Reactivity studies of Organostibonic acids: Isolation of discrete molecular clusters and Polyoxometalates framework

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A Thesis

Submitted for the degree of

DOCTOR OF PHILOSOPHY

by

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(08CHPH15)

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Dedicated

To

Beloved god,
Parents
&
Teachers

STATEMENT

I hereby declare that the matter embodied in the thesis entitled ***"Reactivity studies of Organostibonic acids: Isolation of discrete molecular clusters and Polyoxometalates framework"*** is the result of investigations carried out by me in the School of Chemistry, University of Hyderabad, India under the supervision of **Dr. Viswanathan Baskar**. This work is also free from plagiarism. I hereby agree that my thesis can be submitted in Shodhganga/INFLIBNET.

In keeping with the general practice of reporting scientific investigations, the acknowledgements have been made wherever the work described is based on the findings of other investigators. Any omission or error that might have crept in is regretted.

April 2016

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CERTIFICATE

Certified that the work embodied in the thesis entitled ***"Reactivity studies of Organostibonic acids: Isolation of discrete molecular clusters and Polyoxometalates framework"*** has been carried out by **Mr. M. Santhana raj prabhu** under my supervision and the same has not been submitted elsewhere for any degree.

Viswanathan Baskar
(Thesis Supervisor)

Dean
School of Chemistry
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M. Santhana raj prabhu

CONTENT

Abbrevations

PyO	pyridine-N-oxide
DMSO	dimethylsulfoxide
HMPA	hexamethylphosphoramide
Acac	acetylacetone
Trid	tridentate schiff base ligands
H_2Sah	2, $2'$-(methylidynenitrilo) diphenol
H_2Bah	3-(*o*-hydroxyanilino) crotonophenone
H_2Aah	4-(*o*-hydroxyphenylimino)-2-pentanone
H_2O_2	hydrogen peroxide
DCM	dichloromethane
t-Bu	tert-butyl
cyc	cyclo
NaOMe	sodium methoxide
DNA	deoxyribonucleic acid
DCO	2-(Oximido)(N,N-dimethylamido)acetonitrile
ACO	2-cyano-2-isonitrosoacetamide
THF	tetrahydrofuran

SYNOPSIS

This thesis is entitled **“Reactivity studies of Organostibonic acids: Isolation of discrete molecular clusters and Polyoxometalates framework”.** The details of five chapters given below.

Chapters 1

Chapter 1 deals with detailed literature survey about synthesis, characterization and biological activity of organoantimony(V) compounds. This will be followed by a brief introduction to organostibonic acids, its synthesis and depolymerization reactions with various protic ligands.

Chapters 2

Dinuclear and Tetranuclear Organoantimony(V) Oxido clusters stabilized by dianionic ligands

This chapter deals with the synthesis and characterization of a series of neutral tetranuclear organoantimony(V) oxido clusters, which has been synthesized by using substituted phenolic oxime as a protic ligands. Crystal structures of clusters **2.1-2.5** revealed that all are tetranuclear and isostructural [(*p*-chloro-$C_6H_4Sb)_4(O)_4(L_1)_4$] (**2.1**), [(*p*-bromo-$C_6H_4Sb)_4(O)_4(L_1)_4$] (**2.2**), [(3,5-dichloro-$C_6H_3Sb)_4(O)_4(L_1)_4$] (**2.3**), [(*p*-bromo-$C_6H_4Sb)_4(O)_4(L_4)_4$] (**2.4**) and [(*p*-chloro-$C_6H_4Sb)_4(O)_4(L_5)_4$] (**2.5**). A series of five dinuclear organoantimony(V) oxido clusters have also been synthesized by using organoantimony halides, substituted phenolic oxime and Et_3N as a base in 1:1:2 molar ratio in room temperature condition. Sb-C bond cleavage has been observed in **2.6**, **2.9** and **2.10.** Crystal structures of clusters **2.6-2.10** revealed that they are dinuclear and isostructural [$(Ph_2Sb)_2(O)(L_1)$] (**2.6**), [$(Ph_2Sb)_2(O)(L_2)$] (**2.7)** [$(Ph_2Sb)_2(O)(L_3)$] (**2.8**), [$(Ph_2Sb)_2(O)(L_4)$] (**2.9**) and [$(Ph_2Sb)_2(O)(L_5)$] (**2.10**). ESI-MS of clusters **2.1-2.8** and **2.10** shows that structural integrity in solution as well.

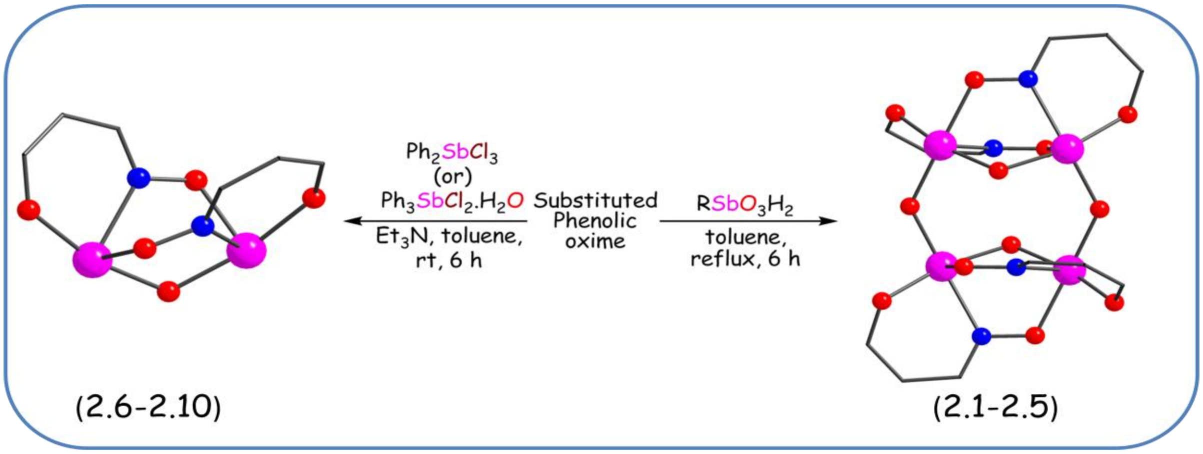


Figure 1: Schematic representation for the preparation of **2.1-2.10**.

Chapters 3

Organoantimony(V) Oxido cubane cluster [(*p*-X-$C_6H_4Sb)_4(O)_4(Ph_2SiO_2)_4$] and [(*m*-$X_2$-$C_6H_3Sb)_4(O)_4(Ph_2SiO_2)_4$] (X = Cl, Br) stabilized by diphenyldisiloxides

This chapter describes the reaction of (*p*-halophenyl)stibonic acid or (*m*-dihalophenyl)stibonic acid with diphenylsilanediol (in ratio 1:1) in refluxing toluene for 6 h which afforded colorless crystalline products in high yields. Single crystal X-ray structural elucidation reveals the formation of the products [(*p*-Cl-$C_6H_4Sb)_4(O)_4(Ph_2SiO_2)_4$] (**3.1**), [(*p*-Br-$C_6H_4Sb)_4(O)_4(Ph_2SiO_2)_4$] (**3.2**) and [(*m*-$Cl_2$-$C_6H_3Sb)_4(O)_4(Ph_2SiO_2)_4$] (**3.3**) respectively. The clusters **3.1**, **3.2** and **3.3** were isostructural; the core consists of a distorted Sb_4O_4 cubane framework with the siloxides acting as bridging ligands across the antimony atoms present at alternate corners of the cube.

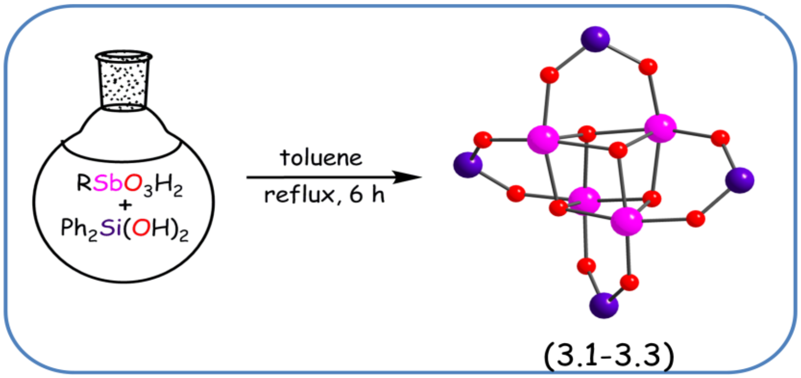


Figure 2: Schematic representation for the preparation of **3.1-3.3**.

Chapters 4

In situ generated polysiloxanes stabilizing μ_3-oxo bridged Sb_3 triangles

This chapter deals with the reaction of $RSbO_3H_2$ with *t*-butylsilanetriol leading to the isolation of organoantimony (V) based molecular triangle stabilized by siloxane frameworks$\{[C_5H_5NH].[(p\text{-}Cl\text{-}C_6H_4Sb)_3\{(t\text{-}Bu)_4Si_4O_9\}\{(t\text{-}Bu)_2Si_2O_5\}(\mu_3\text{-}O)(\mu\text{-}OH)]\}$(**4.1**), $\{[C_5H_5NH].[(p\text{-}Br\text{-}C_6H_4Sb)_3\{(t\text{-}Bu)_4Si_4O_9\}\{(t\text{-}Bu)_2Si_2O_5\}(\mu_3\text{-}O)(\mu\text{-}OH)]\}$(**4.2**) and $\{[C_5H_5NH].[(3,5\text{-}Cl_2\text{-}C_6H_3Sb)_3\{(t\text{-}Bu)_4Si_4O_9\}\{(t\text{-}Bu)_2Si_2O_5\}(\mu_3\text{-}O)(\mu\text{-}OH)]\}$(**4.3**). A combination of a disiloxane and a tetrasiloxane frameworks were generated *in situ* leading to the stabilization of the rare Sb_3 triangles observed. ESI-MS studies reveal that the structural integrity is maintained in solution also.

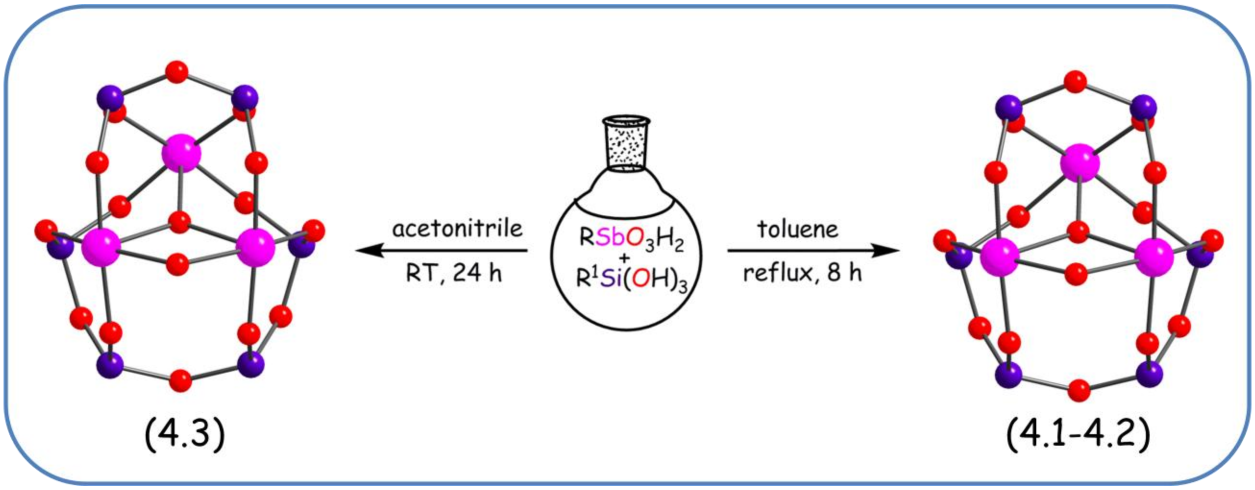


Figure 3: Schematic representation for the preparation of **4.1-4.3**.

Chapters 5

Isolation of high nuclearity isopolyoxostibonates using base

This chapter describes the self-condensation of $RSbO_3H_2$ in presence of a base (tetramethylammonium hydroxide pentahydrate) in ratio 1:1. Single crystal X-ray structural elucidation reveals the formation of $\{(NMe_4)_2[(p\text{-}Cl\text{-}C_6H_4Sb)_{16}(O)_{30}(OH)_6]\}$ (**5.1**), $\{(NMe_4)_3[Na_2(p\text{-}Br\text{-}C_6H_4Sb)_{12}(O)_{23}(OH)_7.4H_2O_{(coord)}]\}$ (**5.2**) and $\{(NMe_4)_4[Na(m\text{-}Cl_2\text{-}C_6H_3Sb)_{12}(O)_{23}(OH)_7]\}$ (**5.3**) respectively. Isopolyoxostibonate acts as inorganic crown type ligands encapsulating Na ion in **5.2** and **5.3.**

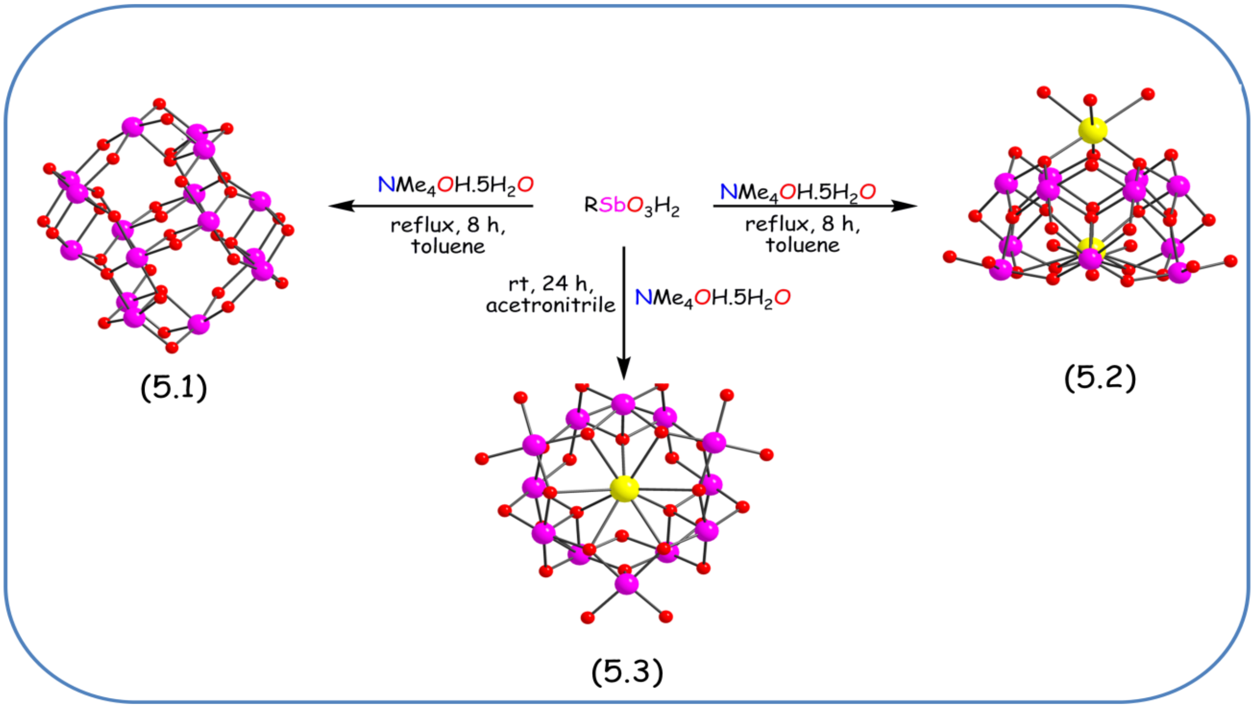


Figure 4: Schematic representation for the preparation of **5.1-5.3**.

++++++++++++++++++ **The end of synopsis** ++++++++++++++++++

INTRODUCTION

Chapter

1

1.1 Introduction:

Antimony is a semi metallic element which exists in two forms, the metallic form is bright, silvery, hard and brittle while the non-metallic form is a grey powder. Antimony resides in the nitrogen family (group 15) and has an electronegativity of 2.05. Antimony is usually obtained from the ores of sulfide mineral stibnite (Sb_2S_3). ^{121}Sb and ^{123}Sb are the two stable isotopes with a natural abundance of 57.36% and 42.64% respectively. Diodes and infrared detectors are certain types of semiconductor devices which are made from very pure antimony. Antimony compounds are used to make fire retardants, pottery, glass, ceramic enamels and paints. Among other products antimony alloys are also used in batteries, low friction metals and for cable sheathing. Antimony was alloyed with tin and lead which increases the properties of the alloys and is used in solders, bullets and plain bearings. Use of antimony in the field of microelectronics is an emerging application. In ancient times antimony compounds were used for cosmetics. Antimony was used in the form of stibnite. In ancient times Egyptians used Sb for black eye make-up. During the fifteenth and sixteenth centuries antimony was widely used as a medicine. Use of antimony in medicine field continues even today, it was used in homeopathic ointments in order to treat chapped skin and also to treat hemorrhoids.[1]

Antimony complexes have been used in the field of medicine and cosmetics.[2,3] For the treatment of various parasitic diseases antimony containing compounds are commonly used. For example, sodium antimony(V) gluconate is being used as a drug.[4] Due to the fascinating structural diversity varying from discrete monomeric molecular species to supramolecular assemblies the chemistry of organoantimony(V) complexes has attracted significant attention in recent times.[5] Similar to that of *cis*-platin, organoantimony derivatives also exhibit significant antimicrobial properties as well as antitumor activities[6] which is associated with cytostatic activity.[7] The biological toxicity of Sb is less than Pt and Pd based anticancer substances. In addition, organoantimony derivatives also show important functions as biocides, fungicides, catalyst components and antioxidants. Antimony in the oxidation state of +5 is interesting considering its hypervalent nature.[8] In organic synthesis organoantimony(V) compounds have been used either as reagents or as catalysts extensively.[9]

1.2 Biological activity:

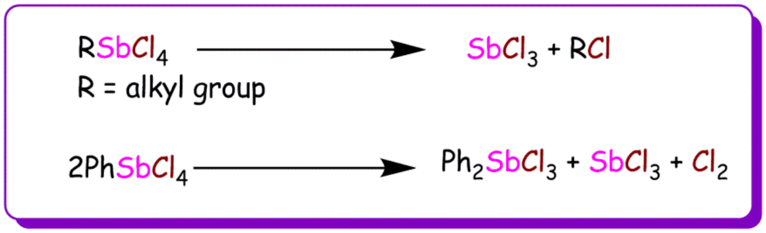
Antimonials Since 1913, has been used in the field of therapeutic agent with the introduction of Sb(III) potassium tartarate in the treatment of leishmaniasis. Pentavalent antimonials have replaced trivalent antimonials due to less toxic nature of Sb(V) compounds such as meglumine antimoniate for treating diseases. Meglumine antimoniate is recommended by WHO as a first choice medicine for leishmaniasis therapy.[10] Bayer in 1915 introduced the first organometallic fungicides Upsulun which is an organomercurial compound. Since organomecurial compounds are environment unfriendly, Beiter and Leebrick 1963 chose a series of tri and pentavalent organoantimony and organobismuth compounds and examined their activity against fungicides. It was found that organoantimony are moderately fungitoxic and more effective than organobismuth compounds. Burrell and Corke in 1980 studied the fungitoxicity of organo antimony compounds and found that fungal toxicity activity increased with increasing the molecular weight of organic compound attached to group VA element.[11]

Cristian Silvestru *et al* investigated the organoantimony(III) derivatives of dithiophosphorus ligand which were found to shows antitumor properties in both *in vitro* and *in vivo* studies.[12] Cytotoxic activity to vascular endothelical cell was diminished when they replaced the bismuth atom by antimony atom in 2-(N,N-dimethylaminomethyl)phenylbis(4-methyl phenyl)bismuthane (DAPBi).[13] $(C_6F_5)_2SbPh$ shows antifungal, antibacterial and insecticidal activities. This compound has also been used as pesticide and insecticide for plant diseases as reported by R. Kant *et al.* Later the group also synthesized the diaryl antimony(III) amide which exhibits antitumor activity against mammary cancer cell line and human breast adenocarcinoma cell line. In addition it also shows antibacterial activity against *Pseudomonas aeruginosa, Staphylococcus aureus, and Klebsiela pneumonia.* It exhibits significant antifungal properties against *Aspergillus flavus and Aspergillus niger*.[14]

Organoantimony(V) derivatives from Schiff bases exhibits higher antimicrobial activity than organoantimony(III) derivatives against *Aspergillus flavus and Escherichia coli*.[15] Potent antimicrobial properties are revealed in three discrete organoantimony(III) containing heteropolytungstates which was recently documented by U. Kortz *et al*.[16] Organostibonic acids have also been used as potential anticancer agents, which inhibits the DNA binding[17a,b] group of B-ZIP proteins at micromolar concentration have been recently reported by Vinson *et al*.[17c-e]

1.3 Monoorganoantimony Compounds:

Monoorganoantimony(V) halides, due to their unstable nature, structural aspects of mono-alkyl and arylantimony(V) chlorides are not fully understood.[18] For example at room temperature phenylantimony tetrachloride tends to disproportionate. Monoalkylantimony tetrachlorides also undergoes decomposition ready.



Scheme 1

In order to stabilize the monoorganoantimony(V) chlorides, addition of neutral oxo donor ligands have been used which stabilize the compound at room temperature. On the basis of spectral analysis such as IR and ^{1}H NMR it was suggested that the antimony atom is hexacoordinated. In solution state, $CH_3SbCl_4{\cdot}L$ (L = PyO or 4-CH_3PyO) exists as monomer in *cis* and *trans* forms. Above 70 ˚C $CH_3SbCl_4.L$, it undergo decomposition giving rise to CH_3Cl and $SbCl_3L$.[19]

1.3.1 *β*-diketones derivatives:

Monoorganoantimony (acetylacetonato) trichlorides have been synthesized either by the reactions of phenylstibonic acid in HCl or monoorganoantimony(V) chloride with acetylacetone at low temperature condition.[20] In solution state, monoorganoantimony(acetylacetonato) trichlorides are monomeric. The IR spectra reveal that these compounds show acetylacetone bidentate ligation. On the basis of the observed doublet and singlet for acetylacetone-CH_3 in the ^{1}H NMR spectra, Okawara and co-workers have suggested an asymmetric octahedral structure for $PhSb(acac)Cl_3$ and a symmetric structure for $MeSb(acac)Cl_3$ in which methyl group occupys an axial position (Figure 1). Kawasaki *et al* have studied ^{1}H NMR for $PhSb(acac)Cl_3$ which shows asymmetric octahedral structure were the phenyl group occupies an equatorial position.

For $MeSb(acac)Cl_3$ the magnitude of the separation between methyl resonance increases in aromatic solvents indicating an enhancement in the non-equivalance of two acetylacetone-CH_3 groups as a result of the aromatic ring current effect on asymmetrically solvated solute molecule. The dipole moment data also supports the asymmetric geometry for these compounds. Later the single crystal X-ray diffraction analysis of $MeSb(acac)Cl_3$ support the asymmetric structure with distorted octahedral geometry.[21]

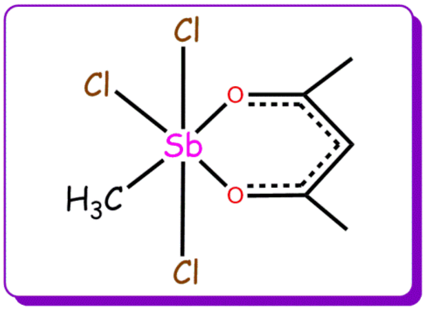
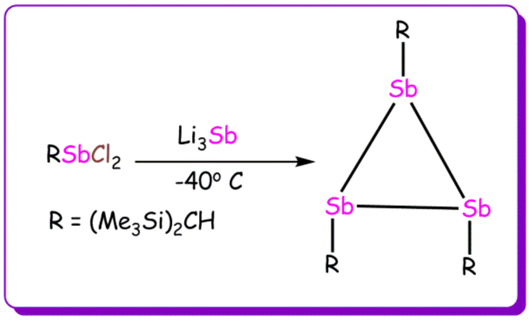


Figure 1: Asymmetric structure of an $MeSb(acac)Cl_3$

The three-membered organoantimony ring cyclo-Sb_3R_3 [R = $(Me_3Si)_2CH$][22a] was prepared by Breunig and co-workers by reaction of $RSbCl_2$ with Li_3Sb at -40 °C. The alkyl groups are occupying *cis* and *trans* positions. The *cis-trans* positions of the substituents are identified by ^1H and ^{13}C NMR spectra in solution state. The three antimony atoms present almost resemble an equilateral triangular motif (Scheme 2).



Scheme 2

1.3.2 Polyoxometalates:

The first organoantimony-containing POM $[\{PhSbOH\}_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{9-}$, is a sandwich-type tungstophosphate which is dimeric in nature (Figure 2). The polyanion can be synthesized by the direct interaction of diphenylantimony trihalide with three different lacunary tungstophosphate precursors, $Na_9[(A\text{-}\alpha\text{-}PW_9O_{34}]$, $K_7[PW_{11}O_{39}]$, or $K_{10}[P_2W_{20}O_{70}(H_2O)_2]$, in an aqueous acidic medium under hydrothermal conditions. The cluster formation takes place by removal of one of the phenyl group during its reaction with diphenylantimony trihalide.[22b]

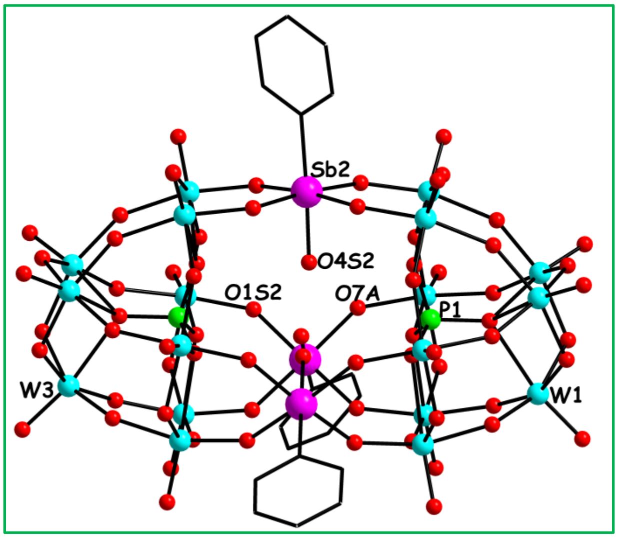
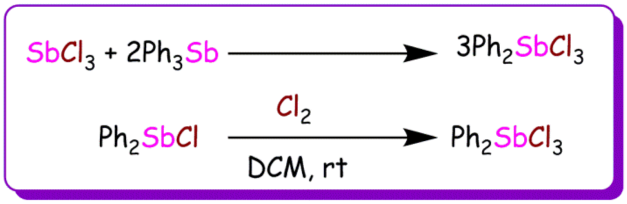


Figure 2: Molecular structure of $[\{PhSbOH\}_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{9-}$

1.4 Diorganoantimony Compounds:

1.4.1 Synthesis of diphenylantimony trichloride:

Diorganoantimony(V) halides have been synthesized by treating antimony(III) chlorides with diazonium salts or by halogenations of diorganoantimony(III) halides R_2SbX with X_2 (X = Cl, Br) (Scheme 3).[23]



Scheme 3

Some of the reducing agents like stannous chloride, sulfur dioxide are used to reduce diorganoantimony(V) halides to diorganoantimony(III) halides.[24]

1.4.2 Dimeric structure of diphenylantimony trichloride:

Michaelis and Reese first synthesized diphenylantimony trichloride where they obtained it as a monohydrate. When heating the monohydrated compound to 100 ˚C they readily obtained the anhydrous compound. Initially there was uncertanity about the structure of Ph_2SbCl_3. Bordner *et al* resolved the ambiguity by examining the single-crystal X-ray diffraction data of the anhydrous Ph_2SbCl_3 and found that it exists as a dimer with chlorine bridges and geometry around antimony was found to be octahedral (Figure 3).[25]

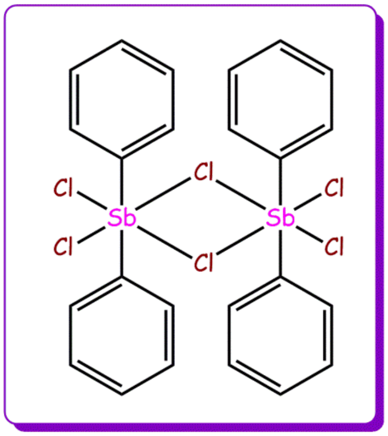


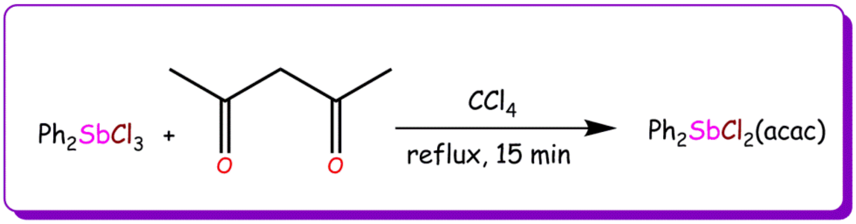
Figure 3: Dimeric structure of diphenylantimony trichloride.

Bone and Sowerby synthesized diarylantimony(V) tribromide (Ph_2SbBr_3) and the two mixed halides Ph_2SbBr_2Cl and $Ph_2SbBrCl_2$.[26] These compounds are monomeric in solid state and geometry around antimony was found to be trigonal-bipyramidal with two phenyl groups and a bromine atom occupying the equatorial positions. Due to weak intermolecular interactions arising between axial halogen atom and antimony, these units are linked to form infinite chains in solid state. On the other hand when compared with above mentioned compounds Ph_2SbCl_3 shows a dimeric nature in solid state.

With various oxygen donor ligands such as DMSO and HMPA diorganoantimony(V) halides forms monomeric covalent adducts ($R_2SbX_3.L$). Octahedral geometry has been proposed on the basis of IR and NMR spectra.[27]

1.4.3 Diorganoantimony *β*-diketone derivatives:

Diorganoantimony trihalide when treated with acetylacetone under reflux condition gave rise to diorganoantimony(V) *β*-diketones, $Ph_2Sb(CH_3COCHCOCH_3)Cl_2$ (Scheme 4) which are monomeric in nature (Figure 4).[28]



Scheme 4

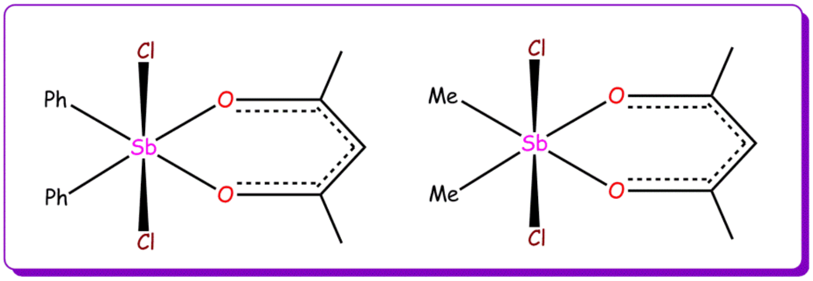
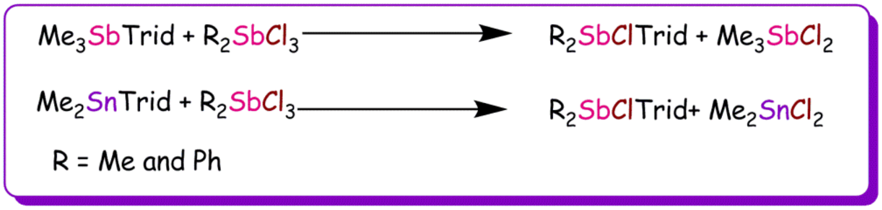


Figure 4: Diphenyldichloro(acetylacetonato)antimony & Dimethyldichloro(acetylacetonato)antimony.

β-diketonate ligand acts as bidentate ligand in both the complexes and the oxygen atoms from acetylacetone bonds to antimony atom. Interpretations drawn from ^1H NMR spectral studies have been confirmed by single crystal X-ray diffraction analysis of $Me_2Sb(acac)Cl_2$ and $Ph_2Sb(acac)Cl_2$.[29,30] $Me_2Sb(acac)Cl_2$ compound possess a slightly distorted octahedral geometry around antimony in which methyl groups occupy equatorial positions and are bent towards the planar acetylacetonato group. In compound $Ph_2Sb(acac)Cl_2$ the geometry around antimony was distorted octahedral in which the two chlorine are arranged trans to each other (Figure 4).

1.4.4 Schiff base derivative of diorganoantimony:

Diorganoantimony(V) complexes with planar tridentate schiff base ligands (Trid) have been prepared by the exchange reactions of diorganoantimony(V) chlorides with corresponding schiff bases of trimethylantimony(V) or dimethyltin(IV) compounds (Scheme 5). These reactions proceed due to greater Lewis acidity of $R_2Sb(V)$ compared to $Me_3Sb(V)$ or $Me_2Sn(IV)$.[31] Planar tridentate ligands (Trid) coordinate to antimony in ONO fashion, the chelating ONO atoms assumed to be arranged in a *meridional* fashion and a linear C-Sb-C skeleton has been proposed based on IR and ^1H NMR studies. Certain compounds such as $Me_2Sb(Sah)Cl$, $Me_2Sb(Bah)Cl$, $Ph_2Sb(Bah)Cl$ and $Ph_2Sb(Aah)Cl$ shows octahedral geometry with *meridional* arrangement as proven by Mossbauer spectroscopy (Figure 5).[32]



Scheme 5

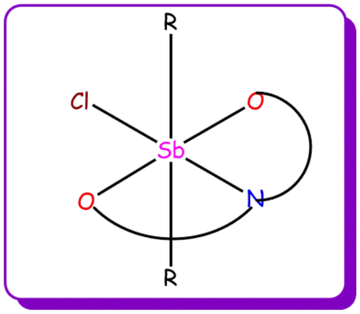
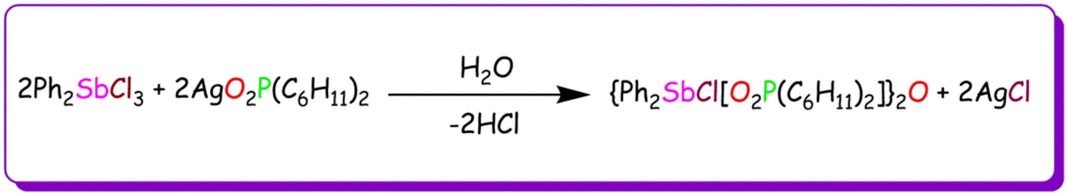


Figure 5: Meridional arrangement of tridentate Schiff base ligand around antimony.

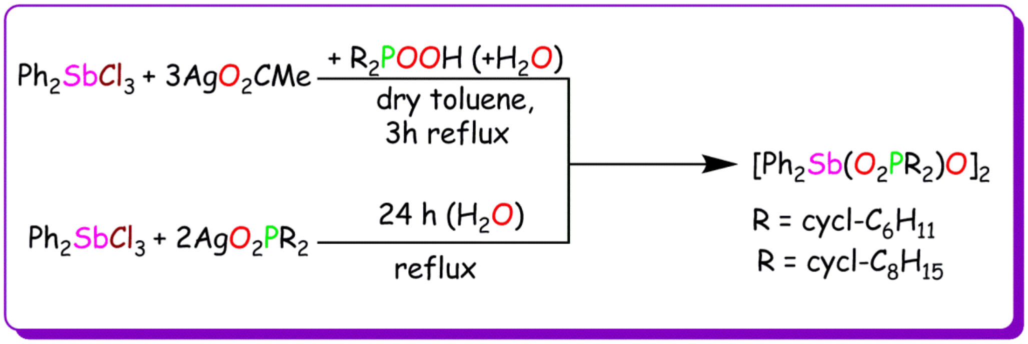
1.4.5 Reaction with Silver salt of phosphinates:

Diphenylantimony trichloride when treated with two equivalents of silver salts of phosphinates leads to the isolation of partially hydrolyzed product $\{SbPh_2Cl[O_2P(C_6H_{11})_2]\}_2O$ (Scheme 6).[8a] Single crystal X-ray diffraction studies reveals that antimony atoms are in octahedral coordination with bridging phophinates *cis* to each other. The phosphinates in this compound only acts a bridging ligand.

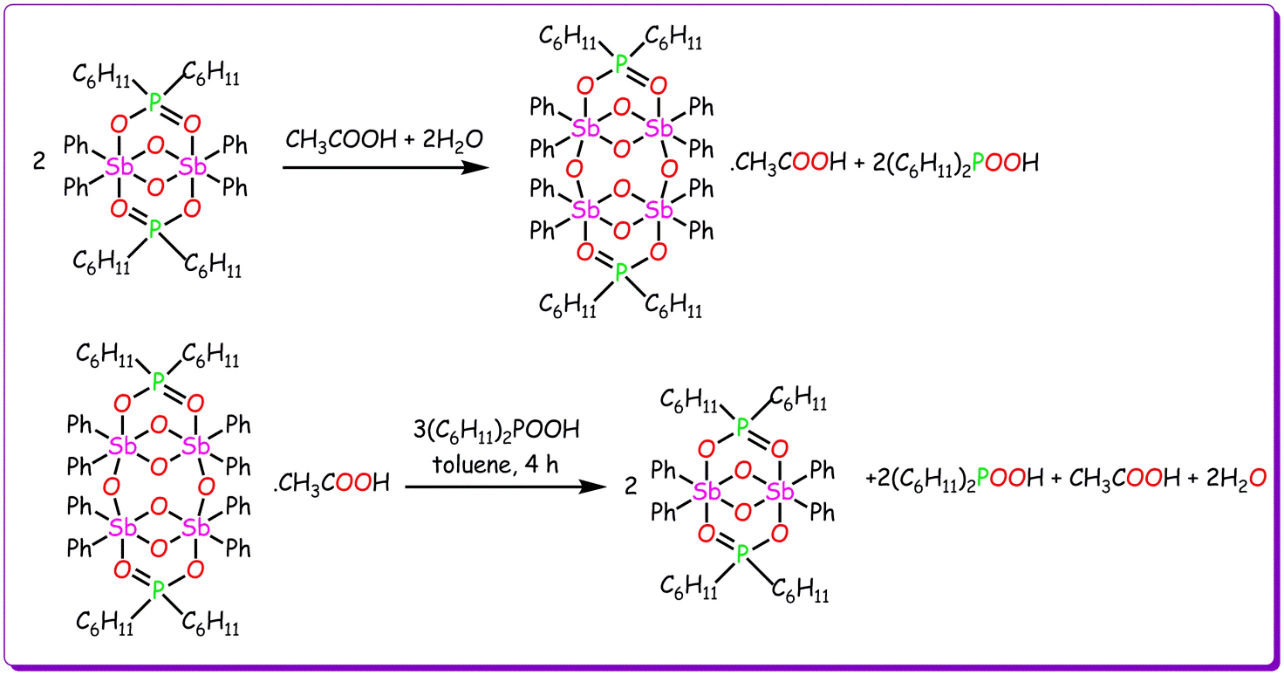


Scheme 6

Kumara Swamy and co-workers reported antimony(V) phosphinates by reacting diphenylantimony trichloride with three equivalence of silver acetate followed by one equivalence of phosphinic acid leading to the isolation of dimeric compounds of formula $[Ph_2Sb(O_2PR_2)O]_2$. Interestingly when the dimer was reacted with acetic acid / water gives the tetra nuclear cage of formula $Ph_8Sb_4O_4(OH)_2(O_2P(C_6H_{11})_2)_2$ (Scheme 7).[33]



Scheme 7

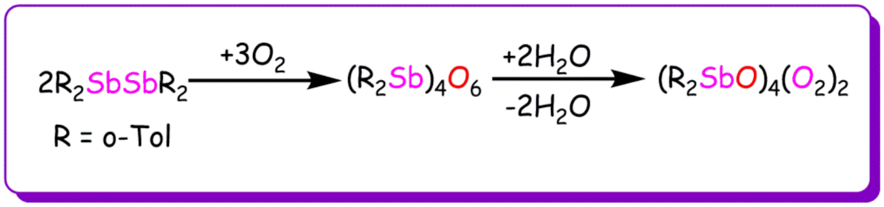


Scheme 8

All the compounds are structurally characterized by single crystal X-ray diffraction analysis. In the di and the tetra nuclear clusters, the antimony atoms are octahedral coordinated with four membered Sb_2O_2 rings. In tetranuclear cluster two Sb_2O_2 rings are linked by oxo bridges on two sides to give a Sb_4O_6 cage (Scheme 8).

1.4.6 Diorganoantimony based μ_4-peroxo complex:

The first main group element μ_4-peroxo complex of antimony was synthesized by treating tetra-*o*-tolyldistibane in air and subsequent reaction with H_2O_2 and the intermediate (*o*-$Tol_2Sb_4)O_6$ (Scheme 9) was identified by mass spectrometry. The complex is stable in solution state. Single crystal X-ray diffraction studies reveal that antimony atoms are arranged as in the vertices of a square planar arrangement (Figure 6).[34]



Scheme 9

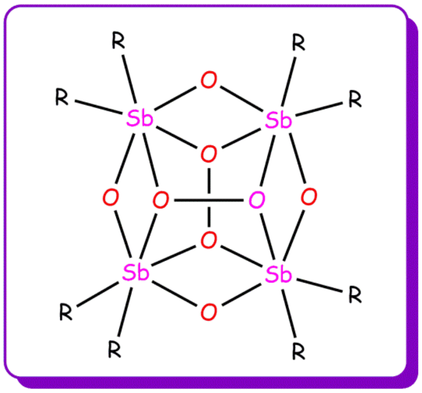


Figure 6: μ_4-peroxo Complex of Antimony

1.4.7 Synthesis of Quadruply bridged diorganoantimony compound:

Quadruply bridged diorganoantimony compounds $[(SbPh_2)_2(\mu\text{-}O)_2(\mu\text{-}O_2AsR_2)_2]$,[35] where R = Me or Ph have been synthesized by reacting $[(SbPh_2BrO)_2]$ with 2 moles of either $Na(O_2AsMe_2)$ or $Na(O_2AsPh_2)$ in DCM and the mixture was refluxed for 24 h. The compounds have been characterized by a various spectroscopic methods and analytical methods (Figure 7).

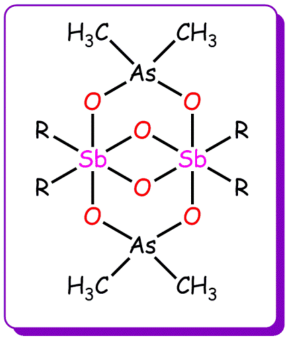
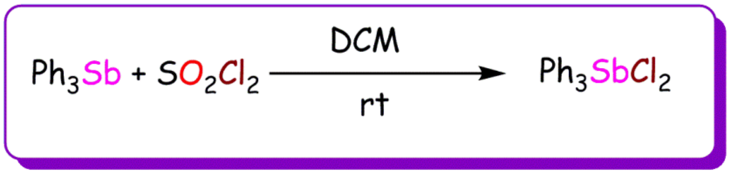


Figure 7: Quadruply bridged diorganoantimony compounds.

1.5 Triorganoantimony Compounds:

1.5.1 Synthesis of triphenylantimony dichloride:

Triorganoantimony(V) halides are the well known organoantimony derivatives and its chemistry is explored in great detail. Though there are many synthetic routes to synthesis triorganoantimony(V) halides, the most common method for preparation of these compounds is the halogenation of the triorganoantimony (Scheme 10).[36]



Scheme 10

Some of the triorganoantimony(V) halides show monomeric behavior in molecular weight calculations. The dipole moments of few of these compounds have also been calculated and correlated with the structures. Parab and Desai determined the diamagnetic susceptibilities of tribenzylantimony(V) halides.[37] Jaffe and Rao *et al* has considered the pπ–dπ resonance in the phenyl derivatives, in between the benzene ring and vacant d-orbitals of the antimony atoms.[38]

On the basis of IR and Raman analysis the geometry around antimony atom in triorganoantimony(V) halides is trigonal bipyramid (Figure 8). The nature of bonding in trialkyl and triarylantimony(V) halides has been elucidated by using NMR spectroscopy. Me_3SbF_2 appeared as single CH_3 proton signal and the splitting at 32° by two equivalent fluorines are consistent with trigonal pyramidal geometry as identified by using ^1H NMR spectroscopy.[39]

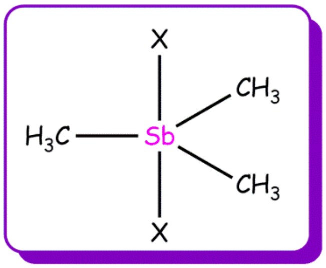
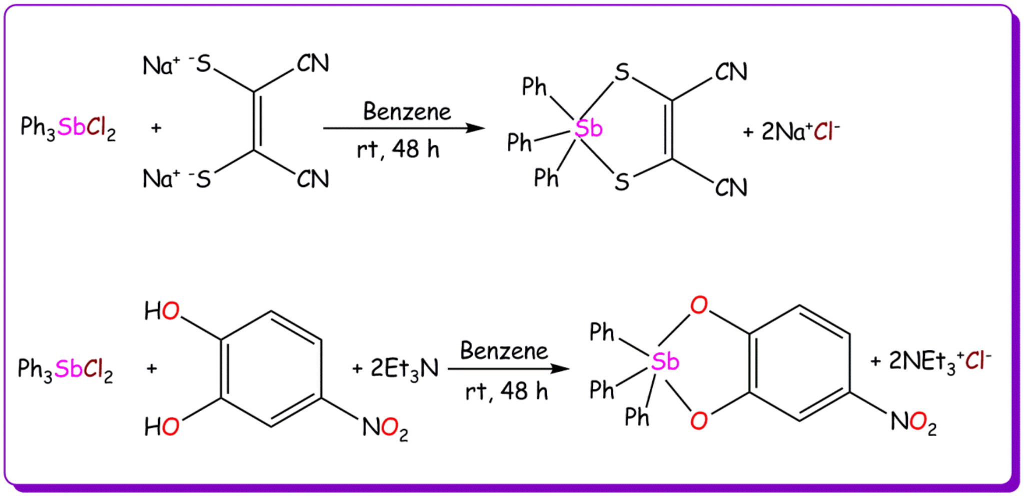


Figure 8: Geometry of Me_3SbX_2.

1.5.2 Reactions with thiols and diols:

Triorganoantimony(V) diolates $R_3Sb(OXO)$, have been found to be monomeric in which antimony is chelated through oxygen atoms from diol groups. These compounds are pentacoordinated and present in trigonal bipyramidal arrangement in which oxygen atoms of the ligand occupy axial and one equatorial positions.[40]

Monocyclic stiboranes were synthesized by Holmes and co-workers[41] by treating Ph_3SbC1_2 with the disodium salt of maleonitriledithiol, 4-nitrocatechol with triethylamine added as a deprotanation reagent. Single crystal X-ray diffraction analysis reveals that the structure around antimony atom in the former case was trigonal bipyramidal while in the later case it was square pyramidal structure. It exists in the solid state as weakly connected dimers which gaving rise to structural displacement toward the square pyramidal structure.



Scheme 11

1.5.3 Reactions with *β*-diketones:

Meinemia *et al* have investigated the stability and the stereochemistry of the compound by substituting the chlorine atoms in organoantimony halides by organic groups. IR and ^1H NMR indicates the weakening of Sb-acac interactions by substituting the chlorine atoms by organic groups. Unambiguously the stereochemistry of various compounds has been deduced from spectroscopic and molecular dipole moment data. Triorganoantimony(V) *β*-diketonates have been prepared by the following reaction route (Scheme 12).

$$R_3SbX_2 + Na(R'COCHCOR'') \longrightarrow R_3SbX(R'COCHCOR'') + NaX$$

Scheme 12

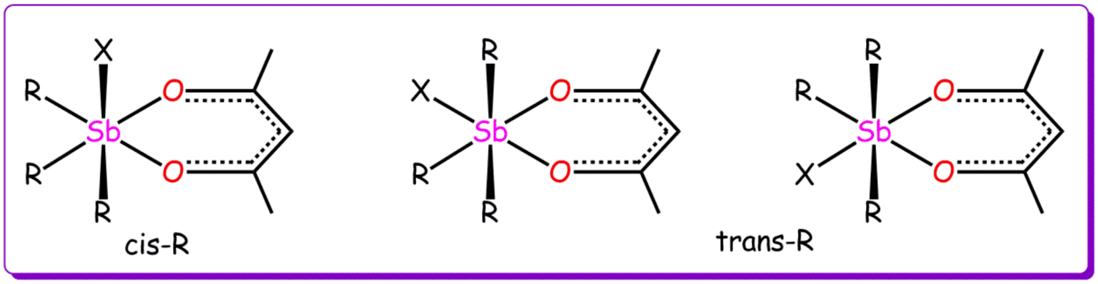
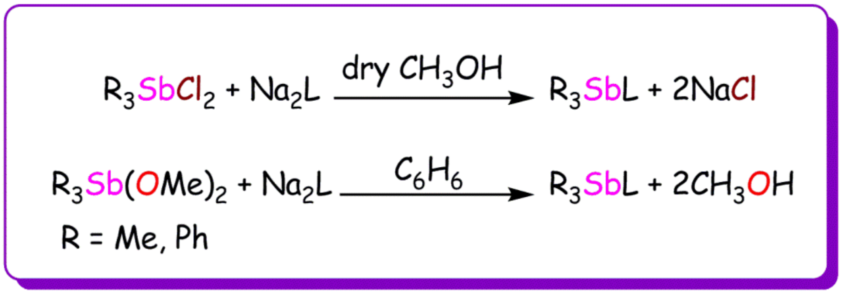


Figure 9: *Cis* and *trans* forms of $R_3Sb(R^1COCHCOR^{11})$.

These compounds are monomeric and the ligands moieties are acting as chelating ligands which was identified by infrared spectra. With the help of ^1H NMR spectroscopy their stereochemistry has been elucidated. Phenyl configuration is in *trans* position for the compounds of the type Ph_3Sb ($R^1COCHCOR^{11}$) (Figure 9).[20d,42]

1.5.4 Reactions with Schiff base:

Triorganoantimony(V) complexes with tridentate schiff bases ligands of ONO and ONS type have been synthesized by the reaction of triorganoantimony dichlorides with the sodium salt of the ligand in dry methanol or treating triorganoantimony dimethoxides with free ligand in benzene solvent (Scheme 13).[43] Molecular weight determination in benzene shows all these compounds are monomeric in nature.



$$R_3SbCl_2 + Na_2L \xrightarrow{\text{dry } CH_3OH} R_3SbL + 2NaCl$$

$$R_3Sb(OMe)_2 + Na_2L \xrightarrow{C_6H_6} R_3SbL + 2CH_3OH$$

R = Me, Ph

Scheme 13

UV and IR data proposed hexacoordinate molecular structures for the complexes R_3SbL in which the dianionic ligand coordinates to the $R_3Sb(V)$ as a planar tridentate ligand. Single crystal X-ray diffraction analysis has revealed that in the crystalline state the antimony atom in $Me_3Sb(Sah)$ shows a distorted octahedral geometry with *meridionally* disposed tridentate ligand and a T- shaped $R_3Sb(V)$ moiety (Figure 10).[44,43b]

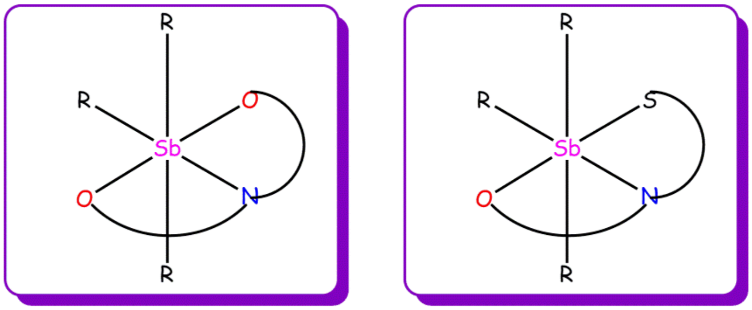
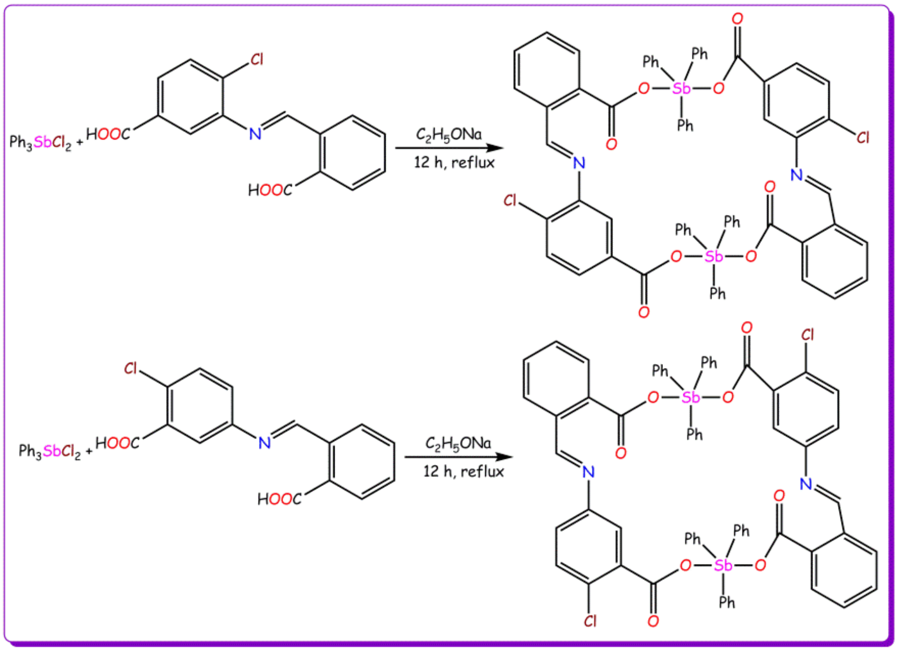


Figure 10: Hexacoordinate structure for the complexes R_3SbL

Yin and co-workers reported the synthesis of highly symmetrical 24-membered macrocyclic organoantimony(V) complexes $[Ph_3SbL^a]_2$ and $[Ph_3SbL^b]_2$ (H_2L^a = 5-{[(2-carboxyphenyl)methylene]amino}-4-chlorobenzoicacid and (H_2L^b=5-{[(2-carboxyphenyl)methylene]amino}-2-chloro benzoic acid) by reacting Ph_3SbCl_2 with schiff bases containing carboxylic acids (Scheme 14).[45] Single crystal X-ray diffraction analysis shows that the antimony atoms are bridged by four terminal carboxylic groups of the schiff base ligands and both antimony atoms show typical five coordinated distorted trigonal bipyramid geometry with two carboxylate O atoms occupied in the axial positions, carbon atoms from the phenyl group occupying the equatorial positions. Both the compounds are stabilized by weak intermolecular



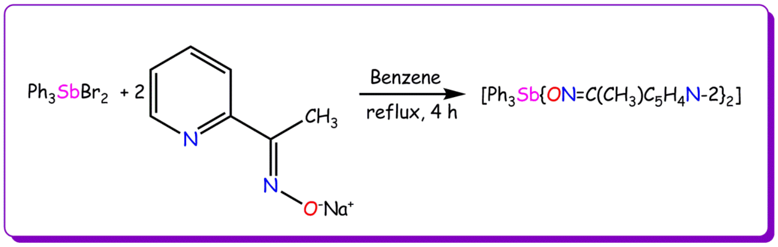
Scheme 14

interactions. Double bridging schiff base ligands linked the two antimony atom resulting in the formation of a 24-membered macrocyclic structure.

1.5.5 Reactions with oximes:

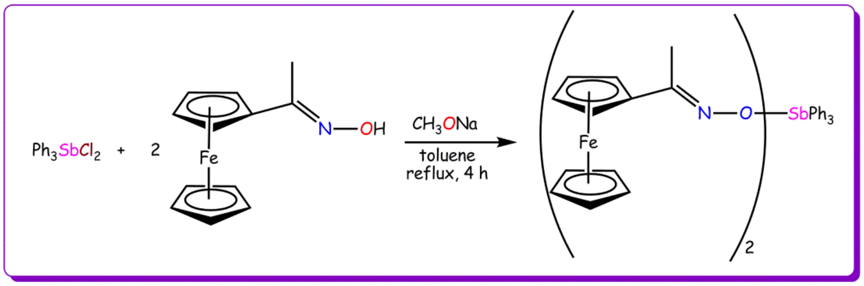
Oxime based multidentate ligands are interesting since they exhibit not only significant variations in their coordination mode but also interesting biocidal activities. Reactive oxime groups are present in the family of Althiomycin antibiotics. Under reduced pressure, oximates of trialkylantimony(V) are volatile. On the other hand corresponding triaryl oximates decomposes to triarylantimony and oximes under the same reaction conditions.

Bohra *et al* prepared trioraganoantimony(V) oximate by treating triphenylantimony(V) dibromide with sodium salt of internally functionalized oxime in 1:2 molar ratio under refluxing condition using dry benzene as a solvent (Scheme 15).[46] Trioraganoantimony(V) oximates structural feature have been characterized by IR, NMR and single crystal X-ray diffraction analysis.



Scheme 15

Yin *et al* synthesized triorganoantimony(V) complex by the reaction of Ph_3SbCl_2 with acetylferroceneoxime in 1:2 molar ratio in dry toluene (Scheme 16). The geometry around the antimony atom was slightly distorted trigonal bipyramidal with the phenyl group attached to antimony in $SbPh_3$ unit occupying equatorial positions and the two oxygen atoms from the oxime group occupies axial positions.[47a]



Scheme 16

Further $[Sb(C_6H_5)_3(C_7H_6NO_2)_2]$ was synthesized by treating salicylaldoxime to a methanol solution of sodium and heating under reflux for 30 minutes. To this solution Ph_3SbCl_2 in benzene was added and the mixture was refluxed for 5 h. Oximate ligand occupies axial positions and the geometry around antimony atom was slightly distorted trigonal bipyramidal (Figure 11).[47b]

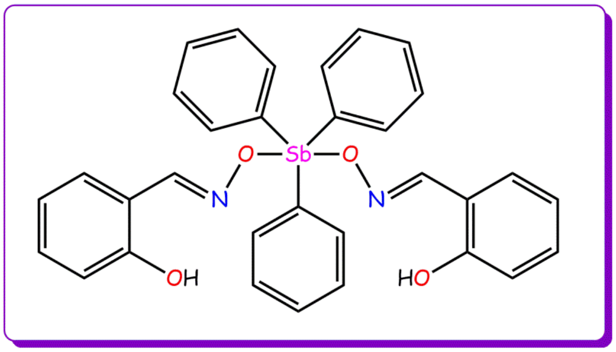


Figure 11: Solid state structure of $[Sb(C_6H_5)_3(C_7H_6NO_2)_2]$

Mononuclear triorganoantimony oximates have been isolated by treating either Ph_3Sb or Me_3Sb with *t*-butyl hydroperoxide in the presence of oxime (Scheme 17). Single crystal X-ray diffraction analyses have revealed that the geometry around antimony atom was trigonal bipyramidal. Molecular weights determination by the cryoscopic method in benzene, shows in good agreement with the calculated values for the metal content.[48]

$$R_3Sb + 2\ HON{=}CR'R'' + Bu^tOOH \longrightarrow R_3Sb(ON{=}CR'R'')_2 + Bu^tOH + H_2O$$

R = Me, Ph; R', R'' = H, alkyl, Ph

Scheme 17

1.5.6 Reactions with diorganophosphinic acids:

Silvestru *et al* investigated the reaction of triorganoantimony halides with sodium salt of the suitable diorganophosphinic acids yielding bis(diorganophosphinato)triorganoantimony(V) complexes $R_3Sb(O_2PR'_2)$ (Scheme 18).

$$R_3SbCl_3 + 2NaOPR'_2 \longrightarrow R_3Sb(O_2PR'_2)_2 + 2NaCl$$

R = Me, Ph
R' = Me, Ph

Scheme 18

These derivatives have been characterized by using IR and multinuclear (^1H, ^{13}C, ^{31}P) NMR spectroscopy. Efforts to crystallize $Me_3Sb(O_2PR'_2)_2$ lead to the partially hydrolyzed product $Me_3Sb(OH)[O(O)PPh_2]$.[49] Coordination around the antimony atom is distorted trigonal bipyramidal.

1.5.7 Reactions with *cyc*-phosphinic acid:

Chandrasekhar *et al* reported the first example of a nonanuclear organostiboxane cage by treating triorganoantimony halides monohydrate with *cyc*-phosphinic acid (*cyc*PO_2) 1,1,-2,3,3-pentamethyltrimethylene phosphinate) in the presence of triethylamine as base which affords a dimer $[(Ph_3Sb)_2(\mu\text{-}O)(\mu\text{-}cycPO_2)_2]$ (Figure 12).

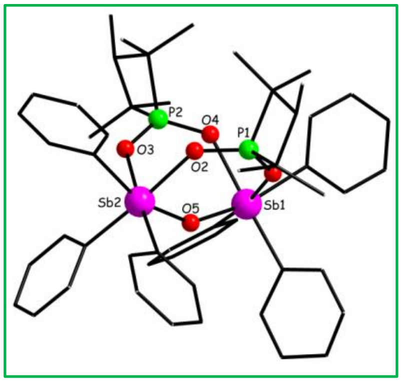


Figure 12: Solid state structure of $[(Ph_3Sb)_2(\mu\text{-}O)(\mu\text{-}cycPO_2)_2]$.

Interestingly this dimer when subjected to mild hydrolysis condition in a mixture of acetonitrile / water mixture (99:1) at 45 ˚C leads to Sb-C bond cleavage resulting in the formation of nonanuclear organostiboxane cage $[(Ph_2Sb)_2(PhSb)_7(\mu\text{-}O)_{11}(\mu_3\text{-}O)_3(\mu\text{-}OH)_2(\mu\text{-}cycPO_2)_2(cycPO_2)_2(H_2O)_2]$ $2CH_3CN$ H_2O which contains a Sb_9O_{16} core (Figure 13).[50]

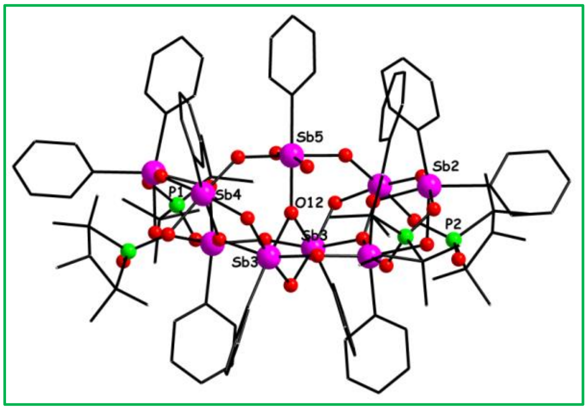


Figure 13: Solid state structure of $[(Ph_2Sb)_2(PhSb)_7(\mu\text{-}O)_{11}(\mu_3\text{-}O)_3(\mu\text{-}OH)_2(\mu\text{-}cycPO_2)_2(cycPO_2)_2(H_2O)_2]$

1.5.8 Reactions with carboxylic acid:

Triphenylorganoantimony(V) carboxylates can be synthesized by treating triphenylantimony halides with carboxylic acids in the presence of NaOMe as base. Badshah and coworkers prepared organoantimony(V) ferrocenyl benzoates[51] by reacting triarylantimony dichloride with (*m,p*)-ferrocenyl benzoic acids in the presence of NaOMe as base. The complexes adopt approximate trigonal bipyramidal geometry around antimony atom. Carboxylic acids are attached to antimony in unidentate fashion which occupied axial positions whereas three phenyl groups occupy equatorial position (Figure 14). The binding activities of this complex towards DNA have been investigated.

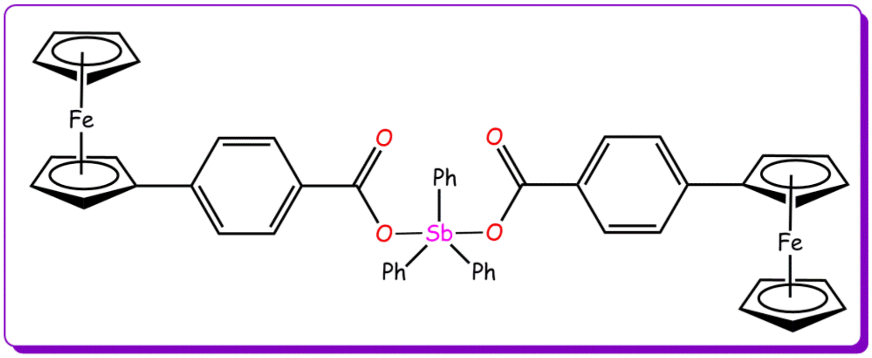


Figure 14: Solid state structure of ($C_5H_5FeC_5H_4COO$)Sb(*p*-$CH_3C_6H_4$)$_3$

Hong *et al* prepared a novel tetranuclearantimony(V) complexes by treating various fluorine atoms substitiuted arylorganoantimony dihalides with (±)mandelic acid in the presence of sodium ethoxide as a base.[52] Single crystal X-ray diffraction analysis reveals the cluster was made of four antimony metal centers in which each metal atom is surrounded by three aryl rings and coordinated to the tridentate $O_2CC(O)(H)Ph$ moiety. DNA binding ability of complexes mainly depends on the position and number of fluoro-substituents present in the complex. A preliminary cytotoxic result shows that *in vitro* studies display remarkably high cytotoxicity toward platin-resistant cancer cell lines (Figure 15).

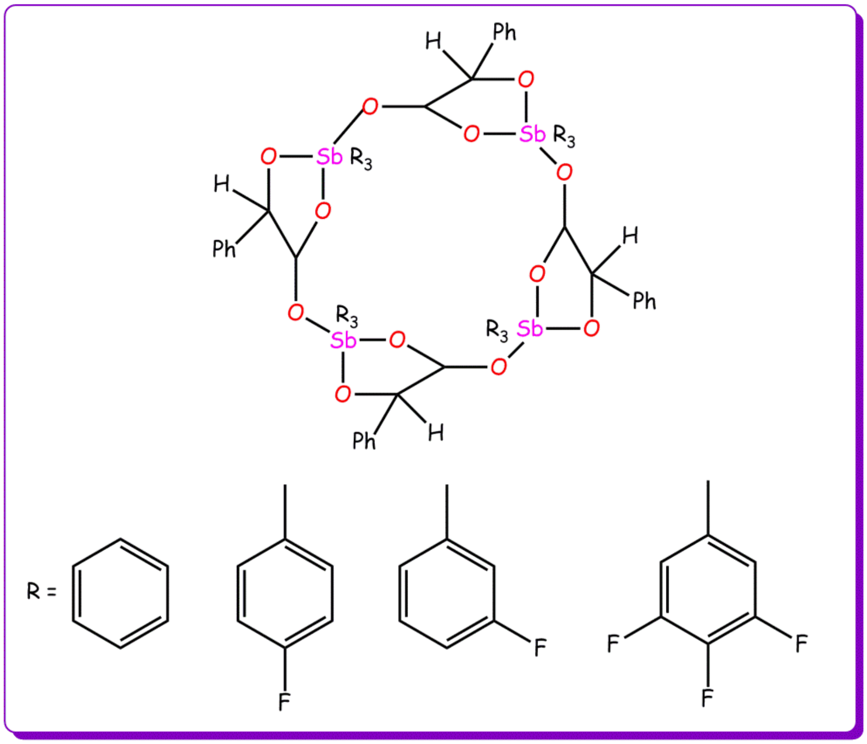


Figure 15: Molecular structure of tetranuclearantimony(V) complexes

1.5.9 Synthesis of dimeric organoantimony(V) imido complex:

Organo-Sb(V) imido complex $[Ph_3Sb(\mu\text{-}NCH_2CH_2Ph)]_2$[53] have been synthesized by using Sb(V) dimethylamido reagents with phenylethylamine ($PhCH_2CH_2NH_2$) (Scheme 19). Single crystal X-ray crystallographic study of $[Ph_3Sb(\mu\text{-}NCH_2CH_2Ph)]_2$ shows it consists of a dimeric unit (Sb_2N_2 core) having a rhombic shape in which Sb(V) centres are present in a highly distorted five-coordinate geometry. Surprisingly the CH_2CH_2Ph chains of the bridging imido groups adopt a *cisoid* orientation with respect to the Sb_2N_2 core as a result of steric and/or crystal packing effects. The angles within the Sb_2N_2 core (Figure 16) are similar to those observed in the antimony (III) dimmers.

$$[Ph_3Sb(NMe_2)_2] + PhCH_2CH_2NH_2 \xrightarrow{\text{toluene}} 1/2[Ph_3Sb(\mu\text{-}NCH_2CH_2Ph)]_2 + 2Me_2NH$$

Scheme 19

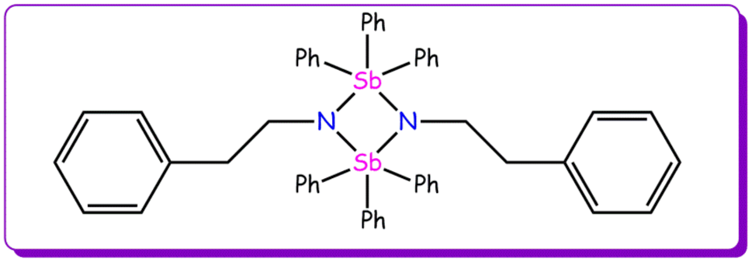


Figure 16: Solid state structure of $Ph_3Sb(\mu\text{-}NCH_2CH_2Ph)]_2$

1.6 Tetraorganoantimony compounds:

1.6.1 Synthesis of bis(tetraphenylantimony) Oxalate $(SbPh_4)_2ox$:

Bis(tetraphenylantimony) Oxalate $(SbPh_4)_2ox$ have been synthesized by Sowerby by treating tetraphenylantimony bromide with silver oxalate and shaking in toluene for 24 h. The structure contains two essentially identical, independent centrosymmetric molecules with antimony in octahedral geometry (Figure 17). Two phenyl groups are *trans* which bent inwards towards the oxalate group.[54]

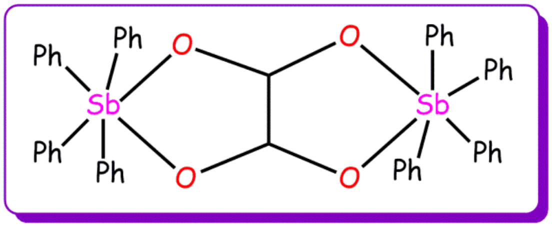


Figure 17: Solid state structure of Bis(tetraphenylantimony) Oxalate $(SbPh_4)_2ox$.

Meinema *et al* have characterized various tetraorgano(oxinato)antimony using UV and NMR spectroscopy. These compounds were obtained by addition of oxine to *a* methanol solution of the either tetralkyl- or tetraphenyhmethoxoantimony compounds. UV data for Me_4SbOx compound (Figure 18) in chloroform solution shows the presence of both the chelated and non-chelated configuration. At 27 °C, methyl protons in $CDCl_3$ shows only one sharp singlet due to rapid equilibrium between stereochemically non-rigid penta- and hexa-coordinate species. At 27 °C in toluene-d_8 this compound show single sharp peak at 0.96 ppm. On reducing the temperature further to -70 °C leads to broadening of the signal. At -100 °C the spectrum gives rise to two individual peaks at 1.04 and 0.50 ppm. This shows that at temperature above -70 °C rapid pseudo-rotation occurs and at -100 °C they have identified that the two different methyl group splits in to two different signals.[55]

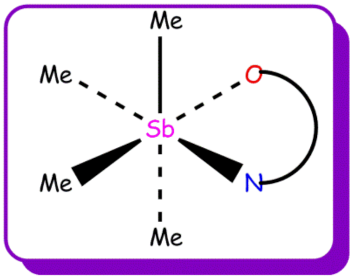
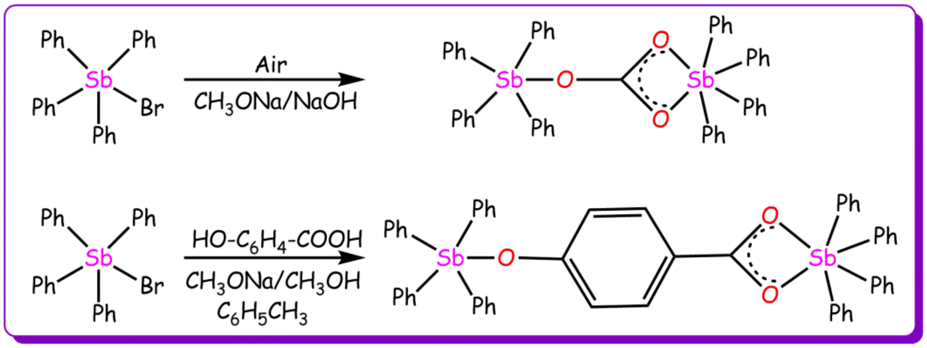


Figure 18: Solid state structure of tetraorgano(oxinato)antimony.

1.6.2 Synthesis of dinuclear tetraorganoantimony carboxylate derivatives:

Yin and coworkers have synthesized novel dinuclear tetraorganoantimony carboxylate derivatives by treating Ph_4SbBr with sodium methoxide in methanol medium which results in the capture of CO_2 from atmosphere to give the dinuclear compound (Scheme 20). In these bimetallic HCO_3^- ion bridged compound, one Sb atom exist in five coordination mode having trigonal bipyramid geometry, and the other Sb atom was six-coordinated displaying distorted octahedron geometry.[56]



Scheme 20

1.6.3 Reaction with cyanoxime ligands:

Gerasimchuk *et al* have prepared 25 different organoantimony(V) cyanoximates of which two compound [Ph_4Sb{ACO} and Ph_4Sb{DCO}] were characterized by single crystal X-ray analysis. Both in solid and solution state all these compounds are monomeric nature. Sb(V) shows distorted trigonal bipyramid geometry with the axial location of the cyanoxime ligand for both compounds (Figure 19).[57]

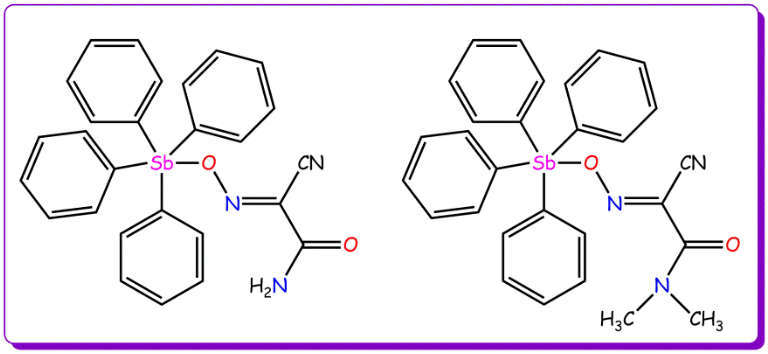
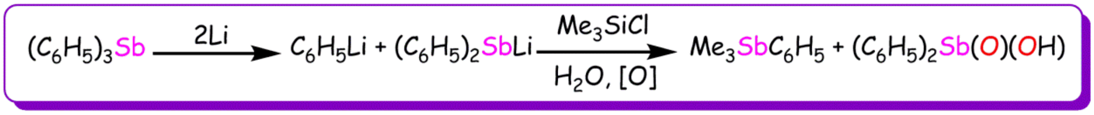


Figure 19: Solid state structure of [Ph_4Sb\{ACO\} and Ph_4Sb\{DCO\}]

1.7 Cleavage of an antimony carbon bond (Sb-C):

1.7.1 Monodearylation from triarylantimony compound:

Cleavage of an antimony carbon bond (Sb-C) was observed initially by Wittenberg who synthesized diphenylstibyllithium from triphenylstibine with lithium in THF. Sb-C cleavage in other triphenyl derivatives in group Vb elements such as triphenylphosphine, triphenylarsine and triphenylstibine have also been reported in literature[58]. Reactions in all these cases are exothermic which gives rise to dark red or brown color products. Further the products from lithium cleavage of triphenylstibine were treated with $(CH_3)_3SiCl$ to give trimethylphenylsilane and diphenylstibinic acid (Scheme 21). Similar reactions are also known for triphenylarsine.



$$(C_6H_5)_3Sb \xrightarrow{2Li} C_6H_5Li + (C_6H_5)_2SbLi \xrightarrow[H_2O,\,[O]]{Me_3SiCl} Me_3SbC_6H_5 + (C_6H_5)_2Sb(O)(OH)$$

Scheme 21

Hewertson and Watson[59] modified the cleavage reagent and observed that much more rapid cleavage was possible in triphenylstibine by using sodium in liquid ammonia as a reagent.

1.7.2 Sb-C bond cleavage at room temperature:

Shawkataly *et al* investigated Sb-C bond cleavage in $Sb(C_6H_5)_3$ at room temperature under nonionic condition by treating $[Ru_3(CO)_{12}]$ and $Sb(C_6H_5)_3$ in THF under nitrogen atmosphere. The reaction was initiated by benzophenone ketyl radical anion. Single crystal X-ray structure reveals the unexpected open triruthenium phenylacyl carbonyl cluster

$[(C_6H_5)_2SbRu_3(COC_6H_5)(CO)_{10}]$ which was obtained by a phenyl group insertion at the carbonyl carbon.[60]

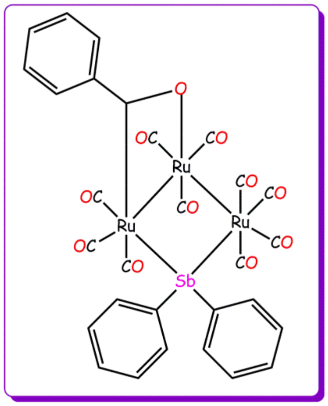


Figure 20: Solid state structure of $[(C_6H_5)_2SbRu_3(COC_6H_5)(CO)_{10}]$

1.7.3 Sb-C bond cleavage in dichlorotrialkylantimony compound:

Meinema and co-workers studied the Sb-C bond cleavage in dichlorotrialkylantimony compounds. The reaction in liquid ammonia solvent of dichlorotrimethylantimony with metallic sodium leads to the formation of dimethylstibylsodium in good yield. The rate of the reaction for antimony-alkyl group cleavage diminished in the order of the stability of the anionic species formed (Scheme 21).[61]

$$(CH_3)_3SbCl_2 + 4Na \xrightarrow{NH_3} (CH_3)_2SbNa + CH_3Na + 2NaCl$$

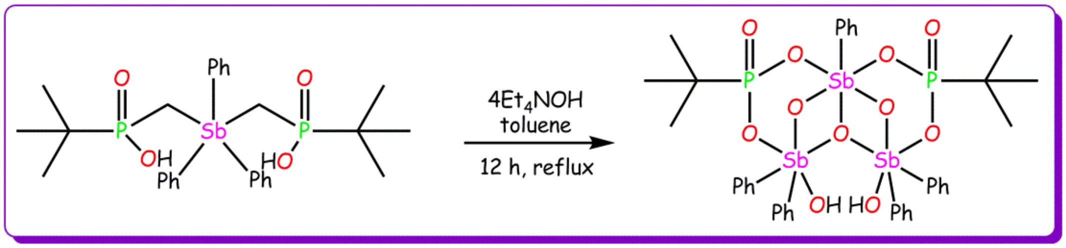
Scheme 21

1.7.4 Sb-C bond cleavage in dimeric $[(Ph_3Sb)_2(\mu\text{-}O)(\mu\text{-}cycPO_2)_2]$:

Chandrasekhar *et al* reported the first example of a nonanuclear organostiboxane cage by treating triorganoantimony halides monohydrate with *cyc*-phosphinic acid (*cyc*PO_2) 1,1,-2,3,3-pentamethyltrimethylene phosphinate) in the presence of triethylamine as a base which affords a dimer $[(Ph_3Sb)_2(\mu\text{-}O)(\mu\text{-}cycPO_2)_2]$ (Figure 12). Interestingly this dimer when subjected to mild hydrolysis condition in a mixture of acetonitrile / water (99:1) at 45 ˚C resulted in Sb-C bond cleavage leading to the formation of nonanuclear organostiboxane cage $[(Ph_2Sb)_2(PhSb)_7(\mu\text{-}O)_{11}(\mu_3\text{-}O)_3(\mu\text{-}OH)_2(\mu\text{-}cycPO_2)_2(cycPO_2)_2(H_2O)_2]$ $2CH_3CN$ H_2O which contains a Sb_9O_{16} core (Figure 13).[50]

1.7.5 *In situ* dearylation:

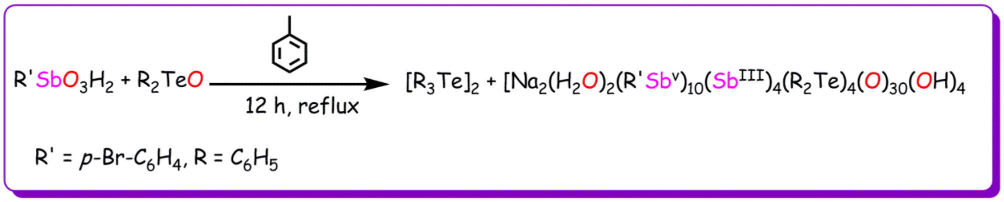
Polymeric triphenylantimony oxide when reacted with *t*-butyl phosphonic acid in 1:2 molar ratio at room temperature also gave rise to a monomeric compound which was characterized by single crystal X-ray studies. On further base hydrolysis, this compound undergoes *in situ* dearylation leading to the formation of novel dianionic trinuclear organoantimony oxido cluster (Scheme 22).[62]



Scheme 22

1.7.6 Complete-dearylation:

Complete-dearylation[63] of arylstibonic acid have also been investigated (Scheme 23) and reported very recently from our group (Figure 21).



Scheme 23

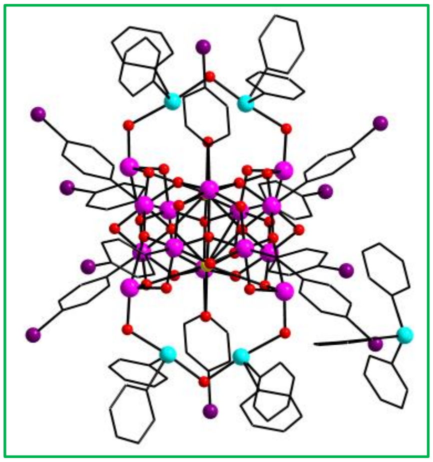
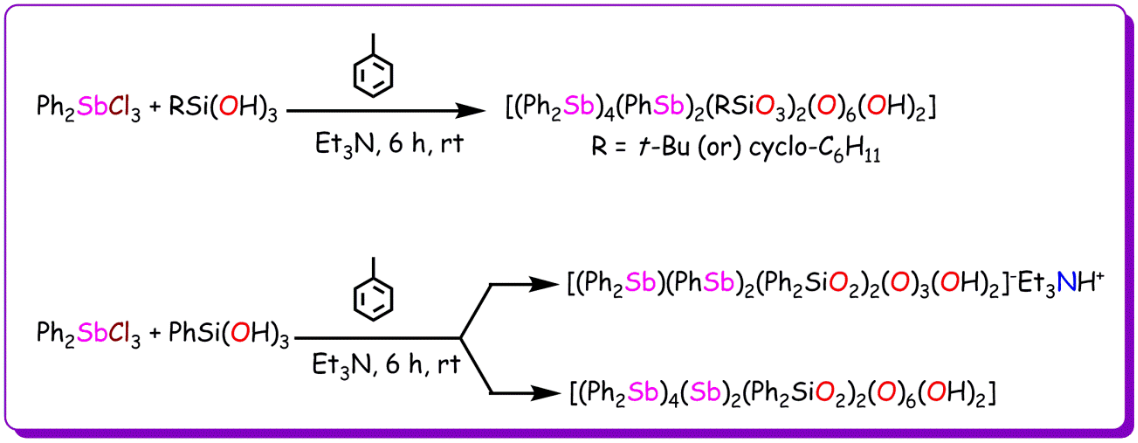


Figure 21: Solid state structure of POM

1.7.7 Synthesis of mixed-valent Sb(III/V):

A series of organoantimony oxo-hydroxo clusters having mixed-valent (III/V)[64] Sb centres (Scheme 24) have been synthesized by treating organoantimony halides with silanols. In all the cases at least one dearylation has been observed, as shown by X-ray diffraction studies.



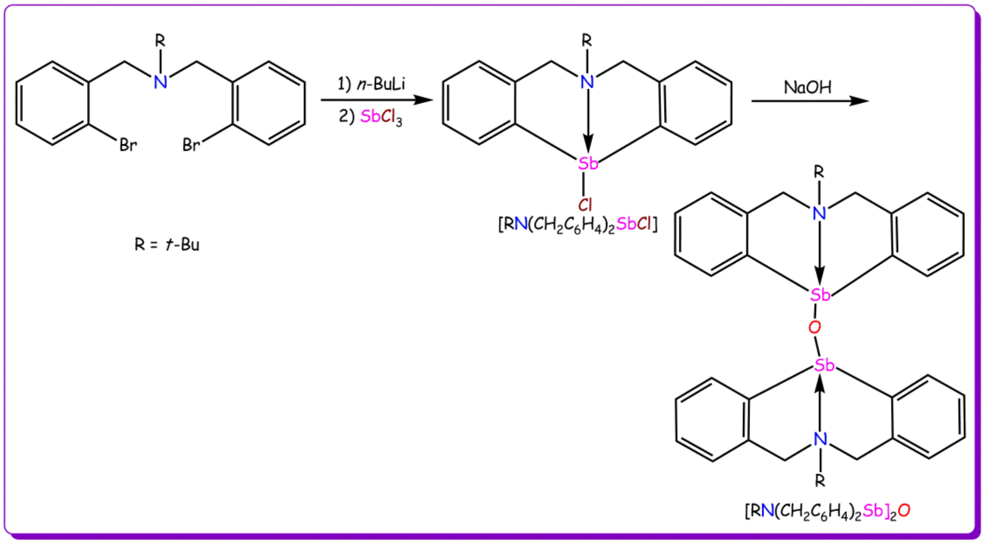
Scheme 24

1.8 HYPERVALENCY:

Musher in 1969 first formally defined hypervalent molecules. Hypervalence was a common phenomenon in antimony chemistry, both the oxidation states +3 or +5 are strong Lewis acids that accept electron pairs from donors.[65a] In most of the cases organoantimony(V) complexes has coordination number of five. In certain cases it shows a coordination number of six or seven even some times it may reach to eight due to the hypervalent nature of the antimony atom. The Martin ligand, 2-dimethylaminophenyl group or tridentate pincer ligands can lead to the formation of hypervalent organoantimony or -bismuth compounds. Hypervalence was promoted with bi- and tridentate ligands and occurs usually when the donor atom of the pendant arm was coordinated through a dative bond to the antimony or bismuth center. Hypervalent compounds can be classify using the N–M–L nomenclature where N = represents the number of valence electrons about the metal, M = Sb, L = number of ligands to the central atom The designation would be 10-Sb-4 for $[SbCl_4]^-$. Use of bi- and tridentate pincer ligands leads to the construction of hypervalent organoantimony.[65b-e]

1.8.1 Synthesis of heterocyclic hypervalent organoantimony compounds:

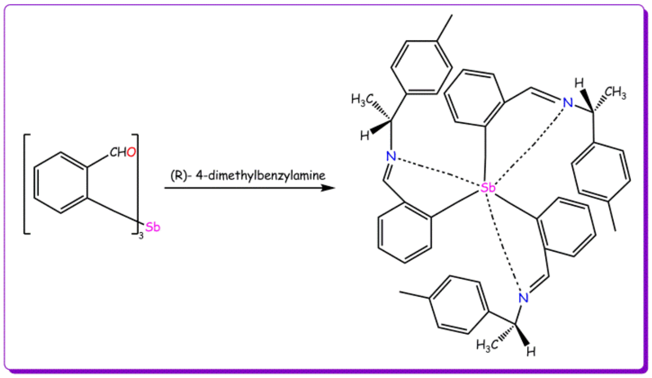
Chen *et al*. have synthesized heterocyclic hypervalent organoantimony chlorides *t*-BuN$(CH_2C_6H_4)_2$SbCl and their chalcogenide derivatives [*t*-BuN$(CH_2C_6H_4)_2$Sb]$_2$O (Scheme 25). Single-crystal X-ray diffraction analysis shows that there is a coordinate bond linking the antimony and the nitrogen atoms in the compounds mentioned. These compounds reveal good anti-proliferation activity towards cancer cells as an outcome of apoptosis and cell cycle arrest. This compound is the first example of hypervalent organoantimony compounds that show the ability to inhibit the growth of human tumor cell lines.[65f]

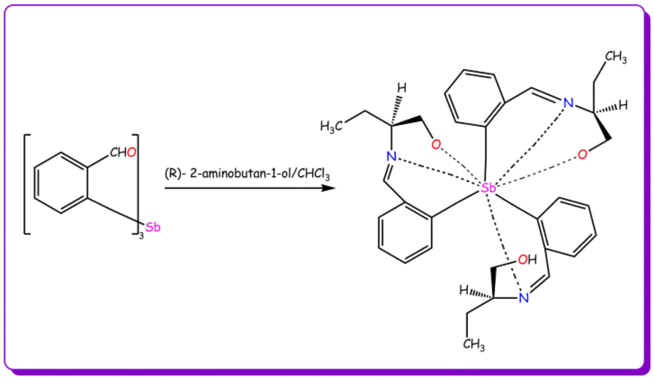


Scheme 25

1.8.2 Synthesis of hypervalent antimoniated schiff base:

Antimoniated schiff bases have been reported by Sharma and coworkers. Reaction of tris(*o*-formylphenyl)stibine with (R)-4-dimethyl benzyl amine (Scheme 26) or (R)-2-aminobutan-1-ol (Scheme 27) respectively gave rise to hypervalent antimoniated schiff base. Single crystal X-ray structures shows two schiff bases present leading to hypervalent interactions between antimony and sp^2 nitrogen atoms. In tris[(R)-2-benzyliden-2-yl-amino)butan-1-ol]stibine, antimony is present in an eight coordination geometry with $C_3O_2N_3$ binding mode.[66]





Scheme 26 **Scheme 27**

1.8.3 Synthesis of arylantimony(V) triphenylgermanylpropionates compound:

Arylantimony(V) triphenylgermanylpropionates is monomer with a Sb present in seven coordination geometry. The geometry around antimony can be described as a distorted pentagonal bipyramid molecular structure (Figure 22).[67]

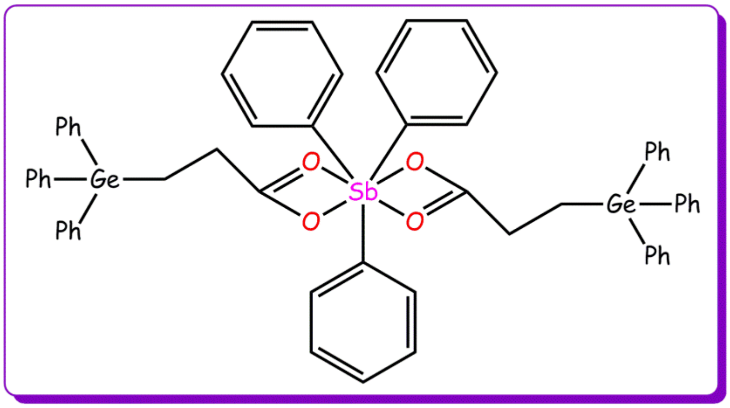


Figure 22: Solid state structure of seven coordinated antimony atom.

1.8.4 Synthesis of seven coordinated $[SbPh_2(O_2CPh)_2]_2O$:

Hypervalent organoantimony compound were readily obtained, when diorganoantimony dihalide was reacted with 3 mole equivalents of silver carboxylates (Figure 23). Single crystal X-ray analysis reveals the formation of oxo-bridged carboxylates $[SbPh_2(O_2CPh)_2]_2O$ in which the Sb atoms are present in seven coordinated geometry with chelating benzoates.[8a]

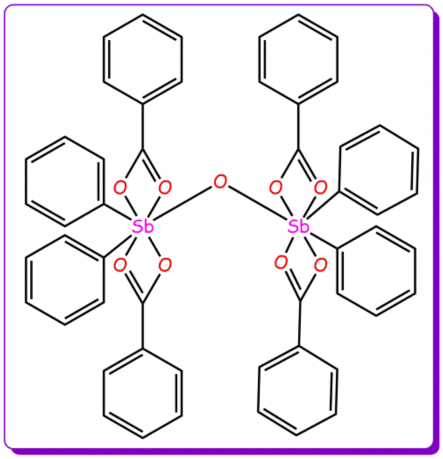


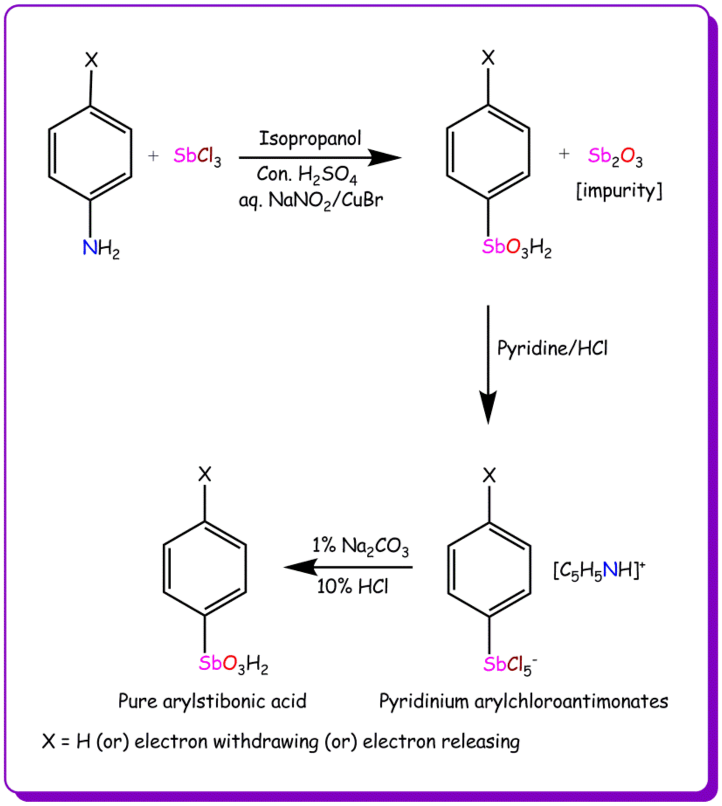
Figure 23: Solid state structure of seven coordinated $[SbPh_2(O_2CPh)_2]_2O$.

1.9 Organostibonic acids:

Organoarsonic acids were first prepared by Bart in 1910. In this preparation an aromatic diazo compound was reacted with As_2O_3 under aqueous alkaline conditions to form organoarsonic acids with the evolution of nitrogen.[68] This method was further used by Schmidt to prepare organostibonic acids[69] to improve the yield and purity of organostibonic acids. Further the procedure was improved by by Scheller and Doak in 1940.[70] The nominal formula for organic stibonic acids can be represented as $RSbO(OH)_2$ (R = alkyl or aryl).[71] Though organostibonic acids have been described in a literatures, the exact chemical structure of these compounds has not been known with certainty. Organostibonic acids are amorphous powders, ill-defined and poorly soluble in common organic solvent. In this way it differs from the very well-defined organoarsonic acids which are mostly soluble and whose solid state structure are known.[72] On the other hand aliphatic stibonic acids are almost nonexistent; expect methanestibonic acid being reported in the chemical literature.[73] Organostibonic acids also exhibits interesting pharmacological properties and lot of reports regarding its anticancer and antimicrobial are found in recent time.[17]

1.9.1 Preparation of organostibonic acids:

The amine of (0.04 mmol) was dissolved or suspended in 150 mL of 2-propanol in a 500 mL beaker which was kept in an ice-bath and stirred. To this solution conc. H_2SO_4 (0.04 mmol) and $SbCl_3$ (0.04 mmol) were added. When the $SbCl_3$ had completely dissolved, diazotization was effected with $NaNO_2$ (0.04 mmol) dissolved in 4 mL of water. The mixture was stirred for 45 minutes, and cuprous bromide of (0.04 mmol) was added and the ice-bath removed. Evolution of nitrogen takes place at the room temperature for 12 hours and the mixtures was steam distilled to remove the alcohol. The crude stibonic acid were obtained by washing with ice cold water then filtered and dried. The crude stibonic acid contains antimony trioxide as an impurity. To purify, organostibonic acid the mixture was dissolved in 40 mL of conc. HCl and then pyridinium hydrochloride solution (4 mL pyridine in 16 mL of conc. HCl) was added under ice-bath condition. The precipitated pyridinium salt was removed by filtration and dried. It was then dissolved in 1% Na_2CO_3 solution followed by addition of activated charcoal which was stirred for an hour and the solution was filtered. The free acid was obtained from the filtrate by the addition of 10% HCl, with rapid stirring. The solution was filtered and then washed with dilute HCl to obtain pure arylstibonic acid.



Scheme 28

1.9.2 Structure of organostibonic acids:

Synthesis of organostibonic acids has been known for over a century and its chemistry has been described in the literature, though their precise molecular structure has been difficult to elucidate. This was due to limited solubility in water and organic solvents. Based on analytical measurement, their behavior as pseudo acids was established and based on the differences in the weight loss obtained on thermal and vacuum drying. Schmidt proposed that the organostibonic acids existed as trimers (I) in the solid state but dissociated under base medium to exist in monomeric form (II) (Figure 23). Depending on different organostibonic acids and the method of preparation, the degree of associated water may vary. Macallum,[74] proposed that they have a monomeric structure which was determined by use of molecular weight. Schmidt's conclusion was favored generally over Macallum proposition.

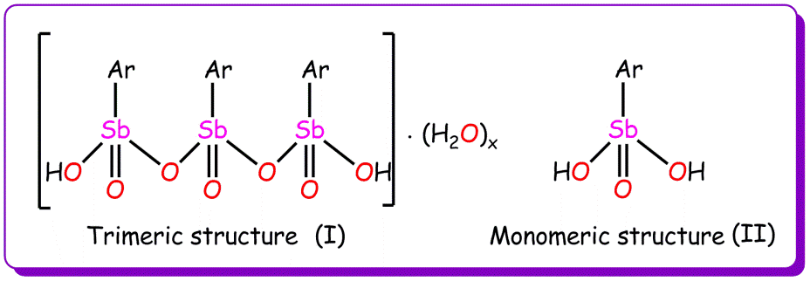
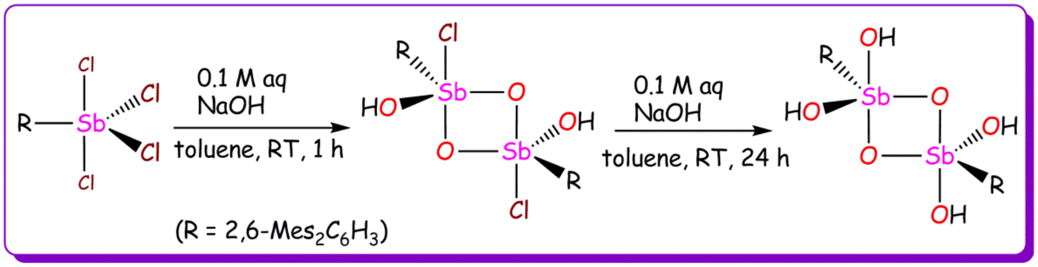


Figure 23: Schmidt proposed organostibonic acid structures.

1.9.3 Synthesis of first well-defined molecular arylstibonic acid:

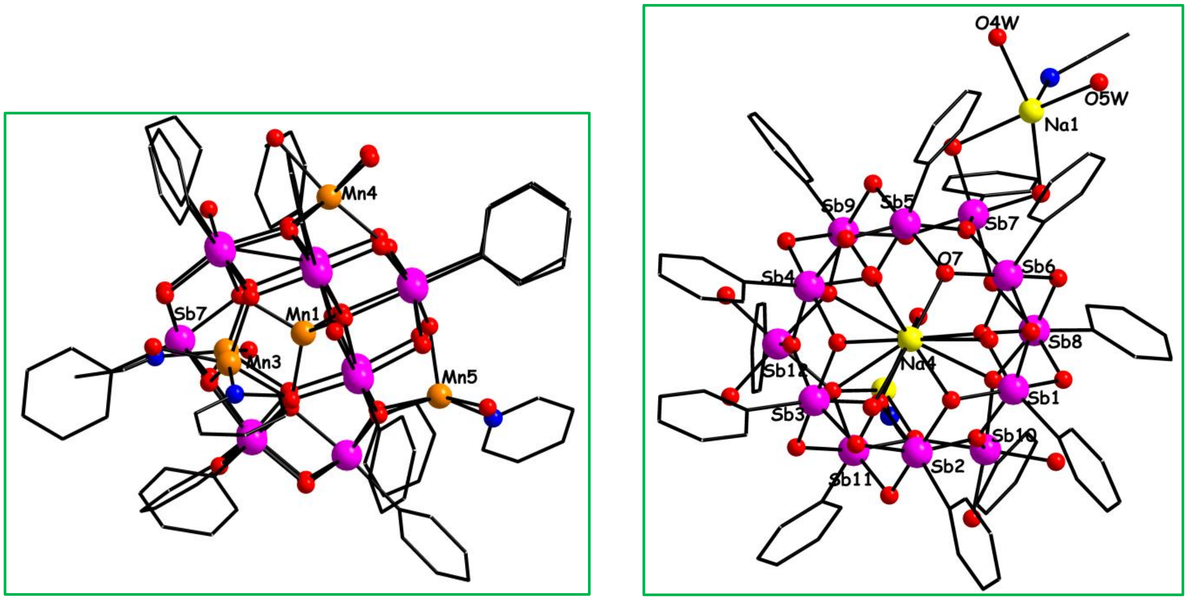
Beckmann *et al* reported the first well-defined molecular organostibonic acid, $[2,6\text{-}Mes_2C_6H_3Sb(O)(OH)_2]_2$ (Mes = mesityl) by kinetically controlled hydrolysis of $2,6\text{-}Mes_2C_6H_3SbCl_4$ under basic conditions (Scheme 29),[75] which crystallized as a dimer with five-coordinate Sb and a Sb_2O_2 core. In this case the bulky R groups prevent the higher aggregation, Hence the organostibonic acid crystallized as a dimer.



Scheme 29

1.9.4 Synthesis of reverse-keggin compounds:

Winpenny *et al* reported the isolation of reverse-keggin frameworks which draws parallels to well established POM chemistry reported by Müller[76] Pope[77] and others.[78] Reverse-keggin ions (Figure 24) have been synthesized under solvothermal condition[79] by treating organostibonic acids with transition metal acetate such as Mn^{2+}, Co^{2+} or Zn^{2+} in presence of base such as pyridine or triethylamine at 100 °C. Here in, the organostibonic acids self-condensed forming POM frameworks which acts as cavitands for incorporating transition metal ions in the cavities.

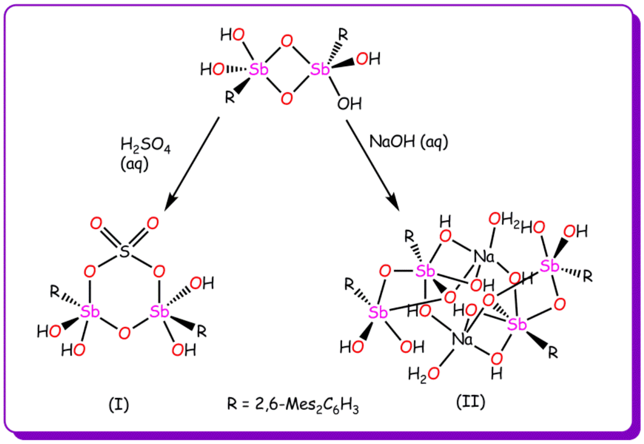


(a) (b)

Figure 24: (a) Manganese with four coordination number (b) Antimony with six coordination number.

1.9.5 Reactivity of organostibonic acid towards H_2SO_4 and NaOH:

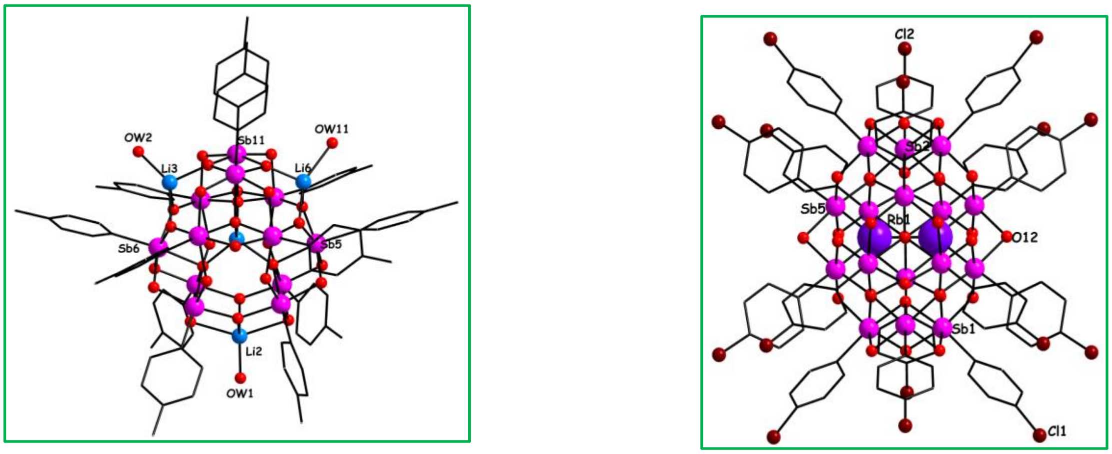
The reactivity of $[2,6\text{-}Mes_2C_6H_3Sb(O)(OH)]_2$ towards H_2SO_4 and NaOH in aqueous medium gave $[(2,6\text{-}Mes_2C_6H_3Sb)_2(O)(OH)_4SO_4]$ (I) and $[(Na_2(2,6\text{-}Mes_2C_6H_3Sb)_4(O)_4(OH)_{10}.2H_2O]$ (II) (Scheme 30).[80] Four-membered Sb_2O_2 undergoes ring opening when treated with aqueous H_2SO_4 gave rise to a six-membered heterocycle (I).



Scheme 30

1.9.6 Synthesis of polyoxometalates:

Organostibonic acids have an ability to act as an inorganic cryptands and it can incorporate alkali metal and alkali earth metals in their cavities, which has been recently well documented by Nicholson *et al* (Figure 25).[81] This group isolated various POM in antimony such as Sb_{11}, Sb_{12} and Sb_{14} under basic condition in aqueous medium. POM stability in solution state was characterized by using ESI-MS which revealed the structure integrity was maintained in solution as well. Mixed valent Sb(III/V) (Figure. 21) have also been isolated by treating organostibonic acid with diphenyltelluric oxide under reflux condition using toluene as a solvent.[63]

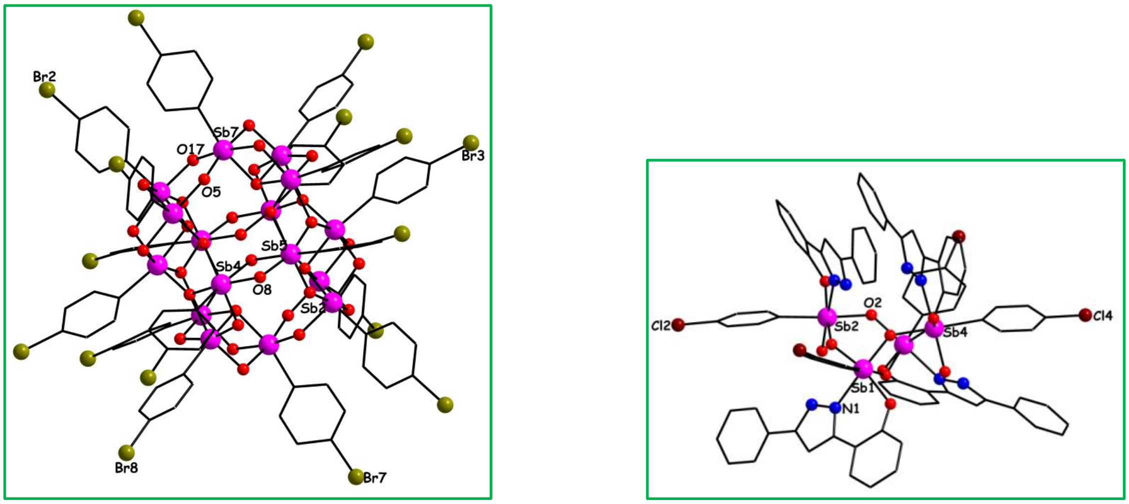


(a) (b)

Figure 25: (a) Dodecanuclear Polyoxostibonate. (b) Hexadecanuclear Polyoxostibonate.

1.9.7 Synthesis of Hexadecanuclear and tetranuclear Organoantimony oxo clusters:

Depolymerisation reactions of organostibonic acids with protic ligand in presence of base have been studied. Reaction of organostibonic acid with phenolic pyrazolyl ligand gave rise to tetranuclear oxido cluster (Figure 26b). In presence of mild base such as 3,5-DMPz, Hexadecanuclear POM (Figure 26a) based organoantimony have been synthesized and structurally characterized.[82]

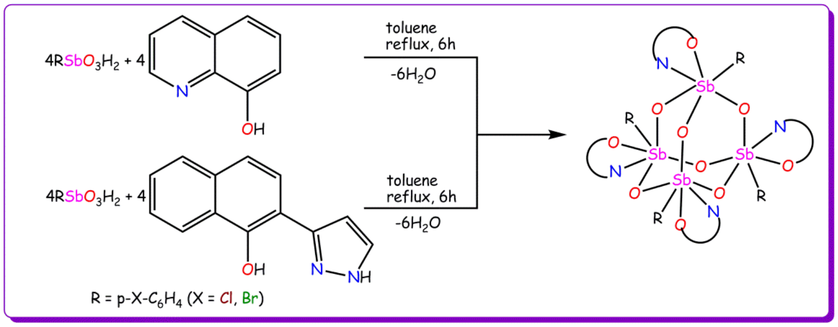


(a) (b)

Figure 26: (a) Hexadecanuclear Polyoxostibonate. (b) Tetranuclear Organoantimony oxo cluster.

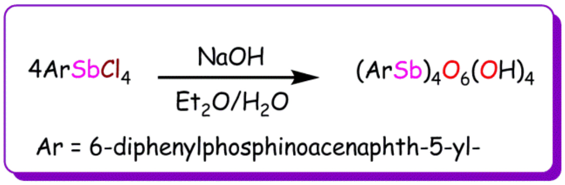
1.9.8 Synthesis of adamantane type structures:

Subsequently, adamantane[83] type structure have been prepared by reacting organostibonic acid with 8-hydroxyquinoline or {2-[1H-pyrazol-5(3)-yl]naphthalene-1-ol} (H_2naphpz) in a 1 : 1 stoichiometry under reflux condition for 6 h (Scheme 31).



Scheme 31

Beckmann *et al* have subsequently reported the second well-defined admantane[84] type structure (Figure 27) by the base hydrolysis of $ArSbCl_4$ (Scheme 32).



Scheme 32

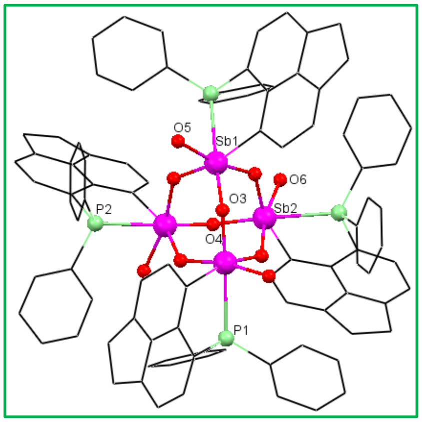
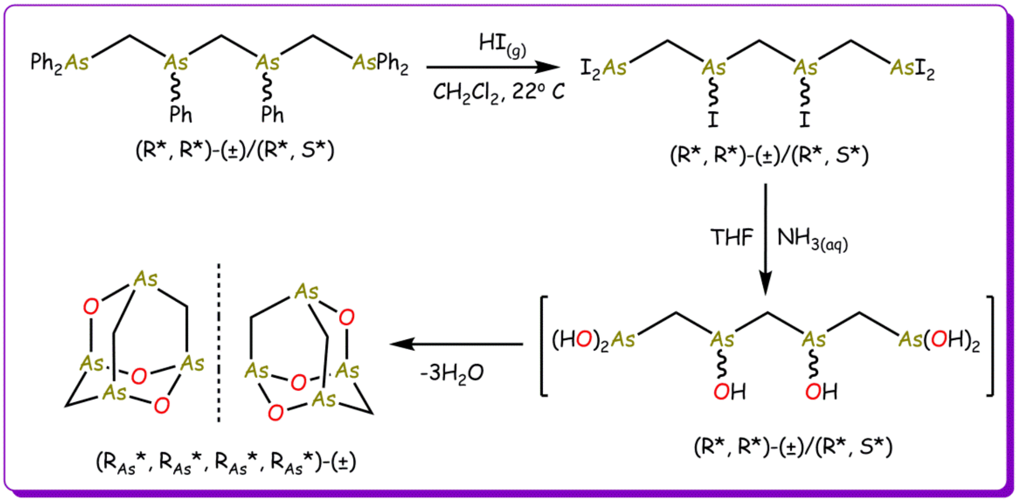


Figure 27: Solid state structure adamantane type tetranuclear arylstibonic acid.

It is interesting here to mention that an arsenic based adamantane framework is known. Arsenicin A was the first natural polyarsenic compound isolated from New Caledonian sponge *Echinochalina bargibanti*[85] in trace amounts and it shows potential bactericidal and fungicidal activities on human pathogenic strains.

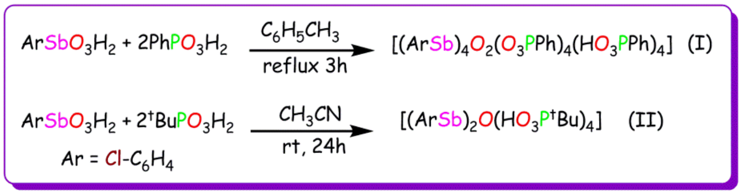


Scheme 33

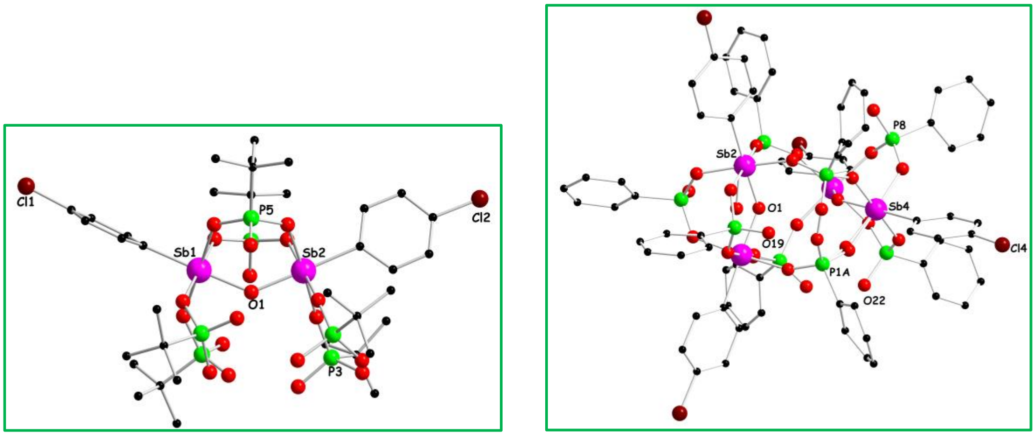
Arsenicin A structure resembles adamantane-type structure As_4O_6 in which three of the oxygen atoms have been replaced by three CH_2 groups in a structure showing C_2-chiral arrangement. It has also been chemically synthesized by Wild *et al*[86] (Scheme 33).

1.9.9 Synthesis of Organoantimony phosphonate clusters:

Novel organoantimony oxo clusters were obtained by treating organostibonic acids with phosphonic acid[87] (Scheme 34). Organoantimony phosphonate clusters have been shown to act as a pro-ligand, which can be used to produce polymetallic complexes towards metal salts under solvothermal reaction conditions (Figure 28).[88]



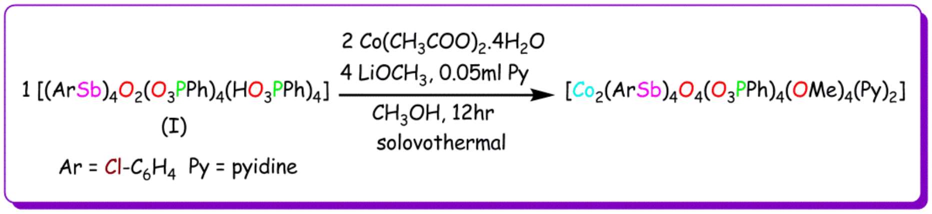
Scheme 34



(a) (b)

Figure 28: (a) Dinuclear antimony cluster. (b) Tetranuclear antimony cluster.

These organoantimony clusters have the ability to acts as proligand (Figure 29) which is being currently investigated in our group (Scheme 35).



Scheme 35

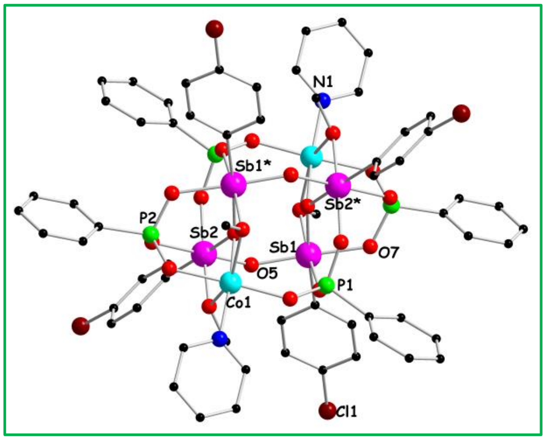
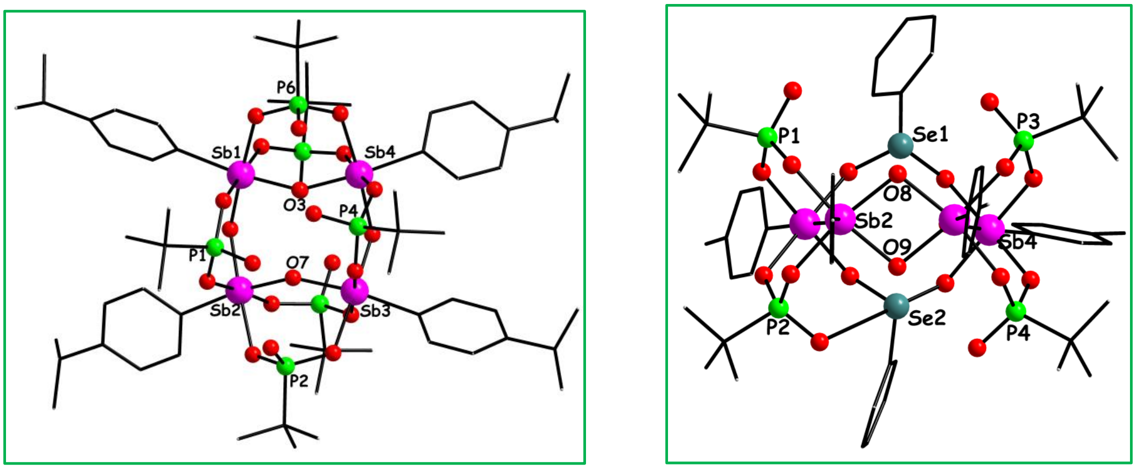


Figure 29: Molecular structure of $[Co_2(SbAr)_4O_4(O_3PPh)_4(OMe)_4py_2]$

1.9.10 Synthesis of monoorganoantimony(V) phosphonate and phosphoseleninate:

Very recently tetra- and dinuclear organoantimony oxo-hydroxo clusters have been synthesized from our group by treating organostibonic acid with organophosphonic acid and phenylseleninic acid and the mole ratios taken in 1 : 2 (or) 1 : 1 : 1 and stirred it for 24 h at room temperature with acetonitrile as solvent (Figure 30).[89]



(a) (b)

Figure 30: (a) Solid state structure of monoorganoantimony(V) phosphonate. (b) monoorganoantimony(V) phosphoseleninate.

These structures just enhance the proligand ability of the clusters by providing an extra ligating group like selininate along with phosphonate. Their ability to act as ligands are also currently being investigated.

1.10 Motivation for the work carried out:

The work reported in this thesis mainly revolves around the investigation of the reactivity of monoorganostibonic acids. Efforts have been made to understand the structure and reactivity of organostibonic acids. Protic ligands have been used to depolymerize organostibonic acids and the results obtained have been studied in detail.

Chapter 2 deals with the reactivity of organostibonic acids when reacted with differently substituted oxime ligands. The first part deals with the reactivity of organostibonic acids with oximes while the latter part deals with the investigation of the reactivity of di- and triorganoantimony halides with various substituted oximes. The results obtained are explained in detail.

Organosilanols have been shown to acts as excellent ligands for synthesing clusters of main group metal ions by reacting them with various organometallic metals like In, Ga, Al, Ge, Sn and etc. Here, silanediols/triols reactions with organostibonic acids have been investigated. Mass spectral data has also been used to prove structure stability in solution. The work carried out and results obtained are given in details in chapter 3 and 4.

Organostibonic acids have been shown to form POM frameworks in aqueous medium from literature reports. Since in the presence of 3,5 DMPz, organostibonic acids self-condensed to form POM, we have investigated organostibonic acids self-condensation in presence of basic medium in organic solvents. The work carried out is given in details in chapter 5.

1.11 References:

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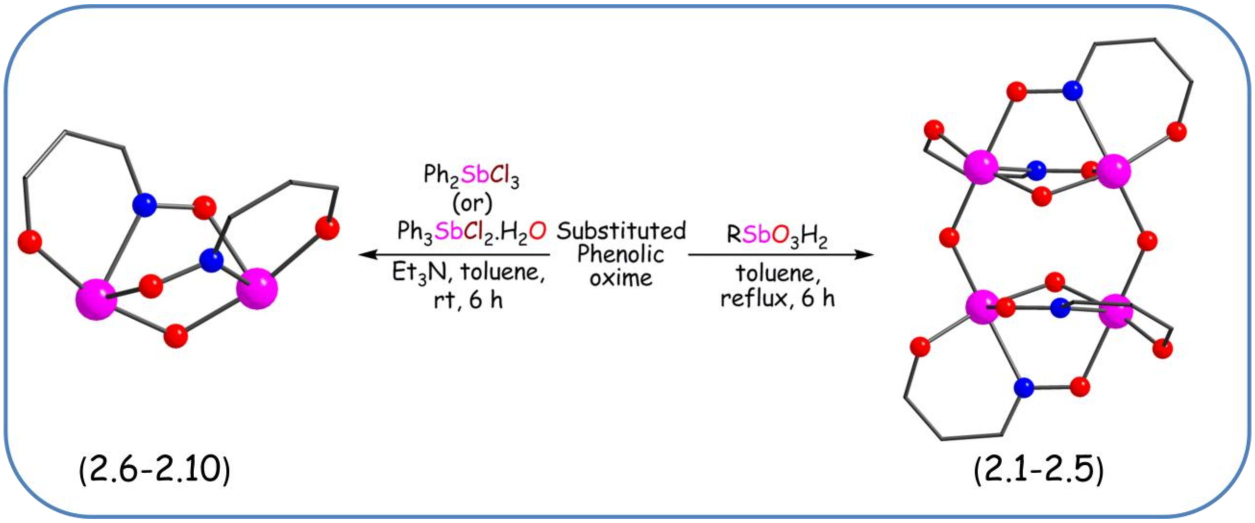
Dinuclear and tetranuclear organoantimony(V) oxido clusters stabilized by dianionic ligands

Chapter 2

Abstract: A series of neutral tetranuclear organoantimony(V) oxido clusters have been synthesized using substituted phenolic oxime as protic ligands in 1:1 ratio under refluxing condition. Crystal structures of**2.1-2.5** revealed that they are tetranuclear and isostructural [(*p*-chloro-$C_6H_4Sb)_4(O)_4(L_1)_4$] (**2.1**), [(*p*-bromo-$C_6H_4Sb)_4(O)_4(L_1)_4$] (**2.2**), [(3,5-dichloro-$C_6H_3Sb)_4(O)_4(L_1)_4$] (**2.3**), [(*p*-bromo-$C_6H_4Sb)_4(O)_4(L_4)_4$] (**2.4**) and [(*p*-chloro-$C_6H_4Sb)_4(O)_4(L_5)_4$] (**2.5**). On the other hand a series of dinuclear organoantimony(V) oxido clusters have been synthesized by using organoantimony halide, substituted phenolic oxime and Et_3N as a base in 1:1:2 molar ratio under room temperature.Sb-C bond cleavage has been observed in **2.6**, **2.9** and **2.10**. Crystal structures of**2.6-2.10** revealed that they are dinuclear and isostructural $[(Ph_2Sb)_2(O)(L_1)]$ (**2.6**), $[(Ph_2Sb)_2(O)(L_2)]$ (**2.7**) $[(Ph_2Sb)_2(O)(L_3)]$ (**2.8**), $[(Ph_2Sb)_2(O)(L_4)]$ (**2.9**) and $[(Ph_2Sb)_2(O)(L_5)]$ (**2.10**).ESI-MS of clusters **2.1-2.8** and **2.10** shows that structural integrity is maintained in solution state also.



2.1 Introduction

Organoantimony compounds are important not only due to the diverse structural chemistry they display, but and also for their potential application in biology and catalysis.[1]Organostibonic acids,have been known for some time now, but thereactivity of organostibonic acid has not been well studied.[2]Molecular structure of organostibonic acid are also not well established due to its polymeric nature and poor solubility. Recently the reactivity of organostibonic acids have started gaining attraction due to the rich structural diversity it exhibits on reactions with various protic ligand systems.[3,7]Isolation of various nuclearity antimony based clusters from Sb_{12} to Sb_{16}under basic condition have beenreported.Under ambient conditions Li^+, Na^+, K^+, $Rb^+$and Ba^{2+}ions have been incorporated in the cage of an isopolyoxoantimonates which act as inorganic crown-type ligandand their ESI-MS showsstructural stability in solution state.[4]First-reverse keggin have been isolated under solvothermal condition.[5] Kinetically controlled base hydrolysis of sterically hindered arylantimony tetrahalide and dihalide led to the isolation of first well defined arylstibonic acid which crystallized as a dimer with a Sb_2O_2core.[6] Mixed valent polyoxostibonates stabilized by telluroxane have also been recently reported from our group.[7]Sb-C bond cleavage has led to formation of interestingmolecular clusters.[8]

Parallely, oxime ligands play animportant role in coordination chemistry of transition metal ions and lanthanides.[9] Depending upon the degree of deprotonation, the oxime ligands have the ability to form a mono/di or poly nuclear complexes as has been reported in literature.[10] On the other hand,the coordination ability ofoximes towards main groupmetal ions are relatively less studies and in particular their reaction with organoantimonyl substrates are less explored.Herein, we report the synthesis and characterization of dinuclear and tetranuclear organoantimony(V) oxido clusters. ESI-MS studies show that the structural integrity is maintained in solution as well.

2.2 Experimental Section

2.2.1 General information:

Solvents and the common reagents were used for the synthesis are purchased from commercial sources. (*p*-halophenyl and*m*-dihalophenyl) stibonic acids (halogen = Cl and Br),

Ph_2SbCl_3, $Ph_3SbCl_2.H_2O$, 2’-hydroxyacetophenone oxime, *o*-Vanillin oxime, 5-bromosalicylaldehyde oxime, 3,5 di-*t*-butylsalicylaldehyde oxime and1’-hydroxy-2’-acetonaphthone oxime were synthesized using literature procedures.[11]

2.2.2 Instrumentation:

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. Singlecrystal X-ray data collection (for **2.1-2.10**) was carried out at 100(2) K on a Bruker Smart Apex CCD area detector system (λ (Mo Kα) = 0.71073 Å), with a graphite monochromotor. The data were reduced using SAINT PLUS and the structures were solved using SHELXS-97[12]and refined using SHELXL-2014/7.[13,14] All non-hydrogen atoms were refined anisotropically.DFIX command was applied to restrain the bond length of the two acetone (C43-C48) solvent molecule in **2.4** and toluene (C73-C78) molecule in **2.5**. Thermal parameters for C43, C46 and C47 were constrained with EDAP instructions. Disorder toluene molecule in **2.7**was removed by SQUEEZE[15] command in the PLATON program.

2.2.3 Synthetic procedures for Compounds 2.1-2.5:

Organostibonic acids and the corresponding oximes were taken in 1:1 stoichiometry in 50mL of toluene and refluxed for 6 h. A Dean Stark apparatus was used to remove the water eliminated in the reaction as an azeotropic mixture. The clear solution that formed was cooled to room temperature, filtered and evaporated under reduced pressure to yield a colorless solid. The molar ratios and weights of the reactants used are as follows:

Compound [(*p*-chloro-$C_6H_4Sb)_4(O)_4(L_1)_4$]2.1:

(*p*-chlorophenyl)stibonic acid (0.300 g , 1.06 mmol) and 2’-hydroxyacetophenone oxime(0.160 g, 1.06 mmol). Colorless crystals suitable for single crystal diffraction analysis were obtained by the diffusion method of chloroform/cyclohexane in a week’s time. Yield:0.197 g (47%, based on the weight of (*p*-chlorophenyl)stibonic acid). Dec pt: 170-171˚C. Anal. Calcd (%) for $C_{56}H_{44}O_{12}N_4Cl_4Sb_4$: C, 42.20; H, 2.78; N, 3.52. Found: C, 42.09; H, 2.71; N, 3.48. IR (cm^{-1}, KBr pellet): 3057(s), 2962(m), 1597(w), 1475(s), 1439(s), 1381(w), 1296(s), 1232(w), 1087(w), 1012(m), 970(m), 862(s), 810(s), 752(m), 567(m), 484(s), 419(m).^1H NMR in $CDCl_3$:

δ 6.83-7.62 (m, 32 H), 2.67 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.66, 157.93, 157.66, 135.18, 134.84, 134.26, 133.90, 129.25, 129.04, 128.95, 128.68, 128.32, 127.90, 127.58, 122.10, 119.05, 118.57, 117.28, 117.17, 15.83, 15.62, 15.13. ESI-MS: *m/z* 1616.7695 $[M+Na]^+$.

Compound [(*p*-bromo-$C_6H_4Sb)_4(O)_4(L_1)_4$]2.2:

(*p*-bromophenyl)stibonic acid (0.300 g , 0.92 mmol) and 2'-hydroxyacetophenone oxime(0.138 g, 0.92mmol). Colorless crystals suitable for single crystal diffraction analysis were obtained by the diffusion method of chloroform/cyclohexane in a week's time. Yield: 0.189 g (47%, based on the weight of (*p*-bromophenyl)stibonic acid). Dec pt: 180-181˚C. Anal. Calcd. (%) for $C_{56}H_{44}O_{12}N_4Br_4Sb_4$: C, 37.97; H, 2.50; N, 3.16. Found: C, 37.85; H, 2.58, N, 3.21. IR (cm^{-1}, KBr pellet): 3061(s), 2924(m), 1597(s), 1562(s), 1475(s), 1440(s), 1377(s), 1298(s), 1182(m), 1132(m), 1057(s), 1006(s), 970(s), 862(m), 808(s), 754(m), 706(w), 569(w), 480(s). ^{1}H NMR in $CDCl_3$: δ 6.77-7.86 (m, 32 H), 2.66 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.67, 135.38, 134.93, 134.41, 133.89, 133.81, 132.60, 132.07, 131.94, 131.25, 130.97, 128.80, 127.58, 124.69, 122.16, 120.88, 120.08, 119.03, 118.58, 117.20, 15.71, 15.15. ESI-MS: *m/z* 1794.5690 $[M+Na]^+$.

Compound[(3,5-dichloro-$C_6H_3Sb)_4(O)_4(L_1)_4$] 2.3:

(*m*-dichlorophenyl)stibonic acid (0.300 g, 0.94 mmol) and 2'-hydroxyacetophenone oxime(0.143 g, 0.94 mmol). Colorless crystals suitable for single crystal diffraction analysis were obtained by the diffusion method of chloroform/cyclohexane in a week's time. Yield: 0.217 g (53%, based on the weight of (*m*-dichlorophenyl)stibonic acid). Dec pt: 120-121˚C.Anal. Calcd. (%) for $C_{56}H_{40}O_{12}N_4Cl_8Sb_4$: C, 38.84; H, 2.33; N, 3.24. Found: C, 38.76; H, 2.36; N, 3.31. IR (cm^{-1}, KBr pellet): 3069(s), 2964(m), 1597(w), 1558(m), 1479(w), 1440(m), 1373(w), 1294(s), 1230(w), 1126(w), 1099(m), 1016(w), 970(w), 860(s), 794(s),752(m), 667(m), 505(s), 419(w). ^{1}H NMR in $CDCl_3$: δ 6.87-7.71 (m, 28 H), 2.43 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.28, 159.07, 157.99, 135.35, 132.27, 131.95, 131.24, 131.15, 130.59, 127.75, 123.62, 121.19, 120.99, 120.52, 15.88. ESI-MS: *m/z* 1732.6113 $[M+H]^+$.

Compound [(*p*-bromo-$C_6H_4Sb)_4(O)_4(L_4)_4$]2.4:

(*p*-bromophenyl)stibonic acid (0.300 g , 0.92 mmol) and 3,5 di-*t*-butylsalicylaldehyde oxime(0.228 g, 0.92 mmol). Colorless crystals were obtained by slow evaporation of acetone solution which is suitable for single crystal diffraction analysis. Yield:0.286 g (58%, based on the weight of (*p*-bromophenyl)stibonic acid). Dec pt: 140-141˚C. Anal. Calcd. (%) for $C_{84}H_{100}O_{12}N_4Br_4Sb_4$: C, 46.61; H, 4.66; N, 2.59. Found: C, 46.72; H, 4.68; N, 2.49. IR (cm^{-1}, KBr pellet): 2953(s), 2871(m), 1605(s), 1556(s), 1479(s), 1435(s), 1391(s), 1358(s), 1260(w), 1205(w), 1172(s), 1008(s), 871(s), 810(s), 707(m), 482(s).^{1}H NMR in $CDCl_3$: δ8.20(s, 4H), 7.01-7.40 (m, 24 H), 1.33 (s, 72 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.22, 154.16, 141.24, 136.48, 126.10, 125.53, 115.75, 35.10, 34.16, 31.49, 31.24. ESI-MS: *m/z* 2165.0465 $[M+H]^+$.

Compound [(*p*-chloro-$C_6H_4Sb)_4(O)_4(L_5)_4$]2.5:

(*p*-chlorophenyl)stibonic acid (0.200 g , 0.71 mmol) and 1’-hydroxy-2’-acetonaphthone oxime(0.142 g, 0.71 mmol). Colorless crystals suitable for single crystal diffraction analysis were obtained by the diffusion method of toluene/cyclohexane in a week’s time. Yield:0.125 g (39%, based on the weight of (*p*-chlorophenyl)stibonic acid). Dec pt: 170-171˚C. Anal. Calcd. (%) for $C_{72}H_{52}O_{12}N_4Cl_4Sb_4$: C, 48.20; H, 2.92; N, 3.12. Found: C, 48.36; H, 2.89; N, 3.28. IR (cm^{-1}, KBr pellet): 3063(s), 2954(m), 1578(w), 1557(m), 1469(s), 1376(s), 1345(s), 1086(w), 1008(s), 884(w), 801(s), 790(s),748(m), 660(m), 511(s), 425(w). ^{1}H NMR in $CDCl_3$: δ 7.33-8.35 (m, 40 H), 2.83 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.28, 159.83, 155.67, 154.88, 137.91, 135.20, 134.41, 133.79, 129.27, 128.86, 128.04, 127.15, 125.98, 125.22, 124.98, 124.47, 123.47, 123.91, 121.91, 119.41, 118.38, 117.52, 11.42, 16.52, 16.28, 15.62. ESI-MS: *m/z* 1794.8693 $[M+H]^+$.

2.2.4 Synthetic procedures for Compounds 2.6-2.10:

The stoichiometric amounts of organoantimony halides ($Ph_3SbCl_2.H_2O$ or Ph_2SbCl_3) was added to a clear solution of oxime and Et_3N in 30 mL of tolueneand a molar ratio of 1:1:2 respectively. The solution was stirred for 6 h at room temperature. Filtration followed by evaporation under reduced pressure furnishes a white crystalline powder.The molar ratios and weights of the reactants used are as follows:

Compound [$(Ph_2Sb)_2(O)(L_1)$]2.6:

$Ph_3SbCl_2.H_2O$ (0.300 g , 0.68 mmol),2’-hydroxyacetophenone oxime(0.103 g, 0.68 mmol) and triethylamine (0.2 mL, 1.36 mmol).Colorless crystals were obtained in a week’s time by slow evaporation of toluene.Yield: 0.230 g (79%, based on the weight of $Ph_3SbCl_2.H_2O$).Dec. pt: 130-131 ˚C.Anal. Calcd (%) for$C_{40}H_{34}O_5N_2Sb_2$: C, 55.46; H, 3.96; N, 3.23.Found: C, 55.38; H, 3.86, N, 3.19.IR (cm^{-1}, KBr pellet): 3046(w), 1621(w), 1589(s), 1473(m), 1435(s), 1358(m), 1293(s), 1254(m), 1156(w), 1068(s), 997(s), 936(s) 734(s), 685(s), 559(m), 449(s).^1H NMR (400 MHz, $CDCl_3$): δ 6.67-7.95 ppm (m, 28H), 3.07 ppm (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ160.23, 158.19, 157.96, 144.06, 136.69, 135.30, 134.64, 133.922, 132.89, 131.29, 130.90, 129.64, 128.75, 128.26, 127.13, 125.32, 122.68, 120.62, 119.38, 118.27, 116.87, 15.09ppm.ESI-MS: *m/z*867.0621 $[M+H]^+$.

Compound $[(Ph_2Sb)_2(O)(L_2)]$2.7:

Ph_2SbCl_3(0.300 g, 0.78 mmol), *o*-Vanillin oxime(0.131 g, 0.78 mmol) and triethylamine (0.22mL, 1.57mmol). Colorless crystals were obtained in a week's time by slow evaporation of toluene which is suitable for single crystal diffraction analysis.Yield: 0.215 g (61%, based on the weight of Ph_2SbCl_3).Dec. pt: 210-211 ˚C.Anal. Calcd. (%)for $C_{40}H_{34}O_7N_2Sb_2$: C, 53.49; H, 3.82; N, 3.12. Found: C, 53.42; H, 3.73; N, 3.07.IR (cm^{-1}, KBr pellet): 3096(m), 1600(s), 1468(m), 1436(m),1364(s), 1260(m), 1222(w), 1107(w), 981(m), 860(m), 811(m),734(m), 690(w)551(m), 439(s).^1H NMR (400 MHz, $CDCl_3$): δ 8.37 ppm (s, 2H), 6.47-7.60 ppm (m, 26H), 3.94 ppm (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.75, 150.88, 145.34, 143.06, 133.81, 132.89, 130.39, 129.74, 128.34, 123.15, 118.96, 114.37, 56.42 ppm.ESI-MS: *m/z*899.0520 $[M+H]^+$.

Compound $[(Ph_2Sb)_2(O)(L_3)]$2.8:

Ph_2SbCl_3(0.300 g, 0.78 mmol),5-bromosalicylaldehyde oxime(0.170 g, 0.78 mmol)andtriethylamine(0.22 mL, 1.57mmol). Colorless crystals were obtained in a week's time by slow evaporation of toluene.Yield: 0.267 g (68%, based on the weight of Ph_2SbCl_3).Dec. pt: 210-211 ˚C.Anal. Calcd. (%)for $C_{38}H_{28}O_5N_2Br_2Sb_2$: C, 45.83; H, 2.83; N, 2.81. Found: C, 45.68; H, 2.89; N, 2.76. IR (cm^{-1}, KBr pellet): 3057(w), 1589(m), 1469(s), 1431(m), 1394(m), 1342(w), 1261(s), 1182(m), 1076(w), 1032(s), 937(w), 812(s), 733(m), 691(w), 511(m), 448(s). ^1H NMR (400 MHz, $CDCl_3$): δ 8.15 ppm (s, 2H), 7.21-8.04 ppm (m, 26H).^{13}C NMR (100 MHz, $CDCl_3$): δ 160.15, 151.70, 149.79, 144.47, 142.41, 137.89, 135.12, 134.14, 133.69, 132.77, 131.78, 130.74, 129.62, 128.67, 125.32, 123.81, 119.05, 118.67, 110.78 ppm.ESI-MS: *m/z*996.8507 $[M+H]^+$.

Compound$[(Ph_2Sb)_2(O)(L_4)]$2.9:

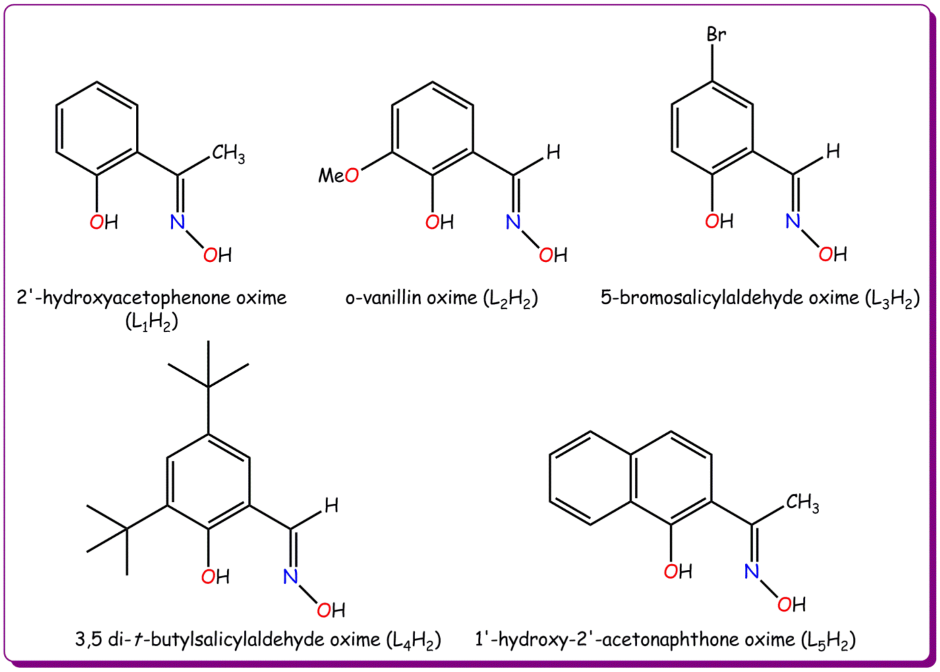
$Ph_3SbCl_2.H_2O$ (0.300 g , 0.68 mmol), 3,5 di-*t*-butylsalicylaldehyde oxime(0.195 g, 0.68 mmol) and triethylamine (0.19 mL, 1.36 mmol).Colorless crystals were obtained in a week's time by slow evaporation of acetone.Yield: 0.254 g (70%, based on the weight of $Ph_3SbCl_2.H_2O$).Dec. pt: 90-91 ˚C.Anal.Calcd. (%) for $C_{52}H_{62}O_5N_2Sb_2$: C, 61.04; H, 5.88; N, 2.64.Found: C, 61.15; H, 5.93; N, 2.59.IR (cm^{-1}, KBr pellet): 3057(w), 1605 (m), (s), 1479 (s), 1430 (s), 1364 (m), 1260(s), 1167(m), 986(w), 882(w), 843(w), 734(s),715(m), 476(s).^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 ppm (s, 2H), 6.95-7.60 ppm (m, 24H), 1.32 ppm (s, 36 H).^{13}C NMR (100 MHz, $CDCl_3$): δ 154.63 154.39, 154.37, 154.02, 140.48, 140.30, 136.50, 136.05, 135.92, 135.42, 134.71, 134.52, 134.17, 133.80, 133.60, 131.75, 131.59, 130.92, 129.69, 129.53, 129.43, 129.25, 125.06, 116.71, 34.11, 31.55, 29.29 ppm.

Compound $[(Ph_2Sb)_2(O)(L_5)]$2.10:

$Ph_3SbCl_2.H_2O$ (0.150 g, 0.34 mmol), 1'-hydroxy-2'-acetonaphthone oxime(0.068 g, 0.34 mmol) and triethylamine (0.09mL, 0.68mmol).Crystals suitable for single crystal diffraction analysis was obtained in a week's timeby diffusion method using dichloromethane/hexane.Yield: 0.112 g (68%, based on the weight of $Ph_3SbCl_2.H_2O$).Dec. pt: 180-181˚C. Anal. Calcd. (%)for $C_{48}H_{38}O_5N_2Sb_2$: C, 59.66; H, 3.96; N, 2.90.Found: C, 59.76; H, 3.91; N, 2.98.IR (cm^{-1}, KBr pellet): 3052(m), 1632(s), 1572(s), 1479(s), 1435(s), 1391(s), 1287(m), 1254(w), 1183(w), 997(w), 953(s), 882(s), 805(s), 734(s), 696(m), 625(m), 597(s), 515(s), 418(m).^{1}H NMR (400 MHz, $CDCl_3$): δ 6.91-8.37 ppm (m, 32H), 2.50 ppm (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.42, 158.32, 155.23, 138.83, 137.26, 136.52, 1135.41, 135.26, 134.66, 131.72, 129.62, 128.35, 128.25, 127.56, 126.90, 124.08, 123.42, 120.69, 117.84, 11.92, 16.36, 16.75, 15.5ppm.ESI-MS: *m/z*967.0840 $[M+H]^+$.

2.3 Results and Discussions

Reaction of organostibonic acid with oximes (1:1 molar ratio) under refluxing condition using toluene as a solvent led to a colorless solution from which five neutral tetranuclear organoantimony(V) oxido clusters**2.1-2.5**(Scheme 2.1) were isolated and whose solid state were established by single crystal X-ray diffraction. Introducing the bulky group in the 3rd position of oxime (**L_2H_2, L_4H_2&L_5H_2**) shows no change in the structure of the product obtained. Ligands used for these syntheses are presented in Chart 2.1.



2'-hydroxyacetophenone oxime (L_1H_2)

o-vanillin oxime (L_2H_2)

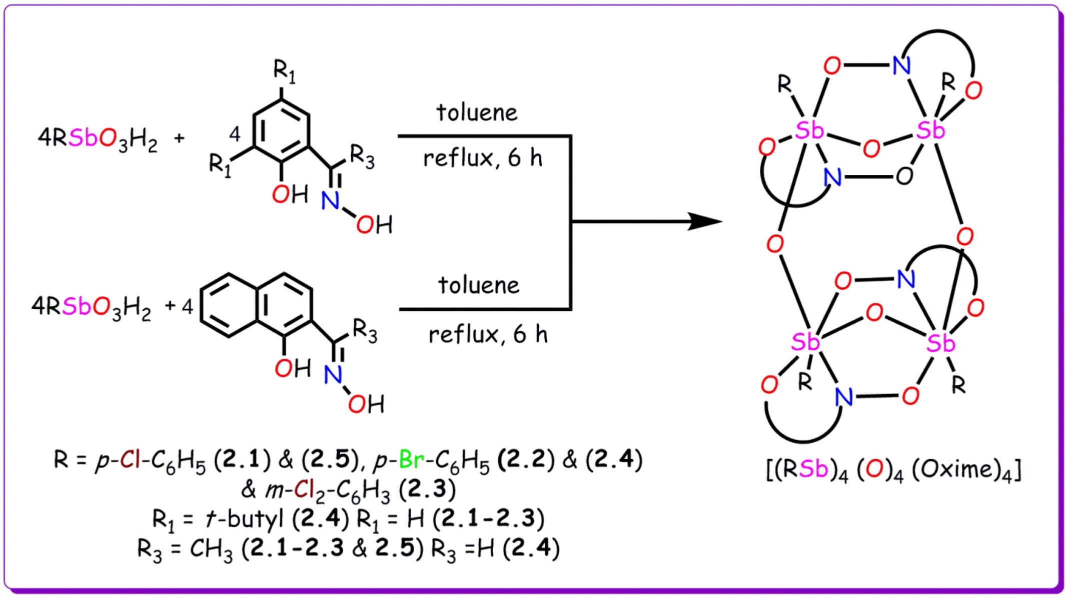
5-bromosalicylaldehyde oxime (L_3H_2)

3,5 di-*t*-butylsalicylaldehyde oxime (L_4H_2)

1'-hydroxy-2'-acetonaphthone oxime (L_5H_2)

Chart 2.1

^{1}H NMR spectra ($CDCl_3$ in solution) for cluster **2.1-2.5** showsmultiplets in the range of 6.77- 8.35 ppmcorresponding to the aromatic protons. For clusters**2.1-2.3** and**2.5**a singlet in the region 2.67, 2.66, 2.43 and 2.83 ppm corresponding to oximic CH_3 protons are observed. Cluster**2.4** shows a singlet in the region of 8.20 ppm assigned foroximic C-H proton. ESI-MS of clusters **2.1** and **2.2**(Figure 2.3)under +ve ion mode shows a molecular ion peak at $[M+Na]^+$ and clusters **2.3-2.5**(Figure 2.3 and 2.4)shows a molecular ion peak under +ve ion mode at $[M+H]^+$.Tetranuclear oxo cluster **2.1-2.4** crystallizes in the triclinic space group*P-1*having half molecule in asymmetric unit(Table 2.1). Cluster **2.5** crystallizes in monoclinic space group*P2(1)/c*(Table 2.2). Cluster**2.1-2.3** crystallizes from the solvent chloroform/cyclohexane. Cluster **2.4** and **2.5** crystallizes in acetone and toluene/cyclohexane respectively. Clusters **2.1-2.5** are isostructural, so the structureof**2.1**isconsidered for explanation. The selected bond lengths (Å) and bond angles (°)of**2.1-2.5** are given in the Table 2.4-2.8.Structural characterization of cluster **2.1** reveals the formation of a tetranuclear organoantimony(V) oxido clusters[(p-chloro-$C_6H_4Sb)_4$ $(O)_4$ $(L_1)_4$]**(2.1)**(Figure 2.1).



Scheme 2.1

The cluster **2.1**contains twelve oxygen atoms, four are$\mu_2$bridging. All oxygen atoms are considered as oxo group for charge neutrality. The structure reveals Sb atoms present in the cluster are six coordinated and present in an octahedral geometry. Core of the structure is constructed by μ_2-oxo group which leds to the formation of eight membered Sb_4O_4 rings (Figure 2.2 (a)) which shows all the Sb atoms are present in almost the same plane and the periphery of core is bridged by N and O atom of oximic ligand. Coordination mode around Sb atom is O_4CN(Figure 2.2 (b)): two coordination from μ_2-oxo group of the core, third from oximic nitrogen, fourth coordination is satisfied by phenolic oxygen atom,fifth coordination is shared through oxygen atom of the neighboring oximic ligand and sixth coordination is from halophenyl carbon atom. Sb-O bond distances found in the cluster **2.1** are three types. The Sb-O distances in the core fall in the range of 1.927(3)-1.960(3) Å. The phenolic oxygen to Sb distances fall in the range of 1.981(3)-1.983(3) Å. Sb-O of oximate oxygen bond distances fall in the range of 2.039(3)-2.072(3) Å.Sb-C fall in the range of 2.099(5)-2.109(5)Å. Sb-N bond distances fall in the range of 2.196(4)-2.234(4)Å. Distances for nonbonding Sb---Sb are 3.306(4)-3.531(3)Å. The Sb-O-Sb bond angles in the core fall in the range of 117.94(16)-130.70(17) °. Four dianionic ligands wrap the eight membered core in an uniform manner. Formations of six membered ringsare due to phenolic oxygen atom and oximate nitrogen atom binding to Sb atom in a chelating mode.

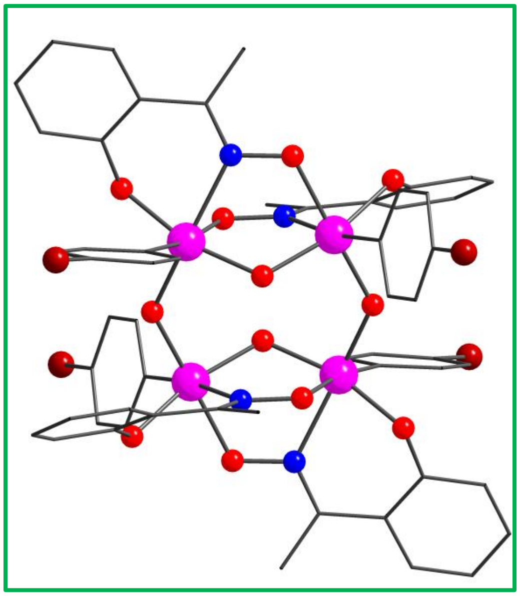
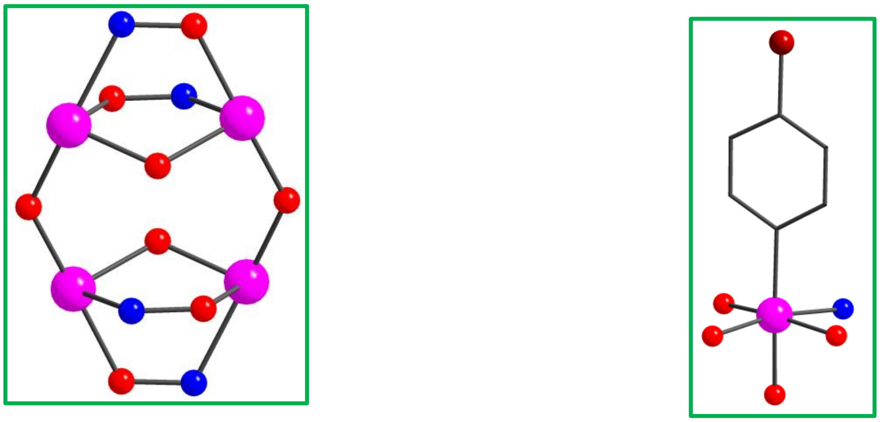


Figure 2.1: Molecular structure of **2.1.** Hydrogen atoms are omitted for clarity.Colour code: Sb magenta, Nblue, O red, Cl brown.



(a) (b)

Figure 2.2:(a) Sb$_4$O$_4$core encapsulatedby four oximate ligands (b) Octahedral geometry around antimony. Colour code: Sb magenta, Nblue, O red, Cl brown.

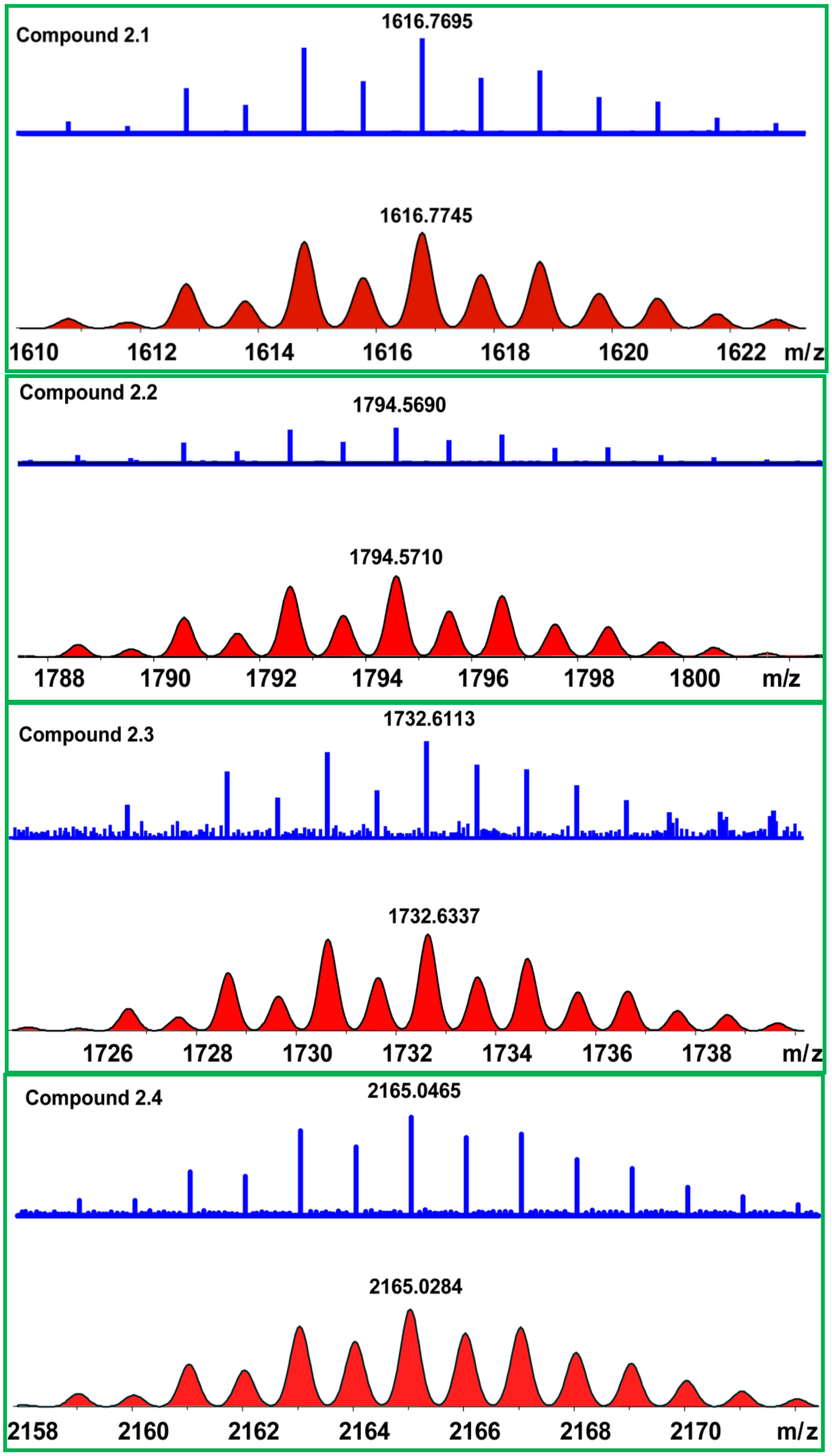


Figure2.3. ESI-MS of compounds**2.1-2.4**. Blue color indicates experimental spectra and red color indicates theoretical simulation spectra.

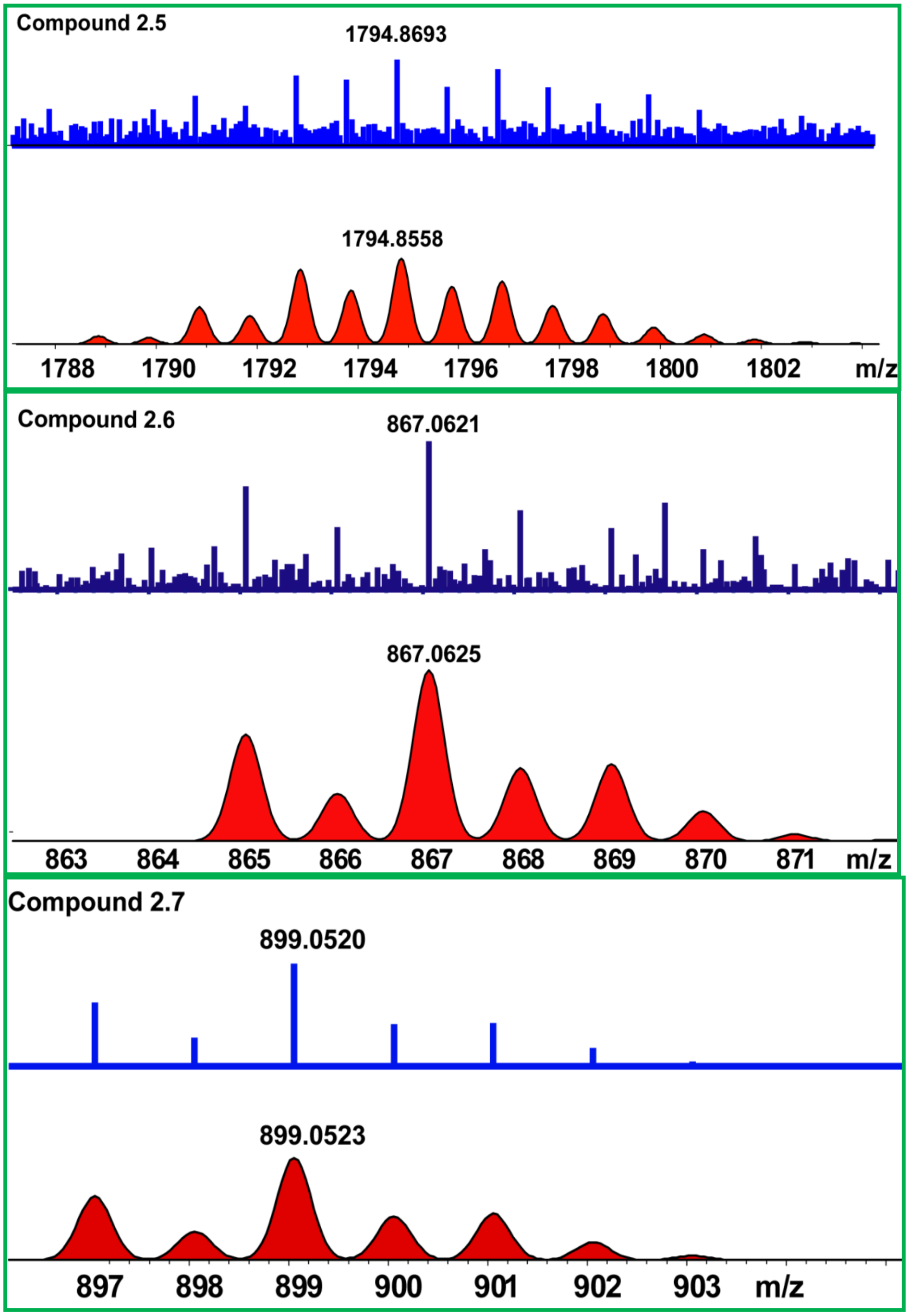


Figure2.4. ESI-MS of compounds**2.5-2.7**. Blue color indicates experimental spectra and red color indicates theoretical simulation spectra.

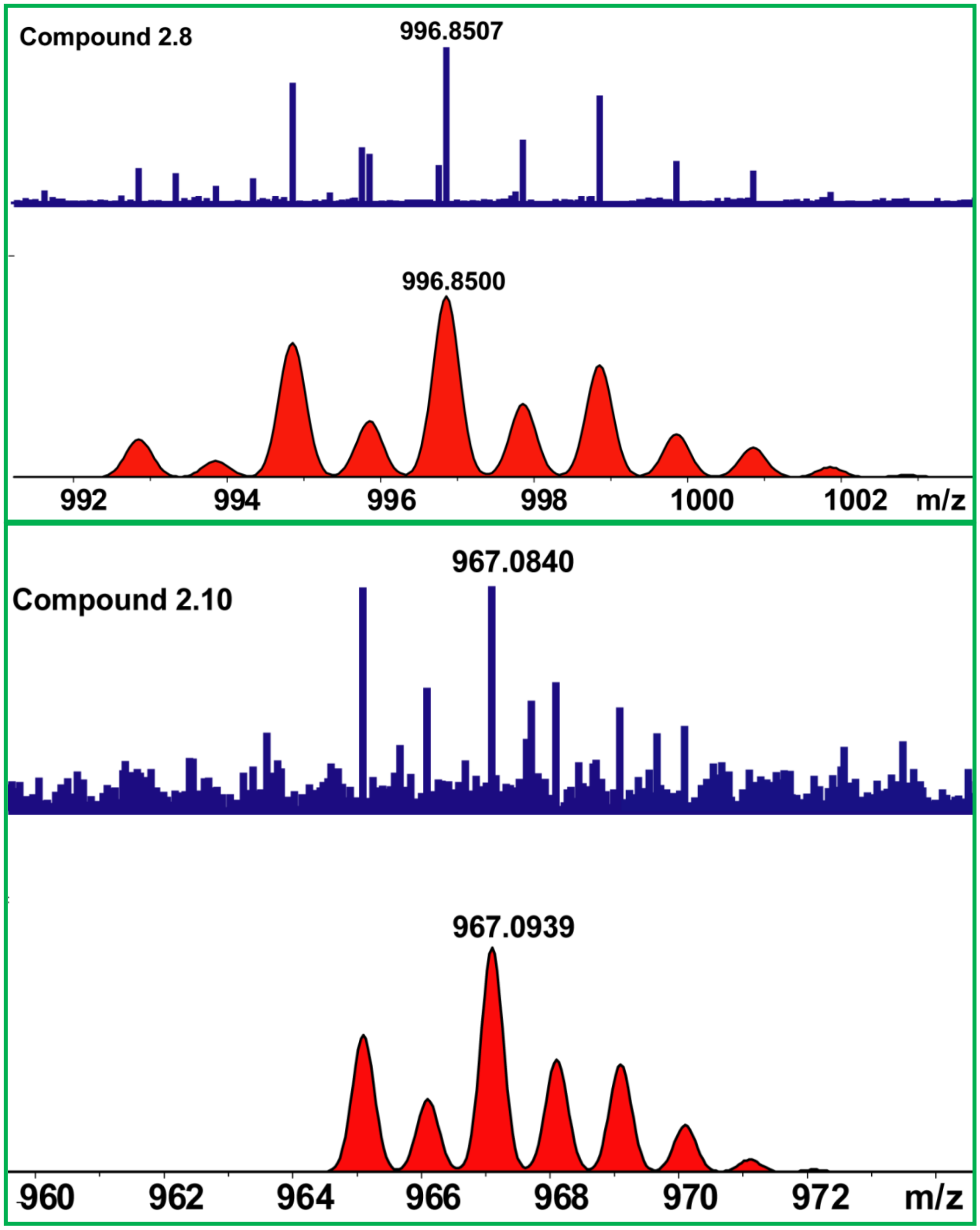


Figure2.5. ESI-MS of compounds**2.8** and **2.10**. Blue color indicates experimental spectra and red color indicates theoretical simulation spectra.

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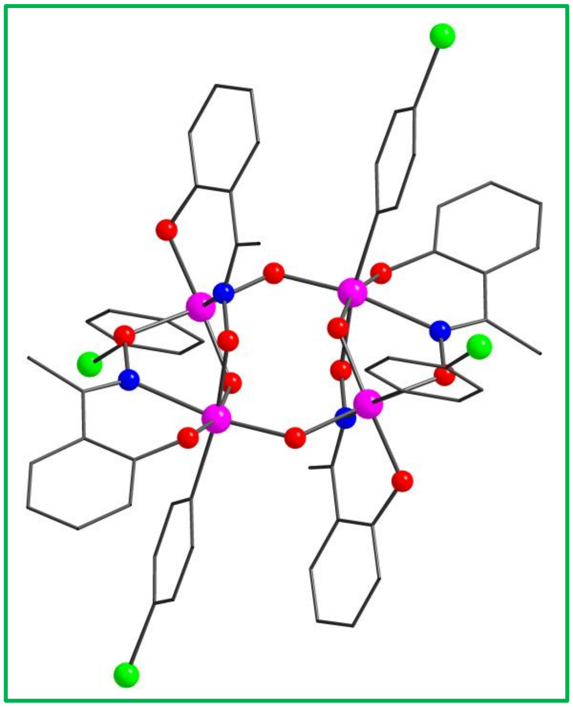


Figure 2.6: Molecular structure of **2.2.** Hydrogen atoms are omitted for clarity.Colour code: Sb magenta, Nblue, O red,Br green.

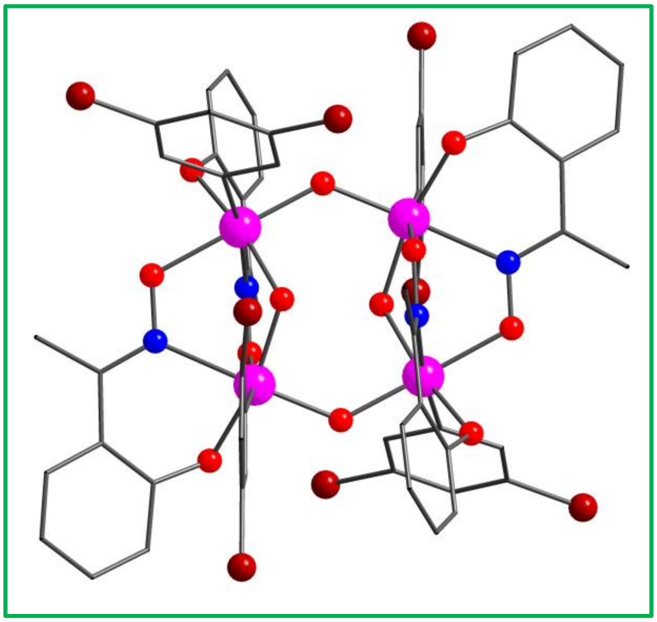


Figure 2.7: Molecular structure of **2.3.** Hydrogen atoms are omitted for clarity.Colour code: Sb magenta, Nblue, O red, Cl brown.

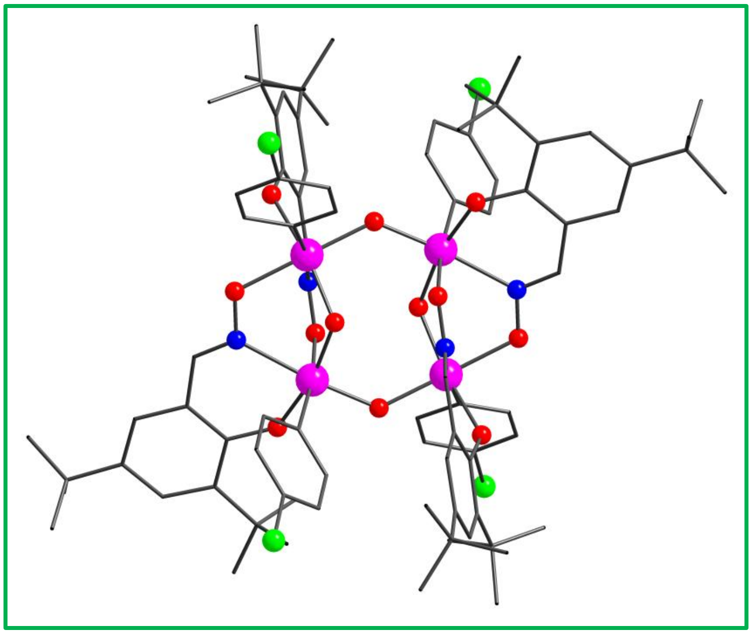


Figure 2.8: Molecular structure of **2.4.** Hydrogen atoms are omitted for clarity.Colour code: Sb magenta, Nblue, O red, Br green.

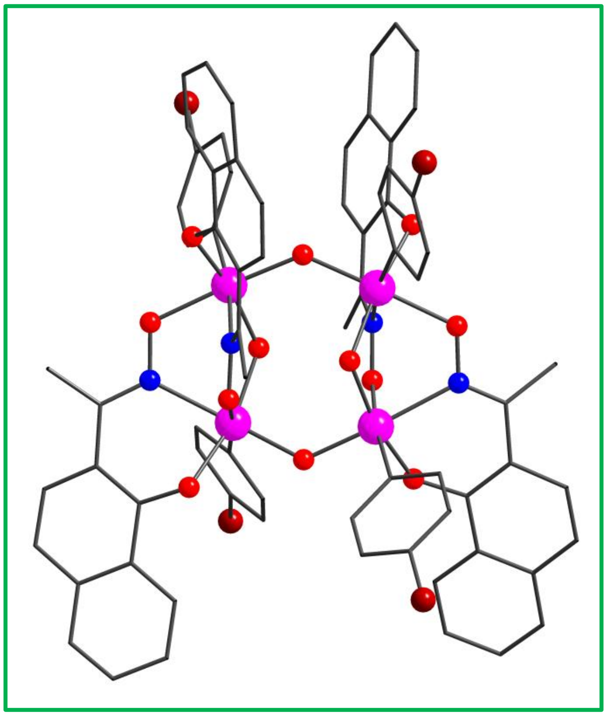
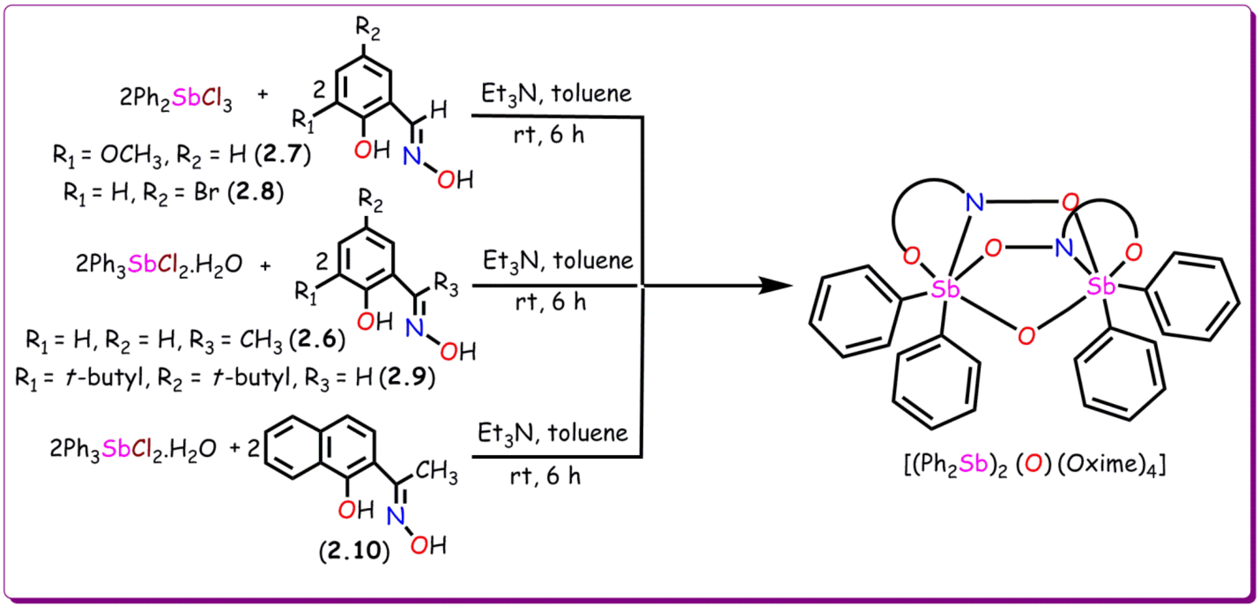


Figure 2.9: Molecular structure of **2.5.** Hydrogen atoms are omitted for clarity.Colour code: Sb magenta, Nblue, O red, Cl brown.

Oximate oxygen atom is linked to neighboring Sb atom in a bridging mode which makes up the polynuclear clusters. Five membered rings are made up of Sb_2O_2N which is nearly perpendicular to each. Phenolic oxygen and oximate nitrogen atom links to Sb atom in *cis* manner and oxime oxygen atoms is in *trans* orientation.

The reaction between Ph_2SbCl_3/$Ph_3SbCl_2.H_2O$ with the appropriately substituted phenolic oxime and Et_3N affords compounds **2.6-2.10**. There were crystallographically identified as $[(Ph_2Sb)_2(O)(L_1)]$ (**2.6**), $[(Ph_2Sb)_2(O)(L_2)]$ (**2.7)** $[(Ph_2Sb)_2(O)(L_3)]$ (**2.8**), $[(Ph_2Sb)_2(O)(L_4)]$ (**2.9**) and $[(Ph_2Sb)_2(O)(L_5)]$ (**2.10**). ^1H NMR spectra ($CDCl_3$ in solution) for cluster **2.6-3.0** shows multiplets in the range of 6.47-8.37 ppm, corresponding to the aromatic protons. Clusters **2.6** and**2.10** shows a singlet in the region 3.07 and 2.50 ppm corresponding to oximic CH_3 protons. Cluster **2.7** shows a singlet in the region 3.94 ppm corresponding to OCH_3 protons. Clusters**2.7, 2.8**and**2.9** shows a singlet in the region 8.37, 8.15and 8.23 ppm assigned to oximic C-H protons. Cluster**2.9** shows a singlet in the region 1.32 ppm corresponding to oximic *t*-butyl protons.ESI-MS of clusters **2.6-2.8** and **2.10**(Figure 2.4 and 2.5) under +ve ion mode showed a molecular ion peak at $[M+H]^+$. Dinuclear oxo cluster **2.6-2.8** crystallizes in the triclinic space group *P-1* (Table 2.2). Cluster **2.9** crystallizes in orthorhombic space group *Fdd2*(Table 2.3) and**2.10** crystallizes in monoclinic space group *P2(1)/c* (Table 2.3).



Scheme 2.2

Clusters **2.6-2.10** are isostructural, (Scheme 2.2)**2.6**is considered forillustrating the solid state structure (Figure 2.10).The selected bond lengths (Å) and bond angles (°)of**2.6-2.10** are given in the Table 2.9-2.13. Structural characterization of cluster **2.6** reveals the formation of a dinuclear organoantimony(V) oxido clusters [$(Ph_2Sb)_2(O)(L_1)$]. All oxygen atoms are considered as oxo group for charge neutrality. Phenolic oxime ligand acts as bidentate ligand binding to antimony atom with both donor atoms. Each antimony atom is hexa coordinated and present in anoctahedral geometry (O_3C_2N mode).

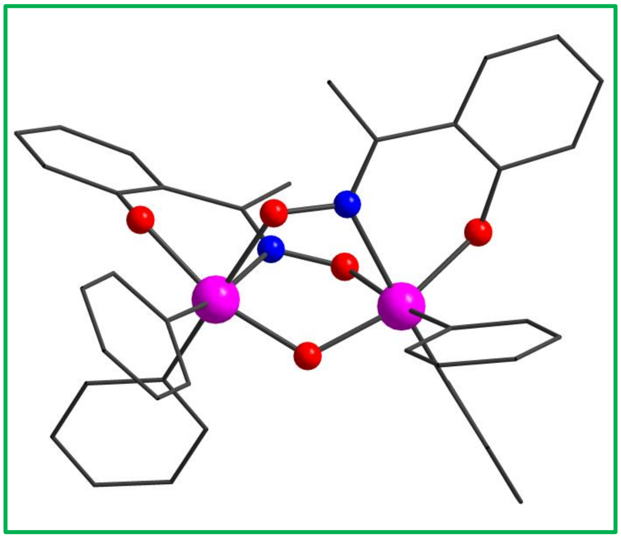


Figure 2.10: Molecular structure of **2.6.** Hydrogen atoms are omitted for clarity.Colour code: Sb magenta, Nblue, O red.

Dearylation from triorganoantimonyl compound gave rise to neutral dinuclear compound. Two diphenyl antimony units are bridged together by μ_2 oxygen atom. Chelation of oxime ligand to two antimony centers led to the formation of five-member ring. The two five-member rings are perpendicular to each other. Each oxime ligand is chelated to the antimony atom through its phenolic oxygen atom and nitrogen atom from oximate and the other antimony atom chelated through oximate oxygen atom and its phenolic oxygen atom. The Sb-O distances fall in the range of 1.941(18)-2.077(19) Å. Sb-C distance lies within the range 2.111(3)-2.133(3) Å. The Sb-N distance falls in the range of 2.238(2)-2.252(2) Å. The Sb---Sb nonbonding distance 3.345(4) Å. The Sb-O-Sb bond angle was 118.27(9)°. These bond lengths and the bond angle found to be similar to that of literature.[21]

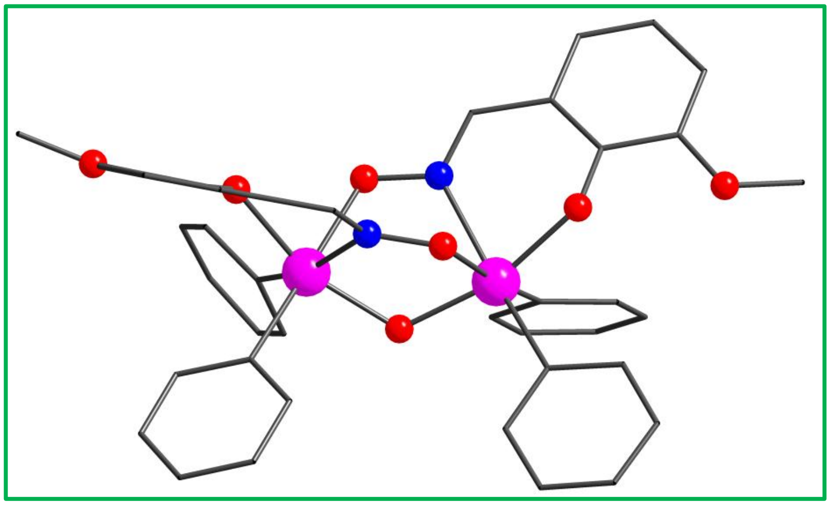


Figure 2.11: Molecular structure of **2.7.** Hydrogen atoms are omitted for clarity.Colour code: Sb magenta, N blue, O red.

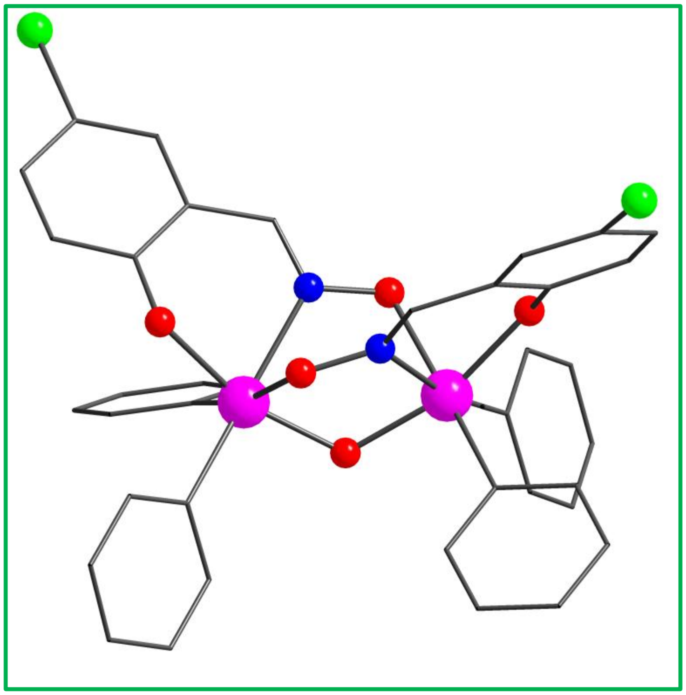


Figure 2.12: Molecular structure of **2.8.** Hydrogen atoms are omitted for clarity.Colour code: Sb magenta, N blue, O red, Br green.

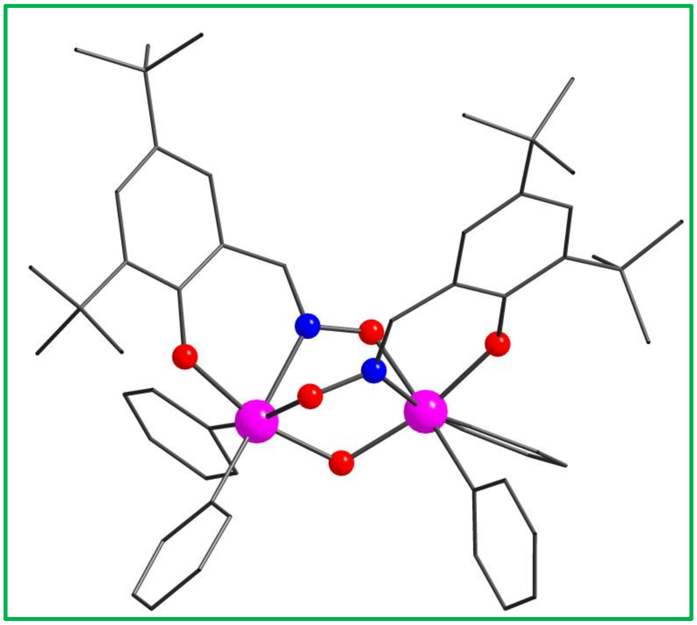


Figure 2.13: Molecular structure of **2.9.** Hydrogen atoms are omitted for clarity.Colour code: Sb magenta, N blue, O red.

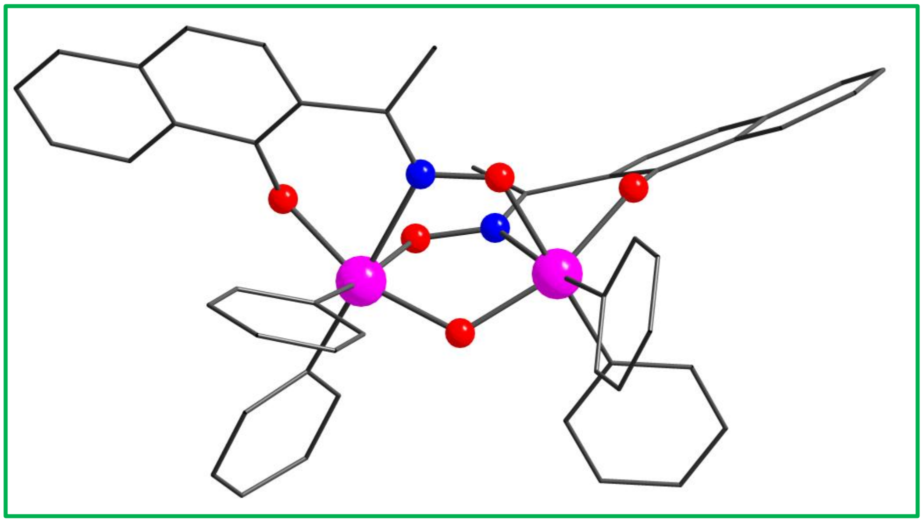


Figure 2.14: Molecular structure of **2.10.** Hydrogen atoms are omitted for clarity.Colour code: Sb magenta, N blue, O red.

2.4 Conclusion

To summarise, di- and tetranuclearorganoantimony(V) oxido clustershave been synthesized and structurally characterized. Depolymerization of arylstibonic acid using dianionic ligands leads to the formation of tetranuclear antimony oxido clusters. Introducing the bulky group in the 3rd position of dianionic ligand shows no change in the structure of the end product obtained. ESI-MS shows that the clustersretain their structural integrity in solution state as well.

Table 2.1: Crystal and refinement data for **2.1-2.4**

	2.1	**2.2**	**2.3**	**2.4**
formula	$C_{58}H_{46}Cl_{10}N_4O_{12}Sb_4$	$C_{58}H_{46}Br_4Cl_6N_4O_{12}Sb_4$	$C_{60}H_{44}Cl_{20}N_4O_{12}Sb_4$	$C_{96}H_{124}Br_4N_4O_{16}Sb_4$
M	1832.49	2010.33	2208.99	2396.62
T(K)	100(2) K	100(2) K	100(2) K	100(2) K
λ (Å)	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
crystal system	Triclinic	Triclinic	Triclinic	Triclinic
space group	*P -1*	*P -1*	*P -1*	*P -1*
a(Å)	9.5821(9)	9.6235(9)	9.8721(8)	12.3752(10)
b(Å)	13.1396(13)	13.1562(12)	13.5500(10)	12.9920(11)
c(Å)	14.3178(14)	14.3786(13)	14.8847(11)	16.9208(14)
α(deg)	66.8910(10)	66.9920(10)	75.6620(10)	87.9120(10)
β(deg)	70.9360(10)	71.5170(10)	84.8390(10)	72.6620(10)
γ(deg)	87.604(2)	87.4460(10)	75.0180(10)	74.5870(10)
V($Å^3$)	1559.3(3)	1582.6(3)	1862.8(2)	2500.8(4)
Z	1	1	1	1
Dcalcd (Mg m^{-3})	1.951	2.109	1.969	1.591
μ (mm^{-1})	2.208	4.531	2.213	2.730
F(000)	892	964	1072	1200
θ range (deg)	1.643-24.962	1.627-24.993	1.413-24.997	1.262 to 25.050
index range	$-11 \leq h \leq 11$	$-11 \leq h \leq 11$	$-11 \leq h \leq 11$	$-14 \leq h \leq 14$
	$-15 \leq k \leq 15$	$-15 \leq k \leq 15$	$-16 \leq k \leq 16$	$-15 \leq k \leq 15$
	$-16 \leq l \leq 16$	$-17 \leq l \leq 17$	$-17 \leq l \leq 17$	$-20 \leq l \leq 20$
reflections collected	15000	15069	17879	24059
data/ restraints /parameter	5444 / 0 / 403	5545 / 0 / 403	6541 / 0 / 461	8798 / 4 / 548
goodness-of-fit (GOF) on F^2	1.072	1.053	1.148	1.047
final R indices	$R_1 = 0.0397$	$R_1 = 0.0390$	$R_1 = 0.0345$	$R_1 = 0.0431$
$R_1[I > 2\sigma(I)]$	$wR_2 = 0.0841$	$wR_2 = 0.0905$	$wR_2 = 0.0768$	$wR_2 = 0.1132$
R indicies (all data)	$R_1 = 0.0500$	$R_1 = 0.0461$	$R_1 = 0.0380$	$R_1 = 0.0508$
	$wR_2 = 0.0882$	$wR_2 = 0.0939$	$wR_2 = 0.0784$	$wR_2 = 0.1180$
large diff. peak and hole (e $Å^{-3}$)	1.063 and -0.468	2.449 and -0.824	1.376 and -0.690	2.808 and -1.290

Table 2.2: Crystal and refinement data for **2.5-2.8**

	2.5	**2.6**	**2.7**	**2.8**
formula	$C_{86}H_{68}Cl_4N_4O_{12}Sb_4$	$C_{47}H_{42}N_2O_5Sb_2$	$C_{40}H_{34}N_2O_7Sb_2$	$C_{45}H_{36}Br_2N_2O_5Sb_2$
M	1978.24	958.32	898.19	1088.08
T(K)	100(2) K	100(2)	100(2)	100(2)
λ (Å)	0.71073 Å	0.71073	0.71073	0.71073
crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
space group	*P 21/c*	*P -1*	*P -1*	*P*-1
a(Å)	15.5663(14)	11.2742(9)	9.8287(19)	15.9270(12)
b(Å)	25.866(2)	11.4658(9)	14.692(3)	16.2634(12)
c(Å)	19.5111(17)	17.4845(13)	15.534(3)	16.6173(12)
α(deg)	90	78.0170(10)	67.171(3)	80.4750(10)
β(deg)	94.6520(10)	77.3940(10)	73.631(3)	82.3060(10)
γ(deg)	90	66.0570(10)	72.225(3)	72.8410(10)
V(Å^3)	7830.0(12)	1997.9(3)	1934.4(7)	4039.5(5)
Z	4	2	2	4
Dcalcd (Mg m^{-3})	1.678	1.593	1.542	1.789
***μ* (mm^{-1})**	1.568	1.402	1.446	3.365
F(000)	3920	960	892	2128
θ range (deg)	1.310-25.071	1.961-25.983	1.448 to 25.112	1.322 to 25.036
index range	$-18 \le h \le 18$	$-13 \le h \le 13$	$-11 \le h \le 11$	$-18 \le h \le 18$
	$-30 \le k \le 30$	$-14 \le k \le 14$	$-17 \le k \le 17$	$-19 \le k \le 19$
	$-23 \le l \le 23$	$-21 \le l \le 21$	$-18 \le l \le 18$	$-19 \le l \le 19$
reflections collected	75231	20720	17847	39200
data/ restraints /parameter	13876 / 3 / 997	7757/0/508	6826 / 0 / 462	14230 / 0 / 1011
goodness-of-fit (GOF) on F^2	1.082	1.066	1.137	1.026
final R indices	$R_1 = 0.0544$	$R_1 = 0.0281$	$R_1 = 0.0439$	$R_1 = 0.0252$
R$_1$[*I* >2σ(*I*)]	$wR_2 = 0.1147$	$wR_2 = 0.0646$	$wR_2 = 0.1178$	$wR_2 = 0.0603$
R indicies (all data)	$R_1 = 0.0693$	$R_1 = 0.0317$	$R_1 = 0.0482$	$R_1 = 0.0292$
	$wR_2 = 0.1216$	$wR_2 = 0.0663$	$wR_2 = 0.1255$	$wR_2 = 0.0619$
large diff. peak and hole (e Å^{-3})	2.186 and -0.821	0.708 and -0.379	1.556 and -2.067	0.753 and -0.484

Table 2.3: Crystal and refinement data for **2.9-2.10**

	2.9	**2.10**
formula	$C_{54}H_{62}N_2O_5Sb_2$	$C_{48}H_{38}N_2O_5Sb_2$
M	1062.55	966.30
T(K)	100(2)	100(2)
λ (Å)	0.71073	0.71073
crystal system	Orthorhombic	Monoclinic
space group	*F d d 2*	*P 21/c*
a(Å)	28.997(3)	11.287(3)
b(Å)	37.748(4)	10.022(3)
c(Å)	17.6707(17)	34.987(9)
α(deg)	90	90
β(deg)	90	98.573(4)
γ(deg)	90	90
V(Å^3)	19342(3)	3913.5(18)
Z	16	4
Dcalcd (Mg m^{-3})	1.460	1.640
μ (mm^{-1})	1.166	1.433
F(000)	8672	1928
θ range (deg)	1.453-25.062	1.177 to 25.072
index range	$-34 \leq h \leq 34$	$-13 \leq h \leq 13$
	$-44 \leq k \leq 44$	$-11 \leq k \leq 11$
	$-21 \leq l \leq 21$	$-41 \leq l \leq 41$
reflections collected	46100	36650
data/ restraints /parameter	8581 / 1 / 580	6930 / 0 / 516
goodness-of-fit (GOF) on F^2	1.073	1.210
final R indices	R_1 = 0.0232	R_1 = 0.0500
$R_1[I > 2\sigma(I)]$	wR_2 = 0.0549	wR_2 = 0.1002
R indicies (all data)	R_1 = 0.0237	R_1 = 0.0583
	wR_2 = 0.0551	wR_2 = 0.1032
large diff. peak and hole (e Å^{-3})	0.831 and -0.239	0.927 and -0.509

Table 2.4: Selected bond lengths (Å) and bond angles (º) in **2.1**

Sb(1)-C(1)	2.109(5)	O(1)-Sb(1)-O(2)	164.91(13)
Sb(2)-C(15)	2.099(5)	O(1)-Sb(1)-O(5)	89.08(13)
Sb(1)-O(1)	1.932(3)	O(2)-Sb(1)-O(5)	80.91(13)
Sb(1)-O(2)	1.983(3)	O(6)#1-Sb(1)-O(5)	88.82(13)
Sb(1)-O(5)	2.039(3)	O(1)-Sb(2)-O(3)	87.00(13)
Sb(1)-O(6)#1	1.925(3)	O(4)-Sb(2)-O(3)	84.57(14)
O(6)-Sb(1)#1	1.925(3)	O(6)-Sb(2)-O(3)	172.21(13)
Sb(2)-O(1)	1.927(3)	O(1)-Sb(2)-O(4)	164.75(14)
Sb(2)-O(3)	2.072(3)	O(6)-Sb(2)-O(4)	90.86(14)
Sb(2)-O(4)	1.981(3)	O(1)-Sb(2)-O(6)	96.01(13)
Sb(2)-O(6)	1.960(3)	O(6)#1-Sb(1)-C(1)	98.13(16)
Sb(1)-N(1)	2.234(4)	O(1)-Sb(1)-C(1)	95.49(16)
Sb(2)-N(2)	2.196(4)	O(2)-Sb(1)-C(1)	93.02(16)
O(6)#1-Sb(1)-N(1)	167.58(14)	O(5)-Sb(1)-C(1)	171.02(16)
O(1)-Sb(1)-N(1)	83.50(14)	O(1)-Sb(2)-C(15)	97.68(16)
O(2)-Sb(1)-N(1)	83.51(14)	O(3)-Sb(2)-C(15)	90.77(16)
O(5)-Sb(1)-N(1)	78.92(13)	O(4)-Sb(2)-C(15)	95.12(16)
O(6)#1-Sb(1)-O(1)	98.38(13)	O(6)-Sb(2)-C(15)	95.93(16)
O(6)#1-Sb(1)-O(2)	92.70(13)	Sb(1)#1-O(6)-Sb(2)	130.70(17)
		Sb(2)-O(1)-Sb(1)	117.94(16)

Symmetry transformations used to generate equivalent atoms: # 1-x+2,-y,-z

Table 2.5: Selected bond lengths (Å) and bond angles (º) in **2.2**

Sb(1)-C(1)	2.110(5)	O(1)-Sb(1)-O(2)	164.87(16)
Sb(2)-C(15)	2.110(5)	O(6)#1-Sb(1)-O(2)	90.65(16)
Sb(1)-O(1)	1.928(3)	O(1)-Sb(1)-O(5)	87.02(15)
Sb(1)-O(2)	1.976(4)	O(2)-Sb(1)-O(5)	84.83(15)
Sb(1)-O(5)	2.077(4)	O(6)#1-Sb(1)-O(5)	172.12(15)
Sb(1)-O(6)#1	1.956(4)	O(1)-Sb(1)-O(6)#1	95.91(15)
O(6)-Sb(1)#1	1.956(4)	O(6)-Sb(2)-O(1)	98.26(15)
Sb(2)-O(1)	1.934(4)	O(1)-Sb(2)-O(3)	89.13(15)
Sb(2)-O(3)	2.041(4)	O(4)-Sb(2)-O(3)	80.91(15)
Sb(2)-O(4)	1.987(4)	O(6)-Sb(2)-O(3)	88.98(15)
Sb(2)-O(6)	1.929(3)	O(1)-Sb(2)-O(4)	165.04(15)
Sb(1)-N(1)	2.202(4)	O(6)-Sb(2)-O(4)	92.72(15)
Sb(2)-N(2)	2.234(4)	O(1)-Sb(1)-C(1)	97.89(18)
O(1)-Sb(1)-N(1)	84.46(16)	O(2)-Sb(1)-C(1)	94.94(19)
O(2)-Sb(1)-N(1)	81.78(16)	O(5)-Sb(1)-C(1)	90.72(19)
O(5)-Sb(1)-N(1)	81.82(15)	O(6)#1-Sb(1)-C(1)	96.10(19)
O(6)#1-Sb(1)-N(1)	91.17(15)	O(1)-Sb(2)-C(15)	95.47(19)
O(1)-Sb(2)-N(2)	83.65(16)	O(3)-Sb(2)-C(15)	170.79(19)
O(3)-Sb(2)-N(2)	78.79(16)	O(4)-Sb(2)-C(15)	92.95(19)
O(4)-Sb(2)-N(2)	83.49(16)	O(6)-Sb(2)-C(15)	98.22(18)
O(6)-Sb(2)-N(2)	167.61(16)	Sb(2)-O(6)-Sb(1)#1	130.72(19)
		Sb(1)-O(1)-Sb(2)	117.81(18)

Symmetry transformations used to generate equivalent atoms: # 1-x+2,-y+1,-z+1

Table 2.6: Selected bond lengths (Å) and bond angles (º) in **2.3**

Sb(1)-C(1)	2.122(4)	O(6)-Sb(1)-O(2)	93.59(11)
Sb(2)-C(15)	2.107(4)	O(1)-Sb(1)-O(5)	88.45(10)
Sb(1)-O(1)	1.930(2)	O(2)-Sb(1)-O(5)	81.86(10)
Sb(1)-O(2)	1.979(2)	O(6)-Sb(1)-O(5)	91.00(11)
Sb(1)-O(6)	1.932(2)	O(1)-Sb(1)-O(6)	97.08(11)
Sb(1)-O(5)	2.048(3)	O(1)-Sb(2)-O(3)	88.49(10)
Sb(2)-O(1)	1.924(2)	O(4)-Sb(2)-O(3)	84.88(11)
Sb(2)-O(3)	2.074(3)	O(6)#1-Sb(2)-O(3)	173.24(11)
Sb(2)-O(4)	1.967(3)	O(1)-Sb(2)-O(4)	165.56(11)
O(6)-Sb(2)#1	1.959(2)	O(6)#1-Sb(2)-O(4)	91.29(11)
Sb(2)-O(6)#1	1.959(2)	O(1)-Sb(2)-O(6)#1	93.97(10)
Sb(1)-N(1)	2.224(3)	O(1)-Sb(1)-C(1)	91.45(13)
Sb(2)-N(2)	2.195(3)	O(2)-Sb(1)-C(1)	96.56(13)
O(1)-Sb(1)-N(1)	83.82(11)	O(5)-Sb(1)-C(1)	171.40(12)
O(2)-Sb(1)-N(1)	84.15(11)	O(6)-Sb(1)-C(1)	97.55(13)
O(5)-Sb(1)-N(1)	79.95(11)	O(1)-Sb(2)-C(15)	95.02(13)
O(6)-Sb(1)-N(1)	170.89(11)	O(6)#1-Sb(2)-C(15)	94.80(13)
O(1)-Sb(2)-N(2)	84.14(11)	O(4)-Sb(2)-C(15)	97.93(13)
O(3)-Sb(2)-N(2)	81.55(11)	O(3)-Sb(2)-C(15)	91.24(13)
O(4)-Sb(2)-N(2)	82.20(11)	Sb(2)-O(1)-Sb(1)	117.73(12)
O(6)#1-Sb(2)-N(2)	92.43(11)	Sb(1)-O(6)-Sb(2)#1	130.04(14)
O(1)-Sb(1)-O(2)	165.70(11)		

Symmetry transformations used to generate equivalent atoms: # 1-x+1,-y+1,-z+1

Table 2.7: Selected bond lengths (Å) and bond angles (º) in **2.4**

Sb(1)-C(1)	2.111(5)	O(1)-Sb(1)-O(2)	166.68(14)
Sb(2)-C(22)	2.101(5)	O(6)#1-Sb(1)-O(2)	91.43(14)
Sb(1)-O(1)	1.938(3)	O(1)-Sb(1)-O(5)	89.60(13)
Sb(1)-O(2)	1.995(3)	O(2)-Sb(1)-O(5)	81.88(13)
Sb(1)-O(5)	2.043(3)	O(6)#1-Sb(1)-O(5)	90.10(13)
Sb(1)-O(6)#1	1.922(3)	O(1)-Sb(2)-O(3)	85.69(13)
Sb(2)-O(1)	1.930(3)	O(4)-Sb(2)-O(3)	86.41(13)
Sb(2)-O(3)	2.095(3)	O(6)-Sb(2)-O(3)	172.56(13)
Sb(2)-O(4)	1.988(3)	O(1)-Sb(2)-O(4)	165.24(13)
Sb(2)-O(6)	1.955(3)	O(6)-Sb(2)-O(4)	90.86(13)
Sb(1)-N(1)	2.224(4)	O(1)-Sb(2)-O(6)	95.42(14)
Sb(2)-N(2)	2.202(4)	O(1)-Sb(1)-C(1)	94.01(16)
O(1)-Sb(1)-N(1)	82.91(14)	O(2)-Sb(1)-C(1)	93.34(16)
O(2)-Sb(1)-N(1)	85.37(14)	O(5)-Sb(1)-C(1)	172.44(16)
O(5)-Sb(1)-N(1)	78.64(14)	O(6)#1-Sb(1)-C(1)	95.90(17)
O(6)#1-Sb(1)-N(1)	168.62(14)	O(1)-Sb(2)-C(22)	101.46(16)
O(1)-Sb(2)-N(2)	84.47(14)	O(3)-Sb(2)-C(22)	91.37(17)
O(3)-Sb(2)-N(2)	81.91(14)	O(4)-Sb(2)-C(22)	91.17(17)
O(4)-Sb(2)-N(2)	82.09(14)	O(6)-Sb(2)-C(22)	95.61(17)
O(6)-Sb(2)-N(2)	90.87(14)	Sb(1)#1-O(6)-Sb(2)	131.13(17)
O(6)#1-Sb(1)-O(1)	98.83(13)	Sb(2)-O(1)-Sb(1)	117.89(16)

Symmetry transformations used to generate equivalent atoms: # 1-x,-y,+1,-z+2

Table 2.8: Selected bond lengths (Å) and bond angles (º) in **2.5**

Sb(1)-C(1)	2.107(5)	O(1)-Sb(1)-O(5)	91.05(16)
Sb(2)-C(19)	2.105(6)	O(1)-Sb(1)-O(6)	174.38(16)
Sb(3)-C(37)	2.111(6)	O(5)-Sb(1)-O(6)	87.49(15)
Sb(4)-C(55)	2.112(6)	O(1)-Sb(2)-O(2)	94.80(16)
Sb(1)-O(1)	1.940(4)	O(2)-Sb(2)-O(8)	85.79(16)
Sb(1)-O(4)	1.935(4)	O(7)-Sb(2)-O(8)	86.69(18)
Sb(2)-O(1)	1.941(4)	O(3)-Sb(3)-O(2)	98.59(17)
Sb(2)-O(2)	1.943(4)	O(3)-Sb(3)-O(9)	90.51(17)
Sb(3)-O(2)	1.944(4)	O(2)-Sb(3)-O(10)	89.22(17)
Sb(3)-O(3)	1.924(4)	O(3)-Sb(4)-O(4)	101.16(16)
Sb(4)-O(3)	1.929(4)	O(3)-Sb(4)-O(11)	91.76(17)
Sb(4)-O(4)	1.934(4)	O(3)-Sb(4)-O(12)	88.25(17)
Sb(1)-N(1)	2.192(5)	O(4)-Sb(4)-O(12)	90.26(16)
Sb(2)-N(2)	2.180(5)	O(1)-Sb(1)-C(1)	95.5(2)
Sb(3)-N(3)	2.218(5)	O(5)-Sb(1)-C(1)	93.73(19)
Sb(4)-N(4)	2.211(5)	O(1)-Sb(2)-C(19)	94.7(2)
O(4)-Sb(1)-N(1)	85.29(17)	O(7)-Sb(2)-C(19)	92.3(2)
O(1)-Sb(1)-N(1)	91.66(17)	O(2)-Sb(3)-C(37)	96.4(2)
O(1)-Sb(2)-N(2)	91.11(17)	O(9)-Sb(3)-N(3)	84.82(18)
O(2)-Sb(2)-N(2)	86.07(18)	O(4)-Sb(4)-N(4)	82.36(17)
O(2)-Sb(3)-N(3)	84.09(18)	O(12)-Sb(4)-N(4)	79.38(17)
O(3)-Sb(3)-N(3)	168.81(19)	Sb(1)-O(1)-Sb(2)	133.4(2)
O(4)-Sb(4)-N(4)	82.36(17)	Sb(2)-O(2)-Sb(3)	116.7(2)
O(11)-Sb(4)-N(4)	83.00(17)	Sb(3)-O(3)-Sb(4)	128.8(2)
O(12)-Sb(4)-N(4)	79.38(17)	Sb(4)-O(4)-Sb(1)	117.66(18)
O(4)-Sb(1)-O(1)	94.92(16)		

Table 2.9: Selected bond lengths (Å) and bond angles (º) in **2.6**

Sb(1)-C(1)	2.113(3)	O(1)-Sb(1)-O(2)	164.16(8)
Sb(1)-C(7)	2.133(3)	O(1)-Sb(1)-O(5)	85.49(7)
Sb(2)-C(27)	2.126(3)	O(2)-Sb(1)-O(5)	82.77(8)
Sb(2)-C(21)	2.111(3)	O(1)-Sb(2)-O(3)	85.68(7)
Sb(1)-O(1)	1.9556(18)	O(4)-Sb(2)-O(3)	83.61(8)
Sb(1)-O(2)	2.0023(18)	O(1)-Sb(2)-O(4)	163.89(8)
Sb(1)-O(5)	2.0771(19)	O(1)-Sb(1)-C(1)	100.22(9)
Sb(2)-O(1)	1.9411(18)	O(2)-Sb(1)-C(1)	89.96(9)
Sb(2)-O(3)	2.0767(18)	O(5)-Sb(1)-C(1)	87.93(9)
Sb(2)-O(4)	1.9997(18)	O(1)-Sb(1)-C(7)	93.88(9)
Sb(1)-N(1)	2.238(2)	O(2)-Sb(1)-C(7)	95.58(9)
Sb(2)-N(2)	2.252(2)	O(5)-Sb(1)-C(7)	168.83(9)
O(1)-Sb(1)-N(1)	84.88(8)	O(1)-Sb(2)-C(21)	100.49(9)
O(2)-Sb(1)-N(1)	82.53(8)	O(3)-Sb(2)-C(21)	87.08(9)
O(5)-Sb(1)-N(1)	79.27(8)	O(4)-Sb(2)-C(21)	90.96(9)
O(1)-Sb(2)-N(2)	84.38(8)	O(1)-Sb(2)-C(27)	94.15(9)
O(4)-Sb(2)-N(2)	82.00(8)	Sb(2)-O(1)-Sb(1)	118.27(9)
O(3)-Sb(2)-N(2)	80.40(8)		

Table 2.10: Selected bond lengths (Å) and bond angles (º) in **2.7**

Sb(1)-C(1)	2.113(3)	O(1)-Sb(1)-O(2)	164.16(8)
Sb(1)-C(1)	2.141(4)	O(1)-Sb(1)-O(7)	86.74(10)
Sb(1)-C(7)	2.123(4)	O(2)-Sb(1)-O(7)	80.70(12)
Sb(2)-C(21)	2.136(4)	O(1)-Sb(2)-O(4)	85.26(10)
Sb(2)-C(27)	2.118(4)	O(5)-Sb(2)-O(4)	85.59(10)
Sb(1)-O(1)	1.943(2)	O(1)-Sb(2)-O(5)	164.07(11)
Sb(1)-O(2)	2.001(3)	O(1)-Sb(1)-C(1)	94.99(13)
Sb(1)-O(7)	2.081(3)	O(2)-Sb(1)-C(1)	94.74(13)
Sb(2)-O(1)	1.952(2)	O(7)-Sb(1)-C(1)	169.97(13)
Sb(2)-O(4)	2.119(3)	O(1)-Sb(1)-C(7)	101.45(13)
Sb(2)-O(5)	2.016(3)	O(2)-Sb(1)-C(7)	93.51(14)
Sb(1)-N(1)	2.261(3)	O(7)-Sb(1)-C(7)	85.33(13)
Sb(2)-N(2)	2.232(3)	O(1)-Sb(2)-C(21)	93.13(13)
O(1)-Sb(1)-N(1)	81.40(11)	O(4)-Sb(2)-C(21)	170.19(12)
O(2)-Sb(1)-N(1)	80.69(11)	O(5)-Sb(2)-C(21)	93.67(13)
O(7)-Sb(1)-N(1)	80.19(11)	O(1)-Sb(2)-C(27)	101.06(13)
O(1)-Sb(2)-N(2)	83.82(11)	C(27)-Sb(2)-O(4)	86.82(13)
O(4)-Sb(2)-N(2)	78.86(10)	O(5)-Sb(2)-C(27)	91.41(13)
O(5)-Sb(2)-N(2)	81.64(11)	Sb(1)-O(1)-Sb(2)	120.05(13)
O(1)-Sb(1)-O(2)	159.62(11)		

Table 2.11: Selected bond lengths (Å) and bond angles (°) in**2.8**

Sb(1)-C(1)	2.134(3)	O(1)-Sb(1)-O(5)	85.48(8)
Sb(1)-C(7)	2.112(3)	O(2)-Sb(1)-O(5)	81.35(8)
Sb(2)-C(20)	2.136(3)	O(1)-Sb(2)-O(3)	86.65(8)
Sb(2)-C(26)	2.112(3)	O(4)-Sb(2)-O(3)	82.05(8)
Sb(1)-O(1)	1.9565(18)	O(1)-Sb(2)-O(4)	162.48(8)
Sb(1)-O(2)	2.0317(19)	O(1)-Sb(1)-C(1)	96.50(10)
Sb(1)-O(5)	2.0833(19)	O(2)-Sb(1)-C(1)	93.69(10)
Sb(2)-O(1)	1.9488(18)	O(5)-Sb(1)-C(1)	168.16(9)
Sb(2)-O(3)	2.0770(19)	O(1)-Sb(1)-C(7)	101.07(9)
Sb(2)-O(4)	2.0286(19)	O(2)-Sb(1)-C(7)	92.86(9)
Sb(1)-N(1)	2.258(2)	O(5)-Sb(1)-C(7)	90.26(9)
Sb(2)-N(2)	2.263(2)	O(1)-Sb(2)-C(20)	96.31(10)
O(1)-Sb(1)-N(1)	82.67(8)	O(3)-Sb(2)-C(20)	168.09(9)
O(2)-Sb(1)-N(1)	81.58(8)	O(4)-Sb(2)-C(20)	92.22(9)
O(5)-Sb(1)-N(1)	80.99(8)	O(1)-Sb(2)-C(26)	97.00(10)
O(1)-Sb(2)-N(2)	82.06(8)	O(3)-Sb(2)-C(26)	89.77(9)
O(3)-Sb(2)-N(2)	80.40(8)	O(4)-Sb(2)-C(26)	96.30(10)
O(4)-Sb(2)-N(2)	82.88(8)	Sb(2)-O(1)-Sb(1)	119.29(9)
O(1)-Sb(1)-O(2)	160.85(8)		

Table 2.12: Selected bond lengths (Å) and bond angles (°) in**2.9**

Sb(1)-C(1)	2.114(4)	O(1)-Sb(1)-O(5)	84.95(12)
Sb(1)-C(7)	2.134(4)	O(2)-Sb(1)-O(5)	88.51(13)
Sb(2)-C(28)	2.121(4)	O(1)-Sb(2)-O(3)	85.44(12)
Sb(2)-C(34)	2.132(4)	O(4)-Sb(2)-O(3)	85.38(13)
Sb(1)-O(1)	1.958(3)	O(1)-Sb(2)-O(4)	164.82(12)
Sb(1)-O(2)	2.028(3)	O(1)-Sb(1)-C(1)	100.32(15)
Sb(1)-O(5)	2.084(3)	O(2)-Sb(1)-C(1)	93.08(15)
Sb(2)-O(1)	1.950(3)	O(5)-Sb(1)-C(1)	87.31(14)
Sb(2)-O(3)	2.082(3)	O(1)-Sb(1)-C(7)	93.28(14)
Sb(2)-O(4)	2.025(3)	O(2)-Sb(1)-C(7)	91.43(15)
Sb(1)-N(1)	2.241(4)	O(5)-Sb(1)-C(7)	172.48(15)
Sb(2)-N(2)	2.234(3)	O(1)-Sb(2)-C(28)	101.14(14)
O(1)-Sb(1)-N(1)	83.88(13)	O(3)-Sb(2)-C(28)	88.28(16)
O(2)-Sb(1)-N(1)	81.44(13)	O(4)-Sb(2)-C(28)	90.64(14)
O(5)-Sb(1)-N(1)	79.94(12)	O(1)-Sb(2)-C(34)	94.20(15)
O(1)-Sb(2)-N(2)	83.41(12)	O(3)-Sb(2)-C(34)	168.57(14)
O(3)-Sb(2)-N(2)	79.41(13)	O(4)-Sb(2)-C(34)	92.41(15)
O(4)-Sb(2)-N(2)	83.04(12)	Sb(2)-O(1)-Sb(1)	118.03(15)
O(1)-Sb(1)-O(2)	164.77(12)		

Table 2.13: Selected bond lengths (Å) and bond angles (°) in **2.10**

Sb(1)-C(1)	2.134(6)	O(1)-Sb(1)-O(5)	85.69(14)
Sb(1)-C(7)	2.119(5)	O(2)-Sb(1)-O(5)	79.54(16)
Sb(2)-C(25)	2.123(5)	O(1)-Sb(2)-O(3)	87.51(15)
Sb(2)-C(31)	2.109(5)	O(4)-Sb(2)-O(3)	80.31(16)
Sb(1)-O(1)	1.936(3)	O(1)-Sb(2)-O(4)	161.88(15)
Sb(1)-O(2)	2.009(4)	O(1)-Sb(1)-C(1)	94.37(19)
Sb(1)-O(5)	2.095(4)	O(2)-Sb(1)-C(1)	97.6(2)
Sb(2)-O(1)	1.951(3)	O(5)-Sb(1)-C(1)	168.17(18)
Sb(2)-O(3)	2.084(4)	O(1)-Sb(1)-C(7)	98.42(18)
Sb(2)-O(4)	2.017(4)	O(2)-Sb(1)-C(7)	93.71(18)
Sb(1)-N(1)	2.240(4)	O(5)-Sb(1)-C(7)	89.65(19)
Sb(2)-N(2)	2.233(4)	O(1)-Sb(2)-C(25)	93.92(18)
O(1)-Sb(1)-N(1)	84.67(15)	O(3)-Sb(2)-C(25)	170.29(18)
O(2)-Sb(1)-N(1)	80.72(16)	O(4)-Sb(2)-C(25)	95.93(18)
O(5)-Sb(1)-N(1)	79.80(16)	O(1)-Sb(2)-C(31)	96.33(17)
O(1)-Sb(2)-N(2)	83.16(15)	O(3)-Sb(2)-C(31)	87.25(18)
O(3)-Sb(2)-N(2)	80.08(15)	O(4)-Sb(2)-C(31)	96.43(18)
O(4)-Sb(2)-N(2)	81.57(15)	Sb(1)-O(1)-Sb(2)	118.68(17)
O(1)-Sb(1)-O(2)	160.81(15)		

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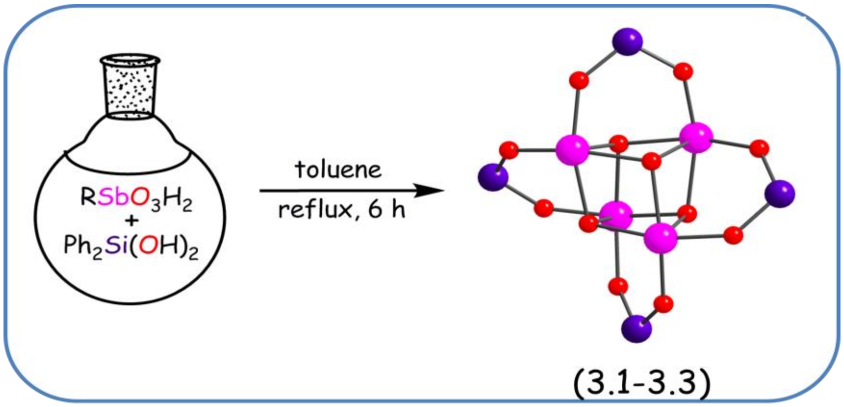
Chapter

3

Organoantimony(V) Oxido Cubane Cluster $[(p\text{-X-}C_6H_4Sb)_4(O)_4(Ph_2SiO_2)_4]$ and $[(m\text{-}X_2\text{-}C_6H_3Sb)_4(O)_4(Ph_2SiO_2)_4]$ (X = Cl, Br) Stabilized Diphenyldisiloxides

Abstract: Reaction of (*p*-halophenyl)stibonic acid or (*m*-dihalophenyl)stibonic acid with diphenylsilanediol (in ratio 1:1) in refluxing toluene for 6 h afforded colorless crystalline products in high yields. Single crystal X-ray structural elucidation reveals the formation of the products $[(p\text{-chloro-}C_6H_4Sb)_4(O)_4(Ph_2SiO_2)_4]$ (**3.1**), $[(p\text{-bromo-}C_6H_4Sb)_4(O)_4(Ph_2SiO_2)_4]$ (**3.2**) and $[(m\text{-dichloro-}C_6H_3Sb)_4(O)_4(Ph_2SiO_2)_4]$ (**3.3**) respectively. The clusters **3.1**, **3.2** and **3.3** were isostructural; the core consists of a distorted Sb_4O_4 cubane framework with the siloxides acting as bridging ligands across the antimony atoms present at alternate corners of the cube.



3.1 Introduction

The study of multinuclear metal-oxo clusters has been fascinating chemists for some time now, owing to the possible generation of precursors for new materials possessing interesting physical and chemical properties.[1] Since multinuclear clusters act as a bridge between molecular and solid state chemistry, they help in understanding the size-dependent physical properties of materials.[2] The cluster chemistry of main-group metals such as tin[3] and bismuth[4] linked through oxo/hydroxo bridges has been explored in detail; their solid-state and solution structures are well understood. In spite of the numerous applications of organoantimonate compounds in the field of catalysis[5] and biology,[6] the cluster chemistry of antimony(V) compounds bridged through oxo/hydroxo linkages are few,[7] though a large number of antimony-thio complexes have been known for years.[8] Since the ability of phenylstibonic acid ($PhSbO_3H_2$) to self-condense and act as an inorganic cryptand incorporating d^5 and d^{10} metals in its cavity was reported recently,[9] there has been an upsurge of interest in understanding the structure and reactivity patterns of organostibonic acids.[10] In this regard, controlled hydrolysis of antimony dihalides and tetrahalides appended with sterically bulky organic substituents on antimony has been carried out, leading to the isolation of molecular arylstibonic acid, $[2,6\text{-}Mes_2C_6H_3Sb(O)(OH)_2]_2$, and antimony-oxido clusters, wherein antimony is found in a mixed (III and V) state of oxidation.[11]

In a recent report,[12] efforts to crystallize a sterically demanding stibine complex, 1,8-bis(R_2-Sb) naphthalene (R=Me), has resulted in serendipitous hydrolysis of the organoantimony(III) compound, resulting in the isolation of a self-assembled tetranuclear cubane cluster in very low yields. Interestingly, phosphonate/antimonate-oxo clusters have also been synthesized, and their utility as proligands for assembling multinuclear cobalt clusters has been investigated.[13] It is worth noting here that a bulky organic group appended on antimony and/or solvothermal synthesis have been employed to get around the poor solubility of the products obtained in the reactions involving stibonic acids, which in our view has hindered the progress of understanding the solid-state and solution chemistry associated with such systems. Further, reaction of hydrated Ph_3SbCl_2 with a cyclic phosphinic acid has been reported recently, resulting in the isolation of a dinuclear organoantimony cluster which on mild hydrolysis undergoes Sb-C bond cleavage, leading to the formation of a novel nonanuclear organostiboxane cage containing a Sb_9O_{16} core.[14] It should be mentioned here that antimony oxido clusters have been studied before in the gas phase or condensed phase by mass spectrometry,[15] and it has been reported that at room temperature the stable solid phase of Sb_2O_3 is the cubic senarmontite which contains a Sb_4O_6 molecule,[16] whereas the high-temperature orthorhombic phase valentinite has a polymeric sheet built up of eight-membered Sb_4O_4 rings.[17] Generally in these clusters antimony atoms are present in both III and V states of oxidation, but at higher oxygen concentrations it has been shown that the formation of oxide clusters containing antimony atoms solely in the V state of oxidation is favored.[18] Organosilanols, on the other hand, have been utilized for synthesizing metallosiloxane frameworks,[19] and in particular the ability of di- and trisilanols to act as ligands toward main-group and transition metals has also been investigated in detail.[20] Reaction of diphenylsilanediol with ECl_3 (E = As, Sb) has resulted in the isolation of interesting arsenic(III) and antimony(III) bicyclic siloxane compounds.[21]

3.2 Experimental Section

3.2.1 General information:

Diphenylsilanediol, solvents, and other common reagents were used as purchased from commercial sources. *p*-halophenyl and *m*-dihalophenylstibonic acids (halogen = Cl and Br), were synthesized using literature procedures.[22]

3.2.2 Instrumentation:

Infrared spectra were recorded on a JASCO-5300 FT-IR spectrometer as KBr pellets. The ^{1}H, ^{13}C, and ^{29}Si solution NMR spectra were recorded on a Bruker DRX 400 instrument. Elemental analysis was performed on a Flash EA Series 1112CHNS analyzer. Single-crystal X-ray data collection (for **3.1** and **3.2**) was carried out at 298(2) K were as **3.3** compound was carried out at 100K on a Bruker Smart Apex CCD area detector system (λ(Mo Kα) = 0.71073 Å), with graphite monochromotor. The data were reduced using SAINT PLUS, and the structures were solved using SHELXS-97[23] and refined using SHELXL-97.[24] All non-hydrogen atoms were refined anisotopically.

3.2.3 Synthetic procedures for Compounds 3.1-3.3:

Compound $[(p\text{-Cl-}C_6H_4Sb)_4(O)_4(Ph_2SiO_2)_4]$ 3.1:

Diphenylsilanediol (0.382 g, 1.76 mmol) and (*p*-chlorophenyl)stibonic acid (0.500 g, 1.76 mmol) were taken up in 50 mL of toluene, and the solution was refluxed for 6 h. A Dean-Stark apparatus was used to remove the water eliminated in the reaction as an azeotropic mixture. The clear solution that formed was cooled to room temperature, filtered to remove any unreacted starting materials present, and evaporated under reduced pressure to yield a colorless solid. Yield: 0.687 g (84%, based on the weight of (*p*-chlorophenyl)stibonic acid). Dec pt: 198-199 °C. Crystals suitable for single crystal X-ray studies were grown from a chloroform solution by diffusion in hexane for 1 week. Anal. Calcd for $C_{72}H_{56}O_{12}Cl_4Si_4Sb_4$: C, 46.63; H, 3.04. Found: C, 46.68; H, 3.10. IR (cm^{-1}, KBr pellet): 3069(m), 1591(s), 1570(s), 1477(s), 1429(s), 1385(s), 1263(s), 1126(w), 1091(w), 1024(w), 904(m), 808(s), 717(m), 698(s), 513(w), 484(w). ^1H NMR in $CDCl_3$: δ 7.92 (d, 16 H), 7.55 (t, 8 H), 7.38 (t, 16 H), 6.75 (d, 8 H), 6.73 (d, 8 H). ^{13}C NMR in $CDCl_3$: δ 139.63, 138.09, 135.20, 134.75, 133.83, 130.39, 128.58, 127.82. $^{29}Si\{^1H\}$ NMR in $CDCl_3$: δ -29.5 ppm.

Compound $[(p\text{-}Br\text{-}C_6H_4Sb)_4(O)_4(Ph_2SiO_2)_4]$ 3.2:

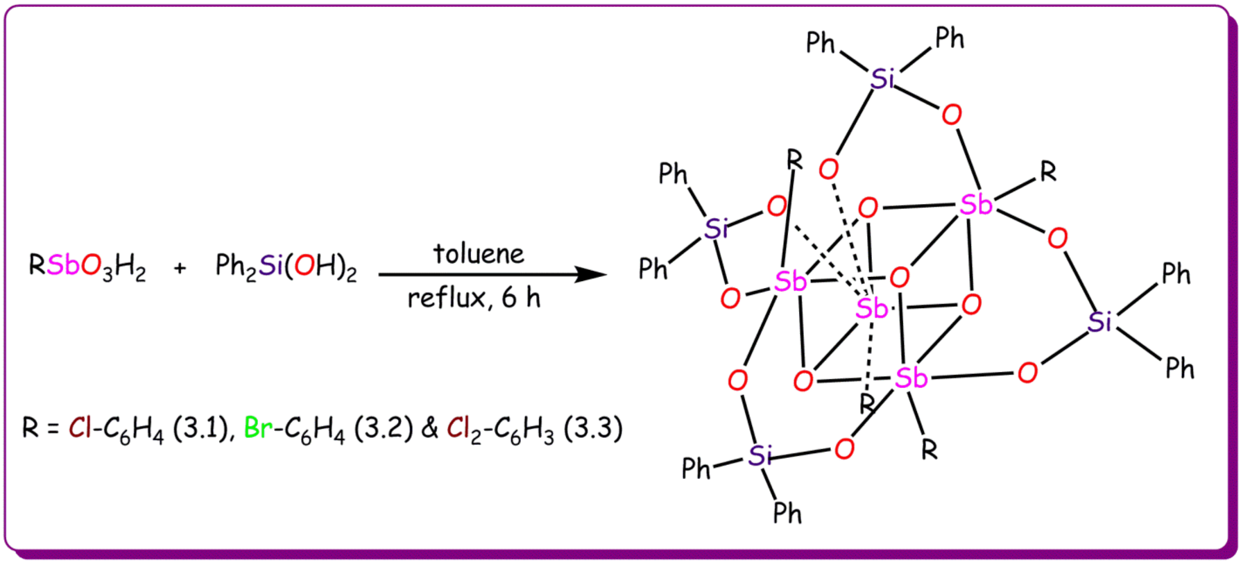
The procedure was similar to that of **3.1**. The molar ratios and weights of the reactants used are as follows: Diphenylsilanediol (0.594 g, 2.74 mmol) and (*p*-bromophenyl) stibonic acid, (0.900 g, 2.74 mmol). Yield: 0.981 g (70% based on (*p*-bromophenyl)stibonic acid). Dec pt: 199-200 °C. Anal. Calcd for $C_{72}H_{56}O_{12}Br_4Si_4Sb_4$: C, 42.55; H, 2.77. Found: C, 42.49; H, 2.75. IR (cm^{-1}, KBr pellet): 3067(w), 2962(w), 1903(w), 1591(s), 1562(s), 1477(s), 1429 (s), 1379(s), 1261(s), 1124(m), 1057(m), 1024(m), 941(m), 900(m), 804(s), 698(s), 511(m). ^1H NMR in $CDCl_3$: δ 7.88 (d, 16 H), 7.52 (t, 8 H), 7.34 (t, 16 H), 6.87 (d, 8 H), 6.65 (d, 8 H). ^{13}C NMR in $CDCl_3$: δ 140.24, 135.17, 134.74, 133.94, 131.51, 130.40, 127.83, 126.75. $^{29}Si\{^1H\}$ NMR in $CDCl_3$: δ -29.5 ppm.

Compound $[(m\text{-}Cl_2\text{-}C_6H_3Sb)_4(O)_4(Ph_2SiO_2)_4]$ 3.3:

The procedure was similar to that of **3.1**. The molar ratios and weights of the reactants used are as follows: Diphenylsilanediol (0.204 g, 0.94 mmol) and (*m*-dichlorophenyl)stibonic acid, (0.300 g and 0.94 mmol). Yield: 0.350 g (64% based on (*m*-dichlorophenyl)stibonic acid). Dec pt: 197-198 °C. Anal. Calcd for $C_{72}H_{52}O_{12}Cl_8Si_4Sb_4$: C, 42.06; H, 2.55. Found: C, 42.14; H, 2.59. IR (cm^{-1}, KBr pellet): 3069(w), 2964(w), 2928(w), 1591(s), 1560(s), 1491(s), 1429(s), 1261(s), 1128(m), 896(m), 796(m), 698(s). ^1H NMR in $CDCl_3$: δ 7.94 (d, 16 H), 7.55 (t, 8 H), 7.37 (t, 16 H), 7.06 (s, 4 H), 6.75 (s, 8 H). ^{13}C NMR in $CDCl_3$: δ 143.54, 135.83, 134.57, 134.23, 131.84, 130.91, 130.27, 128.19, 127.73, 125.35. $^{29}Si\{^1H\}$ NMR in $CDCl_3$: δ -29.3 ppm.

3.3 Results and Discussions

Synthetic methodology adopted for synthesis of **3.1-3.3** and solid-state structure of [(*p*-X-$C_6H_4Sb)_4(O)_4(Ph_2SiO_2)_4$] (X=Cl (**3.1**), Br (**3.2**)) and [*m*-X_2-$C_6H_3Sb)_4(O)_4(Ph_2SiO_2)_4$] (X=Cl (**3.3**)) obtained by refluxing a mixture of (*p*-halophenyl)stibonic acids or *m*-dihalophenylstibonic acids with diphenylsilanediol in a 1:1 molar ratio in toluene (Scheme 3.1).



Scheme 3.1

The clusters (**3.1**, **3.2** and **3.3**) dissolved in a wide range of solvents such as dichloromethane, chloroform, toluene, and xylene. The products were characterized by standard spectroscopic and analytical techniques. The data of the crude products of **3.1**, **3.2** and **3.3** matched well with the data obtained from crystallized products. ^1H NMR in $CDCl_3$ solution for **3.1**, **3.2** and **3.3** showed multiplets in the region 6.74-7.94 ppm, corresponding to the aromatic groups present. Closer examination of the spectra revealed some interesting features. The aromatic region of the ^1H NMR spectrum of **3.1** shows two distinct groupings, the first one consisting of two closely spaced doublets at 6.75 and 6.73 ppm corresponding to the two sets of aromatic protons of the chlorophenyl group attached to antimony and the other consisting of two triplets 7.55 and 7.38 ppm and a doublet 7.92 ppm corresponding to the protons of phenyl groups attached to silicon atom. The ^1H NMR spectrum of **3.2** also shows signals similar to those of **3.1**, except that the two doublets due to the protons of the bromophenyl groups have slightly larger separation between them. Whereas in case of ^1H NMR spectrum of **3.3** protons of phenyl groups attached to silicon atom shows similar signals to that of **3.1**, but in case of aromatic protons of the dichlorophenyl group attached to antimony shows two singlets 7.06 and 6.75. The ^{29}Si NMR in $CDCl_3$ solution spectrum showed a single signal at -29.5 ppm for both **3.1** and **3.2** and -29.3 ppm for compound **3.3**, a small downfield shift compared to the ^{29}Si NMR of $Ph_2Si(OH)_2$ (-34.9 ppm).

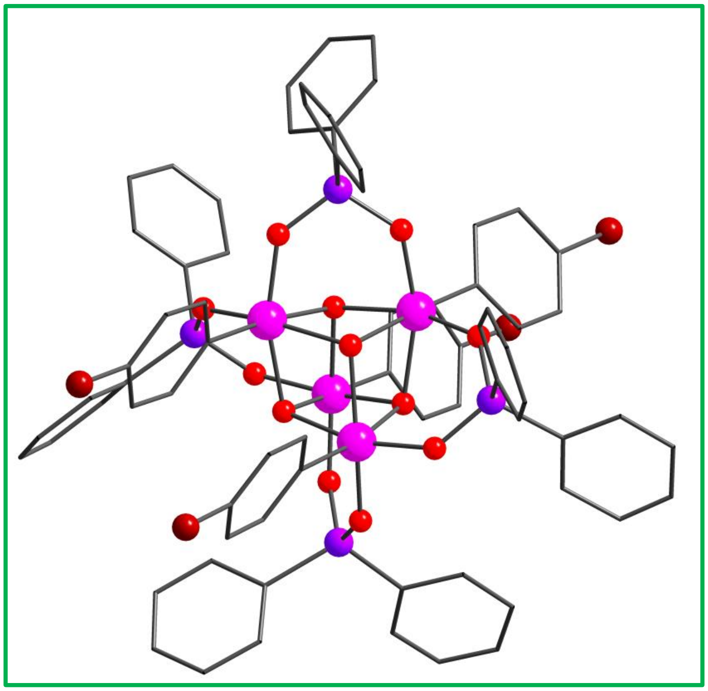
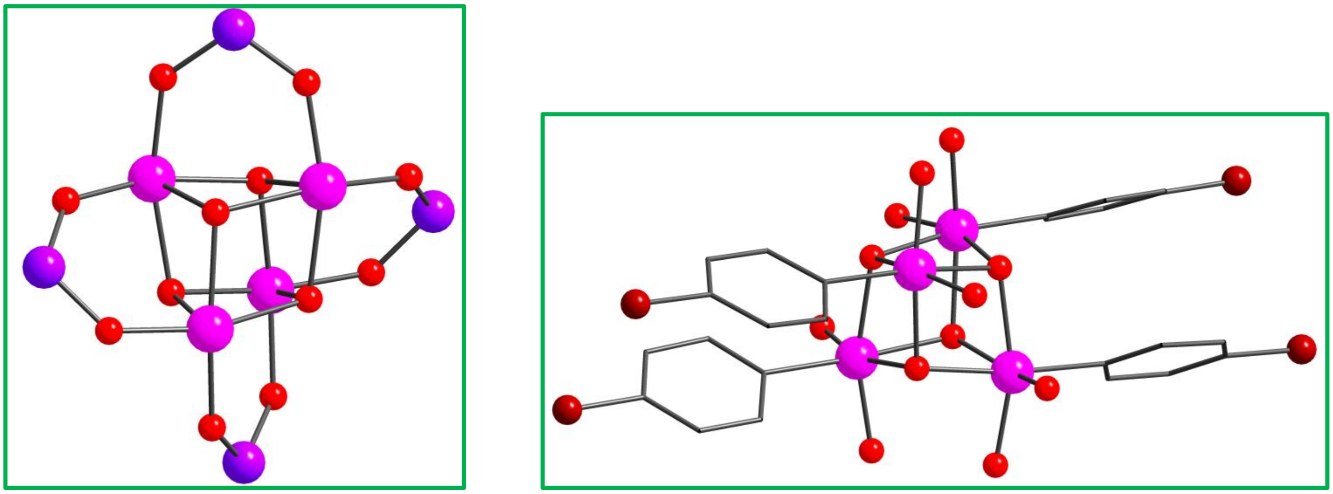


Figure 3.1: Molecular structure of **3.1.** Hydrogen atoms are omitted for clarity. Colour code: Sb magenta, Si purple, O red, Cl brown.

Single crystals of **3.1** and **3.2** were obtained from chloroform solution using hexane as the diffusing solvent over 1 week's time and **3.3** were crystallised from slow evaporation of acetone over 1 week's time. The neutral clusters **3.1** and **3.2** crystallize in the monoclinic space group *C2/c* where as **3.3** crystallize in the monoclinic space group *P21/n* (Table 3.1). As **3.1**, **3.2** and **3.3** are isostructural, we consider the structure of **3.1** for discussion (Figure 3.1). The selected bond lengths (Å) and bond angles (°) of **3.1-3.3** are given in the Table 3.2-3.4. The solid-state structure of **3.1** reveals the formation of the tetranuclear organoantimony(V) oxido cluster $[(p\text{-Cl-}C_6H_4Sb)_4(O)_4(Ph_2SiO_2)_4]$, which contains a central Sb_4O_4 cubane encapsulated by four bridging diphenyldisiloxides (Figure 3.2(a)).

The spatial arrangement around each antimony atom is octahedral with O_5C coordination (Figure 3.2 (b)): three coordinations from μ_3-oxo groups of the cubane core, two from the oxygens of two neighboring bridging siloxide ligands, and one from the carbon of the chloro phenyl group.



(a) (b)

Figure 3.2: (a) Sb_4O_4 cubane encapsulated by four bridging diphenyldisiloxides (b) Octahedral geometry around antimony. Colour code: Sb magenta, Si purple, O red, Cl brown.

The Sb-O distances in the core fall in the range 2.066(9)-2.133(6) Å. The Sb-C distance fall in the range 2.102(1)-2.103(1) Å. The Sb-O-Sb angles in the cubane core fall in the range 100.98(14)-103.49(14) °. The Sb---Sb nonbonding distances are 3.241(2)-3.325(4) Å. The metric parameters (Sb-O bond lengths, Sb-O-Sb bond angles, and the Sb---Sb nonbonding distances) are similar to those of the recently reported Sb_4O_4 cubane cluster.[12] Four dianionic diphenyldisiloxides are present, wrapped around the central cubane core almost in an identical fashion. Of the six faces of the Sb_4O_4 cubane core, two opposite square faces are sterically encumbered by the presence of *p*-chlorophenyl groups on antimony; hence, the bifunctional diphenyldisiloxide ligands approach and bridge the antimony atoms through the remaining four square faces. It should be mentioned here that the condensation reactions of diphenylsilanediol with organotin or organotellurium oxides/hydroxides lead only to Lewis acid or Lewis base catalyzed self-condensation of diphenylsilanediols, yielding $(Ph_2SiO)_3$ or $(Ph_2SiO)_4$ as the major product.[25] However, in the present case we do not encounter such self-condensed products of silanols, probably due to the less acidic nature of stibonic acid compared to that of organotin or organotellurium analogues. It is also possible that the formation of Sb-O-Si bonds is thermodynamically more favorable, leading to the isolation of a rather unexpected product. It is also of interest to note here that in the previously reported compound $[(1,8\text{-}C_{10}H_6)\text{-}(SbMe_2)_2]_2O_4$, which contains a similar Sb_4O_4 cubane core,[12] only two naphthalene dianions bridge the metal atoms in a mutually orthogonal fashion, but in **3.1** four $[Ph_2SiO_2]_2$-ligands bridge the central cubane core. The reason for this is that in the former case the orientation of the two alkyl groups on antimony atom is in such a way that the naphthalene can approach and bind to the metal centers only through two of the six square faces of the cube, whereas in **3.1**, since a monoorgano antimony precursor is used, four of the six square faces of the self-assembled cubane core are accessible for the ligands to bind the metal centers. The Si-O bond distances fall in the range 1.627(5)-1.647(5) Å. The silicon bound O---Sb distance falls in the range 1.927(5)-1.935(5) Å, which is considerably shorter than the Sb-O distances of the central cubane core. The Si-O-Sb angles vary between 131.86(24) and 134.34(24) °. The four tetrahedrally coordinated silicon atoms lie at the vertices of an almost square plane, with the Si---Si distances being 5.592(7)-5.767(7) Å. The isolation of a Sb_4O_4 cubane cluster is significant, since cubane clusters are considered as important secondary building units (SBU's) for synthesizing model compounds for zeolites.[26]

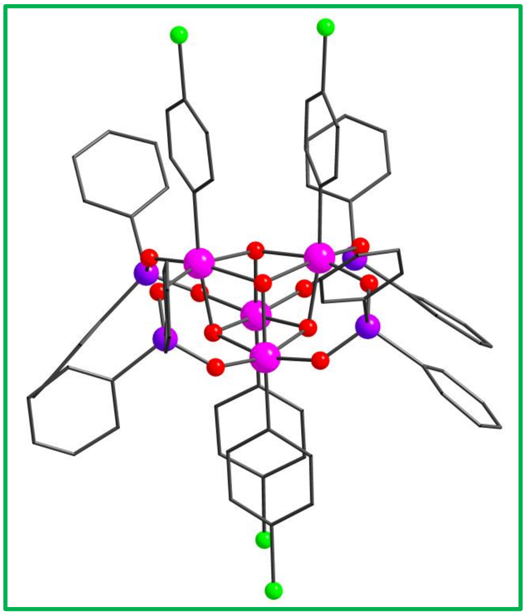


Figure 3.3: Molecular structure of **3.2.** Hydrogen atoms are omitted for clarity. Colour code: Sb magenta, Si purple, O red, Br green.

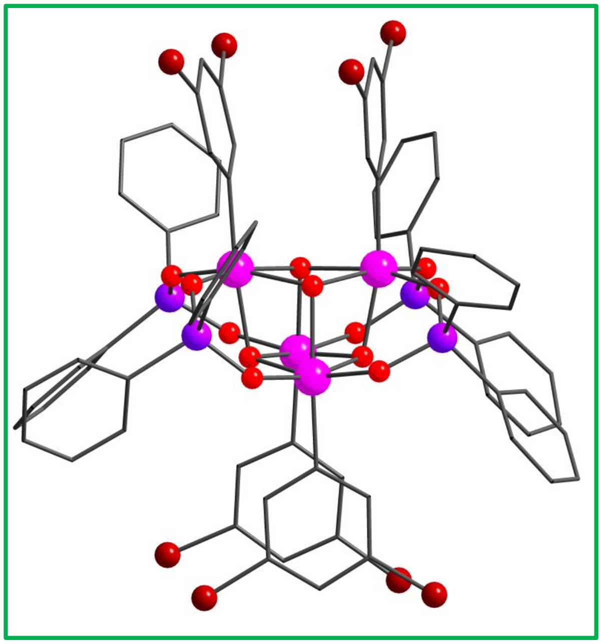


Figure 3.4: Molecular structure of **3.3.** Hydrogen atoms are omitted for clarity. Colour code: Sb magenta, Si purple, O red, Cl brown.

3.4 Conclusion

In conclusion, to the best of our knowledge, this is the first report of organoantimony(V) oxido siloxides containing a Sb^{V}-O-Si^{IV} framework that has been structurally characterized. Silanols generally tend to form metallosiloxane frameworks on reaction with organometal precursors, but in the present case the silanol stabilizes the formation of a rare Sb_4O_4 cubane cluster.

Table 3.1: Crystal and refinement data for **3.1-3.3**

	3.1	**3.2**	**3.3**
formula	$C_{74}H_{62}Cl_{10}O_{14}Sb_4Si_4$	$C_{72}H_{76}Br_4O_{22}Sb_4Si_4$	$C_{75}H_{58}Cl_8O_{13}Sb_4Si_4$
M	2129.10	2212.33	2050.17
T(K)	298(2)	298(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	C2/c	C2/c	P21/n
a(Å)	24.828(13)	24.949(4)	13.7832(7)
b(Å)	15.261(8)	15.262(3)	22.8261(12)
c(Å)	24.943(13)	24.924(4)	24.7430(13)
α(deg)	90	90	90
β(deg)	111.925(7)	111.458(3)	95.7980(10)
γ(deg)	90	90	90
V(Å^3)	8767(8)	8833(3)	7744.7(7)
Z	4	4	4
Dcalcd (Mg m^{-3})	1.613	1.664	1.758
***μ* (mm^{-1})**	1.635	3.139	1.780
F(000)	4192	4336	4032
θ range (deg)	1.66-26.05	1.60-25.11	1.63 to 26.44
index range	$-30 \le h \le 27$	$-29 \le h \le 29$	$-16 \le h \le 16$
	$-16 \le k \le 18$	$-18 \le k \le 18$	$-27 \le k \le 27$
	$-30 \le l \le 30$	$-29 \le l \le 29$	$-29 \le l \le 29$
no of reflections collected	33 146	41 898	73883
goodness-of-fit (GOF) on F^2	1.062	1.087	1.257
R1(F) (I > 2σ(I))	0.0497	0.0511	0.0687
wR2	0.1572	0.1691	0.1238
large diff. peak and hole (e Å^{-3})	1.720/-0.873	1.684/-0.683	1.641/ -1.086

Table 3.2: Selected bond lengths (Å) and bond angles (º) in **3.1**

Sb1-O1	2.121(3)	O1-Sb1-O2*	75.75(13)
Sb1-O2	2.066(9)	O1-Sb1-O2	77.31(13)
Sb1-O3	1.935(5)	O1-Sb1-O6	162.89(16)
Sb1-O2*	2.133(6)	O1-Sb1-O3	91.85(17)
Sb1-O6*	1.927(5)	O2-Sb1-O6	88.35(17)
Sb1*-C1*	2.102(1)	O2-Sb2-O1	88.38(16)
Sb2-O1	2.091(1)	Sb1-O1-Sb2	100.98(14)
Sb2-O2	2.123(3)	Sb2-O1-Sb2*	103.49(14)
Sb2-O1*	2.113(5)	Sb1-O2-Sb2	101.77(14)
Sb2-O4	1.928(7)	Sb1-O3-Si1	131.86(24)
Sb2-O5	1.927(3)	Sb2-O4-Si1	134.34(28)
Si1-O3	1.647(5)	O3-Si1-O4	109.44(24)
Si1-O4	1.627(5)		

Symmetry transformations used to generate equivalent atoms:*1-x+1,y,-z+3/2

Table 3.3: Selected bond lengths (Å) and bond angles (º) in **3.2**

Sb1-O1	2.128(5)	O1-Sb1-O2*	77.21(17)
Sb1-O2	2.098(5)	O1-Sb1-O2	76.32(17)
Sb1-O3	1.921(6)	O1-Sb1-O6	163.27(19)
Sb1-O2*	2.088(6)	O1-Sb1-O3	92.17(18)
Sb1-O6*	1.929(5)	O2-Sb1-O6	89.55(18)
Sb1*-C1*	2.088(7)	O2-Sb2-O1	89.68(17)
Sb2-O1	2.072(5)	Sb1-O1-Sb2	101.40(19)
Sb2-O2	2.132(5)	Sb2-O1-Sb2*	102.79(19)
Sb2-O1*	2.113(6)	Sb1-O2-Sb2	103.15(19)
Sb2-O4	1.924(6)	Sb1-O3-Si1	133.73(32)
Sb2-O5	1.917(5)	Sb2-O4-Si1	131.97(29)
Si1-O3	1.622(6)	O3-Si1-O4	109.96(27)
Si1-O4	1.638(5)		

Symmetry transformations used to generate equivalent atoms: * 1-x+2,y,-z+1/2

Table 3.4: Selected bond lengths (Å) and bond angles (º) in **3.3**

Sb(1)-O(1)	2.083(5)	O(1)-Sb(1)-O(2)	76.89(19)
Sb(1)-O(2)	2.120(5)	O(1)-Sb(1)-O(4)	77.07(19)
Sb(2)-O(1)	2.114(5)	O(1)-Sb(2)-O(3)	75.45(19)
Sb(2)-O(2)	2.063(5)	O(2)-Sb(2)-O(3)	77.33(18)
Sb(3)-O(2)	2.124(5)	O(3)-Sb(3)-O(2)	77.38(18)
Sb(3)-O(3)	2.061(5)	O(4)-Sb(3)-O(2)	75.51(18)
Sb(4)-O(1)	2.094(5)	O(5)-Sb(1)-O(4)	161.8(2)
Sb(4)-O(3)	2.103(5)	Sb(1)-O(1)-Sb(2)	101.0(2)
Si(1)-O(5)	1.641(5)	Sb(2)-O(2)-Sb(1)	101.4(2)
Si(2)-O(7)	1.636(5)	Sb(3)-O(3)-Sb(2)	100.9(2)
Si(3)-O(9)	1.639(6)	Sb(4)-O(3)-Sb(2)	102.8(2)
Si(4)-O(11)	1.638(5)	Si(1)-O(5)-Sb(1)	133.1(3)
Sb(1)-C(1)	2.105(8)	Si(2)-O(7)-Sb(2)	133.4(3)
Sb(2)-C(19)	2.089(8)	Si(3)-O(9)-Sb(3)	132.7(3)
Sb(3)-C(37)	2.088(7)	Si(4)-O(11)-Sb(4)	133.0(3)
Sb(4)-C(55)	2.091(7)	O(6)-Si(1)-O(5)	109.2(3)

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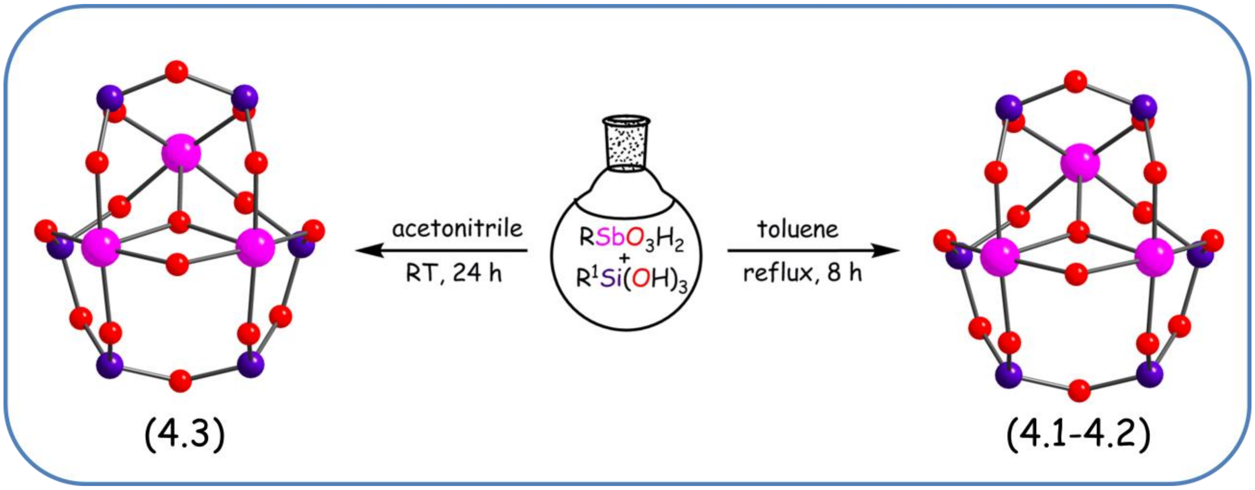
Chapter

4

In situ generated polysiloxanes stabilizing μ_3-oxo bridged Sb_3 triangles

Abstract: Reaction of $RSbO_3H_2$ with *t*-butylsilanetriol has led to the isolation of organoantimony (V) based molecular triangle stabilized by siloxane frameworks$\{[C_5H_5NH].[(p\text{-}Cl\text{-}C_6H_4Sb)_3\{(t\text{-}Bu)_4Si_4O_9\}\{(t\text{-}Bu)_2Si_2O_5\}(\mu_3\text{-}O)(\mu\text{-}OH)]\}$(**4.1**), $\{[C_5H_5NH].[(p\text{-}Br\text{-}C_6H_4Sb)_3\{(t\text{-}Bu)_4Si_4O_9\}\{(t\text{-}Bu)_2Si_2O_5\}(\mu_3\text{-}O)(\mu\text{-}OH)]\}$(**4.2**) and $\{[C_5H_5NH].[(3,5\text{-}Cl_2\text{-}C_6H_3Sb)_3\{(t\text{-}Bu)_4Si_4O_9\}\{(t\text{-}Bu)_2Si_2O_5\}(\mu_3\text{-}O)(\mu\text{-}OH)]\}$(**4.3**). A combination of a disiloxane and a tetrasiloxane framework were generated *in situ* leading to the stabilization of the μ_3-O centred Sb_3 triangle.



4.1 Introduction

Organostibonic acids[1] has started gaining attention in recent years following the first isolation of a reverse Keggin type polyoxometalate[2a] and the subsequent report on the structural elucidation of the first molecular arylstibonic acid which crystallized as a dimer.[2,3] Organostibonic acids have been treated with protic ligands leading to the isolation and structural characterization of interesting discrete metal-oxo frameworks resembling a cubane, adamantane-type structures and butterfly-type tetranuclear cluster.[4] ESI-MS studies have also been used to elucidate the molecular structures of organostibonate in solution.[5] Organostibonic acids in presence of bases self-condense leading to the formation of dodecanuclear / hexadecanuclear POM type frameworks.[4,6] Very recently isolation of mixed valent Sb(V/III) POMs have been reported stabilized by telluroxane ligands.[7] Continuing our interest in the investigation of the reactivity of organostibonic acids, reactivity of organostibonic acids with *t*-butylsilanetriol was investigated. Independently, organosilanols have been used as ligands for generation of a variety of interesting cluster frameworks based on main group metals,[8] transition metals[9] and lanthanides.[10] Single crystal X-ray diffraction studies revealed the formation of oxo-centered organoantimony(V) based triangle stabilized by siloxane frameworks $\{[C_5H_5NH].[(p\text{-}Cl\text{-}C_6H_4Sb)_3\{(t\text{-}Bu)_4Si_4O_9\}\{(t\text{-}Bu)_2Si_2O_5\}(\mu_3\text{-}O)(\mu\text{-}OH)]\}$(**4.1**), $\{[C_5H_5NH].[(p\text{-}Br\text{-}C_6H_4Sb)_3\{(t\text{-}Bu)_4Si_4O_9\}\{(t\text{-}Bu)_2Si_2O_5\}(\mu_3\text{-}O)(\mu\text{-}OH)]\}$(**4.2**) and $\{[C_5H_5NH].[(3,5\text{-}Cl_2\text{-}C_6H_3Sb)_3\{(t\text{-}Bu)_4Si_4O_9\}\{(t\text{-}Bu)_2Si_2O_5\}(\mu_3\text{-}O)(\mu\text{-}OH)]\}$(**4.3**) Interestingly, silanetriol self-condense *in situ* leading to the formation of either a disiloxane or a tetrasilatrioxane framework leading to the stabilization of the first structurally characterized oxo-centered organoantimony (V) based triangular assembly. Though oxo-centered metal triangles are very common in transition metal chemistry,[11] they are a rarity as far as main group metals are concerned.[12] The synthesis and structural characterization will be reported in this communication.

4.2 Experimental Section

4.2.1 General information:

Solvents and the common reagents were used for the synthesis are purchased from commercial sources. *p*-halophenyl and *m*-dihalophenylstibonic acids (halogen = Cl and Br) and *t*-butylsilanetriol were synthesized using literature procedures[13].

4.2.2 Instrumentation:

Infrared spectra were recorded on a JASCO-5300 FT-IR spectrometer as KBr pellets. The ^{1}H, ^{13}C and ^{29}Si solution NMR spectra were recorded on a Bruker DRX 400 instrument. Elemental analysis was performed on a Flash EA Series 1112 CHNS analyzer. HRMS were recorded using electrospray ionization on a Bruker maxis (ESI-TOF analyzer) machine. Single Crystal X-ray data collection (for **4.1-4.3**) was carried out at 100(2) K on a Bruker Smart Apex CCD area detector system (λ (Mo Kα) = 0.71073 Å), with a graphite monochromotor. The data were reduced using SAINT PLUS and the structures were solved using SHELXS-97[14] and refined using SHELXL-2014/7.[15,16] All non-hydrogen atoms were refined anisotropically. The Cl(3) atom for compound **4.1** are found to be positionally disordered and split into two positions with the site occupancy factors of 0.371(18) and 0.629(18) using PART instructions and were restrained using ISOR command. Compound **4.2** Br(3) atom are found to be disordered and split into three positions in a ratio of 0.489(15), 0.084(8) and 0.431(16) according to the PART command and were restrained using DELU and SIMU instructions. C(35) and C(36) of Compound **4.2** are disordered over two positions which were solved by using PART instructions with the site occupancy factors of 0.489(15)/0.511(15) and 0.489(15)/0.511(15), respectively. Additionally SIMU and ISOR instructions were also used for restraint of C(35) and C(36).

4.2.3 General Synthetic procedures for Compounds 4.1-4.3:

Compounds **4.1-4.2** was synthesized from organostibonic acid and *t*-butylsilanetriol refluxing for 8 h in 50mL of toluene. A Dean Stark apparatus was used to remove the water eliminated in the reaction, as an azeotropic mixture. The clear solution that formed was cooled to room temperature, filtered and evaporated under reduced pressure to yield a colorless solid. Compound **4.3** was synthesized by stirring the respective organostibonic acids with *t*-butylsilanetriol in 15 mL of acetonitrile at room temperature for 24 h. The solution was filtered kept for crystallization. The isolated crystals were powdered and subjected to high vaccum for half an hour before being characterized by standard spectroscopic and analytical techniques. Exact stoichiometries of reagents used are given below.

Compound {[C_5H_5NH].[(*p*-Cl-$C_6H_4Sb)_3\{(t\text{-Bu})_4Si_4O_9\}\{(t\text{-Bu})_2Si_2O_5\}(\mu_3\text{-O})(\mu\text{-OH})$]} 4.1:

p-chlorophenylstibonic acid (0.300 g, 1.05 mmol) and *t*-butylsilanetriol (0.096 g, 0.71 mmol). Colorless crystals were obtained in a week's time by diffusion of hexane into a mixture of isopropanol-pyridine (5:1 ratio) solution. Yield: 0.119 g (23 %, based on the weight of *p*-chlorophenylstibonic acid). Dec. pt: 280-281 ˚C. Anal. Calcd (%) for $C_{47}H_{72}O_{16}NCl_3Si_6Sb_3$: C, 36.48; H, 4.69; N, 0.91 Found: C, 36.41; H, 4.73; N, 0.87. IR (cm^{-1}, KBr pellet): 3320(b), 2958(w), 2936(w), 2892(m), 2859(s), 1566(s), 1473(s), 1385(s), 1259(s), 1089(w), 815(s), 722(s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.97 ppm (m, 12H), 0.89 ppm (s, 54 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.90, 136.29, 135.17, 134.54, 133.94, 133.82, 133.47, 129.58, 129.09, 128.91, 128.66, 128.28, 128.02, 30.81, 27.33, 21.51, 18.83, 18.62, 18.50, 18.39, 18.12 ppm. ^{29}Si {^{1}H} NMR in $CDCl_3$: δ -22.20 ppm.

Compound {[C_5H_5NH].[(*p*-Br-$C_6H_4Sb)_3${(*t*-Bu)$_4Si_4O_9$}{(*t*-Bu)$_2Si_2O_5$}(μ_3-O)(μ-OH)]} 4.2:

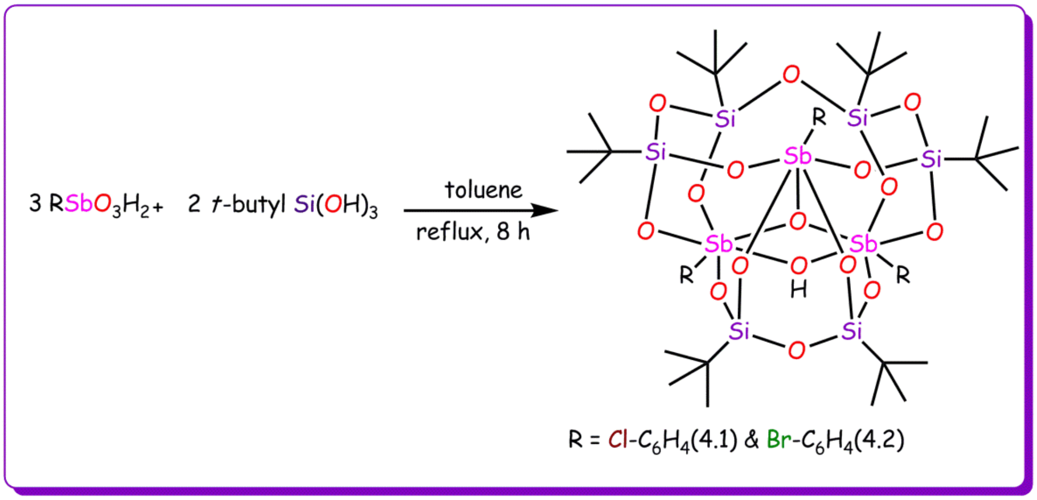
p-bromophenylstibonic acid (0.300 g, 0.92 mmol) and *t*-butylsilanetriol (0.083 g, 0.61 mmol). Colorless crystals were obtained in a week's time by diffusion of hexane into a mixture of isopropanol-pyridine (5:1 ratio) solution. Yield: 0.083 g (17 %, based on the weight of *p*-bromophenylstibonic acid). Dec. pt: 278-279 ˚C. Anal. Calcd. (%) for $C_{47}H_{72}O_{16}NBr_3Si_6Sb_3$: C, 33.59; H, 4.32; N, 0.83. Found: C, 33.46; H, 4.38; N, 0.81. IR (cm^{-1}, KBr pellet): 3408(b), 2934(w), 2858(s), 1566(s), 1475(s), 1379(s), 1251(s), 1055(w), 835(m), 806(s), 706(s), 480(s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-8.04 ppm (m, 12H), 0.91 ppm (s, 54 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.46, 134.12, 131.89, 131.19, 129.06, 128.25, 125.32, 31.62, 26.49, 26.33, 26.04, 22.69, 21.50, 18.21, 18.02 ppm. ^{29}Si {^{1}H} NMR in $CDCl_3$: δ -22.27 ppm.

Compound{[C_5H_5NH].[(3,5-Cl_2-$C_6H_3Sb)_3${(*t*-Bu)$_4Si_4O_9$}{(*t*-Bu)$_2Si_2O_5$}(μ_3-O)(μ-OH)]} 4.3:

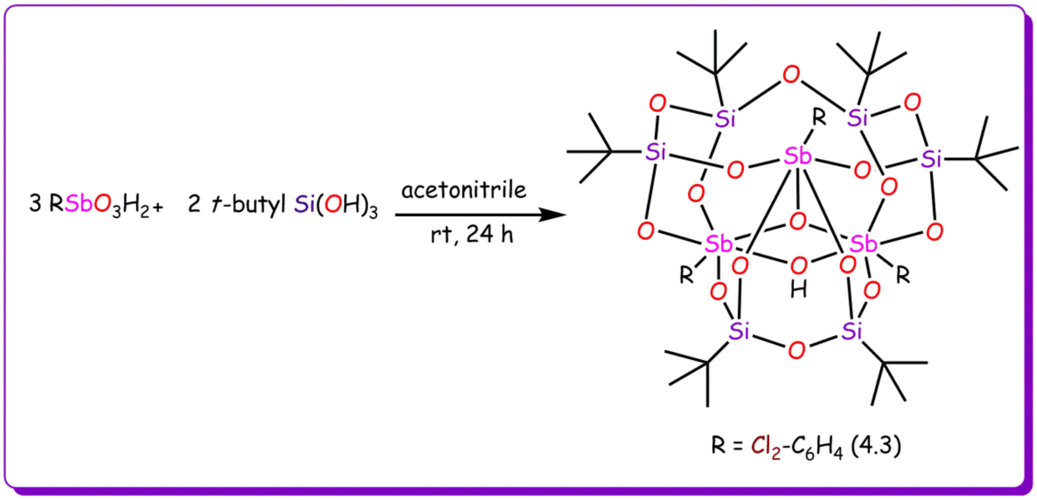
m-dichlorophenylstibonic acid (0.300 g, 0.94 mmol) and *t*-butylsilanetriol (0.086 g, 0.61 mmol). Crystals suitable for single crystal X-ray studies were grown from acetonitrile-pyridine (5:1 ratio) in a week's time. Yield: 0.099 g (20 %, based on the weight of *m*-dichlorophenylstibonic acid). Dec. pt: 282-283 ˚C. Anal. Calcd. (%) for $C_{47}H_{69}O_{16}NCl_6Si_6Sb_3$: C, 34.20; H, 4.21; N, 0.85. Found: C, 34.15; H, 4.26; N, 0.91. IR (cm^{-1}, KBr pellet): 3325(b), 2953(w), 2932(w), 2858(w), 1699(s), 1562(s), 1473(s), 1381(w), 1232(w), 1101(w), 939(m), 794(s), 669(s), 513(w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-8.08 ppm (m, 9H), 0.96 ppm (s, 54H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.92, 129.01, 128.28, 125.35, 27.03, 26.61, 26.39, 26.32, 25.67, 21.51 ppm. ^{29}Si {^{1}H} NMR in $CDCl_3$: δ -16.02 ppm.

4.3 Results and Discussions

Compounds **4.1-4.3** have been synthesized in essentially two ways. First method wherein the appropriate reagents were refluxed in toluene (Scheme 4.1) and the second method wherein cluster **4.3** was synthesized by stirring organostibonic acid and silanetriol in acetonitrile at room temperature (Scheme 4.2). Single crystal structural elucidation revealed that in both cases it lead to the formation of identical structure. Hence as far as polarity of solvent used and the temperature of the reaction does not seem to have any effect in the structure of the end product obtained.



Scheme 4.1



Scheme 4.2

4.1-4.3 was characterized by standard analytical and spectroscopic techniques. IR spectra of compounds **4.1-4.3** shows a broad band at around 3300-3430 cm^{-1} suggesting the present of hydroxyl group in the compounds. The ^{29}Si solution NMR spectra of **4.1-4.3** in $CDCl_3$ show the appearance of single resonance signal at -22.20 (**4.1**), -22.27 (**4.2**) and -16.02 (**4.3**). Crystals suitable for single crystal X-ray diffraction were obtained by slow diffusion of hexane in to a mixture of an isopropanol-pyridine solution for **4.1** and **4.2**. Crystals of **4.3** were grown by slow evaporation from acetonitrile-pyridine mixture.

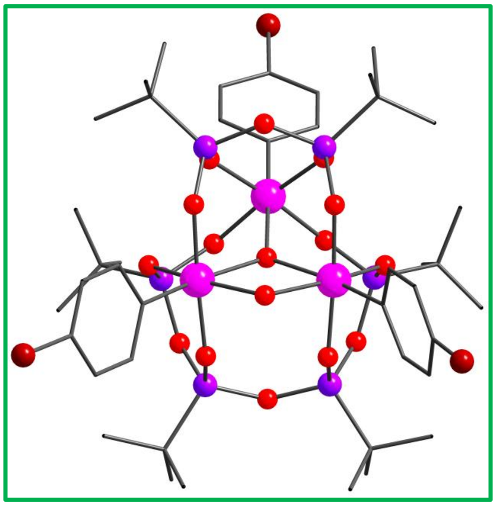
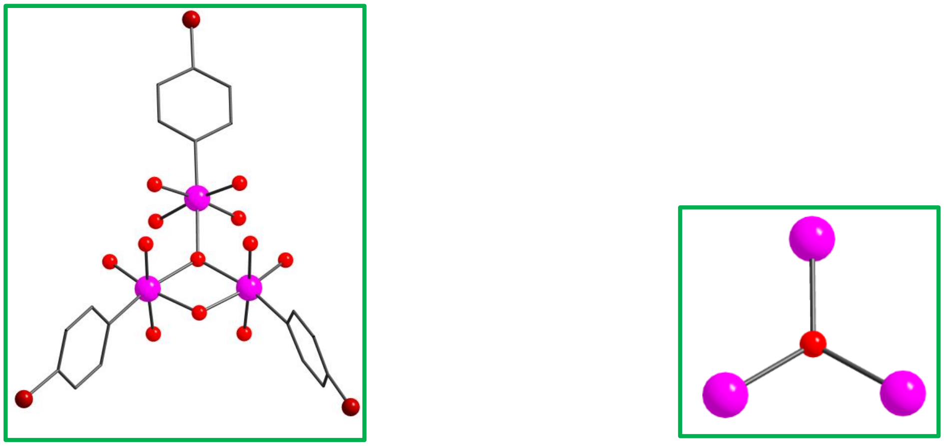


Figure 4.1: Molecular structure of **4.1.** Hydrogen atoms are omitted for clarity. Colour code: Sb magenta, Si purple, O red, Cl brown.



(a)

(b)

Figure 4.2: (a) Octahedral geometry around antimony (b) View of Sb_3 triangles. Colour code: Sb magenta, O red, Cl brown.

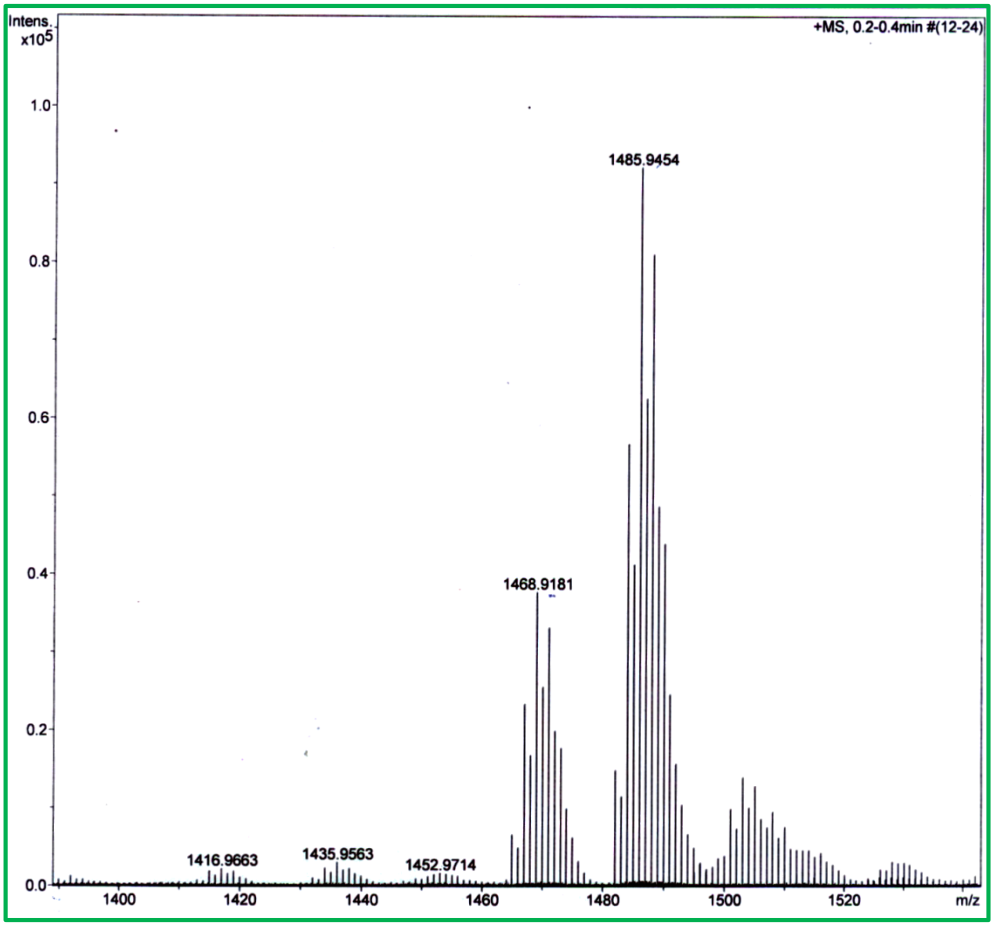


Figure 4.3: ESI-MS of compound **4.1** [*M*+2H]$^+$ calcd 1468.9356; found 1468.9181.

4.1 and **4.2** crystallize in the monoclinic space group *P21/n* and *P21/c* respectively (Table 4.1). **4.3** crystallize in the triclinic space group *P-1* (Table 4.1). Since the molecular structures of **4.1-4.3** are similar, **4.1** is considered for structural discussion. The molecular structure of **4.2** and **4.3** are shown in (Figure. 4.4 and Figure. 4.6). Selected bond lengths (Å) and bond angles (°) of **4.1-4.3** are given in the Table 4.2-4.4. The molecular structure of **4.1** is explained as follows (Figure 4.1). The cluster core is made up of a planar Sb_3O unit stabilized by two condensed siloxane systems. On one side of the Sb_3O unit tetraoxydisiloxane tetra anion is present while a hexaoxytetrasiloxane hexa anion binds to the antimony atoms of the triangular Sb_3O unit from the opposite side. Two of the Sb atoms are further bridged together by a μ-oxo group. The geometry around each antimony atom is six coordinated with octahedral arrangement (Figure. 4.2(a)). Sb_3 triangle representation is shown in Figure. 4.2(b). Sb-C distances fall in the range of 2.112(3)-2.121(3) Å. The Sb-O distances fall in the range of 1.938(2)-2.177(2) Å. Sb-O-Sb angle fall in the range of 105.32(9)-125.59(10) °. Sb-O-Si angle fall in the range of 125.33(13)-134.12(13) °. Si-O-Si angle fall in the range of 124.77(14)-137.97(15) °.

Organotellurium and organotin on reacting with silanols tend to form polymeric silanols leading to formation of condensed siloxane framework.[17] Here again, we have few interesting observation to make. In 3 chapter with silanediol were reacted with organostibonic acids, the silanols just acted as a bridging ligand. The reason for silanols to behave as a discrete ligand is propably due to the less acidic nature of organostibonic acid compared with organotellerium and organotin counter parts. But in this case the silanetriol self condense forming polysiloxanes due to the conditions employed in the synthesis. As, we refluxing the reaction mixture in case of **4.1** and **4.2** and the use of high polar solvent like acetonitrile which is a commonly used solvent in dehydration reaction leads to the formation of condensed siloxane networks ultimate stability the oxo centred molecular triangle. It is also interesting to note that to stabilize the assembled triangular Sb_3O unit the silane triol has self-condensed to form a tetraoxydisiloxane tetra anion and a hexaoxy tetrasiloxane hexa anion Chart 4.1, which acts as a multidentate ligand stabilizing the self-assembly. Based on literature reports, [18] silanetriols self-condense either in the presence of a catalyst or when the reaction system is heated.

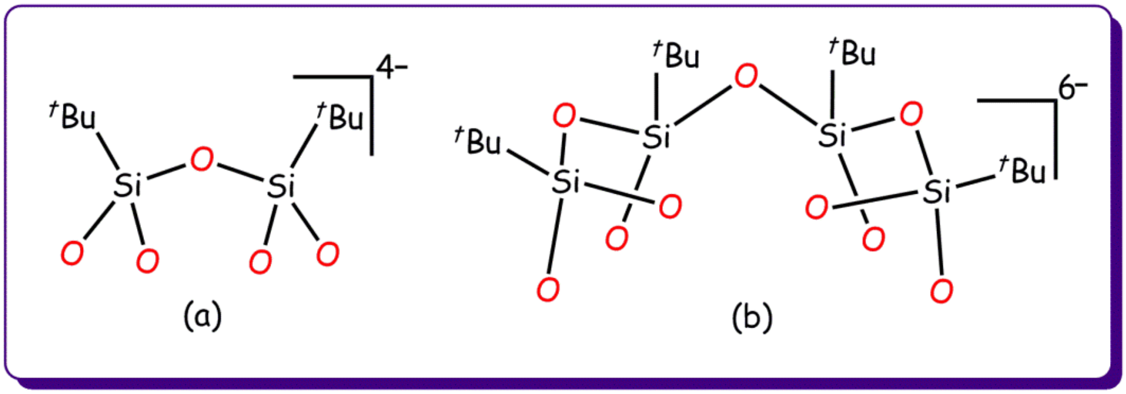


Chart 4.1: *In situ* generated siloxanes (a) tetraoxydisiloxane tetra anion (b) hexaoxytetrasiloxane hexa anion.

ESI-MS of **4.1** (Figure 4.3) and **4.2** (Figure 4.5) shows signals corresponding to formula $[M{+}2H]^+$. For compound **4.3** (Figure 4.7), ESI-MS shows signals corresponding to formula $[M{+}2K{+}3H]^+$ confirming that the structural integrity of **4.1-4.3** are maintained in solution also.

The Sb-O, Sb-C distances, Sb-O-Sb and Sb-O-Si angle in **4.2** and **4.3** falls in the range as present in **4.1**.

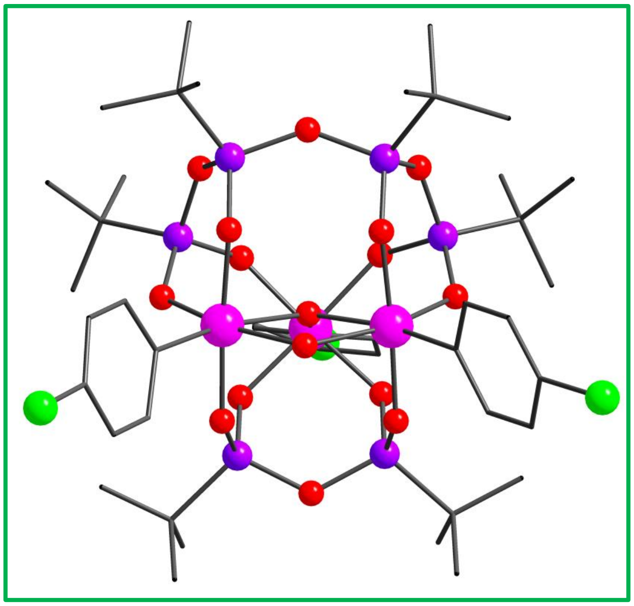


Figure 4.4: Molecular structure of **4.2.** Hydrogen atoms are omitted for clarity. Colour code: Sb magenta, Si purple, O red, Br green.

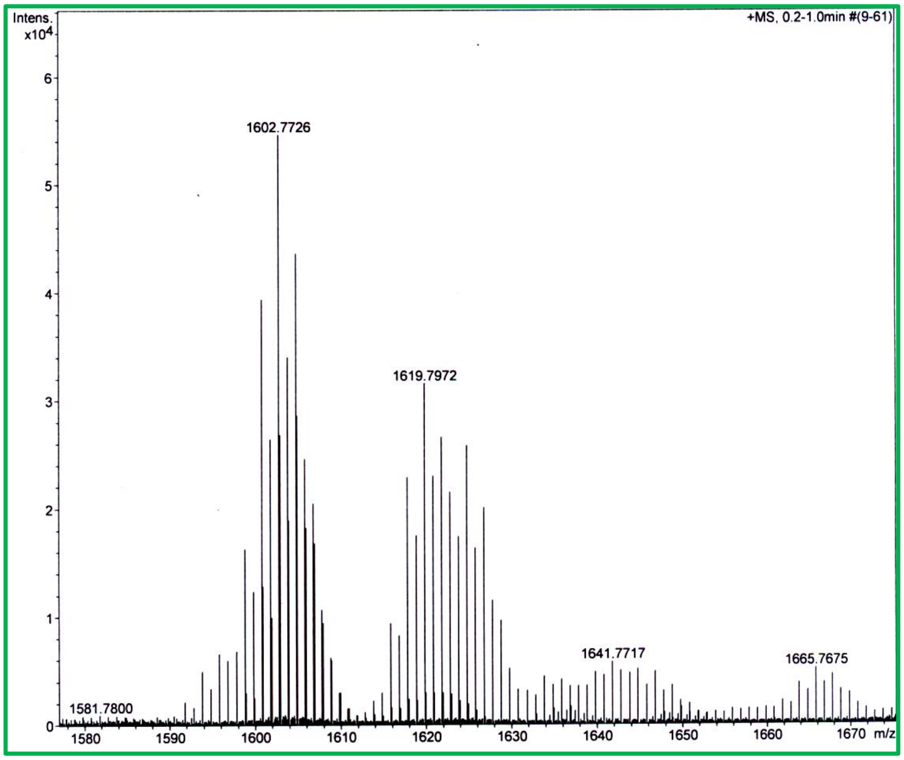


Figure 4.5: ESI-MS of compound **4.2** [*M*+2H]$^+$ calcd 1602.7829; found 1602.7726.

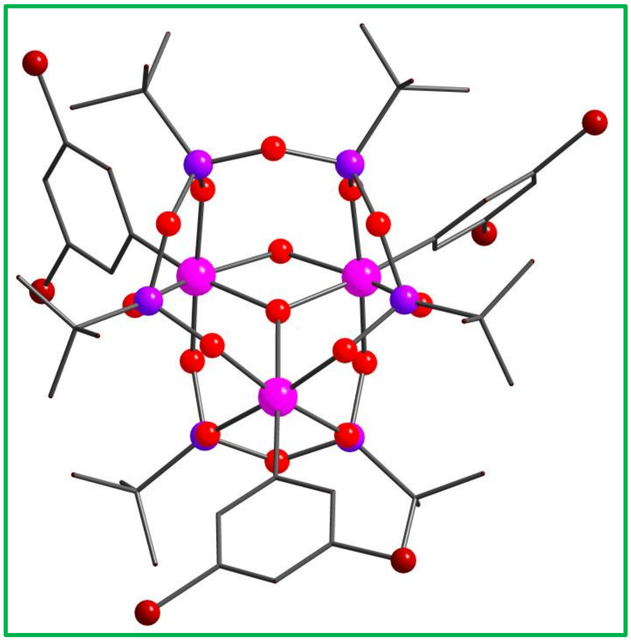


Figure 4.6: Molecular structure of **4.3.** Hydrogen atoms are omitted for clarity. Colour code: Sb magenta, Si purple, O red, Cl brown.

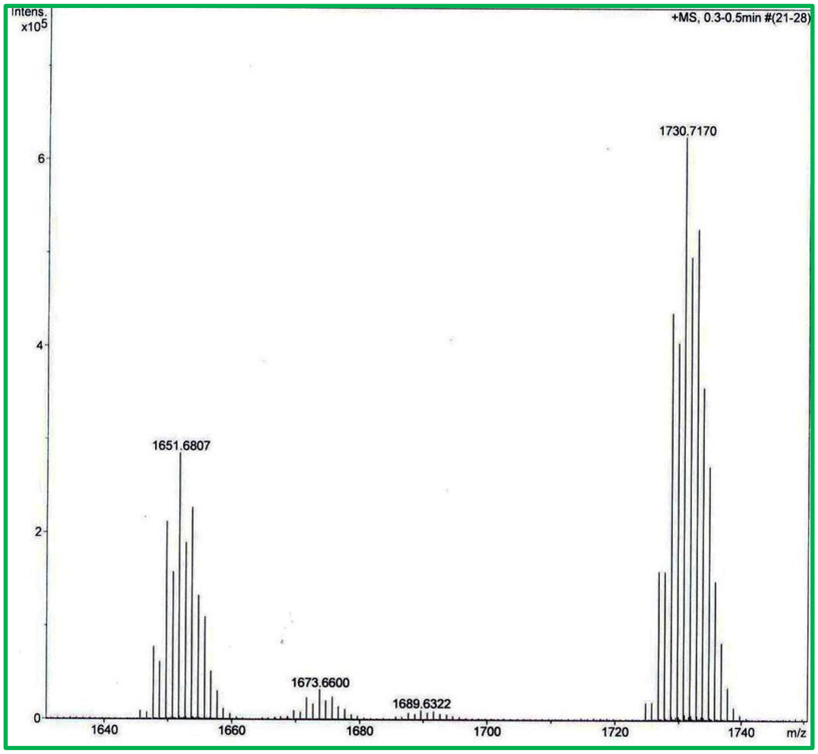


Figure 4.7: ESI-MS of compound **4.3** [*M*+2K+3H]$^+$ calcd 1651.0119; found 1651.6807

4.4 Conclusion

To conclude, a structurally fascinating molecular Sb_3 based oxo triangle has been self-assembled in the presence of *in situ* generated polysiloxanes ligand systems. Mass spectral analysis shows the structural integrity is maintained in solution also.

Table 4.1: Crystal and refinement data for **4.1-4.3**

	4.1	**4.2**	**4.3**
formula	$C_{50}H_{80}Cl_3O_{17}NSb_3Si_6$	$C_{50}H_{80}Br_3O_{17}NSb_3Si_6$	$C_{51}H_{75}Cl_6N_3O_{16}Sb_3Si_6$
M	1607.29	1740.47	1732.63
T(K)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073
crystal system	Monoclinic	monoclinic	Triclinic
space group	*P*2(1)/*n*	*P*2(1)/*c*	*P*-1
a(Å)	11.7571(10)	11.741 (10)	12.3465(14)
b(Å)	28.053(2)	28.21 (2)	13.1911(15)
c(Å)	21.7258 (19)	21.863 (18)	23.155(3)
α(deg)	90	90	99.920(2)
β(deg)	104.9530 (10)	104.994 (14)	95.997(2)
γ(deg)	90	90	105.084(2)
V(Å^3)	6922.9 (10)	6993 (10)	3542.3(7)
Z	4	4	2
Dcalcd (Mg m^{-3})	1.574	1.653	1.624
***μ* (mm^{-1})**	1.442	3.025	1.524
F(000)	3244	3460	1738
θ range (deg)	1.21-25.09	1.20-25.63	1.63 to 26.44
index range	$-14 \le h \le 14$	$-14 \le h \le 14$	$-15 \le h \le 15$
	$-33 \le k \le 33$	$-33 \le k \le 33$	$-16 \le k \le 16$
	$-25 \le l \le 25$	$-25 \le l \le 25$	$-26 \le l \le 28$
reflections collected	66491	67154	28581
goodness-of-fit (GOF) on F^2	1.049	1.092	1.026
final R indices	R_1 = 0.0319	R_1 = 0.0705	R_1 = 0.0414
R$_1$[*I* >2σ(*I*)]	wR_2 = 0.0793	wR_2 = 0.1313	wR_2 = 0.0949
R indicies (all data)	R_1 = 0.0355	R_1 = 0.0998	R_1 = 0.0506
	wR_2 = 0.0814	wR_2 = 0.1425	wR_2 = 0.0998
large diff. peak and hole (e Å^{-3})	1.657 and -0.856	1.611 and -1.282	1.980 and -0.808

Table 4.2: Selected bond lengths (Å) and bond angles (º) in **4.1**

Sb(1)-C(1)	2.121(3)	Si(4)-O(11)	1.625(2)
Sb(2)-C(19)	2.117(3)	Si(4)-O(10)	1.637(2)
Sb(3)-C(33)	2.112(3)	Si(4)-O(9)	1.645(2)
Sb(1)-O(3)	1.938(2)	Si(5)-O(13)	1.626(2)
Sb(1)-O(15)	1.959(2)	Si(5)-O(12)	1.629(2)
Sb(1)-O(5)	1.987(2)	Si(5)-O(14)	1.645(2)
Sb(1)-O(2)	2.089(2)	Si(6)-O(16)	1.620(2)
Sb(1)-O(1)	2.094(2)	Si(6)-O(15)	1.630(2)
Sb(2)-O(11)	1.946(2)	Si(6)-O(14)	1.646(2)
Sb(2)-O(12)	1.953(2)	Sb(1)-O(1)-Sb(2)	105.32(9)
Sb(2)-O(8)	1.978(2)	Sb(1)-O(1)-Sb(3)	124.82(10)
Sb(2)-O(2)	2.085(2)	Sb(2)-O(1)-Sb(3)	125.59(10)
Sb(2)-O(1)	2.109(2)	Sb(2)-O(2)-Sb(1)	106.40(10)
Sb(3)-O(16)	1.951(2)	Si(4)-O(11)-Sb(2)	125.82(13)
Sb(3)-O(13)	1.953(2)	Si(1)-O(3)-Sb(1)	125.33(13)
Sb(3)-O(6)	1.953(2)	Si(6)-O(15)-Sb(1)	130.50(13)
Sb(3)-O(10)	1.983(2)	Si(4)-O(10)-Sb(3)	133.42(13)
Sb(3)-O(1)	2.177(2)	Si(5)-O(12)-Sb(2)	130.13(13)
Si(1)-O(6)	1.621(2)	Si(6)-O(16)-Sb(3)	127.19(13)
Si(1)-O(3)	1.635(2)	Si(2)-O(4)-Si(1)	130.87(15)
Si(1)-O(4)	1.639(2)	Si(2)-O(5)-Sb(1)	132.56(13)
Si(2)-O(5)	1.626(2)	Si(1)-O(6)-Sb(3)	133.35(13)
Si(2)-O(4)	1.631(2)	Si(5)-O(14)-Si(6)	124.77(14)
Si(2)-O(7)	1.638(2)	Si(5)-O(13)-Sb(3)	127.23(13)
Si(3)-O(8)	1.619(2)	Si(3)-O(7)-Si(2)	137.97(15)
Si(3)-O(7)	1.633(2)	Si(3)-O(8)-Sb(2)	134.12(13)
Si(3)-O(9)	1.639(2)	Si(3)-O(9)-Si(4)	129.85(15)

Table 4.3: Selected bond lengths (Å) and bond angles (º) in **4.2**

Sb(1)-C(1)	2.121(8)	Si(4)-O(11)	1.612(6)
Sb(2)-C(19)	2.119(8)	Si(4)-O(9)	1.631(6)
Sb(3)-C(33)	2.103(8)	Si(4)-O(10)	1.640(6)
Sb(1)-O(3)	1.925(5)	Si(5)-O(12)	1.616(6)
Sb(1)-O(15)	1.958(5)	Si(5)-O(13)	1.628(6)
Sb(1)-O(5)	1.979(5)	Si(5)-O(14)	1.642(6)
Sb(1)-O(1)	2.083(5)	Si(6)-O(16)	1.609(6)
Sb(1)-O(2)	2.085(5)	Si(6)-O(15)	1.619(6)
Sb(2)-O(11)	1.943(5)	Si(6)-O(14)	1.636(6)
Sb(2)-O(12)	1.950(5)	Sb(2)-O(2)-Sb(1)	106.2(2)
Sb(2)-O(8)	1.959(6)	Sb(1)-O(1)-Sb(2)	105.5(2)
Sb(2)-O(2)	2.084(5)	Sb(1)-O(1)-Sb(3)	124.6(2)
Sb(2)-O(1)	2.105(5)	Sb(2)-O(1)-Sb(3)	125.6(2)
Sb(3)-O(13)	1.932(5)	Si(3)-O(8)-Sb(2)	134.3(3)
Sb(3)-O(6)	1.944(5)	Si(1)-O(3)-Sb(1)	125.3(3)
Sb(3)-O(16)	1.954(6)	Si(6)-O(15)-Sb(1)	130.6(3)
Sb(3)-O(10)	1.988(5)	Si(2)-O(5)-Sb(1)	132.2(3)
Sb(3)-O(1)	2.170(5)	Si(1)-O(6)-Sb(3)	133.9(3)
Si(1)-O(6)	1.607(6)	Si(3)-O(9)-Si(4)	130.0(3)
Si(1)-O(4)	1.635(6)	Si(5)-O(12)-Sb(2)	130.0(3)
Si(1)-O(3)	1.641(6)	Si(5)-O(13)-Sb(3)	127.4(3)
Si(2)-O(7)	1.627(6)	Si(4)-O(10)-Sb(3)	133.1(3)
Si(2)-O(4)	1.630(6)	Si(4)-O(11)-Sb(2)	125.8(3)
Si(2)-O(5)	1.633(5)	Si(2)-O(4)-Si(1)	131.5(3)
Si(3)-O(8)	1.618(6)	Si(2)-O(7)-Si(3)	138.2(3)
Si(3)-O(9)	1.631(6)	Si(6)-O(16)-Sb(3)	126.9(3)
Si(3)-O(7)	1.636(6)	Si(6)-O(14)-Si(5)	124.5(4)

Table 4.4: Selected bond lengths (Å) and bond angles (º) in **4.3**

Sb(1)-C(1)	2.116(4)	Si(4)-O(10)	1.629(3)
Sb(2)-C(19)	2.134(4)	Si(4)-O(11)	1.629(3)
Sb(3)-C(33)	2.122(4)	Si(4)-O(9)	1.641(3)
Sb(1)-O(3)	1.940(3)	Si(5)-O(13)	1.629(3)
Sb(1)-O(15)	1.961(3)	Si(5)-O(12)	1.633(3)
Sb(1)-O(5)	1.983(2)	Si(5)-O(14)	1.642(3)
Sb(1)-O(1)	2.073(3)	Si(6)-O(16)	1.626(3)
Sb(1)-O(2)	2.087(3)	Si(6)-O(15)	1.632(3)
Sb(2)-O(12)	1.939(3)	Si(6)-O(14)	1.648(3)
Sb(2)-O(11)	1.950(3)	Sb(1)-O(1)-Sb(2)	105.99(11)
Sb(2)-O(8)	1.958(2)	Sb(1)-O(1)-Sb(3)	124.24(12)
Sb(2)-O(1)	2.090(3)	Sb(2)-O(1)-Sb(3)	125.60(12)
Sb(2)-O(2)	2.103(3)	Sb(1)-O(2)-Sb(2)	105.02(12)
Sb(3)-O(16)	1.946(3)	Si(5)-O(12)-Sb(2)	129.47(16)
Sb(3)-O(6)	1.958(3)	Si(6)-O(15)-Sb(1)	129.00(16)
Sb(3)-O(13)	1.959(3)	Si(1)-O(6)-Sb(3)	132.20(16)
Sb(3)-O(10)	1.964(3)	Si(2)-O(5)-Sb(1)	132.71(16)
Sb(3)-O(1)	2.196(3)	Si(3)-O(8)-Sb(2)	133.82(15)
Si(1)-O(6)	1.624(3)	Si(1)-O(3)-Sb(1)	125.68(15)
Si(1)-O(3)	1.632(3)	Si(4)-O(10)-Sb(3)	132.65(16)
Si(1)-O(4)	1.640(3)	Si(5)-O(14)-Si(6)	124.77(17)
Si(2)-O(5)	1.621(3)	Si(5)-O(13)-Sb(3)	128.12(15)
Si(2)-O(4)	1.638(3)	Si(6)-O(16)-Sb(3)	128.20(15)
Si(2)-O(7)	1.641(3)	Si(4)-O(11)-Sb(2)	125.83(15)
Si(3)-O(8)	1.623(3)	Si(2)-O(4)-Si(1)	132.68(18)
Si(3)-O(7)	1.629(3)	Si(3)-O(7)-Si(2)	137.12(18)
Si(3)-O(9)	1.636(3)	Si(3)-O(9)-Si(4)	130.53(18)

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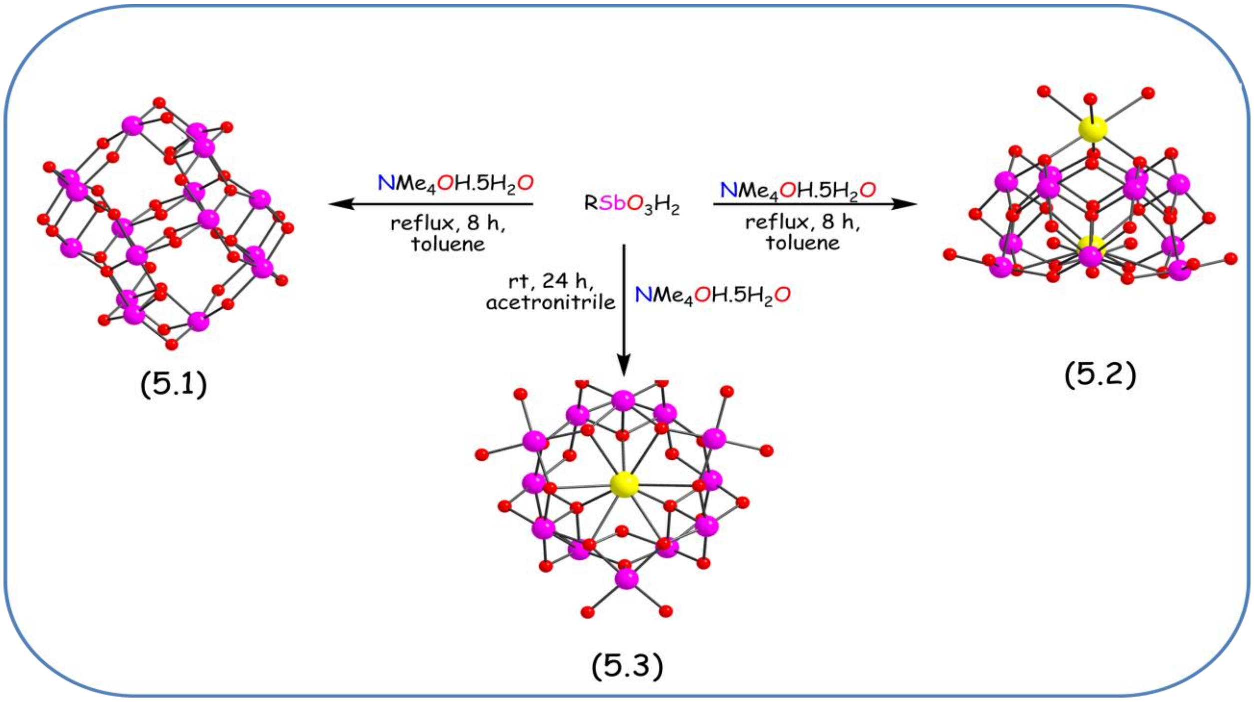
Chapter

5

Isolation of high nuclearity isopolyoxostibonates using base

Abstract: Reaction of organostibonic acids with tetramethylammonium hydroxide pentahydrate (in ratio 1:1) has led to the isolation of organoantimony(V) POM as revealed by single crystal X-ray structural elucidation studies. {$(NMe_4)_2[(p\text{-}Cl\text{-}C_6H_4Sb)_{16}(O)_{30}(OH)_6]$} (**5.1**), {$(NMe_4)_3[Na_2(p\text{-}Br\text{-}C_6H_4Sb)_{12}(O)_{23}(OH)_7.4H_2O_{(coord)}]$} (**5.2**) and {$(NMe_4)_4[Na(m\text{-}Cl_2\text{-}C_6H_3Sb)_{12}(O)_{23}(OH)_7]$} (**5.3**). Isopolyoxostibonate isolated acts as inorganic crown-type ligands towards sodium ion in clusters **5.2** and **5.3**.



5.1 Introduction

Polyoxometalates (POMs) are a metal-oxygen based cluster frameworks. Berzelius reported the first polyoxoanion $H_3PMo_{12}O_{40}$ in 1826.[1] Subsequently synthesis of novel POMs increased tremendeously due to the rich structural diversity they show and the multitude of novel properties they exhibit.[2] Polyoxostibonates on the other hand are relatively few in number and they exhibit interesting structural resemblances with the classical transition metal based POMs as reported by Müller,[3] Pope,[4] and others.[5] POMs show potential applications in the fields as diverse as catalysis to anti-HIV properties.[6] Careful investigations by Cao *et al* showed that framework formation was p^H dependent.[7] In 1978, the first organometallic derivative of polyoxometalates $[(C_5H_5)Ti^{IV}PW_{11}O_{39}]^{4-}$ was reported.[8] The cluster shows application towards homogeneous catalysts for oxidation reaction. Synthesis and characterization of POMs based on organoantimony framework encapsulating 3d metals in its cavity was reported in 2007.[9] These POMs structural resemble the inverse form of keggins structures wherein the position of main group and the transition metal ions position were reversed. Kortz *et al* isolated an organoantimony based POMs under hydrothermal conditions and the isolated polyanion have been subjected to biological studies.[10] In aqueous medium under mild basic condition Nicholson *et al* have isolated Sb_{12} and Sb_{14} based polyoxostibonates which acts as inorganic cryptand encapsulating alkali and alkali earth metals in their cavities.[11] From our group we have recently reported the isolated and structural characterization of POMs by reaction of stibonic acids in presence of mild base like 3,5 DMPz.[12] The reaction of organostibonic acids with diorganotellerium oxides led to the isolation of an intersteing mixed valent POMs system.[13] In this chapter, self-condensation reactions of organostibonic acids in presence of a strong base like tetramethyammoniumhydroxide pentahydrate in organic solvents is detailed. Structural characterization revealed the formation of novel Sb_{12} and Sb_{16} frameworks.

5.2 Experimental Section

5.2.1 General information:

$(NMe_4)_4OH.5H_2O$, solvents, and other common reagents were used as purchased from commercial sources. *p*-halophenyl and *m*-dihalophenylstibonic acids (halogen = Cl and Br), were synthesized using literature procedures.[14]

5.2.2 Instrumentation:

Infrared spectra were recorded on a JASCO-5300 FT-IR spectrometer as KBr pellets. Elemental analysis was performed on a Flash EA Series 1112 CHNS analyzer. Single-crystal X-ray data collection (for **5.1-5.3**) was carried out at 100(2) K on a Bruker Smart Apex CCD area detector system (λ (Mo Kα) = 0.71073 Å), with a graphite monochromotor. The data were reduced using SAINT PLUS and the structures were solved using SHELXS-97[15] and refined using SHELXL-2014/7.[16,17] All non-hydrogen atoms were refined anisotropically.

5.2.3 Synthetic procedures for Compounds 5.1-5.3:

Compound $\{(NMe_4)_2[(p\text{-}Cl\text{-}C_6H_4Sb)_{16}(O)_{30}(OH)_6]\}$ 5.1:

$(NMe_4)_4OH.5H_2O$ (0.096 g, 0.53 mmol) and (*p*-chlorophenyl)stibonic acid (0.150 g, 0.53 mmol) were taken up in 50 mL of toluene, and the solution was refluxed for 8 h. A Dean-Stark apparatus was used to remove the water eliminated in the reaction as an azeotropic mixture. The precipitate formed was cooled to room temperature, filtered and dried. Yield: 0.096 g (65%, based on the weight of (*p*-chlorophenyl)stibonic acid). Dec pt: 210-211°C. Crystals suitable for single crystal X-ray studies were grown from acetonitrile solution by diffusion in hexane for 2 week. Anal. Calcd for $C_{104}H_{86}O_{36}Cl_{16}N_2Sb_{16}$: C, 28.04; H, 1.95; N, 0.63. Found: C, 28.12; H, 1.96; N, 0.68. IR (cm^{-1}, KBr pellet): 3414(b), 1910(s), 1636(m), 1570(m), 1487(s), 1381(s), 1181(w), 1090(s), 1067(s), 1013(s), 949(s), 816(s), 727(m), 490(m).

Compound $\{(NMe_4)_3[Na_2(p\text{-}Br\text{-}C_6H_4Sb)_{12}(O)_{23}(OH)_7.4H_2O_{(coord)}]\}$ 5.2:

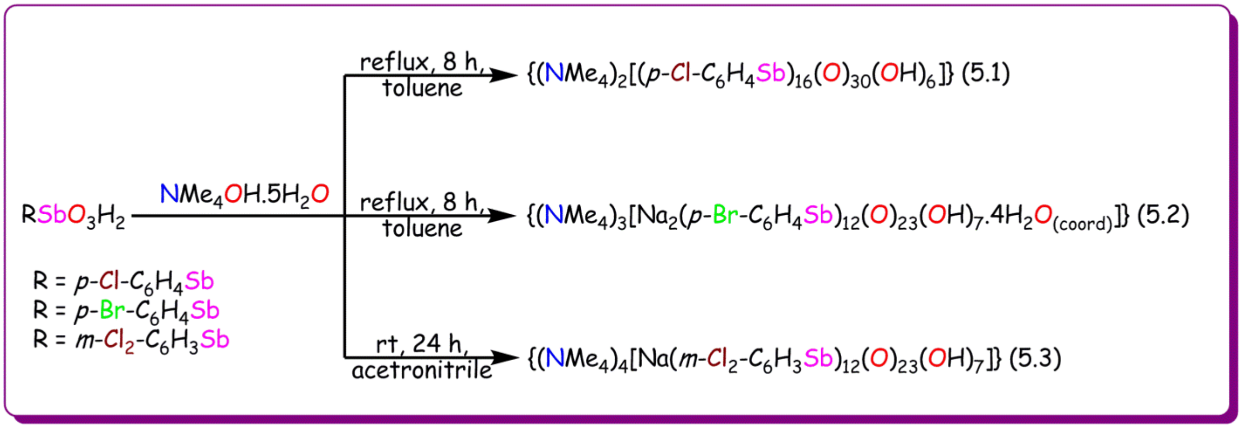
The procedure was similar to that of **5.1**. The molar ratios and weights of the reactants used are as follows: $(NMe_4)_4OH.5H_2O$ (0.083 g, 0.46 mmol) and (*p*-bromophenyl) stibonic acid, (0.150 g, 0.46 mmol). Yield: 0.086 g (54% based on (*p*-bromophenyl)stibonic acid). Dec pt: 220-221°C. Crystals suitable for single crystal X-ray studies were grown from acetonitrile solution by diffusion in hexane for 1 week. Anal. Calcd for $C_{84}H_{99}O_{34}Na_2Br_{12}N_3Sb_{12}$: C, 24.25; H, 2.40; N, 1.01. Found: C, 24.18; H, 2.47; N, 1.07. IR (cm^{-1}, KBr pellet): 3380(b), 3057(w), 1909(w), 1634(m), 1562(s), 1476(s), 1377(s), 1252(m), 1182(m), 1006(s), 947(m), 810(m), 704(s), 480(m).

Compound $\{(NMe_4)_4[Na(m\text{-}Cl_2\text{-}C_6H_3Sb)_{12}(O)_{23}(OH)_7]\}$ 5.3:

(*m*-dichlorophenyl)stibonic acid, (0.150 g and 0.47 mmol) was added to a clear solution of $(NMe_4)_4OH.5H_2O$ (0.086 g and 0.47 mmol) in 30 mL of acetonitrile and a molar ratio of 1:1 respectively. Yield: 0.075 g (47% based on (*m*-dichlorophenyl)stibonic acid). The solution was stirred for 24 h at room temperature. Filtration followed by evaporation under reduced pressure furnishes a white solid. Dec pt: 230-231°C. Crystals suitable for single crystal X-ray studies were grown from acetonitrile solution by diffusion in hexane for 2 week. Anal. Calcd for $C_{88}H_{91}O_{30}NaCl_{24}N_4Sb_{12}$: C, 26.29; H, 2.28; N, 1.39. Found: C, 26.37; H, 2.35; N, 1.32. IR (cm^{-1}, KBr pellet): 3409(b), 3073(w), 1636(w), 1559(s), 1487(s), 1399(m), 1377(m), 1256(w), 1098(m), 949(s), 862(s), 789(m), 671(m), 509(m).

5.3 Results and Discussions

Synthetic methodology for synthesis of **5.1** and **5.2**: $\{(NMe_4)_2[(p\text{-}Cl\text{-}C_6H_4Sb)_{16}(O)_{30}(OH)_6]\}$ (**5.1**) and $\{(NMe_4)_3[Na_2(p\text{-}Br\text{-}C_6H_4Sb)_{12}(O)_{23}(OH)_7.4H_2O(coord)]\}$ (**5.2**) were obtained by refluxing a mixture of (*p*-halophenyl)stibonic acids with $(NMe_4)_4OH.5H_2O$ in a 1:1 molar ratio in toluene, whereas $\{(NMe_4)_4[Na(m\text{-}Cl_2\text{-}C_6H_3Sb)_{12}(O)_{23}(OH)_7]\}$ (**5.3**) was synthesized under ambident condition in a 1:1 molar ratio in acetronitrile (Scheme 5.1).



Scheme 5.1

Crystals suitable for single-crystal X-ray studies for clusters **5.1-5.3** were obtained from acetonitrile solution by diffusion by hexane. The anionic clusters **5.1** crystallize in the monoclinic space group *C2/c* (Table 5.1). The structure of 5.1 along with selected bond lengths (Å) and bond angles (°) are given in Table 5.2. The molecular structure of **5.1** reveals the formation of hexa-decanuclear organoantimony oxo clusters $\{(NMe_4)_2[(p\text{-}Cl\text{-}$

$C_6H_4Sb)_{16}(O)_{30}(OH)_6]\}$ (Figure 5.1), which contains two Sb_2O_2 and four Sb_3O_3 rings which are bridged through oxygen atom. Each Sb_3O_3 moeity was capped by a μ_3-oxygen atom. The spatial arrangement around each Sb atom is octahedral with O_5C coordination manner. In **5.1**, 36 oxo groups were present, of these 28 are μ_2-bridged, remaining eigth oxo groups are μ_3-bridged.

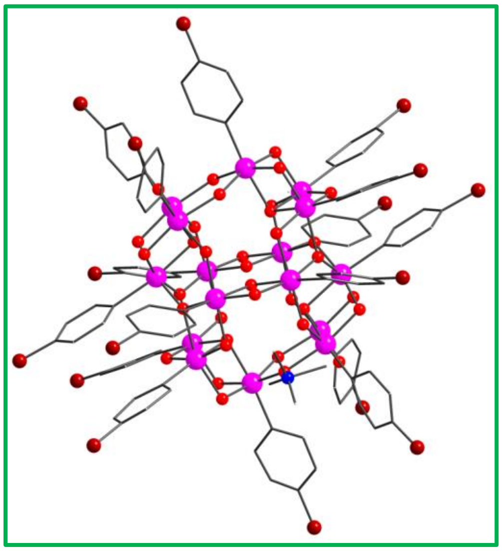
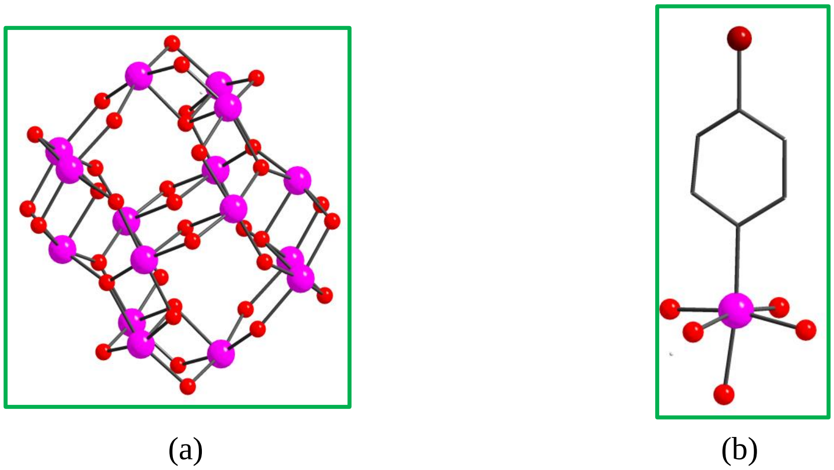


Figure 5.1: Molecular structure of **5.1.** Hydrogen atoms are omitted for clarity. Colour code: Sb magenta, N blue, O red, Cl brown.



(a) (b)

Figure 5.2: (a) Core of hexa-decanuclear cluster (b) Octahedral geometry around antimony. Colour code: Sb magenta, O red, Cl brown.

For charge neutrality concern six μ_3-bridging oxygen atoms are considered as hydroxyl groups. One molecules of (NMe_4) crystallize in the asymmetric unit; hence two molecules of (NMe_4) crystallize along with the anionic hexa-decanuclear polyoxostibonate. The Sb-O distances in the core fall in the range of 1.930(13)-2.151(12) Å. Sb-C distances fall in the range of 2.073(2)-2.132(2) Å. The bond lengths and bond angles were similar to that of previous literature.[13] The spatial arrangement around each antimony atom is octahedral with O_5C coordination (Figure 5.2 (b)).

The anionic cluster **5.2** crystallizes in the triclinic space group *P-1* (Table 5.1). The structure of **5.2** along with selected bond lengths (Å) and bond angles (°) are given in Table 5.3. The molecular structure of **5.2** reveals the formation of dodecanuclear organoantimony oxo cluster $\{(NMe_4)_3[Na_2(p\text{-Br-}C_6H_4Sb)_{12}(O)_{23}(OH)_7.4H_2O_{(coord)}]\}$ (Figure 5.4). For charge neutrality, seven oxygen atoms are considered as hydroxyl groups. Six oxygen atom will associated with the terminal O atoms as OH groups. Four H_2O molecules coordinates to sodium ions few water molecules are also present in the lattices which are poorly defined. The anionic part consists of twelve hexacoordinate *p*-Br-C_6H_4Sb groups (Figure 5.3).

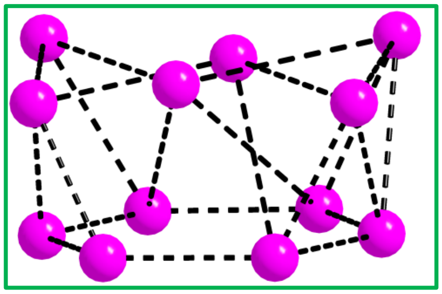


Figure 5.3: Hexagonal antiprismatic arrangement of the 12 Sb atoms in the $\{(NMe_4)_3[Na_2(p\text{-Br-}C_6H_4Sb)_{12}(O)_{23}(OH)_7.4H_2O_{(coord)}]\}$.

Out of 12 antimony atoms present, six of the antimony atoms are located in a puckered hexagonal array whose Sb---Sb nonbonding distances are in the range 3.626(12)-3.654(12) Å, while other six are arranged in a planar hexagonal array whose Sb---Sb nonbonding distances are in the range 3.131(12)-3.139(14) Å. Of the 30 oxo groups present in **5.2**, 18 are μ_2-bridging, 6 are μ_3-bridging and six are terminal. Two sodium atoms are present in the cluster **5.2**. Na(1) is 10-coordinate (Figure 5.5(a)). Planar hexagonal array of the μ_2 oxygen atoms from the puckered Sb layer occupies 6 coordination sites. Three coordination sites are occupied by μ_3 oxygen atoms which link the two antimony layer together, 10th coordination site was occupied by water molecule which is projected to the other side of the hexagon. Na(1) was incorporated within the cavity, herein the stibonate acts as an inorganic cryptand. Na(2) has a coordination number of 6 (Figure 5.5(b)), where μ_2 oxygen atoms occupy three sites and the remaining three sites were occupied by water molecules. The Sb-O distances in the core fall in the range of 1.944(9)-2.123(9) Å. Sb-C distances fall in the range of 2.105(13)-2.152(13) Å. Na-O distances fall in the range of 2.335(10)-2.883(11) Å. The bond lengths and bond angles were similar to that of previous literature.[15]

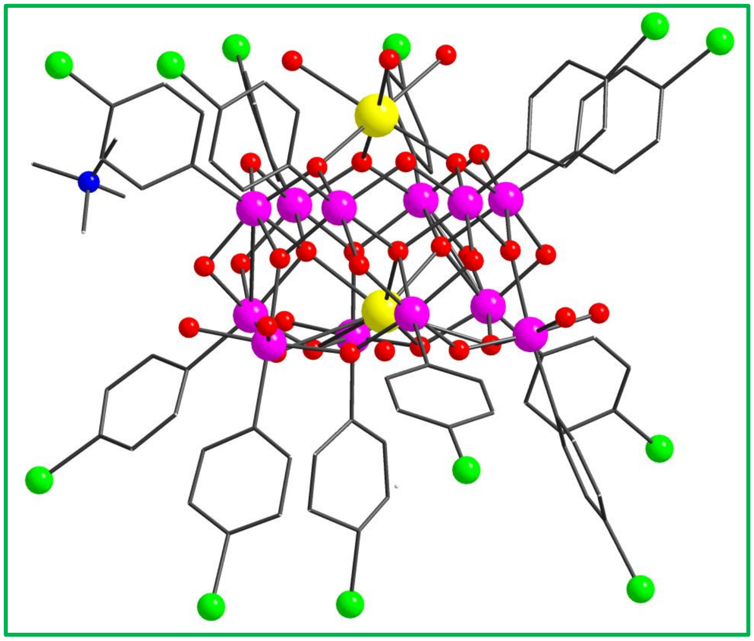
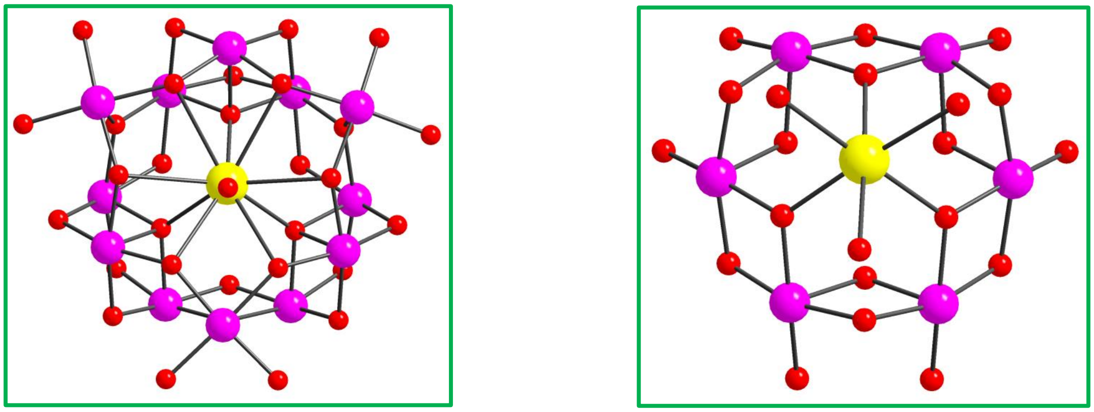


Figure 5.4: Molecular structure of **5.2.** Hydrogen atoms are omitted for clarity. Colour code: Sb magenta, N blue, O red, Na yellow, Br green.



(a) (b)

Figure 5.5: (a) Ten-coordinate Na^+(1) ion (b) Six-coordinate Na^+(2) ion. Colour code: Sb magenta, O red, Na yellow.

The anionic clusters **5.3** crystallize in the monoclinic space group *P21/n* (Table 5.1). The structure of **5.3** along with selected bond lengths (Å) and bond angles (°) are given in Table 5.4. The molecular structure of **5.3** reveals the formation of dodecanuclear organoantimony oxo clusters {$(NMe_4)_4[Na(m\text{-}Cl_2\text{-}C_6H_3Sb)_{12}(O)_{23}(OH)_7]$} (Figure 5.6). For charge neutrality concern seven oxygen atoms are considered as hydroxyl groups. Six oxygen atoms will be associated with the terminal O atoms as OH groups. Few H_2O molecules are also present in the crystal lattice which are poorly defined. The anionic part consists of twelve hexacoordinate *m*-Cl_2-C_6H_3Sb groups at the apices of a hexagonal antiprism, linked by oxygen atoms. Out of 12 antimony atoms, six of the antimony atoms are locate in a puckered hexagonal array whose Sb---Sb nonbonding distances are 3.604(11)-3.626(13) Å, while other six are arranged in a planar hexagonal array whose Sb---Sb nonbonding distances are 3.104(13)-3.139(13) Å. Of the 30 oxo groups present in **5.3**, 18 are μ_2-bridging, 6 are μ_3-bridging and six are present as terminal ones. Sodium has a coordination number of nine (Figure 5.7). Planar hexagonal array of the μ_2 oxygen atoms from the puckered Sb layer occupies 6 coordination sites. Three coordination sites are occupied from the μ_3 oxygen atoms which link the two antimony layer together. Sodium ion incorporated within the cavity which acts as an inorganic cryptand. The Sb-O distances in the core fall in the range of 1.936(12)-2.125(12) Å. Sb-C distances fall in the range of 2.113(5)-2.143(5) Å. Na-O distances fall in the range of 2.439(15)-2.867(13) Å. The bond lengths and bond angles were similar to that of previous literature.[16]

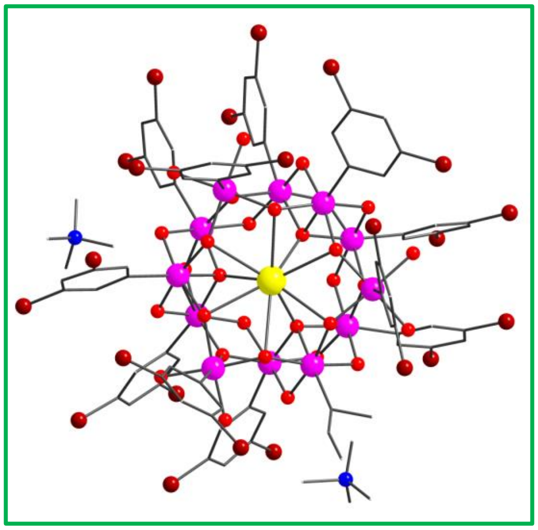


Figure 5.6: Molecular structure of **5.3.** Hydrogen atoms are omitted for clarity**.** Hydrogen atoms are omitted for clarity. Colour code: Sb magenta, N blue, O red, Na yellow, Cl brown.

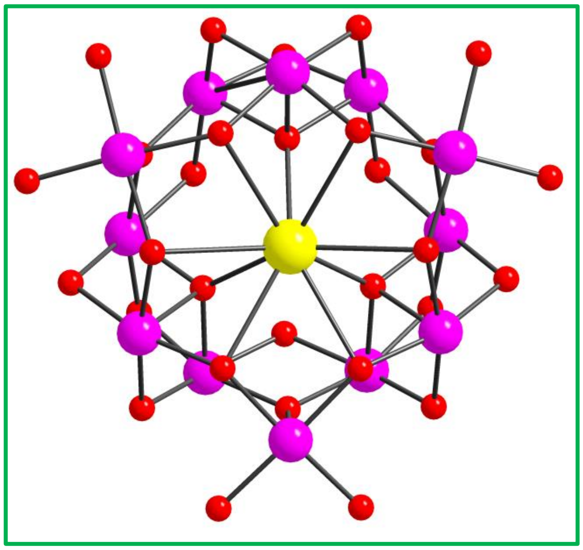


Figure 5.7: Nine-coordinate Na^+ ion. Colour code: Sb magenta, O red, Na yellow.

It should be mentioned here that though no sodium precursor was used in the synthesis of **5.2** and **5.3**, structural elucidation do reveal the presence of Na^+ ions encapsulated by the POM framework. To understand how the sodium ions have crystallized in the cluster, independent reactions using bases like NaOMe were used for the self assembly. When the solutions were kept in teflon container for crystallization, no crystals suitable for X-ray diffraction were obtained. But when the crystallization was carried out in glass vials, crystallization of **5.2** and **5.3** was possible encapsulating Na^+ ions. The only way by which sodium ions could be encapsulated in the cavity is by leaching sodium from glassware where it is present as sodium silicate. Similar observations have also been reported by Nicholson *et al* where in POM frameworks are reported.[11]

The Sb_{12} and Sb_{16} clusters synthesized shows close structural resembles to the reported POMs from our groups[13] and Nicholson group.[11] The most important in present case is the ability to synthesize organoantimony based POM in organic solvents in presence of a base. Though the clusters synthesized are similar to literature reports, a more detailed study varying bases and its stoichiometry would propably pave the way for synthesis of new types of POM frameworks. Changing reaction conditions like employing solvothermal methods would also help in achieving novel structural motifs.

5.4 Conclusion

It has been shown that isopolyoxostibonates formation takes place in alkaline solutions in organic solvents. It has to be mentioned here that in classical transition metal based POMs, self-condensation happen in acidic medium, whereas in the present case involving organoantimonates it happens in basic medium. Cluster **5.2** and **5.3** acts as an inorganic crown moiety towards sodium ion gave rise to more closed Sb_{12} frameworks.

Table 5.1: Crystal and refinement data for **5.1-5.3**

	5.1	**5.2**	**5.3**
formula	$C_{104}H_{86}Cl_{16}O_{36}N_2Sb_{16}$	$C_{88}H_{107}Br_{12}O_{35}N_5Na_2Sb_{12}$	$C_{88}H_{97}Cl_{24}O_{33}N_4NaSb_{12}$
M	4455.20	4260.68	4073.48
T(K)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073
crystal system	Monoclinic	Triclinic	Monoclinic
space group	*C2/c*	*P -1*	*P21/n*
a(Å)	32.628(3)	16.9248(11)	19.5436(19)
b(Å)	17.4439(17)	17.7636(12)	27.314(3)
c(Å)	30.748(3)	26.9751(17)	27.348(3)
α(deg)	90	72.3460(10)	90
β(deg)	115.5580(10)	76.4750(10)	92.888(2)
γ(deg)	90	65.5300(10)	90
V(Å^3)	15788(3)	6978.9(8)	14581(2)
Z	4	2	4
Dcalcd (Mg m^{-3})	1.847	2.028	1.856
***μ* (mm^{-1})**	3.019	5.789	2.690
F(000)	8264	4008	7792
θ range (deg)	1.357-25.117	1.436-25.013	1.054-25.056
index range	$-38 \leq h \leq 38$	$-20 \leq h \leq 20$	$-23 \leq h \leq 23$
	$-20 \leq k \leq 20$	$-21 \leq k \leq 21$	$-32 \leq k \leq 32$
	$-36 \leq l \leq 36$	$-31 \leq l \leq 31$	$-32 \leq l \leq 32$
no of reflections collected	72599	66674	140172
goodness-of-fit (GOF) on F^2	1.092	1.061	1.028
R1(F) (I > 2σ(I))	0.1086	0.0699	0.0702
wR2	0.2834	0.1992	0.1827
large diff. peak and hole (e Å^{-3})	4.552/-3.351	4.276/-2.712	3.150/-2.412

Table 5.2: Selected bond lengths (Å) and bond angles (º) in **5.1**

Sb(1)-C(1)	2.092(2)	Sb(5)-O(11)	1.938(13)
Sb(2)-C(7)	2.114(2)	Sb(5)-O(12)	1.948(16)
Sb(3)-C(13)	2.112(2)	Sb(6)-O(5)#	2.028(14)
Sb(4)-C(19)	2.118(2)	Sb(6)-O(10)	2.071(13)
Sb(5)-C(25)	2.132(2)	Sb(6)-O(11)	1.963(13)
Sb(6)-C(31)	2.073(2)	Sb(6)-O(16)	2.022(13)
Sb(7)-C(37)	2.121(2)	Sb(7)-O(10)	2.113(12)
Sb(8)-C(43)	2.085(3)	Sb(7)-O(12)	1.942(12)
Sb(1)-O(1)	2.094(12)	Sb(7)-O(14)	2.151(12)
Sb(1)-O(2)	1.977(13)	Sb(7)-O(15)	1.958(13)
Sb(1)-O(3)	1.983(13)	Sb(8)-O(9)#	2.142(13)
Sb(1)-O(6)	1.961(13)	Sb(8)-O(14)	2.088(12)
Sb(1)-O(16)#	2.033(14)	Sb(8)-O(15)	1.981(14)
Sb(2)-O(1)	2.082(13)	Sb(8)-O(17)	1.958(14)
Sb(2)-O(4)	1.971(13)	Sb(1)-O(1)-Sb(3)	95.2(5)
Sb(2)-O(7)	2.052(13)	Sb(1)-O(2)-Sb(2)	104.4(6)
Sb(2)-O(14)	2.065(11)	Sb(2)-O(1)-Sb(1)	97.1(5)
Sb(3)-O(1)	2.121(12)	Sb(2)-O(1)-Sb(3)	95.4(5)
Sb(3)-O(3)	1.970(14)	Sb(3)-O(3)-Sb(1)	103.8(6)
Sb(3)-O(17)	1.994(12)	Sb(3)-O(5)-Sb(6)#	137.3(8)
Sb(4)-O(6)	1.930(13)	Sb(4)-O(6)-Sb(1)	133.9(7)
Sb(4)-O(7)	2.089(13)	Sb(4)-O(9)-Sb(8)#	95.7(5)
Sb(4)-O(8)	1.998(12)	Sb(5)-O(8)-Sb(4)	106.7(6)
Sb(4)-O(9)	2.118(12)	Sb(5)-O(11)-Sb(6)	106.9(6)
Sb(4)-O(18)#	1.987(15)	Sb(6)-O(10)-Sb(7)	96.8(5)
Sb(5)-O(7)	2.135(14)	Sb(6)-O(16)-Sb(1)#	136.6(7)
Sb(5)-O(8)	1.974(13)	Sb(7)-O(10)-Sb(5)	95.3(5)
Sb(5)-O(10)	2.115(13)	Sb(8)-O(18)-Sb(4)#	106.2(6)

Symmetry transformations used to generate equivalent atoms # -x+1/2,-y+1/2,-z+1

Table 5.3: Selected bond lengths (Å) and bond angles (º) in **5.2**

Sb(1)-C(1)	2.135(17)	Sb(9)-O(19)	2.0641(8)
Sb(2)-C(7)	2.117(14)	Sb(10)-O(20)	1.982(9)
Sb(3)-C(13)	2.116(16)	Sb(10)-O(29)	1.976(8)
Sb(4)-C(19)	2.123(14)	Sb(11)-O(21)	2.074(9)
Sb(5)-C(25)	2.107(14)	Sb(11)-O(23)	2.062(9)
Sb(6)-C(31)	2.121(13)	Sb(12)-O(13)	2.057(9)
Sb(7)-C(37)	2.129(13)	Sb(12)-O(30)	1.995(9)
Sb(8)-C(43)	2.152(13)	O(4)-Na(1)	2.746(12)
Sb(9)-C(49)	2.105(13)	O(7)-Na(1)	2.800(12)
Sb(10)-C(55)	2.111(13)	O(19)-Na(1)	2.446(11)
Sb(11)-C(61)	2.138(15)	O(23)-Na(1)	2.491(12)
Sb(12)-C(67)	2.121(13)	Na(1)-O(31)	1.012(11)
Sb(1)-O(1)	1.999(10)	O(25)-Na(2)	2.335(10)
Sb(1)-O(13)	2.111(9)	O(27)-Na(2)	2.357(10)
Sb(2)-O(3)	1.948(10)	O(29)-Na(2)	2.349(9)
Sb(2)-O(16)	1.994(9)	Na(2)-O(32)	2.552(11)
Sb(3)-O(5)	1.981(12)	Na(2)-O(33)	2.594(12)
Sb(3)-O(6)	1.967(9)	Na(2)-O(34)	2.616(12)
Sb(4)-O(8)	1.961(8)	Sb(2)-O(3)-Sb(1)	137.1(5)
Sb(4)-O(18)	2.001(9)	Sb(4)-O(8)-Sb(5)	135.0(5)
Sb(4)-O(20)	1.986(10)	Sb(4)-O(7)-Sb(3)	135.7(5)
Sb(5)-O(8)	1.964(9)	Sb(6)-O(11)-Sb(5)	136.5(6)
Sb(5)-O(10)	1.954(11)	Sb(6)-O(12)-Sb(1)	136.2(5)
Sb(5)-O(21)	2.116(9)	Sb(7)-O(13)-Sb(1)	129.3(4)
Sb(6)-O(11)	1.944(9)	Sb(8)-O(15)-Sb(2)	96.9(4)
Sb(6)-O(12)	1.948(10)	Sb(9)-O(19)-Sb(4)	97.2(3)
Sb(6)-O(22)	2.026(10)	Sb(10)-O(19)-Sb(4)	97.5(3)
Sb(7)-O(13)	2.069(8)	Sb(10)-O(21)-Sb(5)	128.8(4)
Sb(7)-O(25)	1.980(9)	Sb(11)-O(29)-Sb(10)	105.7(4)
Sb(8)-O(15)	2.089(9)	Sb(12)-O(13)-Sb(1)	129.1(4)
Sb(8)-O(17)	2.059(8)	Sb(12)-O(24)-Sb(6)	104.7(4)

Table 5.4: Selected bond lengths (Å) and bond angles (º) in **5.3**

Sb(1)-C(1)	2.143(5)	Sb(8)-O(26)	1.991(15)
Sb(2)-C(7)	2.113(5)	Sb(10)-O(19)	2.078(12)
Sb(3)-C(12)	2.133(5)	Sb(10)-O(27)	1.964(11)
Sb(4)-C(18)	2.120 (3)	Sb(10)-O(21)	2.073(13)
Sb(5)-C(24)	2.135(4)	Sb(10)-O(29)	1.966(14)
Sb(6)-C(30)	2.132(4)	Sb(11)-O(21)	2.081(13)
Sb(7)-C(36)	2.123(4)	Sb(11)-O(29)	1.963(11)
Sb(8)-C(42)	2.118(4)	Sb(12)-O(23)	2.080(11)
Sb(9)-C(48)	2.139(13)	Sb(12)-O(30)	1.964(13)
Sb(10)-C(54)	2.130(13)	O(3)-Na(1)	2.867(13)
Sb(11)-C(60)	2.120(14)	O(4)-Na(1)	2.789(11)
Sb(12)-C(66)	2.119(13)	O(7)-Na(1)	2.795(15)
Sb(1)-O(1)	1.981(10)	O(8)-Na(1)	2.769(11)
Sb(1)-O(13)	2.103(13)	O(11)-Na(1)	2.860(14)
Sb(2)-O(3)	1.948(10)	O(12)-Na(1)	2.841(15)
Sb(2)-O(16)	2.009(13)	O(15)-Na(1)	2.455(11)
Sb(3)-O(5)	1.982(12)	O(19)-Na(1)	2.439(15)
Sb(3)-O(6)	1.965(12)	O(23)-Na(1)	2.481(15)
Sb(4)-O(8)	1.952(14)	Sb(2)-O(3)-Sb(1)	134.1(6)
Sb(4)-O(18)	2.010(12)	Sb(2)-O(4)-Sb(3)	135.0(5)
Sb(4)-O(20)	2.012(10)	Sb(4)-O(8)-Sb(5)	135.5(5)
Sb(5)-O(8)	1.965(10)	Sb(4)-O(7)-Sb(3)	136.0(7)
Sb(5)-O(10)	1.978(11)	Sb(6)-O(11)-Sb(5)	134.6(6)
Sb(5)-O(21)	2.107(12)	Sb(6)-O(12)-Sb(1)	135.0(5)
Sb(6)-O(11)	1.9508(11)	Sb(7)-O(13)-Sb(1)	129.6(6)
Sb(6)-O(12)	1.950 (13)	Sb(8)-O(15)-Sb(2)	97.5(6)
Sb(6)-O(22)	2.005(11)	Sb(9)-O(26)-Sb(8)	103.9(6)
Sb(7)-O(13)	2.075(13)	Sb(10)-O(19)-Sb(4)	97.0(5)
Sb(7)-O(25)	1.956(14)	Sb(11)-O(29)-Sb(12)	106.0(7)
Sb(8)-O(15)	2.065(11)	Sb(12)-O(22)-Sb(6)	104.1(6)
Sb(8)-O(26)	1.976(13)	Sb(12)-O(30)-Sb(7)	104.9(6)

5.5 References

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Future Scope of the Present Thesis

Chapter 2-5 shows depolymerization reactions of organostibonic acids in presence of protic ligands/bases and these investigations led to the isolation of novel organoantimony oxo/hydroxo clusters and isopolyoxostibonates.

Chapter 2 tetranuclear clusters have been isolated by treating organostibonic acids with phenolic oxime. These polydentate oxygen donor ligands **2.1-2.5** can be utilized as pro-ligands towards various metal ions such as transition metals and lanthanides to make polymetallic cages. Dinuclear cluster **2.6-2.10** has been isolated in this chapter by reacting organoantimony halides with phenolic oxime. Tetranuclear cluster can be achieved from dinuclear cluster on mild hydrolysis condition by dearylation of one of the phenyl group from dinuclear cluster.

Chapter 3 interesting cubane-type Sb_4O_4 framework (**3.1-3.3**) and in chapter 4 Sb_3 triangle based clusters have been isolated (**4.1-4.3**). This chemistry can be developed, by introducing some polymerizable groups on to the organoantimony or organosilanols precursors, and thus making organoantimony clusters with polymerizable groups which can be used as precursors for synthesizing new inorganic-organic hybrid framework materials. By changing the organic substituents in both precursors, it can be give rise to various novel metallosiloxanes.

Chapter 5 revealed an interesting POMs framework. Organostibonic acids have ability for self condensation in presence of alkali or acidic conditions. For example compound **5.1-5.3** were obtained by the reaction of organostibonic acids in presence of strong base (TMAH.5H_2O), led to the isolation of hexadecanuclear and dodecanuclear isopolyoxostibonates. Encapsulating cation play a vital role in templating different structures as has been proven in our case, so by using varying cations we can end-up with novel structure with varying nuclearites. Such POMs biological application like antiviral and antitumor activities can also be studied.

List of Publications

1. Organoantimony (V) Oxido Cubane Cluster $[(p\text{-X-}C_6H_4Sb)_4(O)_4(Ph_2SiO_2)_4]$ (X = Cl, Br) Stabilized by Diphenylsiloxides
   M. Santhana raj prabhu, Ananda Kumar Jami, and Viswanathan Baskar, O***rganometallics*** **2009**, 28, 3953.

2. Isolation of Tetranuclear Organoantimony Oxo Clusters and Hexa-decanuclear Polyoxostibonates Ananda Kumar Jami, **M. Santhana raj prabhu** and Viswanathan Baskar ***Organometallics*** **2010**, 29, 1137.

3. *In situ* generated polysiloxanes stabilizing μ_3-oxo bridged Sb_3 triangles
   M. Santhana raj prabhu, Uppara Ugandhar and Viswanathan Baskar.
   Dalton Trans. **2016**, DOI: 10.1039/C5DT01590A.

4. Dinuclear and Tetranuclear Organoantimony(V) Oxido clusters stabilized by dianionic ligands **M. Santhana raj prabhu** and Viswanathan Baskar. (Manuscript under preparation)

5. Isolation of high nuclearity isopolyoxostibonates using base **M. Santhana raj prabhu** and Viswanathan Baskar. (Manuscript under preparation)

Poster Presentations

1. Multinuclear Clusters of Lanthanides and Main Group Metals Bridged Through Oxo-Hydroxo Bridges.

    (i) Poster presentation **Modern Trends in Inorganic Chemistry (MTIC-XIII),** held at Indian Institute of Sciences (IISc), Bangalore, December 7-10th 2009.

    (ii) Poster presentation In 7th in-house symposium **“Chemfest-2010”** held at University of Hyderabad**,** Hyderabad, January 8-9th 2010.