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Monoorganoantimony(V) Phosphonates and PhosphoSelininates

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Molecular oxo-hydroxo clusters have been synthesized by reaction of arylstibonic acids with organophosphonic acid and phenylseleninic acid. Single crystal X-ray structural elucidation revealed the formation of [(*p*-*i*-$PrC_6H_4Sb)_4(OH)_4$(*t*-$BuPO_3)_6$](**1**), [(*p*-*t*-$BuC_6H_4Sb)_4(O)_2(PhPO_3)_4(PhPO_3H)_4$](**2**), [(*p*-*i*-$PrC_6H_4Sb)_4(O)_3(OH)(PhSeO_2)_2$(*t*-$BuPO_3)_4$(*t*-$BuPO_3H_2)_2$](**3**), [(*p*-$MeC_6H_4Sb)_4(O)_3(OH)(PhSeO_2)_2$(*t*-$BuPO_3)_4$(*t*-$BuPO_3H_2)_2$](**4**) and [(*p*-*t*-$BuC_6H_4Sb)_2(O)$ $(PhSeO_2)_2$(*t*-$BuPO_3H)_4$](**5**) respectively. Mass spectral studies reveal that the clusters maintain their structural integrity in solution as well. Solution NMR studies (^1H, ^{31}P and ^{77}Se) show spectral patterns which correlates well with the observed solid state structures of **1-5**.

Introduction

The ability of organostibonate-phosphonate cluster to act as pro-ligand for assembling cobalt based molecular clusters has been reported in 2007.[1] Though stibonates and phosphonates can independently act as ligands towards metal ions, the pro-ligand cluster method provides a single source precursor combining the coordinating ability of stibonates and phosphonates motifs, that can serve as a novel ligand platform which could be employed for stabilizing new types of polynuclear metal based oxo hydroxo systems. Synthesis and structural characterization of organoantimony (V) based molecules and clusters have gained attention and is currently an area of active research.[2] Beckmann et al reported the synthesis and structural characterization of organostibonic acids stabilized by bulky organic substituents on the antimony atom.[3] Apart from X-ray structure determination, mass spectrometry has also been used to understand the basic structural motifs involved in the assembly of organostibonate based polyoxometallates (POMs) systems.[4] The biological activity exhibited by organostibonic acids needs a special mention.[5] Recent reports have also suggested the potential application of organostibonic acids as antimicrobial agents.[6]

In this manuscript, synthesis of new organostibonates / phosphonates based molecular clusters and a three component system (Sb/P/Se) involving reactions of organostibonates with phosphonic acid and seleninic acid are discussed. Reaction of *p*-chlorophenylstibonic acid with *t*-butylphosphonic acid led to the isolation of dinuclear organoantimony (V) oxo cluster as reported by Winpenny et al.[7] In the present study, use of *p*-isopropyl and *p*-tertiary butyl substituents on phenylstibonic acid have been used as starting materials. Importantly these organostibonic acids are soluble in common organic solvents unlike the literature reported example wherein the *p*-halophenylstibonic acids are insoluble white powders.[4] The intention of this study is twofold, 1) to investigate the change in reactivity of organostibonic acids with the change in organic substituents on the Sb atom and 2) to analyse the solubility difference of the organostibonic acids would affect the reactivity part on reaction with various protic ligand systems. Synthesis and structural characterization of discrete main group based molecular oxo-hydroxo clusters containing antimony, phosphorus and selenium atoms are reported in this manuscript. ESI-MS studies reveal that the integrity of solid state structures are retained in solution as well.

Results and Discussions

Compound **1** was synthesized by the reaction of *p*-isopropylphenylstibonic acid with *t*-butylphosphonic acid in acetonitrile (Scheme-1). Single crystals suitable for X-ray diffraction were grown from acetonitrile filtrate. Solution NMR of **1** was performed in $CDCl_3$ solvent. ^1H NMR of **1** shows two distinct doublets (at 7.8 and 7.2 ppm) corresponding to the two sets of aromatic protons of the isopropylphenyl group attached to antimony and in the alkyl region, three closely spaced doublets (at 1.2, 1.1 and 0.8 ppm) are present, corresponding to the presence of three sets of *t*-butyl group protons attached to phosphorus. Solution ^{31}P NMR of **1** shows three resonance peaks at δ = 34.5, 32.0 and 25.0 ppm which indicates the presence of three different phosphorus

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Electronic Supplementary Information (ESI) available: Selected metric parameters, crystallographic data and ORTEP diagrams are provided in the supporting information. CCDC reference numbers for 1-5 are 1420219-1420223. See DOI: 10.1039/b000000x/

environments in 1. Reaction of *p*-chlorophenylstibonic acid with *t*-butylphosphonic acid leading to isolation of dinuclear organoantimony (V) oxo cluster was reported by Winpenny et al.7 A change in R group on stibonic acid from *p*-chlorophenylstibonic acid to *p*-isopropylphenylstibonic acid results in the isolation of novel tetranuclear organoantimony (V) oxo cluster.

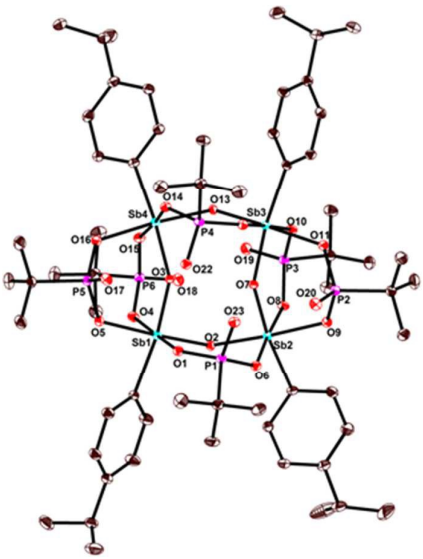


Fig.1: ORTEP view of 1 with thermal ellipsoids shown at 30% probability. H atoms and solvent molecule are omitted for clarity. Cyan: Sb, Purple: P, Red: O, Brown: C

Compound **1** crystalizes in triclinic space group P-1. Molecular structure of **1** (Fig.1) reveals the formation of a puckered eight-membered Sb_4O_4 core held together by six phosphonate ligands. The structure can be described as follows; each Sb is present in an octahedral geometry with the O_5SbC coordination. Of the six phosphonates found in the structure, four phosphonates (two pairs) bridge Sb-O-Sb motifs, while the other two phosphonates link the two Sb-O-Sb units along with the hydroxo group resulting in the formation of a tetranuclear cluster. The phosphonate coordination mode based on Harris notation is 2.110. As mentioned earlier, the solution ^{31}P NMR shows the appearance of three discrete signals corresponding to the three types of phosphonates present in the cluster. ESI-MS data suggests that the structural integrity is maintained solution also [M+H moiety, m/z =1849.1473]. The Sb-O bond lengths involving in the μ_2-hydroxide fall in the range 1.915(14) to 1.942(14)Å. In **1**, the P-O bond distances fall in the range of 1.502(17) to 1.561(17)Å. These P-O distances are found to be similar and comparable with the values reported in an organooxotin phosphonate cage [1.516(2) to 1.556(3)Å][8] and the corresponding distances in gallium phosphonate cages [1.504(2) to 1.555(2)][9] whereas the P-O distances are found to be slightly longer than those found in a borophosphonate cages [1.490(6) to 1.506(5) Å].[10] The Sb-O bond lengths involving phosphonates are in the range of 2.008(15) to 2.098(15)Å which is similar to the Sn-O bond lengths involving phosphonates in an organooxotin phosphonate cage [2.065(2) to 2.095(2)Å][8] whereas the bond lengths are slightly longer than in gallium phosphonate cages [1.908(2) to 1.946(2)Å].[9] The corresponding distances were also longer than those found in a borophosphonate cages [1.452(10) to 1.493(10)Å] reported.[10] The Sb-O-Sb bond angles fall in the range 132.8(8) to 140.1(8)^o.

Solution ^{1}H NMR of **2** shows two regions of aromatic protons**.** Two multiplets (at 7.9 and 7.5 ppm) and one doublet (at 7.6 ppm) corresponding to the protons of the phenyl group attached to phosphorus are present. Second region shows two distinct doublets (at 7.3 and 7.1 ppm) corresponding to two sets of aromatic protons of the *p*-*t*-butyl phenyl group attached to the Sb and in the alkyl region a singlet (at 1.2 ppm) corresponding to the *t*-butyl group protons attached to phenyl ring are observed. Solution ^{31}P NMR of **2** shows two resonance peaks at δ = 12.0 and 0.8 ppm indicating the presence of two different phosphonates present in **2**. Compound **2** crystalizes in tetragonal space group I-4 with ¼ of the molecule present in the asymmetric unit. Solid state structure of **2** is similar to earlier reports, where *p*-chlorophenylstibonic acid is used as starting precursor.[1] When the R group on the stibonic acid was changed to *p*-*t*-butylphenyl stibonate and phosphorus bound organic group has been changed to phenyl, the reaction between the organostibonate and phosphonic acid led to the isolation of structure that is quite different from compound **1**.

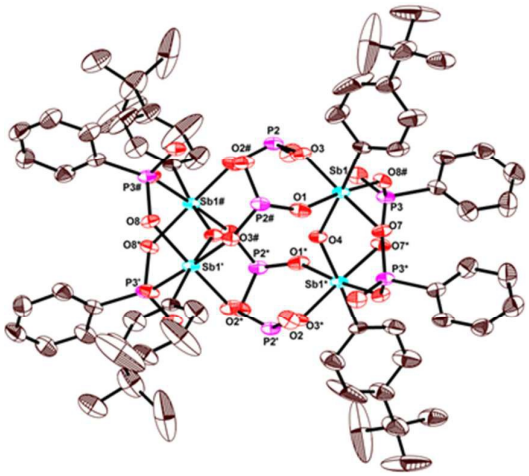
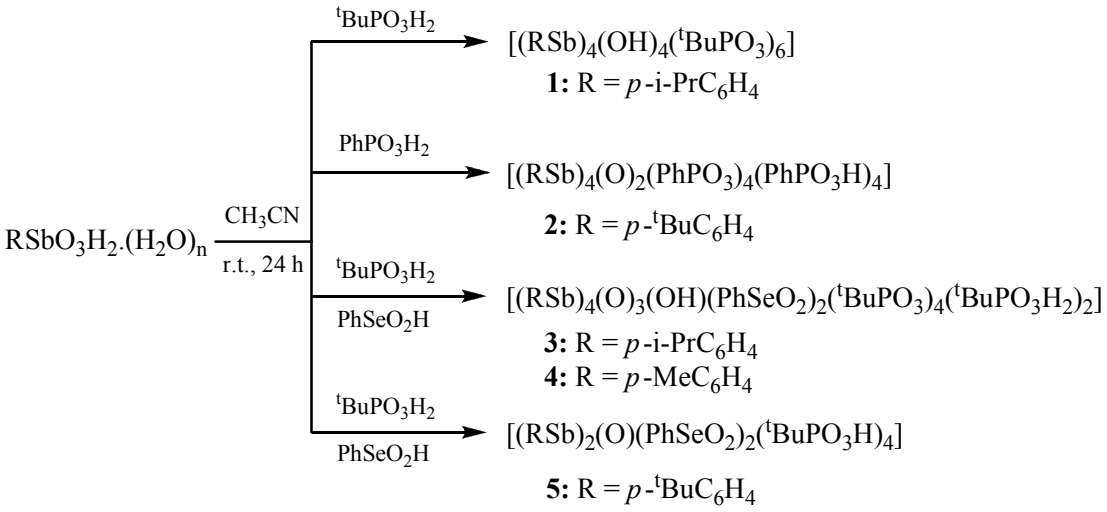


Fig.2: ORTEP view of 2 with thermal ellipsoids shown at 30% probability. H atoms and central phenyl rings are omitted for clarity. Cyan: Sb, Purple: P, Red: O, Brown: C

Molecular structure of **2** (Fig.2) reveals the formation of a tetranuclear organoantimony (V) oxo cluster made up of two Sb-O-Sb frameworks. Two pairs of phosphonate bridge the two Sb-O-Sb units. The two Sb-O-Sb motifs are approximately at right angle to each other. Of the eight phosphonates present, four are in dianionic form while the other four are monoanioinic. Each phosphonate chelate to antimony in 2.110 coordination mode. ESI-MS data reveals the presence of {M-$[(RSb)_2O(PhPO_3)_2]$} +3H (m/z =1469.0205) as a major peak. The spatial arrangement around each antimony atom is in an octahedral geometry with the O_5SbC coordination. The Sb-O bond length involving in the μ_2-oxide is 1.918(5)Å. In **2**, the P-O bond distances fall in the range of 1.504(10) to 1.558(8)Å

similar to those found in an organooxotin phosphonate cage[8] and gallium phosphonate cages[9] whereas the corresponding distances were slightly longer than those found in a borophosphonate cages.[10] The Sb-O bond lengths involving phosphonates fall in the range of 1.982(9) to 2.036(8)Å, similar to those found in Sn-O bond lengths involving phosphonates in an organooxotin phosphonate cage[8] and slightly longer than the gallium phosphonate cages[9] whereas the corresponding distances were relatively longer than those found in a borophosphonate cages.[10] The Sb-O-Sb bond angle is 136.3(7)°.

Compounds **3-5** were synthesized by the reaction of organostibonic acid with phosphonic acid and seleninic acid in acetonitrile (Scheme-1). The idea was to observe the reactivity of organostibonic acid in the presence of phosphonic acid and seleninic acid. Solution NMR studies for compounds **3-5** were performed in $CDCl_3$ solvent. Solution ^{31}P NMR of **3** shows two resonance peaks at δ = 35.0 and 30.3 ppm while ^{77}Se NMR shows a single resonance at δ = 1079.1 ppm, which indicates presence of two different phosphorus environments and a unique selenium environment in **3**. Similarly, solution ^{31}P NMR of **4** also show two resonance peaks at δ = 35.0 and 30.4 ppm and ^{77}Se NMR shows a single resonance at δ = 1081.0 ppm. Solution ^{31}P NMR of **5** also shows two resonance peaks at δ = 32.4, 29.4 ppm and ^{77}Se NMR shows a signal at δ = 1065.0 ppm**.** Compound **3** crystalizes in the orthorhombic space group Pbca and **4** crystalizes in triclinic space group P-1. Since compounds **3** and **4** are isostructural, the structure of **3** is considered for discussion (Fig.3). The structure of **4** along with selected bond lengths (Å) and bond angles (deg) are given in supporting information. The molecular structure of **3** reveals the formation of tetranuclear organoantimony (V) oxo cluster whose structure is described as follows. Each Sb is present in



Scheme- 1

an octahedral geometry with the O_5SbC coordination. The cluster core has four Sb centers, in which two sets of Sb atoms are found in the cluster. The first set of Sb atoms, Sb_1 and Sb_2, are connected between themselves through two μ_2- oxo bridges. The second set of two Sb atoms, Sb_3 and Sb_4, are connected through two phenylseleninic acid O-Se-O bridges. The two different set of Sb atoms are further connected by the two oxo bridges. Four phosphonates bridge to Sb-O-Sb edge in 2.110 coordination mode. The two phenylseleninic acids form a symmetrical bridge between two antimony atoms in a bent on fashion. Interestingly the solid state structure of **3** has two uncoordinated *t*-butylphosphonic acids which crystalize along with the core. These two phosphonic acids sacrifice their bonding to phenylseleninic acid and are free from coordination to Sb and stabilize the cluster core by hydrogen bonding. Out of four μ_2-oxo bridges present, three are considered as oxide bridges and one considered as hydroxyl, this would account for the charge balance and hydrogen bonding present in **3**. As mentioned earlier the solution ^{31}P NMR shows the appearance of two discrete signals corresponding to the two types of phosphonates: one phosphonate group bridges the Sb atoms and other is a free phosphonate. The Sb-O bond lengths involving in the μ_2-oxide fall in the range of 1.911(5) to 2.025(5)Å. In **3**, the P-O bond distances fall in the range of 1.499(6) to 1.567(5)Å) similar to those found in an organooxotin phosphonate cage[8] and gallium phosphonate cages[9] and slightly longer than those found in a borophosphonate cages.[10] The Sb-O bond lengths involving phosphonates fall in the range of 2.005(5) to 2.040(5)Å similar to those found in Sn-O bond lengths involving phosphonates in an organooxotin phosphonate cage[8] and slightly longer than gallium phosphonate[9] whereas the corresponding distances were longer than those found in a borophosphonate cages.[10] The Se-O bond distances fall in the range of 1.725(5) to 1.740(5)Å similar to those found in Mn_7 seleninate cluster [1.703(2) to 1.741(3)Å][11] whereas the corresponding distances were slightly longer than those found in an organotin selininate ester [1.682(5) to 1.696(5)Å][12] and the recently reported selenotelluroxane macrocycle [1.678(4) to 1.690(2)Å].[13] The Sb-O bond lengths involving

phenylseleninates fall in the range of 2.024(5) to 2.033(5)Å, these distances are comparable with reported Mn_7 seleninate cluster [1.944(6) to 2.002(6)Å][11], organotin selininate ester 2.225(5)Å[12] and selenotelluroxane macrocycle [2.329(4) to 2.361(4)Å].[13] Bond angles of Sb-O-Sb, Sb-O-Se and O-Se-O fall in the range of 102.3(2) to 139.7(3)°, 122.7(3) to 124.3(3)° and 99.7(2) to 100.9(2)° respectively. Bond angles of C-Sb-O fall in the range of 174.7(2) to 179.3(3)° clearly indicating that the geometry around each Sb center is regular octahedral (180°). Compounds **3** and **4,** ESI-MS data show M-(2 *t*-$BuPO_3H_2$) (m/z = 1950.9436, 1838.8250 respectively) as a major peak, suggesting structural integrity in solution as well.

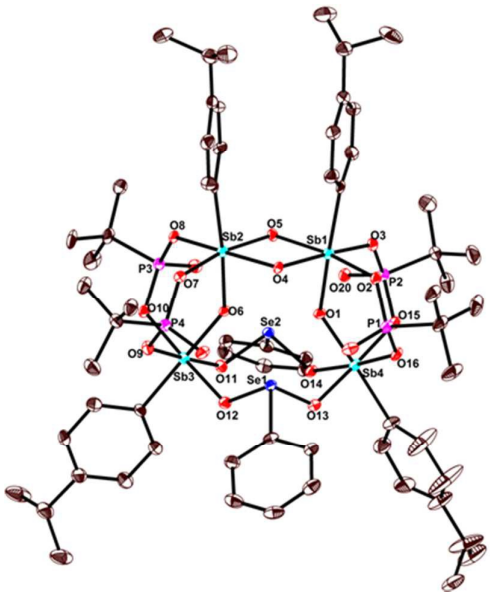


Fig.3: ORTEP view of **3** with thermal ellipsoids shown at 30% probability. H atoms, free t-$BuPO_3H_2$ molecules and solvent molecules are omitted for clarity. Cyan: Sb, Blue: Se, Purple: P, Red: O, Brown: C

Compound **5** crystallizes in monoclinic $P2_1/c$ space group. The solid state structure of **5** (Fig.4) reveals the formation of a dinuclear organoantimony (V) oxo cluster. The molecular structure of **5** is described as follows; two arylstibonates bridged by a μ_2-oxide form Sb-O-Sb edge, and this edge is further chelated by two phosphonic acids in 2.110 coordination mode. Each Sb atom is further connected with one protonated phosphonate and one phenylseleninic acid. As mentioned earlier the solution ^{31}P NMR shows the appearance of two discrete signals corresponding to the two types of phosphonates: one phosphonate group forms a symmetrical bridge between two Sb atoms and other phosphonate form terminal bond with Sb in 1.100 coordination mode. Phenylseleninic acid is bound to Sb in a monodentate fashion. For the charge neutrality of cluster all *t*-butyl phosphonates are considered as protonated phosphonates. The Sb-O bond lengths involving in the μ_2-oxide are 1.929(8) and 1.957(7)Å.

In **5**, the P-O bond distances fall in the range of 1.488(9) to 1.558(8)Å similar to those found in an organooxotin phosphonate cage[8], gallium phosphonate cages[9] and slightly longer than those found in a borophosphonate cages.[10] The Se-O bond distances fall in the range of 1.707(8) to 1.735(8)Å similar to those found in Mn_7 seleninate cluster[11], slightly longer than those found in organotin selininate ester[12] and selenotelluroxane macrocycle.[13] The Sb-O bond lengths involving phenylseleninates fall in the range of 2.023(8) to 2.038(8)Å, these distances are comparable with reported Mn_7 seleninate cluster[11], organotin selininate ester[12] and selenotelluroxane macrocycle.[13] Bond angles of Sb-O-Sb, Sb-O-Se and O-Se-O fall in the range of 134.7(4)°, 123.0(4) to 124.0(4)° and 101.5(4) to 103.9(4)° respectively. ESI-MS data of **5** shows M+H (m/z = 1451.0415) as a major peak.

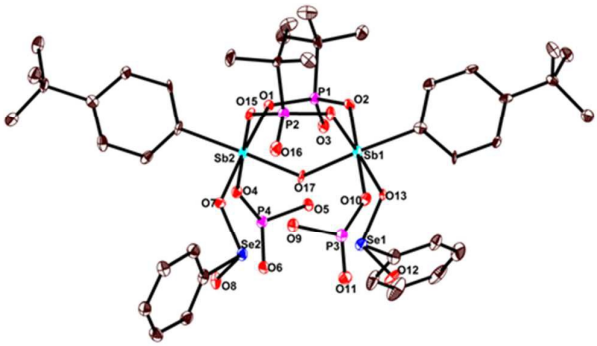


Fig.4: ORTEP view of **5** with thermal ellipsoids shown at 30% probability. H atoms, P3 and P4 attached *t*-butyl groups and solvent molecules are omitted for clarity. Cyan: Sb, Blue: Se, Purple: P, Red: O, Brown: C

Experimental Section

Reagents and General Procedures:

Arylstibonic acids[14] (aryl= *p*-isopropylphenyl, *p*-*t*-butylphenyl and *p*-methylphenyl) and *t*-butylphosphonic acid[15] were synthesized according to literature reports. Phenylseleninic acid, phenylphosphonic acid, solvents and common reagents were purchased from commercial sources.

Instrumentation:

Infrared spectra were recorded with a JASCO-5300 FT-IR spectrometer as KBr pellets. The solution ^1H, ^{13}C, ^{31}P and ^{77}Se NMR spectra were recorded with a Bruker AVANCE^{III} 400 instrument. Elemental analysis was performed with a Flash EA Series 1112 CHNS analyzer. ESI-MS spectra were recorded using Bruker MaXis HRMS (ESI-TOF analyzer) equipment. Single-crystal X-ray data collection for compounds **1–5** was carried out at 100(2) K with a Bruker Smart Apex CCD area detector system [λ (Mo-$K\alpha$) = 0.71073 Å] with a graphite monochromator. The data were reduced using SAINTPLUS, and the structures were solved using SHELXS-97[16] and refined using the program SHELXL-2014/7.[17, 18] All non-hydrogen atoms were refined anisotropically. In **2** the disorder associated with phenyl rings were constrained using EADP, ISOR, DELU, SIMU instructions in SHELXL-2014/7. The compounds **3** have residual electron density owing to solvent of crystallization (acetonitrile) which could not be properly fixed. In, **4** disordered solvent accessible voids are present in the asymmetric unit. These solvent contributions were

removed by using the SQUEEZE[19] command in PLATON[20]. The total electron count 64 (belongs to three disordered acetonitrile solvent molecules) with a void volume of 343 Å^3 (8%) per unit cell in **4** was removed by SQUEEZE.

General synthetic procedures for compounds 1-5: The general synthetic methodology adopted is as follows: The appropriate reagents (Organostibonic acid/Phosphonic acid/Seleninic acid) were taken in 1:2 (or) 1:1:1 mole ratios and stirred in acetonitrile (15mL) for 24 h at room temperature resulting in the formation of white cloudy solution. The solution was filtered and on slow evaporation of acetonitrile, crystals were isolated. The isolated crystals were powdered and subjected to high vaccum for half an hour before being characterized by standard spectroscopic and analytical techniques. Colourless block crystals suitable for single crystal X-ray studies were grown from acetonitrile filtrate in one week's time. The molar ratios of the corresponding reagents used are as follows.

Compound **1**: *p*-Isopropylphenylstibonic acid (0.100g, 0.343 mmol) and *t*-butylphosphonic acid (0.095g, 0.687 mmol). Yield: 0.136 g (86% based on *p*-isopropylphenylstibonic acid). Decp temp: 275-276 ^{o}C. Anal, Calcd (%) for $C_{60}H_{102}O_{22}P_6Sb_4$ (1848.32): C 38.99, H 5.56. Found: C 39.12, H 5.41. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.78 (d, 8H), 7.21(d, 8H), 3.00-2.90 (m, 4H), 1.25(d, 24H), 1.21(d, 18H), 1.14(d, 18H), 0.86(d, 18H).^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.47, 133.09, 125.94, 34.06, 32.42, 30.96, 25.26, 23.93 ppm. ^{31}P NMR (162 MHz, $CDCl_3$) δ: 34.47, 32.09, 24.99 ppm. IR (cm^{-1}, KBr pellet): 3402(wide), 2964(s), 2909(m), 2876(s), 1479(s), 1397(s), 1364(w), 1252(m), 1074(m), 986(m), 816(s), 652(s), 553(s).

Compound **2**: *p*-*t*-Butylphenylstibonic acid (0.100g, 0.327 mmol) and phenylphosphonic acid (0.103 g, 0.655 mmol). Yield: 0.148 g (79% based on *p*-*t*-butylphenylstibonic acid). Decp temp: 267-268 ^{o}C. Anal, Calcd (%) for $C_{88}H_{96}O_{26}P_8Sb_4$ (2304.51): C 45.86, H 4.20. Found: C 45.62, H 4.38. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.90-7.75 (m, 16H), 7.65 (d, 8H), 7.53-7.40(m, 16H), 7.35(d, 8H), 7.15(d, 8H), 1.20(s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.44, 144.68, 132.45, 129.51, 127.67, 126.25, 125.44, 34.69, 31.08 ppm. ^{31}P NMR (162 MHz, $CDCl_3$) δ: 12.09, 0.85 ppm. IR (cm^{-1}, KBr pellet): 3063(wide), 2959(s), 2866(m), 1436(s), 1397(s), 1140(m), 1090(s), 1014(s), 981(s), 822(m), 756(s), 718(m), 690(s), 542(s).

Compound 3: *p*-Isopropylphenylstibonic acid (0.100g, 0.343 mmol), *t*-butylphosphonic acid (0.048g, 0.343 mmol), and phenylseleninic acid (0.065g, 0.343 mmol). Yield: 0.124 g (65% based on *p*-isopropylphenylstibonic acid). Decp temp: 280-281 ^{o}C. Anal, Calcd (%) for $C_{72}H_{114}O_{26}P_6Se_2Sb_4$ (2226.46): C 38.84, H 5.16. Found: C 38.76, H 5.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02-7.80(m, 10H), 7.56(d, 8H), 7.45(d, 8H), 3.35-3.60(m, 4H), 1.36 (d, 24H), 1.19 (d, 18H), 1.03(d, 36H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.28, 149.20, 146.78, 141.69, 133.12, 128.62, 116.35, 34.07, 30.92, 24.92, 23.73 ppm. ^{31}P NMR (162 MHz, $CDCl_3$) δ: 34.97, 30.32 ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$) δ: 1079.14 ppm. IR (cm^{-1}, KBr pellet): 3408(wide), 3035(m), 2958(s), 2926(m), 2904(m), 2871(s), 1669(s), 1489(s), 1397(s), 1364(s), 1240(m), 1118(s), 1030(m), 1008(m), 822(s), 767(s), 734(s), 668(s), 542(s).

Compound 4: *p*-Methylphenylstibonic acid (0.091g, 0.343 mmol), t-butylphosphonic acid (0.048g, 0.343 mmol), and phenylseleninic acid (0.065g, 0.343 mmol). Yield: 0.122 g (68% based on p-methylphenylstibonic acid). Decp temp: 278-279 ºC. Anal, Calcd (%) for $C_{64}H_{98}O_{26}P_6Se_2Sb_4$ (2114.25): C 36.36, H 4.67. Found: C 36.28, H 4.63. 1H NMR (400 MHz, CDCl3) δ: 7.72-7.58(m, 10H), 7.18(d, 8H), 6.80(d, 8H), 2.25(s, 12H), 1.25 (d, 18H), 1.12(d, 36H). 13C NMR (100 MHz, CDCl3) δ: 143.61, 141.24, 138.72, 132.23, 129.30, 128.65, 127.95, 31.59, 30.98, 29.73, 24.88, 21.49 ppm. 31P NMR (162 MHz, CDCl3) δ: 35.01, 30.42 ppm. 77Se NMR (76.3 MHz, CDCl3) δ: 1081.00 ppm. IR (cm-1, KBr pellet): 3430(wide), 3050(m), 2963(s), 2926(m), 2854(m), 1635(s), 1479(s), 1443(m), 1396(s), 1256(m), 1096(s), 799(s), 749(s), 663(s), 559(s).

Compound 5: *p*-*t*-Butylphenylstibonic acid (0.105g, 0.343 mmol), *t*-butylphosphonic acid (0.048g, 0.343 mmol), and phenylseleninic acid (0.065g, 0.343 mmol). Yield: 0.135 g (54% based on *p*-*t*-butylphenylstibonic acid). Decp temp: 269-270 ^{o}C. Anal, Calcd (%) for $C_{48}H_{76}O_{17}P_4Se_2Sb_2$ (1450.44): C 39.75, H 5.28. Found: C 39.68, H 5.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06-8.04(m, 10H), 7.79(d, 4H), 7.56(d, 4H), 1.36(s, 18H), 1.21(d, 18H), 1.05(d, 18H). 13C NMR (100 MHz, CDCl3) δ: 153.44, 143.61, 132.51, 129.24, 127.65, 125.48, 34.87, 32.66, 31.26, 25.32 ppm. . ^{31}P NMR (162 MHz, $CDCl_3$) δ: 32.41, 29.43 ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$) δ: 1065.02 ppm. IR (cm^{-1}, KBr pellet): 3413(br), 3061(m), 2965(s), 2904(w), 2869(m), 1589(m), 1479(s), 1443(m), 1395(s), 1364(s), 1267(m), 1061(m), 1008(s), 822(s), 744(s), 686(s), 665(m), 550(s).

Conclusions

Tetra- and dinuclear organoantimony oxo-hydroxo clusters stabilized by phosphonate and a combination of phosphonate/selininate ligation are reported. ESI-MS data reveals that the structural integrity is maintained in solution as well. ^{31}P and ^{77}Se solution NMR values observed are in accordance to the expected values based on the solid state structure observed and its solution stability. It may thus be noted that clusters **1**-**5** are potentially new main group elements based pro-ligand systems. Their coordination behaviour towards transition metals and lanthanides are currently being investigated.

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Graphical abstract

Synthesis and structural characterization of novel tetra- and dinuclear organoantimony oxo-hydroxo clusters ligated by phosphonates and phosphonates/selininates are reported. Mass spectral studies reveal that the solid state molecular structures of these clusters also retained in solution as well.