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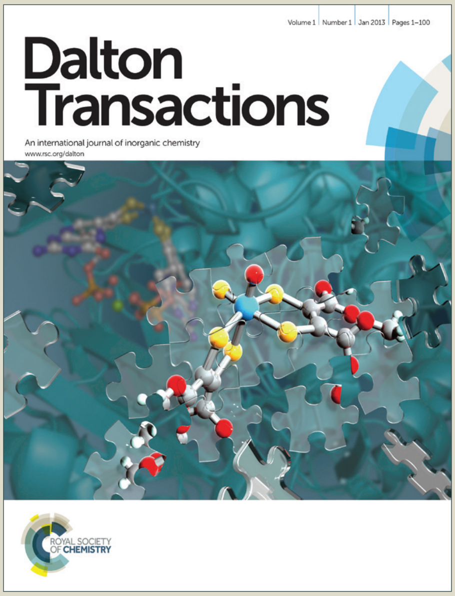

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Assembling Anionic Sb(V)/(III) containing polyoxostibonates stabilized by triphenyltellurium cations

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Abstract: Reactions of diphenyltellurium oxide with organostibonic acid and polymeric triphenylantimony oxide have been investigated independently. Single crystal X-ray diffraction studies have revealed the formation of novel and rare mixed valent Sb(V)/(III) containing polyoxostibonates $\{(C_6H_5)_3Te\}_2\{Na_2(H_2O)_2(p\text{-}Br\text{-}C_6H_4Sb^{V})_{10}(Sb^{III})_4[(C_6H_5)_2Te]_4(O)_{30}(OH)_4]$ **1** and $\{(C_6H_5)_3Te\}_4\{[(C_6H_5)_2Sb^{V}]_4(Sb^{III})_4(O)_{12}(OH)_4\}$ **2**. Solution ^{125}Te NMR supports the solid state structures presented. Interestingly, during the assembly of these POMs several processes happen simultaneously. Rarely observed reduction from Sb(V) to Sb(III), complete dearylation of organoantimony precursors and complexation ability of tetraorganoditelluroxane moiety stabilizing large and novel POM structure(as in **1**) along with formation of triphenyltellurium cations which not only provide charge balance but also stabilize the POM framework (as in **2**) by weak interactions are observed.

Introduction

Polyoxometalates (POMs) of transition metal ions although known since the early nineteenth century,[1] still continue to attract attention due to the rich structural diversity they display and also due to a variety of applications they exhibit.[2] On the other hand POMs which exclusively containing only main group elements were very rare although main group elements substituted heteropolyoxometalates are well documented.[3] Recently polynuclear bismuth clusters showing structural similarities with POMs have been reported.[4] Herein, synthesis and structural characterization of polynuclear bismuth oxido clusters reported by Mehring et al needs a special mention.[5] On the other hand POMs based on antimony are rare.[6] The first report on POMs based on organoantimony were reported in 2007 wherein organostibonic acids were used as starting materials for building POM frameworks encapsulating transition metal ions (Mn or Zn) in their cavity.[7] Organostibonic acids are ill-defined, high molecular weight polymers whose solid state structure has been a matter of considerable debate.[8] Recently, controlled hydrolysis of $2,6\text{-}Mes_2C_6H_3SbCl_4$ under basic conditions leading to the isolation of the first molecular arylstibonic acid which crystallized as a dimer in solid state has been reported.[9] Further to understand in detail about the molecular structures of organostibonic acids, mass spectrometry has been observed to serve as a useful tool.[10] On a parallel view, diorganotellurium oxides R_2TeO (R = alkyl, aryl) have been utilized as mild oxygen transfer reagents in organic and organometallic synthesis.[11] Also needs mentioning is the work of Gabbaï et al on investigation of redox properties of main group / transition metal platforms and study of the *umpolung* nature of Sb-Au, Te-Au, Te-Au bonds.[12] It has been demonstrated that the solutions of diorganotellurium oxide along with diorganotin oxide or dialkyltellurium dihydroxide can readily absorb the atmospheric CO_2 to form stable tellurostanoxane carbonates or telluroxane carbonates.[13] Diorganotellurium oxides are basic in aqueous solutions and in the presence of protic acids they tend to associate and form tetraorganoditelluroxane $[R_2TeOTeR_2]$ moiety.[14] Continuing our interest in investigation of depolymerization reactions of organostibonates,[15] the reactions of organostibonic acid and polymeric triphenylantimony oxide with diphenyltellurium oxide independently were carried out. Synthesis and characterization of $\{(C_6H_5)_3Te\}_2\{Na_2(H_2O)_2(p\text{-}Br\text{-}C_6H_4Sb^{V})_{10}(Sb^{III})_4[(C_6H_5)_2Te]_4(O)_{30}(OH)_4]$ **1** and $\{(C_6H_5)_3Te\}_4\{[(C_6H_5)_2Sb^{V}]_4(Sb^{III})_4(O)_{12}(OH)_4\}$ **2** are reported.

Results and Discussion

Synthetic procedure employed for **1** is as follows (scheme 1). *p*-Bromophenylstibonic acid and diphenyltellurium oxide were taken in 1:1 mole ratio and refluxed in toluene for 12 h resulting in a clear solution. Filtration followed by evaporation of the solvent under reduced pressure resulted in the formation of a colorless solid. Single crystals suitable for X-ray diffraction were grown using dichloromethane / hexane diffusion method. **2** was prepared by reacting polymeric triphenylantimony oxide with diphenyltellurium oxide in 1:2

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Scheme 1

$$\mathrm{R'SbO_3H_2 + R_2TeO \xrightarrow[\text{reflux, 12h}]{\text{toluene}} [R_3Te]_2[Na_2(H_2O)_2(R'Sb^{V})_{10}(Sb^{III})_4(R_2Te)_4(O)_{30}(OH)_4]}\ (\mathbf{1})$$

$$\mathrm{[R_3SbO]_n + 2\ R_2TeO \xrightarrow[\text{reflux, 12h}]{\text{toluene}} [R_3Te]_4[(R_2Sb^{V})_4(Sb^{III})_4(O)_{12}(OH)_4]}\ (\mathbf{2})$$

$$\mathrm{R'} = p\text{-}\mathrm{Br\text{-}C_6H_4,\ R = C_6H_5}$$

mole ratio under toluene reflux condition for 12h which resulted in the formation of a fluffy white solid (scheme 1). Flake like single crystals were grown by diffusion of hexane into a dichloromethane – methanol mixture. **1** and **2** were characterized by standard spectroscopic and analytical techniques. Solution NMR for **1** and **2** were taken in $CDCl_3$ and CD_2Cl_2-CD_3OD mixture respectively. Solution ^{125}Te NMR of **1** shows two resonances at $\delta = 1162$ and 787 ppm which clearly indicates the presence of two different tellurium environments in **1**. Solution ^{125}Te NMR of **2** shows single resonance peak at $\delta = 776$ ppm which indicates the presence of tellurium atom in a unique environment in **2**.

1 and **2** have been characterized by single crystal X-ray diffraction studies. Crystallographic data and selected metric parameters for **1** and **2** are provided in supporting information. **1** crystallizes in monoclinic space group $P2_1/n$ with half of the molecule in asymmetric unit. The molecular structure of **1** represents a dianionic tetradecanuclear organoantimony oxo cluster chelated by two tetraphenylditelluroxane moieties (figure 1). The charge is balanced by the presence of two triphenyltellurium cations which crystallize along with the core. The tetradecanuclear organoantimony oxo cluster can be described as follows. Of the fourteen Sb atoms present, ten are present in +5 state of oxidation displaying six coordination and four Sb atoms are present in +3 state of oxidation displaying pseudo trigonal bipyramidal geometry with stereo chemically active lone pair on antimony occupying one of the equatorial positions.[16] The ten Sb(V) atoms are present as two triads and two diads. Each triad is formed by each polyhedra of the triad sharing an edge with the adjacent polyhedra and further all the three polyhedra sharing a common vertex. The diads are formed by two polyhedra sharing a common edge. Each triad is connected to two diads by two vertex sharing polyhedra with each of the diad. The triads are further also connected in two sides to the diads through a Sb(III) atom. Of the four coordinations present for the Sb(III) atom, three are the oxygen linked to Sb(V) atoms and the fourth coordination comes from the binding tetraphenylditelluroxane unit. The ability of diorganotellurium oxides/dihalides to form tetraorganoditelluroxane $[R_2TeOTeR_2]$ in presence of protic acids is known in literature.[14, 17] The novelty here is the ability of tetraorganoditelluroxane in stabilizing large POM frameworks. The Sb-O distance falls in the range of 1.946(7)Å-2.186(7)Å which are comparable with earlier Sb(V)-O distances reported in literature.[6, 15]

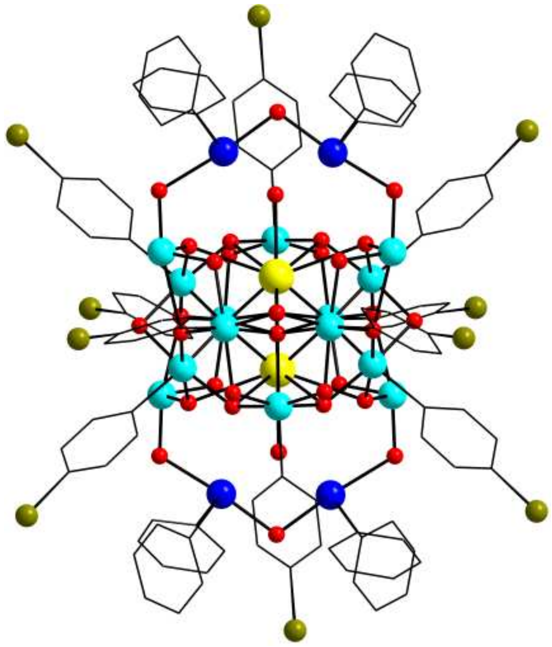
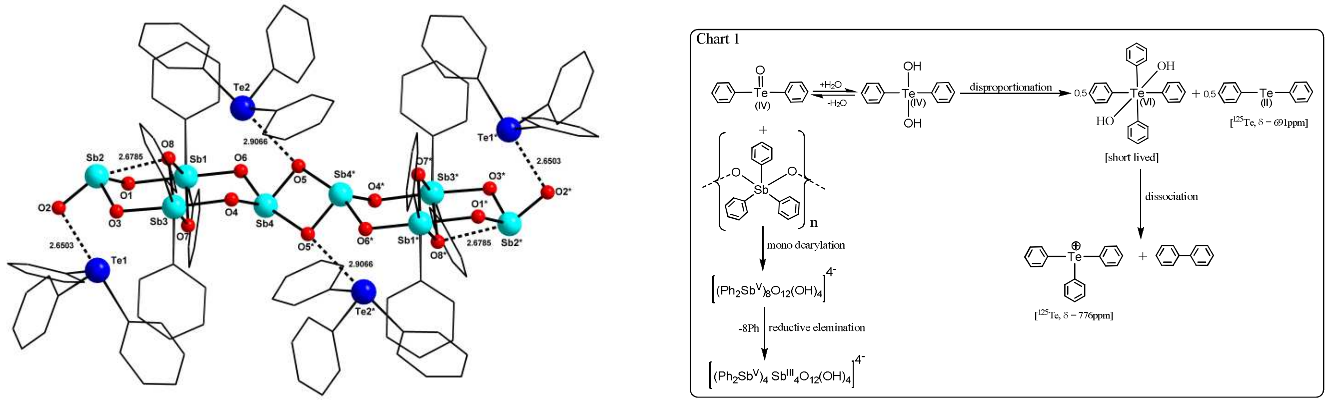


Figure 1: Solid state molecular structure of **1**. Hydrogens, triphenyltellurium cations and dichloromethane solvates are omitted for clarity.

Interestingly mono and di-dearylation of organoantimony compounds have been reported in the literature.[18] To the best of our knowledge complete dearlytion is rare.[19] Herein complete dearylation of organoantimony precursor is reported. BVS calculations have been used for determining the oxidation state of the metal atoms present in the cluster.[20] The oxidation state value in **1** for Sb present in SbO_4 units corresponds to that of +3 state of oxidation. Another interesting aspect about the structure is the partial reduction of the Sb(V) to Sb(III).



(a) (b)

Figure 2: (a) Solid state molecular structure of **2**. Hydrogen atoms are omitted for clarity. (b) chart 1 showing plausible mechanism for the formation **2**

The possible reason for the reduction is dealt with in the latter parts of the manuscript when a similar situation is also encountered in **2**. Sb(III) can readily oxidise to form Sb(V) and recently the synthesis of a mixed valent Sb(III)/Sb(V) oxido cluster in which Sb(III) is oxidised to Sb(V) by air has been reported.[21] Herein reduction of Sb(V) to Sb(III) in presence of diphenyltellurium oxide is observed. Further due to strong affinity of arylstibonates towards Na^+ ion, two Na^+ ions are encapsulated in the Sb_{14} core. With the help of ESI-mass spectroscopy, it has been inferred that these Na^+ ions originated possibly from the glassware due to leaching.[10] The sodium ions are present in eight coordinate geometry. The Na-O bond distances fall in the range 2.355(9)Å -2.912(8)Å. Of the 34 oxo groups present in **1**, 22 are μ_2-bridging and 4 are μ_4-bridging while the other 8 are μ_3-bridging in which 4 of them are considered to be part of hydroxyl ions for charge neutrality. The charge of the Sb_{14} cluster along with the two ligated tetraphenylditelluroxane motifs is dianionic. Two triphenyltellurium cations are found to crystallize outside the core stabilizing the charge on the cluster. Mixed valent Sb_{14} framework reported herein belongs to a novel class of POMs using main group elments as framework atoms.

2 crystallizes in monoclinic space group $P2_1/n$ with half of the molecule present in the asymmetric unit. The molecular structure of **2** corresponds to a tetraanionic octanuclear organoantimony oxo cluster with four triphenyltellurium cations stabilizing the cluster by weak interactions and also providing for charge neutrality (figure 2). The solid state structure of **2** can bedescribed as a dimer of antimony tetramers connected through two μ_2-oxo bridges (O5, $O5^\#$). Each tetramer consists of two Sb(III) and two Sb(V) centres arranged in alternative manner connected through four μ_2-oxo bridges to form a chair-like eight-membered ring. Further the two Sb(V) atoms are connected among themselves by two μ_2-oxo bridges. Polyhedral view of this dimer shows two octahedra around the antimony atoms sharing a common edge. Sb-O distances fall in the range 1.998(4)Å -2.081(4)Å with an average of 2.036Å which are found to be slightly higher when compared to **1**. Each antimony atom in the dimer contains only two phenyl rings as a result of mono dearylation of triphenylantimony oxide polymer which is the starting precursor. The dimer is connected to two Sb(III) centers namely Sb2 and Sb4 through two μ_2-oxo bridges(O1,O3 or O4,O6) at both sides respectively. Interestingly the core of this tetramer resembles the hexa-μ-oxooctaphenyltetraantimony cluster reported in literature.[22] Further this tetrameric core is connected to another identical tetrameric core at Sb4 centre through two μ_2- oxo bridges namely O5 and $O5^\#$ with Sb-O distances 1.871(4)Å, 2.361(4) Å respectively to form a chain like octameric antimony-oxo core with alternate Sb(III) and Sb(V) atoms. The Sb(III) atoms Sb2 and Sb4 are tri coordinate and tetra coordinate with O atoms respectively. The geometry around the tri coordinate Sb2 is considered to be trigonal pyramidal with stereo chemically active lone pair occupying the axial position with Sb-O distance fall in the range 1.886(4)Å -1.901(4)Å with an average 1.876Å which is marginally less when compared to **1**. It has also been observed that this Sb(III) atom is involved in a secondary bonding interaction with O8 (Sb…O, 2.6785 Å). The geometry around tetra coordinate Sb4 is pseudo trigonal bipyramidal with stereo chemically active lone pair on antimony occupying one of the equatorial positions which is the common geometry assigned to antimony with four bonds.[16] The Sb-O distances around Sb4 fall in the range 1.871(4) Å-2.361(4) Å with an average 2.020 Å which is similar to **1**. BVS calculations confirm the +3 oxidation state of Sb2 and Sb4 atoms[20]. **2** contains 16 μ_2-bridging oxo groups. Of the 16, 4 μ_2-oxo bridges which belong to two Sb(V) dimers are considered to be part of hydroxyls for charge neutrality. The overall charge of tetraanionic octanuclear organoantimony oxo cluster is neutralized by the presence of four triphenyltellurium cations present outside the core. These triphenyltellurium cations act as counter ions in both **1** and **2**.

Diphenyltellurium oxide / diphenyl tellurium dihydroxide disproportionates[23] in the presence of organoantimony(V) oxo cluster to diphenyltelluride(II) and tetraphenyl tellurium(VI) dihydroxide. Solution ^{125}Te NMR of the filtrate (in reaction 2) shows a resonance at 691 ppm which confirms the presence of diphenyltelluride[24] as a side product. A resonance corresponding to the presence of Te(VI) was not observed probably because at toluene reflux temperatures tetraphenyltellurium(VI)dihydroxide disintegrates into triphenyltellurium cation and biphenyl.[25] Infact, in solution ^{125}Te NMR a resonance corresponding to the presence of Ph_3Te^+ was observed at 776 ppm. This cation crystallizes out as a counter ion along with the mixed valent organoantimony oxo cluster. The plausible mechanism (chart 1) for assembly of **2** can be proposed as follows, in the presence of diorganotellurium oxide, mono dearylation of the triorganoantimony precursor leading to the formation of diorganoantimony oxo cluster $[(R_2Sb^V)_8O_{16}]^{4-}$ is obtained which further undergoes partial reductive elimination on four antimony atoms leading to the formation of $[(R_2Sb^V)_4Sb^{III}{}_4O_{16}]^{4-}$ whose solid state structure is stabilized by the presence of four triphenyltellurium cations in the crystal lattice.

Experimental Section

Reagents and General Procedures: (P-bromophenyl)stibonic acid, polymeric triphenylantimony oxide and diphenyltellurium oxide were prepared according to literature reports.[26] Solvents and other general reagents were purchased from commercial sources. Compounds **1** and **2** were dried under high vacuum for half an hour before subjected to spectroscopic and elemental analysis.

Instrumentation: Infrared spectra were recorded on a JASCO-5300 FT-IR spectrometer as KBr pellets. The solution ^{1}H, ^{13}C, and ^{125}Te NMR spectra were recorded on Brucker AVANCE^{III} 400 instrument. Elemental analysis was performed on a Flash EA Series 1112 CHNS analyzer. Single Crystal X-ray data collection for **1-2** were collected at 100(2) K on a Bruker Smart Apex CCD area detector system (λ (Mo Kα) = 0.71073 Å) with a graphite monochromator. The data were reduced using SAINTPLUS and the structures were solved using SHELXS-97[27] and refined using SHELXL-97.[28]All non-hydrogen atoms were refined anisotropically. Aryl ring hydrogens were included in calculated positions. Hydrogen atoms of two water molecules which are coordinated to sodium (in case of **1**) and four hydrogens which are associated with hydroxyl ions(in case **1** and **2**) for charge neutrality were included in the final refinement.

*Synthetic procedure for **1***: (*p*-Bromophenyl)stibonic acid(0.100 g, 0.30 mmol) and diphenyltellurium oxide (0.091 g, 0.30 mmol) were refluxed in toluene for 12 h resulting in a clear solution. Dean-Stark apparatus was used to remove the water eliminated in the reaction as an azeotropic mixture. Filtration followed by evaporation of the solvent under reduced pressure resulted in a solid white precipitate which readily dissolves in dichloromethane. Single crystals suitable for X-ray diffraction were grown in dichloromethane/hexane diffusion. Yield: 0.090 g(30.9%) (based on diphenyltellurium oxide). Dec. temp: 200°C. $C_{144}H_{118}Br_{10}Na_2O_{36}Sb_{14}Te_6$ (5739.72):calcd. C 30.13, H 2.07; found C 30.26, H 1.86.^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.47(m, 60H), 7.32(m, 50H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 137.99, 134.48, 131.40, 130.27, 129.52, 128.99, 127.85; ^{125}Te NMR (126.3 MHz, $CDCl_3$, ppm): δ 1162, 787. IR(KBr, cm-1): 3052.1(w), 2964.4(m), 1654.8(w), 1561.6(m), 1473.9(s), 1430.1(s), 1375.3(s), 1260.3(s), 1172.6(w), 1090.4(w), 1052.1(m), 1013.7(m), 800.0(s), 734.2(s), 684.9(m).

*Synthetic procedure for **2***: polymeric triphenylantimony oxide (0.100 g, 0.27 mmol) and diphenyltellurium oxide (0.161 g, 0.54 mmol) were refluxed in toluene for 12 h resulting in a fluffy white solid material. Solvent was removedby filtration and the precipitate dried in air for one day. Flake like single crystals were grown by diffusion of hexane into a dichloromethane –methanol mixture. Yield: 0.170 g (38%) (based on diphenyltellurium oxide). Dec. temp:250°C. $C_{120}H_{104}O_{16}Sb_8Te_4$ (3286.58): calcd. C 43.85, H 3.19; found C 43.76, H 3.23. ^{1}H NMR (400 MHz, CD_2Cl_2-CD_3OD, ppm): δ 7.87(m, 12H), 7.61(m, 62H), 7.38(m, 26H); ^{13}C NMR (100 MHz, CD_2Cl_2-CD_3OD, ppm): δ 134.35, 133.34, 131.92, 130.51, 128.09, 127.69, 125.36; ^{125}Te NMR (126.3 MHz, CD_2Cl_2-CD_3OD, ppm): δ 776. IR(KBr, cm-1): 3046.6(w), 1572.6(m), 1479.4(s), 1430.1(s), 1178.1(m), 1068.5(s), 1019.2(m), 991.8(m), 739.7(s), 684.9(m).

Conclusions

To conclude, in presence of diorganotellurium oxide organostibonic acid and triorganoantimony oxide self-assemble to yield mixed valent organostibonates ligated by tetraorganoditelluroxane (in **1**) and stabilized by weak interactions from triaryltellurium cations (**2**). To the best of our knowledge this is the first instance wherein tetraorganoditelluroxane's ability to act as ligand for stabilizing large POM framework has been observed. Successive reactions like mono / tri-dearylation, reductive elimination and disproportionation have taken place *enroute* to the formation of the novel POM frameworks reported herein.

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†Electronic Supplementary Information (ESI) available: Crystallographic data, selected bond lengths and bond angles, solution ^{125}Te NMR spectra and ORTEP diagrams were given in supporting information. CCDC reference numbers for **1-2** are 1029478-1029479. See DOI: 10.1039/b000000x/

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Table of contents entry

Synthesis and structural characterization of mixed valent polyoxostibonates ligated by tetraorganoditelluroxane and stabilized by weak interactions from triaryltellurium cations are presented herein. Successive reactions like reduction, dearylation and disproportionation have been observed *en route* to the formation of these novel POMs