Organoantimony and Organotellurium based Rings, Macrocycles and Clusters

A Thesis
Submitted for the degree of
DOCTOR OF PHILOSOPHY

By

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April, 2015

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CERTIFICATE

Certified that the work embodied in the thesis entitled **“*Organoantimony and Organotellurium based Rings, Macrocycles and Clusters*”** has been carried out by **Mr. N Kumar Srungavruksham** under my supervision and the same has not been submitted elsewhere for any degree.

Viswanathan Baskar
(Thesis Supervisor)

Dean
School of Chemistry
University of Hyderabad

Dedicated

To

My Parents

Acknowledgements

I sincerely thank my supervisor *Dr. Viswanathan Baskar* for his valuable guidance and encouragement throughout my Ph.D. career. He helped me in many ways, not only in professional front but also in personal life. He gave me so much freedom to think and I learnt many things from our friendly conversations. I also thank his family members for the moral support and the care they shown to me when I was low.

I would like to thank the former and present Dean(s), School of Chemistry, for providing best research facilities and atmosphere. I am thankful to all the faculty members of the school for their help, cooperation and encouragement at various stages.

I am thankful to Dr. K. Muralidharan and Dr. R. Balamurugan for their help in various occasions.

I also thank all the non-teaching staff of the School of Chemistry for their assistance on various occasions. I specially thank Satyanarayana garu, Vijayalakshmi madam, Turabudhin garu for their valuable support given to me to get all the NMR spectra in time. I also thank NMR Venki for his support in acquiring NMR spectra. I thank Dr. Raghaviah (Raghaviah anna) for his valuable suggestions in handling XRD machine. I would like to acknowledge DST funded National Single Crystal X-ray Diffraction Facility, UGC / UPE for providing the basic requirements and DST/UGC/CSIR for the financial support.

Here I would like to take this opportunity to thank all my teachers starting from my first standard to M.Sc. I always feel blessed to have a first teacher like Doraraju sir, who has spotted the best student in me and feel like his blessings brought me to this stage, to get a highest degree in India. I also thank my mathematics teacher Radha madam who has taken away the fear of solving problems in me and she is the responsible person to my early morning study hours in childhood days. I would like to thank my Telugu teachers starting from Venkateswarlu sir, Ramarao sir (8th-10th), Satyanarayana sir (intermediate) and Ravi sir(B.sc) for teaching me the values from mythology and from the biographies of some great personalities. They built up the moral values and good habits in me. I thank my chemistry lecturer Vamsi garu for encouraging me in chemistry subject and he gave all the freedom to do any experiment in chemistry lab, from where I got the initial excitement in doing chemistry experiments and eventually led to come all the way to here. I would also like to thank Prof. Umabala madam (M.Sc.) who treated all of us (my M.Sc. friends) like her kids. I am grateful to Prof. Jayaprakash sir (J.P sir, CSIR coaching institute). In my opinion he is THE BEST organic chemistry teacher and his teachings helped me in qualifying CSIR-NET exam and GATE exam.

Apart from all the above teachers, I also got two wonderful chemistry teachers in the form of *Bachi* (Dr. T. Udaya Bhaskar) and *Saikat Bhayya* (Dr. Saikat Sen) . I am fortunate to study my B.Sc. in S.A.S Govt. Degree College which gave me the opportunity to meet a person called Bhaskar who has made Chemistry as an addiction to me. The amount of time he spends with me and the way he taught chemistry to me is one thing that I will remember for rest of my life. Saikat Bhayya brought the more value to my time I spent here in University of Hyderabad. He is a walking Wikipedia and he is my inspiration. I learnt many things from him and always want to spend time with him. Thanks is a very small word to express my gratitude towards Bachi and Saikat bhayya.

I would like to thank all my School, B.Sc. and M.Sc. friends who have made my life joyful and colorful. On this happy occasion, I would like to remember my best buddies *Balu* and *D.P* with whom I have grown up since my childhood. We three have brought up together and their family members treated me like their own son. I am always very grateful to them.

I would also like to thank my friend's trio Sridhar, Ramana and Kishore with whom I share everything.

I thank my B.Sc. gang Sridhar, Balu, pedda Balaji, lekkala Srinu, Penki, Dharma, Vinod, Vusa Chiru, Subbu, Sitaram, Appu, Murali, Kasu, Prakash, Roja, Devi, Suseela, Siva, Sudha and other friends who have made my B.Sc. days memorable. My degree college days are the best part of my life, instead they have made it best. Thank you so much guys.

I thank my M.Sc. gang Srinu, Rama Krishna, Narayana, Chandu, Suresh, Vali, Badri, Appu, Gangadhar (Scang), Krish, Venky, Aman, Srinu(bic), Anandraj, D.P(physical), Umachakravarthy, Ashok, Bharathi, Gowry and Sowjanya and other friends. I thank all of them for their sweet friendship.

I don’t have words to express my gratitude to my best friends *Srinu*, *Shuvra* (Potti), *Ramakrishna*, *Suresh*, *Narayana* and *Naidu* (Sunny) without whom my life would have been miserable here. They stood by me in all my tough times and I share my best time with them in my life. I can never forget their love and affection and they will be in my memories for the rest of my life.

A special thanks to my wonderful gifted sister Hina. I am always part of her prayers and you will always be in my thoughts too Sis. Thanks for treating me like own brother.

I would like to thank my beloved seniors Anji anna, Anand anna, Balu anna, Santhosh anna, Ajay anna, Kishore anna, Gupta anna, Bharat anna, Nagaraju anna, Nagarjuna anna for their guidance and encouragement throughout my Ph.D. career.

I would like to thank my mess table buddies Chandu, Ashok, Sunil, Sashi, Murali, Bharani, Ramana, Ramaraju and other friends. Their company made the mess food so tasty and I am going to miss the funny discussions we have all the time at mess.

I would like to thank Vikranth and other 200 not out team mates for giving me beautiful memories in the cricket ground. I suppressed all my work burden and stress by playing cricket with these guys and I am very thankful to them.

I am very much grateful to University of Hyderabad. It provided me the best and world class facilities and peaceful environment to achieve my dream degree. I am going to miss this beautiful place; it will always be in my memories.

Dedicating this thesis to my parents is a small gesture of gratitude to them and they are far beyond all the acknowledgements. I always pray my LORD SHIVA to give them a healthy and peaceful life.

Nagarjuna (Arjun).

Contents

INTRODUCTION

Chapter 1

Introduction

Several organotellurium and organoantimony compounds have been used as starting precursors during the course of my Ph.D. work. Hence introduction of my thesis is mainly focussed on different methods of preparation of various organotellurium and organoantimony compounds followed by a brief literature survey on the reactivity of the corresponding starting precursors.

1.1 Organotellurium Compounds:

Tellurium, which belongs to group 16 of the periodic table was first discovered by F. J. Müller von Reichenstein in 1782. Since its discovery, it had been widely thought of as an alloy of bismuth and antimony. But later, M. H. Klaproth had concluded that the metal had its own unique properties and he named it "*tellurium*" which was derived from a latin word *tellus*, meaning earth. The first organotellurium compound, diethyl telluride was prepared by Wöhler in 1840.[1] After this initial work, the organotellurium chemistry remained inactive for several years. Only a few investigations were attempted during the next 70 years. This was mainly due to the dreadful reputation of organotellurium compounds that were known for their foul-smell, air and light sensitivity and handling difficulties.[2] However, it was proved later that only few compounds (for example, alkyl, benzyl and allyl tellurides) were inherently unstable and as far as the foul-smell was concerned, it was shown that organotellurium compounds were no worse than their respective organosulfur or organoselenium analogues. Divalent organotellurium compounds containing less than seven or eight carbons only were found to have penetrating odour and remaining compounds were found to be very stable and easy to handle in normal laboratory conditions.[3]Lederer, with his fruitful synthetic efforts produced large number of aromatic tellurium compounds in the decade between 1910 and 1920. Since then, there has been a growing interest in organotellurium chemistry and eminent scientists like Morgan, Nesmeyanov, Rheinboldt, Petragnani, Irgolic, Zingaro, Schumann, Engman etc. have explored new avenues in this area. However compared to organosulfur and organoselenium chemistry, organotellurium chemistry is less explored.[4]

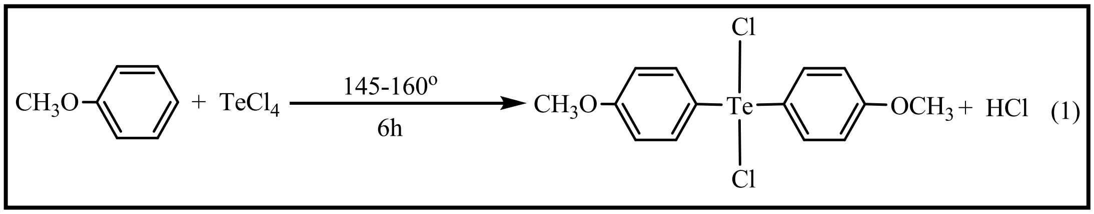
The synthetic applications of organoselenium chemistry prompted development in organtellurium chemistry and in the initial stages the synthetic applications of organotellurium compounds were pursued as an extension of the well-established organoselenium chemistry. But later it was understood that tellurium compounds had their own unique properties and resulted in spectacular transformations in organic chemistry that cannot be met by other reagents. Several applications of organotellurium compounds in synthetic organic chemistry reported so far include carbon-carbon bond formation reactions, oxidation and reduction reaction of many organic compounds and as reagents in many cross-coupling reactions along with other transition metal complexes. Huge number of publications has been published in this field till date. Engman reported first review in 1985 regarding synthetic applications of organotellurium compounds.[5] Later Petragnani and co-workers published consecutive reviews which include the very recent review in 2005.[6]

1.2 Preparation of organotellurium compounds:

Most of the organotellurium compounds were prepared by using Te powder or $TeCl_4$ as starting materials. Generally, aliphatic tellurium compounds are less stable, foul-smelling and difficult to handle in the laboratory conditions when compared to aromatic tellurium compounds. Herein, described are few important preparative methods that were followed for the synthesis of organotellurium compounds.

1.2a Diorganotellurium dichlorides (R_2TeCl_2):

Tellurium tetrachloride reacts with excess amount (6 equivalents) of aromatic compounds bearing activating groups (e.g., RO-, R_2N-, RS- : R = aromatic group) and results in the formation of organotellurium trichlorides (at room temperature)/ diorganotellurium dichlorides (at elevated temperatures) (1) [Note: number in parenthesis represents reaction number].[7] It is a solvent-less method and excess aromatic compound can be separated using high vacuum. Tellurium tetrachloride acts as an electrophilic reagent in this reaction. Less reactive aromatic compounds such as benzene and toluene require high temperatures along with a Lewis acidic catalyst like $AlCl_3$.



(1)

The cleavage of Pb-C bond (2) facilitates the formation of diorganotellurium dihalides when tetraphenyllead reacted with tellurium tetrachloride in aromatic solvents at ambient conditions.[8] The yields of diorganotellurium dihalides in this reaction were excellent and separation of the product also relatively easier as diorganotellurium dihalides dissolve in the aromatic solvent used for the reaction whereas diorganolead dihalides are insoluble.

$$(C_6H_5)_4Pb + TeCl_4 \xrightarrow[\text{room temp}]{\text{benzene/toulene}} (C_6H_5)_2TeCl_2 + (C_6H_5)_2PbCl_2 \quad (2)$$

The cleavage of Sn-C bond also facilitates the formation of diorganotellurium dihalides when tetraphenyltin was treated with tellurium tetrachloride in toluene.[9] But reflux condition has to be maintained to get the diorganotellurium dihalides (4) . The organotellurium trichlorides can be obtained at room temperature (3).

$$(C_6H_5)_4Sn + TeCl_4 \xrightarrow[\text{room temp}]{\text{toulene}} C_6H_5TeCl_3 + (C_6H_5)_3SnCl \quad (3)$$

$$(C_6H_5)_4Sn + TeCl_4 \xrightarrow[\text{reflux}]{\text{toulene}} (C_6H_5)_2TeCl_2 + (C_6H_5)_2SnCl_2 \quad (4)$$

Diorganotellurium dihalides can also be prepared by reacting Te powder or $TeCl_4$ with organometallic reagents like RMgX, RHgCl, RLi or $RN_2^+Cl^-$, $R_2I^+Cl^-$. But often these methods suffer from less yields and formation of other side products like diorganyl tellurides, diorganyl ditellurides or organotellurium trihalides. Tellurium tetrachloride is always preferable as starting precursor since tetrabromide or tetraiodide do not participate in condensation reactions as easily as tetrachloride. Heavier dihalides can be prepared by halogenating the diorganotellurides which are obtained by reduction of diorganotellurium dichlorides.[4]

1.2b Organotellurium trichlorides ($RTeCl_3$):

As discussed above (1), activated aromatics react with tellurium tetrachloride in 1:1 mole ratio and results in the formation of organotellurium trichlorides. However, less reactive aromatics will not give the desired products by this method. In this case reaction of tellurium tetrachloride with aryl mercury chlorides yield the aryl tellurium trichlorides (5).[10] Aryl boronic acids were treated with tellurium tetrachloride in refluxing nitromethane to yield aryltellurium trichlorides (6).[11]

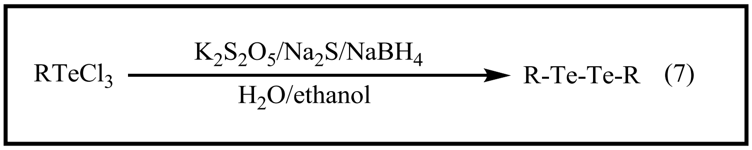
$$\mathrm{R\text{-}HgCl + TeCl_4 \xrightarrow[\text{reflux}]{\text{dioxane}} RTeCl_3 + HgCl_2} \qquad (5)$$

$$\mathrm{RB(OH)_2 + TeCl_4 \xrightarrow[\text{reflux}]{\text{nitromethane}} RTeCl_3} \qquad (6)$$

Recently a solventless reaction has also been reported for the preparation of aryltellurium trichlorides by treating tellurium tetrachloride with corresponding activated aromatic compound.[12]

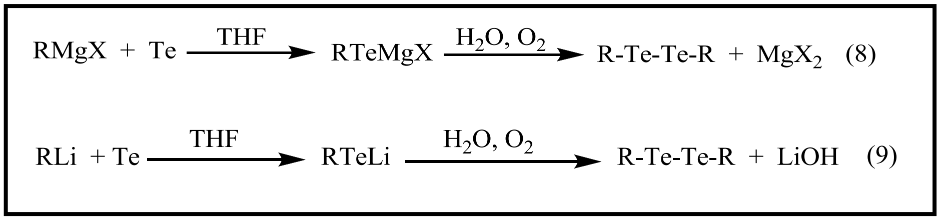
1.2c Diorgano ditellurides (R_2Te_2):

Most of the diorgano ditellurides are prepared by reduction of organotellurium trihalides. Potassium disulfite or sodium sulphide or sodium borohydride can be used as reducing agents (7).[4, 13]



$$RTeCl_3 \xrightarrow[H_2O/ethanol]{K_2S_2O_5/Na_2S/NaBH_4} R\text{-}Te\text{-}Te\text{-}R \quad (7)$$

Aromatic Grignard reagents (8) or aryl lithium (9) compounds react with elemental tellurium in the presence of oxygen to give diorgano ditellurides in quantitative yields.[14]

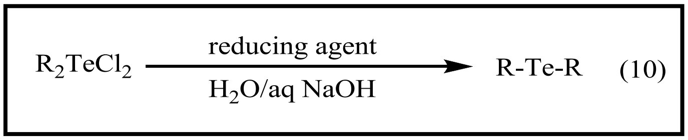


$$RMgX + Te \xrightarrow{THF} RTeMgX \xrightarrow{H_2O,\ O_2} R\text{-}Te\text{-}Te\text{-}R + MgX_2 \quad (8)$$

$$RLi + Te \xrightarrow{THF} RTeLi \xrightarrow{H_2O,\ O_2} R\text{-}Te\text{-}Te\text{-}R + LiOH \quad (9)$$

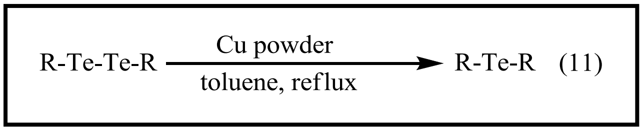
1.2d Diorgano tellurides (R_2Te):

Most of the diorganotellurides are prepared by reduction of diorganotellurium dihalides. Potassium disulfite, sodium hydrogen sulphite or sodium sulfite, sodium thiosulfate, sodium ascorbate, lithium aluminium hydride and zinc dust in glacial acetic acid are the common reducing agents used in this method (10).[4]



$$R_2TeCl_2 \xrightarrow[H_2O/aq\ NaOH]{reducing\ agent} R\text{-}Te\text{-}R \quad (10)$$

Diorganotellurides can also be prepared by the cleavage of Te-Te bond of diarylditellurides with help of freshly prepared electrolytic copper in refluxing toluene (11).[15]



$$R\text{-}Te\text{-}Te\text{-}R \xrightarrow[toluene,\ reflux]{Cu\ powder} R\text{-}Te\text{-}R \quad (11)$$

1.2e Diorganotellurium oxides (R_2TeO):

Hydrolysis of diorganotellurium dihalides in aqueous NaOH solution (2N or 5%) gives diorganotellurium oxides. Small amount of ethanol can be added to the reaction mixture to improve the solubility (12).[16]

$$R_2TeCl_2 \xrightarrow[\text{reflux}]{\text{aq NaOH, ethanol}} R_2TeO \quad (12)$$

Oxidation of diorganotellurides with positive halogenating species like N-bromo-succinamide (NBS), N-chloro-succinamide (NCS) or *tert*-butyl hypochlorite under non-aqueous conditions followed by alkaline hydrolysis gives diorganotellurium oxides in quantitative yields (13).[17]

$$R_2Te \xrightarrow[\substack{\text{at } 0^{O}\text{C} \\ \text{2) 10\% aq NaOH/NaHCO}_3}]{\substack{\text{NCS/NBS/t-BuOCl} \\ \text{1) methanol/dichloromethane(1:1)}}} R_2TeO \quad (13)$$

1.2f Diorgano tellurones (R_2TeO_2):

Diorgano tellurones can be prepared by the oxidation of diorgano telluroxides or diorgano tellurides with sodium periodate or sodium hypochlorite as an oxidant. The solution of telluride or telluroxide in ethanol was treated with aqueous solution of sodium periodate or sodium hypochlorite at room temperature to yield the corresponding diorgano tellurone in excellent yields (14).[18]

$$R_2Te/R_2TeO \xrightarrow[\text{ethanol, at room temp}]{\text{aq NaIO4/NaOCl}} R_2TeO_2 \quad (14)$$

1.3 Structural aspects of diorganotellurium dihalides / diorganotellurium oxides:

Solid state molecular structures of R_2TeCl_2 (R= alky, aryl) exhibits distorted trigonal-bipyramidal geometry around tellurium with chlorine atoms occupying axial positions and stereo chemically active lone pair and two carbon atoms occupying the equatorial positions. But if we also consider the secondary Te…Cl interactions into account, the geometries around Te changes based on the steric demand of organic substituent present on Te. Ph_2TeCl_2 have one Te…Cl interaction in its solid state structure giving a distorted octahedral geometry around Te with sixth position vacant. (p-$MeC_6H_4)_2TeCl_2$ attains distorted pentagonal bipyramidal structure with two primary Cl atoms occupying axial positions (Figure 1).[19]

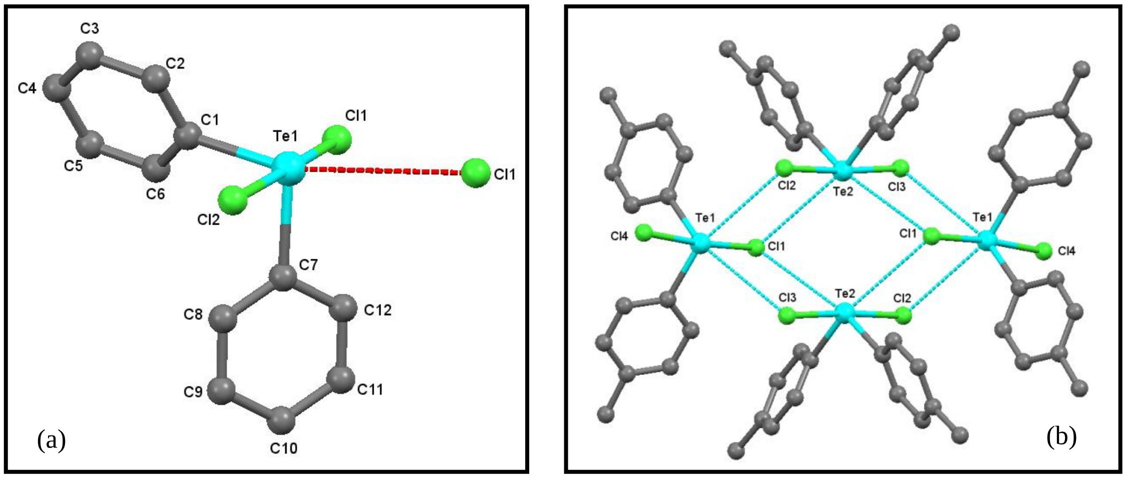


Figure 1: Solid state structures of (a) Ph_2TeCl_2 and (b) $(4\text{-}MeC_6H_4)_2TeCl_2$ showing Te…Cl interactions.

Diorganotellurium oxides R_2TeO (R= aryl) form different structural patterns in solid state based on the aryl group present on the Te. The solid state structure of Ph_2TeO represents a dimer where, two monomers [average Te-O 1.89(1) Å] are linked by short Te…O bonds [average Te-O 2.55(1) Å] that are further associated by longer Te…O bonds [average Te-O 3.77(1) Å]. By considering all these secondary Te…O interactions into account, each Te atom attains a distorted square-pyramidal geometry (Figure 2a).

In contrast to this structure, (p-$MeOC_6H_4)_2TeO$ exists as polymeric chain that contains a zigzag Te-O backbone without any Te…O secondary interactions (Figure 2b). By considering stereo chemically active lone pair into account, Te attains distorted trigonal-bipyramidal geometry with two O atoms occupying axial positions.[16, 20]

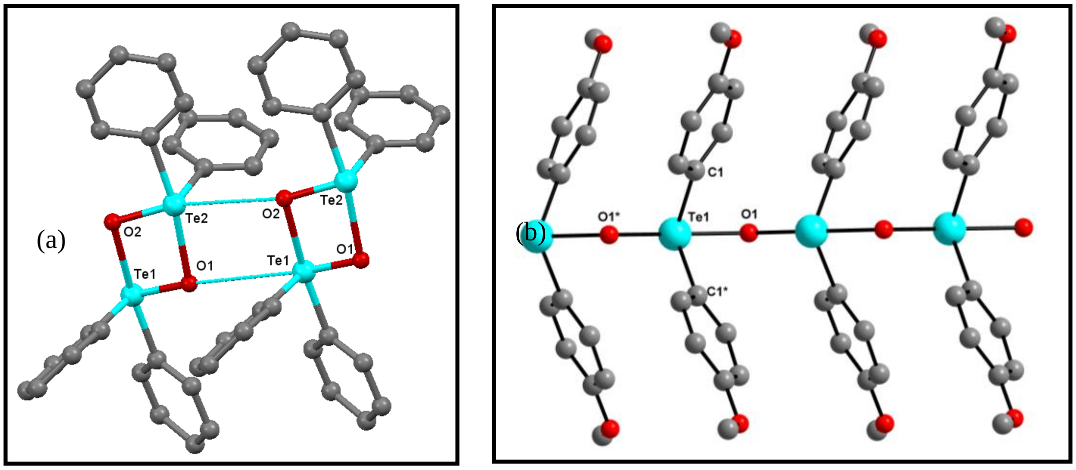


Figure 2: Solid state structures of (a) Ph_2TeO and (b) $(4\text{-}OCH_3\text{-}C_6H_4)_2TeO$.

1.4 Reactions of diorganotellurium dihalides:

1.4a Reactions of diorganotellurium dihalides with thiocarbamates and thiophosphates:

In 1988, Dakternieks et al. reported the molecular structures of $C_8H_8Te(S_2CNEt_2)_2$ (Figure 3a), $C_8H_8Te[S_2P(OEt)_2]_2$ and $C_8H_8Te(S_2COEt)_2$ by treating $C_8H_8TeI_2$ with corresponding sodium salts of ethylene-bis-dithiocarbamate (Etdtc), dithiophosphate (Etdtp) and dithioxanthate (Etxan) respectively, in dichloromethane at room temperature. They showed that dithiocarbamate complex is monomeric in solid state whereas dithiophosphate and dithioxanthate complexes have additional Te-S interactions and form polymeric and dimeric structures respectively, in solid state. With the help of solution ^{125}Te NMR they claimed that the solid state structures of all these complexes were retained in solution too.[21] In another report they had treated orthotelluric acid, $Te(OH)_6$ with $C_8H_8TeI_2$ and dithiphosphate (Etdtp) in 1:6:6 mole ratio in DMF followed by hydrolysis in water, which, yielded a mixed valent Te^{VI}/Te^{IV} compound $Te^{VI}[OTe^{IV}(C_6H_8)(S_2P(OEt)_2)]_6$. This was the first mixed valent Te^{VI}/Te^{IV}

compound prepared under very mild conditions and using solution state ^{125}Te NMR studies, they had proved that secondary interactions that were present in solid state structure persisted in solution too.[22]

In yet another report Dakternieks et al. treated Ph_2TeCl_2 with sodium salts of dithiocarbamate (Etdtc), dithiophosphate (Etdtp) and dithioxanthate (Etxan) in toluene at -40°C resulting in the formation of $Ph_2Te(S_2CNEt_2)_2$, $Ph_2Te[S_2P(OEt)2]_2$ (Figure 3b) and $Ph_2Te(S_2COEt)_2$, respectively. They found that these complexes were unstable in dichloromethane and decomposed to Ph_2Te and $(Etdtc)_2$/$(Etdtp)_2$/$(Etxan)_2$.[23]

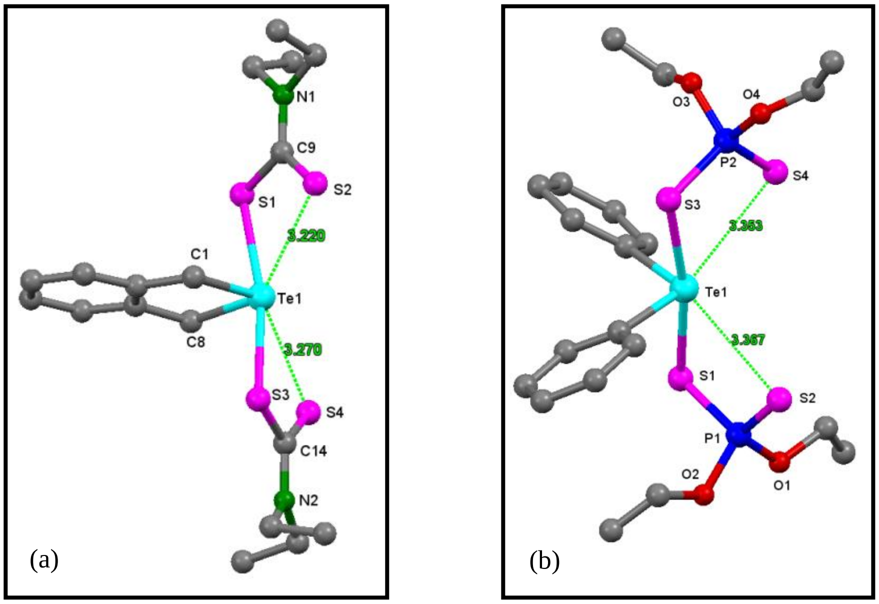


Figure 3: (a) Solid state structure of $C_8H_8Te(S_2CNEt_2)_2$. (b) Solid state structure of $Ph_2Te[S_2P(OEt)_2]_2$

In 1994, Drake and co-workers reported monothiocarbamate derivatives of dimethyltellurium(IV). They had obtained $Me_2Te[SCONR_2]_2$, where $NR_2 = NEt_2$ (Figure 4a), $N(CH_2)_3CH_2$, $N(CH_2)_4CH_2$, by treating Me_2TeCl_2 with two moles of corresponding sodium salt of monothiocarbamate in carbon disulfide at room temperature.

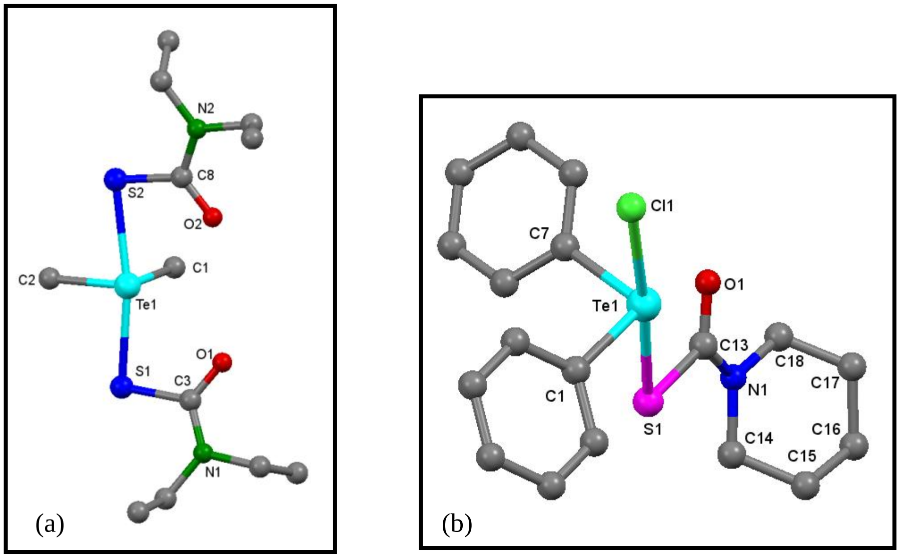


Figure 4: (a) Solid state structure of $Me_2Te[SCONEt_2]_2$. (b) Solid state structure of $Ph_2TeCl[SCONCH_2(CH_2)_3CH_2]_2$.

They also prepared $Me_2TeX[SCONR_2]_2$, where X = Cl, Br, I, by reacting equimolar amounts of appropriate sodium salt of monothiocarbamate and dimethyltellurium dihalide in dichloromethane at room temperature. As a continuation of this work they later reported $Ph_2Te[SCONR_2]_2$ and $Ph_2TeX[SCONR_2]_2$ (Figure 4b) by following the same procedure except the reaction temperatures, here the reaction was carried out at 0°C. In contrast to the monothiocarbamate derivatives of dimethyltellurium(IV), derivatives of diphenyltellurium(IV) were found to be unstable in dichloromethane/carbon disulfide at room temperature and they were also reported to undergo disproportion, reductive elimination to form Ph_2Te and $[SCONR_2]_2$.[24]

1.4b Reactions of diorganotellurium dihalides with carboxylates:

Petragnani et al. reported the reactions of diorganotellurium dihalides with silver carboxylates in refluxing benzene which resulted in the formation of diorganotellurium carboxylates (15).[25] These compounds were also prepared by passing diorganotellurium dihalides through an anion exchange resin in which OH⁻ ions were previously replaced with carboxylate ions.

$$R_2TeCl_2 + 2\ R'CO_2Ag \xrightarrow{\text{benzene}} R_2Te(O_2CR')_2 + 2AgCl \qquad (15)$$

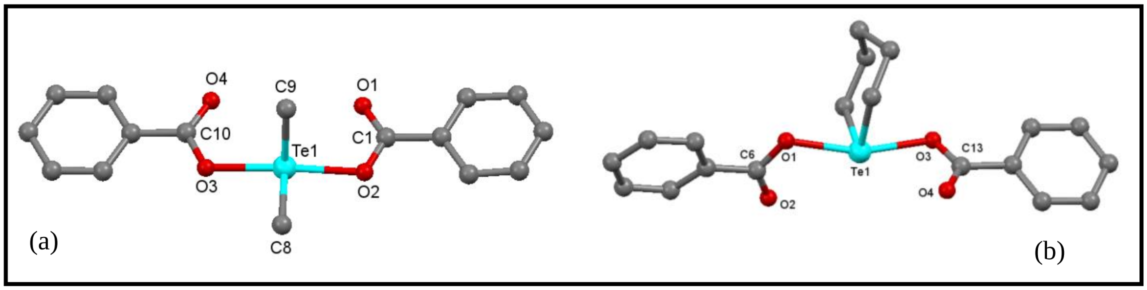


Figure 5: (a) Solid state structure of $Me_2Te[OCOC_6H_5]_2$. (b) Solid state structure of $C_5H_{10}Te[OCOC_6H_5]_2$.

Srivastava and co-workers reported the reactions of acyclic/cyclictellurium dihalides with freshly prepared silver carboxylates to yield corresponding tellurium dicarboxylates (Figure 5).[26] Recently Chandrasekhar et al. reported the reactivity of diorganotellurium dichloride with ferrocenedicarboxylic acid resulting in the formation of a 16-membered tellurium containing macrocycle (Figure 6).[27]

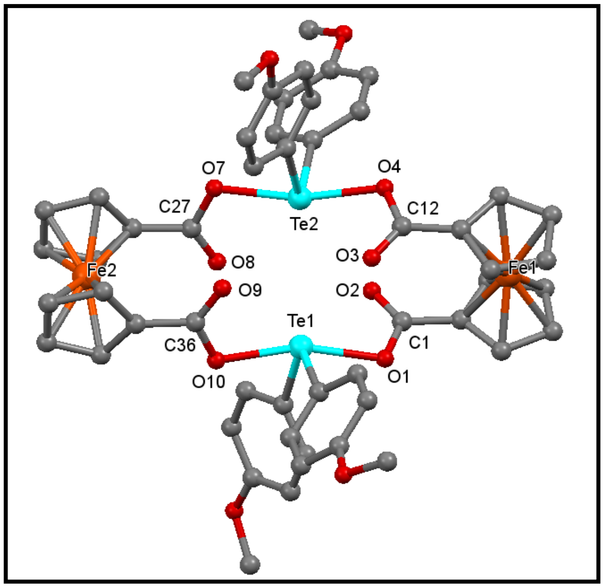


Figure 6: Solid state structure of $[R_2TeL]_2$; R=(4-CH_3O-C_6H_4), LH_2=1,1′-ferrocenedicarboxylic acid.

1.4c Reaction of diorganotellurium dihalide with platinum (II) complex:

In an interesting work, Puddephatt et al. reported the oxidative addition of Ph_2TeCl_2 to a dimethylplatinum(II) complex (Figure 7).

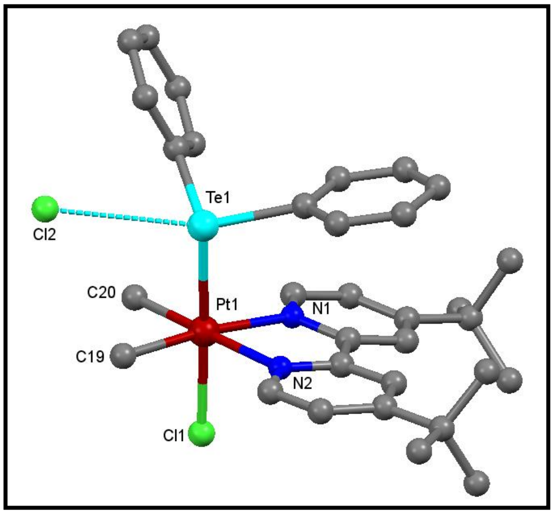


Figure 7: Solid state structure of $[PtClMe_2(TePh_2Cl)(bu_2bpy)]$.

It was known that dialkyl/diaryl tellurides or telluro ethers can form Te-metal bond with many transition metal atoms. But this was the first example that demonstrated the oxidative addition of tellurium-halide bond to a transition metal complex, although oxidative addition of Te-C/Te-M (M= Si, Ge, Sn) were previously reported.[28] In a typical experiment, 1:1 mole ratio reaction of Ph_2TeCl_2 with $[PtMe_2(bu_2bpy)]$ in dichloromethane at room temperature yielded $[PtClMe_2(TePh_2Cl)(bu_2bpy)]$. This product was the result of the trans oxidative addition of Te-Cl bond to platinum(II) complex.[29]

1.4d Reaction of diorganotellurium dihalide with phosphinates

Chandrasekhar et al. reported the reactivity of bis(p-methoxyphenyl)tellurium dichloride with 1,1,2,3,3-pentamethyltrimethylenephosphinic acid in presence of triethylamine base which resulted in the formation of a chloride capped 12-membered tellurium containing macrocycle $[((p\text{-}MeOC_6H_4)_2Te)_2(\mu\text{-}O)(\mu\text{-}cycPO_2)(\mu_4\text{-}Cl)]_2$ (Figure 8).

Although transition metal containing macrocyclic hosts for halides were reported earlier, this was the first report of inorganic tellurium containing macrocycle that could behave as host for halide ions. This macrocycle stabilized the halide ions through Te-halide interactions and with the help of ESI-MS they claimed that these secondary interactions existed in solution too.[30]

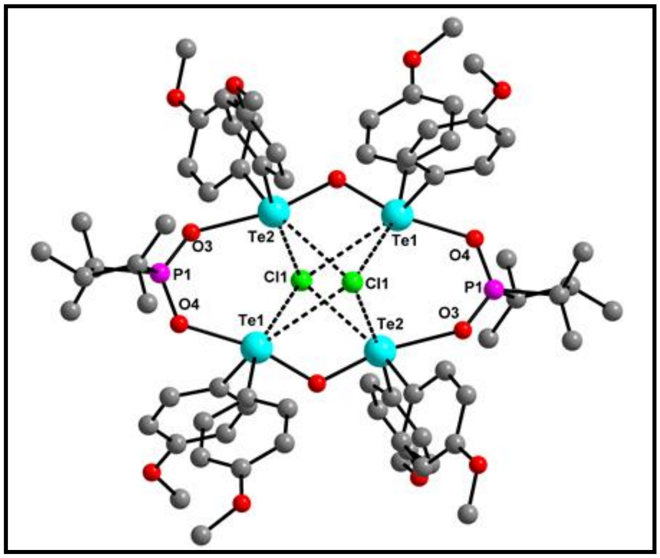


Figure 8: Solid state structure of $[((p\text{-}MeOC_6H_4)_2Te)_2(\mu\text{-}O)(\mu\text{-}cycPO_2)(\mu_4\text{-}Cl)]_2$.

1.5 Reactions of diorganotellurium oxides:

1.5a Reactions of diorganotellurium oxides with Sb(V)/Sn(IV)/Ti(IV) chlorides:

R. K. Chadha et al. in 1981 explored the Lewis base behaviour of diphenyltellurium oxide. They treated the solutions of diphenyltellurium oxide in chloroform with the solutions of Sb(V)/Sn(IV)/Ti(IV) chlorides in the same solvent in 1:1 mole ratio which resulted in a white unidentified precipitate thrown out from the solution. Filtration followed by the slow evaporation of the filtrate gives diphenyltellurium dichloride as crystalline product. This clearly indicates that diphenyltellurium oxide not only acts as Lewis base but also reacts with strong Lewis acids in the manner described below (16).[31]

$$(C_6H_5)_2TeO \; + \; MCl_n \xrightarrow{\text{chloroform}} (C_6H_5)_2TeCl_2 \; + \; MOCl_{n-2} \qquad (16)$$

$$M = Sb(V)/Sn(IV)/Ti(IV)$$

Other metal chlorides like Co(II), Ni(II) and Sn(II) chlorides did not behave as chlorinating agents for diphenyltellurium oxide. Organotellurium trichlorides formed 2:1 addition products with diphenyltellurium oxide.

1.5b Reactions of diorganotellurium oxide with protic acids:

As mentioned above diorganotellurium oxides are basic in nature and several reactions with protic acids have been reported by various groups. Alcock et al. in 1982 reported the reactivity of diphenyltellurium oxide with nitric acid. They did the reaction by dissolving the diphenyltellurium oxide in hot water- concentrated nitric acid mixture followed by repeated heating and cooling that yielded $Ph_2Te(NO_3)_2$ crystals.[32] In 2005, Beckmann et al. investigated the reactivity of $(p\text{-}MeOC_6H_4)_2TeO$ with both triflic acid and diphenylphosphinic acid. In both the cases they found the formation of dicationic tetraorganoditelluroxane moiety $[R_2TeOTeR_2]^{2+}$ stabilized by two triflate or phenylphosphinate ions with secondary Te-O interactions in the solid state crystal structure (Figure 9).[33]

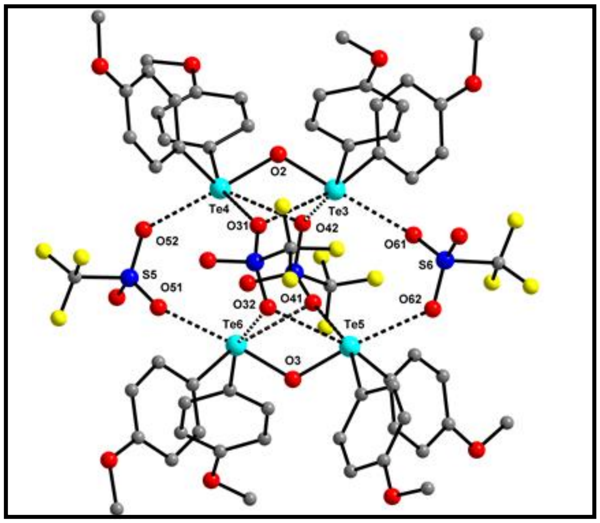


Figure 9: Solid state structure of $(F_3CSO_3)\ R_2TeOTeR_2\ (F_3CSO_3)$, R = $p\text{-}MeOC_6H_4$.

Chandrasekhar's group has been working on reactivity of diorganotellurium oxides with various carboxylic acids. In 2008, they reported the preparation of diorganotellurium ferrocenecarboxylates [$R_2Te(O_2CFc)_2$, R = *p*-$OMeC_6H_4$, *p*-$NMe_2C_6H_4$, Fc = ferrocene] by treating corresponding diorganotellurium oxides with ferrocene carboxylic acid.[34] These compounds showed quasireversible and irreversible redox behaviour at +0.62 and +1.17 V respectively. In another report, they had treated (*p*-$MeOC_6H_4)_2TeO$ with various pyridine carboxylic acids to obtain different organotelluroxane moieties depending on the stoichiometry of the reactants and reaction conditions used. They observed interesting Te-O secondary interactions in some of these compounds which lead to the formation of supramolecular assemblies in the solid state.[35] They also investigated the reactivity of (*p*-$MeOC_6H_4)_2TeO$ with various functionalized carboxylic acids [Pyridine (Figure 10b), pyrazole (Figure 10a), trioazole and Schif base containing carboxylic acids] to form mononuclear organotelluroxane motifs containing multiple coordinating sites.[36]

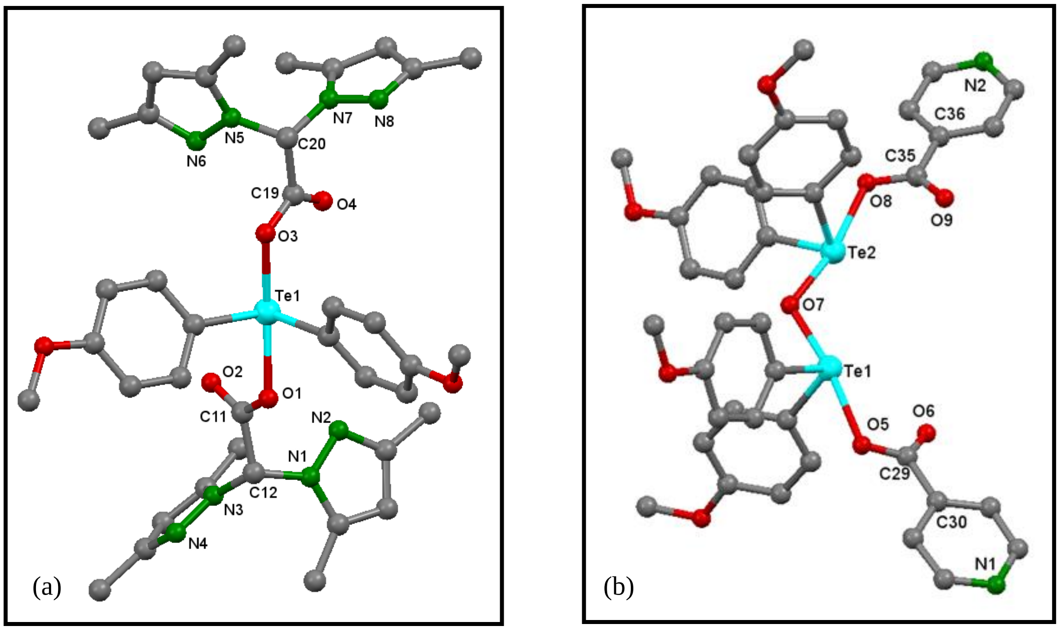


Figure 10: Solid state structures of (a) $R_2Te(O_2CR')_2$ and (b) $R_2Te(O_2C\text{-}C_4H_4N)_2$ where R = *p*-$MeOC_6H_4$, R' = 3,5-dimethyl pyrazole.

1.5c Reactions of diorganotellurium oxide with silanols:

In 2007, Beckmann's group investigated the condensation reaction of t-$Bu_2Si(OH)_2$ with (p-$MeOC_6H_4)_2TeO$ in 1:1.2 mole ratio that resulted in the formation of 12-membered tellurasiloxane ring *cyclo*-[(p-$MeOC_6H_4)_2TeOSi$*t*-$Bu_2O]_3$ (Figure 11). Larger Si/Te precursor ratio reactions resulted in the formation of open-chain tellurasiloxanes which were identified by solution ^{29}Si and ^{125}Te NMR studies.[37]

Later in 2009, Chandrasekhar's group had also investigated the reactivity of diorganotellurium oxides [(p-$MeOC_6H_4)_2TeO$/(p-$NMe_2C_6H_4)_2TeO$] with t-$BuSi(OH)_3$ / tetrahydroxy-1,3-disiloxane / disiloxane-1,3-diol $[Ph_2Si(OH)]_2O$ at varying stoichiometries giving rise to tellurasiloxane containing cages / ring compounds. Interestingly one of the cage structures is reminiscent of secondary building unit framework found in Zeolites.[38]

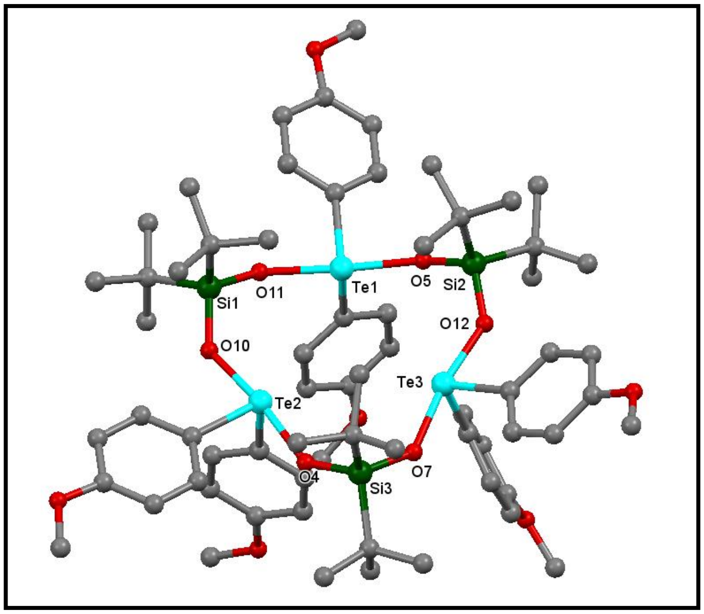
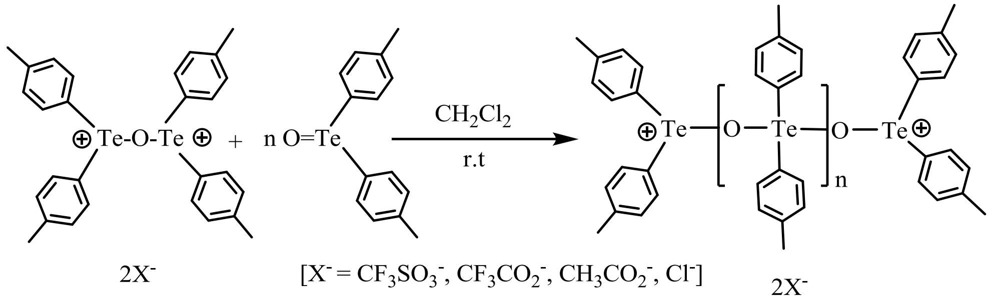


Figure 11: Solid state structures of *cyclo*-[(p-$MeOC_6H_4)_2TeOSi$*t*-$Bu_2O]_3$.

1.5d Reactions of diorganotellurium oxide with ditelluroxanes:

In 1988, Kobayashi et al. reported that tellurium atoms in ditelluroxanes ($R_2TeOTeR_2$) exhibit cationic character in solution. Further they treated these ditelluroxanes with nucleophiles like diorganotellurium oxides to produce oligotelluroxanes. The reaction of the ditelluroxanes $[Ar_2TeOTeAr_2]^{2+}[X]^{2-}$ (Ar = p-tolyl, X = CF_3SO_3, CF_3CO_2, CH_3CO_2, Cl) with one, two, three, or four equivalents of di(p-tolyl)telluroxide yielded tritelluroxane, tetratelluroxane, pentatelluroxane and hexatelluroxane, respectively. These oligotelluroxanes could be converted to diorganotellurium oxides by treating with aqueous NaOH (17).[39]



(17)

1.5e Diorganotellurium oxides as oxygen transfer reagents:

Diorganotellurium oxides have been used as mild and selective oxidising reagents for several organic substrates.[40] Phosphines can be converted to phosphine oxide by treating with di(*p*-anisyl)tellurium oxides (18). Similarly thiocarbonyl compounds can be transformed to their corresponding oxo analogues (19). In both the reactions di(*p*-anisyl)telluride is the by-product which can be easily separated by column chromatography.[41]

$$R_3P + (p\text{-OMe-}C_6H_4)_2TeO \xrightarrow{CHCl_3} R_3P{=}O + (p\text{-OMe-}C_6H_4)_2Te \quad (18)$$

$$R_2C{=}S + (p\text{-OMe-}C_6H_4)_2TeO \xrightarrow{\text{methanol}} R_2C{=}O + (p\text{-OMe-}C_6H_4)_2Te \quad (19)$$

Diorganotellurium oxides' ability to act as oxygen transfer reagents for various transition-metal carbonyl complexes have been reported.[42]The mechanism of this reaction involves nucleophilic attack by O atom of Te-O bond on the C atom of M-CO bond and simultaneous bond breakages between M-CO and Te-O. The reaction of $Cr(CO)_6$ with $(p\text{-MeO-}C_6H_4)_2TeO$ in the presence of pyridine as an entering ligand afforded $Cr(CO)_5py$ and $(p\text{-MeO-}C_6H_4)_2Te$ with release of CO_2 gas from the reaction mixture (20).[43]

$$\boxed{Cr(CO)_6 + py + (P\text{-MeO-}C_6H_4)_2TeO \xrightarrow{CHCl_3} Cr(CO)_5py + CO_2 + (P\text{-MeO-}C_6H_4)_2Te \qquad (20)}$$

In the absence of pyridine, the same reaction of $Cr(CO)_6$ with $(p\text{-MeO-}C_6H_4)_2TeO$ afford $Cr(CO)_5Te(p\text{-MeO-}C_6H_4)_2$ (Figure 12).

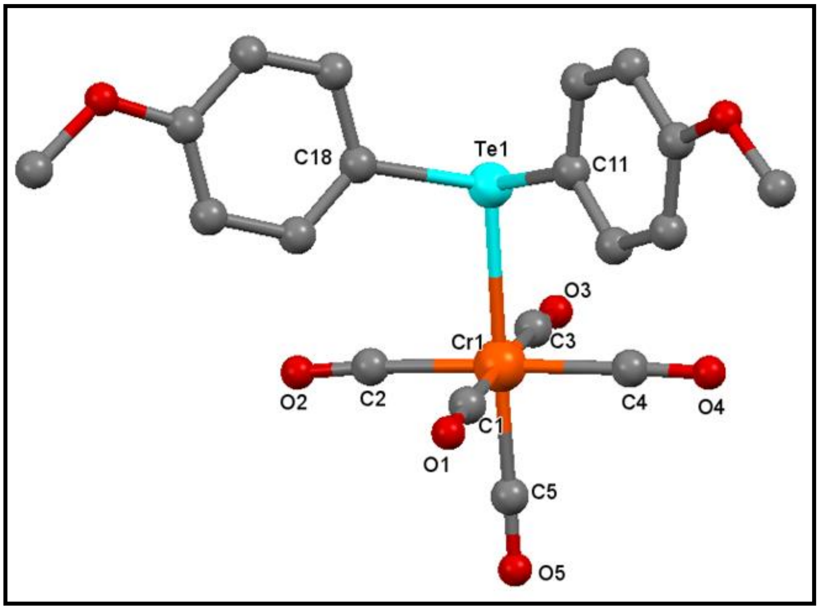


Figure 12: Solid state structure of $Cr(CO)_5Te(p\text{-MeO-}C_6H_4)_2$.

Oxygen transfer reactions of diorganotellurium oxides with various heterometallic carbonyl clusters have also been reported.[44]

Very recently Beckmann et al. reported oxygen atom transfer from diorganotellurium oxide to acetonitrile (21).[45] The reaction of intra-molecularly coordinated diorganotellurium oxide $(8\text{-}Me_2NC_{10}H_6)_2TeO$ with acetonitrile resulted in the formation of zwitterionic diorganotellurium(IV) acetamide $(8\text{-}Me_2NC_{10}H_6)_2TeNC(O)CH_3$ (Figure 13) in good yield. Further, hydrolysis of this zwitterionic complex with hydrochloric acid affords acetamide and diorganohydroxytelluronium(IV) chloride $[(8\text{-}Me_2NC_{10}H_6)_2Te(OH)]Cl$. Propionitrile and benzonitrile also gave the corresponding amide products when they were treated with $(8\text{-}Me_2NC_{10}H_6)_2TeO$. However nitriles did not react with other diorganotellurium oxides, R_2TeO (R = Ph, $4\text{-}MeOC_6H_4$, Mes), probably because of the lack of intramolecularly coordinating N donor substituents.

$$R_2TeO + CH_3CN \xrightarrow{\text{6 h reflux}} R_2TeNC(O)CH_3 \xrightarrow{\text{aq HCl}} [R_2Te(OH)]Cl + CH_3C(O)NH_2 \qquad (21)$$

$$R = (8\text{-}Me_2NC_{10}H_6)$$

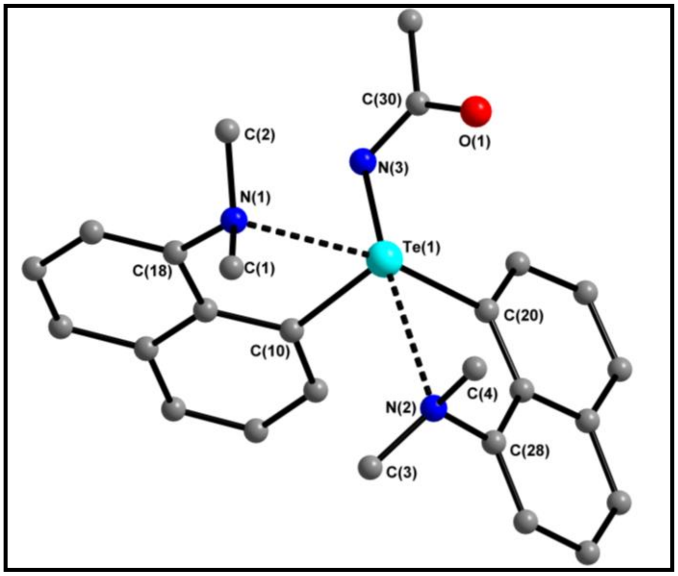


Figure 13: Solid state structure of $(8\text{-}Me_2NC_{10}H_6)_2TeNC(O)CH_3$.

1.6 Organoantimony compounds:

Antimony belongs to group 15 of the periodic table and is known since ancient times. The chemical symbol Sb has been derived from its Latin name *stibium*. It is found in nature as a sulphide mineral stibnite, Sb_2S_3. The first organoantimony compound, a tertiary stibine R_3Sb (R = alkyl, aryl) was prepared in 1850 by reacting Grignard reagent RMgX and $SbCl_3$ in ether or tetrahydrofuran medium. Aryl stibines are air stable solids whereas alkyl stibines are volatile liquids, especially lower members being spontaneously flammable in air.[46]

Organoantimony compounds have several applications in the field of synthetic organic chemistry. They have been used as catalysts or reagents or useful starting precursors for many organic reactions. Triphenylantimony dicarboxylates $Ph_3Sb(O_2CR)_2$ have a monodentate Sb-OC(O) linkage which can act as active ester source for amides synthesis when they are treated with amines.[47] Triphenylantimony oxide (Ph_3SbO) along with P_4S_{10} catalyzed the aminolysis of N-protected amino acids with amino acid esters.[48] The same catalyst system (Ph_3SbO/ P_4S_{10}) was also used for esterification reaction of various carboxylic acids with corresponding alcohols and amidation of carboxylic acids by amines.[49] Trialkylstibines are found to be effective reagents for the formation of double bond between α-halogeno carboxylic derivatives (includes esters, amides and nitriles) and carbonyl compounds to obtain α,β-unsaturated esters, amides and nitriles.[50]

α-Enones can be prepared by treating aldehydes and α-bromo ketones in the presence of tri-*n*-butylstibine. Huang et al. reported the reactions of quaternary stibonium salts with strong nucleophilic base such as RLi or less nucleophilic base such as LDA/potassium *tert*-butoxide to yield pentaorganyl stiboranes or stibonium ylides, respectively. Pentaorganyl stiboranes (λ^5-stibanes) further react with aldehydes followed by consequent hydrolysis to give secondary alcohols. Stibonium ylides react with carbonyl compounds to produce olefins or epoxides.[51] Kurita et al. have reported the use of organoantimony compounds as substrates in palladium-catalysed cross-coupling reactions.[52]

1.7 Preparation of organoantimony compounds:

1.7a Preparation of organoantimony(III) halides:

Organoantimony(III) halides of the type R_2SbX or $RSbX_2$ (X = Cl, Br) can be prepared by the redistribution reaction between R_3Sb and SbX_3. It is a solvent-less reaction. 2:1 mole ratio reaction of Ph_3Sb and $SbCl_3$ at room temperature for 3 hours gives a pale viscous oil of Ph_2SbCl which solidifies on standing (22). The same reaction between Ph_3Sb and $SbBr_3$ gives Ph_2SbBr. Since $SbBr_3$ has higher melting point than $SbCl_3$, the reaction mixture has to be slightly warmed (35-40°C) to make the reaction progress. Similarly 1:2 mole ratio reactions between Ph_3Sb and $SbCl_3$ (23) or Ph_3Sb and $SbBr_3$ give $PhSbCl_2$ or $PhSbBr_2$, respectively. All these reactions give sufficiently pure organoantimony(III) chlorides for further reactions, otherwise it can be purified by recrystallization from either dichloromethane or warm glacial acetic acid.[53]

$$2\ Ph_3Sb + SbCl_3 \longrightarrow 3\ Ph_2SbCl \qquad (22)$$

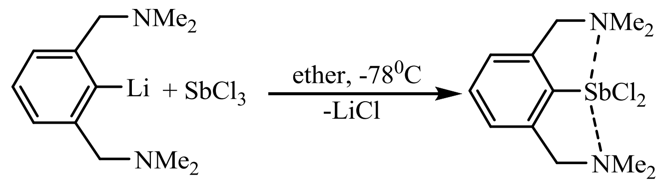
$$Ph_3Sb + 2\ SbCl_3 \longrightarrow 3\ PhSbCl_2 \qquad (23)$$

Other substituted triphenylstibines also give corresponding organoantimony(III) halides with the same procedure but to ensure the completion of reaction, elevated temperatures have to be maintained for overnight. However this method has not been useful for the preparation of alkylantimony(III) halides. Thermolysis of trialkylantimony dihalides or halogenation of distibines have been used for the preparation of alkylantimony(III) halides (24 & 25).[54]

$$Et_3SbBr_2 \xrightarrow[400\ \text{mm Hg}]{240^0C} Et_2SbBr \qquad (24)$$

$$Me_2Sb\text{-}SbMe_2 \xrightarrow{SO_2Cl_2} 2\ Me_2SbCl \qquad (25)$$

NCN chelated organoantimny(III) dichlorides can be prepared by reacting Li[2,6-$(Me_2NCH_2)_2C_6H_3$] with $SbCl_3$ in ether medium at lower temperatures (26).[55]



(26)

1.7b Preparation of organoantimony(V) halides:

Organoantimony(V) halides ranging from R_4SbX to $RSbX_4$ have been prepared using various methods. Tetraorganoantimony(V) halides R_4SbX can be prepared by reacting trialkylantimony with alkyl halides (27). Reaction of pentaorganoantimony compounds with halogen sources also gives R_4SbX (28). They usually have ionic structures like $R_4Sb^+X^-$.[56]

$$R_3Sb + R'X \longrightarrow R_3(R')SbX \quad (27)$$

$$(R = R' = \text{alkyl};\ X = Br, I)$$

$$Ph_5Sb \xrightarrow{Cl_2} Ph_4SbCl \quad (28)$$

Triorganoantimony(V) dihalides R_3SbX_2 can be prepared by the addition of 1.0 M SO_2Cl_2 solution to corresponding triorganostibines in dichloromethane (29). Other substituted triorganostibines also give corresponding triorganoantimony(V) dihalides by the same procedure.[57]

$$Ph_3Sb \xrightarrow[CH_2Cl_2,\ r.t]{SO_2Cl_2} Ph_3SbCl_2 \quad (29)$$

Diorganoantimony(V) Trihalides R_2SbX_3 are prepared by halogenation of corresponding diorganoantimony(III) halides R_2SbX with X_2 (X = Cl, Br) (30).[58]

$$\boxed{\mathrm{Ph_2SbCl} \xrightarrow[\mathrm{CH_2Cl_2,\ r.t}]{\mathrm{Cl_2}} \mathrm{Ph_2SbCl_3} \quad (30)}$$

Diorganoantimony(V) trihalides can also be prepared by treating $SbCl_5$ with arylating reagents such as tetraaryltin or tetraaryllead (31).[59]

$$\boxed{\mathrm{SnPh_4 + SbCl_5} \xrightarrow[\mathrm{reflux,\ 2h}]{\mathrm{CCl_4}} \mathrm{Ph_2SbCl_3 + Ph_2SnCl_2} \quad (31)}$$

Monoorganoantimony(V) tetrahalides are less stable and they show strong Lewis acid character. Only few of such compounds have been isolated.

1.7c Preparation of organoantimony(III) oxides:

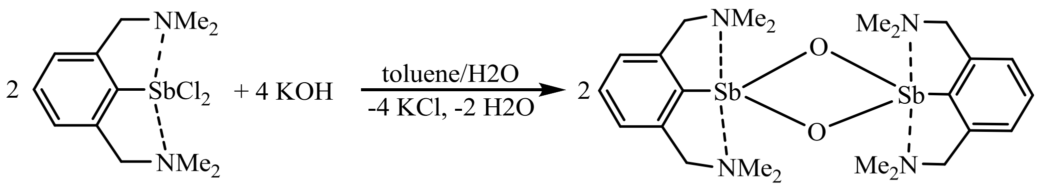
Organoantimony(III) oxides can be obtained by hydrolysis/oxidation of oraganoantimony(III) halides. Hydrolysis of R_2SbCl with aq. $NaOH/Na_2CO_3$ gives $(R_2Sb)_2O$ (31). Controlled oxidation of tetraorganodistibines $(R_2Sb)_2$ with O_2 gives $(R_2Sb)_2O$ (32).[60]

$$\boxed{\begin{array}{lll} \mathrm{t\text{-}Bu_2SbCl} \xrightarrow{\mathrm{aq\ NaOH}} \mathrm{(t\text{-}Bu_2Sb)_2O} & & (31) \\ \mathrm{(Me_2Sb)_2} \xrightarrow{\mathrm{1/2\ O_2}} \mathrm{(Me_2Sb)_2O} & & (32) \end{array}}$$

Hydrolysis of $RSbCl_2$ (R = aryl) with aq. NaOH at 0°C gives a polymeric RSbO in high yield.[61]

$$\boxed{\mathrm{PhSbCl_2} \xrightarrow{\mathrm{aq\ NaOH}} \mathrm{(PhSbO)_n} \quad (33)}$$

NCN chelated organoantimony(III) oxides can be prepared by treating $RSbCl_2$ (R = NCN chelating ligand) with aq. KOH in toluene at ambient temperature (34).[62]



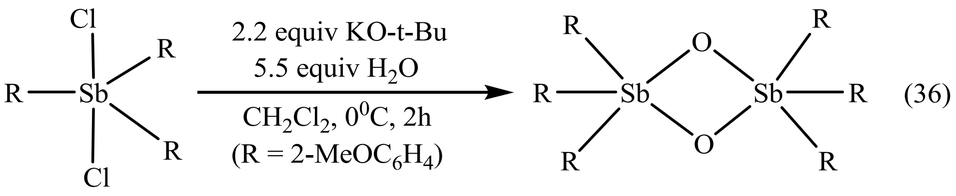
(34)

1.7d Preparation of organoantimony(V) oxides:

Organoantimony(V) oxides can be obtained by treating triarylantimony/ triarylantimony dihalides with peroxides/alkaline bases. The reaction of triphenylantimony with 30% H_2O_2 in ice-cold acetone gives an insoluble white fluffy solid material which is characterized as polymeric triphenylantimony oxide (35).[63]

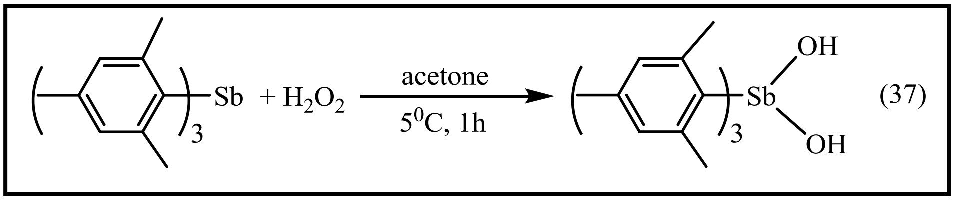
$$Ph_3Sb + H_2O_2 \xrightarrow[0\text{-}5^0C]{\text{acetone}} (Ph_3SbO)_n \quad (35)$$

The reaction of tris(2-methoxyphenyl)antimony dichloride with potassium *tert*-butoxide in the presence H_2O in dichloromethane at low temperature leads to the formation of tris(2-methoxyphenyl)antimony oxide dimer (36).[64]



(36)

Trimesitylantimony dihydroxide monomer can be obtained by treating trimesitylantimony with 30% H_2O_2 in acetone at 5°C (37).[65]



(37)

When tetraaryldistibines $R_2Sb\text{-}SbR_2$ are treated with O_2 followed by the oxidation with H_2O_2 resulted in the formation of tetranuclear organoantimony (V) oxides of the type $(R_2Sb)_4O_6$ with peroxo bridges in its solid state molecular structure.[66]

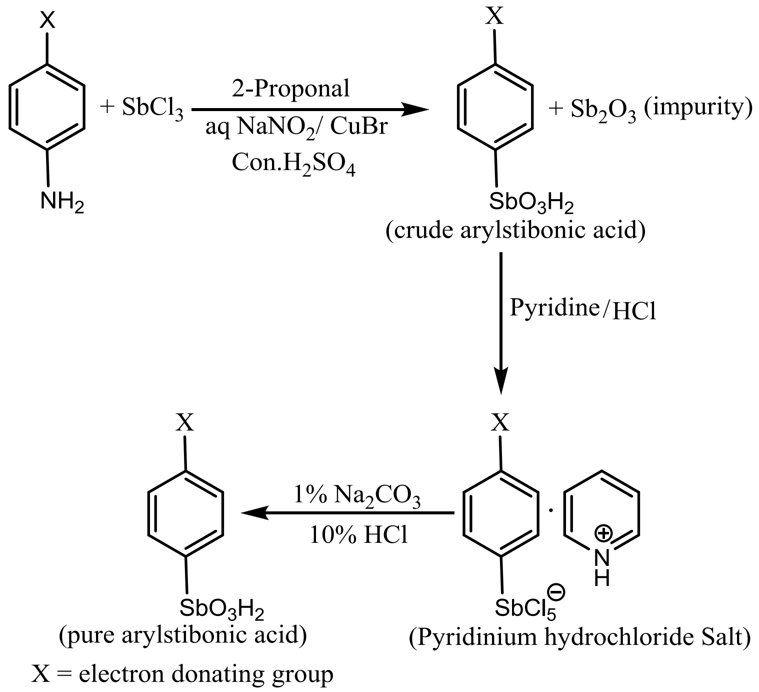
1.7e Preparation of arylstibonic acids:

The initial motivation for exploring the chemistry of arylstibonic acids was driven from excellent pharmaceutical applications of arylarsonic acids. Arylarsonic acids were first prepared by Barton reaction, in which an aromatic diazo compound was reacted with As_2O_3 under alkaline conditions to form arylarsonic acids.[67]However the yields and purity of the final products were not so encouraging and several modifications have been attempted to overcome these issues. Later Scheller introduced some major changes by using organic solvent to dissolve aromatic amine and aqueous $NaNO_2$ as a diazotisation reagent. He also used $AsCl_3$ in place of As_2O_3 and Cu(I) salt as catalyst. All these changes improved the yields tremendously. Scheller reaction was also employed to synthesize arylstibonic acids.[68]

1.7e.1 Preparation of arylstibonic acids by Scheller reaction:

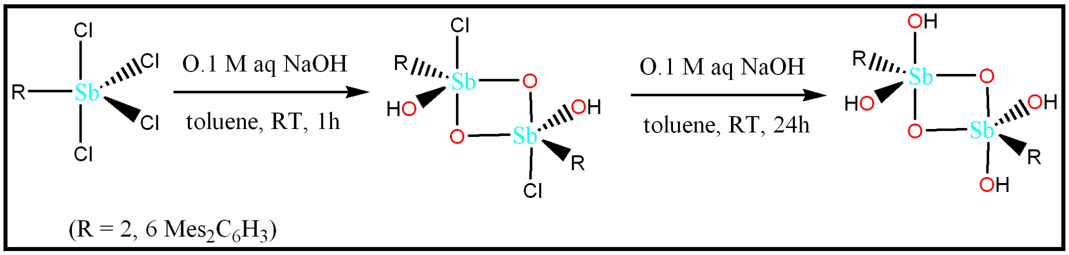
Aromatic amine was dissolved/suspended in 2-propanol in a beaker kept in an ice-bath. To this solution conc. H_2SO_4 and $SbCl_3$ were added followed by addition of aqueous $NaNO_2$ to initiate the diazotisation reaction. Stirring was continued for one hour and the ice-bath removed after addition of CuBr (catalytic amount). Nitrogen gas evolved spontaneously and the reaction mixture was kept at room temperature for one day to ensure the complete evolution of nitrogen gas. After that the reaction mixture was steam-distilled to remove the solvent (2-prpanol) to yield crude stibonic acid. Later, this crude stibonic acid was washed with ice cold water and air dried for one day. In order to purify this crude arylstibonic acid, it was dissolved in conc. HCl and then pyridinium hydrochloride solution was added under ice-bath condition. The precipitated pyridinium salt of arylstibonic acid was separated by vacuum filtration and washed several times with conc. HCl and air dried for 2-3 days. Later this pyridinium salt of arylstibonic acid was dissolved in 1% Na_2CO_3 solution. Stirring was continued for few hours after addition of activated charcoal to this solution after which the solution was filtered. Pure arylstibonic acid was obtained from this filtrate as fluffy white solid by drop wise addition of dilute HCl while rapid stirring was continued. This solution was then filtered and washed with dilute HCl to obtain pure arylstibonic acid.

Schematic representation for the preparation of arylstibonic acids:



1.7e.2 Preparation of well-defined arylstibonic acids:

In general arylstibonic acids are amorphous, ill-defined and insoluble in most organic solvents. But in a break-through result, Beckmann et al. reported the controlled hydrolysis of 2,6-$Mes_2C_6H_3SbCl_4$ under basic conditions leading to the formation of a dinuclear arylstibonic acid [2,6-$Mes_2C_6H_3Sb(O)(OH)_2]_2$.[69]



1.8 Structural aspects of organoantimony(V) dihalides / trihalides, organoantimony(V) oxides and arylstibonic acids:

1.8a Structure of triphenylantimony(V) dichloride / diphenylantimony(V) trichloride:

In solid state structure of triphenylantimony dichloride (Figure 14a), Sb exhibits trigonal bipyramidal-geometry with axial positions occupied by chlorine atoms.[70] Anhydrous diphenylantimony trichloride exists as a dimer in solid state with chlorine bridges where Sb is in trigonal-bipyramidal geometry with two phenyl groups occupying the axial positions (Figure 14b).[71] There is an ambiguity in the solid state structure of diphenylantimony trichloride monohydrate. In 1961 Polynova and co-workers reported a trigonal-bipyramidal structure for diphenylantimony trichloride monohydrate with two phenyl groups occupying equatorial positions.[72]But later the same authors' stated octahedral geometry for the same compound. In 1973 Gukasyan et al. with help of ^{121}Sb Mössbauer study, reported trigonal bipyramidal geometry with three chlorine atoms occupying equatorial positions.[73]

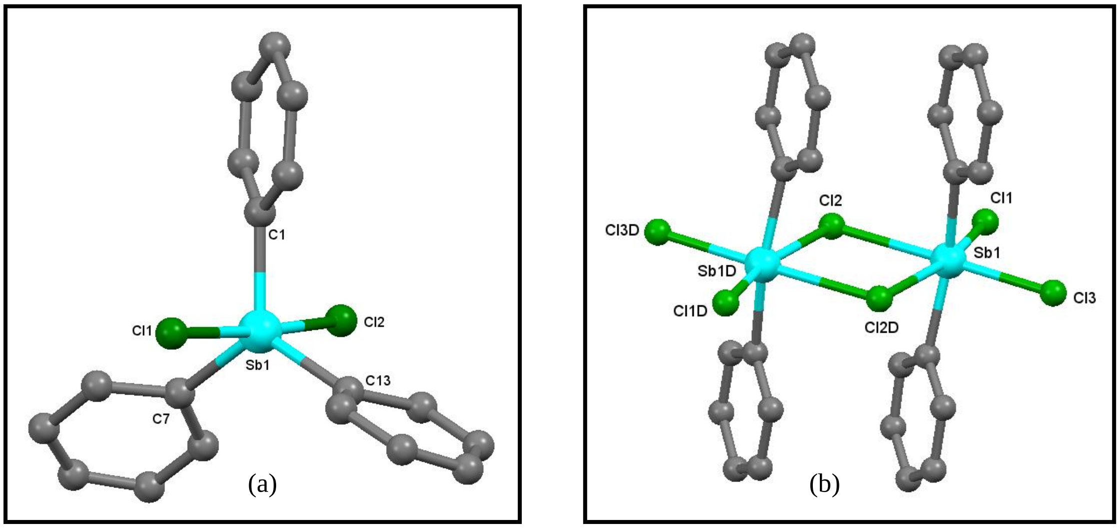
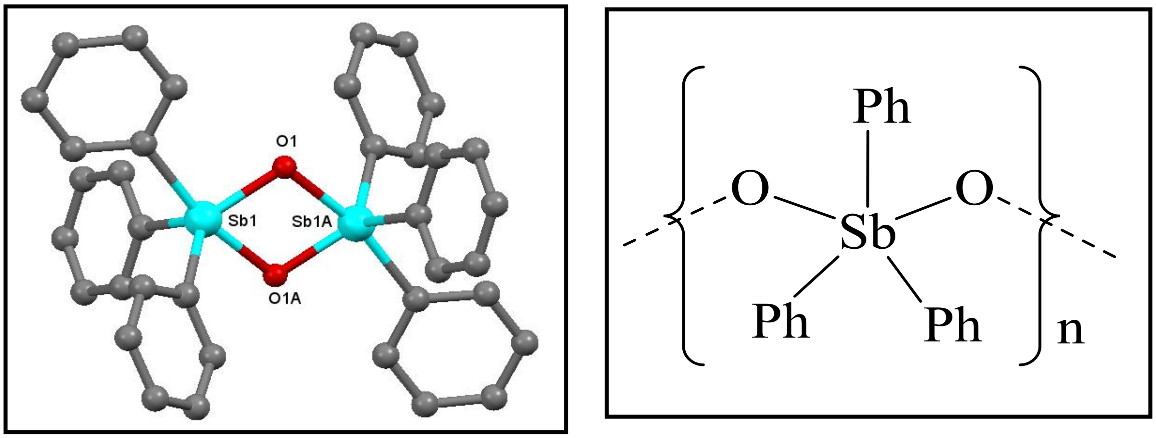


Figure 14: Solid state structures of (a) Ph_3SbCl_2 and (b) Ph_2SbCl_3.

1.8b Structure of triphenylantimony(V) oxides:

Solid state structure of triphenylantimony oxide has been a matter of considerable debate since it was prepared in 1922 by Schmidt.[74]The structure greatly depends on the starting precursor used and the method of preparation adopted. When triphenylantimony was treated with H_2O_2 in cold acetone, it resulted in the formation of a white fluffy material which is sparingly soluble in common organic solvents. When different solvents were used (other than acetone) or the reaction performed at room temperature it leads to the isolation of products with different melting points. In 1986 Doak et al reported the crystal structure of dimeric triphenylantimony oxide in which each antimony center is in trigonal pyramidal geometry with planar Sb_2O_2 ring (Figure 15a). However, Doak et al. have also prepared various amorphous forms of triphenylantimony oxide and based on its insoluble nature in all common organic solvents, they proposed a polymeric structure for triphenylantimony oxide.[63] Recently with the help of EXAFS spectroscopy, Orpen et al. stated that the resulting compound obtained in the reaction between triphenylantimony and H_2O_2 in cold acetone is polymeric triphenylantimony oxide in which each trigonal bipyramidal Ph_3SbO_2 unit is bridged through their axial oxygen atom in a polymeric or oligomeric array (Figure 15b).[75]



(a

(b

Figure 15: (a) Solid state dimeric structure of Ph_3SbO. (b) Polymeric array of Ph_3SbO.

Introducing a substituent (OMe) at ortho position of the phenyl rings attached to Sb resulted in the isolation of a dimeric $[(OMe\text{-}C_6H_4)_3SbO]_2$ with a flat Sb_2O_2 ring in the solid state (Figure 16a). Sb attains distorted trigonal-bipyramidal geometry with two ipso carbon atoms and oxygen at equatorial positions.[64]

When a bulky substituent like mesityl group was attached to Sb, it resulted in the isolation of a monomeric $Mes_3Sb(OH)_2$ in solid state with two hydroxyl groups occupying the axial positions (Figure 16b).[65]

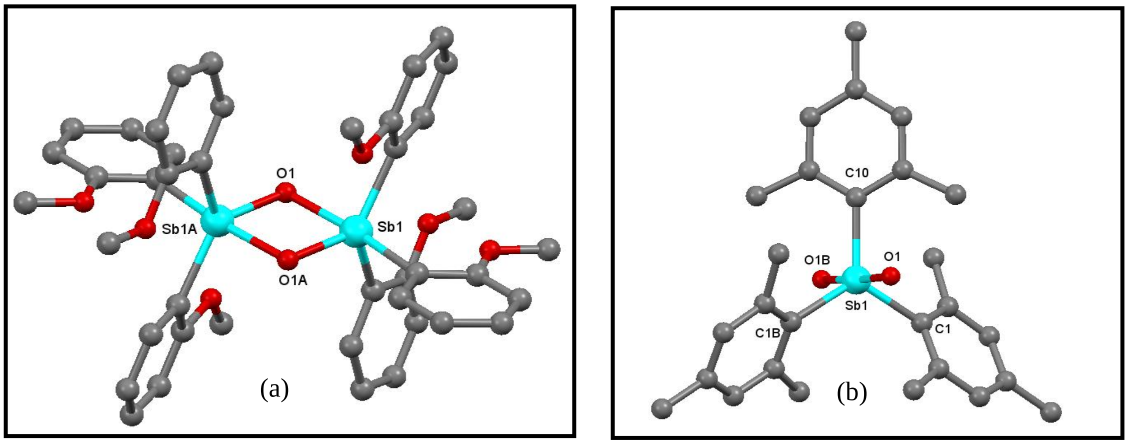


Figure 16: Solid state structures of (a) $[(OMe\text{-}C_6H_4)_3SbO]_2$ and (b) $Mes_3Sb(OH)_2$.

1.8c Structure of arylstibonic acids:

Despite the fact that arylstibonic acids are known for last 100 years and have potential applications in biology and catalysis, their solid state structure has been a matter of debate. All the arylstibonic acids are amorphous, ill-defined and insoluble in most common organic solvents. Lack of solubility and distinct melting points and difficulty in separation by filtration (as they tend to form colloids when washed with water) makes the determination of exact solid state structure of arylstibonic acids impossible.

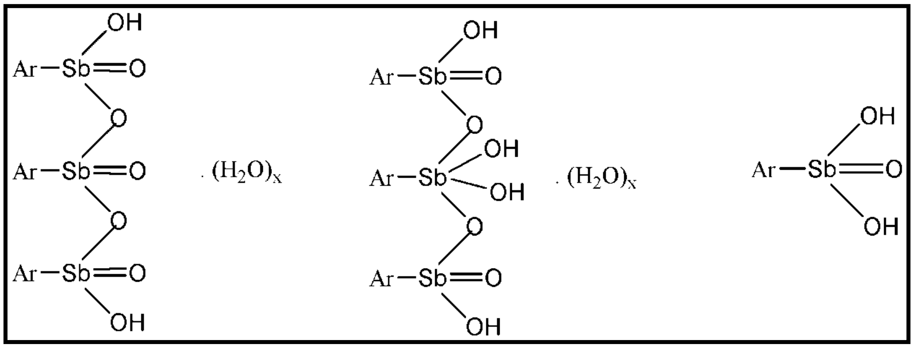


Figure 17: Schematic representation of various structures proposed for arylstibonic acids.

Schmidt proposed a trimeric structure for arylstibonic acids from which a monomeric structure can be obtained when the former dissociates in alkali solution.[76] Macallum proposed monomeric structure by using molecular weight determination methods.[77] But Doak disagreed with Schmidt and Macallum and further suggested that arylstibonic acids exist as high molecular weight polymeric aggregates in solid state which are linked by hydrogen bonding.[78] Through ^{121}Sb Mössbauer study, Bowen et al. concluded that arylstibonic acids have trigonal-bipyramidal geometry around Sb with bridging oxygen atoms in epical positions.[79]

Recent report of Beckmann et al. on solid state structure of dinuclear arylstibonic acid (Figure 18) where Sb bearing a bulky substituent (2,6-$Mes_2C_6H_3$) further in agreement with previous reports on the trigonal-bipyramidal geometry of arylstibonic acids.[69]

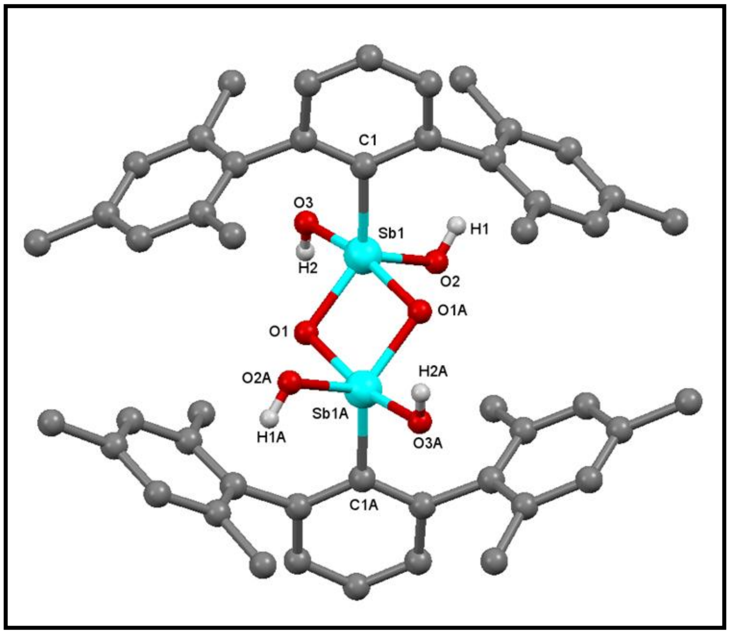


Figure 18: Solid state structure of [2,6-$Mes_2C_6H_3Sb(O)(OH)_2]_2$.

1.9 Reactions of triorganoantimony(V) dihalides /diorganoantimony(V) trihalides:

1.9a Reactions of R_3SbCl_2 / R_2SbCl_3 with diols and dithiols:

When triorganoantimony dihalides were reacted with *gem* or *vicinal* diols, it resulted in the formation of triorganostiboranes. Complexes of the type $R_3Sb(R'R''CO_2)$, (where R= phenyl, p-tolyl; R', R''= CF_3, CF_3; CF_3, H) have been prepared by treating R_3SbCl_2 with corresponding *gem* diols. These compounds were characterised by IR and NMR studies and it was revealed that *gem*-diolato group bond to the Sb bidentately through oxygen atoms.[80] Similarly when Ph_3SbCl_2 was treated with sodium salt of maleonitriledithiol or 4-nitrocatechol in the presence of Et_3N it resulted in the formation of $Ph_3Sb[S_2C_2(CN)_2]$ or $Ph_3Sb[O_2C_6H_3\text{-4-}NO_2]$ (Figure 19) with trigonal-bipyramidal and square-pyramidal geometries around Sb, respectively.[81] Chandrasekhar et al. demonstrated the reaction of Ph_2SbCl_3 with disodium salt of maleonitriledithiolate in dichloromethane and isolated $[Ph_2SbCl\{S_2C_2(CN)_2\}]$ which showed several hydrogen bonding interactions in solid state leading to the formation of a supramolecular zig-zag polymeric network.[82]

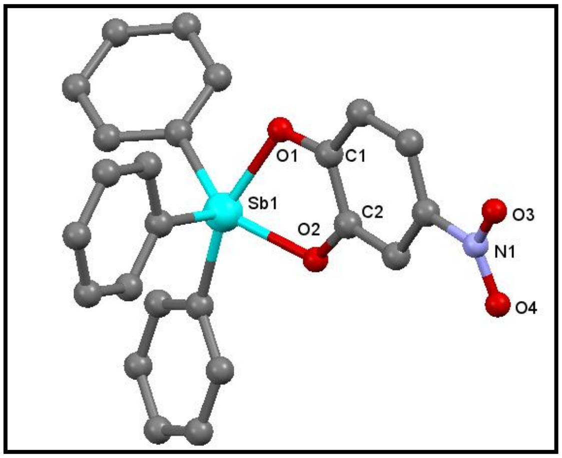


Figure 19: solid state structure of $Ph_3Sb[O_2C_6H_3\text{-}4\text{-}NO_2]$

1.9b Reactions of R_3SbCl_2 / R_2SbCl_3 with β-diketones:

When R_3SbCl_2 and R_2SbCl_3 was reacted with acetylacetone (Acac), it resulted in the formation of complexes $R_3SbCl(Acac)$ and $R_2SbCl_2(Acac)$, respectively. These complexes were characterized by NMR and IR studies. In both the complexes β-diketonate ligand acts as bidentate ligand and bonds to Sb through oxygen atoms. In $R_3SbCl(Acac)$ (Figure 20a) chlorine atom occupies equatorial position whereas in $R_2SbCl_2(Acac)$ (Figure 20b) aryl groups occupy equatorial positions and chlorine atoms occupy axial positions. Further complexes of the type $R_nSbCl(Acac)$ (R=Me, Ph and n=1-4) have also been synthesized and characterized.[83]

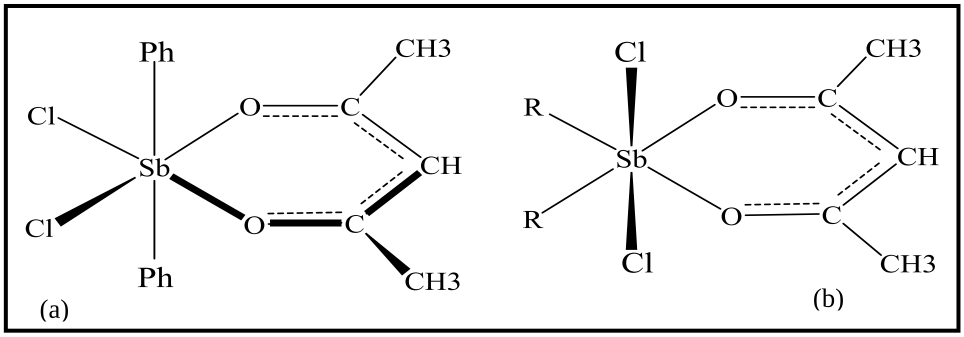


Figure 20: (a) Schematic diagram of $Ph_3SbCl(Acac)$. (b) Schematic diagram of $R_2SbCl_2(Acac)$.

1.9c Reactions of R_3SbCl_2 / R_2SbCl_3 with Schiff base ligands:

A series of organoantimony(V) compounds of the type R_3Sb(trid) / R_2SbCl(trid) (R=Me or Ph; trid^{2-} = tridentate Schiff base ligands with ONO or SNO donor atoms) have been prepared by treating R_3SbCl_2/R_2SbCl_3 with corresponding Schiff base ligands. Various Schiff base ligands used for this study are 2,2'-(methylidynenitrilo)diphenol (H_2Sab), 2-(o-hydroxyphenyl)benzothiazoline (H_2Sat), 3-(o-hydroxyanilino)crotonophenone (H_2Bah), 4-(o-hydroxyphenylimino)-2-pentanone (H_2Aah) and 2-acetonyl-2-methylbenzothiazoline (H_2Aat). All these complexes are characterized by UV, IR and NMR studies and monomeric hexacoordinate molecular structures were suggested. X-ray diffraction studies revealed the solid state molecular structure of Me_3SbSab in which Sb atom is in distorted octahedral geometry with meridional arrangement of ONO ligand around antimony center (Figure 21).[84] ^{121}Sb Mössbauer study of other complexes revealed the same fact that antimony has octahedral geometry with meridionally arranged ONO or SNO Schiff base ligands.[85]

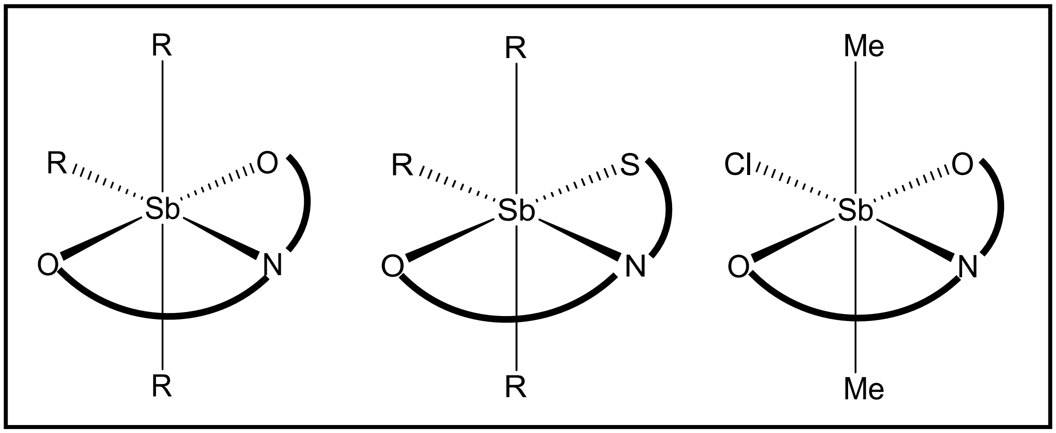


Figure 21: Schematic representation of octahedral geometry around Sb and meridional arrangement of tridentate Schiff base ligand around antimony.

Recently Han-Dong Yin et al. reported the reactions of triphenylantimony dichloride with Schiff base ligands resulting in the formation of triorganoantimony(V) complexes of the type, Ph_3SbL' / Ph_3SbL'', where H_2L'= Schiff base ligand possessing terminal carboxyl group, 5-{[(2-carboxyphenyl)methylene]amino}-4-chlorobenzoic acid and H_2L''=5-{[(2-carboxyphenyl)methylene]amino}-2-chlorobenzoic acid, respectively. X-ray diffraction studies revealed the formation of 24-membered macrocyclic organoantimony complex in which two Sb atoms are bridged by four terminal carboxyl groups of Schiff base ligands.[86]

1.9d Reactions of R_3SbCl_2 / R_2SbCl_3 with carboxylates:

Organoantimony(V) carboxylates have been extensively studied not only owing to their structural diversity but also due to their biological activities, especially for their antitumor activities.[87]Sowerby et al. investigated the reaction of triphenylantimony dichloride with silver oxalate in toluene/methanol at different temperatures that led to the formation of $[SbPh_4][SbPh_2(ox)_2]$ (Figure 22) and $[SbPh_3(OMe)]_2ox$ (where ox= oxalate), respectively.[88]

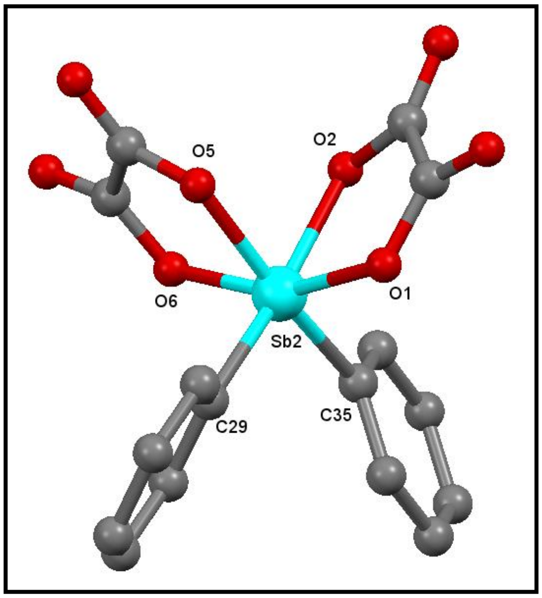


Figure 22: Solid state structure of $[SbPh_2(ox)_2]^-$.

Han-Dong Yin et al. investigated the reactions of triorganoantimony(V) dichlorides with various carboxylic acids like fluoromethylbenzoic acids, (±)-mandelic acid and arylcarboxylic acids to look into the aspects of structural information and nature of bonding in the resultant complexes.[89] They have also reported the reactions of diphenylantimony(V) trichloride with arylcarboxylic acids possessing electron withdrawing groups resulting in the formation of cage-like tetranuclear organoantimony carboxylates $(SbPh_2)_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(\mu\text{-}O_2CR)_2$ [R= 2-CHO-$C_6H_4COO^-$ (Figure 23), 2,3-2F-$C_6H_4COO^-$, 4-CF_3-$C_6H_4COO^-$]. In the solid state structure four diorganoantimony centers are bridged together by oxo- and hydroxo-bridges to form a cage like architecture which are terminally bridged by two carboxyl groups.[90]

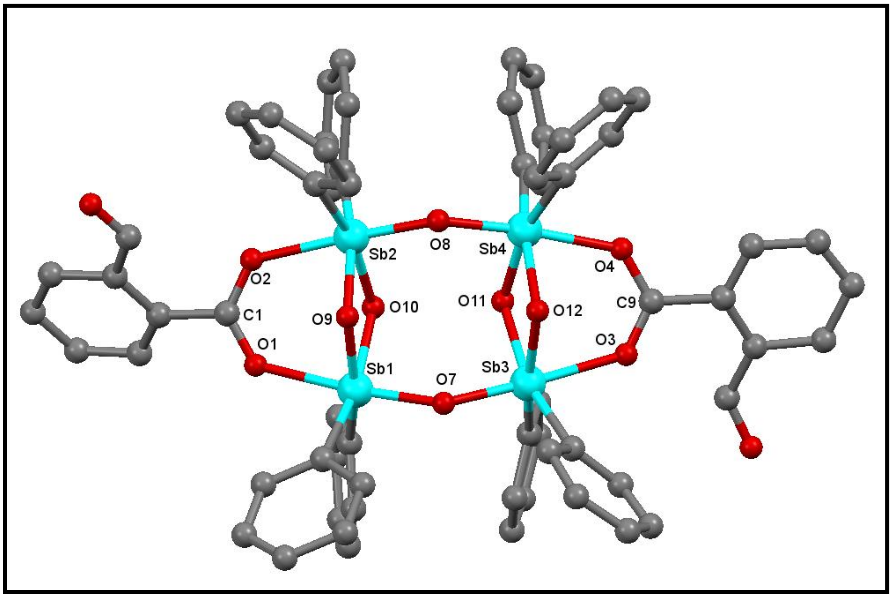


Figure 23: Solid state structure of $(SbPh_2)_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(\mu\text{-}O_2C\text{-}C_6H_4\text{-}CHO)_2$.

1.9e Reactions of R_3SbCl_2 / R_2SbCl_3 with phosphinates:

Silvestru and co-workers reported the reactions of R_3SbCl_2 (R= Me, Ph) with sodium salts of diphenylphosphinates ($Ph_2PO_2^-$) or diphenylmonothiophosphinates ($Ph_2P(S)O^-$) or diphenyldithiophosphinates ($Ph_2PS_2^-$) resulting in the formation of monomeric complexes of the type $R_3Sb(O_2PPh_2)_2$ / $R_3Sb(O(S)PPh_2)_2$ / $R_3Sb(S_2PPh_2)_2$ in which two phosphinate / monothiophosphinate / thiophosphinate ligands coordinate to central antimony ion in monodentate fashion in trans direction to each other.[91]

In 1996, the same group has also reported the reactions of Ph_2SbCl_3 with alkali salts of oxo- and thioimidodiphosphinic acids, $M[(OPPh_2)(XPPh_2)N]$ (M=Na, K; X=O, S) that resulted in the formation of novel inorganic SbO_2P_2N / $SbOSP_2N$ ring containing complexes $Ph_2SbCl_2[(OPPh_2)(XPPh_2)N]$ (X=O,S) respectively. In both the complexes imidodiphosphinato ligand bonds to central antimony through chalcogen atoms, Sb being in distorted octahedral geometry.[92]

Kumara Swamy et.al investigated the reactions of Ph_2SbCl_3 with silver salts of dicyclohexylphosphinic acid / dicyclooctylphosphinic acid in dry toluene at reflux conditions and isolated the dinuclear organoantimony(V) phosphinates $[Ph_2Sb(O_2PR_2)O]_2$ [R= cycl-C_6H_{11} (Figure 24) and cycl-C_8H_{15}] respectively. When these compounds are further hydrolyzed with acetic acid/ water mixture at reflux temperature it resulted in the formation of a tetranuclear cage $[Ph_2Sb(O_2P(C_6H_{11})_2)(O_2CMe)]_2O$. This tetranuclear cage can convert back to dinuclear cage by treating it with excess amount of dicyclohexylphosphinic acid. Both these di and tetranuclear cages possess four membered Sb_2O_2 rings and in tetranuclear cage the two Sb_2O_2 rings are further connected through oxo-bridges on both sides to form Sb_4O_6 cage.[93]

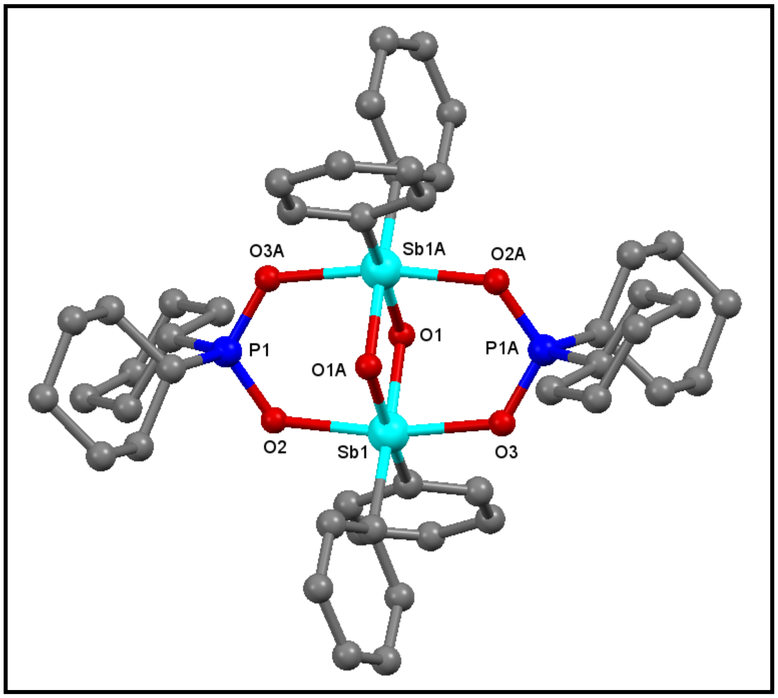


Figure 24: Solid state structure of $[Ph_2Sb(O_2P(C_6H_{11})_2)O]_2$.

In a recent report, Chandrasekhar et al. investigated the reaction of Ph_2SbCl_3 with 1,1,2,3,3-pentamethyltrimethylenephosphinic acid (*cyc*PO_2H) to yield an oxo-bridged dinuclear organoantimony(V) phosphonate $[(Ph_3Sb)_2(\mu\text{-}O)(\mu\text{-}cycPO_2)_2]$ (Figure 25). Further, Sb-C bond cleavage followed by hydrolysis of this compound in acetonitrile/water mixture (99:1) at 45°C afforded a novel nonanuclear organostiboxane cage $[(Ph_2Sb)_2(PhSb)_7(\mu\text{-}O)_{11}(\mu_3\text{-}O)_3(\mu\text{-}OH)_2(\mu\text{-}cycPO_2)_2(cycPO_2)_2(H_2O)_2]$. Unlike the earlier reported mixed-valent Sb(III)/Sb(V) cage by Beckmann, this nonanuclear Sb_9O_{16} cage possess all Sb centers in +5 oxidation state. Interestingly, two *insitu* generated stibinic acid moieties are trapped in this Sb_9O_{16} cage.[94]

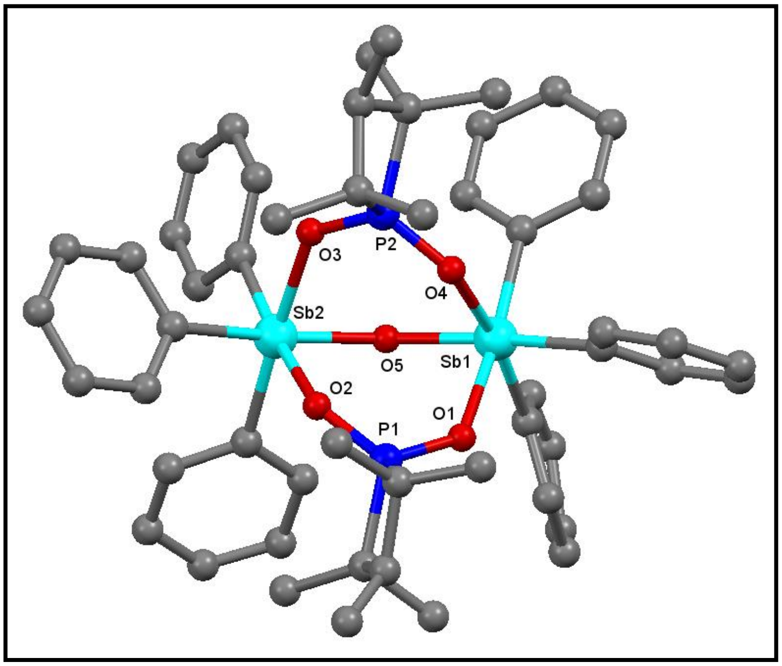


Figure 25: Solid state structure of $[(Ph_3Sb)_2(\mu\text{-}O)(\mu\text{-}cycPO_2)_2]$.

1.10 Reactions of arylstibonic acids:

Polyoxometalates (POMs) of transition metal ions have been known since the early nineteenth century whereas POMs which exclusively contain main group elements are very rare. Arylstibonic acids are proven to be the best starting precursors for self-assembling of antimony containing POMs. The first report on organoantimony containing POM was published in 2007 by Winpenny's group.[95] They reported reactions of arylstibonic acid with various transition metal ion sources in acetonitrile in the presence of a base (pyridine or trimethylamine) at 100°C under solvothermal conditions yielding the formation of novel dodecanuclear polyoxostibonates which encapsulates a transition metal ion at the centre (Figure 26). These POMs are termed as reverse keggin ions as they are structurally similar to the well-known keggin ions of the formula $[EM_{12}O_{40}]^{x-}$ (where, E= p-block element, M= d-block element) but with the positions of the p- and d-block elements reversed. Several transition metal containing POMs incorporating p-block elements at its core or periphery[96] are known but this is the first report of POM built from organoantimony (p-block element) that encapsulates a transition metal ion at its core.

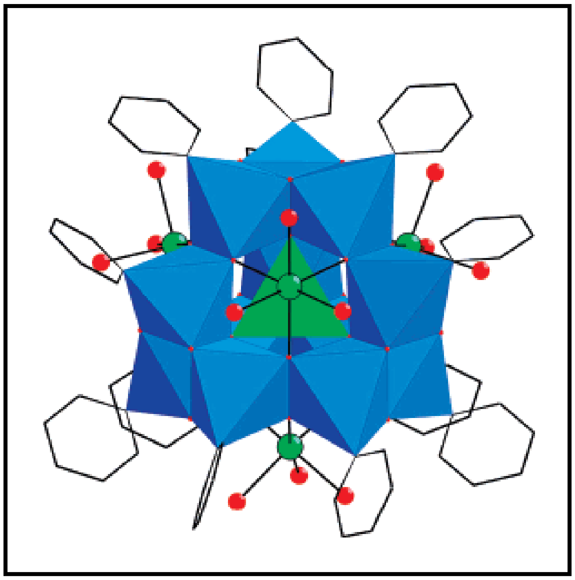


Figure 26:Polyhedral representation of dodecanuclear polyoxostibonate $[Mn(PhSb)_{12}O_{28}\{Mn(H_2O)_3\}_2\{Mn(H_2O)_2(AcOH)\}_2]$

Nicholson’s group has also been working on synthesis and characterization of arylstibonic acids. They prepared various derivatives of arylstibonic acids by employing different para substituted aryl amines in Scheller reaction. Further, arylstibonic acids were purified by dissolving in water/aq. NH_3 mixture in a plastic beaker and diffusing CH_3COOH into the solution in a closed desiccator to obtain sodium or potassium free arylstibonic acids. However, they found the presence of Na^+ ions in *p-*

nitrophenylstibonic acid even after two diffusion purifications. With the help of Electrospray Ionization Mass Spectrometry (ESI-MS), they found that most of these arylstibonic acids exists as dodecanuclear aggregates $[H_8(RSb)_{12}O_{28}]$ in acetonitrile. They also observed that if a small amount of NaOH is added or if the solutions of the pure arylstibonic acids are left standing in normal glassware, sodium adducts of arylstibonic acids like $[NaH_5(RSb)_{12}O_{28}]^{2-}$/ $[Na_2H_4(RSb)_{12}O_{28}]^{2-}$/ $[Na_3H_3(RSb)_{12}O_{28}]^{2-}$ were found in ESI-MS spectra which explains the strong affinity of arylstibonic acids towards Na^+ ions. When aqueous solutions of arylstibonic acid are neutralized with NaOH or KOH in the presence of organic cations like tetraphenylphosphonium or benzyltrimethylammonium ions, formation of dodecanuclear organoantimony assemblies of the formula $[M_2H_{10-x}(RSb)_{12}O_{30}]^{x-}$ (where M=Na, K) were observed.

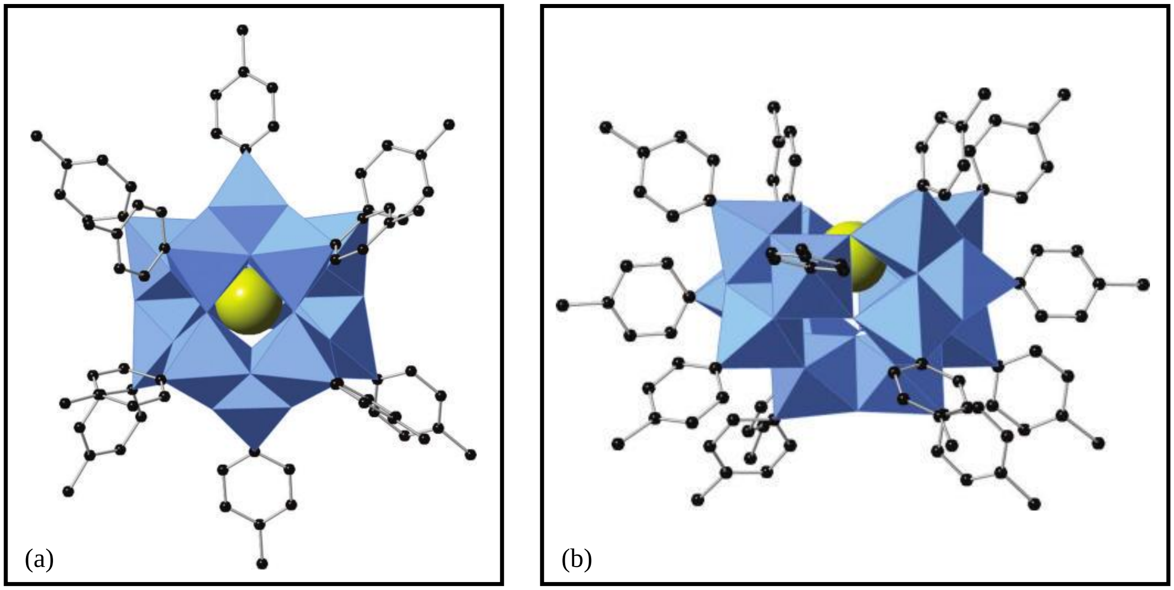


Figure 27: Polyhedral representations of (a) $[LiH_3(p\text{-}MeC_6H_4Sb)_{12}O_{28}]^{4-}$ and (b) $[BaH_{10}(p\text{-}MeC_6H_4Sb)_{14}O_{34}]$.

Single crystal X-ray diffraction studies revealed the solid state molecular structures of these compounds in which Na^+ or K^+ ions were encapsulated in a hexagonal antiprismatic array of Sb atoms. They have also demonstrated that the size of the cation is important in templating the polyoxometalate formation. When arylstibonic acids are neutralized with LiOH, where Li^+ ion is smaller than Na^+ ion, it resulted in the formation of dodecanuclear polyoxostibonate $[LiH_3(p\text{-}MeC_6H_4Sb)_{12}O_{28}]^{4-}$with more closed geometry in which Li^+ ion is fully enclosed (Figure 27a). The core of this structure $\{Sb_{12}O_{28}\}$ resembles γ Keggin ion geometry. When arylstibonic acids are treated with $BaCl_2/BaO$ in aqueous medium, it resulted in the formation of tetradecanuclear polyoxostibonate $[BaH_{10}(p\text{-}MeC_6H_4Sb)_{14}O_{34}].4H_2O$ with bowl-shaped geometry (Figure 27b). Interestingly, all these polyoxostibonates are formed in alkaline medium whereas traditional transition metal containing POMs were formed under acidic conditions. Another interesting feature of these clusters is that they retain their structural integrity in solution too which is proven by ESI-MS of these clusters in acetonitrile solvent.[97]

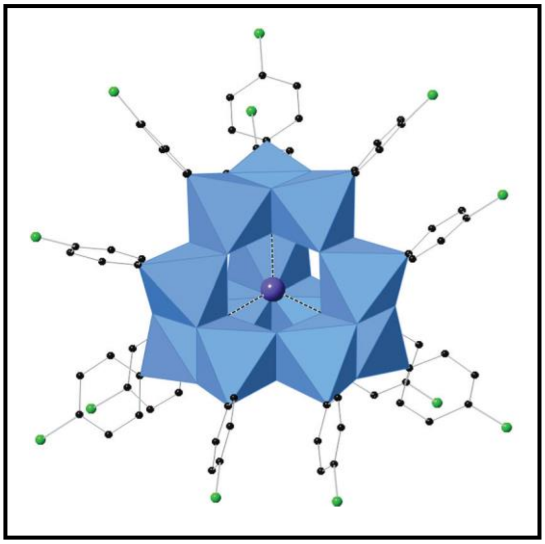


Figure 28: Polyhedral representation of dodecanuclear polyoxostibonate $[(ClC_6H_4Sb)_{12}O_{28}Zn_5Cl_4]^{2-}$.

Nicholson et al. have also reported the reactivity of arylstibonic acids in water/NH_3 mixture with transition metal (Co, Zn) chlorides resulting in the formation of dodecanuclear polyoxostibonate clusters in which Co^{2+}, Zn^{2+} ions (Figure 28) occupy the central tetrahedral sites. These structures belong to the class of ε Keggin ion geometry which are in resemblance with previously reported reverse Keggin ion by Winpenny's group. All these results suggest that polycondensation products of arylstibonic acids can act as inorganic cryptands for various transition/alkali metal ions.[98]

Winpenny et al. investigated the reactivity of arylstibonic acids with *tert*-butylphosphonic/phenylphosphonic acids leading to the formation of di/tetranuclear organoantimonate-phosphonate clusters. Further, they also utilized these clusters as pro-ligands for the preparation of polymetallic cobalt (II) complexes in hydrothermal conditions.[99]

Our group has been working on the depolymerisation reactions of arylstibonic acids with various protic ligands. 1:1 mole ratio reaction of arylstibonic acids with diphenylsilanediol in toluene at reflux conditions leads to the formation of organoantimony cubane clusters $[(p\text{-X-}C_6H_4Sb)_4(O)_4(Ph_2SiO_2)_4]$ [X = Cl (Figure 29a), Br) stabilized by siloxides acting as bridging ligands across the antimony atoms present at alternative corners of Sb_4O_4 cube. This is the first complex that contains $Sb^V\text{-O-}Si^{IV}$ framework that has been structurally characterized.[100]

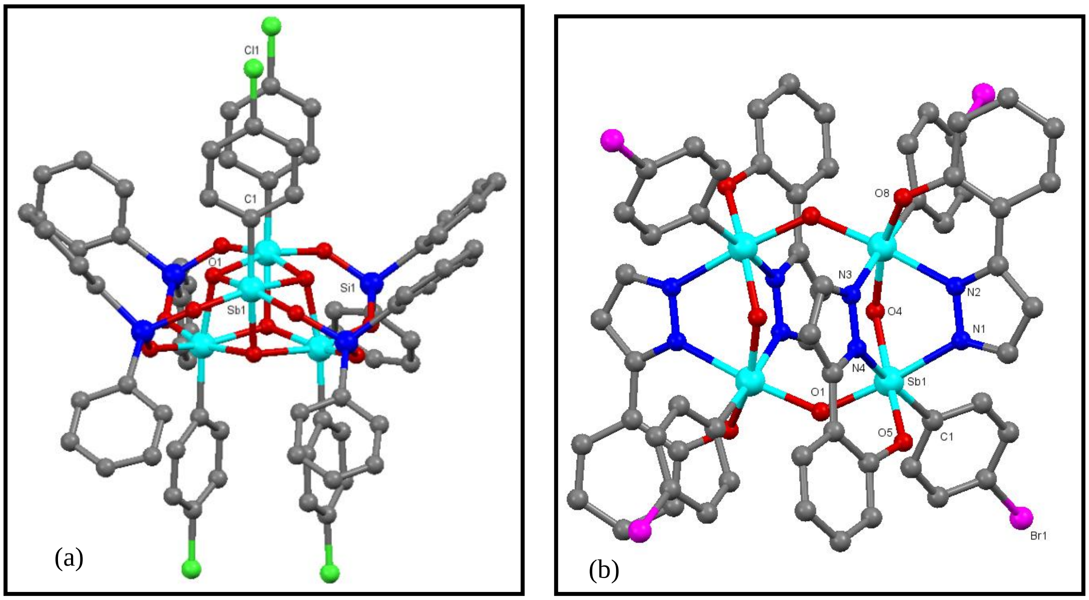


Figure 29: Solid state structures of (a) $[(p\text{-Cl-}C_6H_4Sb)_4(O)_4(Ph_2SiO_2)_4]$ and (b) $[(p\text{-Br-}C_6H_4Sb)_4(O)_4(PhPz)_4]$.

Reaction of arylstibonic acids with pyrazolyl ligands (1:1 mole ratio) with substitution at 3, 5 positions in toluene at reflux conditions yielded novel tetranuclear organoantimony oxo clusters $(RSb)_4O_4(OH)_2L_4$/ $(RSb)_4O_4L_4$ (R= $p\text{-Cl-}C_6H_4$ or $p\text{-Br-}C_6H_4$, L= pyrazole ligand) where, depending on the steric bulk present at the pyrazole ring, either one or two of the ring nitrogen atoms were found to be coordinated to antimony centres. Interestingly, reaction of 3,5-DMPz with arylstibonic acids led to the formation of hexadecanuclear polyoxostibonates $[(p\text{-X-C}_6H_4Sb)_{16}(O)_{28}(OH)_8](3,5\text{-DMPz})_6$ (X= Cl/Br) (Figure 30a).[101]

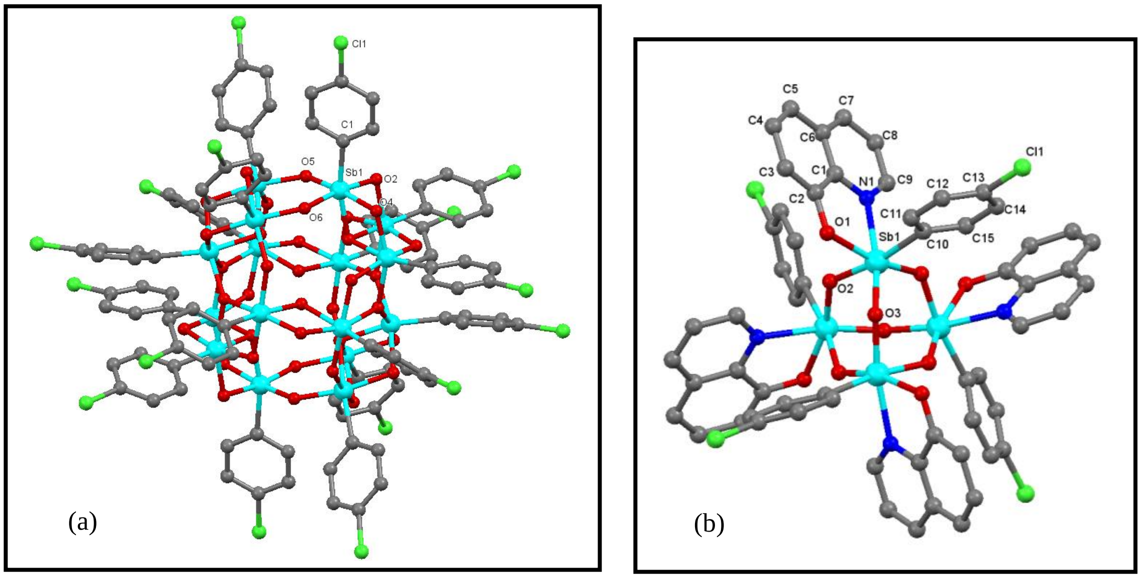


Figure 30: Solid state structures of (a) hexadecanuclear polyoxostibonate $[(p\text{-Cl-C}_6H_4Sb)_{16}(O)_{28}(OH)_8]$ and (b) $[(p\text{-Cl-C}_6H_4Sb)_4(O)_6(Q)_4]$, QH = 8-hydroxyquinoline.

Depolymerisation reactions of arylstibonic acids with 8-hydroxyquinoline (8-HQ)/ napthylphenolic pyrazole (H_2naphpz) [1:1 mole ratio] in toluene at reflux conditions has been performed to obtain tetranuclear adamantane-type $L_4(RSb)_4O_6$ organoantimony oxo clusters (Figure 30b). Interestingly, Sb_4O_6 adamantane-type framework is structurally in resemblance with dimeric form of antimony oxide Sb_2O_3 and its mineral senarmontite.[102]

1.11 Motivation for the Work:

As already mentioned, there is an ambiguity in the solid state structure of triphenylantimony oxide and considerable debate has been going on since it was synthesized by treating triphenylantimony with H_2O_2 which resulted in the formation of an amorphous white powder, poorly soluble in common organic solvents. Despite the fact that triorganoantimony(V) complexes have several applications in biology and organic catalysis, the complete information regarding structural aspects is less known. Hence we thought it would be interesting to explore this particular area and started investigating the depolymerization reactions of triphenylantimony oxide with various protic ligands. We were able to isolate interesting eight membered organoantimony rings or open chain organoantimony(V) complexes which are completely soluble in all common organic solvents. These details are presented in chapter 2.

As we discussed in the introduction part, diorganotellurium dihalides tend to form cationic ditelluroxane frame works in the presence of protic acids and are able to form novel macrocyclic structures. Hypervalent nature of tellurium atom has been observed in many organotellurium(IV) complexes which led to the formation of interesting supramolecular networks in solid state. A recent report on the isolation of a 12-membered $Te_4P_2O_6$ macrocyclic core that is stabilized by halide ions prompted us in investigating the reaction of analogus acids of selenium, say benzeneseleninic acid with bis(p-methoxyphenyl)tellurium dihalides (Cl, Br, I) in presence of triethylamine. The details are presented in chapter 3.

Arylstibonic acids are ill-defined, polymeric in nature and insoluble in most organic solvents. But they do have several applications in biology and catalysis. Arylstibonic acids tend to form soluble multinuclear organoantimony oxo clusters when treated with acidic or basic ligands. By keeping the fact in mind that diorganotellurium oxides are basic in solution, we have investigated the independent reactions of diphenyltellurium oxide with organostibonic acid and triphenylantimony oxide which resulted in the formation of novel and rare mixed valent Sb(V)/(III) containing polyoxostibonates stabilzed by triphenyltellurium cations in the solid state. These details are presented in chapter 4.

Organoantimony(V) halides are Lewis acidic in nature. On the other hand mono and di-dearylation in triphenylantimony(V) compounds is very common and can be utilized as tool for assembling multinuclear antimony oxo clusters. Organometallic compounds containing Sb-O-Te frameworks is a rarity, hence we thought it would be interesting to explore the possibility of formation of Sb-O-Te building blocks by treating diorganotellurium oxides with organoantimony(V) halides. Details are presented in chapter 5.

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Organoantimony(V) Phosphinates, Phosphonates and Seleninates

Chapter 2

Reaction of polymeric triphenylantimony oxide with various protic ligands like phenylphosphinic acid, diphenylphosphinic acid, tert-butyl phosphonic acid and phenylseleninic acid has been investigated. Single crystal X-ray structural elucidation revealed the formation of $[Ph_3Sb(HPhPO_2)_2]_2$ 2.**1**, $[Ph_3Sb(Ph_2PO_2)_2]$ 2.**2**, $[Ph_3Sb(tert\text{-}BuPO_3H)_2]$ 2.**3**, $[Ph_3Sb(PhSeO_2)_2]_2$ 2.**4**, and $[(Ph_3Sb)_2(\mu\text{-}O)(\mu\text{-}PhSeO_2)_2]$ 2.**5** respectively. Hydrolysis and dearylation of 2.**3** yielded $[(Ph_2Sb)_2(PhSb)(\mu_3\text{-}O)(\mu_2\text{-}O)_2(OH)_2(\mu\text{-}t\text{-}BuPO_3)_2[(C_2H_5)_4N]_2]$ 2.**6** possessing *insitu* generated $Ph_2Sb(O)(OH)$ and $PhSbO_3H_2$ moieties. ^{31}P solution NMR spectrum of 2.**1** shows the observation of P-H three-bond coupling for the first time in organophosphorus based compounds. Further ^{31}P NMR at lower temperatures revealed 2.**1** to be fluxional molecule. ^{77}Se NMR indicates the formation of different molecular clusters from crystallization process carried out under varying solvent conditions.

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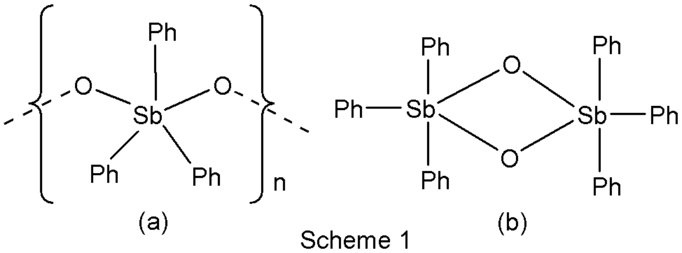
2.1 Introduction

Group 15 elements in pentavalent state of oxidation has the ability to form double bond with oxygen atom resulting in the formation of triorganylpnictogen oxides of the formula $R_3M{=}O$ (R=P, As, Sb, Bi). Depending on the central atom present, they exist as either monomer or polymer in solid state. Heavier elements of the group, bismuth and antimony forms dimeric or polymeric triarylantimony oxides (Scheme 1) depending on the starting precursor used and the synthetic procedure adopted.[1] In 1986 Doak et al reported the crystal structure of dimeric triphenylantimony oxide which crystallized as a dimer in solid state.[2] However the solid state structure of triphenylantimony oxide was a matter of considerable debate since an attempt to synthesize triphenylantimony oxide by treating triphenylantimony with H_2O_2 resulted in the formation of an amorphous white powder poorly soluble in common organic solvents.[3] With the help of EXAFS studies, Orpen and coworkers proposed that the resulting compound is polymeric triphenylantimony oxide in which each trigonal bipyramidal Ph_3SbO_2 unit is bridged through their axial oxygen atom in to a polymeric array.[4] It has to be mentioned here that Huber et al has reported the oxidation of trimesitylantimony resulting in the formation of trimesitylantimony dihydroxide which upon reaction with sulphonic and carboxylic acids forms adducts.[5] They also carried out the reactions of polymeric triphenylantimony oxide with veriety of sulphonic acids to form open-chain monomeric antimony complexes.[6] In another interesting observation, Breunig et al reported the oxidation of tetraaryldistibanes with air and H_2O_2 resulting in the formation of monoxides $[(R_2Sb)_2O]$, hexoxides $[(R_2Sb)_4O_6]$ and peroxo clusters $[(R_2SbO)_4(O_2)_2]$.[7]



Scheme 1

Organoantimony compounds have generated continued interest due to their interesting structural chemistry which leads to the isolation of intriguing metal oxo clusters and polyoxometallates.[8] Recently our group and others have been involved in investigating the reactions of polymeric organostibonic acid by carry out depolymerisation reactions using various protic ligands with an aim of understanding the basic building blocks that are responsible for formation of cluster frameworks.[9] In a break through result, Beckmann et al reported the solid state structure of a well-defined stibonic acid which crystallized as a dimer.[10] Dinuclear and tetranuclear diorganoantimony carboxylates and phosphinates have been reported earlier by carrying out reactions between diorganoantimony trihalides and silver salts of corresponding carboxylates and phosphinates.[11] In another report, synthesis of an oxo bridged dimeric antimony-*tert.*butylphosphonate and its hydrolysis leading to assembly of a novel nonanuclear organostiboxane cage has been reported.[12] Synthesis of $[LSbO]_2$ type Sb(III) compounds have been reported employing NCN-chelating ligand systems.[13] Continuing our work in the field of organoantimony(V) compounds, herein the synthesis and structural characterization of organoantimony(V) based phosphinates, phosphonates and seleninates are reported.

2.2 Experimental Section

2.2.1 General Information:

Phenylphosphinc acid, diphenylphosphinic acid, phenylseleninic acid, tetraethylammonium hydroxide, solvents and other general reagents were purchased from commercial sources. Tertiary butylphosphonic acid and polymeric triphenylantimony oxide were synthesized according to literature reports.[6,14]

2.2.2 Instrumentation:

Infrared spectra were recorded on a JASCO-5300FT-IR spectrometer as KBr pellets. The solution ^{1}H, ^{13}C, ^{31}P, ^{77}Se NMR spectra were recorded on Brucker AVANCE^{III} 40 instrument. Elemental analysis was performed on a Flash EA Series 1112 CHNS analyzer. Single Crystal X-ray data collection for 2.**1**-2.**4** were collected at 100(2) K and 2.**5**, 2.**6** were carried out at 298(2) K on a Bruker Smart Apex CCD area detector system (λ (Mo Kα) = 0.71073Å) with a graphite monochromator. The data were reduced using SAINTPLUS and the structures were solved using SHELXS-97[15] and refined using SHELXL-97.[16] In 2.**4** the selenium attached phenyl ring (C25, C26, C27, C28, C29, C30) was disordered over two positions A and B with occupancies 0.60 and 0.40 respectively. Solvate dichloromethane (C31 CL1 CL2) was also found to be disordered over two positions A and B with occupancies 0.55 and 0.45 respectively. All non-hydrogen atoms were refined anisotropically.

2.2.3 Synthetic procedures

2.2.3a Synthetic procedure for compounds 2.1-2.5:

Compound 2.**1:** Triphenylantimony oxide (0.200 g, 0.54 mmol) was added to 25 mL of dichloromethane to get a white colored suspension. To this phenylphosphinic acid (0.154 g, 1.08 mmol) was added and stirring continued for 12 h at room temperature resulting in the formation of a clear solution. The solution was filtered and concentrated under reduced pressure to which was added equal volume of hexane to obtain block like crystals overnight at room temperature. Yield: 78.44% (based on triphenylantimony oxide). M.P: 150^{o}C. $C_{60}H_{54}O_8P_4Sb_2$ (1270.43):calcd. C 56.72, H 4.28; found C 56.61, H 4.32. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.12(d, J = 7.2 Hz, 12H), 7.95(d, J = 548 Hz, 4H), 7.57(m, 18H), 7.39(m, 12H), 7.27(m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 135.52, 134.34, 134.22, 134.10, 132.46(d, J = 106 Hz), 129.86(d, J = 12 Hz), 128.25(d, J = 13 Hz); ^{31}P NMR (162 MHz, $CDCl_3$, ppm): δ13.42, at low tempratures: (at 0^{o}C) δ 13.66, 13.63, (at -50^{o}C) δ 14.05, 14.00, 13.93. ^{31}P{^{1}H}NMR (162 MHz, $CDCl_3$, ppm): δ 15.20(dt, J = 545.9, 13.0 Hz). IR(KBr, cm^{-1}): 3051.6(m), 2388.1(w), 2324.4(w), 1666.6(w), 1591.4(w), 1574.1(w), 1481.5(s), 1433.2(s), 1313.6(m), 1219.1(s, PO), 1184.4(w), 1145.8(w), 1124.6(w), 1072.5(m), 964.5(w), 736.9(s), 690.6(s), 549.8(s), 457.2(m).

Compounds 2.**2**, 2.**3**, 2.**4**, 2.**5** were also prepared by the same procedure as compound 2.**1**. The mole ratios of the corresponding reagents used are as follows.

Compound 2.**2**: Triphenylantimony oxide (0.200 g, 0.54 mmol), diphenylphosphinic acid (0.236 g, 1.08 mmol), yield: 82.04%. M.P: 302°C. $C_{42}H_{35}O_4P_2Sb$(787.40): calcd C 64.06, H 4.48; found C 64.21, H 4.56. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.09(m, 6H), 7.47(m, 22H), 7.15(m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 137.00, 135.64, 135.42, 134.37, 131.83(d, J = 148 Hz), 131.00(d, J = 10 Hz), 129.56, 127.84(d, J = 13 Hz); ^{31}P NMR (162 MHz, $CDCl_3$, ppm): δ 21.06. IR(KBr, cm^{-1}): 3055.5(w), 1589.5(w), 1483.4(m), 1437.1(s), 1311.7(w), 1275.1(w), 1201.8(s, PO), 1163.2(m), 1124.6(m), 1068.7(m), 943.3(w), 756.2(m), 723.4(w), 696.4(m), 547.8(w), 516.9(w), 428.2(w).

Compound 2.**3**: Triphenylantimony oxide (0.200 g, 0.54 mmol), *tert*-butylphosphonic acid (0.150 g, 1.08 mmol), yield: 83.84%. M.P: 277°C. $C_{26}H_{35}O_6P_2Sb$(627.26): calcd C 49.78, H 5.62; found C 49.65, H 5.51. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.76(s, 2H), 8.15(d, J = 8 Hz, 6H), 7.41(m, 9H), 0.70(d, J = 16 Hz, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 134.92, 134.63, 131.89, 129.53, 32.12(d, J = 145 Hz), 25.06; ^{31}P NMR (162 MHz, $CDCl_3$, ppm): δ 29.02. IR(KBr, cm^{-1}): 3059.4(w), 2970.6(w), 2359.1(m), 1664.7(br, POH), 1479.5(s), 1439.0(s), 1392.7(m), 1363.8(m), 1334.86(m), 1240.3(m, PO), 1149.7(w), 995.4(m), 939.4(m), 829.5(m), 734.9(s), 690.6(s), 652.0(s), 493.8(s), 459.1(s)

Compound 2.**4**: Triphenylantimony oxide (0.200 g, 0.54 mmol), phenylseleninic acid (0.204 g, 1.08 mmol), crystals isolated from dichloromethane-hexane mixture. Yield: 75.93%, M.P: 187°C. $C_{60}H_{50}O_8Se_4Sb_2$(1458.41): calcd C 49.41, H 3.45; found C 49.62, H 3.36. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.06(d, J = 6 Hz, 10H), 7.53(m, 40H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.96, 135.49, 134.80, 132.05, 131.42, 129.90, 129.05, 127.67, 125.50; ^{77}Se NMR (76.3 MHz, $CDCl_3$, ppm): δ 1185. IR(KBr, cm^{-1}): 3053.6(m), 1971.4(w), 1900.1(w), 1820.9(w), 1574.1(m), 1475.7(s), 1433.2(s), 1305.9(m), 1182.5(m), 1157.4(w), 1068.6(s), 1020.4(m), 997.3(s), 923.9(w), 881.55(s), 773.5(w), 690.6(w), 505.4(m), 468.7(w).

Compound 2.**5**: Crystals were grown in acetonitrile-hexane mixture. Yield: 84.03%. M.P: 229^{o}C. $C_{48}H_{40}O_5Se_2Sb_2$(1098.22): calcd C 52.49, H 3.67; found C 52.31, H 3.75. ^{1}H NMR (400 MHz, CD_3OD - $CDCl_3$, ppm): δ 7.98(m, 12H), 7.85(m, 4H), 7.64(m, 24H); ^{13}C NMR (100 MHz, CD_3OD - $CDCl_3$, ppm): δ 143.56, 134.58, 134.33, 132.60, 132.31, 131.22, 129.57, 129.21, 129.16, 125.91; ^{77}Se NMR (76.3 MHz, CD_3OD - $CDCl_3$, ppm): δ 1215. IR(KBr, cm^{-1}): 3051.6(w),1961.8(w), 1886.5(w), 1817.1(w), 1574.1(m), 1477.6(s), 1440.9(s), 1429.4(s), 1304.0(m), 1265.4(w), 1182.5(m), 1155.5(w), 1066.7(s), 1020.4(m), 997.3(s), 916.3(w), 767.7(w), 734.9(w), 694.4(s), 486.1(m), 462.9(w).

2.2.3b Synthetic procedure for compound 2.6:

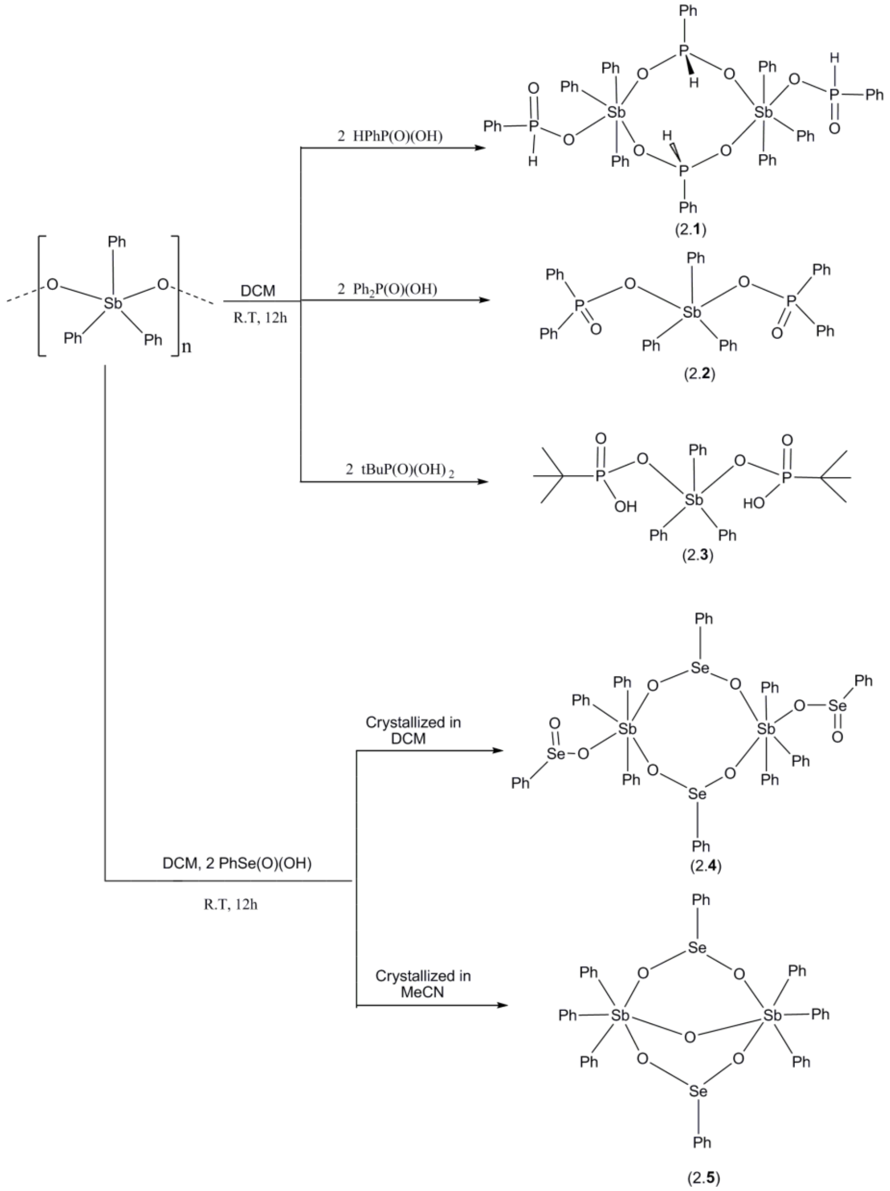
Tetraethylammonium hydroxide (0.19 mL, 1.34 mmol) was added to a solution of 2.**3** (0.21 g, 0.33 mmol) in 30 mL of toluene and the solution was refluxed for 12h. Dean-stark apparatus was used to remove the water eliminated in the reaction as an azeotropic mixture. This resulted in a white gel like precipitate and stuck to the bottom of the flask. The solution was filtered and the resultant precipitate dried under vacuum. Crystals were grown by dichloromethane / hexane diffusion method. Yield: 65.65% (based on 2.**3**). M.P: 252^{o}C. $C_{54}H_{85}N_2O_{11}P_2Sb_3$(1365.44): calcd C 47.49, H 6.27, N 2.05; found C 47.56, H 6.23, N 2.12; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.01(m, 2H), 7.85(d, J = 7.6 Hz, 4H), 7.64(d, J = 7.2 Hz, 4H), 7.32(d, J = 6 Hz, 3 H), 7.15(m, 6H), 6.68(br, 3H), 6.60(m, 4H), 3.19(m, 17H), 1.13(t, 7.2 Hz, 24H), 1.01(d, J = 14.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.73, 152.94, 134.48, 134.38, 138.14, 129.25, 127.84, 127.58, 127.03, 126.54, 126.05, 51.892, 32.43(d, J = 144.8 Hz), 27.03, 7.54; ^{31}P NMR (162 MHz, $CDCl_3$, ppm): δ 23.99. IR(KBr, cm^{-1}): 3059.4(w), 2966.8(w), 1658.9(w), 1579.8(m), 1481.5(s), 1433.2(m), 1394.6(m), 1263.5(s, PO), 1149.7(s), 1074.4(m), 983.8(m), 800.5(w), 734.9(s), 694.4(s), 659.7(m), 634.6(w), 532.4(m), 499.6(m), 464.9(s).

2.3 Results and Discussion

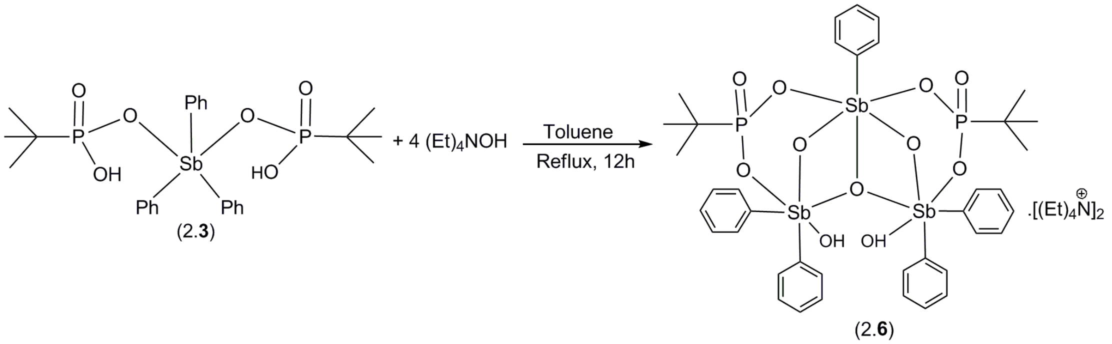
General synthetic procedures employed for synthesis of 2.**1**-2.**5** are as follows. Polymeric triphenylantimony oxide and the protic acids were taken in 1:2 molar ratios and stirred in dichloromethane for 12 h at room temperature resulting in a clear solution. Filtration was followed by evaporation to reduce the volume of the filtrate to half of the initial value to which was added equivalent volume of hexane. Colorless block like crystals of compound 2.**1**-2.**4** were obtained in high yields. Interestingly when the reaction product of the reaction between polymeric triphenylantimony oxide and phenylseleninic acid was crystallized from acetonitrile-hexane mixture yielded 2.**5** (Scheme 2). Base induced hydrolysis and *insitu* dearylation of 2.**3** results in the formation of 2.**6** (Scheme 3).

Compounds (2.**1**-2.**6**) were characterized by standard spectroscopic and analytical techniques. Solution NMR of the compounds 2.**1**-2.**4** were performed in $CDCl_3$, 2.**5** was collected in mixture of CD_3OD-$CDCl_3$ and 2.**6** in DMSO-D_6. ^1H NMR spectrum of 2.**1** shows a doublet resonance peak at δ = 7.95 ppm, with a coupling constant of 548 Hz between ^{31}P and ^1H ($^1J_{P,H}$ = 548 Hz) clearly showing the presence of PH group in the 2.**1**. Though one expected a doublet in the proton coupled ^{31}P NMR spectrum for the PH group, interestingly a doublet of triplet at δ = 15.20 ppm was observed (Figure 1). Coupling constant of 545.9 Hz ($^1J_{H,P}$ = 545.9 Hz) for the doublet can be assigned to one-bond coupling between P and H and a coupling constant of 13.0 Hz($^3J_{H,P}$ = 13.0 Hz) in the triplet can be assigned to three-bond coupling between P and two *ortho* hydrogens on the phenyl ring attached to phosphorus atom. To the best of our knowledge this is the first report for observation of such three bond PH coupling in ^{31}P NMR spectrum though the three-bond coupling between hydrogen and phosphorus atom in ^1H NMR are well documented.[17] Further proton decoupled ^{31}P NMR spectrum shows single resonance peak at δ = 13.42 ppm which indicates the presence of phosphorus atom in an unique environment in 2.**1**.

Scheme 2



Scheme 3



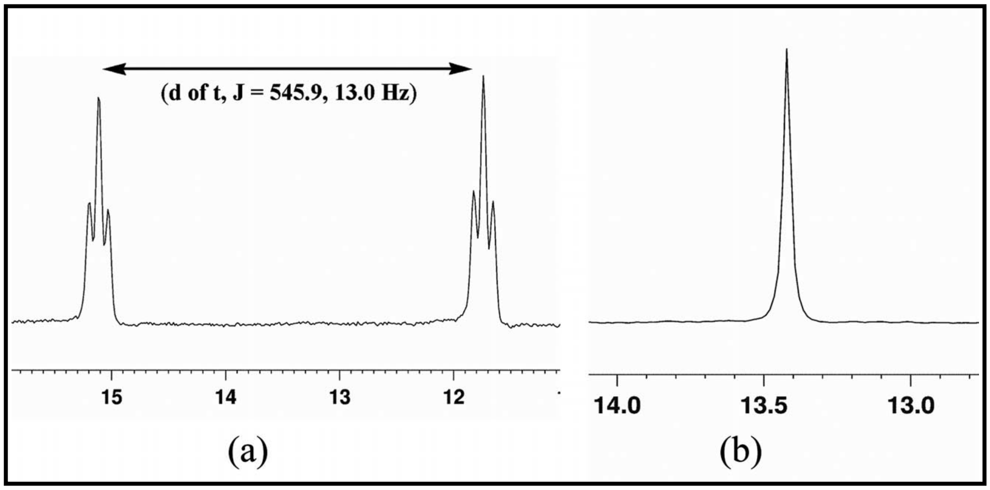


Figure 1: (a) Proton coupled ^{31}P NMR of 2.**1** showing a doublet of triplet indicating the three bond P-H coupling (b) Proton decoupled ^{31}P NMR of 2.**1**.

^{31}P NMR spectra of 2.**2**, 2.**3** and 2.**6** shows single resonance peaks at δ = 21.06, 29.02 and 23.99 ppm respectively, indicating the presence of unique environment for phosphorus atoms. Further ^{1}H NMR spectrum of 2.**3** shows a broad peak at δ = 9.76 ppm which is assigned to the presence of P-OH group. ^{77}Se solution NMR spectrum of 2.**4** and 2.**5** shows single resonance at δ = 1185 ppm and 1215 ppm respectively. This indicates that the environment of selenium atoms in 2.**4** and 2.**5** differ. ^{13}C NMR spectra of all the compounds (2.**1**-2.**6**) are in agreement with proposed structures (Scheme 2 and 3). Further one-bond, two-bond and three-bond coupling between ^{31}P and ^{13}C nuclei have been observed in ^{13}C NMR of compounds 2.**1**, 2.**2**, 2.**3** and 2.**6**. IR spectrum of compound 2.**1** shows a medium peak at 2324 cm^{-1}, which supports the presence of PH group.[18] Broad peaks at 2359 cm^{-1} and 1664 cm^{-1} shows the presence of POH group in the 2.**4**.[13b, 19] Medium or strong peaks in the range of 1200-1260 cm^{-1} reflects the Presence of PO group[20] in the spectra of the compounds 2.**1**, 2.**2**, 2.**3** and 2.**6** respectively.

The compounds (2.**1**-2.**6**) were characterized by single crystal X-ray diffraction studies. Crystallographic data and selected bond distance and bond angle parametres for

2.**1**-2.**6** are given in tables 4-7. Compound 2.**1** crystallizes in triclinic space group P-1 with half of the molecule in asymmetric unit. The molecular structure of 2.**1** consists of two triphenylantimony subunits bridged by two phenylphosphinates in 2.11 coordination mode[21] hence resulting in the formation of an eight-membered ring $Sb_2P_2O_4$ ring. Further two more terminal phenylphosphinates are present in the structure, each binding to antimony atom in a monodentate fashion (Figure 2).

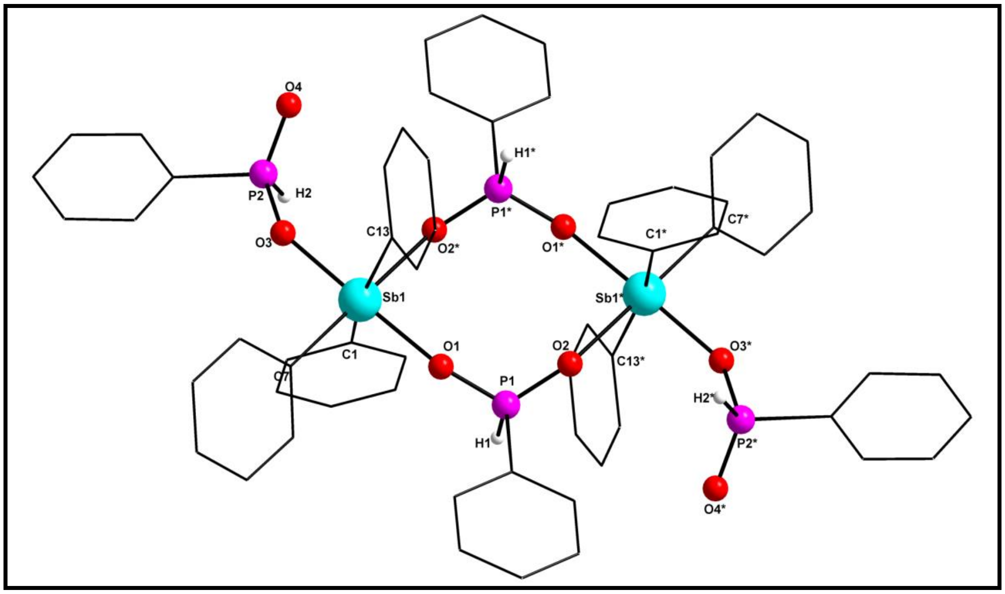


Figure 2: Solid state structure of 2.**1**. Hydrogen atoms except those bonded to phosphorus are omitted for clarity.

The structure of 2.**1** resembles closely to earlier reports of similar $Sb_2P_2O_4$ eight-membered rings reported in literature.[22] The geometry around each antimony in 2.**1** is a distorted octahedron. Of the six coordinations present, two are from oxygens of bridged phosphinates, one from oxygen of terminal phosphinate and one carbon of phenyl ring occupying the equatorial positions. Remaining two axial positions are occupied by two carbons of phenyl rings which makes an angle of 161.52(18)° (C1-Sb1-C13) indicating the extent of deviation from regular octahedron (180°). In contrast to the solution studies, solid state structure of compound 2.**1** revealed that it contains two kind of phosphinates, among them one phosphinate (P1) group forms a nonsymmetrical bridge between two antimony(V) ions with the bond lengths corresponding to Sb1-O1 = 2.109(3)Å, O1-P1 = 1.514(3) Å or Sb1*-O2 = 2.318(3) Å, O2-P1 = 1.499(4) Å and the other phosphinate (P2) forms a terminal bond with the bond lengths corresponds to Sb1-O3 = 2.041(3) Å and O3-P2 = 1.541(4) Å. It should be mentioned here that though the crystal structure indicates the presence of two types of phosphinates, the solution ^{31}P NMR at room temperature could not distinguish between the two kinds of phosphorus atoms present probably due to fast exchange between the terminal and bridged phosphinates in the NMR time scale. Low temperature NMR studies (0°C and -50°C) showed the appearance of two (δ = 13.66 ppm, 13.63 ppm) and three (δ = 14.05 ppm, 14.00 ppm, 13.93 ppm) signals respectively indicating the fluxional behavior of 2.**1** at room temperature (Figure 3). The appearance of two signals at 0˚C can be designated for the presence of two kinds of phosphinates in 2.**1**(bridging and dangling). The three signals at -50°C can be accounted for by considering the following option, middle signal of the three corresponding to a pair of bridging phosphinate while the other two signals from the two hanging phosphinates with phosphorus atom present in slightly different environment to each other.

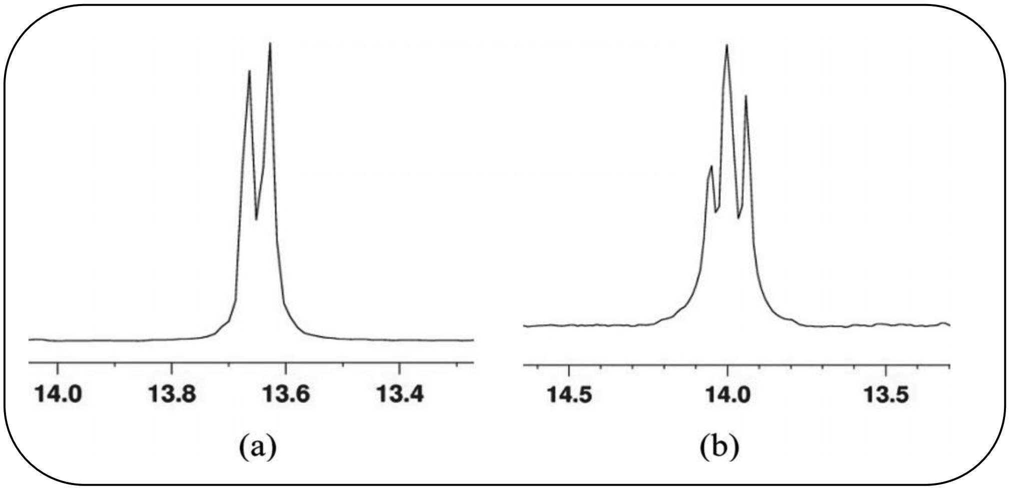


Figure 3: (a) Proton decoupled ^{31}P NMR for 2.**1** at 0˚C. (b) Proton decoupled ^{31}P NMR for 2.**1** at -50˚C

It is of interest to compare 2.**1** with an earlier report in organotin chemistry wherein a diorganotin phosphonate possessing two kinds of phosphonates in the solid state was found to be fluxional.[23] The eight-membered ring $Sb_2P_2O_4$ looks almost planar, with Sb1, P1, O1 and O2 deviating ±0.050 Å, ±0.256 Å, ±0.120 Å, ±0.241 Å respectively from the mean plane defined by the eight membered ring. The average Sb-O bond length are 2.156(3) Å which is slightly less than that of reported Sb(III) phosphinate Sb-O bond length of 2.213(3) Å.[13c]

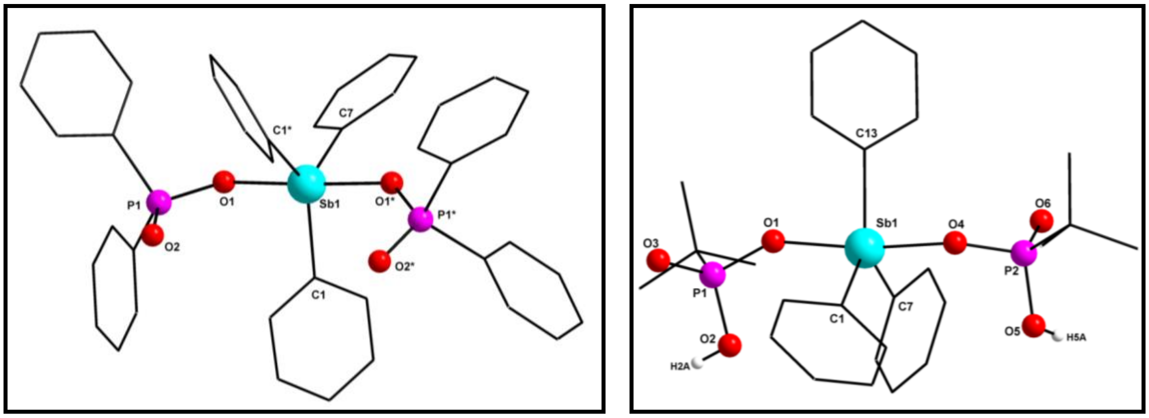


Figure 4: (left) Solid state structure of 2.**2**. (right) Solid state structure of 2.**3**. Hydrogen atoms are omitted for clarity.

Compound 2.**2** crystallizes in monoclinic space group C2/c and the structure corresponds to a triphenylantimony monomer [Figure 4(left)] in which two diphenylphosphinates coordinates to the central antimony ion in unidentate fashion. The phosphinates are present in *trans* direction to each other as revealed by O-Sb-O angle of 176.35(11)°. The geometry around the central antimony seems to be a slightly distorted trigonal bipyramidal, in which three phenyl groups occupies equatorial positions and two phosphinates oxygen atoms located at axial positions. Compound 2.**3** crystallizes in monoclinic $P2_1/n$ space group. The molecular structure [Figure 4(right)] is similar to that of compound 2.**2**. Two *tert*-butyl phosphonates binds to the central antimony ion in monodentate fashion mutually *trans* to each other making an angle of 170.96(17)° at O-Sb-O unit, which is more close to the ideal axial bond angle in a trigonal bipyramidal geometry. Each phosphonate has one free OH group which remains non-coordinating. The average Sb-O bond lengths in 2.**2** and 2.**3** are 2.078(2) Å and 2.058(2) Å respectively, which are close to the value for Sb(V)-O bonds[24] and slightly less when compared to the reported Sb(III) diphenylphosphinates and phosphonates respectively.[13b]

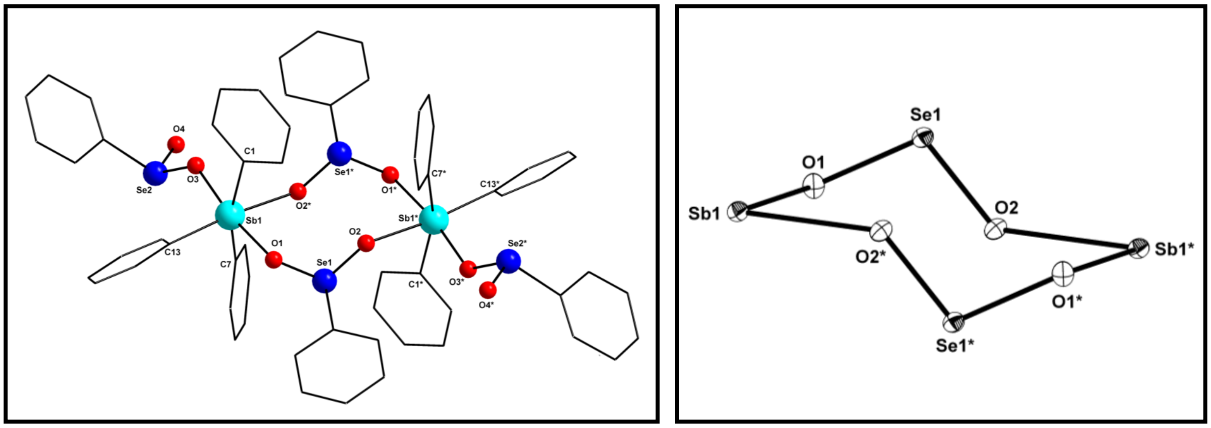


Figure 5: (left) Solid state structure of 2.**4**. Hydrogen atoms are omitted for clarity. (right) Puckered eight membered $Sb_2Se_2O_4$ core of 2.**4**.

Compounds 2.**4** and 2.**5** are the products of the reaction between polymeric triphenyantimony oxide and phenylseleninic acid but crystallized from different solvent systems, namely dichloromethane-hexane mixture and acetonitrile-hexane mixture respectively. Solution NMR studies indicate to the isolation of varied products which was confirmed by single crystal X-ray crystallography. Compound 2.**4** crystallizes in monoclinic space group $P2_1/n$. Structure of 2.**4** [Figure 5(left)] resembles exactly with that of compound 2.**1**, where phenylseleninates replaces the phenylphosphinates present in 2.**1** leading to the formation of an eight-membered $Sb_2Se_2O_4$ ring. The eight-membered ring is highly puckered [Figure 5(right)] when compared to the eight-membered ring of the 2.**1**, which is almost planar. Mean plane deviation results show that this ring is more puckered in comparison to that of 2.**1**(table 1). As in the case of 2.**1,** in contrast to solution studies, the solid state structure reveals the presence of two kinds of phenylseleninates. Low temperature NMR studies (0°C and -50°C) were carried out to correlate the solid state structure of 2.**4** and solution NMR studies, but unlike in the case of 2.**1**, the NMR spectrum of 2.**4** showed the appearance of only a single resonance indicating fast exchange between the terminal and bridged seleninates in the NMR time scale. One of the phenylseleninate forms a non-symmetrical bridge between two antimony ions while the other phenylseleninate is terminal and is bound in a monodentate fashion.

Table 1: Mean plane deviation of each atom in $Sb_2Se_2O_4$ ring

Label	D/A	Label	D/A	Label	D/A	Label	D/A
Sb1	0.014	O1	0.309	Se1	0.573	O2	0.457
Sb1*	-0.014	O1*	-0.309	Se1*	-0.573	O2*	-0.457

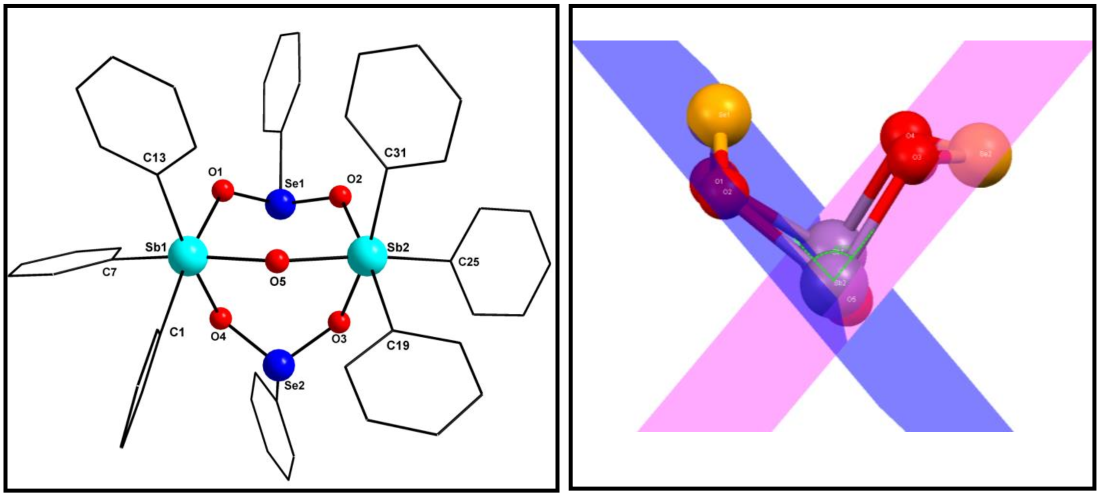


Figure 6: (left) Solid state structure of 2.**5**. Hydrogen atoms are omitted for clarity. (right) Showing the dihedral angle of 80.59º between the two mean planes in bicyclic core of 2.**5**.

Compound 2.**5** crystallizes in triclinic space group P-1. The major difference in the solid state structure when compared to the 2.**4** is the absence of terminal phenylseleninates and the charge balance comes from the presence of a μ-oxo bridge (O5) which connects two antimony(V) ions namely Sb1 and Sb2 [Figure 6(left)]. Chelating non symmetrical bridged phenylseleninates are present in 2.11 coordination mode.[11b, 12, 25] The structure of 2.**5** can be visualized as follows; two six-membered Sb_2O_3Se rings, which are nearly perpendicular to each other with dihedral angle 80.09° [Figure 6(right)] and sharing a common Sb-O-Sb bridge. Each six-membered ring by itself is not planar and can be clearly observed by deviation of each atom from the mean plane (tables 2-3). Interestingly the average Sb-O bond lengths of 2.**4** and 2.**5** [2.150(3) Å, 2.153(6) Å] are very similar to the recently reported organoantimony(III) selenite.[26] The average Se-O bond length of 2.**4** [1.780(2) Å] is also found similar to the recently reported organoantimony(III) selenite .[26]

Table 2: Mean plane deviation of each atom in six-membered Sb1O1Se1O2Sb2O5 ring of 2.**5**.

Label	D/A	Label	D/A	Label	D/A
Sb1	-0.151	O1	0.359	Se1	-0.417
O2	0.232	Sb2	-0.076	O5	0.053

Table 3: Mean plane deviation of each atom in six-membered Sb1O4Se2O3Sb2O5 ring of 2.**5**.

Label	D/A	Label	D/A	Label	D/A
Sb1	-0.097	O4	-0.349	Se2	0.549
O3	-0.305	Sb2	-0.128	O5	0.331

The presence of two free OH groups on the phosphonate ligands in 2.**3** and earlier reports on the facile cleavage of Sb-C bonds in triorganoantimony(V) compounds [12, 27] prompted us to investigate if one can assemble larger clusters from 2.**3**. Hence base induced hydrolysis of 2.**3** was carried out in toluene in the presence of excess tetraethylammonium hydroxide at reflux temperature. Single crystal studies revealed the assembly of a novel dianionic trinuclear organoantimony oxido cluster along with two molecules of tetraethylammonium cations in the crystal lattice. Compound 2.**6** crystallizes in monoclinic space group C2/c. In the dianionic core (Figure 7), the antimony ions exist in an octahedral geometry. Due to facile cleavage of the Sb-C bonds at higher temperatures, mono and di-dearylation followed by elimination of water molecules from the free OH present in phosphonate and subsequent self-assembly leads to the formation of the trinuclear metal oxo core.

The structure of 2.**6** can be visualized as follows. The antimony ions are connected through a μ_3-oxo bridge (O1) and further each Sb2 and Sb2* ions are also connected to the Sb1 ion through a μ_2-oxo bridge (O2 or O2*) resulting in the formation of two four- membered Sb_2O_2 rings that are then fused through a common Sb-O bond (Figure 7b). One *tert*-butyl phosphonate ligand is involved in binding in a bidentate fashion at both ends of these four-membered Sb_2O_2 rings to form two bicyclic systems, each one composed of one six-membered Sb_2PO_3 ring and a four-membered Sb_2O_2 ring (Figure 7c). Each Sb2 and Sb2* ion also consists of a free OH group that is involved in weak hydrogen bonding with P=O of the *tert*-butylphosphonate group (P=O….H, 1.950Å). Mono and di-dearylation has led to the observation of *insitu* generated diphenylstibinic acids [$Ph_2Sb(O)OH$] and phenylstibonic acid [$PhSb(O)(OH)_2$] residues in the solid state structure of 2.**6**. Weak intramolecular π- π stacking[28] between phenyl ring attached to Sb2 with that of phenyl ring attached to Sb2* is also observed. π- π stacking distance between the phenyl centroids is 3.946Å which is slightly greater than the van der Waals radii (3.800 Å).

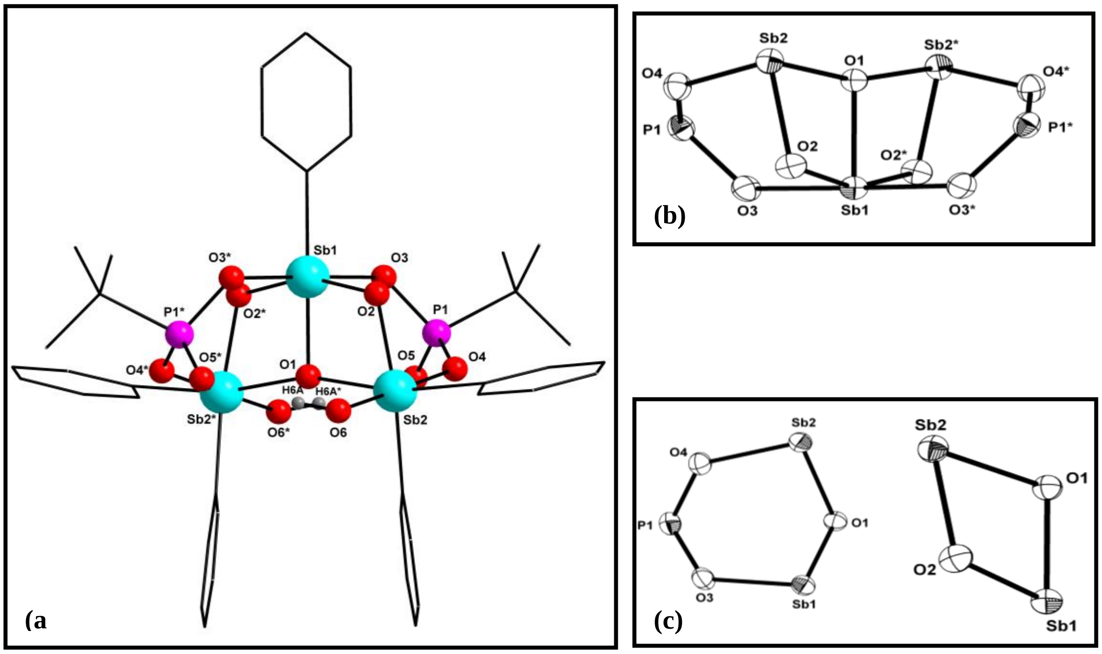


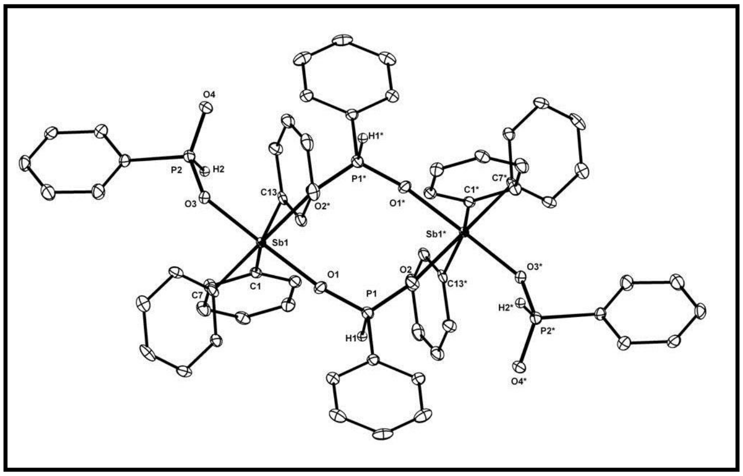
Figure 7: (a) Solid state structure of 2.**6**. Hydrogen atoms except those bonded to Sb-O and tetraethylammonium cations are omitted for clarity. (b) Core of the compound 2.**6** showing two Sb2PO3 fused rings through Sb-O. (c) Six-membered Sb2PO3 ring and four- membered Sb2O2 ring

2.4 Conclusion

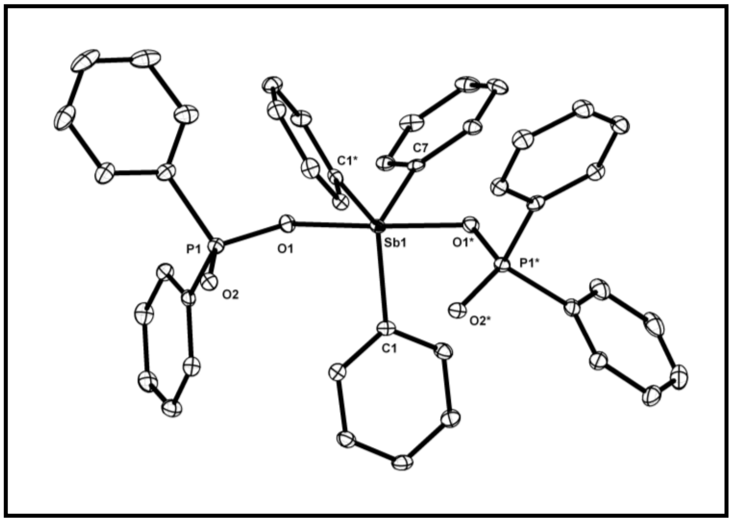
Depolymerization of triphenylantimony oxide in presence of protic ligands have led to the isolation of interesting eight membered organoantimony rings incorporating either phosphorus or selenium atom as a part of the ring system. Depending on the crystallization process adopted, isolation of varying products has been observed when phenylseleninic acid was used as the ligand. Dearylation and hydrolysis of 2.**3** leads to the isolation of a novel trinuclear organoantimony based oxo cluster possessing *insitu* generated phenylstibinic and phenylstibonic acid residues. ^{31}P and ^{77}Se solution NMR reveals interesting insights about the structures of the products isolated.

2.5 ORTEP diagrams of 2.**1**-2.**6**:

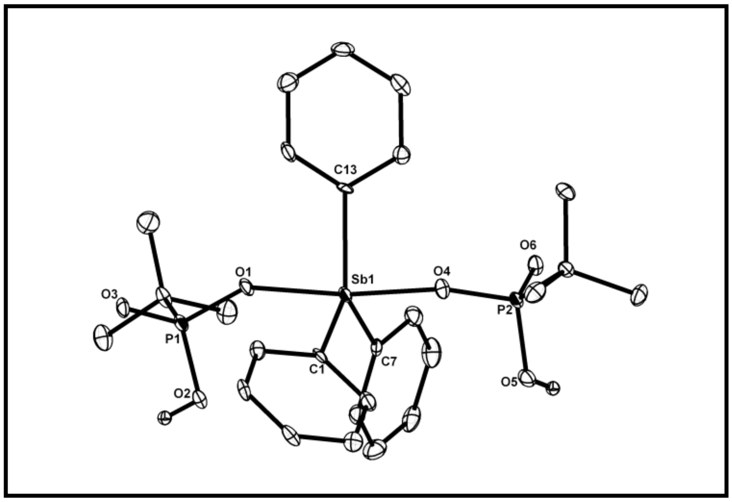
2.**1**



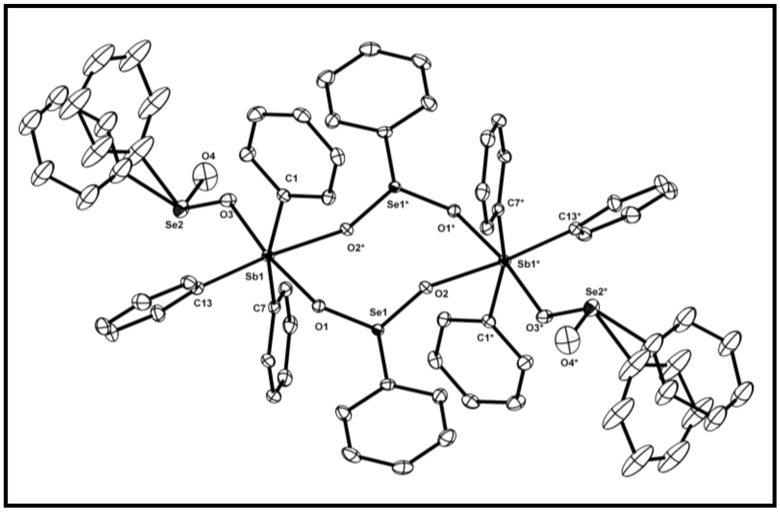
2.**2**



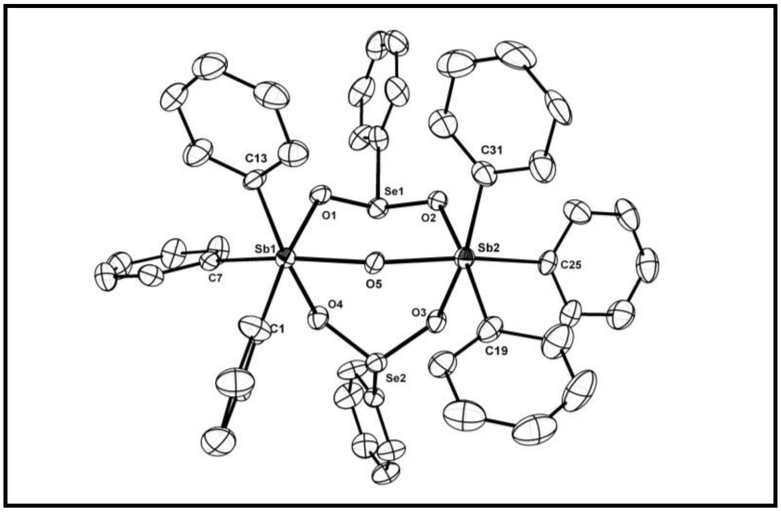
2.**3**



2.**4**


O4
C1
Se1*
C7*
C13*
Se2
O3
O1*
O2*
Sb1*
Sb1
C13
C7
O1
Se1
O2
C1*
O3*
Se2*
O4*

2.**5**


C13
C31
Se1
O1
O2
Sb1
Sb2
C7
O5
C25
O4
O3
C1
C19
Se2

2.**6**

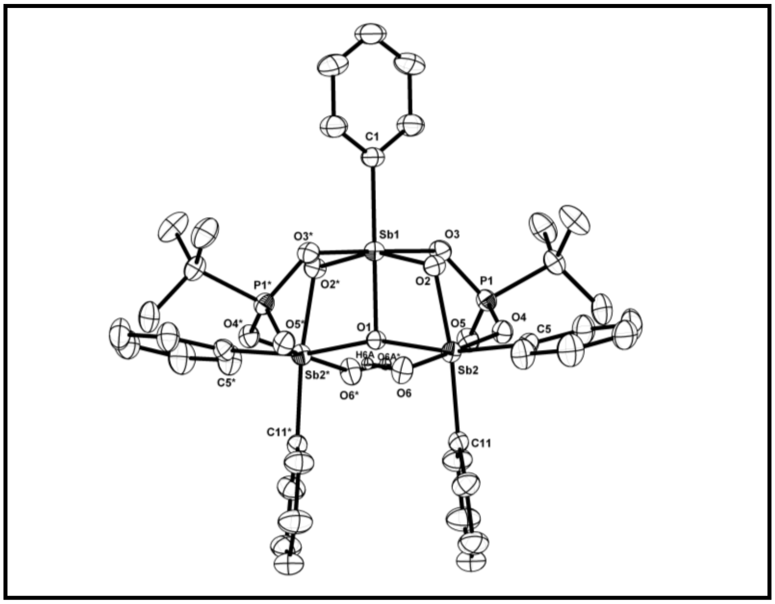

C1
O3*
Sb1
O3
P1*
O2*
O2
P1
O4*
O5*
O1
O5
O4
C5
H6A
O6A*
C5*
Sb2*
Sb2
O6*
O6
C11*
C11

Table 4: Crystal and Refinement data for 2.**1**-2.**3**

	2.**1**	2.**2**	2.**3**
Formulae	$C_{60} H_{54} O_8 P_4 Sb_2$	$C_{42} H_{35}$ O4 P_2 Sb	$C_{26} H_{37} O_7 P_2$ Sb
Fw.g mol^{-1}	1270.41	787.39	645.25
Cryst syst	Triclinic	Monoclinic	Monoclinic
Cryst size.mm	0.34 x 0.32 x 0.30	0.20 x 0.16 x 0.10	0.14 x 0.10 x 0.10
Space group	P-1	C2/c	$P2_1/n$
a, Å	10.794(5)	23.350(19)	10.054(16)
b, Å	10.990(5)	9.651(8)	15.879(3)
c, Å	12.743(5)	15.204(12)	18.744(3)
α, deg	81.31(6)	90.00	90
β, deg	69.38(6)	94.34(10)	103.593(3)
γ, deg	73.62(6)	90.00	90
v, Å^3	1355.2(10)	3416.3(5)	2908.5(8)
Z	1	4	4
Dcacld.Mgm^{-3}	1.557	1.531	1.474
T.K	100	100	100
µ, mm^{-1}	1.171	0.945	1.099
F(000)	640	1600	1320
θ range,deg	1.71 to 25.20°	1.75 to 24.99°	1.70 to 26.47°.
Index ranges	-12<=h<=12 -13<=k<=13 -15<=l<=15	-27<=h<=27 -11<=k<=11 -18<=l<=18	-12<=h<=12 -19<=k<=19 -23<=l<=23
No. of.refln colled	12730	15868	30741
Completeness to θ max	99.1 %	99.9 %	99.9 %
No. of. indep refln/R_{int}	4839	2998	6001
GooF(F^2)	1.190	1.091	1.132
R_1 (F) (I>2σ(I))	0.0480	0.0322	0.0535
wR_2 (F^2) (All data)	0.1084	0.0753	0.1133
Largest diff peak/hole,e Å^{-3}	2.568 / -1.529	0.700 / -0.280	2.213 / -0.784

Table 5: Crystal and Refinement data for 2.**4**-2.**6**

	2.**4**	2.**5**	2.**6**
Formulae	$C_{62}H_{54}Cl_4O_8Sb_2Se_4$	$C_{48}H_{40}O_5Sb_2Se_2$	$C_{55}H_{87}Cl_2N_2O_{11}P_2Sb_3$
Fw.g mol^{-1}	1626.18	1098.22	1450.36
Cryst syst	Monoclinic	Triclinic	Monoclinic
Cryst size.mm	0.20 x 0.16 x 0.12	0.16 x 0.12 x 0.10	0.22 x 0.16 x 0.12
Space group	$P2_1/n$	P-1	C2/c
a, Å	10.845(12)	10.257(3)	27.906(2)
b, Å	15.593(18)	11.236(3)	31.231(2)
c, Å	17.890(2)	19.128(5)	18.343(13)
α, deg	90.00	104.25(4)	90.00
β, deg	90.85(2)	91.19(4)	128.26(10)
γ, deg	90.00	98.12(4)	90.00
v, Å^3	3024.9(6)	2111.6(9)	12553.6(15)
Z	2	2	8
Dcacld.Mgm^{-3}	1.785	1.727	1.535
T.K	100	298	298
μ, mm^{-1}	3.531	3.050	1.473
F(000)	1588	1076	5888
θ range,deg	1.73 to 25.02°	1.89 to 25.13°	1.14 to 25.04°
Index ranges	12<=h<=12 -18<=k<=18 -21<=l<=21	-12<=h<=12 -13<=k<=13 -22<=l<=22	-33<=h<=33 -37<=k<=37 -21<=l<=21
No. of.refln colled	28171	20258	60220
Completeness to θ max	99.7 %	98.3 %	99.8 %
No. of. indep refln/R_{int}	5327	7431	11095
GooF(F^2)	1.051	1.128	1.031
R_1 (F) (I>2σ(I))	0.0303	0.0787	0.0294
wR_2 (F^2) (All data)	0.0798	0.1518	0.0822
Largest diff peak/hole,e Å^{-3}	1.602 / -0.868	1.220 / -1.183	0.757 / -0.468

Table 6: Selected bond lengths(Å) and bond angles(°) in 2.**1**-2.**4**

2.**1**	**2.2**	**2.3**	**2.4**
Sb1-O1 = 2.109(3)	Sb1-O1 = 2.078(2)	Sb1-O1 = 2.041(4)	Sb1-O1 = 2.108(3)
Sb1-O2* = 2.318(3)	Sb1-C1 = 2.089(3)	Sb1-O4 = 2.075(4)	Sb1-O2* = 2.293(3)
Sb1-03 = 2.041(3)	Sb1-C7 = 2.085(4)	Sb1-C1 = 2.095(6)	Sb1-O3 = 2.050(3)
P1-O1 = 1.514(4)	P1-O1 = 1.549(2)	Sb1-C7 = 2.080(6)	Sb1-C1 = 2.140(4)
P1-O2 = 1.499(4)	P1-O2 = 1.479(2)	Sb1-C13 = 2.102(6)	Se1-O1 = 1.723(3)
P1-H1A = 1.44(5)	O1-Sb1-O1*=176.35(11)	P1-O1 = 1.536(4)	Se1-O2 = 1.690(3)
P2-O3 = 1.541(4)	O1-Sb1-C1 = 91.28(10)	P1-O2 = 1.545(5)	Se2-O3 = 1.748(3)
O1-Sb1-O3 = 178.07(14)	O1-Sb1-C7 = 88.17(5)	P1-O3 = 1.478(4)	Se2-O4 = 1.611(4)
O1-Sb1-O2* = 88.99(13)	O1-Sb1-C1* = 90.32(10)	P2-O4 = 1.531(4)	C1-Sb1-C7 = 162.53(16)
O3-Sb1-O2* = 90.62(13)	C1-Sb1-C7 = 115.88(8)	P2-O5 = 1.559(5)	O1-Sb1-O3 = 171.76(12)
C1-Sb1-C13 = 161.52(18)	Sb1-O1-P1 = 133.31(12)	P2-O6 = 1.483(5)	C13-Sb1-O2*=174.37(14)
C1-Sb1-C7 = 97.93(18)	O1-P1-O2 = 116.36(12)	O1-Sb1-O4=170.96(17)	O1-Sb1-O2* = 84.80(11)
C1-Sb1-O1 = 90.33(16)		O1-Sb1-C1 = 92.7(2)	C1-Sb1-C13 = 98.07(17)
O1-P1-O2 = 117.2(2)		O4-Sb1-C7 = 93.5(2)	O3-Sb1-C1 = 86.69(15)
O3-P2-O4 = 116.6(2)		C1-Sb1-C7 = 114.3(2)	O1-Se1-O2 = 104.29(11)
Sb1-O1-P1 = 156.3(2)		P1-O1-Sb1 = 148.0(3)	O3-Se2-O4 = 105.10(2)
P2-O3-Sb1 = 140.8(2)		P2-O4-Sb1 = 140.6(3)	Sb1-O1-Se1 = 120.34(15)
		O1-P1-O2 = 105.2(3)	Se1-O2-Sb1*=130.64(16)
		O4-P2-O5 = 106.6(3)	Sb1-O3-Se2 = 128.44(17)

Symmetry transformations used to generate equivalent atoms:*=1-x+2,-y+2,-z+1(2.**1**); 1-x+1,y,-z+3/2(2.**2**); 1-x,1-y,-z(2.**4**).

Table 7: Selected bond lengths(Å) and bond angles(°) in 2.**5**-2.**6**

2.**5**		2.**6**	
Sb1-O1 = 2.145(6)	O1-Sb1-O4 = 83.5(2)	Sb1-O1 = 2.012(3)	Sb1-O3-P1 = 127.60(11)
Sb1-O4 = 2.157(6)	O1-Sb1-O5 = 84.9(2)	Sb1-O2 = 1.951(18)	Sb2-O4-P1 = 130.99(11)
Sb2-O2 = 2.123(6)	C1-Sb1-C7 = 98.5(4)	Sb1-O3 = 2.059(19)	C1-Sb1-O1 = 180.00(1)
Sb2-O3 = 2.189(6)	C31-Sb2-O3 = 166.2(3)	Sb2-O1 = 2.146(4)	O2-Sb1-O2*= 159.15(11)
Sb1-O5 = 1.982(6)	C25-Sb2-O5 = 163.6(3)	Sb2-O2 = 1.994(19)	O3-Sb1-O3*= 179.14(10)
Sb2-O5 = 1.967(6)	C19-Sb2-O2 = 173.9(3)	Sb2-O4 = 2.098(18)	O1-Sb1-O2 = 79.57(6)
Sb1-C1 = 2.143(9)	O2-Sb2-O3 = 81.3(2)	Sb2-O6 = 1.952(19)	O1-Sb1-O3 = 89.57(5)
Sb2-C19 = 2.130(10)	O2-Sb2-O5 = 88.2(2)	Sb1-C1 = 2.126(4)	C1-Sb1-O2 = 100.43(6)
Se1-O1 = 1.686(6)	C19-Sb2-C25 = 96.3(4)	Sb2-C5 = 2.149(3)	O2-Sb2-C11 = 164.27(10)
Se1-O2 = 1.679(6)	O1-Se1-O2 = 102.7(3)	Sb2-C11 = 2.134(3)	O1-Sb2-C5 = 167.97(11)
Se2-O3 = 1.665(6)	O3-Se2-O4 = 104.4(3)	P1-O3 = 1.556(2)	O4-Sb2-O6 = 179.17(8)
Se2-O4 = 1.693(6)	Sb1-O1-Se1 = 123.3(3)	P1-O4 = 1.543(2)	O2-Sb2-O4 = 85.66(8)
Sb1-O5-Sb2 = 150.4(3)	Sb2-O2-Se1 = 125.5(3)	P1-O5 = 1.488(2)	O1-Sb2-O2 = 75.44(9)
C13-Sb1-O4 = 169.4(3)	Sb2-O3-Se2 = 118.0(3)	Sb1-O1-Sb2 = 98.13(7)	C5-Sb2-C11 = 100.48(11)
C1-Sb1-O1 = 173.1(3)	Sb1-O4-Se2 = 117.9(3)	Sb1-O2-Sb2=105.62(9)	Sb2-O1-Sb2*=163.74(13)
C7-Sb1-O5 = 160.6(3)			

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

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$Te_4Se_2O_6$ Macrocycle Stabilizing Anions of Varying Size and Geometry

Chapter 3

The reaction of benzeneseleninic acid with bis(p-methoxyphenyl)tellurium dihalide in benzene for 12 h at room temperature in presence of triethylamine as a base leads to the formation of a 12-membered macrocycle $[(p\text{-}MeOC_6H_4)_2Te(\mu\text{-}O)(\mu\text{-}PhSeO_2)(\mu_4\text{-}X)]_2$ (X = Cl (3.**1**), Br (3.**2**)) where the halogens are found capping the macrocycle on both sides stabilized by Te-X interactions. Reaction of NaI with 3.**1** afforded the iodo capped macrocycle $[(p\text{-}MeOC_6H_4)_2Te(\mu\text{-}O)(\mu\text{-}PhSeO_2)(\mu_4\text{-}I)]_2$ (3.**3**) in good yield. Notable conformational changes have been observed in the solid state structure starting from macrocycle 3.**1** to 3.**3** which are quantified in terms of torsion angles and alignment of phenyl ring attached to selenium. Further reaction of methaneseleninic acid with bis(p-methoxyphenyl)tellurium dichloride in methanol in presence of triethyl amine as a base also afforded a 12-membered macrocycle $[(p\text{-}MeOC_6H_4)_2Te(\mu\text{-}O)(\mu\text{-}MeSeO_2)(\mu_4\text{-}Cl)]_2$ 3.**4** structurally similar to 3.**1**-3.**3**. Anion exchange reactions of Cl-macrocycle 3.**1** $[(p\text{-}MeOC_6H_4)_2Te)_2(\mu\text{-}O)(\mu\text{-}PhSeO_2)(\mu_4\text{-}Cl)]_2$ with $AgNO_3$, $AgClO_4$ and $AgBF_4$ yielded colorless solids whose single crystal X-ray diffraction studies revealed the formation of 12-membered macrocycles $[(p\text{-}MeOC_6H_4)_2Te)_2(\mu\text{-}O)(\mu\text{-}PhSeO_2)(\mu\text{-}X)]_2$ [X=NO_3 (3.**5**), ClO_4(3.**6**), BF_4(3.**7**)]. ESI-MS studies revealed that macrocycles retain their integrity in solution. Solution ^{125}Te NMR spectrum of 3.**7** shows the appearance of a triplet ($^1J_{Te\ldots F}$ = 568 Hz) that can be assigned to coupling between ^{125}Te nuclei and two fluorine atoms in BF_4^- ions.

Nagarjuna Kumar Srungavruksham, Viswanathan Baskar, *Eur. J. Inorg. Chem.*, **2012**, 136-142.

Nagarjuna Kumar Srungavruksham, Viswanathan Baskar *Dalton Trans.*, **2015,** *44*, 4554.

3.1 Introduction

Deliberations in the synthesis of anion receptors document unique challenges in supramolecular host-guest chemistry with respect to designing a host molecule for anions. Typically the synthesis of anion receptors is hindered by the large variation in size, geometry and also due to their limited stability to certain pH ranges.[1] Since anions are electron rich and act as Lewis base, macrocyclic hosts that contain Lewis acidic metals such as tin, silicon, boron and mercury have been synthesized and structurally charecterized.[2] Few recent literature reports have revealed the role of halide ions (chloride/bromide) as templates in assembling transition / lanthanide metal containing cages.[3] Pioneering work of Hawthorne et al. on halide templated synthesis of [12]mercuracarborand-4, a charge-reversed analogue of the well-known [12]crown-4, called as the anti-crown needs a special mention.[4] Mercuracarborand is a multidentate carborane containing Lewis acidic host assembled by reacting 1,2-dilithiocarborane with $HgCl_2$ in ethereal solvent. The free host molecule, tetranuclear [12]mercuracarborand-4 can be readily obtained by removing the halide ions. With this free host molecule, complexation behaviour of other anions (Br^-, $C_2H_5O^-$, $B_{10}H_{10}^{2-}$ and NO_3^-) has also been demonstrated. Despite the above mentioned reports on anion templated syntheses, self-assembled host molecules for complexation of anions comprising heavier main group metals are still a rarity.

On the other hand, diorganotellurium oxides have been of immense interest to chemists owing to their extensive applications in organic synthesis as oxygen transfer reagents.[5] Another interesting aspect of diorganotellurium oxide / halides is its ability to form macrocycles resulting in the isolation of novel telluroxane frameworks.[6] Beckmann and coworkers have done pioneering work in this field by carrying out reactions of diorganotellurium oxides with various protic ligands like carboxylates, phosphinates, sulfonates and diorganosilane diols resulting in the formation of products showing rich structural variations.[7] Very recently Chandrasekhar and coworkers have investigated the reaction of a cyclic phosphinic acid with diorganotellurium dihalide leading to the assembly of an unprecedented 12-membered macrocycle capped by halogens on both sides.[8] The authors suggested that these macrocycles can be considered as analogues to the family of "inverse crowns"[9] and "anti crowns".[10] It has to be mentioned here that H.B.Singh and coworkers have carried out condensation reaction of bis(o-formylphenyl)selenide/telluride with primary amines followed by reduction leading to the formation of fused macrocycles which can bind to a variety of transition metal ions.[11] Despite these efforts on the isolation of interesting tellurium and selenium based macrocycles, compounds containing Se-O-Te motifs are rare.[12]

Hence, by keeping the fact in mind that host molecules for anions comprising heavier main group metals and macrocycles that contain tellurium and selenium are rare, we started investigating the reactivity of diorganotellurium dihalides with organoseleninic acids in presence of base to obtain 12-membered macrocycles $[(p\text{-}MeOC_6H_4)_2Te(\mu\text{-}O)(\mu\text{-}RSeO_2)(\mu_4\text{-}X)]_2$ (R = Ph (3.**1**, 3.**2** & 3.**3**), Me (3.**4**); X = Cl (3.**1**), Br (3.**2**), I (3.**3**) & Cl (3.**4**)) stabilized by halide ions (chloride, bromide, iodide). We have also investigated the anion exchange reactions of chloro-macrocycle 3.**1** with different anions displaying varying geometry around a central element (for example nitrate, perchlorate and tetrafluoroborate ions) to check the stability and flexibility of 12-membered macrocyclic host. Herein, synthesis and characterization of macrocycles $[(p\text{-}MeOC_6H_4)_2Te)_2(\mu\text{-}O)(\mu\text{-}PhSeO_2)(\mu\text{-}X)]_2$ [X=NO_3(3.**5**), ClO_4(3.**6**), BF_4(3.**7**)] are reported.

3.2 Experimental Section

3.2.1 General Information:

Tellurium tetrachloride, benzeneseleninic acid, methaneseleninic acid and silver salts were purchased from Sigma Aldrich Ltd. Solvents and other general reagents were purchased from commercial sources and purified according to standard procedures. Bis(p-methoxyphenyl)tellurium dihalide ($p\text{-}MeOC_6H_4TeCl_2$ or $p\text{-}MeOC_6H_4TeBr_2$) was synthesized according to literature procedure.[13]All the compounds were dried under high vacuum for half an hour and these dried samples (free of benzene solvates) were subjected to spectroscopic and elemental analysis.

3.2.2 Instrumentation:

Infrared spectra were recorded on a JASCO-5300FT-IR spectrometer as KBr pellets. The solution ^{1}H, ^{13}C, ^{19}F, ^{77}Se, ^{125}Te NMR spectra were recorded on Brucker AVANCE^{III} 400 instrument. Elemental analysis was performed on a Flash EA Series 1112 CHNS analyzer. ESI-MS spectra were recorded using Bruker MaXis HRMS (ESI-TOF analyzer) equipment. Single Crystal X-ray data collection for 3.**1**-3.**7** were collected at 100(2) K on a Bruker Smart Apex CCD area detector system (λ (Mo Kα) = 0.71073Å) with a graphite monochromator. All the compounds have atleast one benzene as a solvate in their crystall lattice. These solvates are loosely bound in the lattice and the moment crystals are taken out of the crystallization vial, they tend to loose their benzene solvates becuase of which hey lose thier crystallanity. Hence, crystals were carefully transfered into a petty dish which filled with benzene solvent and suitable single crystals were picked and immediately mounted on goniometer under liquid nitrogen flow. The data were reduced using SAINTPLUS and the structures were solved using SHELXS-97[14] and refined using SHELXL-97.[15] All non-hydrogen atoms were refined anisotropically. In 3.**6** and 3.**7** the disordered solvent molecules in the asymmetric units were removed using the BYPASS algorithm, implemented as the SQUEEZE[16] option in PLATON.[17] The total electron count removed by SQUEEZE corresponded to 146 with void volume of 528.2 Å^3 (20.5%) per unit cell in 3.**6** and 118 with void volume of 587 Å^3 (23.1%) per unit cell in 3.**7** respectively.

3.2.3 Synthetic procedures

3.2.3a Synthetic procedure for compounds 3.1-3.2:

In 15 mL of benzene, benzeneseleninic acid and triethylamine were added and stirred for 5 min till a clear solution was obtained. To this solution appropriate bis(p-methoxyphenyl)tellurium dihalide(p-$MeOC_6H_4TeCl_2$ or p-$MeOC_6H_4TeBr_2$) was added and the solution immediately turned turbid. Stirring was continued for a period of 12 h. The solution was filtered to remove the triethylamine hydrochloride formed during the course of the reaction. The filtrate was kept for crystallization in room temperature to grow colorless block like crystals in a week's time. Molar ratios and weights of the reactants used are as follows.

[(*p*-MeOC$_6$H$_4$)$_2$Te)$_2$(μ-O)(μ-PhSeO$_2$)(μ$_4$-Cl)]$_2$ (3.1): Benzeneseleninic acid (0.15 g, 0.80 mmol), triethylamine (0.12 mL, 0.88 mmol), bis(p-methoxyphenyl)tellurium dichloride (0.33 g, 0.80 mmol). Yield: 0.17 g (46%, based on bis(p-methoxyphenyl)tellurium dichloride). Mp: 150–152 °C. Anal.Calcd for $C_{68}H_{66}Cl_2O_{14}Se_2Te_4$(1846.47): C, 44.23; H, 3.60. Found: C, 44.16; H, 3.68. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 7.75 (d, 16 H), 7.37 (m, 10 H), 6.80 (d, 16 H), 3.80 (s, 24 H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 161.18, 135.08, 130.78, 129.27, 128.78, 128.33, 125.90, 114.50, 55.32. ^{77}Se NMR (76.3 MHz, CDCl$_3$, ppm): δ 1167(s). ^{125}Te NMR (126.3 MHz, CDCl$_3$, ppm): δ 1211(s). IR (KBr, cm^{-1}): 3057.4(w), 2930.1(w), 1585.6(s), 1564.4(m), 1493.0(s), 1452.5(m), 1292.4(s), 1253.8(s), 1178.6(s), 1057.1(m), 1020.4(m), 823.7(m), 788.9(m), 748.4(m), 659.0 (w).

[(*p*-MeOC$_6$H$_4$)$_2$Te)$_2$(μ-O)(μ-PhSeO$_2$)(μ$_4$-Br)]$_2$ (3.2): Benzeneseleninic acid (0.15 g, 0.80 mmol), triethylamine (0.12 mL, 0.88 mmol), bis(p-methoxyphenyl)tellurium dibromide (0.40 g, 0.80 mmol). Yield: 0.22 g (53% based on bis(p-methoxyphenyl)tellurium dibromide). Mp: 230–232 °C. Anal.Calcd for $C_{68}H_{66}Br_2O_{14}Se_2Te_4$(1935.37): C, 42.20; H, 3.43. Found: C, 42.31; H, 3.38. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 7.78 (d, 16 H), 7.42 (m, 5 H), 7.20 (m, 5 H), 6.76 (d, 16 H), 3.79 (s, 24 H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 160.88, 135.96, 130.73, 129.29, 128.75, 128.34, 125.98, 114.03, 55.25. ^{77}Se NMR (76.3 MHz, CDCl$_3$, ppm): δ 1167 (s). ^{125}Te NMR (126.3 MHz, CDCl$_3$, ppm): δ 1196(s). IR (KBr, cm^{-1}): 3063.2(w), 2943.6(w), 2831.8(m), 1585.6(s), 1575.9(m), 1493.0(s), 1460.2(m), 1439.0(m), 1402.4(m), 1294.3(s), 1253.8(s), 1176.7(s), 1059.0(m), 1020.4(m), 821.7(m), 788.9(m), 748.4(w), 653.9(w).

3.2.3b Synthetic procedure for $[(p\text{-}MeOC_6H_4)_2Te)_2(\mu\text{-}O)(\mu\text{-}PhSeO_2)(\mu_4\text{-}I)]_2$ (3.3):

Sodium iodide (0.008 g, 0.053 mmol) was added to a solution of 3.**1** (0.052 g, 0.028 mmol) in benzene (15 mL) and then stirred for 24h. The solution turns to orange- yellow colour. The mixture was filtered and the filtrate kept for crystallization in room temperature to grow colorless block like crystals. Yield: 0.05 g (69 % based on3. **1**). Mp: 216–218 °C. Anal.Calcd for $C_{68}H_{66}I_2O_{14}Se_2Te_4$(2029.37): C, 40.24; H, 3.27. Found: C, 40.14; H, 3.32. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.83 (m, 16 H), 7.24 (m, 10 H), 6.78 (d, 16 H), 3.80 (s, 24 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 160.87, 136.26, 131.51, 130.97, 129.19, 128.93, 126.00, 113.96, 55.26. ^{77}Se NMR (76.3 MHz, $CDCl_3$, ppm): δ 1166(s). ^{125}Te NMR (126.3 MHz, $CDCl_3$, ppm): δ 1182(s). IR (KBr, cm^{-1}): 3065.3(w), 2959.9(w), 2932.9(w), 2835.6(m), 1584.4(m), 1567.7(s), 1492.0(s), 1493.3(s), 1438.8(m), 1293.7(s), 1252.7(s), 1177.3(s), 1088.8(w), 1060.3(m), 1022.9(m), 821.6(s), 788.7(m), 749.2(w), 649.5(w), 588.0(m).

3.2.3c Synthetic procedure for $[(p\text{-}MeOC_6H_4)_2Te)_2(\mu\text{-}O)(\mu\text{-}MeSeO_2)(\mu_4\text{-}Cl)]_2$ (3.4):

In 15 mL of methanol methaneseleninic acid (0.123 g, 0.968 mmol) and triethylamine (0.15 mL, 1.08 mmol) were added and stirred for 5 min till a clear solution was obtained. To this solution bis(p-methoxyphenyl)tellurium dichloride (0.400 g, 0.968 mmol) was added and the solution warmed for some time to get a clear solution. Stirring was continued at room temperature for a period of 12 h. Solution was filtered and the solvent removed from the filtrate under reduced pressure to obtain a white solid. This solid material was dissolved in benzene and the solution was filtered to remove triethylamine hydrochloride. The filtrate was kept for slow evaporation at room temperature to afford colorless block like crystals in a period of 2 days. Yield: 0.23 g (55% based on bis(p-methoxyphenyl)tellurium dichloride). Mp: 180–182 °C. Anal.Calcd for $C_{58}H_{62}Cl_2O_{14}Se_2Te_4$(1722.33): C, 40.45; H, 3.63. Found: C, 40.35; H, 3.68. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.8 (d, 16 H), δ 6.8 (d, 16), δ 3.8 (s, 24), δ 2.2 (s, 6). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 161.00, 135.75, 128.34, 114.26, 55.29, 40.99. ^{77}Se NMR (76.3 MHz, $CDCl_3$, ppm): δ 1182(s). ^{125}Te NMR (126.3 MHz, $CDCl_3$, ppm): δ 1182(s). IR (KBr, cm^{-1}): 3067.1(w), 2934.0(w), 2833.7(w), 1585.6(m), 1493.0(s), 1460.2(w), 1400.4(m), 1292.4(s), 1249.9(s), 1176.7(s), 1060.9(w), 1022.4(m), 873.8(w), 823.7(s), 787.0(m), 750.4(m), 671.3(m), 588.3(w).

3.2.3d Synthetic procedure for compounds 3.**5**-3.**7:** Cl-macrocycle 3.**1** was dissolved in 20 mL of benzene. To this, two equivalents of corresponding silver salts were added and stirring continued for 12h at room temperature. White silver chloride precipitate which is formed during the course of the reaction was separated from the reaction mixture by filtration and slow evaporation of filtrate gives block like crystals in a week's time. Molar ratios and weights of the reactants used are as follows.

$[(p\text{-}MeOC_6H_4)_2Te)_2(\mu\text{-}O)(\mu\text{-}PhSeO_2)(\mu\text{-}NO_3)]_2$ (3.**5):** Cl-macrocycle 3.**1** (0.100 g, 0.054 mmol), silver nitrate (0.018 g, 0.106 mmol), yield: 0.078 g (76 % based on 3.**1**). MP: 184-186°C. $C_{68}H_{66}N_2O_{20}Se_2Te_4$ (1899.57): calcd. C 43.00, H 3.50, N 1.47; found C 43.15, H 3.58, N 1.41. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.69(m, 28H), 6.81(m, 14H), 3.78(s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 161.33, 134.94, 129.29, 129.02, 125.95, 125.67, 115.06, 114.53, 55.32; ^{125}Te NMR (126.3 MHz, CDCl3, ppm): δ 1171; ^{77}Se NMR (76.3 MHz, CDCl3, ppm): δ 1087. IR(KBr, cm^{-1}): 3063.0(w), 2958.9(w), 2936.9(w), 2832.8(w), 1589.0(s), 1490.4(s),1353.4(m), 1304.1(m), 1260.2(s), 1172.6(s), 1063.0(m),1019.1(m), 821.9(m).

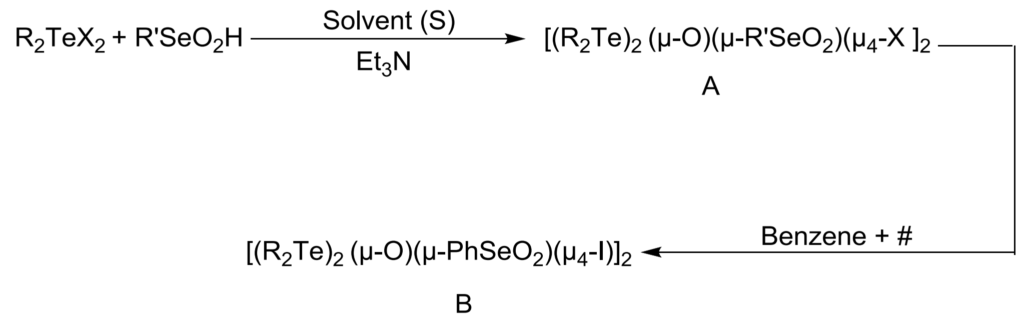
$[(p\text{-}MeOC_6H_4)_2Te)_2(\mu\text{-}O)(\mu\text{-}PhSeO_2)(\mu\text{-}ClO_4)]_2$ (3.**6):** Cl-macrocycle 3.**1** (0.100 g, 0.054 mmol), silver perchlorate (0.022 g, 0.106 mmol), yield: 0.082 g (77 %). MP: 203-205°C. $C_{68}H_{66}Cl_2O_{22}Se_2Te_4$ (1974.46): calcd. C 41.36, H 3.37; found C 41.26, H 3.31. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.65(m, 14H), 7.42(m, 14H), 6.81(m, 14H) 3.79(s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.18, 134.10, 132.91, 129.45, 129.22, 128.10, 126.17, 125.69, 115.23, 55.25; ^{77}Se NMR (76.3 MHz, CDCl3, ppm): δ1117. IR(KBr, cm^{-1}): 3047.3(w), 2936.9(w), 2839.8(w), 1584.5(s), 1492.7(s), 1436.3(s), 1305.1(s), 1253.3(s), 1177.4(m), 1058.6(s), 1021.1(m), 821.0(m), 787.9(m).

[(*p*-MeOC$_6$H$_4$)$_2$Te)$_2$(μ-O)(μ-PhSeO$_2$)(μ-BF$_4$)]$_2$ (3.7): Cl-macrocycle 3.**1** (0.100 g, 0.054 mmol), silver tetrafluoroborate (0.021 g, 0.108 mmol), yield: 0.080 g (76 %). MP: 194-196°C. $C_{68}H_{66}B_2F_8O_{14}Se_2Te_4$ (1949.17): calcd. C 41.90, H 3.41; found C 42.06, H 3.49. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 7.89(m, 7H), 7.60(m, 20H), 7.05(m, 7H), 6.86(m, 8H), 3.83(s, 24H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 161.97, 134.80, 132.99, 132.20, 129.45, 125.91, 115.46, 115.14, 55.25; ^{19}F NMR(376 MHz, CDCl$_3$, ppm) δ -127; ^{11}B NMR (128.4 MHz, CDCl$_3$, ppm): δ -0.7; ^{125}Te NMR (126.3 MHz, CDCl3, ppm): δ 1145(t, J = 568 Hz); ^{77}Se NMR (76.3 MHz, CDCl3, ppm): δ1119. IR(KBr, cm^{-1}): 3057.5(w), 2936.9(w), 2838.3(m), 1594.5(s), 1484.9(s), 1298.6(m), 1254.7(s), 1183.5(s), 1052.0(m), 1024.6(m), 827.4(m), 783.5(m).

3.3 Results and Discussion

Synthetic methodology for macrocycles 3.**1**-3.**3** were adopted from literature methods.[8] Benzeneseleninic acid and bis(p-methoxyphenyl)tellurium dihalide [Halide = Cl(3.**1**), Br(3.**2)**] were stirred in benzene for 12 h at room temperature in the presence of triethylamine as a base (Scheme 1). Filtration followed by slow evaporation of the solvent afforded colourless crystals in moderate yield. Unlike 3.**1** and 3.**2** the iodo capped macrocycle 3.**3** could not be synthesized by reaction of the corresponding diorganotellurium dihalide with benzeneseleninic acid. Hence 3.**3** was synthesized by replacement of chloride from macrocycle 3.**1** by reacting with sodium iodide (Scheme 1).[8] Macrocycle 3.**4** was synthesized following similar methods to 3.**1** and 3.**2** except that methanol was used as solvent in place of benzene.

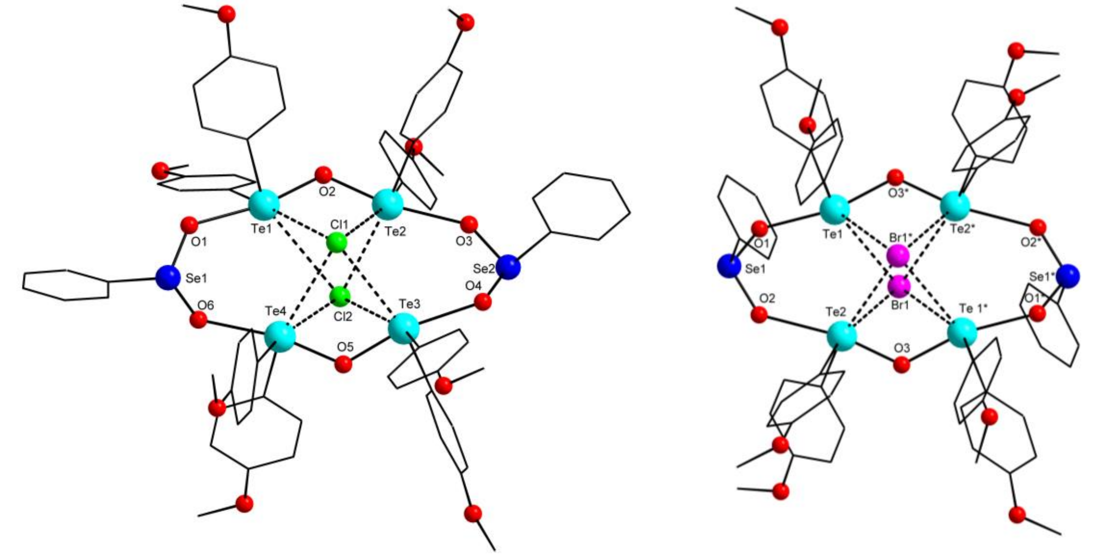
Macrocycles 3.**1**-3.**4** were characterized by standard analytical and spectroscopic techniques. ^{77}Se NMR (in CDCl$_3$) shows single resonances at nearly identical chemical shift values for 3.**1**, 3.**2** and 3.**3** at δ = 1167 ppm suggesting the presence of selenium atoms in an identical environment. The ^{125}Te NMR (in CDCl$_3$) also shows single resonance in CDCl$_3$ but a slight upfield shift is observed starting from 3.**1** to 3.**3** with the chemical shift values being δ = 1211, 1196 and 1182 ppm respectively. The observed variation in the chemical shifts values in ^{125}Te NMR spectra can be assigned to the decrease in electronegativity starting from chlorine to bromine to iodine, as has been reported earlier.[18] ^{77}Se NMR and ^{125}Te NMR (in $CDCl_3$) for 3.**4** shows single resonances at 1182 ppm suggesting the presence of selenium and tellurium atoms in an identical environment.



S = Benzene(3.**1**,3.**2**), Methanol(3.**4**) ; A; R = $MeOC_6H_4$, R' = Ph(3.**1**,3.**2**), Me(3.**4**), X = Cl(3.**1**,3.**4**), Br(3.**2**); B(3.**3**); R = $MeOC_6H_4$; # = 3.**1** + NaI

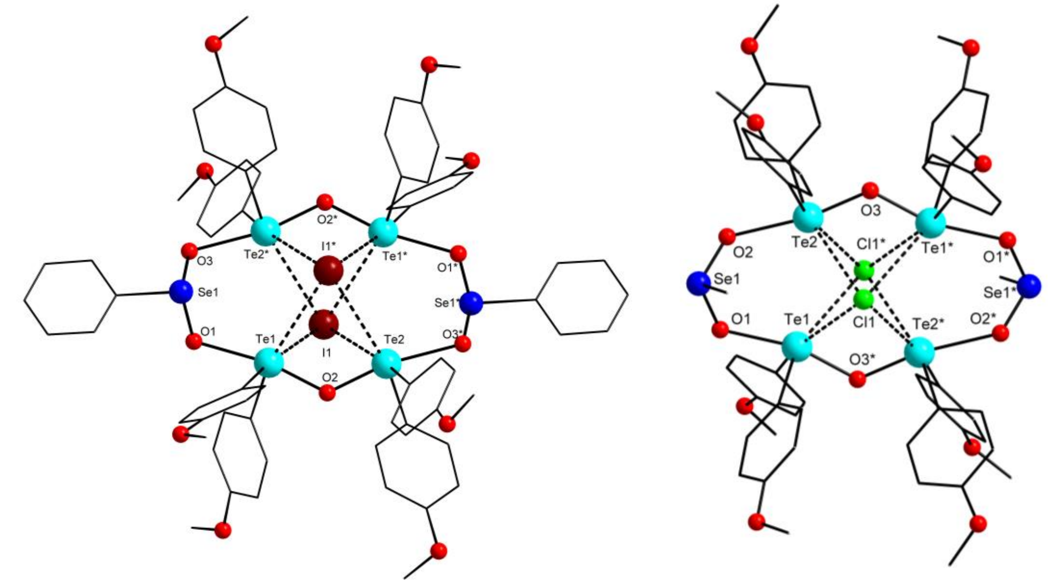
scheme1

Single crystal X-ray diffraction studies revealed the formation of a 12-membered macrocycles $[(p\text{-}MeOC_6H_4)_2Te(\mu\text{-}O)(\mu\text{-}RSeO_2)(\mu_4\text{-}X)]_2$ [R = Ph (3.**1**, 3.**2** and 3.**3**), Me (3.**4**) and X = Cl (3.**1,** 3.**4**), Br (3.**2**), I (3.**3**)] where the halogens are found capping the macrocycle on both sides stabilized by Te-X interactions. The crystallographic data and the selected metric parameters for 3.**1**-3.**4** are given in tables 4-9. Macrocycles 3.**1**-3.**4** crystallize in triclinic space group P-1 and are 12-membered rings that consist of a $Te_4Se_2O_6$ framework, which is built from two ditelluroxane units and two seleninate groups [figure 1]. Charge neutralization for the dicationic marocycle comes from the halide ions present on top and bottom of the macrocycle in a capping fashion held together by Te-X interactions. The average Te-X distances in 3.**1**, 3.**2**, 3.**3** and 3.**4** are 3.380 Å, 3.465 Å, 3.688 Å and 3.362 Å respectively. These Te-X distances fall in the range as reported in literature.[8,19]



Solid state structure of 3.**1**

Solid state structure of 3.**2**



Solid state structure of 3.**3**

Solid state structure of 3.**4**

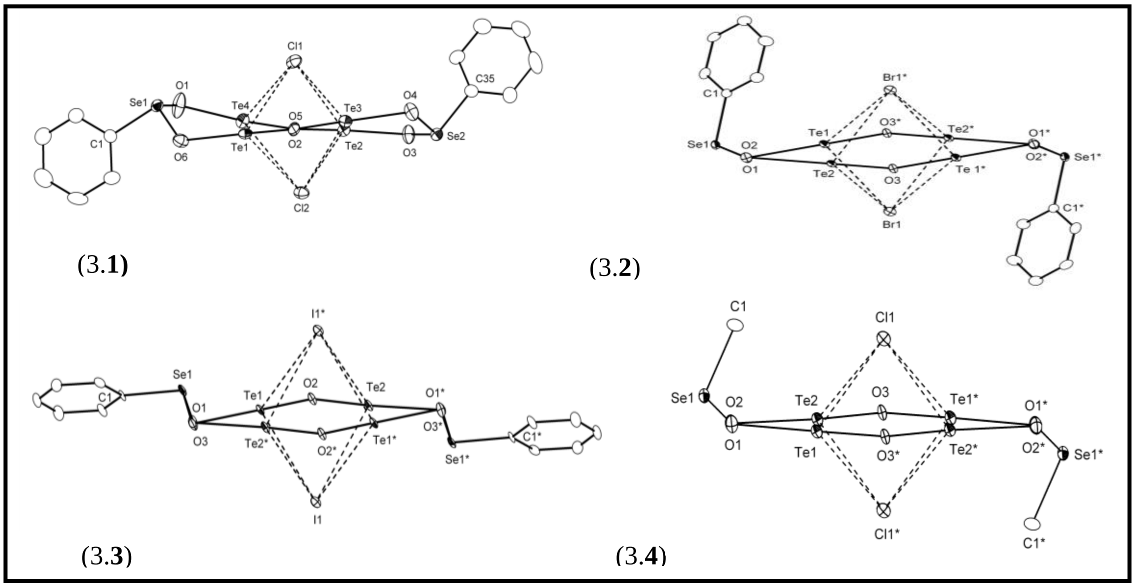
Figure 1: Solid state molecular structures of 3.**1**-3.**4**. Hydrogen atoms and benzene solvates are omitted for clarity.

The average Te-O distances of the ditelluroxane units in 3.**1**, 3.**2**, 3.**3** and 3.**4** are 1.980(3) Å, 1.977(2) Å, 1.989 (4) Å and 1.979(3) Å respectively. The Te-O distances are slightly longer than the ones found in the sulfonate based macrocycle[7b] and is almost similar to the distances founds in the ditelluroxane macrocycles based on phosphinate ligands.[7b,8] Te-O-Te angles in 3.**1**, 3.**2**, 3.**3** and 3.**4** are 123.88(2)°, 126.90(1)°, 122.15(2)° and 126.70(13)° respectively, and O-Te-O angles in 3.**1**, 3.**2**, 3.**3** and 3.**4** are 168.12(1)°, 166.62(7)°, 168.43(2)° and 166.95(10)° respectively. These parameters are in the range as reported in literature.[8,20] The average Se-O distances in 3.**1**, 3.**2**, 3.**3** and 3.**4** are 1.678(4) Å, 1.690(2) Å, 1.690 (4) Å and 1.683(3) Å respectively, and O-Se-O bond angles in 3.**1**, 3.**2**, 3.**3** and 3.**4** fall in the range 105.5° - 107.7°. The Se-O distances are in similar range when compared to the organotin seleninate ester.[21]

The major change in the solid state structure on going from the Cl- capped macrocycle 3.**1** to the Br-capped macrocycle 3.**2** and the I-capped macrocycle 3.**3** is the orientation of the Se-Ph group which changes dramatically with respect to the macrocyclic core (Figure 2). These conformational changes in the 12-membered $Te_4Se_2O_6$ macrocyclic cores on going from 3.**1**-3.**3** can be quantified in terms of torsion angles making at Se centres.

The torsion angles in case of 3.**1** for C2-C1---Se1-O1 and C2-C1---Se1-O6 are -100.3(5)° and 151.8(4)° which falls in the range classified as *–syn-clinal* and *+anti-periplanar* respectively. The torsion angles for the Se-O to the carbon atom of the ring on the other side (ie. C1 and C6) are -26.6(5)° (for C6-C1---Se1-O6) and 81.3(5)° (for C6-C1---Se1-O1) respectively, and falls in the range classified as *–syn-periplanar* and *+syn-clinal* respectively. In 3.**1,** as the entire macrocycle is present in the asymmetric unit, the torsion angles between the oxygen atoms bound to the other selenium atom (say, O3-Se2 and O4-Se2) and the carbons of the phenyl ring (C40-C35 and C36-C35) differ from those that involve Se1, those that involve Se2 fall in the ranges classified as *+anti-clinal, -anti-clinal, +syn-clinal* and *–syn-clinal* respectively. In macrocycles 3.**2** and 3.**3**, as only half of the macrocycle appear in the asymmetric unit, investigating the torsion angles of the oxygen atoms bound to selenium and the carbons of the selenium-bound phenyl ring of the macrocycle is sufficient to understand the orientation of the selenium attached phenyl group with respect to the macrocycle. In 3.**2**, the torsion angles for C2-C1---Se1-O1 and C2-C1---Se1-O2 are –70.8(3)° and 178.5(3)°

respectively, which can be classified as –*syn-clinal* and +*anti-periplanar* respectively. Although the torsion angles in 3.**2** fall in the same classification as that of **1**, the values of the torsion angles themselves varies considerably (nearly 30˚) when compared with identical atoms in 3.**1**. If one looks at the torsion angles for the Se-O to the carbon atoms of the ring on the other side, the angles are -4.3(3)˚ (for C6-C1---Se1-O2) and 106.4(3)˚ (for C6-C1---Se1-O1). Here the torsions angles falls in the range classified as –*syn-periplanar* and +*anti-clinal* respectively. For macrocycle 3.**3**, the torsion angles for C2-C1---Se1-O3 and C2-C1---Se1-O1 are –17.6(5)˚ and -124.8(5)˚ falling in the range classified as –*syn-periplanar* and -*anti-clinal* respectively. Hence on comparing with 3.**1** and 3.**2** the classification of the torsion angle for similar atoms in case of 3.**3** vary considerably. The torsion angles for the Se-O to the carbon atom of the ring on the other side are 57.9(5)˚ (for C6-C1---Se1-O1) and 165.13(5)˚ (for C6-C1---Se1-O3) which falls in the range classified as +*syn-clinal* and +*anti-periplanar* respectively. These values of torsion angles and their classification for **1**, **2** and **3** clearly indicates the dramatic change in the orientation of the selenium bound phenyl with respect to the macrocyclic ring.



(3.**1**) (3.**2**)

(3.**3**) (3.**4**)

Figure 2: ORTEP representaions of 3.**1**-3.**4** showing the orientaion of Se-Ph (3.**1**-3.**3**) and Se-Me (3.**4**) with rspect to macrocycle. Hydrogen atoms and benzene solvates are omitted for clarity.

This variation in the position of the Se atom and the subsequent orientation of the Se-Ph group with the macrocyclic core leads to the observation of interesting weak interactions in solid state. In the case of macrocycle 3.**2**, intramolecular π- π stacking[22] is observed between the phenyl ring attached to selenium with that of one of the aromatic rings attached to the tellurium atom (Figure 3). Further an *edge to face* CH-π interactions[23]between the tellurium attached phenyl rings and the benzene present as solvent of crystallization is also observed (Figure 3). The π- π and *edge to face* CH-π bond distances are 3.957 Å and 2.826 Å respectively. Though the observed intramolecular π- π stacking distance between the phenyl centroids (3.957 Å) is slightly greater than the van der Waals radii (3.800 Å), it can be considered as a weak π- π interactions since aromatic rings are attached to strong electron withdrawing groups. The dihedral angle between the two interacting aromatic ring planes is 16.51° which is in agreeable limits for the interaction to be considered as π- π stacking.

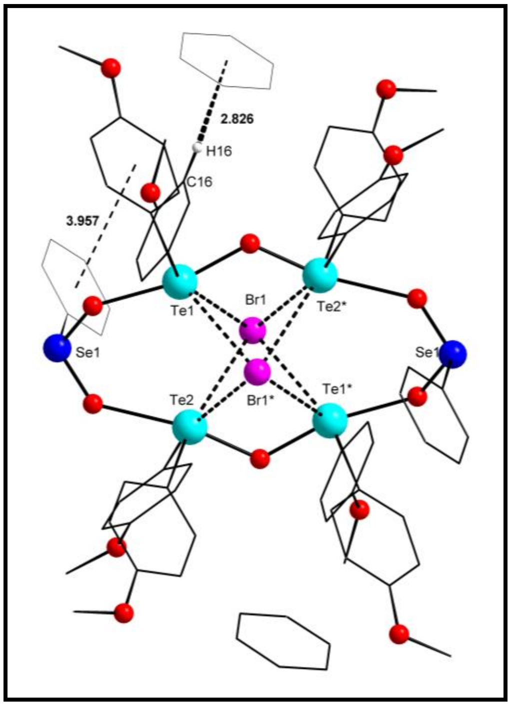


Figure 3: Bromo capped macrocycle(3.**2)** showing intramolecular π- π stacking and *edge to face* CH-π interactions.

The consequence of the variation in the orientation of the selenium attached phenyl ring to the macrocycle leads to another interesting intramolecular interaction which leads to the formation of a polymeric supramolecular structures in case of macrocycle 3.**3** (Figure 4). This supramolecular structure in 3.**3** arises due to the Se- π interactions (3.508 Å), the distance of which is much lesser than the sum of the van der Waals radii (3.80 Å). Though Te-π interactions are well documented,[24] Se-π interactions are very rare.[25] Hence the supramolecular pattern observed in 3.**3** is a rare example of Se- π interactions between a tetravalent selenium to the π cloud of an aromatic ring.

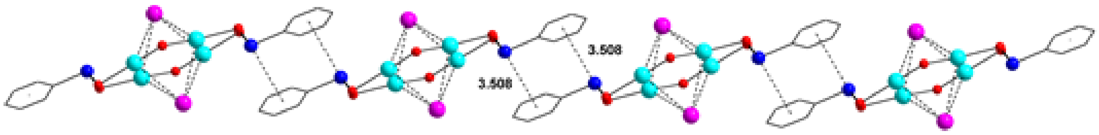


Figure 4: Supramolecular structure of 3.**3** showing Se- π interactions.

After observing interesting conformational changes in the solid state structures of 12-membered macrocycles from 3.**1** to 3.**3**, where different sized spherical ions namely chloride, bromide and iodide respectively, stabilized the dicationic macrocyclic core, we were curious to study the effect of varying geometry of the anion around a central element on the stability and flexibility of this 12-membered $Te_4Se_2O_6$ macrocyclic host. Hence, we investigated the anion exchange reactions of Cl-macrocycle 3.**1** with $AgNO_3$, $AgClO_4$ and $AgBF_4$ which afforded colourless solids in good yields (Scheme 2).

$$[(R_2Te)_2\,(\mu\text{-O})\,(\mu\text{-PhSeO}_2)\,(\mu_4\text{-Cl})]_2 \xrightarrow[\text{2AgX}]{\text{Benzene}} [(R_2Te)_2\,(\mu\text{-O})(\mu\text{-PhSeO}_2)(\mu\text{-X})]_2$$

(3.**1**)

$R = MeOC_6H_4$

$X = NO_3$(3.**5**), ClO_4(3.**6**), BF_4(3.**7**)

Scheme 2

Single crystal X-ray diffraction studies revealed the molecular structures of 3.**5**-3.**7** $[(p\text{-MeO-}C_6H_4)_2Te)_2(\mu\text{-O})(\mu\text{-PhSeO}_2)(\mu\text{-X})]_2$ [X=NO_3(3.**5**), ClO_4(3.**6**), BF_4(3.**7**)]. The compounds were also characterized by standard spectroscopic and analytical techniques. ^{77}Se NMR spectra of 3.**5**, 3.**6** and 3.**7** showed single resonances at 1087, 1117 and 1119 ppm, respectively. These chemical shifts were slightly shifted upfield when compared to ^{77}Se NMR chemical shift of 3.**1** (1167 ppm). Solution ^{125}Te NMR of 3.**5** showed a single resonance signal at 1171 which was also shifted upfield when compared to that of 3.**1** (1211 ppm). Interestingly, in the ^{125}Te NMR of 3.**7** (Figure 5), a triplet was observed at 1145 ppm with a coupling constant of 568 Hz ($^1J_{Te\ldots F}$ = 568 Hz). ^{19}F NMR spectrum of 3.**7** (Figure 5) in $CDCl_3$ shows single resonance at -127 ppm which is considerably lower when compared to that of ^{19}F NMR chemical shift of $AgBF_4$ solution (-149 ppm) in $CDCl_3$. Importantly, we do see the appearance of tellurium satellites in ^{19}F NMR of 3.**7**. ^{11}B NMR of 3.**7** in $CDCl_3$ showed a peak at -0.7 ppm which corresponds to the presence of BF_4^- group.[26]

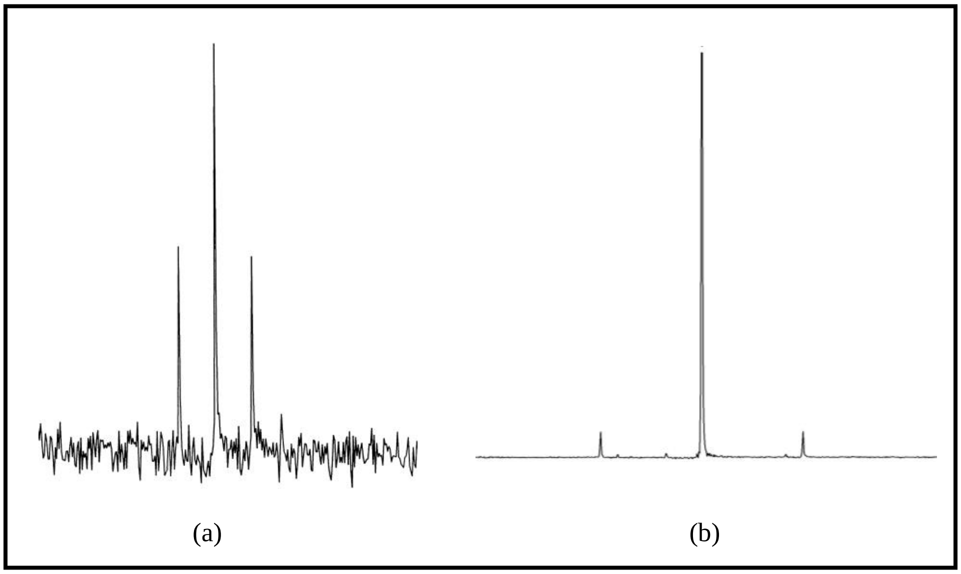


Figure 5: (a) Solution ^{125}Te NMR of 3.**7** showing a triplet. (b) Solution ^{19}F NMR of compound 3.**7** with Te satellites on both sides.

ESI-MS of 3.**5** and 3.**6** (positive ion mode) showed peaks at 1839.8871 and 1876.8369, respectively (Figure 6). These values correspond to the loss of an anion from

3.**5** and 3.**6** and can be assigned to the formulae [{(*p*-MeO-$C_6H_4)_2Te)_2$(μ-O)(μ-$PhSeO_2$)}$_2${X}]$^+$, where X = NO_3(3.**5**), ClO_4(3.**6**). These mass spectra data suggest that macrocycles 3.**5** and 3.**6** retain their structural integrity in solution as well. ESI-MS of 3.**7** showed a peak at 888.9347(m/z = 888.9347, z = 2) which corresponds to a di-positive 12-membered $Te_4Se_2O_6$ macrocyclic core.

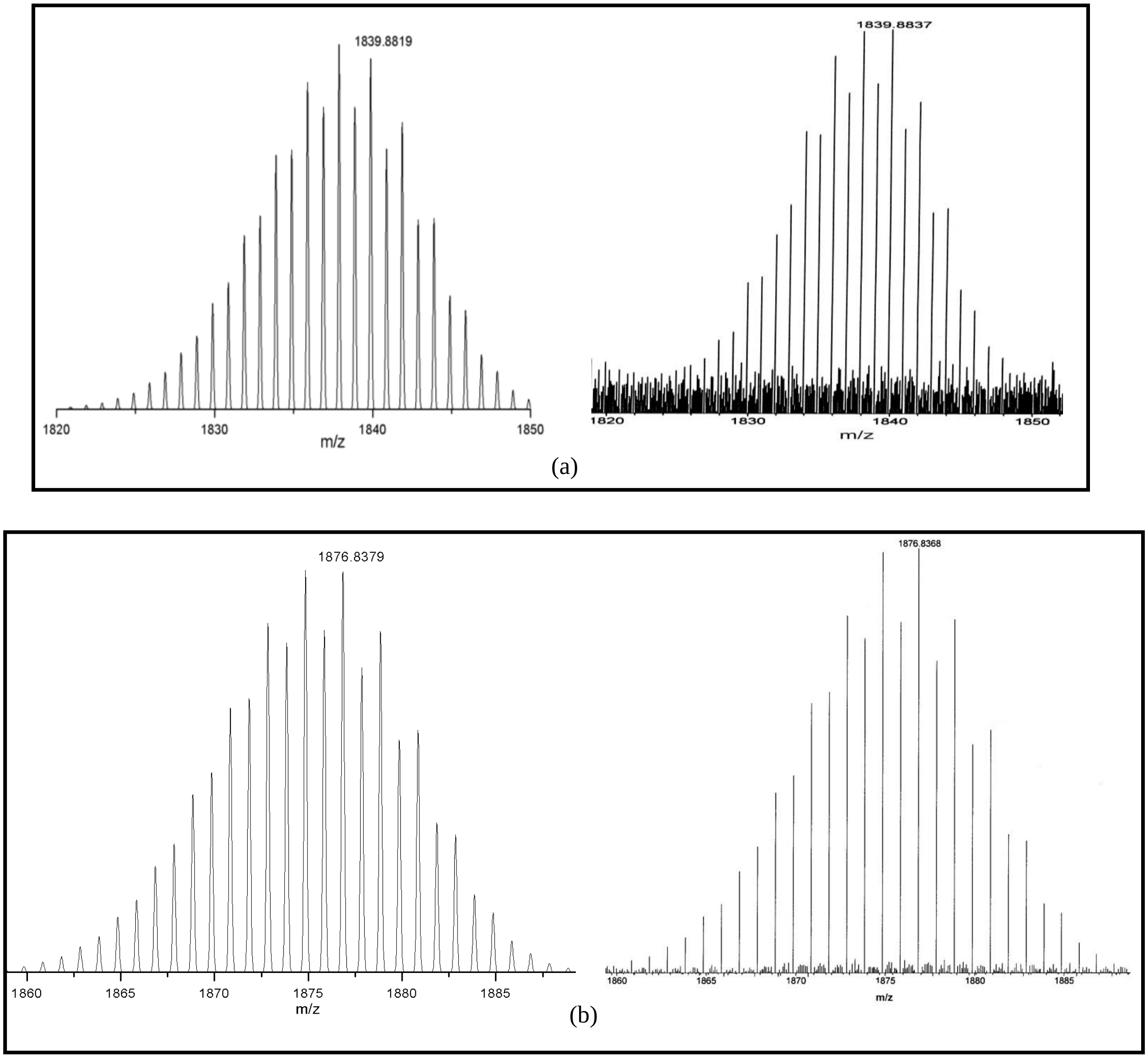


Figure 6: (a) Theoretical (left) and experimental (right) ESI-MS (positive ion mode) of 3.**5**. (b) Theoretical (left) and experimental (right) ESI-MS (positive ion mode) of 3.**6**.

The molecular structures of 3.**5**, 3.**6** and 3.**7** correspond to a 12-membered macrocycle containing $Te_4Se_2O_6$ framework, built from two ditelluroxane units and two phenylseleninates, which are further stabilized by Te-O and Se-O interactions in case of NO_3^-macrocycle (3.**5**), ClO^-_4macrocycle (3.**6**) and Te-F, Se-F interactions in case of BF_4-macrocycle (3.**7**).

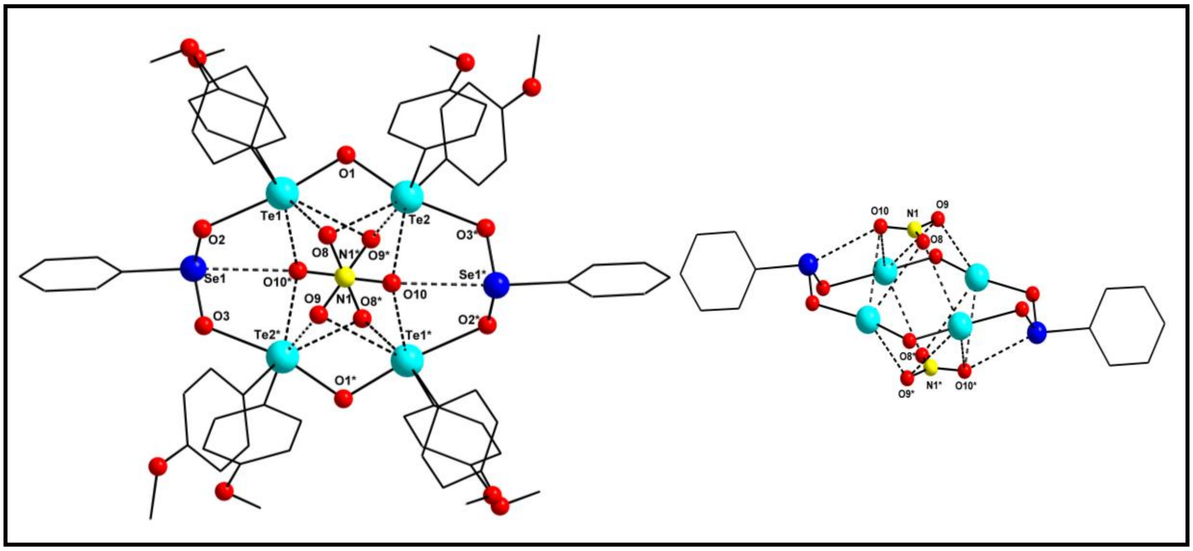


Figure 7: (left) Solid state molecular structure of 3.**5**. Hydrogen atoms and benzene solvates are omitted for clarity. (right) 12-membered $Te_4Se_2O_6$ ring of 3.**5** showing interactions with nitrate ions.

Macrocycles 3.**5**-3.**7** crystallize in triclinic space group *P*-1 with half of the molecule present in the asymmetric unit. In 3.**5** (Figure 7), Se-O interactions are observed involving one of the oxygen atoms of nitrate ion with a Se atom stabilizing the nitrate ions present above and below the plane of the 12-membered macrocycle. The Se-O interacting distance in 3.**5** is 3.041(2) Å which is marginally less when compared to the sum of the van der Walls radii (3.42 Å) and slightly higher on comparison with the reported divalent intramolecular Se-O interacting distances.[27] The Te-O interactions in 3.**5** fall in the range 2.983(2)-3.468(2) Å with an average of 3.172(2) Å which is marginally less when compared to the sum of the van der Walls radii (3.58Å) and slightly higher when compared to the earlier reported Te-O secondary interactions.[28] The12-membered ring $Te_4Se_2O_6$ in 3.**5** is almost planar, with selenium atoms (±0.6304

Å) and one of the oxygen atoms (O2 ±0.539 Å) deviating from the mean plane (Table 1).

Table 1: Deviation of each atom from the mean plane (Å) in 12-membered $Te_4Se_2O_6$ ring

Label	3.**5**	3.**6**	3.**7**
Te1	± 0.0894(4)	± 0.1188(4)	± 0.1204(3)
Te2	± 0.1006(4)	± 0.1050(4)	± 0.1108(3)
Se1	± 0.6304(4)	± 0.6221(5)	± 0.6244(3)
O1	± 0.2203(17)	± 0.1757(17)	± 0.1850(14)
O2	± 0.5391(17)	± 0.4585(18)	± 0.4704(15)
O3	± 0.0791(18)	± 0.1309(18)	± 0.1170(14)

The average Te-O bond length of ditelluroxane unit in 3.**5** is 2.0028(14), which is slightly higher than the previously reported average Te-O bond lengths of 12-membered macrocyles.[8] The average O-Te-O angle 169.2(6)° is similar to previous reports and Te-O-Te angle is 114.39(7)° which is considerably less when compared to previously reported 12-membered macrocycles (123.10° -126.90°). The average Se-O bond length in 3.**5** is 1.6975(15) Å which is similar to earlier reports whereas O-Se-O angle is 103.91(8)° which is slightly less when compared to that of 3.**1**-3.**3**(105.70°- 107.77°).

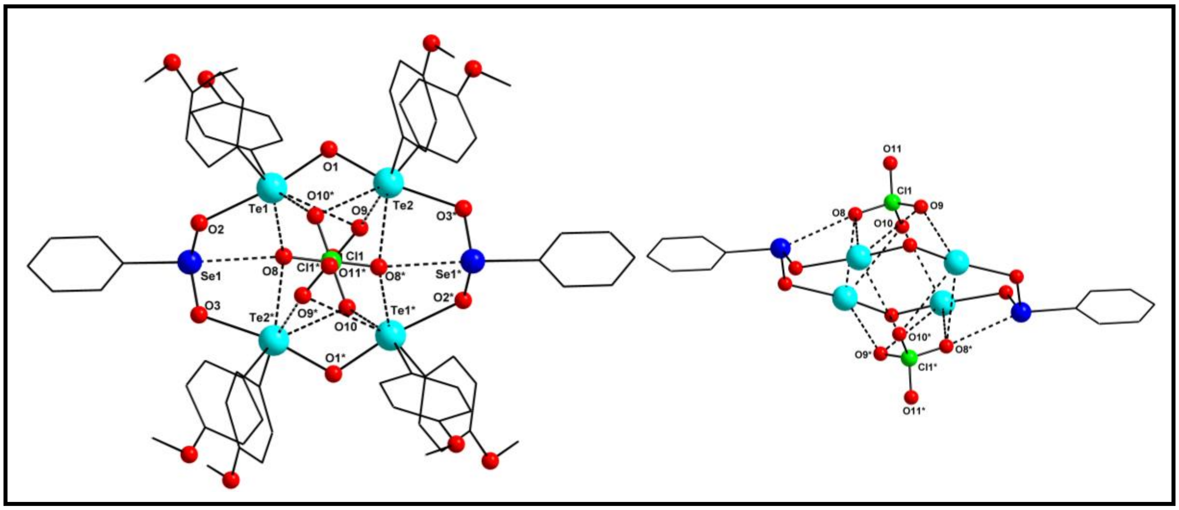


Figure 8: (left) Solid state molecular structure of 3.**6**. Hydrogen atoms and benzene solvates are omitted for clarity. (right) 12-membered $Te_4Se_2O_6$ ring of 3.**6** showing interactions with perchlorate ions.

Macrocycles 3.**6** (Figure 8) and 3.**7** (Figure 9) resulted from replacement of spherical chloride ions in 3.**1** by perchlorate and tetrafluoroborate ions, respectively. The Te-O interactions in 3.**6** fall in the range 3.0078(18) - 3.581(3) Å with an average of 3.208(2) Å which is lesser when compared to the sum of the van der Walls radii (3.58 Å) and slightly higher in comparison to the previously reported Te-O interactions.[28] The tetrahedral geometry of the perchlorate ion brings one of its oxygen atoms close to selenium centre as a result of which Se-O interactions were observed with a distance of 2.9237(19) Å which is considerably less in comparison to the sum of the van der Walls radii (3.42 Å) and slightly less with that observed in 3.**5**. The Te-F interactions in 3.**7** fall in the range 2.9864(12)-3.4598(16) with an average of 3.1562(13) Å which is considerably less when compared to the sum of the van der Walls radii (3.53 Å) of the interacting atoms.

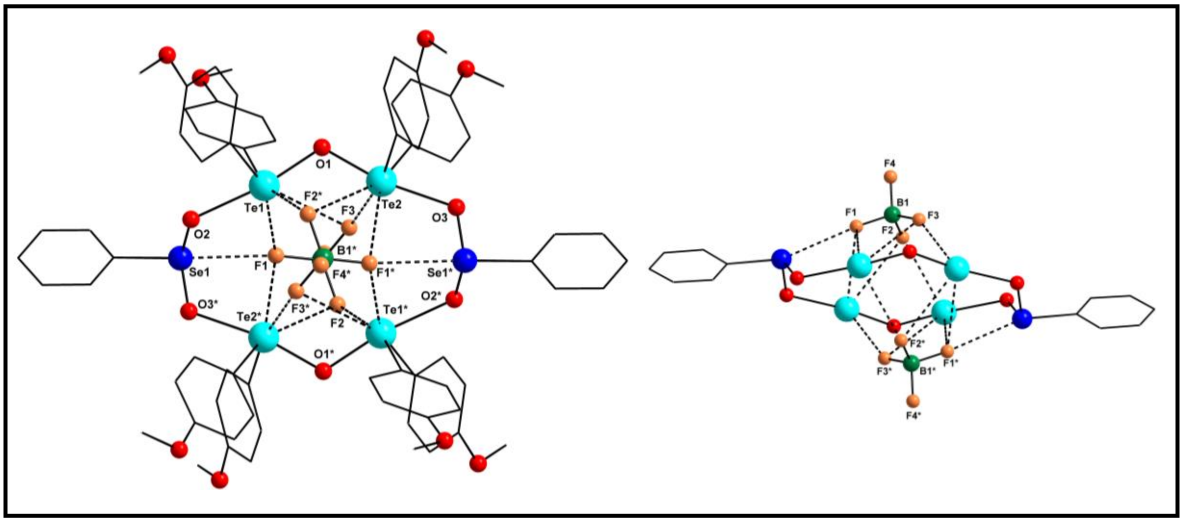


Figure 9: (left) Solid state molecular structure of 3.**7**. Hydrogen atoms and benzene solvates are omitted for clarity. (right) 12-membered $Te_4Se_2O_6$ ring of 3.**7** showing interactions with tetrafluoroborate ions.

The Te-F interacting distances are found to be shorter when compared to earlier reported Te-F secondary interactions in diphenyltellurium difluoride (3.208Å)[29] and higher when compared to bis(pentafluorophenyl)tellurium difluoride (2.846-2.952Å).[30] These strong secondary interactions are also reflected in the solution ^{125}Te NMR spectrum of 3.**7**, where a triplet with coupling constant of 568 Hz ($^{1}J_{\mathrm{Te}\ldots\mathrm{F}}$ = 568 Hz) is observed. This triplet can be assigned to coupling between ^{125}Te nuclei and two fluorine atoms namely F2 and F2* from the BF_4^- ions. Interestingly, this coupling constant is almost similar to that observed in diphenyltellurium difluoride ($^{1}J_{\mathrm{Te\text{-}F}}$ = 548 Hz),[29] where two fluorine atoms are covalently bonded with tellurium with a bond distance of 2.006(2)Å. Though molecular ion peak with loss of an anion could not be observed using mass spectral data, the very strong coupling observed in ^{125}Te solution NMR actually suggest the solution stability of 3.**7**. Se-F interactions have also been observed in 3.**7** with an average distance of 2.9363(13) Å (sum of van der Walls radii is 3.37 Å) which is in conformity with the ranges reported in literature.[31]

Table 2: Torsion angles list in 3.**5**-3.**7**

	3.**5**	3.**6**	3.**7**
At Se1			
C30-C29-Se1-O3	45.8(2) [+sc]	-76.8(3) [-sc]	-75.65(19) [-sc]
C30-C29-Se1-O2	-59.7(2) [-sc]	176.3(3) [+ap]	177.57(18) [+ap]
C34-C29-Se1-O2	121.17(18) [+ac]	-1.9(2) [-sp]	-0.66(17) [-sp]
C34-C29-Se1-O3	-133.32(18) [-ac]	105.0(2) [+ac]	106.12(17) [+ac]
At Te1			
C2-C1-Te1-O2	29.8(2) [+sp]	-135.6(2) [-ac]	-135.92(18) [-ac]
C2-C1-Te1-O1	-153.8(2) [-ap]	38.4(2) [+sc]	37.84(18) [+sc]
C6-C1-Te1-O1	29.0(2) [+sp]	-141.3(2) [-ac]	-140.75(18) [-ac]
C6-C1-Te1-O2	-147.4(2)[-ac]	44.8(2) [+sc]	45.49(17) [+sc]
At Te2			
C16-C15-Te2-O3	-148.0(2) [-ac]	136.1(3) [+ac]	136.17(19) [+ac]
C16-C15-Te2-O1	42.5(2) [+sc]	-35.4(3) [-sc]	-35.56(18) [-sc]
C20-C15-Te2-O1	-140.1(2) [-ac]	145.1(3) [+ac]	143.06(19) [+ac]
C20-C15-Te2-O3	29.38(19) [+sp]	-43.5(3) [-sc]	-45.21(18) [-sc]

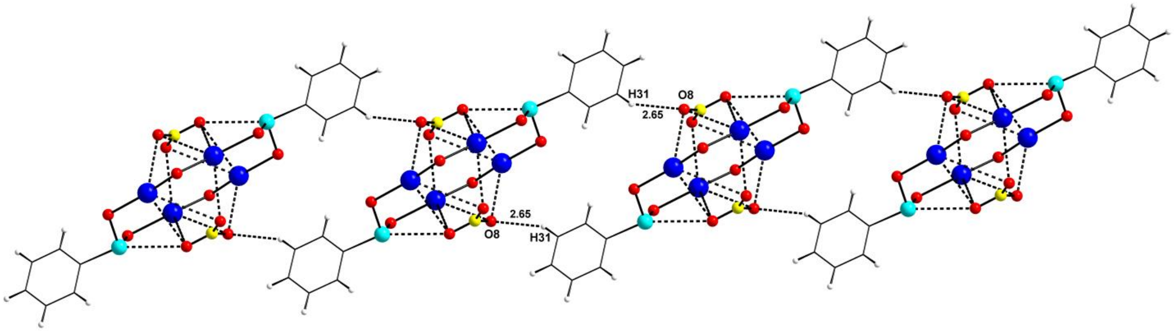
NOTE: [sp] = *syn-periplanar*; [sc] = *syn-clinal*; [ac] = *anti-clinal*; [ap] = *anti-periplanar*.

The 12-membered ring $Te_4Se_2O_6$ of 3.**6** and 3.**7** are also almost planar with selenium atoms (±0.622 Å for 3.**6**, ±0.624 Å for 3.**7**) and one of the oxygen atoms namely O2 (±0.458 Å for 3.**6**, ±0.470 Å for 3.**7**) deviating from the mean plane (Table 1). Conformational changes have been observed in the 12-membered rings of 3.**5**-3.**7** when compared to that of 3.**1** due to change in the geometry of the anions around central element (trigonal planar/tetrahedral). These can be quantified in terms of torsional angles at Se / Te centres (Table 2). The average Te-O bond lengths of ditelluroxane units in 3.**6** and 3.**7** are 1.9975(15), 1.9974(12) respectively, which are slightly high when compared to that of previous reports.[8] The average O-Te-O angles are 170.66(6)°, 170.45(6)° for 3.**6** and 3.**7**, respectively which are also higher when compared to the previous results. The average Se-O bond length and O-Se-O angles in 3.**6** are 1.6976(17) Å and 105.29(9)° respectively and in 3.**7** are 1.7017(13) Å, 105.16(7)° respectively. These bond angles are almost similar to earlier reports whereas bond lengths are on slightly higher side.[8]

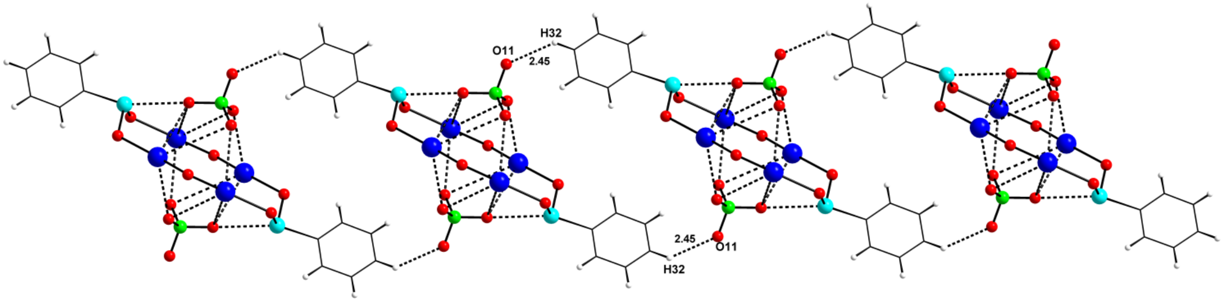
Weak intermolecular C-H…O interactions[32] in 3.**5**, 3.**6** and C-H…F interactions[33] in 3.**7** have been observed during analyses of the solid state packing of the crystal structures. The C-H…O interactions in 3.**5**, 3.**6** arises between selenium attached phenyl CH of one macrocycle and one of the oxygen atoms of nitrate anion (or) one of the oxygen atoms of perchlorate anion of the another macrocycle. The C-H…F interactions in 3.**7** arises between selenium attached phenyl CH of one macrocycle and one of the fluorine atoms of tetrafluoroborate anion of another macrocycle. These weak interactions have led to the formation of interesting polymeric supramolecular assemblies in solid state (Figure 10). The C-H…O, C-H…F distances and the angles at hydrogen in 3.**5**-3.**7** are given in the table 3.

Table 3: D-A distances and angles making at H in 3.**5**-3.**7**

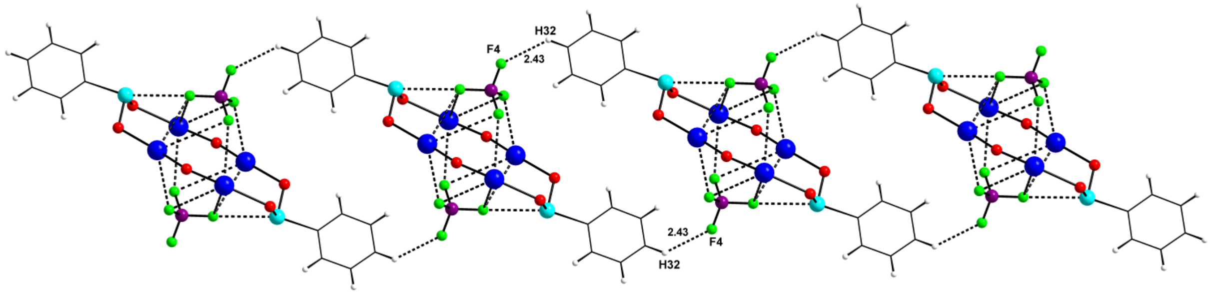
	H…O(Å)	C…O(Å)	C-H…O(deg)
3.5	2.65	3.50	154
3.6	2.45	3.13	130
	H…F(Å)	C…F(Å)	C-H…F(deg)
3.7	2.43	3.10	128



Supramolecular structure of 3.**5** showing C-H…O interactions



Supramolecular structure of 3.**6** showing C-H…O interactions



Supramolecular structure of 3.**7** showing C-H…F interactions

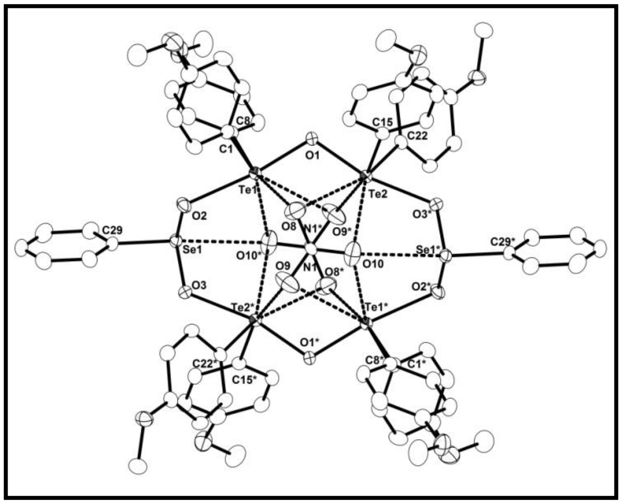
Figure 10: Supramolecular assemblies of 3.**5**-3.**7** showing secondary interactions. Anisyl rings attached to tellurium are omitted for clarity.

3.4 Conclusion

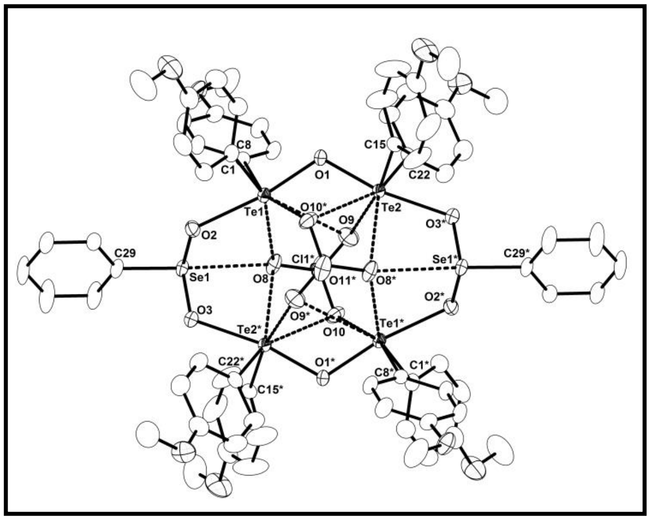
12-membered macrocycles consisting of $Te_4Se_2O_6$ framework have been isolated and structurally characterized. Halogen atoms stabilized by Te-X interactions [X = Cl(3.**1**,3.**4**), Br(3.**2**), I(3.**3**)] cap both sides of the cationic macrocycle providing charge neutrality. We have also successfully demonstrated the anion exchange reactions of Cl-macrocycle 3.**1** with nitrate ion (trigonal planar geometry, 3.**5**), perchlorate and tetrafluoroborate ions (tetrahedral geometry, 3.**6** and 3.**7** respectively). To the best of our knowledge, 3.**1**–3.**7** are the first structurally characterized examples of compounds that contain both Te–O–Te and Se–O–Te units and hence belong to a unique class of macrocycles. ESI-MS spectra of 3.**5**-3.**7** proved that 12-membered $Te_4Se_2O_6$ macrocycles retained their solid state structures in solution too. ^{125}Te NMR of 3.**7** showed the presence of interesting coupling between Te and F nuclei. Macrocycle 3.**3** (I-macrocycle) showed rare Se-π interactions leading to the formation of supramolecular polymeric networks in solid state. Weak intermolecular C-H…O interactions in 3.**5**, 3.**6** and C-H…F interactions in 3.**7** has led to the formation of interesting polymeric supramolecular assemblies in solid state.

3.5 ORTEP diagrams of 3.5-3.7:

3.5



3.6



3.7

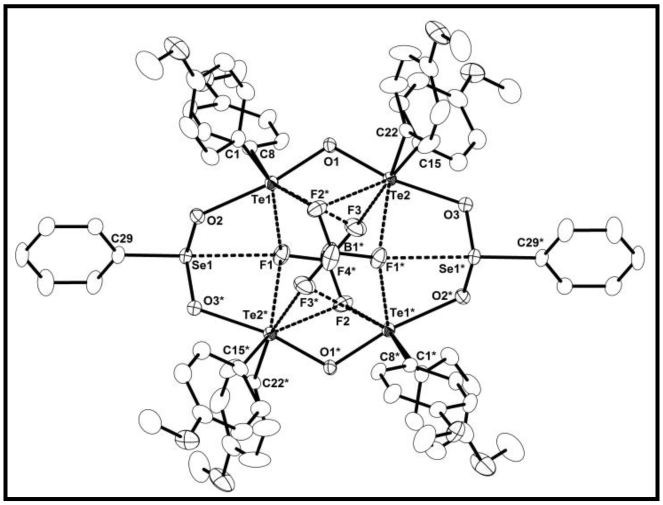


Table 4: Crystal and Refinement data for 3.**1**-3.**2**

	3.**1**	3.**2**
Formula	$C_{68}H_{66}Cl_2O_{14}Se_2Te_4$	$C_{92}H_{90}Br_2O_{14}Se_2Te_4$
fw	1846.43	2247.78
Temperature [K]	100(2)	100(2)
Crystal system	triclinic	Triclinic
Space group	P-1	P-1
Crystal size [mm]	0.18 x 0.16 x 0.10	0.20 x 0.16 x 0.12
a [Å]	13.943(3)	13.400(12)
b [Å]	15.726(3)	13.813(12)
c [Å]	17.826(3)	13.964(12)
α[°]	83.057(3)	105.21(1)
β[°]	69.493(3)	100.85(1)
γ[°]	67.539(2)	113.06(1)
V [$Å^3$]	3382.8(10)	2168.1(3)
Z	2	1
$d_{calcd.}$ [Mgm^{-3}]	1.813	1.722
μ [mm^{-1}]	2.926	3.156
F (000)	1792	1100
θ range for data collection [°]	1.22 to 25.12	1.60 to 25.02
Index ranges	-16<=h<=16 -18<=k<=18 -21<=l<=21	-15<=h<=15 -16<=k<=16 -16<=l<=16
Reflections collected/unique	32316 / 11937	14953 / 7568
R(int.)	0.0533	0.0198
Data/restraints/parameters	11937 / 0 / 819	7568 / 0 / 518
GoF on F^2	0.987	1.087
R_1/wR_2 [I>2σ(I)]	0.0411 / 0.0988	0.0248 / 0.0646
R_1/wR_2 [all data]	0.0535 / 0.1057	0.0268 / 0.0656
Largest diff peak/hole [$eÅ^{-3}$]	2.083 / -1.377	0.831 / -1.105

Table 5: Crystal and Refinement data for 3.**3** and 3.**4**

	3.**3**	3. **4**
Formula	$C_{110}H_{108}I_2O_{14}Se_2Te_4$	$C_{70}H_{74}Cl_2O_{14}Se_2Te_4$
fw	2576.08	1878.51
Temperature [K]	100(2)	100(2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
Crystal size [mm]	0.20 x 0.16 x 0.12	0.16 x 0.16 x 0.10
a [Å]	13.466(2)	10.958(9)
b [Å]	14.102(2)	11.839(10)
c [Å]	15.170(2)	14.670(12)
α[°]	91.41(3)	107.63(1)
β[°]	115.60(2)	94.69(2)
γ[°]	93.75(3)	104.30(1)
V [$Å^3$]	2588.0(6)	1732.1(2)
Z	1	1
$d_{calcd.}$ [Mgm^{-3}]	1.653	1.801
μ [mm^{-1}]	2.477	2.859
F (000)	1262	916.0
θ range for data collection [º]	1.45 to 25.07	1.48 to 25.13
Index ranges	-16<=h<=16 -16<=k<=16 -18<=l<=18	-13<=h<=13 -14<=k<=14 -18<=l<=18
Reflections collected/unique	24560 / 9119	16845/6127
R(int.)	0.0548	0.0476
Data/restraints/parameters	9119 / 0 / 599	6127/0/420
GoF on F^2	1.023	1.013
R_1/wR_2 [I>2σ(I)]	0.0507 / 0.1290	0.0338/0.0756
R_1/wR_2 [all data]	0.0630 / 0.1367	0.0400/0.0785
Largest diff peak/hole [$eÅ^{-3}$]	2.829 / - 2.074	1.072/-0.525

Table 6: Crystal and Refinement data for 3.**5**-3.**7**

	3.**5**	3.**6**	3.**7**
Formula	$C_{80}H_{78}N_2O_{20}Se_2Te_4$	$C_{86}H_{84}Cl_2O_{22}Se_2Te_4$	$C_{86}H_{84}B_2F_8O_{14}Se_2Te_4$
fw	2055.76	2208.75	2183.47
Temperature [K]	100	100	100
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
Crystal size [mm]	0.40 x 0.28 x 0.12	0.80 x 0.46 x 0.28	0.40 x 0.30 x 0.14
a [Å]	11.9793(8)	12.2163	12.1225(9)
b [Å]	13.0047(9)	14.8089(13)	14.7726(11)
c [Å]	14.3277(10)	15.9691(14)	15.9277(12)
α[°]	107.5360(10)	71.3950(10)	71.2340(10)
β[°]	109.9690(10)	70.1130(10)	70.0790(10)
γ[°]	92.5130(10)	82.3580(10)	82.4160(10)
V [$Å^3$]	1973.4(2)	2573.7(4)	2538.3(3)
Z	1	1	1
$d_{calcd.}$ [Mgm^{-3}]	1.730	1.425	1.428
μ [mm^{-1}]	2.459	1.942	1.922
F (000)	1008	1086	1070
θ range for data collection [°]	1.61 to 25.01	1.42 to 26.37	1.42 to 25.50
index ranges	-14<=h<=14 -15<=k<=15 -17<=l<=17	-15<=h<=15 -18<=k<=18 -19<=l<=19	-14<=h<=14 -17<=k<=17 -19<=l<=19
Reflections collected/unique	18995/6948	27402/10449	25469/9431
R(int.)	0.0171	0.0260	0.0182
Data/restraints/parameters	6948 / 0 / 491	10449 / 0 / 527	9431 / 0 / 527
GoF on F^2	1.091	1.035	1.028
R_1/wR_2 [$I>2\sigma(I)$]	0.0198/0.0493	0.0275/0.0730	0.0196/0.0500
R_1/wR_2 [all data]	0.0208/0.0498	0.0293/0.0740	0.0210/0.0506
Largest diff peak/hole [$eÅ^{-3}$]	0.614/-0.480	1.832/-0.641	0.573/-0.369

Table 7: Selected bond lengths(Å) and bond angles(°) in 3.**1**-3.**2**

3.**1**				3.**2**	
Te(1)-O(1)	2.329(4)	Se(2)-O(4)	1.688(4)	Te(1)-O(1)	2.2976(2)
Te(1)-O(2)	1.982(3)	O(1)-Te(1)-O(2)	169.20(1)	Te(1)-O(3)*	2.0067(2)
Te(1)-C(7)	2.124(5)	C(7)-Te(1)-C(14)	96.73(2)	Te(1)-C(7)	2.110(3)
Te(1)-C(14)	2.136(5)	O(2)-Te(2)-O(3)	167.57(1)	Te(1)-C(14)	2.107(3)
Te(2)-O(2)	1.994(3)	C(21)-Te(2)-C(28)	96.72(2)	Te(2)-O(2)	2.506(2)
Te(2)-O(3)	2.348(4)	O(4)-Te(3)-O(5)	167.60(1)	Te(2)-O(3)	1.9477(2)
Te(2)-C(21)	2.126(5)	C(41)-Te(3)-C(48)	97.32(2)	Te(2)-C(21)	2.112(3)
Te(2)-C(28)	2.131(5)	O(5)-Te(4)-O(6)	168.11(1)	Te(2)-C(28)	2.113(3)
Te(3)-O(4)	2.342(4)	C(55)-Te(4)-C(62)	99.91(2)	Se(1)-O(1)	1.7101(2)
Te(3)-O(5)	1.975(3)	C(1)-Se(1)-O(1)	101.4(2)	Se(1)-O(2)	1.671(2)
Te(3)-C(41)	2.132(5)	C(1)-Se(1)-O(6)	98.4(2)	Se(1)-C(1)	1.937(3)
Te(3)-C(48)	2.108(5)	O(1)-Se(1)-O(6)	105.7(2)	O(1)-Te(1)-O(3)*	165.12(7)
Te(4)-O(5)	1.970(3)	C(35)-Se(2)-O(3)	100.2(2)	C(7)-Te(1)-C(14)	94.45(1)
Te(4)-O(6)	2.361(4)	C(35)-Se(2)-O(4)	98.5(2)	O(2)-Te(2)-O(3)	168.12(7)
Te(4)-C(55)	2.106(5)	O(3)-Se(2)-O(4)	107.45(2)	C(21)-Te(2)-C(28)	93.99(1)
Te(4)-C(62)	2.112(5)	Te(1)-O(1)-Se(1)	130.7(2)	O(1)-Se(1)-O(2)	107.77(1)
Se(1)-C(1)	1.938(5)	Te(1)-O(2)-Te(2)	123.69(2)	C(1)-Se(1)-O(1)	100.04(1)
Se(1)-O(1)	1.677(4)	Te(2)-O(3)-Se(2)	143.7(2)	C(1)-Se(1)-O(2)	101.89(1)
Se(1)-O(6)	1.681(4)	Te(3)-O(4)-Se(2)	126.32(2)	Se(1)-O(1)-Te(1)	124.77(1)
Se(2)-C(35)	1.920(5)	Te(3)-O(5)-Te(4)	124.07(2)	Se(1)-O(2)-Te(2)	135.98(1)
Se(2)-O(3)	1.668(4)	Te(4)-O(6)-Se(1)	124.31(2)	Te(2)-O(3)-Te(1)*	126.90(1)

Symmetry transformations used to generate equivalent atoms:*=1-x,1-y,1-z

Table 8: Selected bond lengths(Å) and bond angles(°) in 3.**3**-3.**4**

3.**3**		3.**4**	
Te(1)-O(1)	2.357(4)	Te(1)-O(1)	2.283(3)
Te(1)-O(2)	1.989(4)	Te(1)-O(3)#	1.994(3)
Te(1)-C(7)	2.102(6)	Te(1)-C(2)	2.110(4)
Te(1)-C(14)	2.100(6)	Te(1)-C(9)	2.121(4)
Te(2)-O(2)	1.989(4)	Te(2)-O(2)	2.409(3)
Te(2)-O(3)*	2.349(4)	Te(2)-O(3)	1.964(3)
Te(2)-C(21)	2.113(6)	Te(2)-C(16)	2.112(4)
Te(2)-C(28)	2.119(6)	Te(2)-C(23)	2.126(4)
Se(1)-O(1)	1.689(4)	Se(1)-O(1)	1.689(3)
Se(1)-O(3)	1.691(4)	Se(1)-O(2)	1.677(3)
Se(1)-C(1)	1.925(6)	Se(1)-C(1)	1.928(4)
O(1)-Te(1)-O(2)	168.84(2)	O(3)#-Te(1)-O(1)	164.48(1)
C(7)-Te(1)-C(14)	95.0(2)	C(2)-Te(1)-C(9)	99.65(2)
O(2)-Te(2)-O(3)*	168.02(2)	O(2)-Te(2)-O(3)	169.43(1)
C(21)-Te(2)-C(28)	94.6(2)	C(16)-Te(2)-C(23)	93.95(2)
O(1)-Se(1)-O(3)	105.5(2)	O(1)-Se(1)-O(2)	107.04(1)
C(1)-Se(1)-O(1)	98.8(2)	C(1)-Se(1)-O(1)	100.12(2)
C(1)-Se(1)-O(3)	98.7(2)	C(1)-Se(1)-O(2)	101.49(2)
Se(1)-O(1)-Te(1)	110.62(2)	Se(1)-O(1)-Te(1)	125.50(1)
Te(1)-O(2)-Te(2)	122.15(2)	Se(1)-O(2)-Te(2)	129.82(1)
Se(1)-O(3)-Te(2)*	113.6(2)	Te(2)-O(3)-Te(1)#	126.70(1)

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

Table 9: Selected bond lengths(Å) and bond angles(°) in 3.**5**-3.**7**

3.**5**		3.**6**		3.**7**	
Te1-O1	1.9952(14)	Te1-O1	1.9925(16)	Te1-O1	1.9917(13)
Te1-O2	2.3475(15)	Te1-O2	2.3294(16)	Te1-O2	2.3260(13)
Te2-O1	2.0105(15)	Te2-O1	2.0025(15)	Te2-O1	2.0032(12)
Te2-O3*	2.2909(15)	Te2-O3*	2.3083(16)	Te2-O3	2.3102(13)
Te1-C1	2.108(2)	Te1-C1	2.101(2)	Te1-C1	2.0996(19)
Te1-C8	2.100(2)	Te1-C8	2.099(2)	Te1-C8	2.1021(18)
Te2-C15	2.110(2)	Te2-C15	2.106(2)	Te2-C15	2.1117(19)
Te2-C22	2.101(2)	Te2-C22	2.108(2)	Te2-C22	2.1037(18)
Se1-O2	1.6989(15)	Se1-O2	1.6934(17)	Se1-O2	1.6974(13)
Se1-O3	1.6961(15	Se1-O3	1.7018(17)	Se1*-O3	1.7060(13)
Se1-C29	1.919(2)	Se1-C29	1.925(2)	Se1-C29	1.9280(19)
O2-Se1-O3	103.91(8)	O2-Se1-O3	105.29(9)	O2-Se1-O3*	105.16(7)
O1-Te1-O2	172.73(6)	O1-Te1-O2	171.68(6)	O1-Te1-O2	171.26(5)
O1-Te2-O3*	167.11(6)	O1-Te2-O3*	169.64(6)	O1-Te2-O3	169.65(7)
Te1-O1-Te2	114.39(7)	Te1-O1-Te2	116.63(8)	Te1-O1-Te2	116.86(6)
Te1-O2-Se1	112.12(7)	Te1-O2-Se1	118.23(8)	Te1-O2-Se1	118.00(7)
Se1-O3-Te2*	122.68(8)	Se1-O3-Te2*	119.72(8)	Se1*-O3-Te2	119.24(7)

Symmetry transformations used to generate equivalent atoms:*=1-x+1,-y+1,-z+1(3.**5**); 1-x+1, -y+1, -z(3.**6**); 1-x+2, -y+1, -z(3.**7**).

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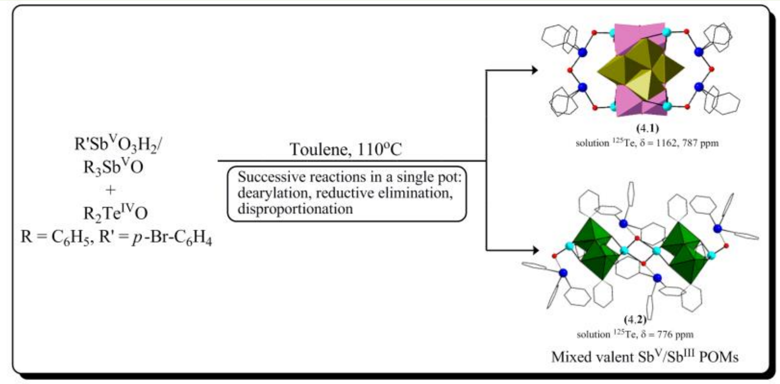
Assembling Anionic Sb(V)/(III) containing Polyoxostibonates Stabilized by Triphenyltellurium Cations

Chapter 4

Reactions of diphenyltellurium oxide with organostibonic acid and polymeric triphenylantimony oxide have been investigated independently. Single crystal X-ray diffraction studies have revealed the formation of novel and rare mixed valent Sb(V)/(III) containing polyoxostibonates $\{(C_6H_5)_3Te\}_2\{Na_2(H_2O)_2(p\text{-}Br\text{-}C_6H_4Sb^V)_{10}(Sb^{III})_4[(C_6H_5)_2Te]_4(O)_{30}(OH)_4]$ 4.**1** and $\{(C_6H_5)_3Te\}_4\{[(C_6H_5)_2Sb^V]_4(Sb^{III})_4(O)_{12}(OH)_4\}$ 4.**2**. Solution ^{125}Te NMR supports the solid state structures presented. Interestingly, during the assembly of these POMs several processes happen simultaneously. Rarely observed reduction from Sb(V) to Sb(III), complete dearylation of organoantimony precursors and complexation ability of tetraorganoditelluroxane moiety stabilizing large and novel POM structure(as in 4.**1**) along with formation of triphenyltellurium cations which not only provide charge balance but also stabilize the POM framework (as in 4.**2)** by weak interactions are observed.



Naragjuna Kumar Srungavruksham, Viswanathan Baskar, *Dalton Trans.*, **2015**, DOI: 10.1039/C4DT03319A.

4.1 Introduction

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

Continuing our interest in investigation of depolymerization reactions of organostibonates,[15] the reactions of organostibonic acid and polymeric triphenylantimony oxide with diphenyltellurium oxide independently were carried out. Synthesis and characterization of $\{(C_6H_5)_3Te\}_2\{Na_2(H_2O)_2(p\text{-}Br\text{-}C_6H_4Sb^{V})_{10}(Sb^{III})_4[(C_6H_5)_2Te]_4(O)_{30}(OH)_4$ 4.**1** and $\{(C_6H_5)_3Te\}_4\{[(C_6H_5)_2Sb^{V}]_4(Sb^{III})_4(O)_{12}(OH)_4\}$ 4.**2** are reported.

4.2 Experimental Section

4.2.1 General Information:

(P-bromophenyl)stibonic acid, polymeric triphenylantimony oxide and diphenyltellurium oxide were prepared according to literature reports.[16] Solvents and other general reagents were purchased from commercial sources. Compounds 4.**1** and 4.**2** were dried under high vacuum for half an hour before subjected to spectroscopic and elemental analysis.

4.2.2 Instrumentation:

Infrared spectra were recorded on a JASCO-5300 FT-IR spectrometer as KBr pellets. The solution ^{1}H, ^{13}C, and ^{125}Te NMR spectra were recorded on Bruker AVANCE^{III} 400 instrument. Elemental analysis was performed on a Flash EA Series 1112 CHNS analyzer. Single Crystal X-ray data collection for 4.**1**-4.**2** were collected at 100(2) K on a Bruker Smart Apex CCD area detector system (λ (Mo Kα) = 0.71073 Å) with a graphite monochromator. The data were reduced using SAINTPLUS and the structures were solved using SHELXS-97[17] and refined using SHELXL-97.[18]All non-hydrogen atoms were refined anisotropically. Aryl ring hydrogens were included in calculated positions. Hydrogen atoms of two water molecules which are coordinated to sodium (in case of 4.**1**) and four hydrogens which are associated with hydroxyl ions (in case 4.**1** and 4.**2**) for charge neutrality were included in the final refinement.

4.2.3 Synthetic Procedures:

4.2.3a Synthetic procedure for compound 4.1:

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

4.2.3b Synthetic procedure for compound 4.2:

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

4.3 Results and Discussion

Synthetic procedure employed for 4.**1** is as follows (scheme 1). *p*-Bromophenylstibonic acid and diphenyltellurium oxide were taken in 1:1 mole ratio and refluxed in toluene for 12 h resulting in a clear solution. Filtration followed by evaporation of the solvent under reduced pressure resulted in the formation of a colorless solid. Single crystals suitable for X-ray diffraction were grown using dichloromethane / hexane diffusion method. 4.**2** was prepared by reacting polymeric triphenylantimony oxide with diphenyltellurium oxide in 1:2 mole ratio under toluene reflux condition for 12h which resulted in the formation of a fluffy white solid (scheme 1). Flake like single crystals were grown by diffusion of hexane into a dichloromethane – methanol mixture. 4.**1** and 4.**2** were characterized by standard spectroscopic and analytical techniques. Solution NMR for 4.**1** and 4.**2** were taken in $CDCl_3$ and CD_2Cl_2-CD_3OD mixture respectively. Solution ^{125}Te NMR of 4.**1** shows two resonances at δ = 1162 and 787 ppm which clearly indicates the presence of two different tellurium environments in 4.**1**. Solution ^{125}Te NMR of 4.**2** shows single resonance peak at δ= 776 ppm which indicates the presence of tellurium atom in a unique environment in 4.**2**.

Scheme 1

$$\mathbf{R'SbO_3H_2 + R_2TeO \xrightarrow[\text{reflux, 12h}]{\text{toluene}} [R_3Te]_2[Na_2(H_2O)_2(R'Sb^{V})_{10}(Sb^{III})_4(R_2Te)_4(O)_{30}(OH)_4](4.1)}$$

$$\mathbf{[R_3SbO]_n + 2\ R_2TeO \xrightarrow[\text{reflux, 12h}]{\text{toluene}} [R_3Te]_4[(R_2Sb^{V})_4(Sb^{III})_4(O)_{12}(OH)_4]\ (4.2)}$$

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

4.**1** and 4.**2** have been characterized by single crystal X-ray diffraction studies. Crystallographic data and selected metric parameters for 4.**1** and 4.**2** are provided in tables 1-4. 4.**1** crystallizes in monoclinic space group $P2_1/n$ with half of the molecule in asymmetric unit. The molecular structure of 4.**1** represents a dianionic tetradecanuclear organoantimony oxo cluster chelated by two tetraphenylditelluroxane moieties (Figure

1). The charge is balanced by the presence of two triphenyltellurium cations which crystallize along with the core.

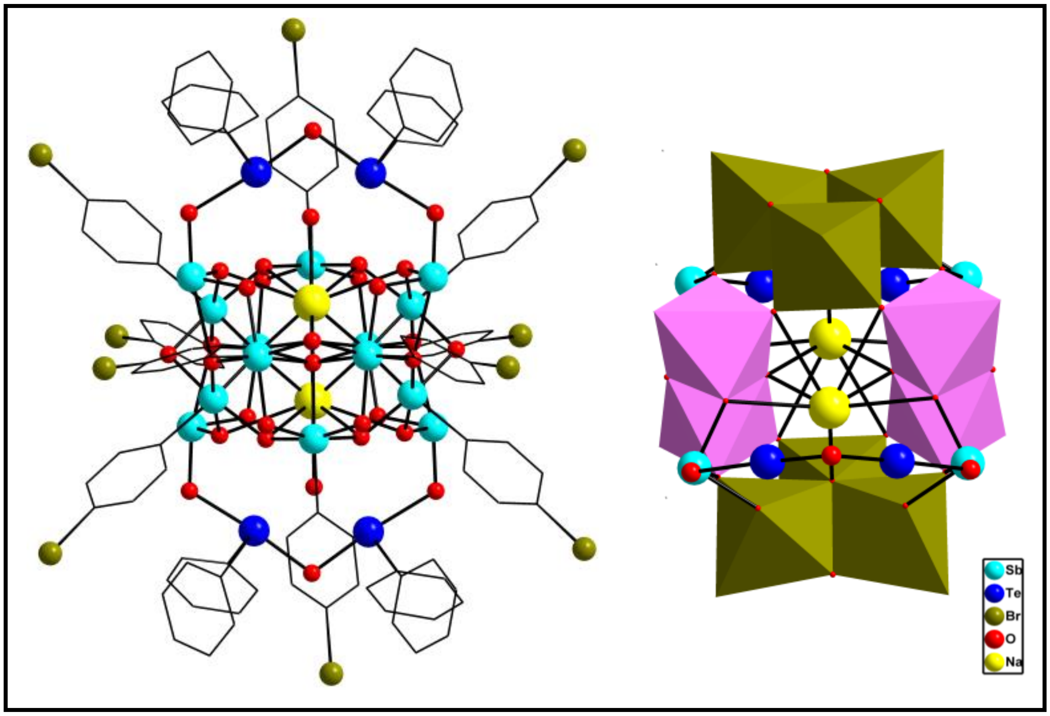


Figure 1: (left) Solid state molecular structure of 4.**1**. Hydrogens, triphenyltellurium cations and dichloromethane solvates are omitted for clarity. (right) Polyhedral view of 4.**1**. Aryl groups attached to Sb/Te are omitted for clarity.

The tetradecanuclear organoantimony oxo cluster can be described as follows. Of the fourteen Sb atoms present, ten are present in +5 state of oxidation displaying six coordination and four Sb atoms are present in +3 state of oxidation displaying pseudo trigonal bipyramidal geometry with stereo chemically active lone pair on antimony occupying one of the equatorial positions.[19] The ten Sb(V) atoms are present as two triads and two diads. Each triad is formed by each polyhedra of the triad sharing an edge with the adjacent polyhedra and further all the three polyhedra sharing a common vertex. The diads are formed by two polyhedra sharing a common edge. Each triad is connected to two diads by two vertex sharing polyhedra with each of the diad. The triads are further also connected in two sides to the diads through a Sb(III) atom. Of the

four coordinations present for the Sb(III) atom, three are the oxygen linked to Sb(V) atoms and the fourth coordination comes from the binding tetraphenylditelluroxane unit. The ability of diorganotellurium oxides/dihalides to form tetraorganoditelluroxane [$R_2TeOTeR_2$] in presence of protic acids is known in literature.[14,20] The novelty here is the ability of tetraorganoditelluroxane in stabilizing large POM frameworks. The Sb-O distance falls in the range of 1.946(7)Å-2.186(7)Å which are comparable with earlier Sb(V)-O distances reported in literature.[6, 15]

Interestingly mono and di-dearylation of organoantimony compounds have been reported in the literature.[21] To the best of our knowledge complete dearlytion is rare.[22] Herein complete dearylation of organoantimony precursor is reported. BVS calculations have been used for determining the oxidation state of the metal atoms present in the cluster.[23] The oxidation state value in 4.**1** for Sb present in SbO_4 units corresponds to that of +3 state of oxidation. Another interesting aspect about the structure is the partial reduction of the Sb(V) to Sb(III).

Sb(III) can readily oxidise to form Sb(V) and recently the synthesis of a mixed valent Sb(III)/Sb(V) oxido cluster in which Sb(III) is oxidised to Sb(V) by air has been reported.[24] Herein reduction of Sb(V) to Sb(III) in presence of diphenyltellurium oxide is observed. Further due to strong affinity of arylstibonates towards Na^+ ion, two Na^+ ions are encapsulated in the Sb_{14} core. With the help of ESI-mass spectroscopy, it has been inferred that these Na^+ ions originated possibly from the glassware due to leaching.[10] The sodium ions are present in eight coordinate geometry. The Na-O bond distances fall in the range 2.355(9)Å -2.912(8)Å. Of the 34 oxo groups present in 4.**1**, 22 are μ_2-bridging and 4 are μ_4-bridging while the other 8 are μ_3-bridging in which 4 of them are considered to be part of hydroxyl ions for charge neutrality. The charge of the Sb_{14} cluster along with the two ligated tetraphenylditelluroxane motifs is dianionic. Two triphenyltellurium cations are found to crystallize outside the core stabilizing the charge on the cluster. Mixed valent Sb_{14} framework described herein belongs to a novel class of POMs using main group elments as framework atoms.

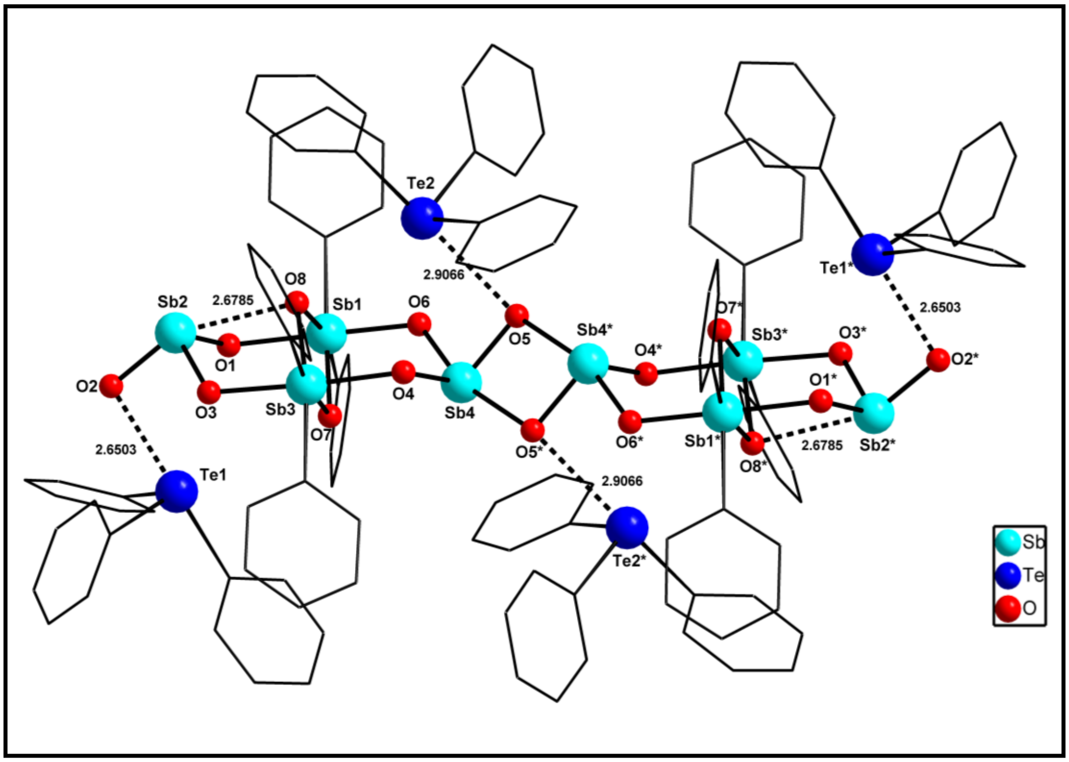


Figure 2: Solid state molecular structure of 4.**2**. Hydrogen atoms are omitted for clarity.

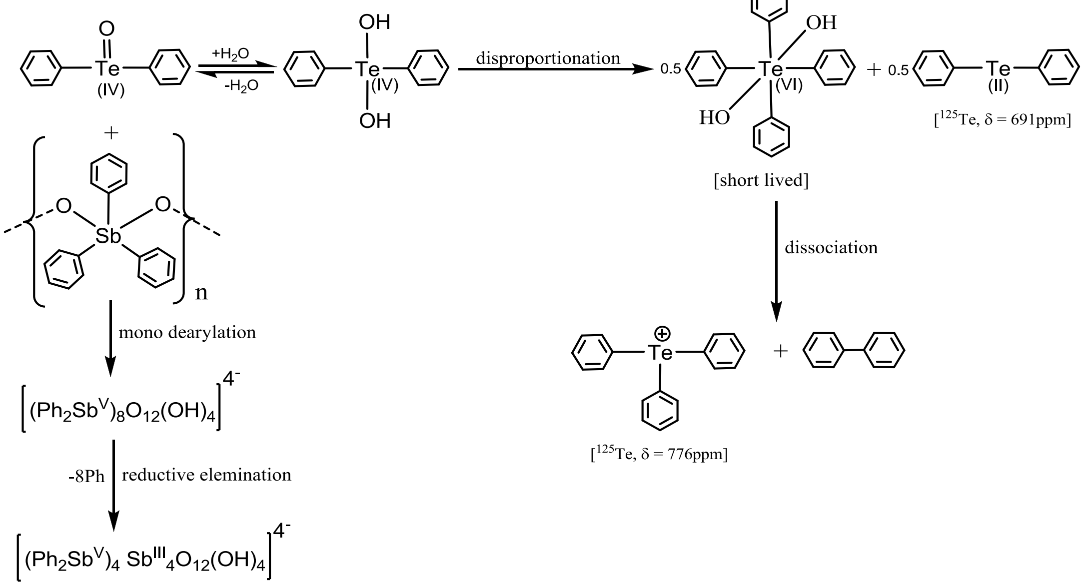
4.**2** crystallizes in monoclinic space group $P2_1/n$ with half of the molecule present in the asymmetric unit. The molecular structure of 4.**2** corresponds to a tetraanionic octanuclear organoantimony oxo cluster with four triphenyltellurium cations stabilizing the cluster by weak interactions and also providing for charge neutrality (Figure 2). The solid state structure of 4.**2** can be described as a dimer of antimony tetramers connected through two μ_2-oxo bridges (O5, O5$^{\#}$). Each tetramer consists of two Sb(III) and two Sb(V) centres arranged in alternative manner connected through four μ_2-oxo bridges to form a chair-like eight-membered ring. Further the two Sb(V) atoms are connected among themselves by two μ_2-oxo bridges. Polyhedral view of this dimer shows two octahedra around the antimony atoms sharing a common edge.

Sb-O distances fall in the range 1.998(4)Å -2.081(4)Å with an average of 2.036Å which are found to be slightly higher when compared to 4.**1**. Each antimony atom in the dimer contains only two phenyl rings as a result of mono dearylation of triphenylantimony oxide polymer which is the starting precursor. The dimer is connected to two Sb(III) centers namely Sb2 and Sb4 through two μ_2-oxo bridges(O1,O3 or O4,O6) at both sides respectively. Interestingly the core of this tetramer resembles the hexa-μ-oxooctaphenyltetraantimony cluster reported in literature.[25] Further this tetrameric core is connected to another identical tetrameric core at Sb4 centre through two μ_2- oxo bridges namely O5 and O5[#] with Sb-O distances 1.871(4)Å, 2.361(4) Å respectively to form a chain like octameric antimony-oxo core with alternate Sb(III) and Sb(V) atoms. The Sb(III) atoms Sb2 and Sb4 are tri coordinate and tetra coordinate with O atoms respectively. The geometry around the tri coordinate Sb2 is considered to be trigonal pyramidal with stereo chemically active lone pair occupying the axial position with Sb-O distance falling in the range 1.886(4)Å -1.901(4)Å with an average 1.876Å which is marginally less when compared to 4.**1**.

It has also been observed that this Sb(III) atom is involved in a secondary bonding interaction with O8 (Sb…O, 2.6785 Å). The geometry around tetra coordinate Sb4 is pseudo trigonal bipyramidal with stereo chemically active lone pair on antimony occupying one of the equatorial positions which is the common geometry assigned to antimony with four bonds.[19] The Sb-O distances around Sb4 fall in the range 1.871(4) Å-2.361(4) Å with an average 2.020 Å which is similar to 4.**1**. BVS calculations confirm the +3 oxidation state of Sb2 and Sb4 atoms[23]. 4.**2** contains 16 μ_2-bridging oxo groups. Of the 16, 4 μ_2-oxo bridges which belong to two Sb(V) dimers are considered to be part of hydroxyls for charge neutrality. The overall charge of tetraanionic octanuclear organoantimony oxo cluster is neutralized by the presence of four triphenyltellurium cations present outside the core. These triphenyltellurium cations act as counter ions in both 4.**1** and 4.**2**.

Diphenyltellurium oxide / diphenyl tellurium dihydroxide disproportionates[26] in the presence of organoantimony(V) oxo cluster to diphenyltelluride(II) and tetraphenyl tellurium(VI) dihydroxide. Solution ^{125}Te NMR of the filtrate (in reaction 2, Scheme 1) shows a resonance at 691 ppm which confirms the presence of diphenyltelluride[27] as a side product. A resonance corresponding to the presence of Te(VI) was not observed probably because at toluene reflux temperatures tetraphenyltellurium(VI)dihydroxide disintegrates into triphenyltellurium cation and biphenyl.[28] In fact, in solution ^{125}Te NMR a resonance corresponding to the presence of Ph_3Te^+ was observed at 776 ppm. This cation crystallizes out as a counter ion along with the mixed valent organoantimony oxo cluster. The plausible mechanism (chart 1) for assembly of 4.**2** can be proposed as follows, in the presence of diorganotellurium oxide, mono dearylation of the triorganoantimony precursor leading to the formation of diorganoantimony oxo cluster $[(R_2Sb^V)_8O_{16}]^{4-}$, which further undergoes partial reductive elimination on four antimony atoms leading to the formation of $[(R_2Sb^V)_4Sb^{III}{}_4O_{16}]^{4-}$ whose solid state structure is stabilized by the presence of four triphenyltellurium cations in the crystal lattice.

Chart 1



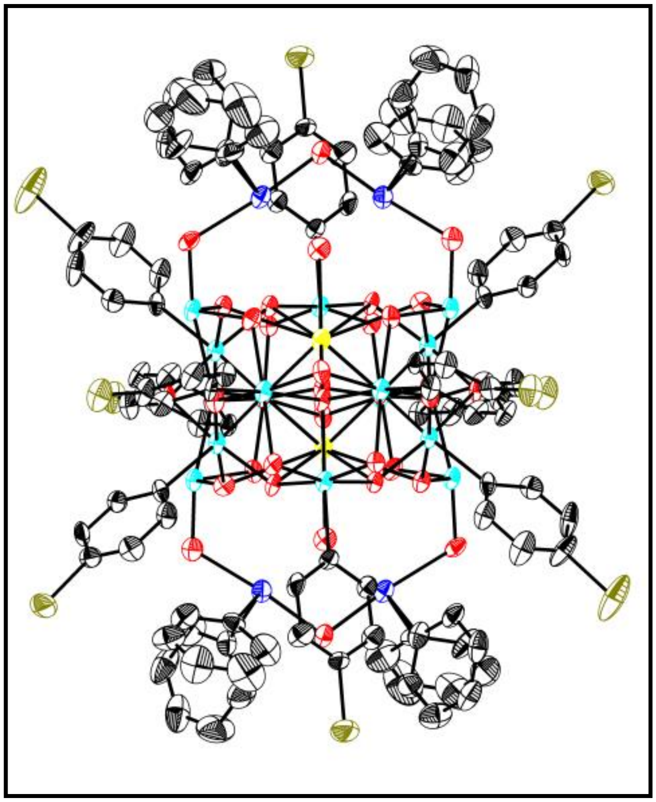
4.4 Conclusion

To conclude, in presence of diorganotellurium oxide, organostibonic acid and triorganoantimony oxide self-assemble to yield mixed valent organostibonates ligated by tetraorganoditelluroxane (in 4.**1**) and stabilized by weak interactions from triaryltellurium cations (4.**2**). To the best of our knowledge this is the first instance wherein tetraorganoditelluroxane's ability to act as ligand for stabilizing large POM framework has been observed. Successive reactions like mono / tri-dearylation, reductive elimination and disproportionation have taken place *enroute* to the formation of the novel POM frameworks.

4.5 ORTEP diagrams of 4.1-4.2:

Thermal ellipsoids are shown at 50% probability.

4.**1**



4.**2**

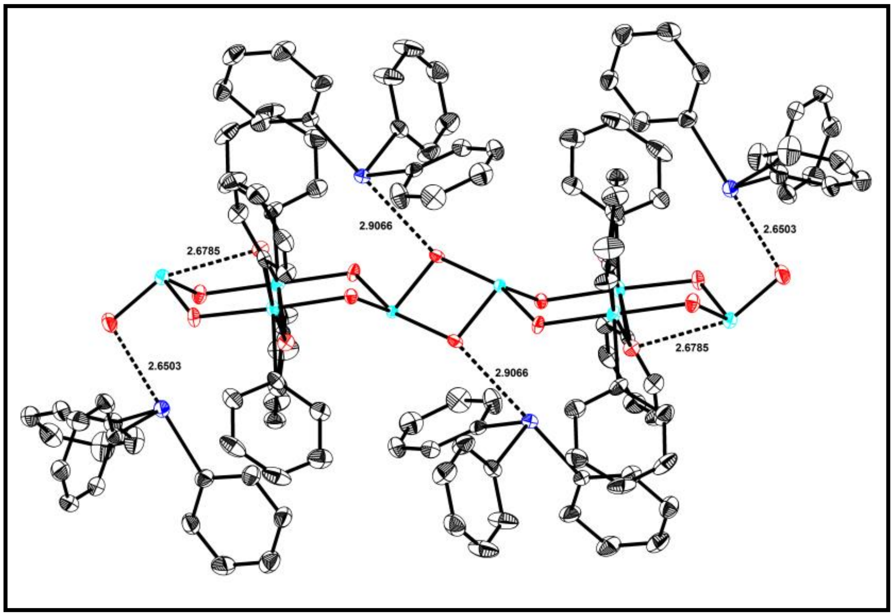


Table 1: Crystal and Refinement data for 4.**1**-4.**2**

	4.1	**4.2**
Formulae	C_{148} $H_{126}Br_{10}$ Cl_8 Na_2 O_{36} Sb_{14}	C_{120} H_{104} O_{16} Sb_8 Te_4
Fw.g mol^{-1}	6079.27	3286.43
Cryst syst	Monoclinic	Monoclinic
Cryst size.mm	0.16 x 0.12 x 0.08	0.22 x 0.14 x 0.08
Space group	$P2_1/n$	$P2_1/n$
a, Å	19.1789(13)	16.709(2)
b, Å	22.2219(15)	16.711(2)
c, Å	20.1740(13)	19.386(2)
α, deg	90	90
β, deg	91.9930(10)	90.193(2)
γ, deg	90	90
v, Å^3	8592.8(10)	5413.0(11)
Z	2	2
Dcacld.Mgm^{-3}	2.350	2.016
T.K	100	100
μ, mm^{-1}	5.685	3.087
F(000)	5672	3136
θ range,deg	1.36 to 25.07	1.61 to 26.49
Index ranges	-22<=h<=22 -26<=k<=26 -24<=l<=24	-20<=h<=20 -20<=k<=20 -24<=l<=24
No. of.refln colled	82138	56992
Completeness to θ max	99.8 %	99.7 %
No. of. indep refln/R_{int}	15219	11162
GooF(F^2)	1.030	1.123
R_1 (F) ($I>2\sigma(I)$)	0.0554	0.0442
wR_2 (F^2) (All data)	0.1503	0.1061
Largest diff peak/hole,e Å^{-3}	2.897/ -1.861	2.802/ -1.824

Table 2: Selected bond lengths(Å) and bond angles(°) in 4.**1**

Sb1-O5 = 2.186(7)	Sb4-O14* = 2.091(7)	Te1-O15 = 2.175(8)	C7-Sb2-O5 = 168.3(3)
Sb1-O1 = 1.966(6)	Sb5-O1* = 1.962(7)	Te2-O16 = 2.258(8)	C7-Sb2-O10* = 99.8(3)
Sb1-O2 = 1.984(7)	Sb5-O11 = 2.080(7)	Te1-O17 = 2.053(8)	O2-Sb2-O13 = 167.8(3)
Sb1-O4 = 1.996(6)	Sb5-O10 = 2.004(7)	Te2-O17 = 2.008(8)	C13-Sb3-O5 = 170.7(3)
Sb1-O6 = 1.946(7)	Sb5-O7 = 1.977(6)	Te1-C31 = 2.128(12)	O4-Sb3-O12 = 169.8(3)
Sb2-O2 = 1.955(7)	Sb5-O9 = 1.993(7)	Te2-C43 = 2.131(13)	C19-Sb4-O7 = 171.6(3)
Sb2-O3 = 1.981(7)	Sb6-O8 = 2.504(7)	Te3-C55 = 2.112(11)	C25-Sb5-O7 = 169.0(3)
Sb2-O5 = 2.081(7)	Sb6-O12 = 1.906(7)	C4-Br1 = 1.895(11)	O1*-Sb5-O9 = 168.0(3)
Sb2-O10* = 2.006(7)	Sb6-O11 = 1.871(7)	Na1-O1 = 2.912(8)	O12-Sb6-O11 = 97.2(3)
Sb2-O13 = 2.039(7)	Sb6-O16 = 1.865(7)	Na1-O5 = 2.379(8)	O8-Sb6-O16 = 165.8(3)
Sb3-O3 = 1.978(7)	Sb7-O10* = 2.428(7)	Na1-O7 = 2.355(9)	O12-Sb6-O16 = 95.8(3)
Sb3-O5 = 2.088(6)	Sb7-O13 = 1.915(7)	Na1-O7* = 2.359(8)	O15-Sb7-O10* = 164.5(3)
Sb3-O4 = 1.969(7)	Sb7-O14 = 1.849(7)	Na1-O6* = 2.962(7)	Na1-O7-Na1* = 95.9(3)
Sb3-O12 = 2.044(7)	Sb7-O15 = 1.875(8)	Na1-O14 = 2.851(8)	Te1-O17-Te2 = 107.6(4)
Sb3-O8 = 1.984(7)	Sb1-C1 = 2.119(11)	Na1-O18 = 2.494(9)	Te2-O16-Sb6 = 117.8(3)
Sb4-O6 = 1.962(7)	Sb2-C7 = 2.109(11)	Na1-O11 = 2.779(8)	Te1-O15-Sb7 = 118.2(4)
Sb4-O8 = 2.017(7)	Sb3-C13 = 2.120(10)	C1-Sb1-O5 = 173.9(3)	Sb4*-O14-Sb7 = 131.8(4)
Sb4-O9 = 1.980(6)	Sb4-C19 = 2.102(10)	C1-Sb1-O1 = 94.0(3)	Sb7*-O10-Sb2* = 94.5(3)
Sb4-O7 = 1.996(7)	Sb5-C25 = 2.097(11)	O6-Sb1-O2 = 167.3(3)	Sb5-O11-Sb6 = 131.6(4)

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

Table 3: Selected bond lengths(Å) and bond angles(°) in 4.**2**

Sb1-O6 = 2.003(4)	Sb4-O5 = 1.871(4)	C1-Sb1-O8 = 164.6(2)	O5-Sb4-O6 = 88.28(17)
Sb1-O1 = 2.072(4)	Sb4-O6 = 1.943(4)	C7-Sb1-O1 = 93.0(2)	O6-Sb4-O5* = 164.37(15)
Sb1-O7 = 2.019(4)	Sb4-O4 = 1.906(4)	O7-Sb1-O8 = 78.89(16)	O4-Sb4-O6 = 97.49(16)
Sb1-O8 = 2.038(4)	Sb4-O5* = 2.361(4)	O1-Sb2-O2 = 95.1(2)	Sb1-O8-Sb3 = 99.81(17)
Sb2-O1 = 1.886(4)	Sb1-C1 = 2.143(6)	O1-Sb2-O3 = 102.79(18)	Sb1-O1-Sb2 = 116.9(2)
Sb2-O2 = 1.842(4)	Sb1-C7 = 2.150(6)	O2-Sb2-O3 = 94.83(19)	Sb3-O4-Sb4 = 120.26(19)
Sb2-O3 = 1.901(4)	Sb3-C13 = 2.149(6)	C13-Sb3-O8 = 167.18(19)	Sb4-O5-Sb4*= 130.69(17)
Sb3-O3 = 2.081(4)	Sb3-C19 = 2.141(6)	C19-Sb3-O7 = 169.3(2)	
Sb3-O4 = 2.059(4)	Te1-C25 = 2.134(6)	C13-Sb3-O4 = 94.89(19)	
Sb3-O7 = 1.998(4)	Te1-C43 = 2.124(6)	O3-Sb3-O7 = 91.83(17)	
Sb3-O8 = 2.025(4)	C1-Sb1-O7 = 167.9(2)	O4-Sb4-O5 = 96.66(17)	

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

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Reactions of Diorganotellurium Oxides with Organoantimony (V) Halides

Chapter 5

This chapter details the reactions of diorganotellurium oxides with organoantimony(V) halides. Reaction of diphenyltellurium oxide with diphenylantimony trichloride in (1:1 mole ratio) refluxing toluene yielded Ph_2TeCl_2 (5.**1**) as a major product and $[(PhSb)_4(O)_4(Ph_2ClSbO_2)_4]$ (5.**2**) as a minor product whereas a similar reaction between dimesityltellurium oxide and diphenylantimony trichloride yielded an adduct $Ph_2SbCl_3.Mes_2TeO$ (5.**3**) as the only product. Further reactions of triphenylantimony dichloride with diphenyltellurium oxide and dimesityltellurium oxide were investigated independently and the products obtained are given in detail in this chapter.

5.1 Introduction

Lewis acid catalysts which includes various main group elements have been used extensively to catalyze several types of organic reactions.[1] Macrocyclic systems that contain Lewis acidic main group elements have been utilized as host molecules for several anions.[2] Recently, pnictogen-based Lewis acids were found to show variety of applications in synthetic organic chemistry.[3] Herein it is worth mentioning about the pioneering work of Gabbai et al. on fluorescence sensing of fluoride ions in protic solvents by using Lewis acidic organoantimony(V) compounds.[4] Diorganoantimony trichloride is a strong Lewis acid and tend to form adducts with water, acetonitrile, methanol and triphenylphosphine oxide.[5] On the other hand, diorganotellurium oxides have been used as an oxygen transfer reagents in organic synthesis.[6] Diorganotellurium oxides are basic in aqueous solutions and in the presence of protic acids they tend to associate and form tetraorganoditelluroxane [$R_2TeOTeR_2$] moiety.[7] Beckmann and coworkers reported the reactivity of diorganotellurium oxide with various protic ligands like carboxylates, phosphinates, sulfonates and diorganosilane diols which resulted in the formation of products showing rich structural variations.[8] In a very recent report, they demonstrated the oxygen transfer reaction of diorganotellurium oxide to acetonitrile.[9] When intramolecularly coordinated diorganotellurium oxide $(8\text{-}Me_2NC_{10}H_6)_2TeO$ was treated with acetonitrile, it resulted in the formation of zwitterionic diorganotellurium(IV) acetamide $(8\text{-}Me_2NC_{10}H_6)_2TeNC(O)CH_3$ which when further hydrolysed with HCl afforded acetamide and diorganohydroxytelluronium(IV) chloride $[(8\text{-}Me_2NC_{10}H_6)_2Te(OH)]Cl$.

We have been working on self-assembly of multinuclear antimony-oxo clusters. We reported previously the base induced hydrolysis of triphenylantimony diphosphonate in refluxing toluene in which mono and di-dearylation followed by elimination of water molecules lead to the formation of the trinuclear organoantimony oxo cluster.[10] Although inorganic weakly coordinating anions that contain Sb-O-Te moieties are well known[11], organometallic compounds containing Sb-O-Te frameworks is a rarity. We also recently demonstrated the ligating capacity of a tetraorganoditelluroxane [$R_2TeOTeR_2$] moiety in stabilizing large organometallic Sb_{14} polyoxostibonate cluster.[12] In continuation of our efforts in preparing organometallic Sb-O-Te frameworks, in this work, we investigated the independent reactions of diphenylantimony trichloride and triphenylantimony dichlorides with diorganotellurium oxides to afford Ph_2TeCl_2(5.**1**), [$(PhSb)_4(O)_4(Ph_2ClSbO_2)_4$](5.**2**), Ph_2SbCl_3.Mes_2TeO (5.**3**), Ph_3TeCl (5.**4**) and $(Mes)_2ClTeOTeCl(Mes)_2$ (5.**5**).

5.2 Experimental Section

5.2.1 General Information:

Triphenylantimony, $TeCl_4$, Te powder, 2-bromomesityline, other reagents and solvents were purchased from commercial sources. Diphenylantimony trichloride, triphenylantimony dichloride, diphenyltellurium oxide, dimesityltellurium oxide were prepared according to literature reports.[13]

5.2.2 Instrumentation:

Infrared spectra were recorded on a JASCO-5300 FT-IR spectrometer as KBr pellets. The solution ^{1}H, ^{13}C, and ^{125}Te NMR spectra were recorded on Bruker AVANCE^{III} 400 instrument. Elemental analysis was performed on a Flash EA Series 1112 CHNS analyzer. Single Crystal X-ray data collection for 5.**2**-5.**5** were collected at 298(2) K on a Bruker Smart Apex CCD area detector system (λ (Mo Kα) = 0.71073 Å) with a graphite monochromator (for 5.**2**) and Oxford CCD X-ray diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å for 5.**4**, 5.**5**) and Cu Kα radiation (λ = 1.5418 Å for 5.**3**). The data were reduced using SAINTPLUS, CrysAlisPro 171.33.55[14] and the structures were solved using SHELXS-97[15] and refined using SHELXL-97[16]. All non-hydrogen atoms were refined anisotropically. Aryl ring hydrogens were included in calculated positions. In 5.**2** the disordered solvent molecules in the asymmetric units were removed using the BYPASS algorithm, implemented as the

SQUEEZE[17] option in PLATON[18]. The total electron count removed by SQUEEZE corresponded to 314 with void volume of 1388.7 Å^3 (17.2%) per unit cell in 5.**2**.

5.2.3 Synthetic procedures:

5.2.3a Synthetic procedure for compound 5.1-5.3:

Diphenylantimony trichloride (Ph_2SbCl_3, 0.100 g, 0.26 mmol) and diphenyltellurium oxide (Ph_2TeO, 0.078 g, 0.26 mmol) were refluxed in toluene for 12 hours resulting in a clear solution. Filtration followed by evaporation of the solvent under reduced pressure resulted in a solid white precipitate which readily dissolves in dichloromethane. Compounds 5.**1** and 5.**2** were isolated from the reaction mixture by crystallization in dichloromethane / hexane diffusion.

Compound 5.**1**:

Yield: 0.060 g (65.2%) (based on diphenyltellurium oxide). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.12 (m, 4H), 7.56 (6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 135.54, 133.80, 131.77, 130.06. ^{125}TeNMR (126.3 MHz, $CDCl_3$, ppm): δ 914. IR (KBr, cm^{-1}): 3052.7(w), 1572.6(w), 1468.5(m), 1435.6(s), 1331.5(w), 1178.1(w), 1101.4(m), 1052.0(m), 991.8(s), 838.4(m), 739.7(s), 673.9(m).

Compound 5.**2**:

Yield: 0.010 g (13.7 %) (based on diphenylantimony trichloride), Dec. temp: 290°C. $C_{72}H_{60}Cl_4O_{12}Sb_8$(2233.13): calcd C 38.72, H 2.71; found C 38.65, H 2.76. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.73(d, 2H), 8.32(m, 12H), 7.58(m, 14H), 7.09(m, 32H). IR (KBr, cm^{-1}): 2960.9(m), 1477.8(m)1434.1(s), 1259.3(s), 1016.5(m), 864.2(w), 794.2(s), 792.3(s).

Compound 5.**3** was also prepared by the same procedure as compound 5.**1**. The mole ratios of the corresponding reagents used are as follows.

Diphenylantimony trichloride (Ph_2SbCl_3, 0.100 g, 0.26 mmol), dimesityltellurium oxide (0.100 g, 0.26 mmol), Yield: 0.150 g (75.4 %), Dec. temp: 200°C. $C_{30}H_{32}Cl_3OSbTe$(764.29): calcd C 47.14, H 4.22; found C 47.26, H 4.15. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.33(m, 2H), 7.54(m, 5H), 7.31(m, 2H), 7.08(m, 5H), 2.93(s, 6H), 2.59(s, 6H), 2.36(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.62, 141.98, 140.81, 135.33, 134.58, 131.11, 130.62, 129.81, 25.03, 24.13, 20.99. ^{125}TeNMR (126.3 MHz, $CDCl_3$, ppm): δ 794. IR (KBr, cm^{-1}): 2958.9(w), 1589.0(w), 1561.6(w), 1430.1(w), 1369.9(m), 1287.7(m), 1254.8(s), 1095. 9(w), 1024.6(w), 849.3(m), 794.5(s), 739.7(s),695.89(m).

5.2.3b Synthetic procedure for compound 5.**4**-5.**5**:

Triphenylantimony dichloride (Ph_3SbCl_2, 0.100 g, 0.23 mmol), diphenyltellurium oxide (Ph_2TeO, 0.070 g, 0.23 mmol) were refluxed in toluene for 12 hours resulting in the formation of a clear solution. Filtration followed by evaporation of the solvent under reduced pressure resulted in a solid white precipitate which readily dissolves in dichloromethane. Single crystals suitable for X-ray diffraction studies were grown in dichloromethane / hexane diffusion.

Compound 5.**4**:

Yield: 0.055 g (59.1%) (based on diphenyltellurium oxide), Dec. temp: 210°C. $C_{18}H_{15}ClTe$(394.36): calcd C 54.82, H 3.83; found, C 54.76, H 3.91. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.81(m, 5H), 7.57(m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 135.02, 133.82, 131.58, 130.45. ^{125}Te NMR (126.3 MHz, $CDCl_3$, ppm): δ 735. IR (KBr, cm^{-1}): 3046.6(w), 1572.6(m), 1473.97(s), 1430.1(s), 1260.3(m), 1178.1(w), 1057.5(w), 991.8(m), 728.7(s), 679.4(s).

Compound 5.**5** was also prepared by the same procedure as compound 5.**4**. The mole ratios of the corresponding reagents used are as follows.

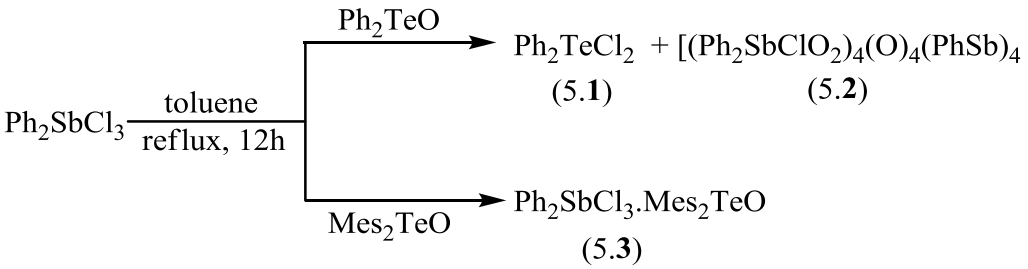
Yield: 0.050 g (57.3%) (based on dimesityltellurium oxide), Dec. temp: 235°C. $C_{36}H_{44}Cl_2OTe_2$(818.84): calcd C 52.80, H 5.42; found C 52.65, H 5.48. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.08 (m, 8H), 2.59 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 133.50, 130.54, 129.26, 128.33. ^{125}Te NMR (126.3 MHz, $CDCl_3$, ppm): δ 995. IR (KBr, cm^{-1}): 2960.5(w), 1594.3(m), 1450.4(m), 1293.2(s), 1261.7(s), 1098.8(w), 1018.6(w), 852.5(s), 801.7(m), 755.5(m), 637.8(m).

5.3 Results and Discussion

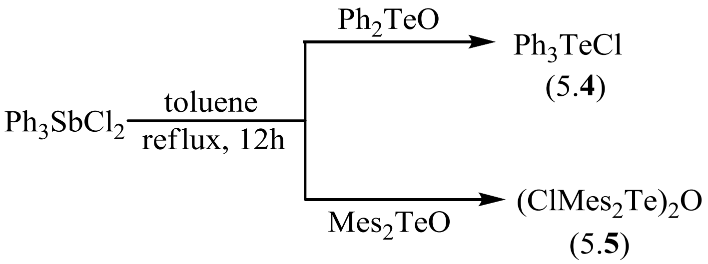
General synthetic procedures employed for the preparation of the compounds 5.**1**-5.**5** are dipicted in schemes 1 and 2. The reaction of diphenylantimony trichloride with diphenyltellurium oxide was performed by refluxing in toluene for 12 hours which resulted in the formation of a clear solution. Filtration followed by evaporation of the solvent under reduced pressure resulted in a colorless solid. Crystallization of this white solid material from dichloromethane-hexane diffusion have lead to the isolation of two types of crystals with varying morphologies. The major yield is identified as 5.**1** and minor yield is identified as 5.**2**. The same reaction with dimesityltellurium oxide resulted in the formation of a Lewis acid-base adduct 5.**3**. The reactions of triphenylantimony dichloride with diphenyltellurium oxide / dimesityltellurium oxide in refluxing toluene for 12 hours resulted in the fromation of clear solutions. Filtration followed by the evaporation of the solvent and subsequent crystallization in dichloromethane/hexane diffusion lead to the isolation of compounds 5.**4** and 5.**5**, respectively.

Compounds 5.**1**-5.**5** were characterised by standard spectroscopic and analytical techniques. Solution ^{125}Te NMR of 5.**1** in $CDCl_3$ showed a single resonance at δ = 914 ppm which cofirmed compound 5.**1** to be Ph_2TeCl_2[19] whereas compound 5.**2** did not show any signal which confirmed the absence of tellurium atom in 5.**2**. Solution ^{125}Te NMR of 5.**3**-5.**5** in $CDCl_3$ showed single resonances at δ = 794, 735 and 995 ppm, respectively.

Scheme 1



Scheme 2



Finally, all the compounds (5.**2**-5.**5**) were characterized by single crystal X-ray diffraction studies. Crystallographic data and selected bond distance and bond angle parametres for 5.**2**-5.**5** are given in Tables 1-3. Compound 5.**2** crystallizes in monoclinic space group $P2_1/c$. The molecular structure of 5.**2** represents an octanuclear organoantimony oxo cluster $[(Ph_2SbClO_2)_4(O)_4(PhSb)_4]$ which contains a central Sb_4O_4 cubane encapsulated by four diphenylchlorostibinates bridging antimony atoms present at alternate corners of the Sb_4O_4 cube (Figure 1).

The geometry around each antimony atom in Sb_4O_4 cubane is octahedral with CO5 coordination among which, three are from μ_3-oxo groups of the cubane core, two are from μ_2-oxo groups of adjacent diphenylchlorostibinate and one carbon from the phenyl ring attached to antimony. The Sb-O distances and Sb-O-Sb angles of the Sb_4O_4 cubane core fall in the range 2.062(4)-2.145(4) Å with an average of 2.103(4) Å and 100.15(17)-103.64(17)°, respectively. These values are similar to those of earlier reported Sb_4O_4 cubane clusters[20]. Of the six faces of the Sb_4O_4 cubane core, two opposite faces [Sb1-O1-Sb3-03 and Sb2-O2-Sb4-O4] are sterically hindered by phenyl groups present on antimony atoms and remaining four faces are approached by four diphenylchlorostibinate moieties, each of them bridging alternate antimony atoms of the Sb_2O_2 square face.

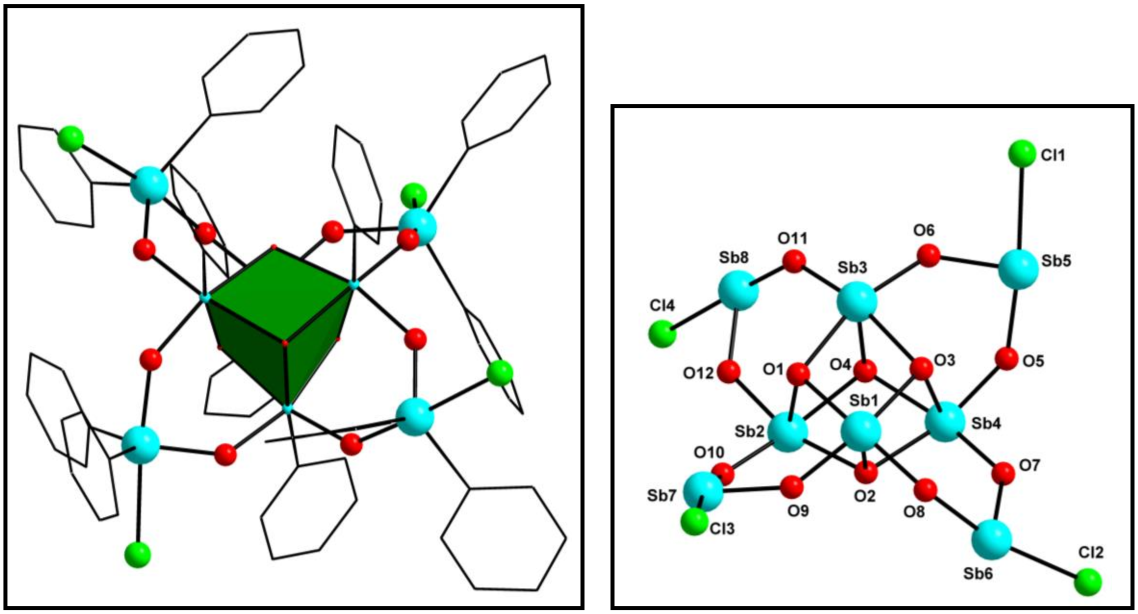


Figure 1: (left) Solid state molecular structure of 5.**2**. Hydrogen atoms are omitted for clarity. (right) cubane core of 5.**2** encapsulated by four diphenylchlorostibinates.

Although cubane cores containing transition or lanthanide metal atoms are very well-known [21], main group elements containing cubane core structures are very rare.[22]Till now there are only two Sb_4O_4 cubane cores structures reported where naphthalene dianions / diphenyldisiloxides stabilize the core by chelation[20]. This is the first instance where novel and rare diphenylchlorostibinate moieties stabilizing a Sb_4O_4 cubane core has been observed. Hence the bridging nature of this diphenylchlorostibinate moiety can be compared to that of carboxylate groups. The geometry around antimony in diphenylchlorostibinate is trigonal-bipyramidal with one chlorine atom, one μ_2-oxo group occupying the axial positions and two carbons of the phenyl groups, one μ_2-oxo group occupying equatorial positions. The Sb-O and Sb-Cl distances of diphenylchlorostibinates fall in the ranges 1.910(4)-1.978(5) Å and 2.470(2)-2.4893(19) Å, respectively. The Sb-O bond distances involving diphenylchlorostibinate oxygen atoms and antimony atoms of Sb_4O_4 cubane fall in the range 1.913(4)-1.954(4) Å with an average of 1.932(4) Å which is slightly less when compared to that of Sb-O distances of cubane core.

The plausible mechanism for the formation of diphenylchlorostibinate and Sb_4O_4 cubane core from Ph_2SbCl_3 in the presence of diphenyltellurium oxide can be explained in the following manner. Initially, diphenylantimony trichloride transfers two chloride ions to diphenyltellurium oxide resulting in the formation of diphenyltellurium dichloride and *insitu* generated diphenylchlorostibine oxide (Ph_2ClSbO). It is already known in literature that strong Lewis acids like Sb(V)/Sn(V)/Ti(IV) halides can transfer two halogen atoms to diorganotellurium oxide to form diorganotellurium dihalides[23]. Some amount of the diphenylchlorostibine oxide undergoes partial hydrolysis by adventitious water and forms diphenylchlorostibinate ($Ph_2SbClO_2^-$) and remaining part of diphenylchlorostibine oxide undergoes complete hydrolysis to form diphenylstibinic acid which further undergoes di-dearylation followed by the elimination of water leading to the formation of $(PhSb)_4O_4$ cubane core. Mono and di-dearylation is very common in triorganoantimony(V) compounds[24] and very recently we have reported the formation of a dianionic triorganoantimony oxo cluster which contains *insitu* generated diphenylstibinic and phenylstibonic acid residues that resulted from mono and di-dearylation followed by the elimination of water from triphenylantimony diphosphonate.[10] The yield of the cubane cluster $[(Ph_2SbClO_2)_4(O)_4(PhSb)_4]$ is very low and we could only isolate very less amount of cubane cluster by hand picking method from the crystallization vial since it tends to crystallize along with diphenyltellurium dichloride. Efforts are in progress to improve the yield of the cluster 5.**2**.

Compound 5.**3** crystallizes in monoclinic space group $P2_1/c$. The molecular structure of 5.**3** represents a Lewis acid-base adduct $Ph_2SbCl_3.Mes_2TeO$ (Figure 2). The geometry around antimony is octahedral with two phenyl groups occupying axial positions. The Sb-O bond length is 2.091(6) Å which falls in the range of literature reported Sb(V)-O bond length values.[12] The Te-O bond length is 1.899(6) Å which is slightly higher when compared to that of dimesityltellurium oxide[25] [1.855(4) Å]. The Sb-O-Te bond angle is 124.1(3)° which is considerably higher than previous reports. Here we would like to propose that a similar kind of Lewis acid-base adduct [$Ph_2SbCl_3.Ph_2TeO$] might be forming as an intermediate species during the formation of 5.**2** in which two chloride ions from antimony have been transfered to tellurium to form diphenyltellurium dichloride and *insitu* generated diphenylchlorostibine oxide. But, in the present case, since mesityl groups are bulky, they hinder the transformation of chloride ions from antimony to tellurium atom.

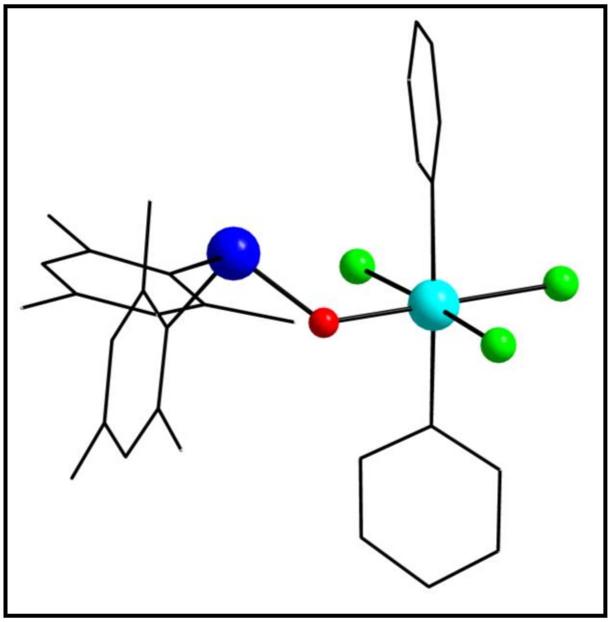


Figure 2: Solid state molecular structure of 5.**3**. Hydrogen atoms are omitted for clarity

Compounds 5.**4** ($Ph_3Te^+Cl^-$) and 5.**5** [$(ClMes_2Te)_2O$] are the products isolated in the reactions between triphenylantimony dichloride and diphenyltellurium oxide / dimesityltellurium oxide, respectively. In both the reactions despite repeated efforts the products corresponding to antimony precursor could not be isolated. But the solution ^{125}Te NMR of the clear solution obtained from the reaction between Ph_3SbCl_2 and Mes_2TeO showed an additional peak at $\delta = 793$ ppm apart from a peak at 995 ppm(which correspond to 5.**5**). Interestingly this additional peak (δ 793 ppm) exactly matches with the ^{125}Te NMR of 5.**3** ($Ph_2SbCl_3.Mes_2TeO$). It should be mentioned here that triphenylantimony dichloride is less Lewis acidic when compared to that of diphenylantimony trichloride. In both the cases they act as halogen transfer reagents to diorganotellurium oxides.

Compound 5.**4** crystallizes in triclinic space group P-1 with two $Ph_3Te^+Cl^-$ molecules in asymmetric unit. Secondary Te...Cl interactions forms a dimeric structure in solid state (Figure 3). Te...Cl interacting distances fall in the range 3.198(10)-3.342(3) Å with an average of 3.275 Å which is slightly less when compared to earlier reported Te…Cl secondary interactions[26].

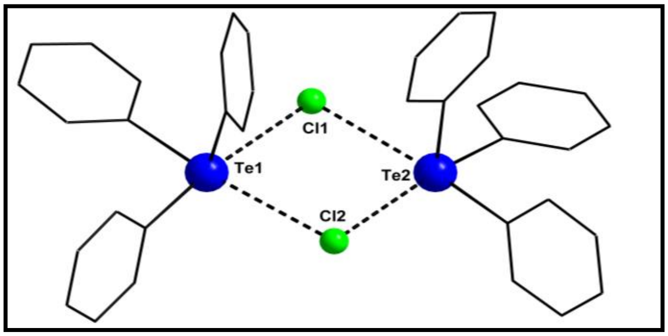


Figure 3: Solid state dimeric molecular structure of 5.**4**. Hydrogen atoms and dichloromethane solvate are omitted for clarity.

Compound 5.**5** crystallizes in orthorhombic Pbcn space group. The molecular structure corresponds to a tetramesitylditelluroxane dichloride $ClMes_2Te\text{-}O\text{-}TeMes_2Cl$ (Figure 4) which presumably formed by the partial hydrolysis followed by the elimination of water molecule from Mes_2TeCl_2, a product originated by halogen transfer from Ph_3SbCl_2 to Mes_2TeO. This kind of tetraoragnoditelluroxane moieties are well known in literature.[27] Very recently we have reported the ability of tetraphenylditelluroxane ($Ph_2TeOTePh_2$) in stabilizing tetradecanuclear polyoxostibonate framework.[12]

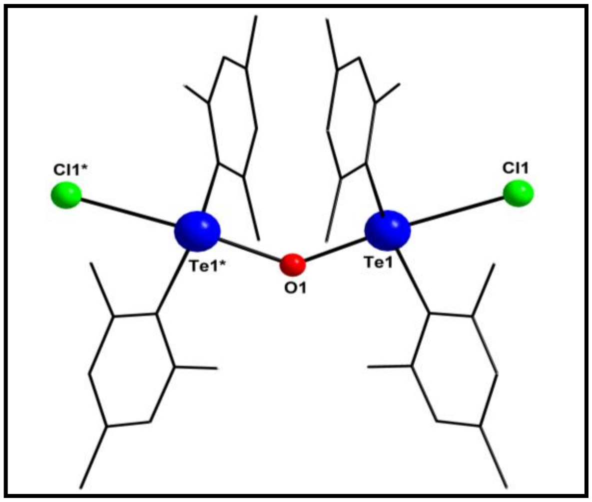


Figure 4: Solid state molecular structure of 5.**5**. Hydrogen atoms are omitted for clarity.

The Te-O bond length and Te-O-Te bond angles are 1.981(3) Å and 135.8(5)° respectively, which are very close to that of recently reported tetramesitylditelluroxane dicyanide.[28] The Te-Cl bond length is 2.636(2) Å which is considerably higher than Te-Cl bond length [2.144(2) Å] of Mes_2TeCl_2.[29]

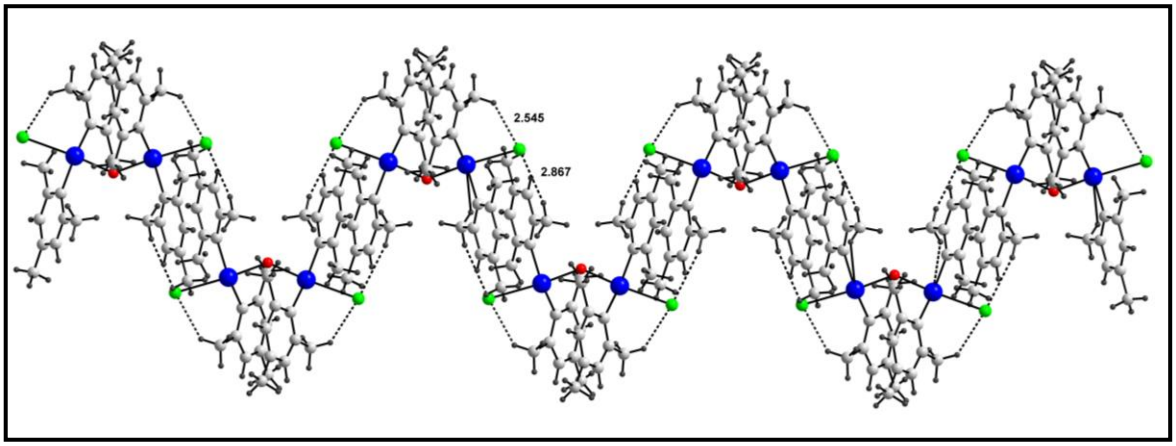


Figure 5: Wave-like supramolecular structure of 5.**5** showing inter and intra molecular C-H…Cl secondary interactions.

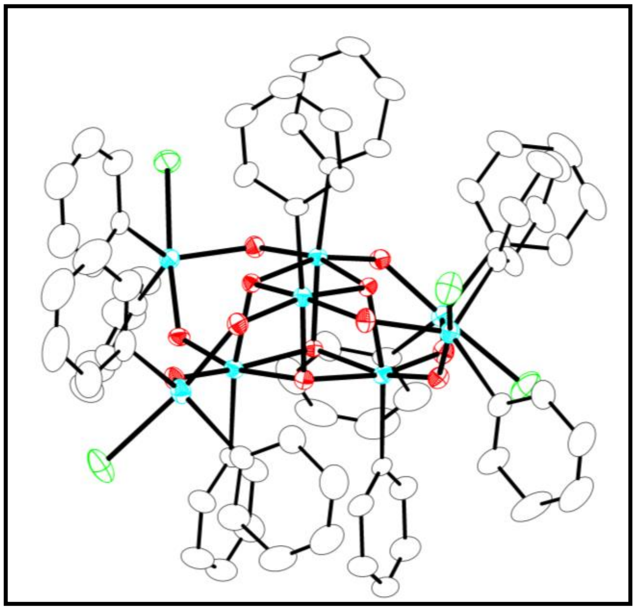
We have also observed inter and intra molecular C-H…Cl secondary interactions [inter molecular C-H…Cl, 2.867 Å and intra molecular C-H…Cl, 2.545 Å] in 5.**5** which led to the formation of interesting wave-like supramolecular structure in solid state (Figure 5). These secondary interactions arise between tellurium attached mesityl C-H and chlorine atom attached to the same tellurium / tellurium atom of another molecule. These interacting distances are very well in agreement with earlier reports.[30]

5.4 Conclusion

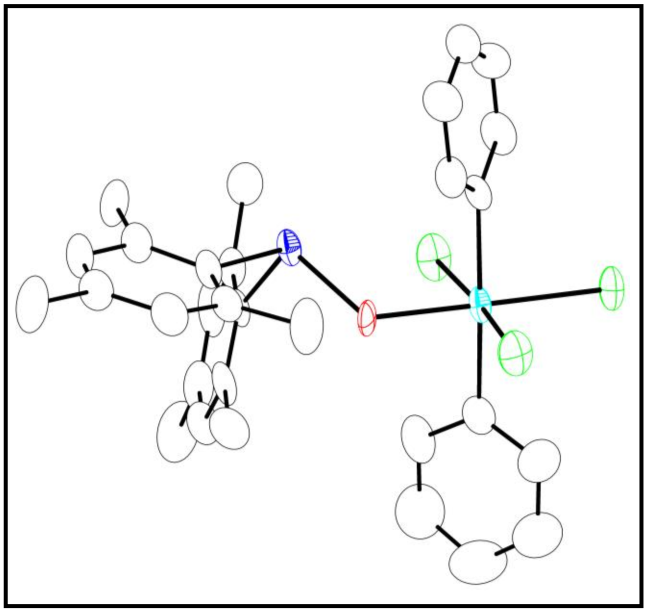
In conclusion, diphenylantimony trichloride / triphenylantimony dichloride acts as halogen transfer reagents to diorganotellurium oxides. Interestingly, in presence of diphenyltellurium oxide, diphenylantimony trichloride self assemled to form a novel octanuclear organoantimony oxo cluster $[(PhSb)_4(O)_4(Ph_2ClSbO_2)_4]$(5.**2**) in which central Sb_4O_4 cubane core is encapsulated by four diphenylchlorostibinates. Dimesityltellurium oxide forms a Lewis acid-base adduct 5.**3** $[Ph_2SbCl_3.Mes_2TeO]$ with diphenylantimony trichloride. Secondary C-H…Cl interactions in 5.**5** $[(ClMes_2Te)_2O]$ have led to formation of interesting wave-like supramolecular structure in solid state.

5.5 ORTEP diagrams of 5.**2**-5.**5**:

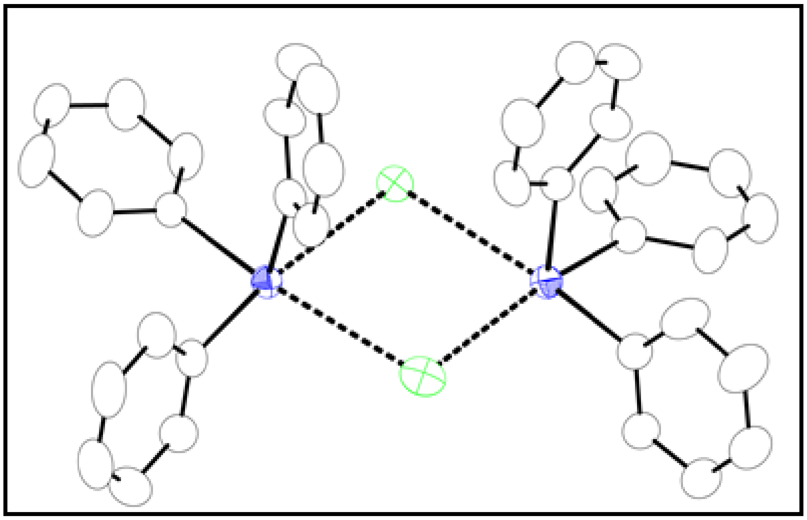
5.**2**



5.**3**



5.**4**



5.**5**

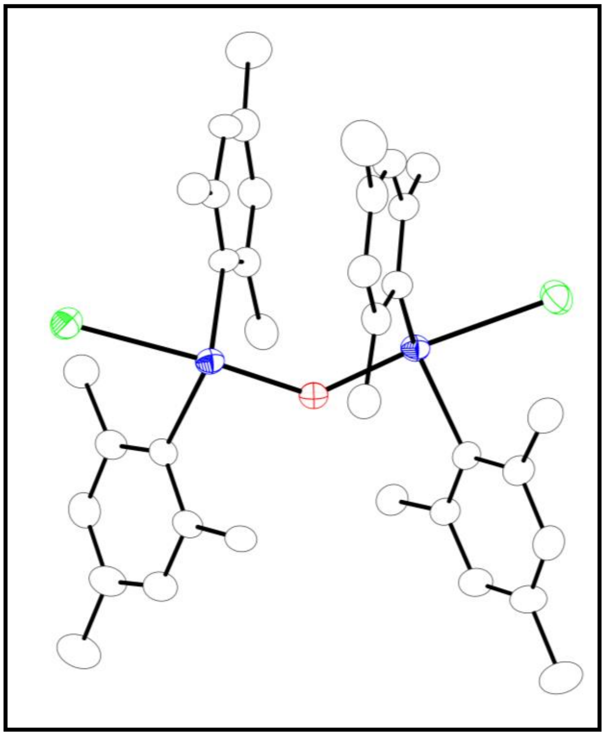


Table 1: Crystal and Refinement data for 5.**2**-5.**3**

	5.**2**	5.**3**
Formulae	$C_{72}H_{60}Cl_4O_{12}Sb_8$	$C_{30}H_{32}Cl_3OSbTe$
Fw.g mol^{-1}	2233.00	764.26
Cryst. Syst.	Monoclinic	Monoclinic
Cryst size.mm	0.16 x 0.12 x 0.10	0.30 x 0.26 x 0.26
Space group	$P2_1/c$	$P2_1/c$
a, Å	13.586(3)	9.8931(2)
b, Å	13.559(3)	18.0830(4)
c, Å	43.799(8)	16.5707(4)
α, deg	90	90
β, deg	90.245(3)	91.482(2)
γ, deg	90	90
v, Å^3	8068(3)	2963.46(11)
Z	4	4
Dcacld.Mgm^{-3}	1.838	1.713
T.K	298(2)	298(2)
μ, mm^{-1}	2.822	17.647
F(000)	4256	1496
θ range, deg	1.50 to 26.43	3.62 to 69.99
Index ranges	-16<=h<=16 -16<=k<=16 -54<=l<=54	-11<=h<=7 -21<=k<=18 -20<=l<=17
No. of.refln colled	85090	7760
Completeness to θ max	99.7 %	84.4 %
No. of. indep refln/R_{int}	16502	4735
GooF(F^2)	1.237	1.095
R_1 (F) (I>2σ(I))	0.0553	0.0902
wR_2 (F^2) (All data)	0.1132	0.2632
Largest diff peak/hole,e Å^{-3}	1.011 / -0.779	2.584 / -2.581

Table 2: Crystal and Refinement data for 5.**4**-5.**5**

	5.**4**	5.**5**
Formulae	$C_{37}H_{32}Cl_4Te_2$	$C_{36}H_{44}Cl_2OTe_2$
Fw.g mol^{-1}	873.63	818.81
Cryst. Syst.	Triclinic	Orthorhombic
Cryst size.mm	0.26 x 0.24 x 0.20	0.22 x 0.20 x 0.18
Space group	P -1	Pbcn
a, Å	11.7038(7)	15.921(2)
b, Å	12.8658(7)	17.004(3)
c, Å	12.9020(6)	15.004(2)
α, deg	77.700(4)	90
β, deg	82.104(5)	90
γ, deg	66.022(5)	90
v, Å^3	1731.55(16)	4061.9(11)
Z	2	4
Dcacld.Mgm^{-3}	1.676	1.339
T.K	298(2)	298(2)
μ, mm^{-1}	2.019	1.590
F(000)	852	1624
θ range, deg	2.84 to 26.37	2.72 to 26.37
Index ranges	-14<=h<=14 -16<=k<=09 -16<=l<=15	-19<=h<=19 -21<=k<=17 -18<=l<=17
No. of.refln colled	12770	12385
Completeness to θ max	99.8 %	99.9 %
No. of. indep refln/R_{int}	7071	4153
GooF(F^2)	1.030	1.099
R_1 (F) (I>2σ(I))	0.0316	0.0678
wR_2 (F^2) (All data)	0.0840	0.2510
Largest diff peak/hole,e Å^{-3}	0.979 / -0.930	1.831 / -0.885

Table 3: Selected bond lengths(Å) and bond angles(°) in 5.**2**-5.**5**

5.**2**		**5.3**	**5.4**
Sb1-O1=2.141(4)	Sb1-O1-Sb3=103.64(17)	Sb1-O1=2.091(6)	Te1-C1=2.129(3)
Sb2-O2=2.091(4)	Sb1-O2-Sb4=100.58(17)	Te1-O1=1.899(6)	Te1-C7=2.127(3)
Sb3-O3=2.145(4)	Sb3-O3-Sb4=100.53(17)	Sb1-Cl1=2.427(2)	Te1-C13=2.123(3)
Sb4-O4=2.107(4)	Sb2-O4-Sb4=103.03(17)	Sb1-Cl2=2.445(2)	C7-Te1-C1=91.25(13)
Sb1-O8=1.920(4)	O2-Sb1-C1=169.8(2)	Sb1-Cl3=2.485(2)	C13-Te1-C7=94.61(13)
Sb2-O10=1.913(4)	O7-Sb6-C43=114.6(2)	Sb1-C1=2.114(11)	
Sb3-O11=1.924(4)	Cl1-Sb5-O6=83.66(15)	Sb1-C7=2.108(13)	5.**5**
Sb4-O5=1.913(4)	O1-Sb1-O3=75.59(16)	Te1-C13=2.174(10)	Te1-O1=1.981(3)
Sb5-O5=1.978(5)	O7-Sb6-O8=90.88(18)	Te1-C22=2.129(11)	Te1-Cl1=2.636(2)
Sb6-O7=1.910(4)		C1-Sb1-C7=178.4(4)	Te1-C1=2.132(9)
Sb7-O9=1.918(4)		C1-Sb1-Cl1=91.7(3)	Te1-C10=2.140(8)
Sb8-O11=1.965(4)		Cl1-Sb1-O1=87.68(19)	O1-Te1-Cl1=173.44(17)
Sb5-Cl1=2.477(2)		Te1-O1-Sb1=124.1(3)	Te1-O1-Te1*=135.8(5)
Sb6-Cl2=2.482(2)		C13-Te1-C22=101.3(4)	O1-Te1-C1=89.2(3)

Symmetry transformations used to generate equivalent atoms:*= -x+1, y, -z+3/2 (5.**5**)

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List of Publications

[1] 12-Membered Macrocycles Containing Ditelluroxane and Selenotelluroxane Units. Nagarjuna Kumar Srungavruksham and Viswanathan Baskar, *Eur. J. Inorg. Chem.*, **2012**, 136-142.

[2] Organoantimony(V) Phosphinates, Phosphonates and Seleninates. Nagarjuna Kumar Srungavruksham and Viswanathan Baskar, *Eur. J. Inorg. Chem.*, **2013**, 4345-4352.

[3] Assembling Anionic Sb(V)/(III) containing polyoxostibonates stabilized by triphenyltellurium cations. Nagarjuna Kumar Srungavruksham and Viswanathan Baskar, *Dalton Trans.*, **2015**, *44*, 6358. (***Cover picture contribution***)

[4] $Te_4Se_2O_6$ Macrocycle Stabilizing Triangular Planar and Tetrahedral Anions. Nagarjuna Kumar Srungavruksham and Viswanathan Baskar, *Dalton Trans.*, **2015**, *44*, 4554.

[5] Reactions of Diorganotellurium Oxides with Organoantimony (V) Halides. Nagarjuna Kumar Srungavruksham and Viswanathan Baskar, (*Manuscript to be submitted*).

Poster and Oral Presentations / Workshops

[1] Presented **poster** entitled “12-Membered Macrocycles Containing Ditelluroxane and Selenotelluroxane Unit” at **3rd Asian Conference on Coordination Chemistry** (**ACCC-3**), October-2011, New Delhi, India.

[2] Presented **poster** entitled “Diorganotelluroxane rings and Star shaped molecules” at **Modern Trends in Inorganic Chemistry** (**MTIC- XIV**), University of Hyderabad, Hyderabad, India, December-2011

[3] Attended “**Oxford Diffraction Users Meet**” a workshop on crystallography, April-2012, IIT Indore, Indore, India

[4] **Oral and Poster presentation** on “Organoantimony(V) Phosphinates, Phosphonates and Seleninates” at **Chemfest-2014**, 11th Annual In-House Symposium, February-2014, University of Hyderabad, India

Volume 44 | Number 14 | 14 April 2015 | Pages 6299–6656

Dalton Transactions

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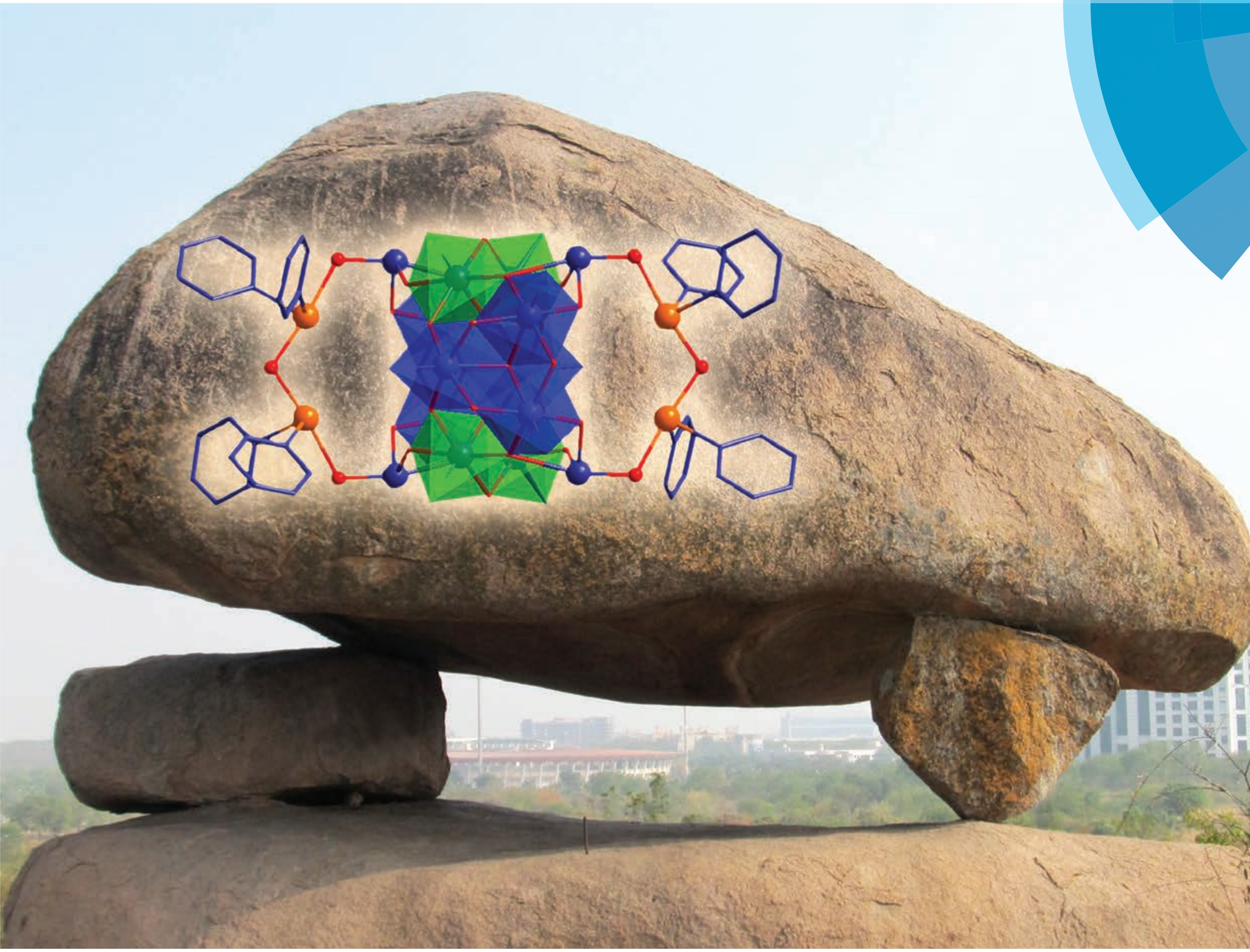


ISSN 1477-9226

ROYAL SOCIETY OF CHEMISTRY

PAPER

Nagarjuna Kumar Srungavruksham and Viswanathan Baskar

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

SYNOPSIS

This thesis is entitled as “**Organoantimony and Organotellurium based Rings, Macrocycles and Clusters**”. It is divided into 5 chapters. Detailed description of each of the chapters is given below.

Chapter 1

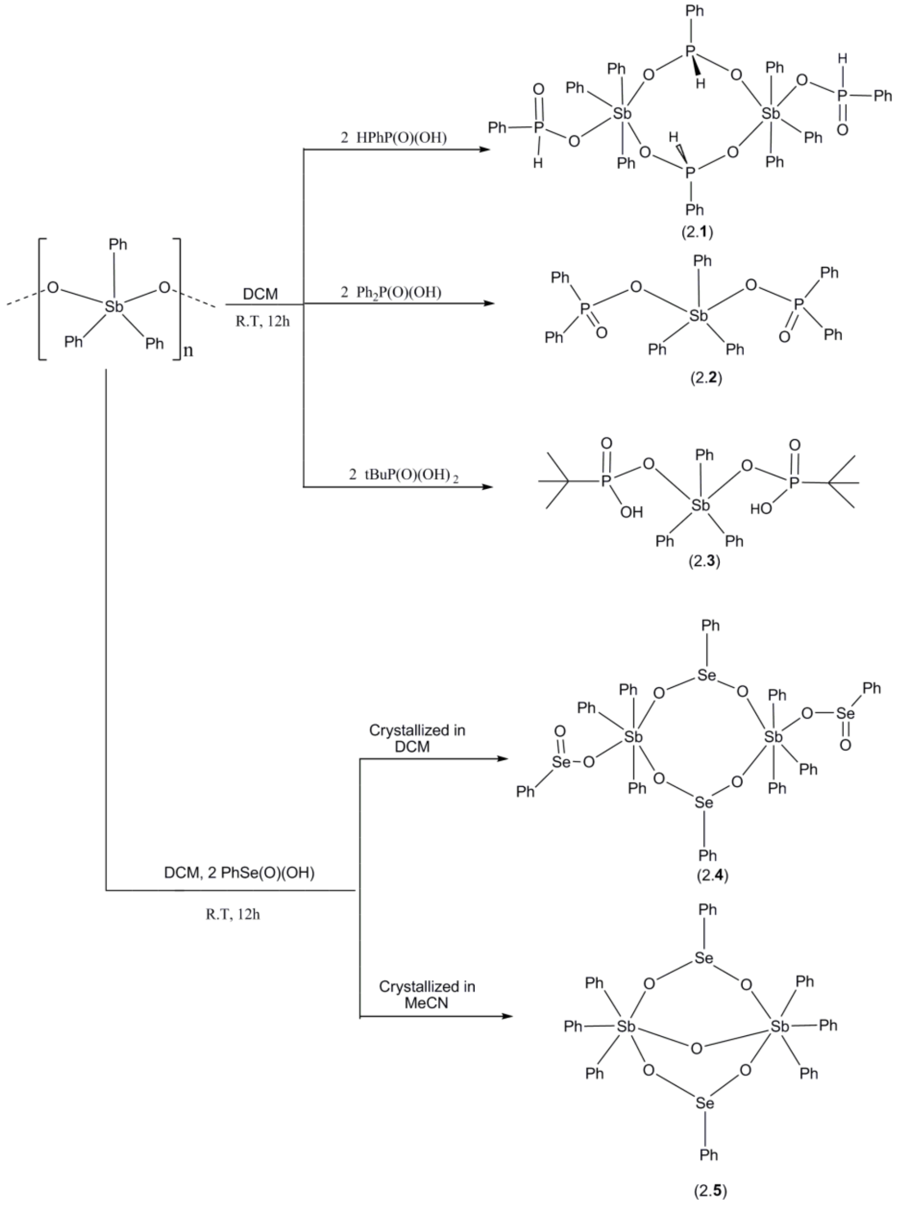
Introduction: Literature surveys of organotellurium and organoantimony compounds are dealt with in detail. Synthetic methodologies adopted for the preparation of various important organoellurium and organoantimony compounds with a reference to applications of these compounds are given in detail. The introduction part concludes with the motivation for the present work that has been carried out which will be reported in the thesis.

Chapter 2

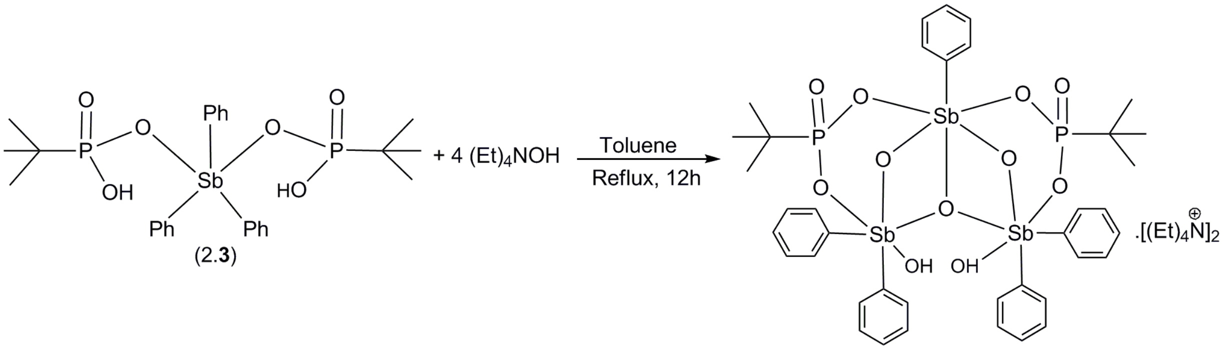
Organoantimony(V) Phosphinates, Phosphonates and Seleninates

This chapter deals with the depolymerisation reactions of triphenylantimony oxide with various protic ligands. Reaction of polymeric triphenylantimony oxide with various protic ligands like phenylphosphinic acid, diphenylphosphinic acid, tert-butyl phosphonic acid and phenylseleninic acid leads to the formation of $[Ph_3Sb(HPhPO_2)_2]_2$ 2.**1**, $[Ph_3Sb(Ph_2PO_2)_2]$ 2.**2**, $[Ph_3Sb(\text{tert-}BuPO_3H)_2]$ 2.**3**, $[Ph_3Sb(PhSeO_2)_2]_2$ 2.**4**, and $[(Ph_3Sb)_2(\mu\text{-}O)(\mu\text{-}PhSeO_2)_2]$ 2.**5** respectively (scheme 1). Hydrolysis and dearylation of 2.**3** yielded $[(Ph_2Sb)_2(PhSb)(\mu_3\text{-}O)(\mu_2\text{-}O)_2(OH)_2(\mu\text{-t-}BuPO_3)_2[(C_2H_5)_4N]_2]$ 2.**6** possessing *insitu* generated $Ph_2Sb(O)(OH)$ and $PhSbO_3H_2$ moieties (scheme 2). Single crystal X-ray diffraction studies revealed the solid state molecular structures for 2.**1**-2.**6**. ^{31}P solution NMR spectrum of 2.**1** shows the observation of P-H three-bond coupling for the first time in organophosphorus based compounds. Further ^{31}P NMR at lower temperatures revealed 2.**1** to be fluxional molecule. ^{77}Se NMR indicates the formation of different molecular clusters from crystallization process carried out under varying solvent conditions.

Scheme 1



Scheme 2



Chapter 3

$Te_4Se_2O_6$ Macrocycle Stabilizing Anions of Varying Size and Geometry

This chapter describes the synthesis and structural characterization of 12-membered inorganic macrocycle $Te_4Se_2O_6$ stabilizing anions of varying size and geometry. Reaction of benzeneseleninic acid with bis(p-methoxyphenyl)tellurium dihalide (chloride/bromide) in benzene for 12 h at room temperature in presence of triethylamine leads to the formation of 12-membered macrocycle $[(p\text{-}MeO\text{-}C_6H_4)_2Te(\mu\text{-}O)(\mu\text{-}PhSeO_2)(\mu_4\text{-}X)]_2$ (X = Cl (3.**1**), Br (3.**2**)) where the halogens are found capping the macrocycle on both sides, stabilized by Te-X interactions (Scheme 3). Reaction of NaI with 3.**1** afforded the iodo capped macrocycle $[(p\text{-}MeO\text{-}C_6H_4)_2Te(\mu\text{-}O)(\mu\text{-}PhSeO_2)(\mu_4\text{-}I)]_2$ (3.**3**) (Scheme 4). Notable conformational changes have been observed in the solid state structure starting from macrocycle 3.**1** to 3.**3** which are quantified in terms of torsion angles and alignment of phenyl ring attached to selenium. Further reaction of methaneseleninic acid with bis(p-methoxyphenyl)tellurium dichloride in methanol in presence of triethyl amine as a base also afforded a 12-membered macrocycle $[(p\text{-}MeO\text{-}C_6H_4)_2Te(\mu\text{-}O)(\mu\text{-}MeSeO_2)(\mu_4\text{-}Cl)]_2$ 3.**4** structurally similar to 3.**1**-3.**3**.

$$R_2TeX_2 \;+\; R'SeO_2H \xrightarrow[Et_3N]{\text{Benzene}(3.\mathbf{1},3.\mathbf{2})/\text{MeOH}(3.\mathbf{4})} [(R_2Te)_2\,(\mu\text{-}O)(\mu\text{-}R'SeO_2)(\mu_4\text{-}X\,]_2$$

$R = MeOC_6H_4$
$R' = Ph(3.\mathbf{1},3.\mathbf{2}), Me(3.\mathbf{4})$
$X = Cl(3.\mathbf{1},3.\mathbf{4}),\ Br(3.\mathbf{2})$

Scheme 3

$$[(R_2Te)_2\,(\mu\text{-}O)\,(\mu\text{-}PhSeO_2)\,(\mu_4\text{-}Cl)\,]_2 \xrightarrow[\text{NaI}]{\text{Benzene}} [(R_2Te)_2\,(\mu\text{-}O)(\mu\text{-}PhSeO_2)(\mu_4\text{-}I)]_2$$

(3.**1**) (3.**3**)

Scheme 4

$R = MeOC_6H_4$

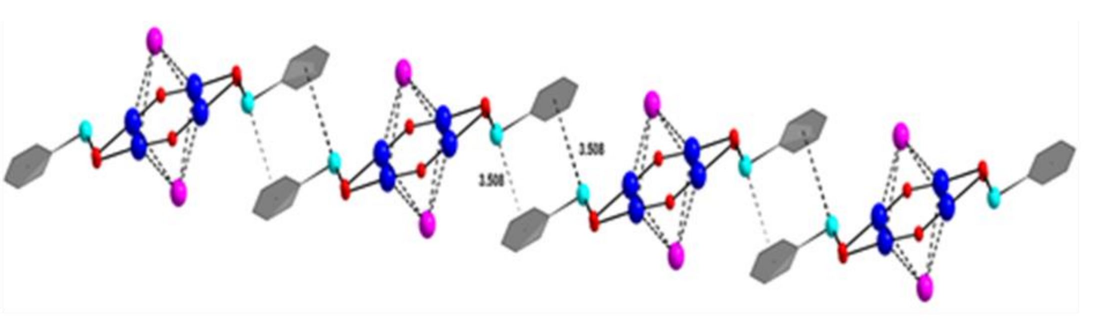


Figure 1: Supramolecular structure of 3.**3** showing Se- π interactions. Anisyl rings attached to Te and hydrogens are omitted for clarity.

After observing interesting flexible behaviour of 12-membered macrocyclic core when varied the size of the anion (from Cl, Br to I), we were curious to study the effect of varying geometry of the anion around a central element on the stability and flexibility of this 12-membered macrocyclic host. Hence we performed the anion exchange reactions of Cl-macrocycle 3.**1** $[(p\text{-MeO-C}_6\text{H}_4)_2\text{Te})_2(\mu\text{-O})(\mu\text{-PhSeO}_2)(\mu_4\text{-Cl})]_2$ with $AgNO_3$, $AgClO_4$ and $AgBF_4$ (scheme 5) which lead to the formation of 12-membered macrocycles $[(p\text{-MeO-C}_6\text{H}_4)_2\text{Te})_2(\mu\text{-O})(\mu\text{-PhSeO}_2)(\mu\text{-X})]_2$ [X=NO_3 (3.**5**), ClO_4(3.**6**), BF_4(3.**7**)]. Single crystal X-ray diffraction studies revealed the solid state molecular structures for 3.**1**-3.**7**. Macrocycle 3.**3** shows rare Se-π interactions leading to the formation of supramolecular polymeric networks. Weak intermolecular C-H…O interactions in 3.**5**, 3.**6** and C-H…F interactions in 3.**7** has led to the formation of interesting polymeric supramolecular assemblies in solid state. ESI-MS studies revealed that macrocycles retain their structures in solution. Solution ^{125}Te NMR spectrum of 3.**7** shows the appearance of a triplet ($^1J_{\text{Te...F}}$ = 568 Hz) that can be assigned to coupling between ^{125}Te nuclei and two fluorine atoms in BF_4^- ions.

$$[(\text{R}_2\text{Te})_2\,(\mu\text{-O})\,(\mu\text{-PhSeO}_2)\,(\mu_4\text{-Cl})\,]_2 \xrightarrow[\text{2AgX}]{\text{Benzene}} [(\text{R}_2\text{Te})_2\,(\mu\text{-O})(\mu\text{-PhSeO}_2)(\mu\text{-X})]_2$$

(3.**1**)

R = $MeOC_6H_4$

Scheme 5

X = NO_3(3.**5**), ClO_4(3.**6**), BF_4(3.**7**)

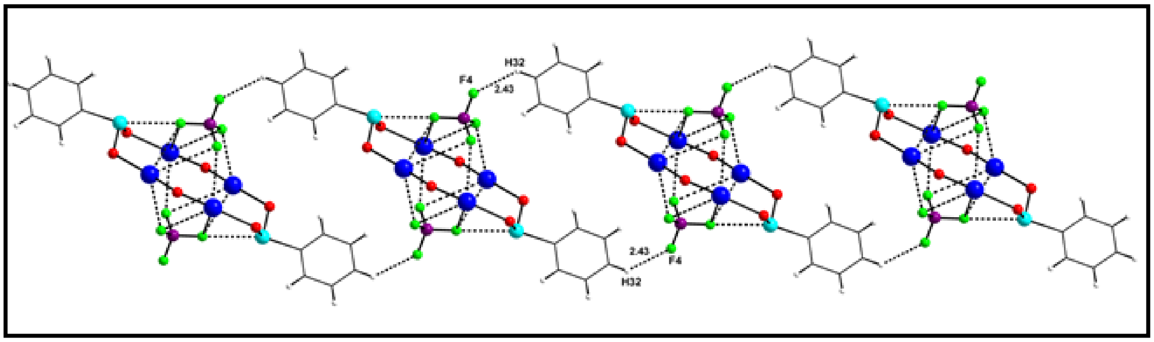


Figure 2: Supramolecular structure of 3.**7** showing C-H…F interactions. Anisyl rings attached to Te and hydrogens are omitted for clarity.

Chapter 4

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

In this chapter, the reactions of diphenyltellurium oxide with organostibonic acid and polymeric triphenylantimony oxide have been investigated independently. Single crystal X-ray diffraction studies have revealed the formation of novel and rare mixed valent Sb(V)/(III) containing polyoxostibonates $\{(C_6H_5)_3Te\}_2\{Na_2(H_2O)_2(p\text{-}Br\text{-}C_6H_4Sb^{V})_{10}(Sb^{III})_4[(C_6H_5)_2Te]_4(O)_{30}(OH)_4]$ 4.**1** and $\{(C_6H_5)_3Te\}_4\{[(C_6H_5)_2Sb^{V}]_4(Sb^{III})_4(O)_{12}(OH)_4\}$ 4.**2**. Solution ^{125}Te NMR supports the solid state structures presented. Interestingly, during the assembly of these POMs several processes happen simultaneously. Rarely observed reduction from Sb(V) to Sb(III), complete dearylation of organoantimony precursors and complexation ability of tetraorganoditelluroxane moiety stabilizing large and novel POM structure(as in 4.**1**) along with formation of triphenyltellurium cations which not only provide charge balance but also stabilize the POM framework (as in 4.**2**) by weak interactions are observed.

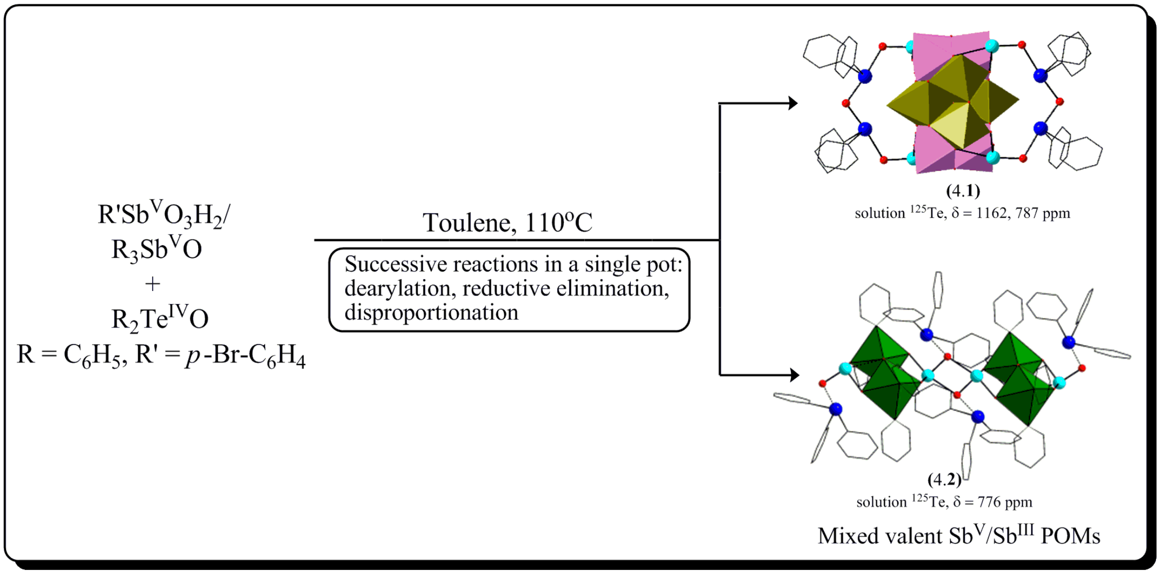
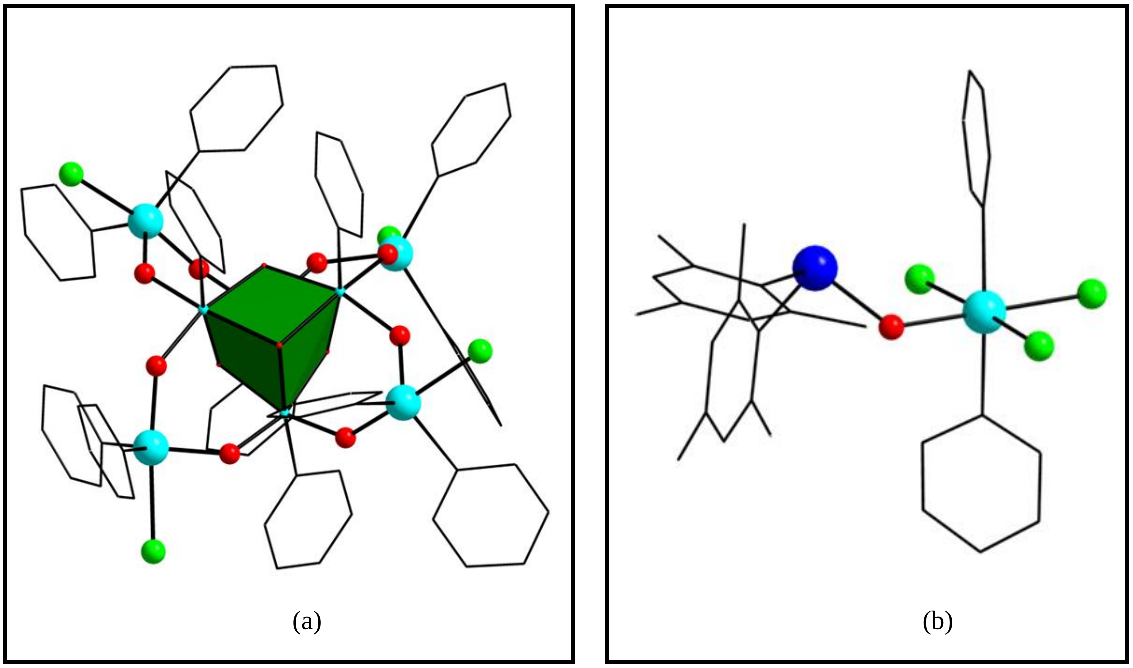


Figure 3: Schematic representation for the preparation of 4.**1** and 4.**2**.

Chapter 5

Reactions of Diorganotellurium Oxides with Organoantimony(V) Halides

This chapter deals with the reactions of diorganotellurium oxides with organoantiony(V) halides. 1:1 mole ratio reaction of diphenyltellurium oxide with diphenylantimony trichloride in refluxing toluene conditions for 12 h resulted in the formation of Ph_2TeCl_2(5.**1**) as a major product and $[(PhSb)_4(O)_4(Ph_2ClSbO_2)_4]$(5.**2**) as a minor product. Similar reaction between dimesityltellurium oxide and diphenylantimony trichloride yielded an adduct $Ph_2SbCl_3.Mes_2TeO$ (5.**3**). Single crystal X-ray diffraction studies revealed the formation of novel octanuclear organoantimony-oxo cluster (5.**2)** which contains a central Sb_4O_4 cubane encapsulated by four diphenylchlorostibinates bridging antimony atoms present at alternate corners of the Sb_4O_4 cube. The work carried out regarding the isolation of these systems will be described in detail.



(a)

(b)

Figure 4: The solid state molecular structures of 5.**2** (a) and 5.**3**(b).

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