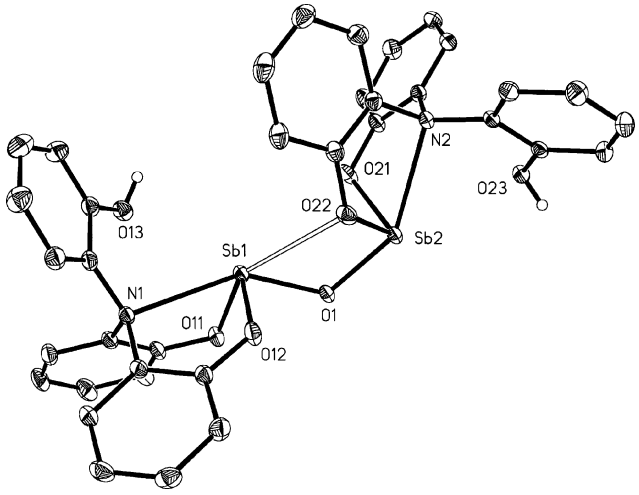


Fig. 4 Dinuclear portion of the molecular structure of {{[η^3-N(*o*-C_6H_4OH)(*o*-$C_6H_4O)_2$]Sb}$_2$(μ_2-O)}$_2$. Selected bond lengths (Å): Sb1–O11 2.015(2), Sb1-O12 1.980(2), Sb1–O1 1.992(2), Sb1–N1 2.601(2), Sb1–O22 2.912(2), Sb2–O21 2.013(2), Sb2–O22 2.011(2), Sb2–O1 1.976(2), Sb2–N2 2.619(2). Selected bond angles (°): C16–N1–C118 116.7(2), C112–N1–C118 116.7(3), C16–N1–C112 111.4(2), C212–N2–C218 117.9(2), C26–N2–C218 115.9(2), C26–N2–C212 111.5(2).

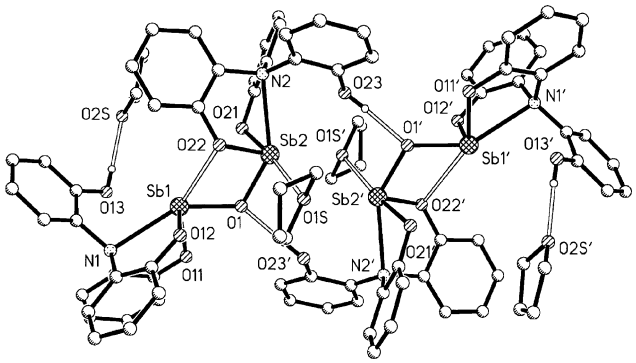


Fig. 5 Extended structure of {{[η^3-N(*o*-C_6H_4OH)(*o*-$C_6H_4O)_2$]Sb}$_2$(μ_2-O)}$_2$. Selected distances (Å): O13···O2S 2.742(4), O1–O23′ 2.634(3), Sb2–O1S 2.804(4). The atoms marked with a prime (′) are related to the corresponding unprimed atoms *via* an inversion center located at the centroid of the Sb–O1S–Sb′–O1S′ rectangle.

a longer O···O distance of 2.74 Å, thereby indicating that the oxo ligand is a better hydrogen bond acceptor than a THF molecule in this system. Finally, the Sb–N distance increases from the value of 2.43 Å in [η^4-N(*o*-$C_6H_4O)_3$]Sb($OSMe_2$) (**2**) to 2.60 Å and 2.62 Å in {{[η^3-N(*o*-C_6H_4OH)(*o*-$C_6H_4O)_2$]Sb}$_2$(μ_2-O)}$_2$ (**3**). The increase in Sb–N bond length is also accompanied by a reduction in the pyramidal nature of the nitrogen atom, as illustrated by comparison of the sum of the C–N–C bond angles for [η^4-N(*o*-$C_6H_4O)_3$]Sb($OSMe_2$) (**2**) ($\Sigma_{C\text{-}N\text{-}C} = 340.5°$) and {{[$\eta^3$-N(*o*-$C_6H_4OH$)(*o*-$C_6H_4O)_2$]Sb}$_2$($\mu_2$-O)}$_2$ (**3**) ($\Sigma_{C\text{-}N\text{-}C} = 344.8°$ and 345.3).

Although antimony(III) oxide compounds are precedented, the majority of these are organoantimony derivatives,[35,36] as illustrated by $(R_2Sb)_2O$.[37] An interesting feature of the structures of $(R_2Sb)_2O$ pertains to the conformational preferences of the two R_2Sb fragments, of which the two extreme *syn–syn* and *syn–anti* conformations are illustrated in Fig. 6.[37–40] While the direct comparison with {{[η^3-N(*o*-C_6H_4OH)(*o*-$C_6H_4O)_2$]Sb}$_2$(μ_2-O)}$_2$ (**3**) is complicated by the fact that the antimony exhibits a higher coordination number due to interaction with the nitrogen and the bridging aryloxide group, it is evident that the dinuclear unit {[η^3-N(*o*-C_6H_4OH)(*o*-$C_6H_4O)_2$]Sb}$_2$(μ_2-O)} is best described as having a *syn–anti* conformation with respect to the Sb–OAr interactions (Fig. 7).

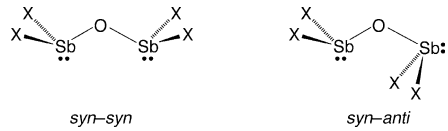


Fig. 6 Conformations of bridging oxo complexes indicating the presumed location of the lone pairs on antimony.

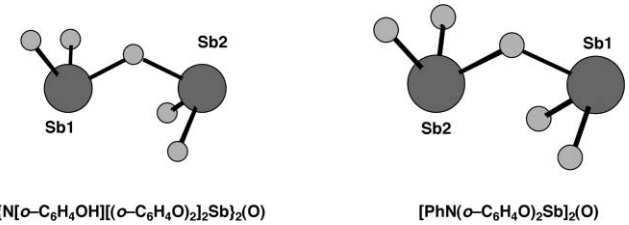
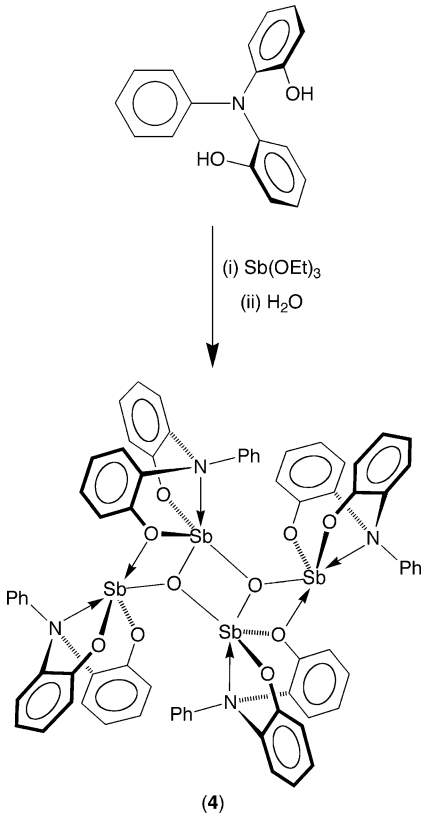


Fig. 7 *Syn–anti* conformations with respect to the Sb–OAr interactions for the dinuclear moiety in {{[η^3-N(*o*-C_6H_4OH)(*o*-$C_6H_4O)_2$]Sb}$_2$(μ_2-O)}$_2$ and {[η^3-PhN(*o*-$C_6H_4O)_2$]Sb}$_4$(μ_3–O)$_2$.

Synthesis and structural characterization of the oxo complex {[η^3-PhN(*o*-$C_6H_4O)_2$]Sb}$_4$(μ_3-O)$_2$

In view of the existence of a hydrogen bonding interaction to the bridging oxo ligand within {{[η^3-N(*o*-C_6H_4OH)(*o*-$C_6H_4O)_2$]Sb}$_2$(μ_2-O)}$_2$ (**3**), it was of interest to ascertain how

the nature of the complex would be modified in the absence of a hydrogen bond donor. For this purpose, the analogue in which the phenolic-OH group is formally replaced by H, *i.e.* $\{[\eta^3\text{-PhN}(o\text{-C}_6\text{H}_4\text{O})_2]\text{Sb}\}_4(\mu_3\text{-O})_2$ (**4**), was synthesized by treatment of Sb(OEt)_3 with $\text{PhN}(o\text{-C}_6\text{H}_4\text{OH})_2$ followed by addition of H_2O (Scheme 2).[41] The molecular structure of $\{[\eta^3\text{-PhN}(o\text{-C}_6\text{H}_4\text{O})_2]\text{Sb}\}_4(\mu_3\text{-O})_2$ (**4**) has been determined by X-ray diffraction (Figs. 8 and 9). Comparison of Figs. 4 and 8 indicates that the basic dinuclear $[\text{PhN}(o\text{-C}_6\text{H}_4\text{O})_2\text{Sb}]_2(\text{O})$ unit is similar to that of $\{[\eta^3\text{-N}(o\text{-C}_6\text{H}_4\text{OH})(o\text{-C}_6\text{H}_4\text{O})_2]\text{Sb}\}_2(\mu_2\text{-O})\}$. Furthermore, the dinuclear moiety $[\text{PhN}(o\text{-C}_6\text{H}_4\text{O})_2\text{Sb}]_2(\text{O})$ also exhibits a *syn–anti* conformation with respect to the Sb–OAr



(**4**)

Scheme 2

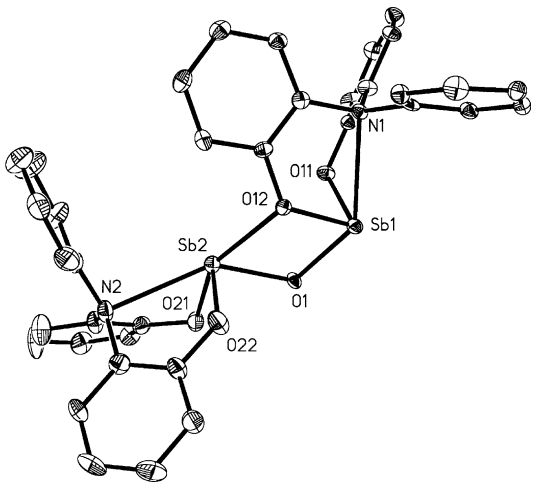


Fig. 8 Molecular structure of the dinuclear portion of $\{[\eta^3\text{-PhN}(o\text{-C}_6\text{H}_4\text{O})_2]\text{Sb}\}_4(\mu_3\text{-O})_2$. Selected bond lengths (Å): Sb1-O11 2.001(6), Sb1–O12 2.121(6), Sb1–O1 1.992(5), Sb1–N1 2.723(7), Sb2–O21 2.005(7), Sb2–O22 1.986(7), Sb2–O1 1.989(6), Sb2–O12 2.538(6), Sb2–N2 2.684(8). Selected bond angles (°): C112–N1–C113 115.8(7), C112–N1–C16 112.6(7), C113–N1–C16 117.2(7), C212–N2–C213 117.7(9), C212–N2–C26 115.2(9), C213–N2–C26 119.7(9).

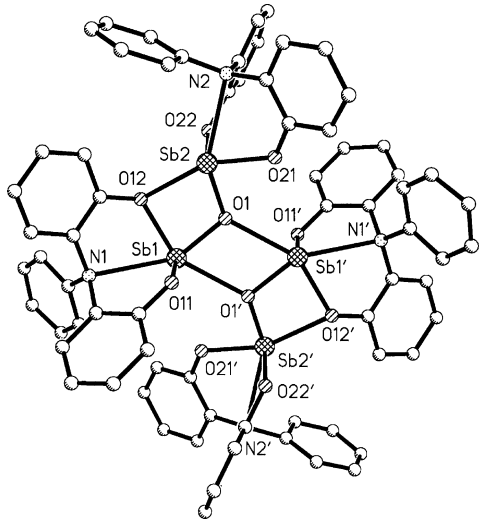


Fig. 9 Molecular structure of $\{[\eta^3\text{-PhN}(o\text{-C}_6\text{H}_4\text{O})_2]\text{Sb}\}_4(\mu_3\text{-O})_2$. Selected bond lengths (Å): Sb1–O1′ 2.446(6), Sb2–O1 1.989(6), Sb1–O1 1.992(5).

interactions (Fig. 7). Despite these similarities, a significant difference in the structures of $\{[\eta^3\text{-PhN}(o\text{-C}_6\text{H}_4\text{O})_2]\text{Sb}\}_4(\mu_3\text{-O})_2$ (**4**) and $\{[\eta^3\text{-N}(o\text{-C}_6\text{H}_4\text{OH})(o\text{-C}_6\text{H}_4\text{O})_2]\text{Sb}\}_2(\mu_2\text{-O})\}$ results from the fact that there is no hydrogen bond donor in the former molecule to provide a stabilizing interaction with the bridging oxo ligand. As a consequence, the oxo ligand interacts with a third antimony, thereby resulting in a discrete tetranuclear complex, with Sb–O bond lengths of 1.992(5) Å, 1.989(6) Å, and 2.446(6) Å (Fig. 9). Trigonal planar μ_3-oxo ligands are not common in antimony chemistry but a related motif is observed within the infinite chain of $[(\text{Me}_2\text{Sb})_2\text{O}]_n$, for which the bridging oxo ligand exhibits two short [1.99 and 2.10 Å] and one long bond [2.59 Å] to three antimony atoms; a similar μ_3-oxo ligand environment is also observed in valentinite, an orthorhombic modification of Sb_2O_3.[39] Another interesting example of an antimony complex with a trigonal planar μ_3-oxo ligand is provided by $\{[\text{Me}_2\text{Sb}]_3(\mu_3\text{-O})\}^+$, for which the three Sb–O distances are identical, 2.116(1) Å.[42]

Finally, with respect to the coordination of the $[\text{PhN}(o\text{-C}_6\text{H}_4\text{O})_2]$ ligand, the Sb–N distances [2.68 Å and 2.72 Å] are longer than those of $\{\{[\eta^3\text{-N}(o\text{-C}_6\text{H}_4\text{OH})(o\text{-C}_6\text{H}_4\text{O})_2]\text{Sb}\}_2(\mu_2\text{-O})\}_2$ (**3**) [2.60 Å and 2.62 Å], and the nitrogen atoms are less pyramidal, with $\Sigma_{\text{C-N-C}} = 345.6°$ and 352.6°. On the basis of these observations, it is evident that by comparison to $[\text{N}(o\text{-C}_6\text{H}_4\text{O})_3]$, the nitrogen atom of the $[\text{PhN}(o\text{-C}_6\text{H}_4\text{O})_2]$ ligand shows a reduced tendency to serve as a donor.

Summary

In conclusion, a series of antimony compounds that feature multidentate aryloxide ligands has been synthesized using $\text{N}(o\text{-C}_6\text{H}_4\text{OH})_3$ and $\text{PhN}(o\text{-C}_6\text{H}_4\text{OH})_2$. While $[\eta^4\text{-N}(o\text{-C}_6\text{H}_4\text{O})_3]\text{Sb}(\text{OSMe}_2)$ (**2**) exists as a discrete mononuclear species, treatment with water results in a dinuclear bridging oxo complex $\{\{[\eta^3\text{-N}(o\text{-C}_6\text{H}_4\text{OH})(o\text{-C}_6\text{H}_4\text{O})_2]\text{Sb}\}_2(\mu_2\text{-O})\}_2$ (**3**) in which the oxo ligand participates in a hydrogen bonding interaction with an OH group. In the absence of a hydrogen bond donor, the bridging oxo ligand interacts with an additional antimony center, such that $\{[\eta^3\text{-PhN}(o\text{-C}_6\text{H}_4\text{O})_2]\text{Sb}\}_4(\mu_3\text{-O})_2$ (**4**), exists as a tetranuclear complex. The structures of $\{\{[\eta^3\text{-N}(o\text{-C}_6\text{H}_4\text{OH})(o\text{-C}_6\text{H}_4\text{O})_2]\text{Sb}\}_2(\mu_2\text{-O})\}_2$ (**3**) and $\{[\eta^3\text{-PhN}(o\text{-C}_6\text{H}_4\text{O})_2]\text{Sb}\}_4(\mu_3\text{-O})_2$ (**4**), therefore, indicate that an oxo ligand bridging two Sb^{III} centers is sufficiently electron rich that it serves as both an effective hydrogen bond acceptor and as a ligand for an additional Sb^{III} center.

Experimental

General considerations

All manipulations were performed using a combination of glovebox, high-vacuum and Schlenk techniques under a nitrogen or argon atmosphere, except where stated otherwise. Solvents were purified and degassed by standard procedures. NMR spectra were measured on Bruker 300wb DRX, Bruker Avance 400 DRX, and Bruker Avance 500 DMX spectrometers. IR spectra were recorded as Nujol mulls on KBr plates on a Perkin-Elmer Paragon 1000 spectrometer. $N(o\text{-}C_6H_4OH)_3$[14] and $PhN(o\text{-}C_6H_4OH)_2$[25] were prepared by the literature methods. $Sb(OEt)_3$ was obtained from Strem. Elemental analyses were performed by Robertson Microlit Laboratories Inc., Madison, NJ 07940.

Synthesis of $[\eta^4\text{-}N(o\text{-}C_6H_4O)_3]Sb(OSMe_2)$ (2)

A mixture of $Sb(OEt)_3$ (0.876 g, 3.4 mmol) and $N(o\text{-}C_6H_4OH)_3$ (1.000 g, 3.4 mmol) was dissolved in CH_2Cl_2 (*ca.* 25 mL). The mixture was stirred and a white precipitate started to form after about 30 s of stirring. The mixture was concentrated to *ca.* 10 mL and then stirred for 18 h at room temperature. The mixture was filtered and the precipitate was washed with CH_2Cl_2 (2 × 10 mL) and dried *in vacuo* giving $[N(o\text{-}C_6H_4O)_3]Sb$ (**1**) as a white solid (0.370 g, 26%). Anal. Calcd. for $C_{18}H_{12}NO_3Sb$: C, 52.5%; H, 2.9%; N, 3.4%. Found: C, 52.3%; H, 2.8%; N, 3.2%. IR Data (Nujol, cm^{-1}): 1926 (w), 1794 (w), 1590 (s), 1211 (m), 1194 (m), 1161 (w), 1146 (m), 1113 (m), 1102 (s), 1040 (m), 1030 (s), 964 (w), 945 (w), 931 (m), 918 (m), 908 (m), 894 (w), 858 (s), 832 (s), 767 (s), 755 (s), 746 (s), 703 (m), 654 (m), 640 (m), 633 (s), 622 (s), 611 (s), 598 (s), 587 (s), 571 (m), 550 (m), 533 (w), 517 (m), 504 (s), 477 (m), 456 (m), 447 (w). $[N(o\text{-}C_6H_4O)_3]Sb$ (**1**) is insufficiently soluble for ^1H NMR spectroscopic analysis, but a sample degraded in CD_3OD with 2 drops DCl (20% in D_2O) revealed the presence of $N(o\text{-}C_6H_4OD)_3$ and the absence of ethanol. Crystals of $[\eta^4\text{-}N(o\text{-}C_6H_4O)_3]Sb(OSMe_2)$ (**2**) suitable for X-ray diffraction were obtained by slow cooling of a warm solution of $[N(o\text{-}C_6H_4O)_3]Sb$ (**1**) in Me_2SO.

Synthesis of $\{\{[\eta^3\text{-}N(o\text{-}C_6H_4OH)(o\text{-}C_6H_4O)_2]Sb\}_2(\mu_2\text{-}O)\}_2$ (3)

A mixture of $Sb(OEt)_3$ (0.219 g, 0.85 mmol) and $N(o\text{-}C_6H_4OH)_3$ (0.250 g, 0.85 mmol) was dissolved in $CHCl_3$ (*ca.* 50 mL). The mixture was stirred and a white precipitate started to form after about 30 s of stirring. The mixture was stirred at room temperature for 18 h, after which period H_2O (10 μL, 0.56 mmol) was added and the mixture was stirred for 3 days. After this period, the mixture was concentrated to *ca.* 25 mL and cooled to 0 °C with an ice-water bath. The mixture was filtered and the precipitate was washed with $CHCl_3$ (5 mL) and dried *in vacuo* giving $\{\{[\eta^3\text{-}N(o\text{-}C_6H_4OH)(o\text{-}C_6H_4O)_2]Sb\}_2(\mu_2\text{-}O)\}_2$ (**3**) as a white solid (0.254 g, 71%). Anal. Calcd. for $C_{36}H_{26}N_2O_7Sb_2$: C, 51.3%; H, 3.1%; N, 3.3%. Found: C, 51.2%; H, 2.5%; N, 3.1%. IR Data (Nujol, cm^{-1}): 1924 (w), 1792 (w), 1590 (s), 1213 (m), 1194 (s), 1161 (m), 1148 (m), 1144 (m), 1114 (m), 1102 (s), 1040 (m), 1030 (s), 963 (w), 946 (w), 931 (m), 920 (m), 908 (m), 860 (s), 831 (s), 767 (s), 758 (s), 728 (m), 703 (m), 654 (m), 641 (s), 634 (s), 622 (s), 611 (s), 598 (s), 587 (s), 572 (m), 550 (m), 534 (w), 517 (m), 504 (s), 476 (m), 457 (m), 447 (w). $\{\{[\eta^3\text{-}N(o\text{-}C_6H_4OH)(o\text{-}C_6H_4O)_2]Sb\}_2(\mu_2\text{-}O)\}_2$ (**3**) is insufficiently soluble for ^1H NMR spectroscopic analysis, but a sample degraded in CD_3OD with 2 drops DCl (20% in D_2O) revealed the presence of $N(o\text{-}C_6H_4OD)_3$ and the absence of ethanol. Crystals suitable for X-ray diffraction were obtained from THF.

Synthesis of $\{[\eta^3\text{-}PhN(o\text{-}C_6H_4O)_2]Sb\}_4(\mu_3\text{-}O)_2$ (4)

$Sb(OEt)_3$ (0.185 g, 0.72 mmol) was added to a solution of $PhN(o\text{-}C_6H_4OH)_2$ (0.200 g, 0.72 mmol) in THF (*ca.* 15 mL) and the mixture was stirred at room temperature for 18 h. H_2O (3 μL, 0.17 mmol) was added and the mixture was stirred for a further 24 h. After this period, the mixture was concentrated to *ca.* 3 mL, thereby resulting in the slow formation of a white precipitate. The mixture was filtered and the precipitate was dried *in vacuo* giving $\{[\eta^3\text{-}PhN(o\text{-}C_6H_4O)_2]Sb\}_4(\mu_3\text{-}O)_2\cdot 2THF$ as a white solid (0.275 g, 80%). Anal. Calcd. for $C_{36}H_{26}N_2O_5Sb_2\cdot THF$: C, 54.5%; H, 3.9%; N, 3.2%. Found: C, 56.0%; H, 3.7%; N, 3.0%. IR Data (Nujol, cm^{-1}): 1590 (s), 1228(s), 1154 (w), 1105 (m), 1062 (m), 1034 (m), 914 (m), 856 (m), 839 (m), 824 (m), 778 (m), 752 (s), 704 (w), 696 (m), 644 (m), 604 (s), 530 (m), 504 (m), 496 (m), 484 (s), 472 (m), 450 (w). $[\eta^3\text{-}PhN(o\text{-}C_6H_4O)_2Sb]_4(\mu_3\text{-}O)_2$ is insufficiently soluble for ^1H NMR spectroscopic analysis, but a sample degraded in CD_3OD with 2 drops DCl (20% in D_2O) revealed the presence of $PhN(o\text{-}C_6H_4OH)_2$ and THF in a 2 : 1 ratio, and the absence of ethanol. Crystals suitable for X-ray diffraction were obtained from THF.

X-Ray structure determinations

X-Ray diffraction data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector; crystal data, data collection and refinement parameters are summarized in Table 1. The structures were solved using direct methods and

Table 1 Crystal, intensity collection and refinement data.

	$[N(o\text{-}C_6H_4O)_3]Sb(OSMe_2)$	$\{\{[\eta^3\text{-}N(o\text{-}C_6H_4OH)(o\text{-}C_6H_4O)_2]Sb\}_2\text{-}(\mu_2\text{-}O)\}_2\cdot 2.18THF$	$\{[\eta^3\text{-}PhN(o\text{-}C_6H_4O)_2]Sb\}_4\text{-}(\mu_3\text{-}O)_2\cdot 2THF$
Lattice	Triclinic	Triclinic	Triclinic
Formula	$C_{20}H_{18}NO_4Sb$	$C_{36}H_{26}N_2O_7Sb_2\cdot 2.18(C_4H_8O)$	$C_{80}H_{68}N_4O_{12}Sb_4$
Formula weight	490.16	999.27	882.19
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.452(1)	13.1256(7)	9.763(1)
b/Å	8.734(1)	13.3738(8)	10.852(2)
c/Å	13.960(2)	14.4188(8)	17.345(3)
α/°	96.289(2)	111.544(1)	85.217(3)
β/°	90.953(2)	99.969(1)	76.467(3)
γ/°	112.482(2)	108.335(1)	88.987(3)
V/Å^3	944.4(2)	2111.9(2)	1780.5(5)
Z	2	2	1
Temperature/K	243	243	243
Radiation λ/Å	0.71073	0.71073	0.71073
ρ (calcd.)/g cm^{-3}	1.724	1.571	1.646
μ (Mo-Kα)/mm^{-1}	1.597	1.337	1.568
θ_{max}/°	28.0	28.3	28.3
No. of data	4058	9236	7863
No. of parameters	247	532	452
R_1	0.0395	0.0335	0.0681
wR_2	0.1083	0.0880	0.1785
GOF	1.032	1.007	1.039

standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 5.10).[43] Crystals of $\{\{[\eta^3\text{-N}(o\text{-C}_6\text{H}_4\text{OH})(o\text{-C}_6\text{H}_4\text{O})_2]\text{Sb}\}_2(\mu_2\text{-O})\}_2$ (**3**) were obtained from THF, and three crystallographically independent THF molecules are present in the asymmetric unit. Of these, one molecule is weakly coordinated to antimony, one is involved in hydrogen bonding to the o-C_6H_4OH group, and a third is not involved in any specific interaction and exhibits only partial occupancy (0.18).

CCDC reference numbers 268879–268881.

See http://www.rsc.org/suppdata/dt/b5/b505308k/ for crystallographic data in CIF or other electronic format.

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