Ferrocene Anchored Ln-O Clusters and Main Group Based Rings and Macrocycles

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A Thesis

Submitted for the degree of

DOCTOR OF PHILOSOPHY

by

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Dedicated

to

My Family

STATEMENT

I hereby declare that the matter embodied in the thesis entitled **“*Ferrocene Anchored Ln-O Clusters and Main Group Based Rings and Macrocycles*”** is the result of investigations carried out by me in the School of Chemistry, University of Hyderabad, India under the supervision of **Dr. Viswanathan Baskar**.

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

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CERTIFICATE

Certified that the work embodied in the thesis entitled **“*Ferrocene Anchored Ln-O Clusters and Main Group Based Rings and Macrocycles*”** has been carried out by **Mr. Pilli. V. V. N. Kishore** under my supervision and the same has not been submitted elsewhere for any degree.

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Kishore

CONTENTS

Abbreviations

SMM	single molecule magnet
Sao	dianion of the salicylaldoxime
ROP	ring opening polymerization
bafca	α-benzamido-β-ferrocenylacrylic acid
Hfca	ferrocene carboxylic acid
Hfcacacph	benzoyl ferrocenylmethane
HFca	1-ferrocenyl-1,3-butanedione
Hfctp	(z)-3-hydroxy3-ferrocenyl-1-(thioph-2-yl) prop-2-en-1-one
Hfctfa	1-ferrocenyl-4,4,4-trifluorobutane-1,3-dione
Hfcpfa	1-ferrocenyl-4,4,5,5,5-pentafluoroproane-1,3-dione
PNO	pyridine-n-oxide
DMSO	dimethylsulfoxide
HMPA	hexamethylphosphoramide
Acac	acetylacetone
Trid	tridentate schiff base ligands
H_2Sah	2, 2^1-(methylidynenitrilo) diphenol
H_2Sat	2-(o-hydroxyphenyl) benzothiazoline
H_2Bah	3-(o-hydroxyanilino) crotonophenone
H_2Aah	4-(o-hydroxyphenylimino) -2-pentanone
H_2Aat	2-acetonyl-2-methylbenzothioziline

Cyc	cyclo
Tert	tertiary
THC	tetrahedral character
H_2PhPzh	2-(1H-pyrazol-3-yl) phenol
H_2PhPztBu	2-(5-tert-butyl-1H-Pyrazole-3-yl) phenol
H_2PhPzme	2-(5-methyl-1H-pyrazole-3-yl) phenol
H_2PhPzNP	2-(1-H-pyrazol-3-yl) naphthalene-1-ol

SYNOPSIS

This thesis entitled "Ferrocene Anchored Ln-O Clusters and Main Group Based Rings and Macrocycles" will be presented in two parts. Part A deals with synthesis, structural characterization and magnetic properties of ferrocene anchored lanthanide based oxo-hydroxo clusters. Part B gives in detail the work carried out on the synthesis and structural characterization of organoantimony and boron based oxo-hydroxo clusters.

PART A

Chapter 1

Introduction: A General Overview on Lanthanide Oxo-Hydroxo Clusters and Single Molecule Magnets (SMMs):

This chapter will begin with an overall discussion on SMMs, its general definition, about the isolation of the first SMM Mn_{12}-AC and its characterization protocols. This will be followed by a brief introduction to ferrocene and a detailed literature survey on various multi ferrocene containing self assemblies.

Chapter 2

Redox Shield Enfolding a Magnetic Core

This chapter deals with assembling bi-functional molecular architectures containing redox active ferrocenes and lanthanide oxo-hydroxo core displaying single molecule magnet (SMM) behavior. Ferrocenyl beta diketones were reacted with hydrated lanthanide trihalides in presence of a base to yield solids whose single crystal characterization revealed the formation of nona- and tetranuclear lanthanide oxo-hydroxo clusters with sixteen (2.1), eight (2.2) and six ferrocene (2.3-2.6) units anchored on lanthanide oxide surface. Magnetism studies of dysprosium oxo-hydroxo cluster (2.1) containing sixteen ferrocenes shows slow relaxation of magnetization at lower temperatures. This is apparently the second largest ferrocene assembly reported till date and the first example wherein redox active ferrocenes are appended on a lanthanide cluster which displays SMM behavior. The dimensions of the isolated discrete molecular clusters falls in nano range.

Details of the synthesis, structural characterization and magnetism studies are given in detail.

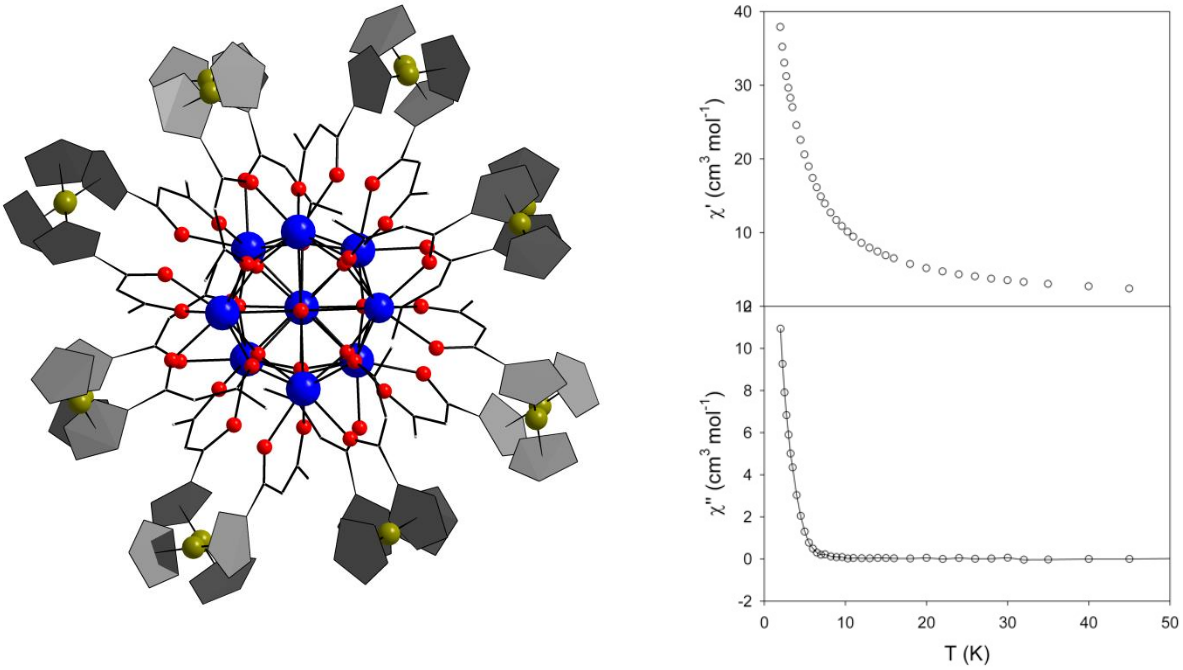


Figure 1: Solid state structure of 2.1 and AC magnetic susceptibility plot at 1000 Hz (ball and stick representation) viewed through the z axis. Colour code: blue (Dy), red (O), green (Fe).

PART B

Chapter 3

Diorganoantimonyl Phenolic Pyrazolates

A brief survey of organoantimony compounds is included to facilitate the reader to appreciate the work reported in the chapter. Reaction of tri- and diorganoantimony halides with phenolic pyrazoles HRPzR^1 (R = phenolic, and naptholic: R^1 = phenyl and hydrogen) afforded colorless products whose structures were characterized by single crystal X-ray diffraction technique. Structural analysis revealed the formation of mono-, di- and tetranuclear antimony oxo-hydroxo compounds / clusters $[(Ph_2SbCl_2)(HPhPzPh)]$ (3.1), $[(Ph_2Sb)_2(O)(PhPz)_2]$ (3.2), $[(Ph_2Sb)_2(O)(PhPzPh)_2]$ (3.3), $[(Ph_2Sb)_2(O)(NpPz)_2]$ (3.4) and $[(Ph_2Sb)_4(HPhPzPh)_2(O)_4(OH)_2]$ (3.5). The details are reported in the chapter.

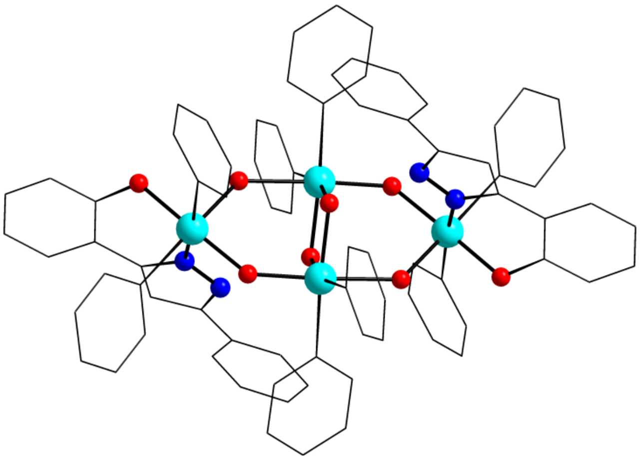


Figure 2: The solid state structure of $[(Ph_2Sb)_4(HPhPzPh)_2(O)_4(OH)_2]$

Chapter 4

Hexa- and Trinuclear Organoantimony Oxo Clusters Stabilized by Organosilanols

Chapter 4 contains a literature survey on organoantimony (v) compounds, in particular the reactions of di/triorganoantimony (v) halides with protic acids. This chapter describes the reactions of Ph_2SbCl_3 with $RSi(OH)_3$ [R = ^tBu, *cyclo*-C_6H_{11}] and $Ph_2Si(OH)_2$ in toluene in the presence of base triethylamine as HCl scavenger which leads to isolation of colorless crystalline products. Single crystal X-ray structural elucidation reveals the formation of hexanuclear antimony(V) and mixed valent antimony (III/V) oxo-hydroxo clusters with incomplete cubane like structures of formulae $[(Ph_2Sb)_4(PhSb)_2(C_4H_9SiO_3)_2(O)_6(OH)_2]$ (4.1), $[(Ph_2Sb)_4(PhSb)_2(C_6H_{11}SiO_3)_2(O)_6(OH)_2]$ (4.2), $[(Ph_2Sb)_4(Sb)_2(Ph_2SiO_2)_2(O)_6(OH)_2]$ (4.3) and $[(Ph_2Sb)(PhSb)_2(Ph_2SiO_2)_2(O)_3(OH)_2]^{-}Et_3NH^{+}$(4.4) respectively. Interestingly in all the above cases, atleast one Sb-C bond cleavage is observed.

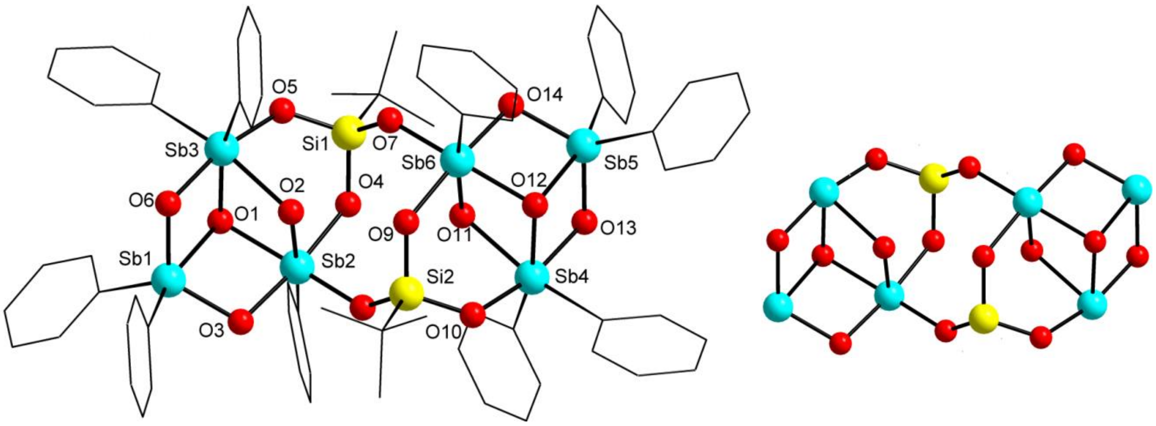


Figure 3: The solid state structure and core of $[(Ph_2Sb)_4 (PhSb)_2(C_4H_9SiO_3)_2(O)_6(OH)_2]$

Chapter 5

Investigations on the Reactivity of Arylboronic Acid with Phenolic Pyrazoles

The chapter begins with a brief introduction to boronic acids and its chemistry related towards organic and inorganic applications in general. This chapter specifically describes the reactions of phenylboronic acid with phenolic pyrazole which were carried out in 1:1 stochiometry using toluene as a solvent. Depending on the steric bulk of the group present on the pyrazole ring, [PhB(HPhPzPh)(OEt)] (5.1), [(PhB)(PhPzHt-Bu)(OH)][$(PhB)_2$$(PhPzt\text{-}Bu)_2$(O)] (5.2) and $(PhBPhPz)_2$ (5.3) were isolated. Compound 5.3 is an example of cis-isomer of pyrazabole crystallized in a boat conformation for the B_2N_4 heterocycle. Interestingly changing the phenyl boronic acid to bulky ferrocene boronic acid also leads to the isolation of an pyrazabole ring.

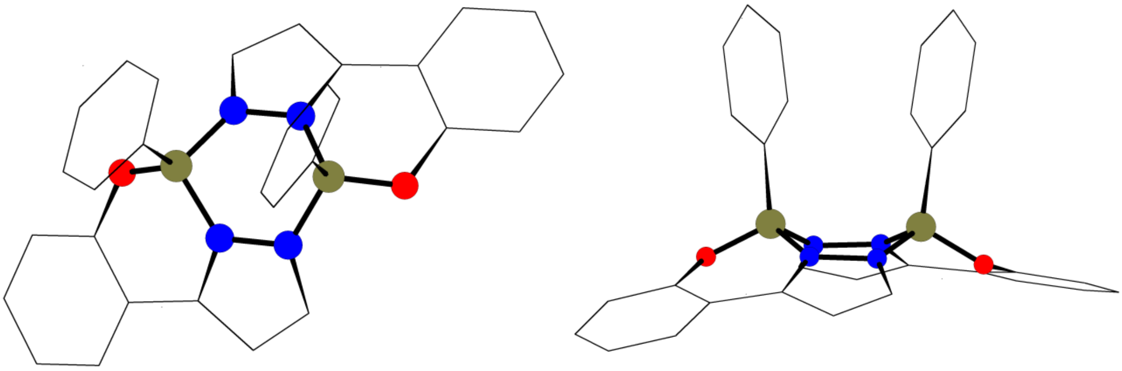


Figure 4: (a) The solid state structure of $(PhBPhPz)_2$ (b) boat form of B_2N_4 pyrazabole

Chapter 6

Twelve-Membered $B_2Si_4O_6$ BoraSiloxane Macrocycles

A one pot three component reaction of boric acid, diphenylsilane diol and functionalized alcoholic pyrazole in 1:1:1 stochiometry using toluene as a solvent under reflux conditions afforded twelve-membered borasiloxane macrocycle $[(Ph_2Si)_4(O)_6(BR^1PzR)_2]$ in moderate yields. Single crystal X-ray elucidation revealed the formation of a puckered twelve-membered ring system. ESI-MS studies indicate the stability of these macrocyclic systems in solution. The details of the synthesis and structural characterization are given in detail in this chapter.

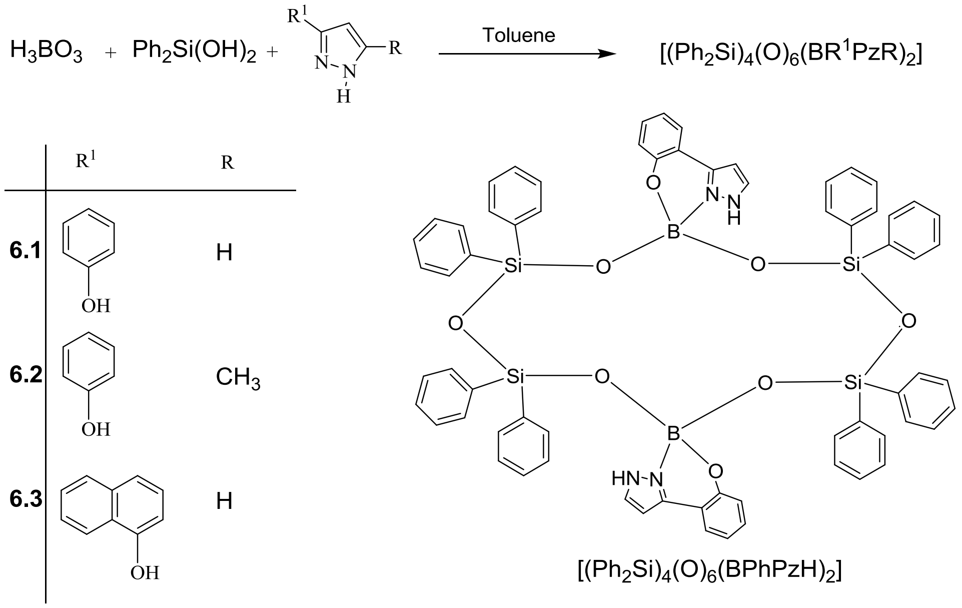


Figure 5: The chemdraw figure of **6.1**

PART-A

INTRODUCTION

Chapter

1

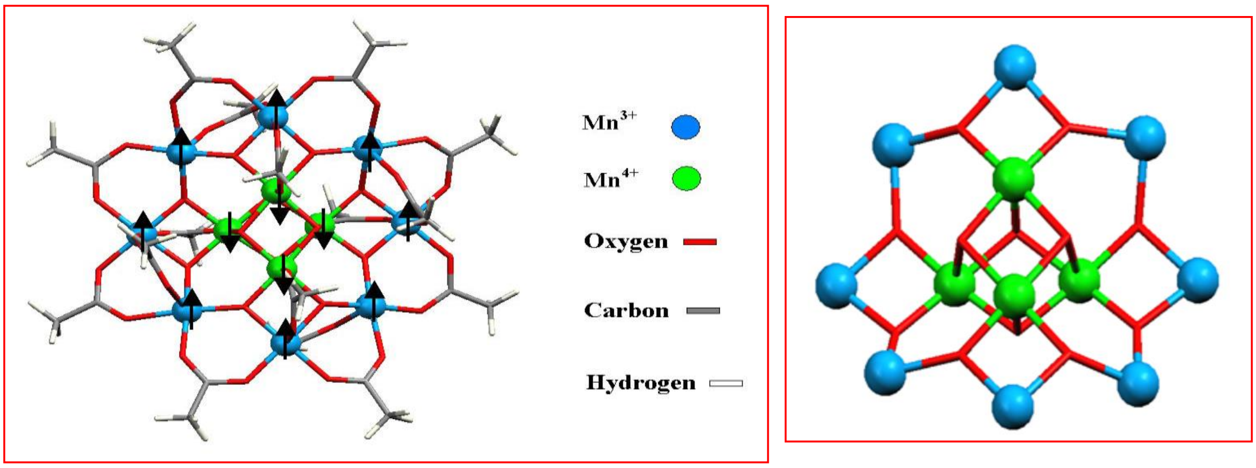
1.1 Introduction

A single molecule magnet is a molecule that can be magnetized in a magnetic field, and the molecule retains its magnetization even after switching off the magnetic field. It shows slow relaxation of the magnetization of purely molecular origin. This property associated with the molecules is not due to bulk phenomenon as in traditional magnets but it is the property which is completely due to single molecule itself. There need not be any interactions between the molecules for this phenomenon to occur. This makes single molecule magnets fundamentally different from traditional bulk magnets. The paramagnetic metal ions are bridged together by simple bridging ligands such as O_2^-, OH^-, OCH_3^-, F^-, Cl^-, $RCOO^-$. This bridge creates a super exchange pathway giving rise to an isotropic exchange coupling. The organic ligands surrounding the metal ions shield the exchange coupled cluster from the environment, especially with respect to exchange interactions. This super paramagnetic behavior is observed below certain temperatures called blocking temperatures. Single molecule magnets have numerous potential applications in information storage devices, spintronics, quantum computation and refrigerants.

1.2 Origin of Single-Molecule Magnetism and its Characterization

Lis reported the synthesis and structure of $[Mn_{12}O_{12}(MeCO_2)_{16}(H_2O)_4]\ 2MeCO_2H\cdot 4H_2O$, a compound containing an unique dodecanuclear cluster with a disc-shaped geometry in 1980 (Figure 1).[1] The structure resembles a central $Mn^{IV}{}_4O_4$ cubane unit enclosed by a ring of eight Mn^{III} centers connected through bridging oxo ligands. Bridging acetate and terminal water ligands surrounds the metal surface, such that each Mn center acquires an approximate octahedral coordination environment. The magnetic data was not collected that time but Lis suggested, this unique compound may have interesting magnetic properties. Nearly after a decade, magnetization data for this compound was collected at high magnetic field strengths and low temperatures. The data suggests an S =10 ground state with large axial anisotropy.[2,3]

The oxo donors coordinating the Mn atoms are weak-field ligands, so the electron configurations of Mn^{IV} and Mn^{III} will be $t_{2g}{}^3e_g{}^0$ and $t_{2g}{}^3e_g{}^1$, imparting local spins of S = 3/2 and S = 2 respectively. The total spin of the ground state S =10 can be obtained from a situation in which the spins of the four central Mn^{IV} centers are all aligned antiparallel to the spins of the eight external Mn^{III} centers, to give $S = |(4 \times 3/2) + (8 \times -2)| = 10$ (Figure 1a).



(a) (b)

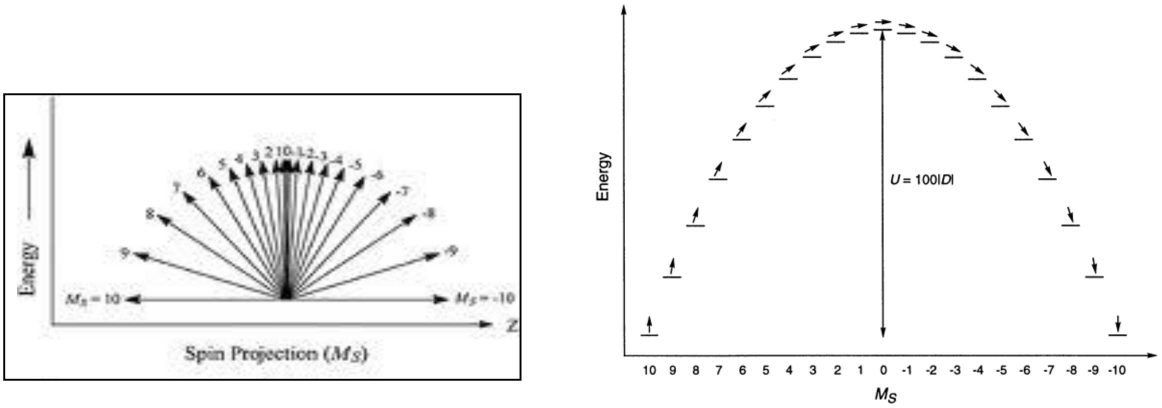
Figure 1: (a) Ball and stick model of Mn12-Ac with spin orientations. (b) core of Mn12-Ac

Later it was shown that the reduced magnetization curves for the compound were deviated significantly from a simple Brillouin function, suggesting that the S = 10 ground state experiences a zero-field splitting (D) with a magnitude of $|D| = 0.5\ cm^{-1}$. High-field, high-frequency EPR spectra are also consistent with this value, and further indicate the sign of D to be negative.

Due to this negative axial zero-field splitting the degeneracy in the M_S levels of the ground state (Figure 2a) are removed placing the higher magnitude levels lower in energy as shown in Figure 2b and with a selection rule of $\Delta M_S = \pm 1$ for allowed transitions results in an energy barrier U separating the two lowest energy levels of $M_S = +10$ and $M_S = -10$. Normally, for an integral spin state, the energy barrier will be $U = S^2|D|$, while for a half-integral spin state it will be $U = (S^2 - 1/4)|D|$. Thus, for the S = 10 ground state of the Mn_{12} cluster, the spin-reversal energy barrier is $U = S^2|D| = 10^2|-0.5\ cm^{-1}| = 50\ cm^{-1}$.

As a result of this energy barrier U which is due to the S = 10 spin ground state and negative axial zero-field splitting, the magnetization of the Mn12 cluster can be pinned along one direction (spin–up), and then relaxes slowly (spin-down) at very low temperatures as shown in Figure 3.

This relaxation of magnetization of the molecule and its relaxation times can be investigated readily through AC magnetic susceptibility measurements. Here the susceptibility of a sample



(a) (b)

Figure 2: (a) The degenerate 2S+1 orientations of the S=10 ground state (b) Energy level diagram for an S=10 ground state with an negative axial zero field splitting, D in the absence of applied magnetic field.

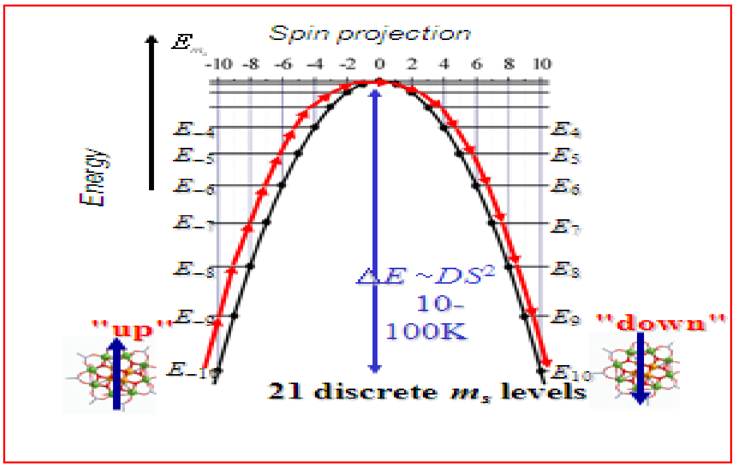


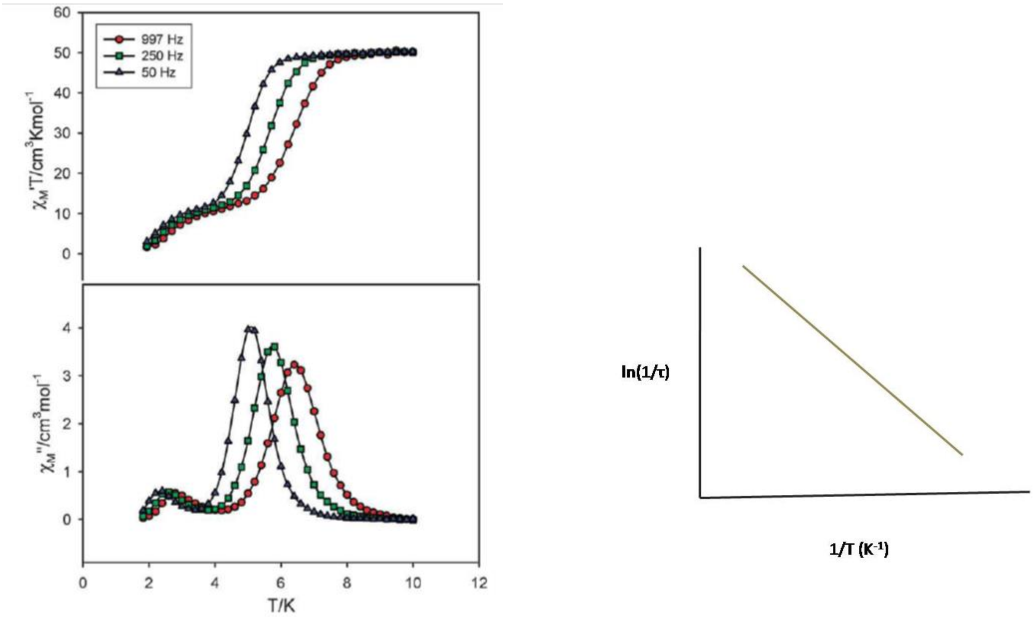
Figure 3: Energy level diagram showing spin reversal energy barrier.

is calculated using a weak magnetic field (usually of ca. 1 G) that switches direction at a fixed frequency. As the switching frequency increases and starts to approach the relaxation rate for the magnetization within the molecules, the measured susceptibility — referred to as the in-phase or real component of the AC susceptibility and represented as χ’ will start decreasing. Accordingly, the portion of the susceptibility that cannot sustain with the switching field—referred to as the out-of-phase or imaginary component of the AC susceptibility and represented as χ”—gradually increases. If just a single relaxation process is equipped in the squid magnetometer instrument, then a plot of χ” versus temperature will show a peak with maximum height at the temperature where the switching of the magnetic field matches the relaxation rate, 1/ τ , for the magnetization of the molecules. Furthermore, since 1/ τ increases with temperature, this peak should move to higher temperature when the switching frequency is raised (Figure 4a).This was what is exactly observed in $[Mn_{12}O_{12}(MeCO_2)_{16}(H_2O)_4]\cdot 2MeCO_2H\cdot 4H_2O$.[3]

The relaxation time for the magnetization in a single-molecule magnet generally follows an Arrhenius relationship

$$\tau = \tau_0 \exp(U_{eff}/KT)n \text{ or } \ln(\tau) = \ln(\tau_0) + U_{eff}/KT$$

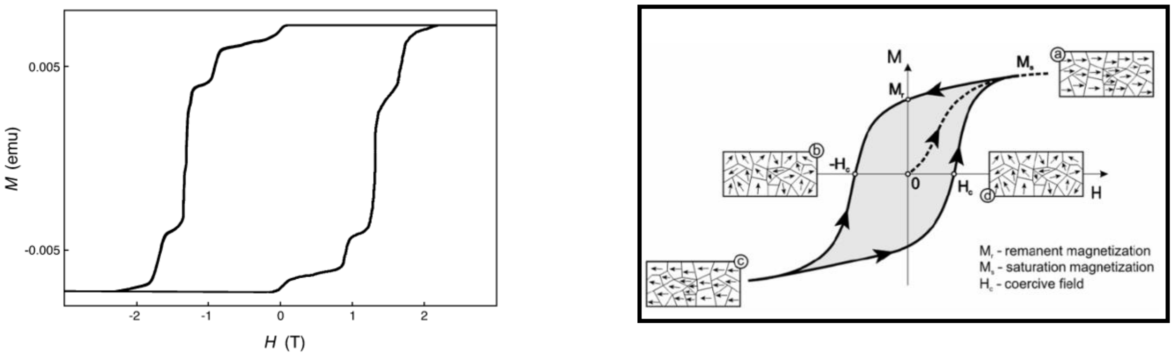
where the preexponential term τ_0 is the relaxation attempt frequency, K is Boltzmann constant, and T is temperature. Thus, a plot of lnτ versus 1/T should be linear (Figure 4b), where the U_{eff} and τ_0 can be calculated from slope and intercept. Analysis of data gave U_{eff} = 42 cm^{-1} and $\tau_0 = 2.1 \times 10^{-7}$s.[4] In general the effective energy barrier U_{eff} obtained is slightly lower than the intrinsic spin reversal barrier U calculated from S and D, owing to the effects of quantum tunneling of the magnetization.



(a) (b)

Figure 4: (a) In-phase and out –phase of phase ac susceptibility of Mn12-Ac. (b) Arrhenius plot ln(τ) vs 1/T

Other than the AC magnetic susceptibility measurements the slow relaxation can also readily probed through magnetic hysteresis loops. The $[Mn_{12}O_{12}(MeCO_2)_{16}(H_2O)_4]\cdot 2MeCO_2H\cdot 4H_2O$ at 2.1K [5] shows a magnetic hysteresis loop (Figure 5a). This hysteresis has a completely different phenomenon from that in an ordered ferromagnet where there will be inducing domain wall motion (Figure 5b), but in SMM on increasing the applied magnetic field there will be shifts in the relative energies of the M_S levels (Figure 6), there by decreasing the thermal activation barrier for reversing spin direction and allows the relaxation process. As a consequence, the coercivity of the sample changes dramatically with temperature. The remarkable steps apparent in the hysteresis curve are due to quantum tunneling of the magnetization



(a) (b)

Figure 5: (a) Magnetic hysteresis loop observed for Mn12 Ac at 2.1K. (b) Orientations of electrons in each domain at different points in the hysteresis loop

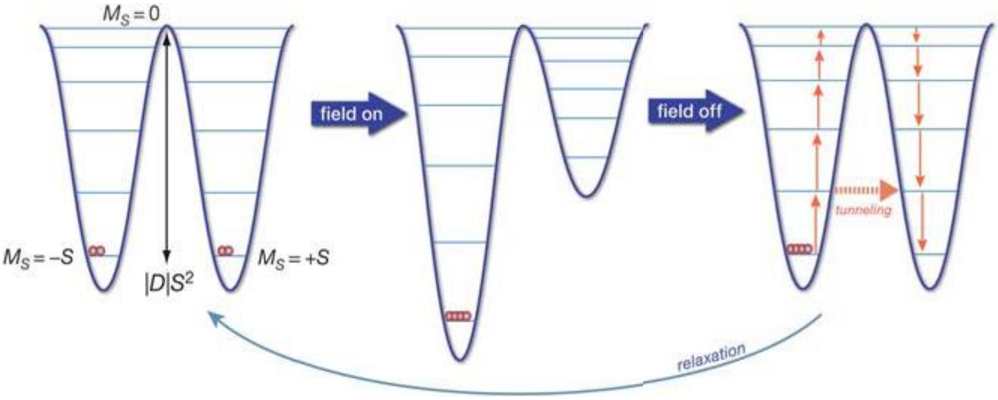


Figure 6: Double well diagram to explain relaxation process in SMM

An explanation for the unusual step in the magnetic hysteresis loops obtained from samples of $[Mn_{12}O_{12}(MeCO_2)_{16}(H_2O)_4]\cdot 2MeCO_2H\cdot 4H_2O$ [5-7] was given in 1996. The location of steps is independent on temperature, suggesting that they are not of the thermal origin. Finally, it was decided the relaxation has occurred through quantum tunneling mechanism, which means that tunneling occurs when there is an energy coincidence of the M_S levels on the opposite parts of the double-well potential diagram, fulfilling the resonance condition (figure 7). The tunneling of magnetization not only occurs between the pair of levels lowest in energy, but also between the pair of levels highest in energy infact the chance of tunneling increases as one progresses upward toward $M_S = 0$. Thus, much loss of magnetization is a result of thermally-assisted tunneling between higher energy levels. As the strength of the applied magnetic field is increased, the M_S levels shift in energy, with the lower levels going up on one side and down on the other side of double-well potential diagram until finally the spin reversal barrier disappears. Between these two extremes lie a number of field strengths at which a resonance again occurs and then allows tunneling of the magnetization. Consequently, the positions of the steps in the hysteresis loops can be used to find the M_S energy levels of the ground state.

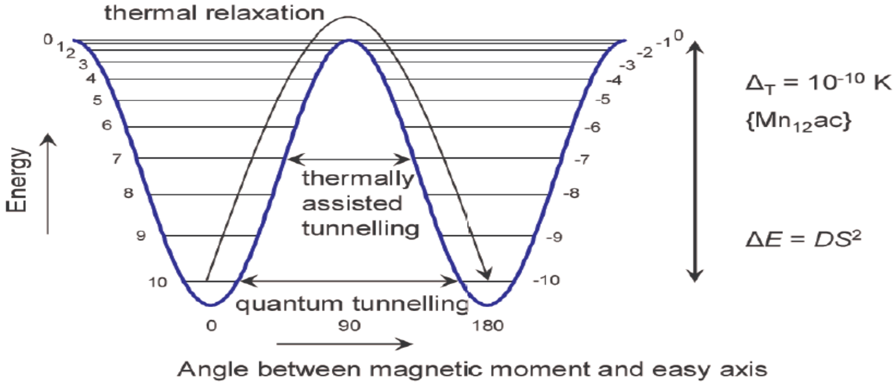


Figure 7: Double well diagram showing various relaxation process in SMM

The presence of an energy barrier for reversing spin magnetization suggests the possibility of storing a bit of information. Thus the Mn12 cluster exhibits a magnetization relaxation half-life of more than 2 months at 2 K. The other important applications are in spintronics, quantum computation and in refrigerants.[8] So for the molecules to be capable of storing information at more convenient temperatures there is a clear requirement for clusters possessing a larger spin reversal barrier U. To meet this challenge, one would like to synthesize molecules bearing ground states with remarkably high spin ground state S and a large negative axial anisotropy D.

1.3 Why lanthanides preferred over transition metals ?

Many examples of SMMs with transition metals have been reported after the first isolation of Mn_{12}–Ac SMM, but their energy barrier for spin reversal and blocking temperature are quite low as compared to the first [$LnPc_2$] reported by Ishikawa et al[9] and other lanthanide based SMMs whose nuclearity ranging from monomer[10] to Ln_{2-60}.[11-13] These SMMs have the larger energy barriers and blocking temperatures compared to the TM based SMMs (Figure 8).

From the above discussion it was evident that for any complex to show slow relaxation of magnetization it must have large energy barrier for relaxation. This energy barrier indeed depends on the large spin ground state (S) and easy axis type negative magnetic anisotropy.

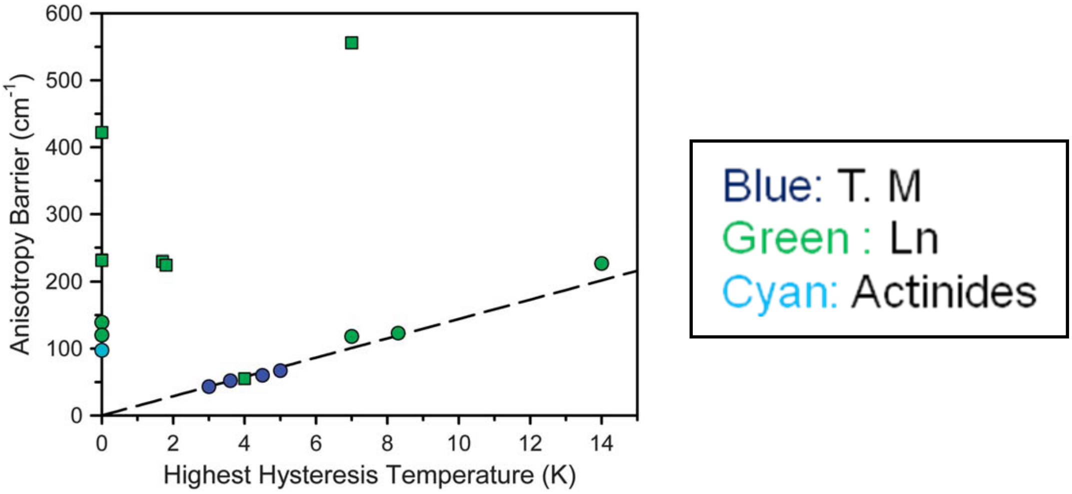


Figure 8: Plot of the highest recorded hysteresis temperature vs. the anisotropy barrier for the selected single molecule magnets.

In case of 3d based SMMs large spin ground state arises from the ferro magnetic or ferri magnetic arrangement of spins of various paramagnetic metal centers present in complexes. The splitting of ground state S into their individual m_s levels provides a high energy barrier for the spin reversal (up to down). This energy barrier frequently depends on the anisotropy of individual spin centers present in the complex/clusters, and orientation of anisotropy axes on the individual metal centers. Even though presence of a good magnetic coupling interactions between transition metal ions via ligand orbital's, due to lack of strong spin–orbit coupling [notable exception in case of Co (II)] transition metal ions did not provide large anisotropies. So that in transition metal based SMMs the highest effective energy barrier have S =10 and anisotropies D between 0.5 and 0.9 cm^{-1}.

Where as in lanthanide elements 4f orbital's are deeply buried and are not involved in bonding with ligand orbitals, as a result magnetic coupling exchange interaction between the lanthanide metal centers are very weak or almost not considerable. However, f-orbital's have almost complete degeneracy as a consequence it provides large unquenched orbital angular momentum to the lanthanide elements. The ground states terms of the lanthanide ions defined in terms of total angular momentum J [spin angular momentum (S) + orbital angular momentum (L)], where as in transition metals spin angular momentum is taken into consideration. Due to the presence of this strong spin orbital coupling [14] results in large magnetic anisotropies for the lanthanide ions particularly Tb, Ho and Dy. For the lanthanides after gadolinium J= L+S is the lowest energy term and which leads to ground states with large J, as result large magnetic moments. The splitting of ground state term into the individual M_j levels leads to an energy barrier. So the factors that control this splitting are key in deciding the magnitude of the energy barriers. In this regard the crystal field (local crystal field) in which lanthanide ions is situated has a significant effect on the electronic structure of the lanthanide ions. Hence the crystal field interacts with the ground state removes the 2J+1 degeneracy of the ground state as result which influence on the magnetic properties of lanthanide ions. Finally the slow relaxation of lanthanide ions depends on the spin-orbit coupling and local crystal field. Because of these intrinsic properties of lanthanide ions, which are chosen as best candidates to construct the improved SMM parameters.

1.4 3d and 4f based Single Molecule Magnets with highest energy barriers so far

Manganese is most common one in making transition based SMMs because, in most of the cases metal ions present in the different oxidation states (Mn^{2+}, Mn^{3+}, and Mn^{4+}) leads to an antiferromagnetic interactions between the metal centers results in a non zero ground state. So the complexes containing Mn ions are likely to have large spin ground states (S). Another important fact why Mn is preferred over the other transition metal ions, Mn^{3+} ($3d^4$) ions undergoes Jahn–Teller distortion which leads to a reduction in symmetry from Oh to D_{4h}, consequently anisotropy (D) of complexes increases. So the combination of these two factors leads to appreciable energy barriers.

Brechin et al reported family of hexanuclear complexes by treating the manganese salts with various salicylaldoximes in presence of different carboxylic acids results in Mn_6 clusters with general formula as {$[Mn_6O_2(sao)_6(O_2CR)_2L_4]$[14a, 14b] (where R = H, Me, Ph; sao = dianion of the salicylaldoxime; L= solvent ; MeOH or EtOH)}. They noticed that by altering the alkyl substituent's attached to salicylaldioxime ligands/carboxylates, it was possible to increase the spin ground state of the molecules from S = 4 to S =12. In the process they reported another family of Mn_6 clusters with substituted oximes and carboxylates having the general formula {$[Mn_6O_2(R\text{-}sao)_6(O_2CR')_2L_{4\text{-}6}]$[14c] (where R, R' = H, Me, Et, Ph; L= MeOH, EtOH, MeCN, H_2O). These Mn_6 molecules exhibited enhanced SMM parameters. The possible reason was changing simple $saoH_2$ to substitute R-$saoH_2$ causes the slight structural distortion to the metal oxo core of the molecules, which further leads to increase in the twisting of the oxime moiety (Mn-N-O-Mn). The torsion angle of Mn-N-O-Mn increased approximately above 31.3˚. So that presence of this twist in angle leads to exchange between metal centers transform from the weakly antiferromagnetic to weakly ferromagntic. Due to torsion angle in one of the complex known [Mn_6] molecule [Mn_6O_2(Et-sao)$_6$(O_2CPh(Me)$_2$)$_2$(EtOH)$_6$] switches the dominant magnetic exchange from antiferromagnetic to ferromagnetic resulting in a molecule possessing an S = 12 ground state with D = -0.43cm^{-1}. Relaxation studies on both powdered samples and on single crystals reveal the complex to be a single-molecule magnet with a record value of the effective energy barrier to magnetization reversal (U_{eff}) of 86.4 K and a blocking temperature of ~4.5 K, finally breaking the long-standing record held by the Mn_{12} family of molecules (figure 9).

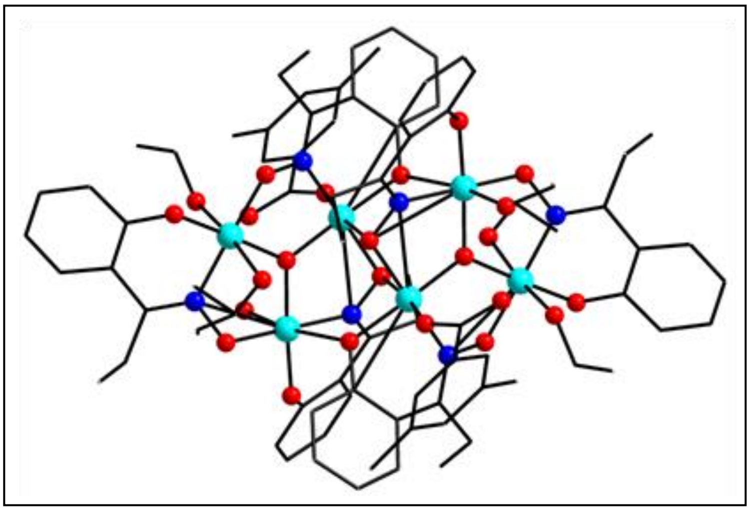


Figure 9: Ball and stick model of [Mn_6O_2(Et-sao)$_6$(O_2CPh(Me)$_2$)$_2$(EtOH)$_6$] with U_{eff} =86.4 K

In 4f based SMM’s the Dy element plays a very important role. The electronic configuration of Dy(III) ion is [Xe] 4f^9, it has 5 unpaired electrons. Since there is strong spin-orbit coupling present in lanthanides the ground state term for the Dy(III) is given as $^6H_{15/2}$ ($^{2S+I}L_J$). The spin multiplicity in Dy(III) atoms is 16 fold degenerate that comes from 2J+1 (2x15/2+1), this degeneracy can be removed by surrounding crystal filed into new sublevels states i.e doubly degenerate ± m_j states. For Dy(III) the total m_j states are ±15/2 ±13/2 ±11/2 ±9/2 ±7/2 ±5/2 ±3/2 ±1/2. But the degeneracy of theses ±mj levels cannot be removed by crystal fields because of spin–parity effect of kramers ion (odd number of 4f electrons). The doublets called as kramers doublets. Because of large separation between ground m_j state to other m_j states, requires more energy for the spin relaxation from one state to other.

Winpenny et al reported the polymetallic lanthanide alkoxide complexes and their doped yttrium analogues by treating anhydrous lanthanide (III) chlorides with three equivalents of potassium iso-propoxide or potassium tert-butoxide in toluene, yielding $[Ln_5(\mu\text{-}O)(OiPr)_{13}]$[15a] and $[Ln_4K_2O(OtBu)_{12}].C_6H_{14}$ (Ln = Sm, Gd, Tb, Dy, Ho, Er).[15b] They suggested that a strongly axial crystal field can lead to thermal relaxation via higher excited states, this leads to higher values for U_{eff}. The relaxation barrier of $[Dy_5(\mu\text{-}O)(OiPr)_{13}]$ system is 530K and further $\{Dy_4K_2\}$ complex show the highest U_{eff} found for any polymetallic complex, and those for the Dy-doped Y complexes reach even higher energies (800 K) (figure 10).

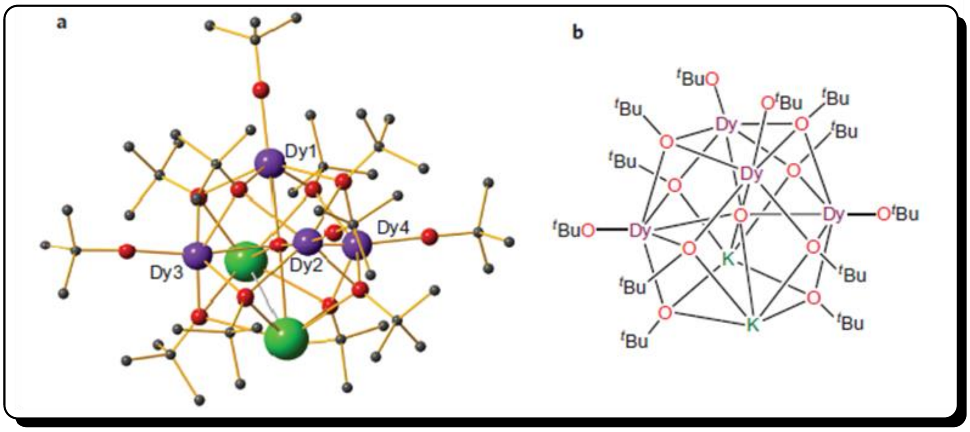


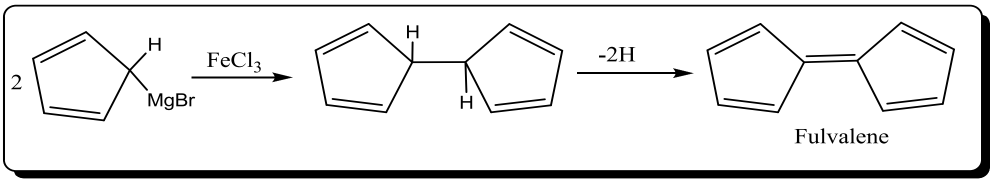
Figure 10 : Ball and stick model of $[Dy_4K_2O(OtBu)_{12}]$

The objective of the work reported in this thesis is to utilize the interesting magnetic properties exhibited by the lanthanide ions and anchor ferrocene on the surface of such cluster essentially synthesizing bifunctional clusters. Hence before going in to multiferrocene assembly, a slight introduction about ferrocene is given as preface.

1.5 Ferrocene: Structure and Bonding

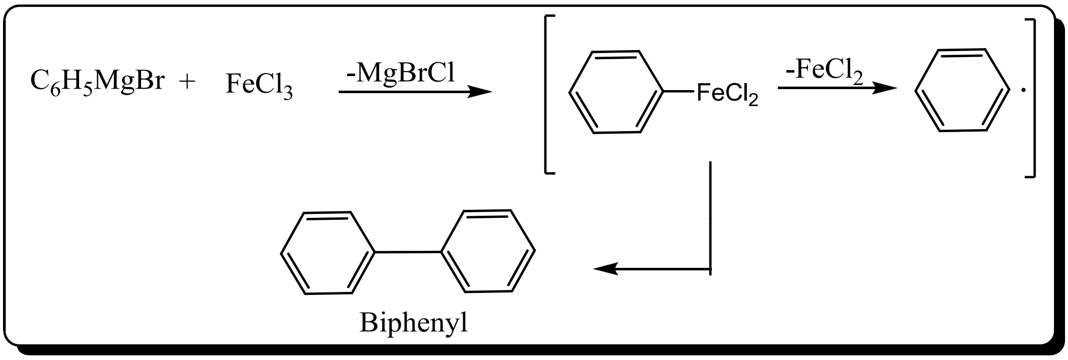
Ferrocene is also called bis(η5-cyclopentadienyl)iron, the earliest and best known of the so-called sandwich compounds. It is organometallic chemical compound consisting of two cyclopentadieyl rings bound on opposite sides of a central iron atom. Its molecular formula is $(C_5H_5)_2Fe$.

The discovery of ferrocene was one of those fortuitous incidents that was wholly unpredictable. The kind of discovery which, over and over again, has changed the course of science. In 1951 Pauson was trying to synthesize fulvalene by first coupling two molecules of cyclopentadienylmagnesium bromide with $FeCl_3$ and then dehydrogenating the product (scheme 1).



Scheme 1

But the coupling reaction of phenylmagnesium bromide with $FeCl_3$ gives high yields of biphenyl, most probably by way of an unstable phenyliron compound (scheme 2).



Scheme 2

And the other reaction product was a beautifully crystalline, highly stable, orange substance, $C_{10}H_{10}Fe$, which Pauson formulated as a simple combination of two cyclopentadienide anions and ferrous ion with two C-Fe bonds, However, the product soon was shown by a variety of physical methods to have the sandwich structure (figure 11).

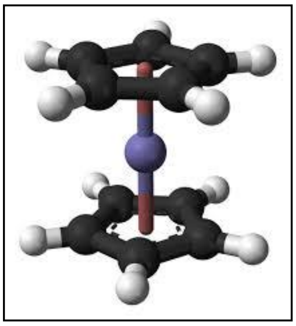


Figure 11: Ball and stick representation of ferrocene

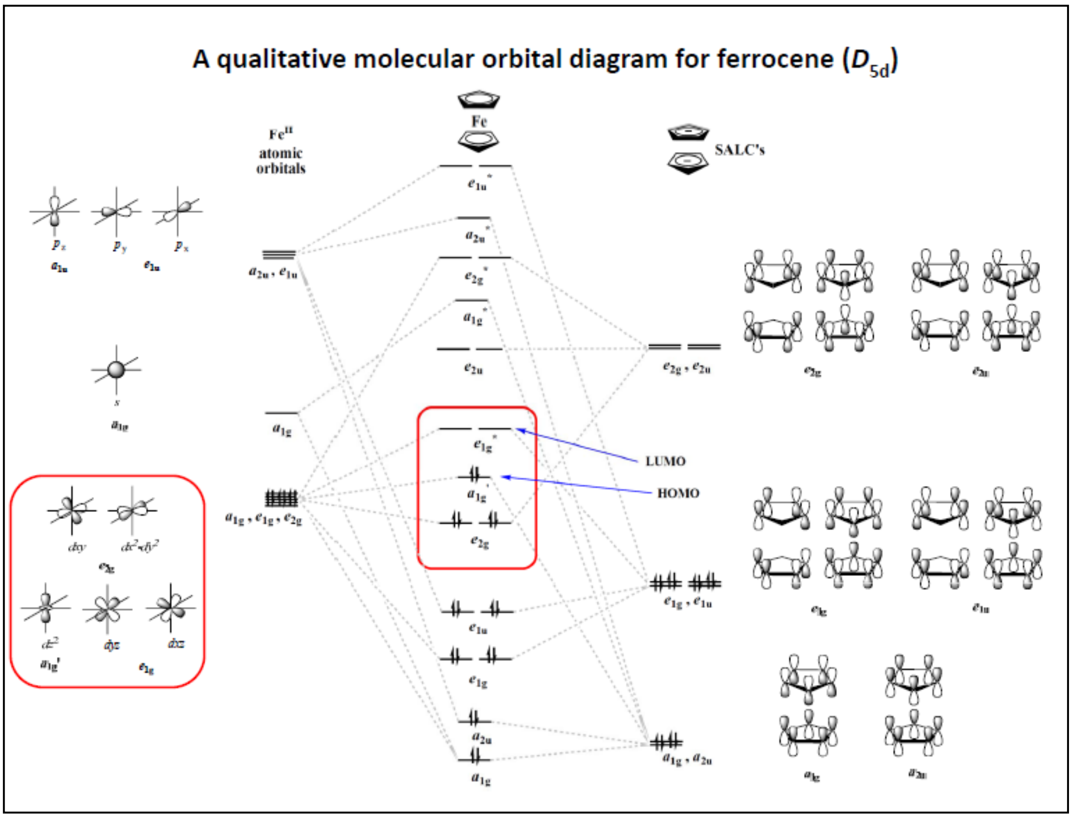
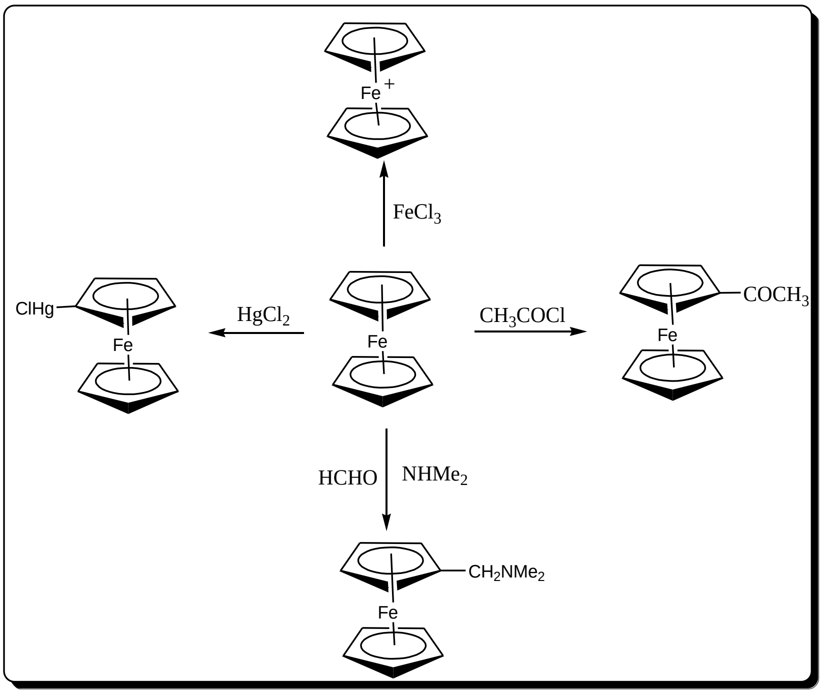


Figure 12: Molecular orbital diagram of ferrocene

The bonding between the metal and the cyclopentadiene rings involves the n-electrons of the two rings, all carbons being equally bonded to the central ferrous ion. The latter, in accepting a share of 12 n-electrons from two cyclopentadienyl anions, achieves the 18 outer-shell electron configuration of the inert gas, krypton.

Above molecular orbital diagram (figure 12) shows that iron(0) has 8 electrons in the 4s and 3d orbitals. Ferrous ion (Fe^{+2}) then will have 6 outer-shell electrons. This 6 and the 12 n-electrons of the two cyclopentadienide rings makes the 18-electron total and attains stable krypton electronic configuration.

Analysis of the structure of crystalline ferrocene shows that when looking down on the molecule along the ring-iron-ring axis the cyclopentadiene rings are seen to be staggered with respect to one another, ferrocene has mp 173° and, although stable to sulfuric acid, it is readily oxidized by nitric acid to the less stable ferricinium ion. Like benzene, ferrocene does not react easily by addition reactions but does undergo electrophilic substitution very readily (scheme 3).



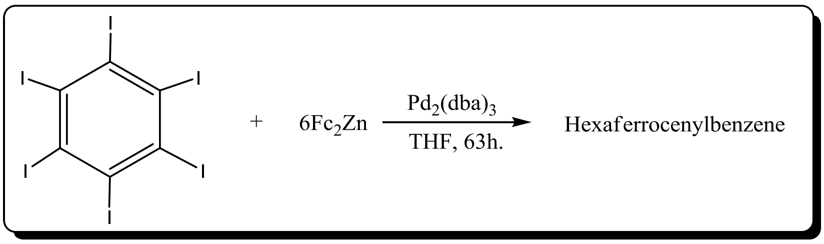
Scheme 3: Electrophilic substitution reactions on ferrocene

1.6 Ferrocene self assemblies :

Design and synthesis of molecules having multi ferrocene assemblies bearing redox active centers at nano dimension level has been a matter of active research due to their potential applications in fields of nano scale organometallics, conducting polymers, specialty electrodes, anion recognition and in magnetism. In literature most of the strategies used for making multiferrocene assemblies include aromatic, polymers and surface of metal nanoparticles. Completely in a different synthetic methodology P. J. Stang and group adopted coordination driven self assembly approach, bringing the interaction between ferrocene containing donor and acceptor molecules to construct metallacyclic polygons containing ferrocene units. The incorporation of ferrocene moieties in to molecular assembly can also be achieved by constructing core kind of frame works. Among the different core frame works known to date, mostly multiferrocene assemblies have been prepared as metallodendrimers in which generally a central benzene type aromatic cores were constructed and ferrocenes were grafted at the peripheries either by convergent or divergent routes, the advantage being that metallodendrimers can incorporate maximum number of ferrocene units, due to its large surface area to volume ratio of each molecule. On the other side dendrimers requires multistep synthesis and great synthetic efforts. In addition to that they often results in the products with amorphous nature and of very low yields. So in order to overcome these difficulties, in recent years many efforts have been devoted around the world in constructing multi ferrocene assemblies supported by inorganic cores. Different groups around the world have successfully employed the inorganic cores such as stannoxanes, cyclophosphazenes, aluminum–nitrogen/carbide skeleton frames, metal chalcogenates, and multi nuclear metal oxide surfaces that support multi ferrocene assemblies. The detailed discussion and the reactions of ferrocene self assemblies are discussed below.

1.6.1 Aromatic Cores supporting ferrocene assemblies:

Vollhard et al used cyclopentadiene and benzene kind of cores for ferrocene self assemblies.[16a,b] They incorporated six bulky ferrocene groups around the benzene by Negishi type ferrocenylation of hexabromo or hexaiodobenzene in which six equivalents of diferroceneylzinc was treated with hexa iodo benzene in the presence of 30% Tris(dibenzylideneacetone)dipalladium(0) at the refluxing temperature of THF (scheme 4). The reaction often gives in mixture of products hexaferrocenyl benzene and pentaferrocenyl with 4% and 56% yields. These two compounds were separated by repeated chromatography on silica.



Scheme 4

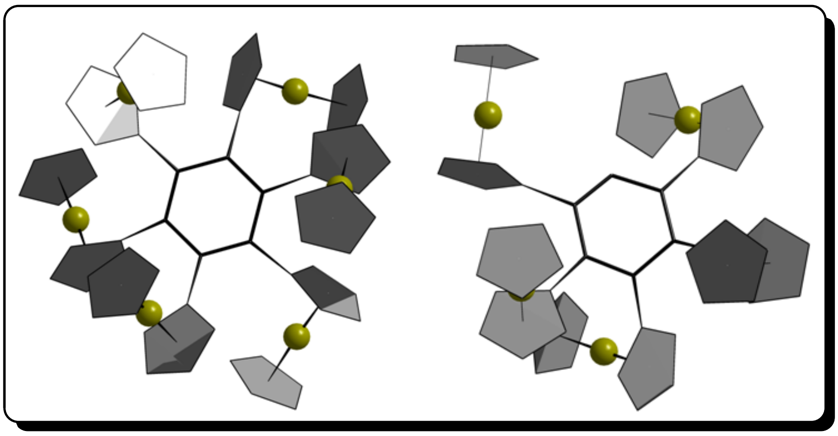
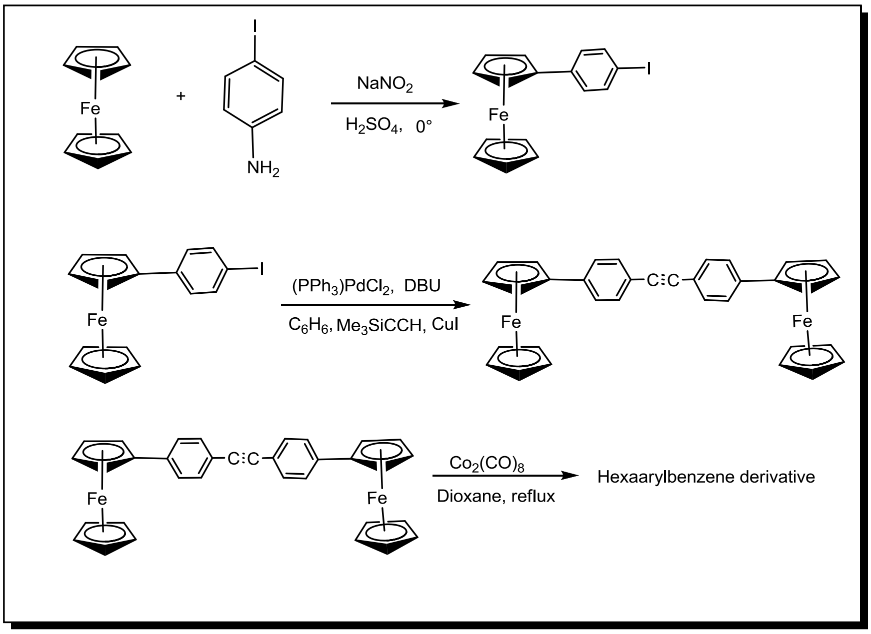


Figure 13: Ball and stick model of hexaferrocenyl benzene and pentaferrocenyl benzene

Later Rajendra Rathore and group utilized the hexaphenylbenzene core as a platform for the high yield synthesis of multiferrocene assemblies.[16c] They followed a three step route to accomplish the hexa aryl benzene derivative core containing ferrocenes at the periphery (scheme 5).



Scheme 5

Initially 4-ferrocenyl-iodobenzene was readily prepared by diazotization reaction and was coupled in the presence of Pd with trimethylsilylacetylene to from bis(4-ferrocenylphenyl) acetylene. Interestingly the bis(4-ferrocenylphenyl) acetylene was trimerized in the presence of catalytic amount of $Co_2(CO)_8$ and allows an easy access to hexaarylbenzene derivatives decorated with six ferrocenes (figure 14).

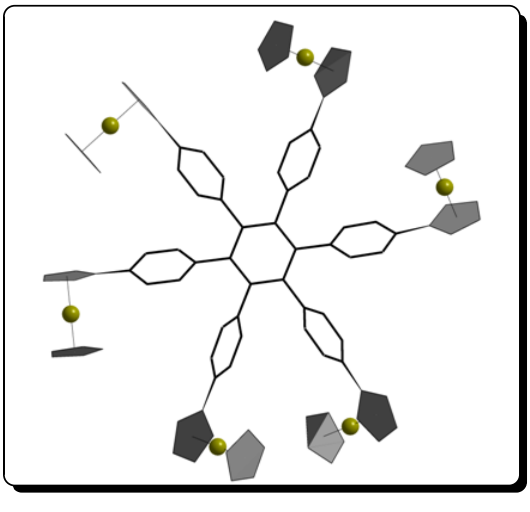


Figure 14: Ball and stick model of hexapenyl benzene core containing six ferrocenes

1.6.2 Coordination driven self-assembly approach for multi ferrocene assemblies:

P. J. Stang et al utilized coordination-driven self-assembly approach method for self-assembling large, rigid multi ferrocene systems with well-defined shapes, sizes, and geometries.[17a-f] The approach brings together the highly directional dative metal-ligand bonds between the ferrocene substituted electron-poor metal centers and electron-rich organic donors to provide a wide variety of discrete two dimensional (2D) and three dimensional (3D) polygonal and polyhedral coordination assemblies containing multiferrocenes. In particular, electron-poor square planar Pt (II) and Pd (II) metals are often used in combination with electron-rich nitrogen-containing moieties such as substituted pyridines and nitriles (chart 1). Thus coordination-driven self-assembly is a dynamic process carried out under thermodynamic control, ultimately leading to the most stable supramolecular structure.

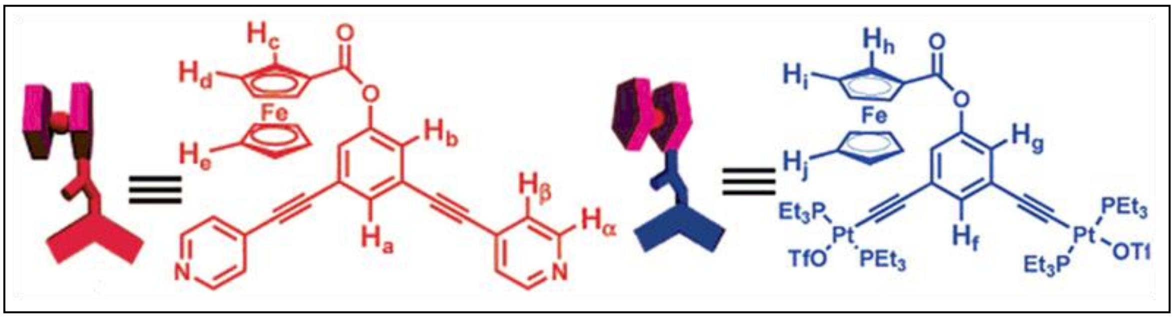


Chart 1: The molecular structures of 120˚ ferrocenyl donor and acceptor.

The two most significant structural factors that largely dictate the supramolecular structure obtained from coordination-driven self-assembly are the shape and size of individual component building blocks. The shape of donor and/or acceptor building blocks is dominated by the turning angle defined as the angle formed between the two open valences of a ditopic donor or acceptor. Below figure 15 demonstrates how the directional-bonding approach to coordination-driven self assembly provides a means of synthesizing 2D metallacyclic polygons such as squares, rectangles, rhomboids, triangles, and hexagons.

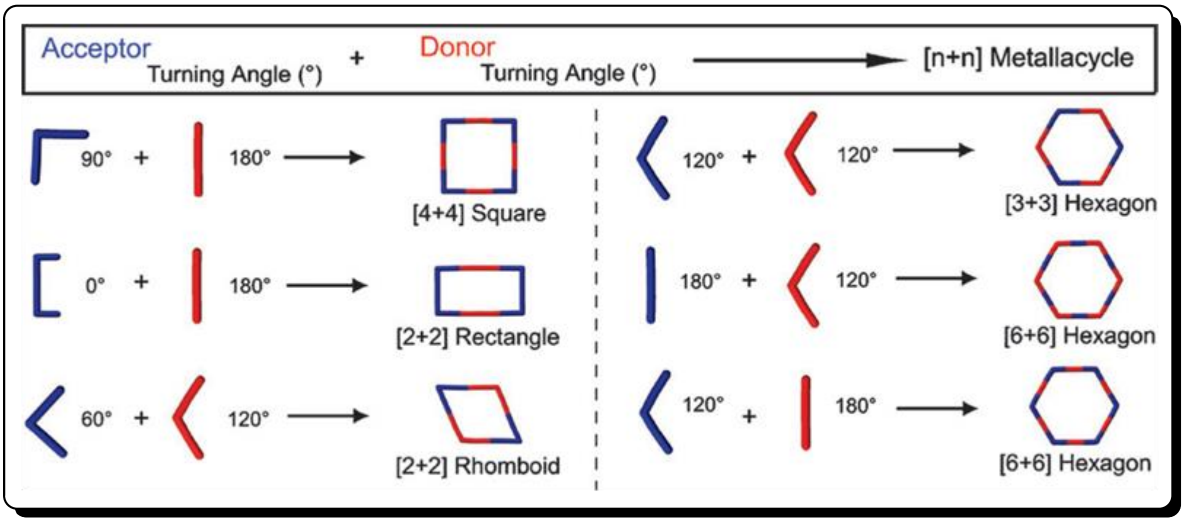
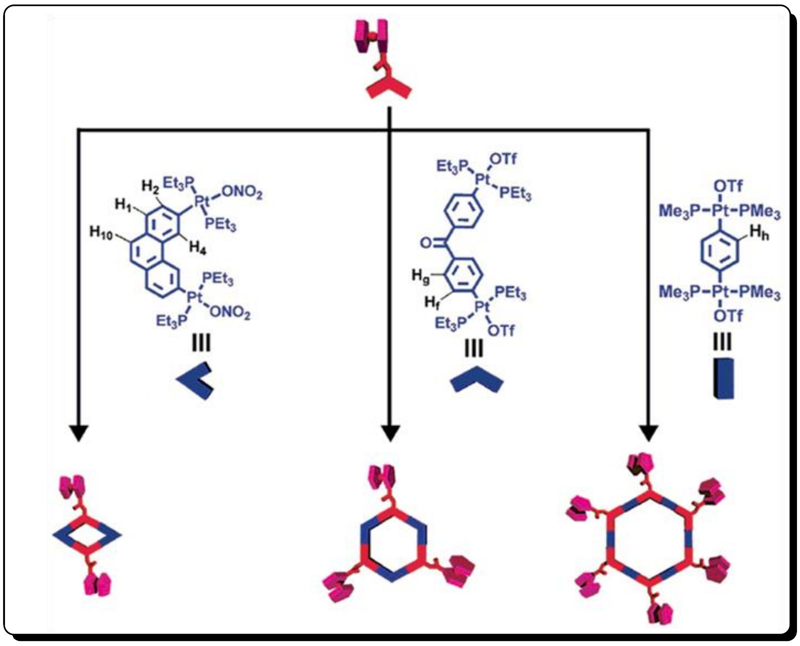


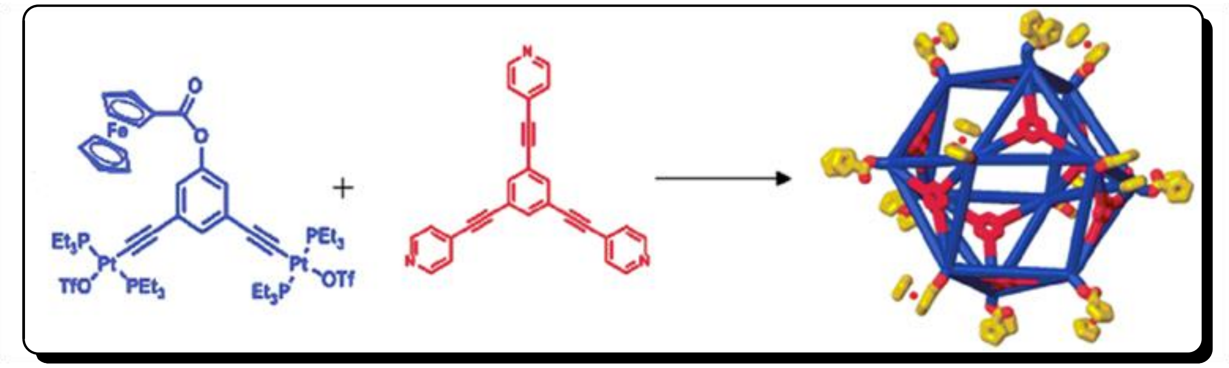
Figure 15: Directional-bonding approach to coordination-driven self-assembly

For example when the ferrocenyl 120˚donor precursor was treated with 60˚, 120˚, or 180˚ di-Pt(II) acceptor in a 1:1 ratio resulted in the formation of the [2+2] rhomboid , the [3+3] hexagon, and the [6+6] hexagon, respectively with pendant ferrocene groups at donor vertexes (scheme 6).



Scheme 6: coordination-driven self assembly of the [2+2] rhomboid, [3+3] hexagon, and the [6+6] hexagon

Similarly stirring a mixture of 120˚ acceptor with the linear tritopic donor in a 3:2 ratio resulted in the formation of cubooctahedral complexes with 12 pendant ferrocenes at the vertexes (scheme 7).



Scheme 7: Coordination-driven self assembly of cubooctahedral complexes with 12 pendant ferrocenes.

Thus by synthesizing ferrocene functionalized donor and acceptor building blocks, coordination-driven self assembly is able to afford a facile and versatile strategy for the preparation of multi-ferrocenyl assemblies that allows accurate control over shape, size and the distribution of ferrocene moieties.

1.6.3 Ferrocenyl dendrimers :

Dendrimers are built around a central focal point or a core from which bonds are grafted radially with a regular branching pattern. Not all regularly branched molecules are dendrimers. To be classified as a dendrimer, a globular molecule must have a low viscosity in solution. This property can be achieved only if the molecule possesses a certain critical size.

In general two different synthetic methodologies have been developed for the preparation of dendrimers. The divergent synthesis (from the core of the molecule to its periphery) and the convergent synthesis (from the periphery to the core). Ferrocene dendrimers can be synthesized by both convergent and divergent methods. The first poly-branched molecules containing ferrocenes were synthesized using the hexa-allylation and hexa-alkylation of hexamethylbenzene[18] or the $CpFe^+$-induced nona-allylation of mesitylene[19] was accompanied by visible-light decomplexation[20] and subsequent recovery of the organo-iron group. Various possibilities for grafting ferrocenes of the terminal double bonds were explored. The commercial diaminobutane (DAB) dendrimers was functionalized up to fifth generation by Casado et al. using ferrocenylcarbonyl chloride.[21] The phosphorus based[22] and arene-centered[23] dendrimers (1 - 3 connectivity) containing large number of ferrocenes were synthesized by Toulouse, Astruc and Newkome group. Astruc and group synthesized ferrocenyl dendrimers containing gold nanoparticle cores,[24] cluster cores,[25] arene cores[26] and silica cores.[27] It was shown with arene cores, the powerful 1-3 connectivity has been extended to the 7th dendrimer generation, G7, for which the actual number of ferrocenyl termini was approximately 14000 ± 1000, and these dendrimers were characterized by a large number of classic and nanoscience techniques including AFM and dynamic light scattering. Recently, the ferrocenyl group has been introduced by the very efficient ‘‘click’’ reaction, i.e. Cu(I)-catalyzed alkyne azide 1,3-dipolar cycloaddition (CuAAC), which has allowed the synthesis of the first metallodendrimers synthesized by ‘‘click’’ chemistry.[28] There are three basic categories that ferrocene-containing dendrimers can be placed in: (a) dendrimers with ferrocene cores (b) dendrimers with peripheral ferrocene groups, (chart 2) and (c) dendrimers with ferrocene at the core and the peripheral (chart 3).

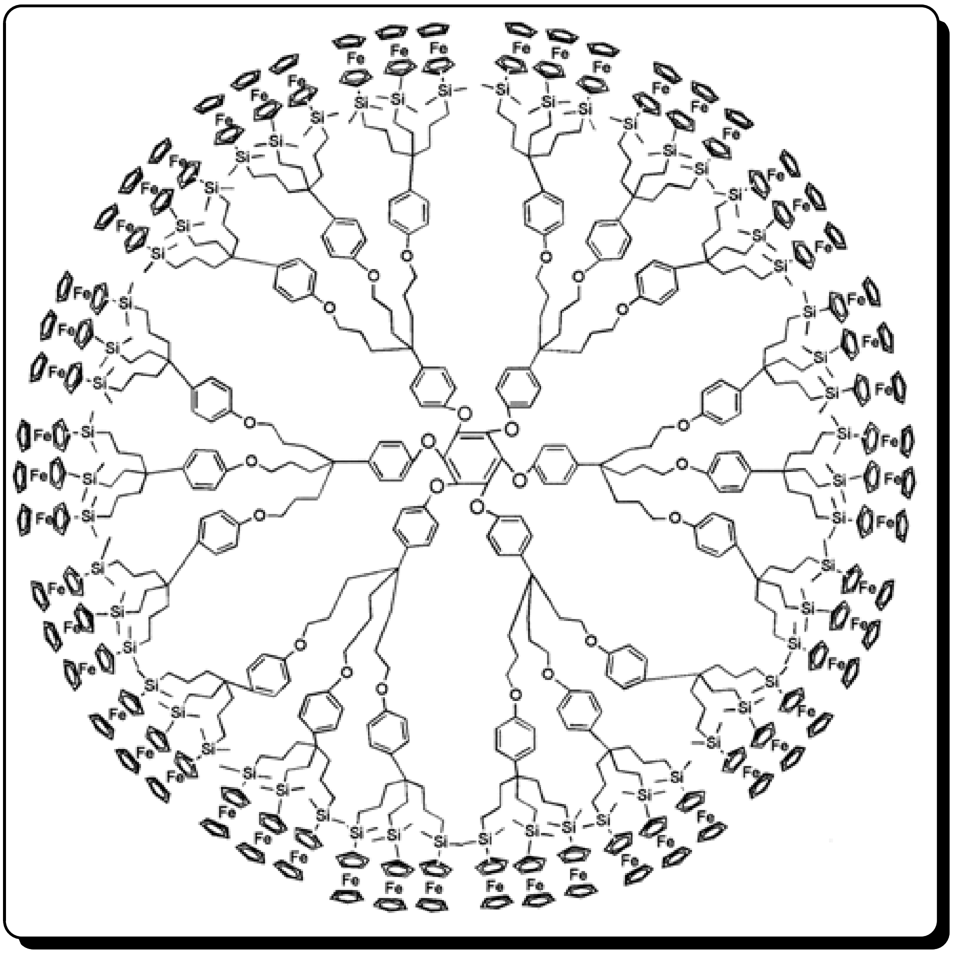


Chart 2: A 54 ferrocene dendrimer

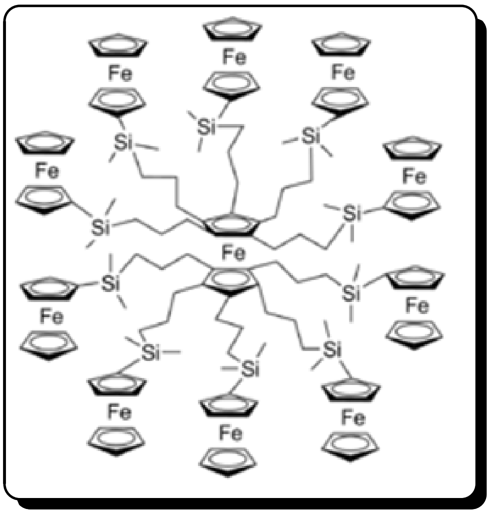


Chart 3: Decaferrocenyl ferrocene

1.6.4 Trimethylsilylchalcoginide reagents for multi ferrocene assemblies :

J. F. Corrigan and group have found that well-defined silylated chalcogen reagents can be used as useful supports for polyferrocenyl assemblies.[29a-g] The silylated reagents are shown to be very effective at incorporating a tailored surface onto metal-chalcogen clusters. Silylated chalcogen reagents of the type $FcESiMe_3$ (Fc=Ferrocene; E = S, Se, Te) (chart 4) are soluble in most common organic solvents and allows for homogeneous reaction conditions and thus have the benefit of introducing various functionalities, into metal-chalcogen architectures.

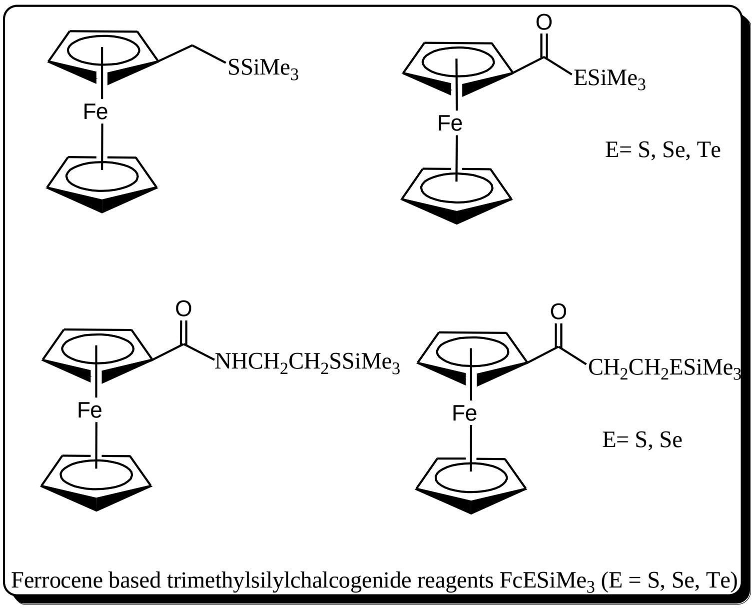


Chart 4: Ferrocene based trimethylsilylchalcogenide reagents

These silylated reagents react with metal salts through the thermodynamically favorable formation of $XSiMe_3$ (X = Cl, OAc) to yield metal–chalcogenolate (M–ER) and chalcogenide(M–E) bonds (E = S, Se, Te). Importantly, the soluble $XSiMe_3$ does not obstruct the formation and crystallization of the nano-sized cluster complexes. The size of the cluster product attained in the reactions of silylated chalcogen reagents with metal salts often depends on the ratio of starting reagents, the steric demands of the chalcogenolate ligand and that of ancillary ligands used. The tunability of the substituent R presents the opportunity to control the characteristics of the ligands that stabilize the surface of the cluster and allow the incorporation of the chemical functionalities.

Metal–chalcogenolate supported multiferrocene assemblies are readily prepared in a reaction involving a silylated ferrocene–chalcogen reagent and a metal salt. Synthesis and structural characterization of a fascinating molecular cluster built on Ag_2S framework $[Ag_{48}(\mu_4\text{-}S)_6(\mu_{2/3}\text{-}SCH_2Fc)_{36}]$ and $[Ag_{14}(PPh_3)_6S\text{-}(SCH_2CH_2O(O)CFc)_{12}]$ anchoring thirty six ferrocenes and twelve ferrocenes have been reported (scheme 8,9). In fact till date these are the largest multiferrocene architectures that has been characterized by using single crystal X-ray diffraction technique (figure 16, 17).

$$(Ph_3P)_2\,.\,AgoAc + FcCH_2SSiMe_3 \longrightarrow [Ag_{48}(\mu_4\text{-}S)_6\,(\mu_{2/3}\text{-}SCH_2Fc)_{36}] + OAcSiMe_3 + (FcCH_2)_2S$$

Scheme 8

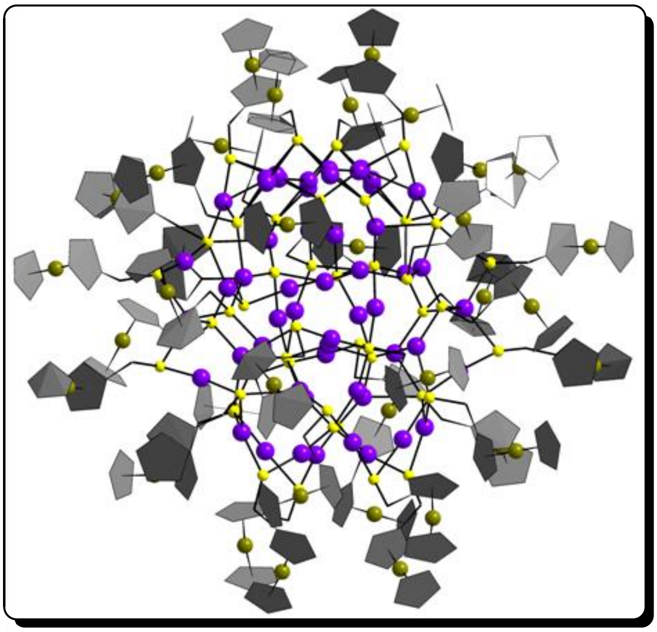


Figure 16: ball and stick representation of $[Ag_{48}(\mu_4\text{-}S)_6(\mu_{2/3}\text{-}SCH_2Fc)_{36}]$

$$(Ph_3P)_2\,.\,AgoAc + Fc(CO)OCH_2CH_2SSiMe_3 \longrightarrow [Ag_{14}(PPh_3)_6S\text{-}(SCH_2CH_2O(O)CFc)_{12}]$$

Scheme 9

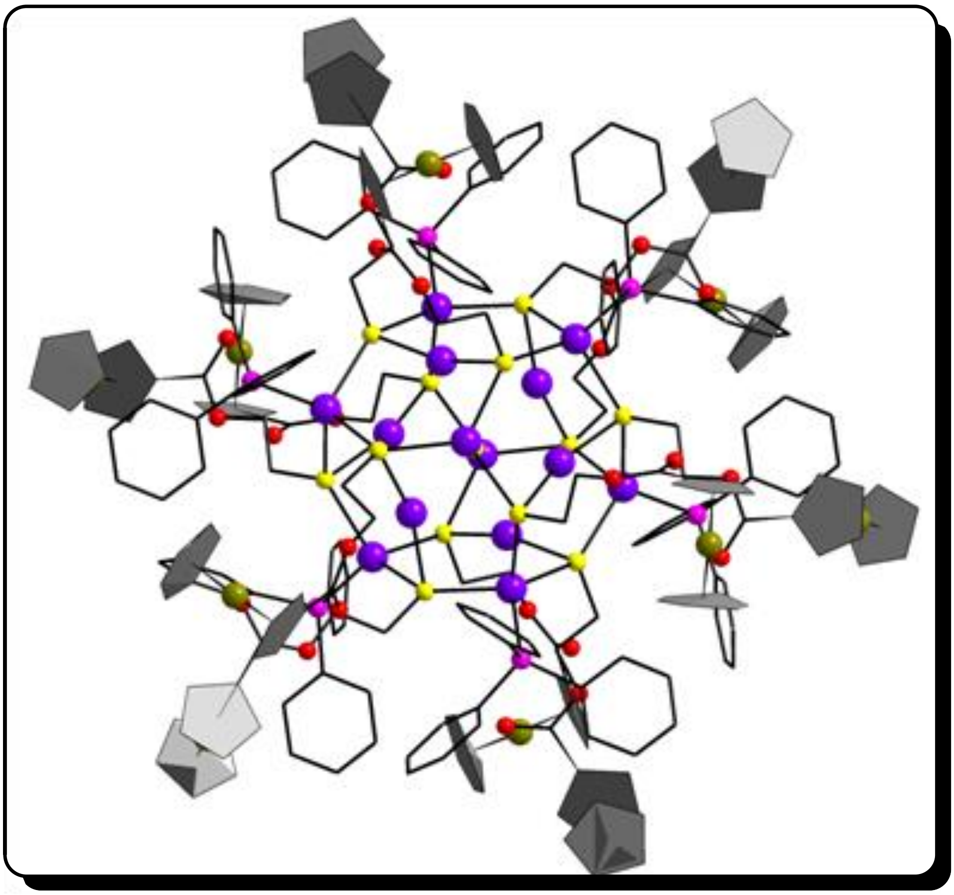


Figure 17: ball and stick representation of $[Ag_{14}(PPh_3)_6S\text{-}(SCH_2CH_2O(O)CFc)_{12}]$

1.6.5 Ring opening polymerization (ROP) of strained Metallocenophanes:

ROP reactions usually takes place via a chain growth mechanism and therefore represent a particularly attractive route for the preparation of high molecular weight poly(ferrocenes). A key requirement for a classical ROP process is a strained cyclic monomer. Metallocenophanes have been known since 1975 in which a single atom bridges the two cyclopentadienyl ligands (i.e metallocenophanes) possess strained ring-tilted structures (chart 5). Such species possess tilt-angles between the planes of the Cp ligands of 6-32˚, but no successful ROP reactions for these species had been reported until very recently.

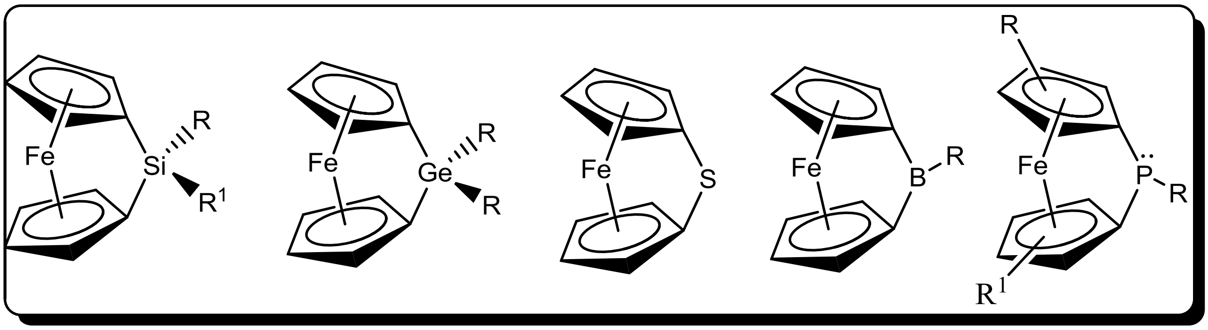
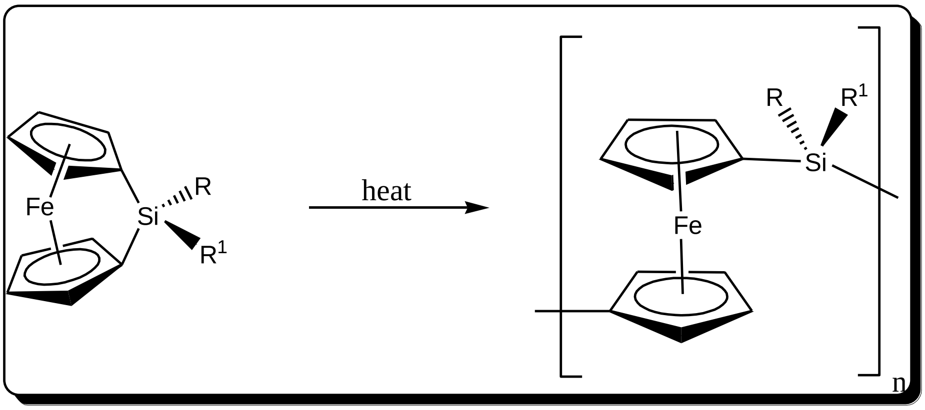


Chart 5: Various strained Metallocenophanes

1.6.6 Thermal ring opening polymerization of Silicon- Bridged Ferrocenophanes:

The first examples of the use of ROP of strained metallocenophanes to prepare high molecular weight poly(metallocenes) (Mn > 10^5) involved organosilane-spacers.[30a,b] Specifically, poly(ferrocenylsilanes) such as ($R = R^1 = Me$) were prepared via the thermal ring-opening polymerization of strained, ring-tilted ferrocenophanes (scheme 10). These high polymeric materials were prepared by heating the silicon bridged ferrocenophanes at 130-220˚C in evacuated tubes.[31] The thermal ROP route is very general and a wide range of glassy, semicrystalline, or elastomeric poly- (ferrocenylsilanes) have been prepared from silicon bridged ferrocenophanes with a range of different substituents at silicon or the cyclopentadienyl rings. These polymers have been fully characterized using a range of spectroscopic and analytical methods and their molecular weights (Mw) which have been established by absolute methods such as low angle laser light scattering, lie in the 10^5-10^6 range with polydispersity indices of ca. 2.



Scheme 10: Thermal ring opening polymerization of strained Metallocenophanes

1.6.7 Thermal ring opening polymerization of other strained Ferrocenophanes:

Later this thermal ROP methodology has been extended to other strained metallocenophanes (chart 6) in making high molecular weight poly(ferrocenylgermanes),[32] poly(ferrocenylphosphines),[33] poly(ferrocenylsulfides)[34,35] and poly(ferrocenylboranes)[36,37] have been reported.

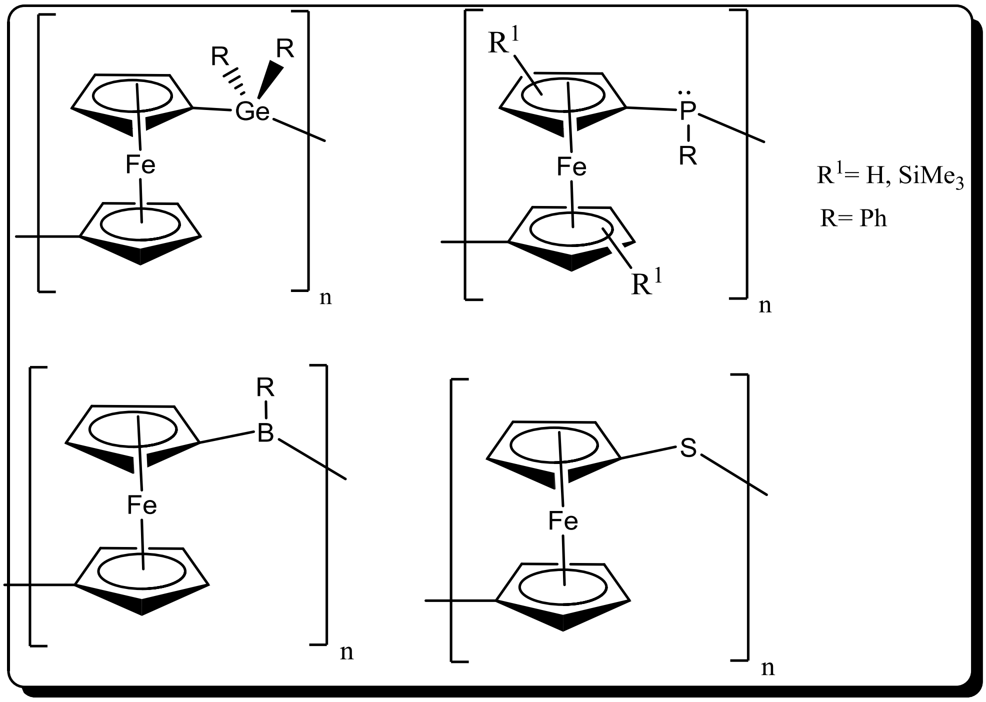
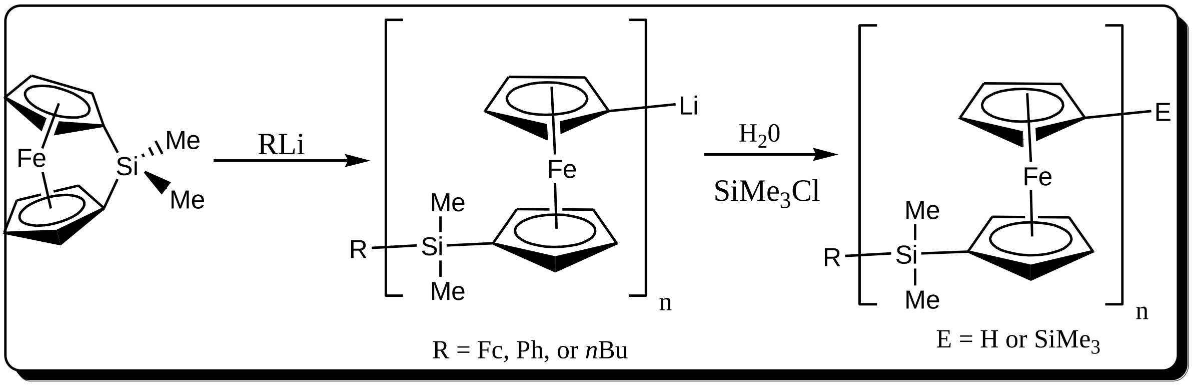


Chart 6: Various strained polymetallocenophanes

1.6.8 Anionic Ring-Opening Polymerization of Strained Metallocenophanes:

The first anionic ROP reactions for metallocenophanes were reported in 1994. Initially it was shown silicon-bridged ferrocenophanes (R = R^1= Me) were oligomerized with lithioferrocene as initiator,[38] but later they found by decreasing the initiator concentration, poly(ferrocenylsilanes) can be produced. Moreover, using extremely pure monomer and rigorous reaction conditions the anionic ROP was shown to be living.[39] Poly(ferrocenylsilanes) with controlled molecular weights (Mw) up to ca. 120000 and with very narrow polydispersities (PDI= 1.05- 1.10) were formed depending on the monomer-to-initiator ratio. Further quenching of the living polymer with either $SiMe_3Cl$ or H_20 yielded the H- or $SiMe_3$-capped poly-(ferrocenylsilanes) (scheme 11).



Scheme 11: Anion ring opening polymerization of strained Metallocenophanes

1.6.9 Organostannoxane-Supported Multiferrocenyl Assemblies:

Chandrasekhar et al have adopted a completely different and simple synthetic strategy to assemble multi-ferrocene units on strong stannoxane supports (scheme 12). This is based on the principles of organotin chemistry. Thus, the reaction of n-butylstannonic acid and n-BuSn(O)OH with either ferrocenecarboxylic acid or ferrocenylacetic acid afforded drum like hexa-ferrocene assemblies $[n\text{-}BuSn(O)OC(O)C_5H_4\text{-}Fe\text{-}C_5H_5]_6$ and $[n\text{-}BuSn(O)OC(O)CH_2C_5H_4\text{-}Fe\text{-}C_5H_5]_6$ in nearly quantitative yields (figure 18).[40a] Another interesting feature of this result is that it is a single-step synthesis which obtained from commercially available starting materials.

$$6\ BuSn(O)OH\ +\ 6\ FcCOOH\ \xrightarrow[80°C]{C_6H_6}\ [\{BuSn(O)OC(O)Fc\}_6]\ +\ 6H_2O$$

Scheme 12

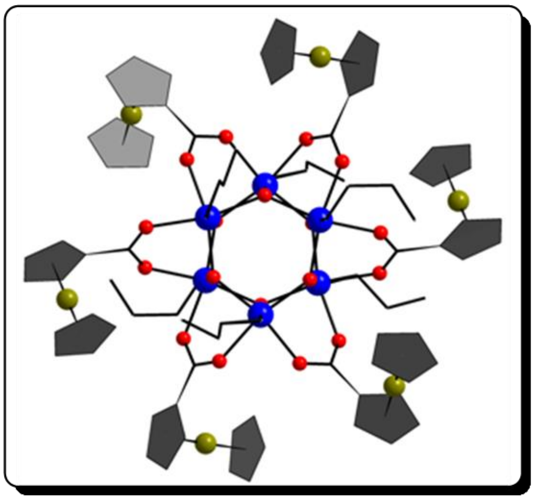


Figure 18: Ball and stick model of $[n\text{-}BuSn(O)OC(O)C_5H_4\text{-}Fe\text{-}C_5H_5]_6$

Later J. F. Ma intended to prepare new multiferrocene compounds based on tin–oxygen cluster by using solvothermal methods and they reported a new multiferrocene compound in which the six ferrocene units are held together by an mixed valence Sn^{II}_4–$Sn^{III}_4O_4$ cluster for the first time (scheme 13). The reaction of n-Bu_2SnO with 1,1'-ferrocenedicarboxylic acid in a 1:1 stoichiometry in toluene was carried out in a teflon-lined autoclave at 180˚C for four days. The reaction proceeded with complete dealkylation of nBu_2SnO, and the compound $Sn_8O_4L_6$ was obtained (figure 19).[41]

$$\text{n } Bu_2SnO \quad + \quad H_2L \quad \xrightarrow[180°C]{\text{Toluene}} \quad Sn_8O_4L_6 \quad (L = 1,1^1\text{- Ferrocenedicarboxylic acid})$$

Scheme 13

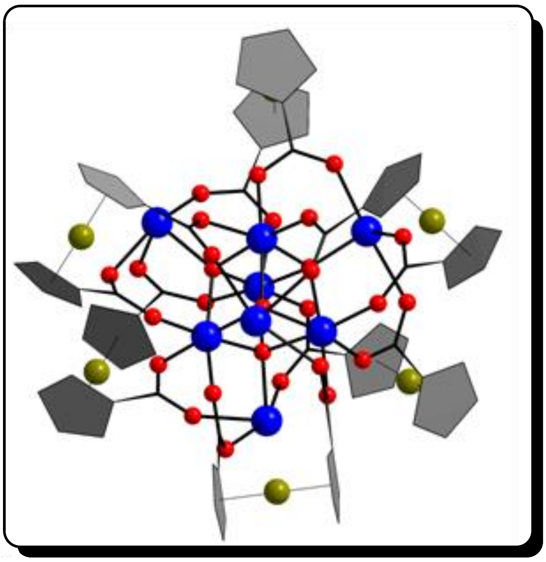
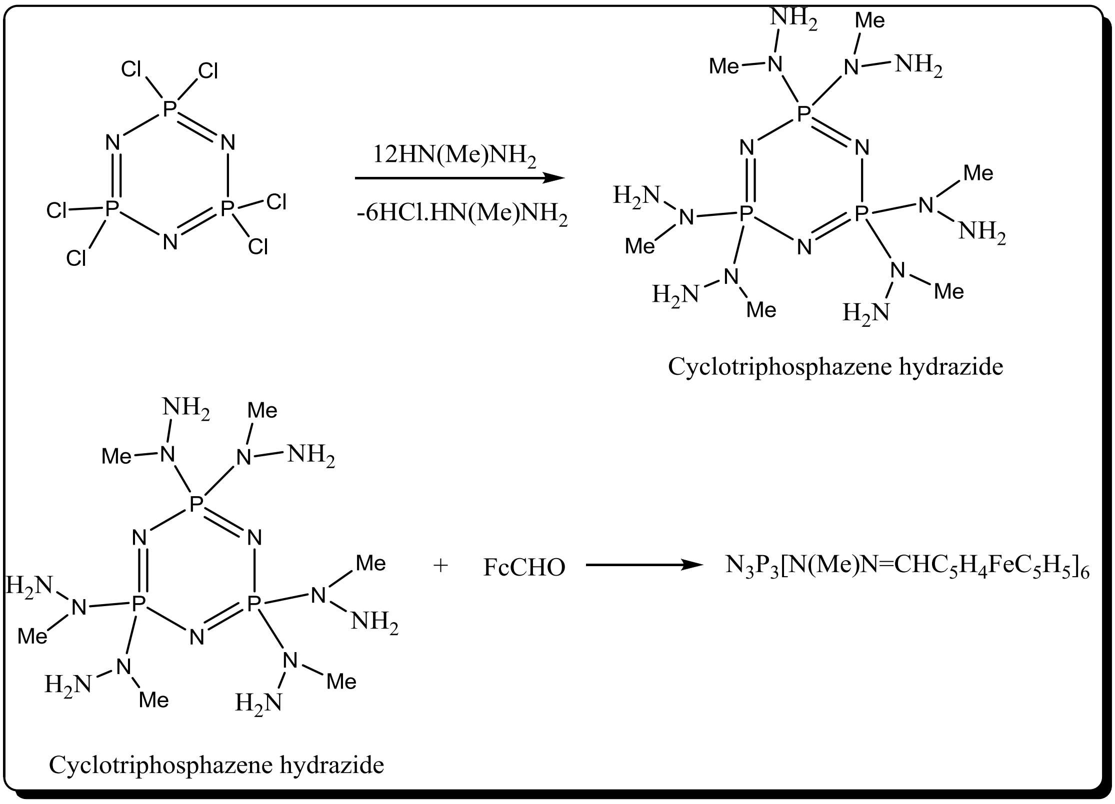


Figure 19: Hexa ferrocene assembly on tin oxo core

1.6.10 Cyclophosphazene Hydrazides as Scaffolds for Multi-Ferrocenyl Assemblies:

More convenient synthetic strategy of using cyclophosphazenes as scaffolds for supporting ferrocenes has been reported by Chandrasekhar et al. Their method consists of first converting chlorocyclotriphosphazenes to the corresponding cyclotriphosphazene hydrazides which contain reactive -NH_2 groups. These hydrazides can further treated with ferrocene carboxaldehyde to afford the corresponding hydrazones (scheme 14). This strategy allowed synthesizing a cyclophosphazene derivative containing six ferrocene units (figure 20).[42]



Scheme 14

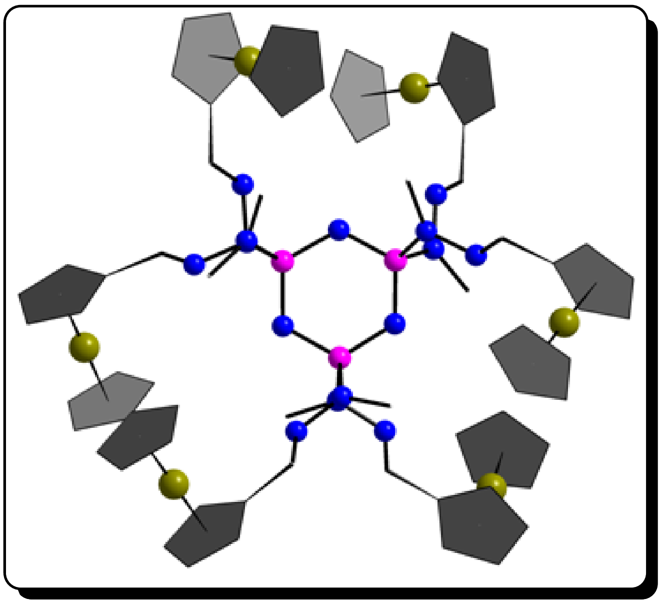
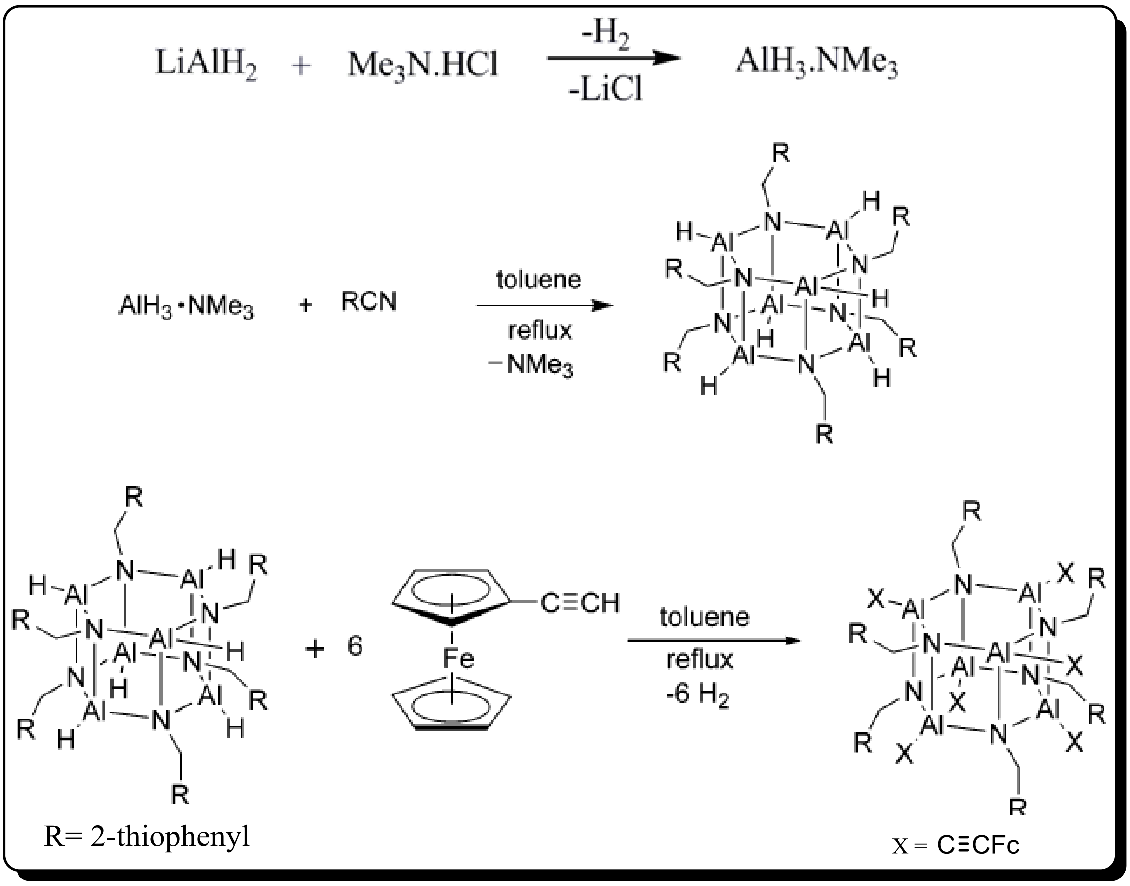


Figure 20: Ball and stick model of $N_3P_3[N(Me)N{=}CHC_5H_4FeC_5H_5]_6$

1.6.11 Aluminium Nitride (Al-N) and Aluminium Carbide (Al-C) Frame works for Ferrocene Assemblies:

H. W. Roesky and group synthesized the first Al-N cluster containing an assembly of six ferrocenylacetylene moieties and structurally characterized. The reaction proceeds in three steps, first step involves the making of $AlH_3.NMe_3$, later hydroalumination of RCN with $AlH_3.NMe_3$ in refluxing toluene resulted in $(HAlNCH_2R)_6$ (scheme 15). The reaction between stoichiometric amounts of $(HAlNCH_2R)_6$ and ferrocenylacetylene under reflux conditions in the presence of toluene leads to the formation of ferrocene assembly containing Al-N skeleton frame work (Figure 21).[43] All six hydridic hydrogens were replaced by six ferrocenylacetylene moieties. The reaction mixture was refluxed until the evolution of H_2 had ceased. The product is obtained in quantitative yields. The Al-N framework remained intact during the substitution. These are the first model compounds for the fixation of metal-containing ligands on an Aluminum Nitride cluster.



R= 2-thiophenyl

X = C≡CFc

. **Scheme 15:** Construction of ferrocene assembly of aluminium nitride frame work

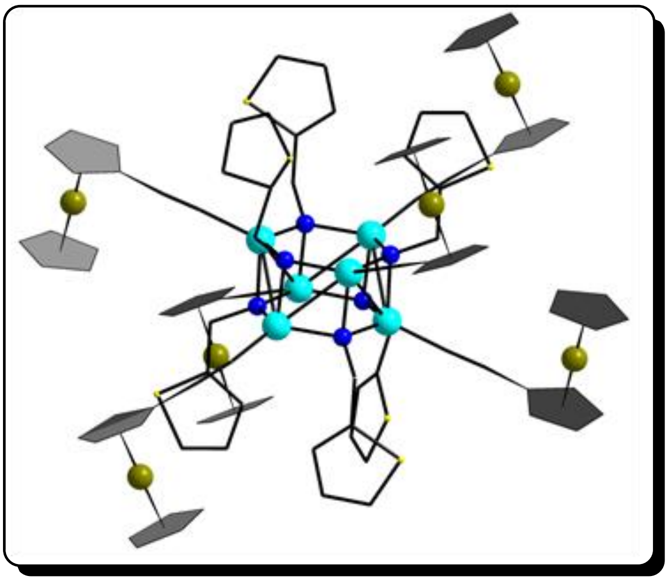
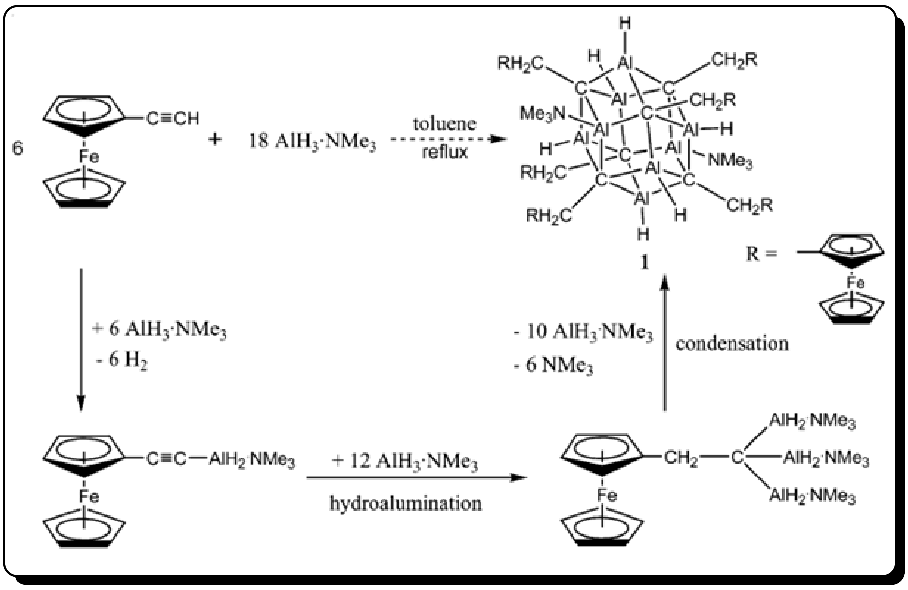


Figure 21: Hexa ferrocene assembly of Al-N frame work

The same group shows the Al–C frame works supporting multi ferrocene assemblies. The reaction of ferrocenylacetylene with an excess of $AlH_3.NMe_3$ in refluxing toluene resulted in the formation of $[(AlH)_6(AlNMe_3)_2(CCH_2C_5H_4FeC_5H_5)_6]$.[44] During the reaction, evolution of NMe_3 and H_2 was observed.



Scheme 16: scheme showing ferrocene assembly on aluminium carbide frame work

The mechanism of hydroalumination of ferrocenylacetylene is believed to be, as in scheme16 the first step is predicted as the formation of $FcC\equiv CAlH_2NMe_3$ accompanied by the elimination of H_2. Subsequent hydroalumination of this intermediate would lead to the formation of $FcCH_2C(AlH_2.NMe_3)_3$, which undergoes a condensation reaction to give the carballane containing six ferrocenes on the periphery of the frame work (figure 22).

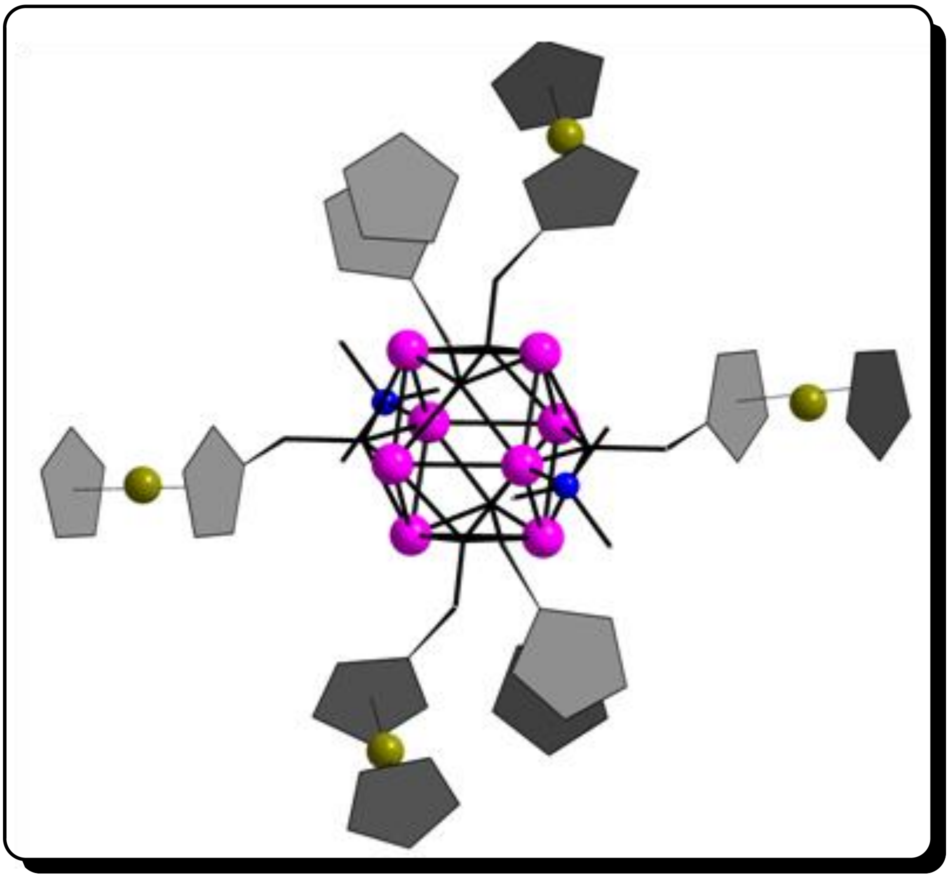


Figure 22: Hexa ferrocene assembly of Al-C frame work

1.6.12 Transition metal cores for multi ferrocene assemblies:

Making use of covalent bonds, interesting examples based on aromatic units or dendritic architectures bearing several ferrocenyl groups have been explained in the above context. Concerning the incorporation of the ferrocenyl moiety through coordination bonds, the ferrocene group must contain at least one coordinating site. Many ferrocene derivatives bearing a variety of coordination sites have been prepared (chart 7) and used as ligands in the construction of homo- and heterometallic complexes.[45] Some the reported derivatives include strongly coordinating groups such as pyridyl, pyrimidyl, pyrazole and carboxylic acid groups. Surprisingly, the tendency of the carbonyl group to form coordination bonds with metal centres has also been reported. The list of ferrocenyl ligands containing coordination sites and their reactions (scheme 17-22) with transition metals are listed below (figure 23-28).

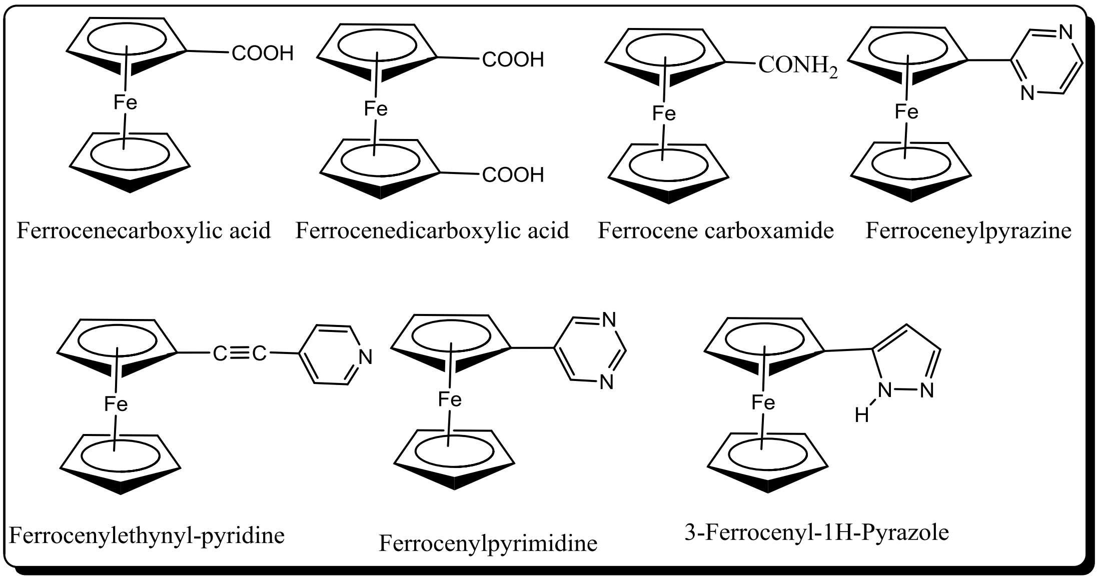
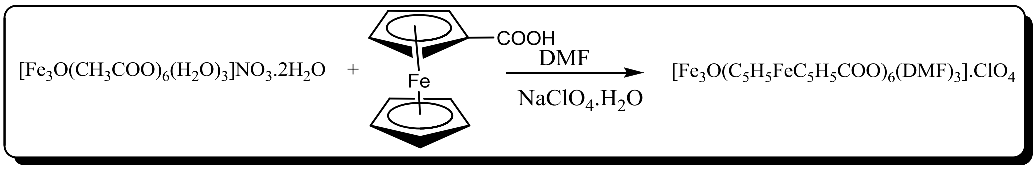


Chart 7: Ferrocenyl ligands bearing a variety of coordination sites



$$[Fe_3O(CH_3COO)_6(H_2O)_3]NO_3.2H_2O + C_5H_5FeC_5H_4COOH \xrightarrow[NaClO_4.H_2O]{DMF} [Fe_3O(C_5H_5FeC_5H_5COO)_6(DMF)_3].ClO_4$$

Scheme 17

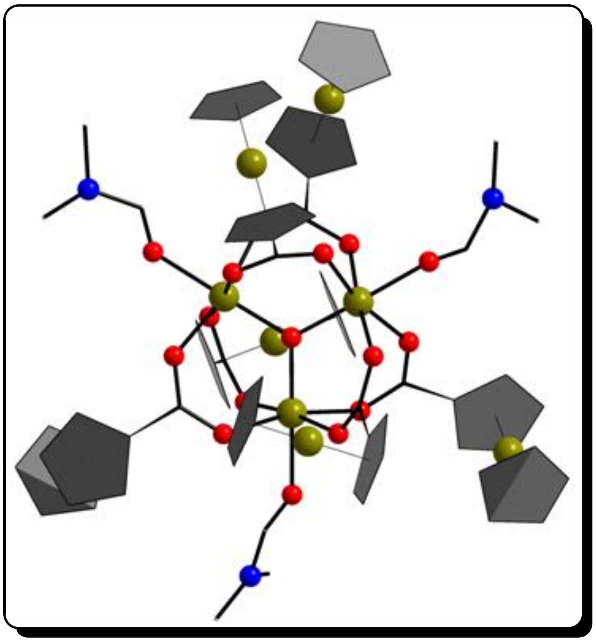
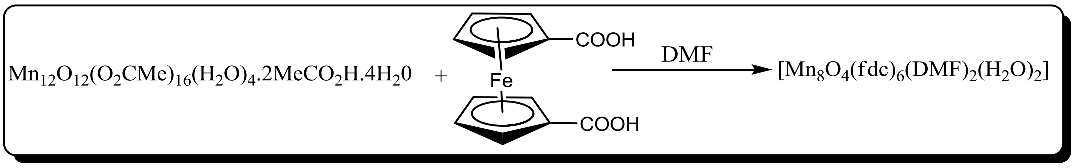


Figure 23: Ball and stick model of $[Fe_3O(C_5H_5FeC_5H_5COO)_6(DMF)_3].ClO_4$



Scheme 18

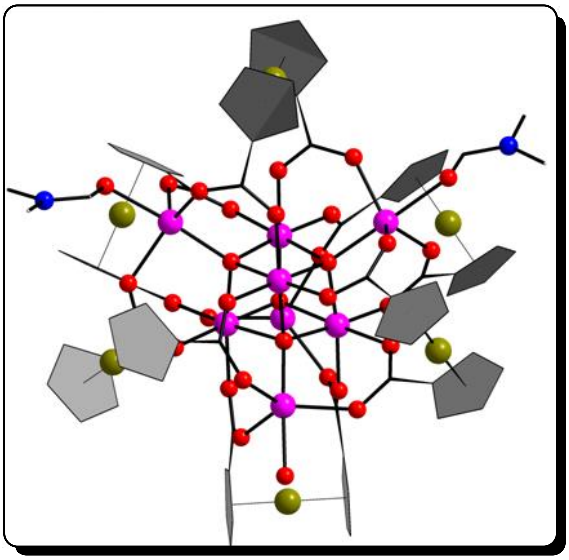
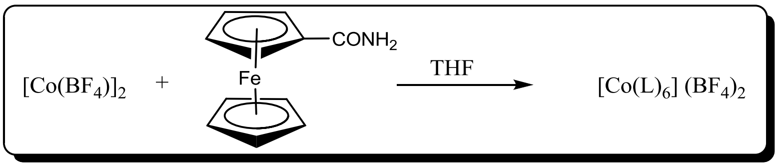


Figure 24: Ball and stick model of $[Mn_8O_4(fdc)_6(DMF)_2(H_2O)_2]$



Scheme 19

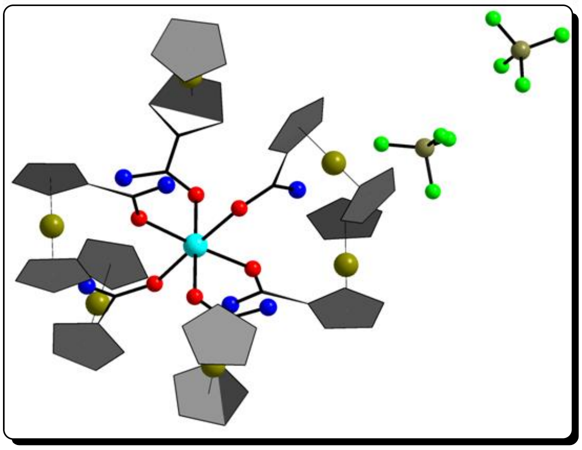
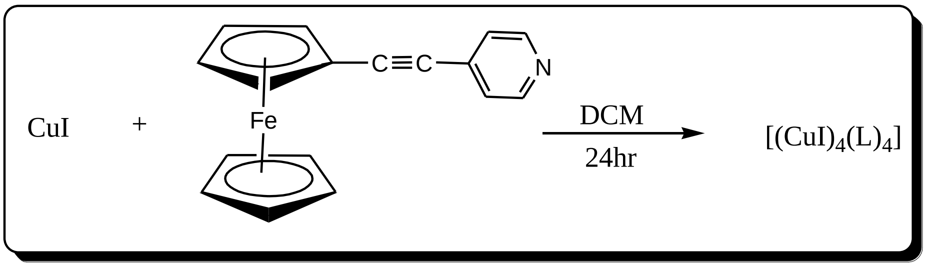


Figure 25: Ball and stick model of $[Co(L)_6(BF_4)_2]$



Scheme 20

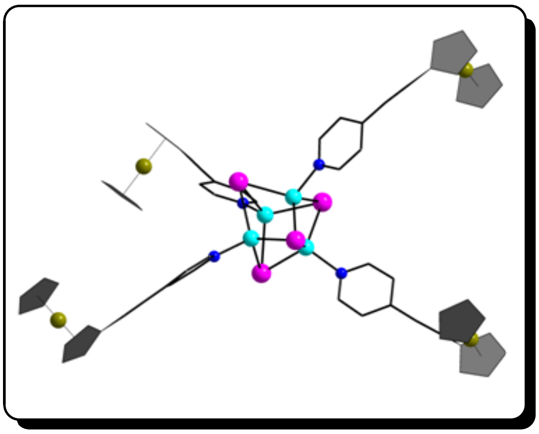
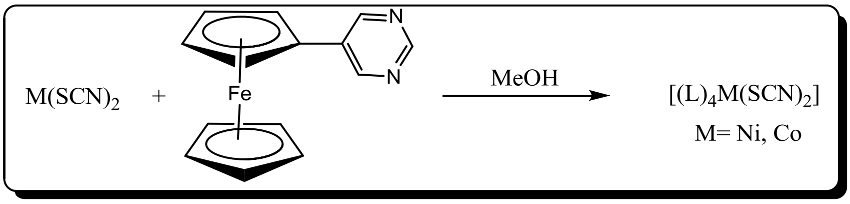


Figure 26: Ball and stick model of $[(CuI)_4(L)_4]$



Scheme 21

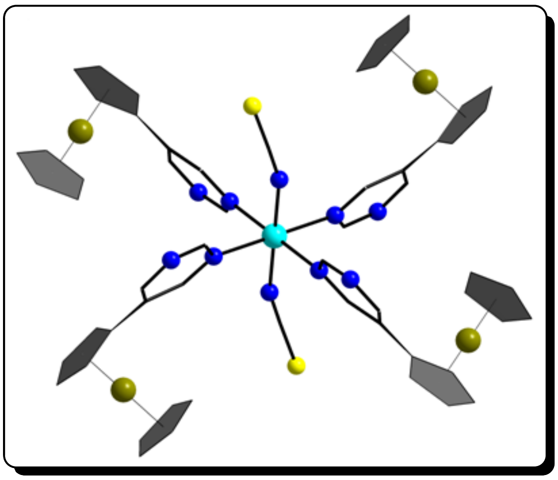
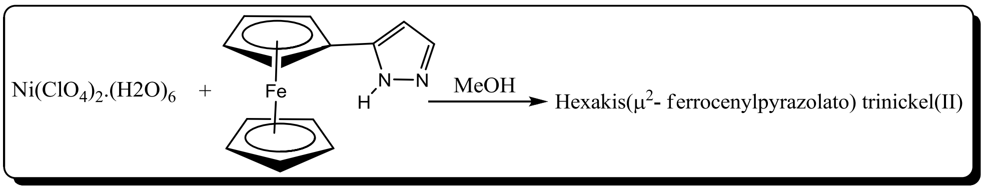


Figure 27: Ball and stick model of $[M(SCN)_2(L)_4]$



Scheme22

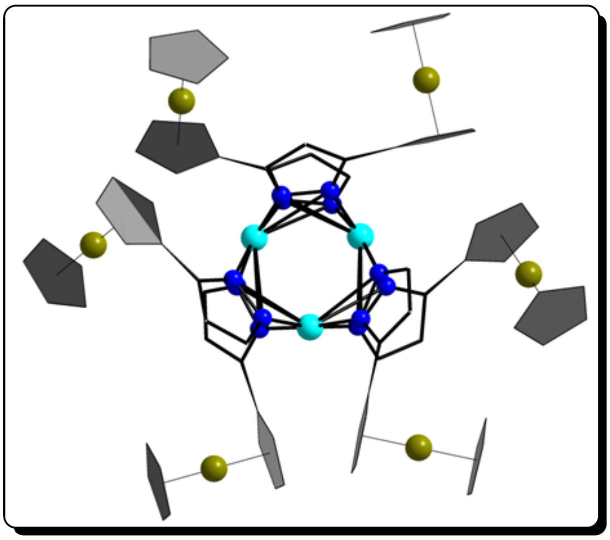
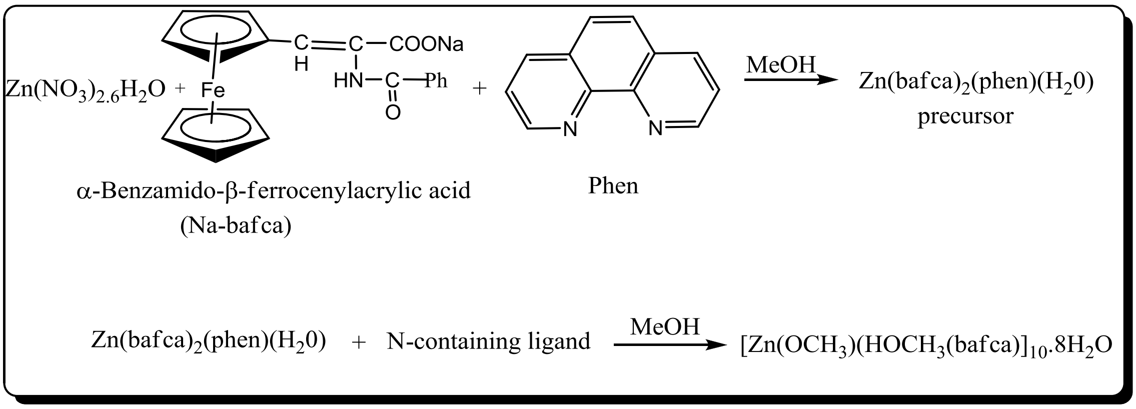


Figure 28: Ball and stick model of hexakis(μ_2-ferrocenylpyrazolato) trinickel(II)

1.6.13 Oligimerization for self assembly of ferrocenes from multifunctional precursors:

A unique multifunctional precursor complex $Zn(bafca)_2(phen)(H_2O)$ was synthesized by Liu etal (scheme 23). whose multifunctional behavior is confirmed by its reactions with organic ligands or metal ions. In the presence of basic N-containing ligands precursor acts as an acceptor and takes part in the oligimerization in methanol to produce a discrete supramolecular species, $[Zn(OCH_3)(HOCH_3)(bafca)]_{10}$ $8H_2O$,[46] containing ten ferrocene units which is a novel circular decanuclear Zn(II) complex with a wheel structure (figure 29); while in the presence of $Cd(NO_3)_2$, the precursor acts as a donor and experience an unusual central metal ion exchange reaction (scheme 24), resulting in a new binuclear Cd(II) skeleton, $[Cd(bafca)_2(phen)]_2$ $8H_2O$ (figure 30), similar decanuclear Cd(II) complex, $[Cd(OCH_3)(HOCH_3)(bafca)]_{10}$ $8H_2O\cdot 6CH_3OH$, is obtained by using the similar method to that for the preparation of zinc. The results indicate that the oligimerization of metal-carboxylate complexes with methanol under basic conditions is a relatively reliable synthetic route to produce wheel structures. In addition, the important function of N-containing ligands in the formation of complexes is verified further by the strong electrochemical responses of precursors to 1,1′-(1,4-butanediyl)bis-1Hbenzotriazole (bbbt) (N-Containing ligand).



Scheme 23

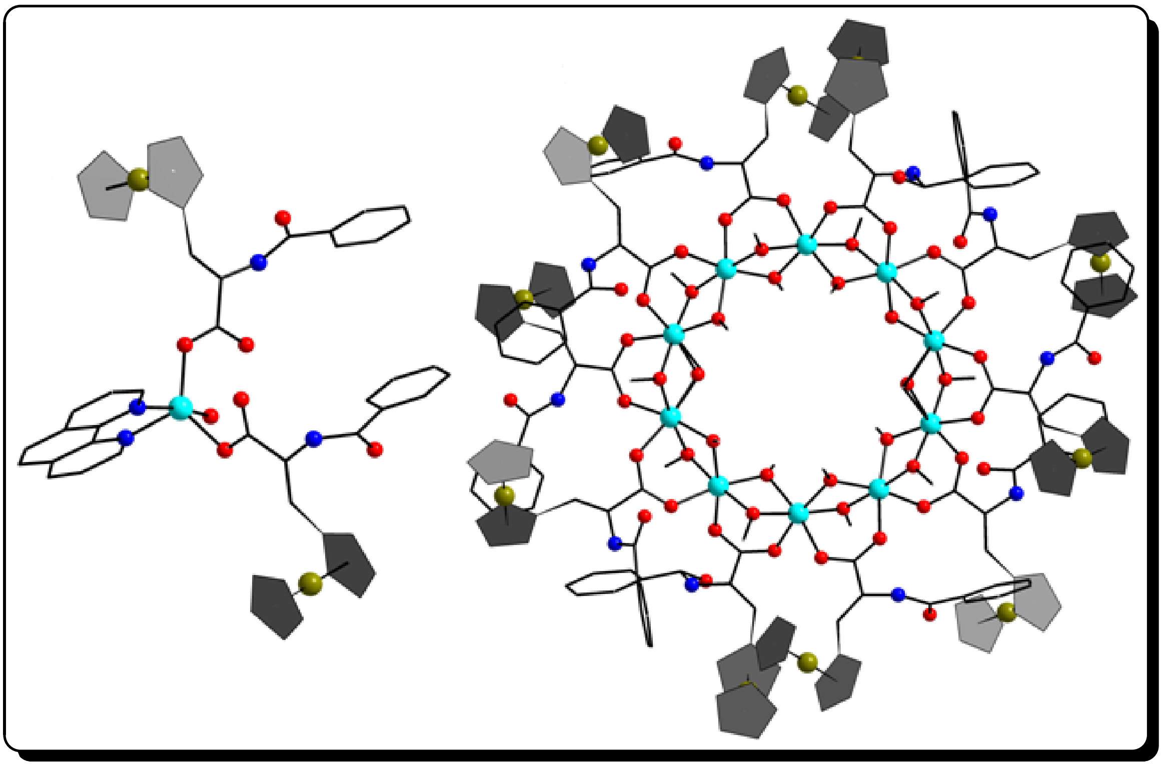


Figure 29: Ball and stick model of $[Zn(bafca)_2(phen)_2(H_20)$, $[Zn(OCH_3)(HOCH_3)(HOCH_3(bafca)]_{10}.8H_20$,

$Cd(NO_3)_24H_2O$ + $Zn(bafca)_2(phen)(H_20)$ $\xrightarrow[H_2O]{MeOH}$ $[Cd(bafca)_2(phen)]_2.\ 8H_20$

precursor

$[Cd(bafca)_2(phen)]_2.\ 8H_20$ + N-containing ligand $\xrightarrow{MeOH}$ $[Cd(OCH_3)(HOCH_3(bafca)]_{10}.8H_2O$

Scheme 24

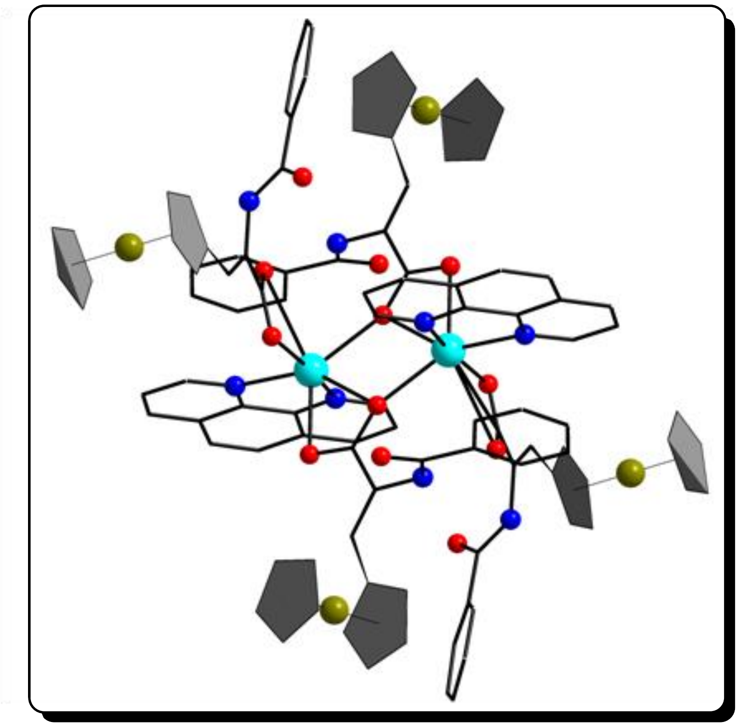
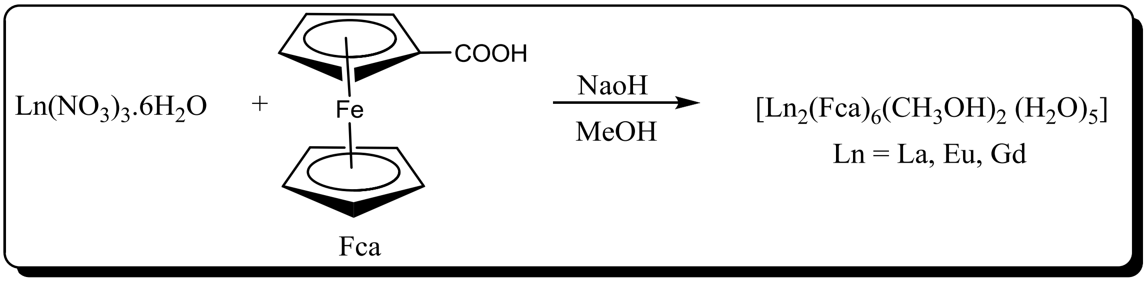


Figure 30: Ball and stick model of $[Cd(bafca)_2(phen)]_2.8H_2O$

1.6.14 Lanthanide oxide surfaces supporting Multi ferrocene assemblies:

Some groups focussed on multi-nuclear lanthanide oxide core as useful inorganic frameworks to support the ferrocene units.

Dong etal shows that the reaction of lanthanide ions with the ferrocene carboxylic acid (scheme 25) resulted in three isostructural heterodinuclear windmill-shaped compounds $Ln_2(fca)_6(CH_3OH)_2(H_2O)_5$ [(Ln) = La, Eu, and Gd] (figure 31) by simply diffusing the solutions of lanthanide ions into the mixture of ferrocene carboxylic acid and NaOH, respectively.[47]



Scheme 25

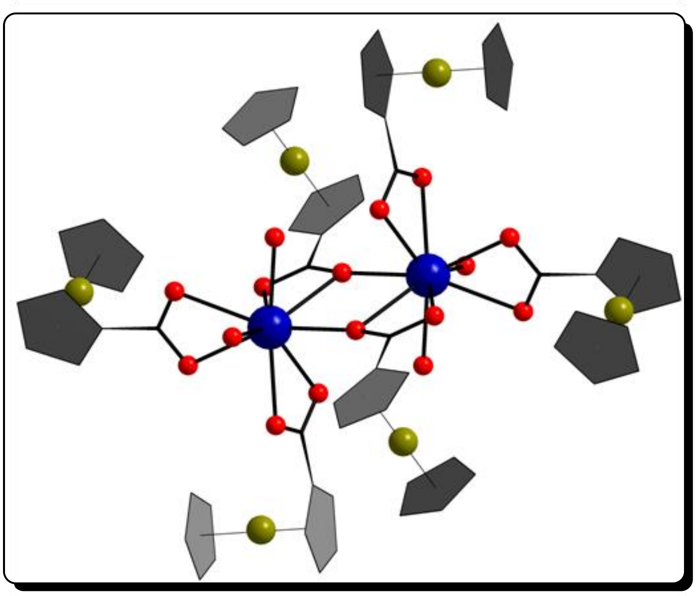
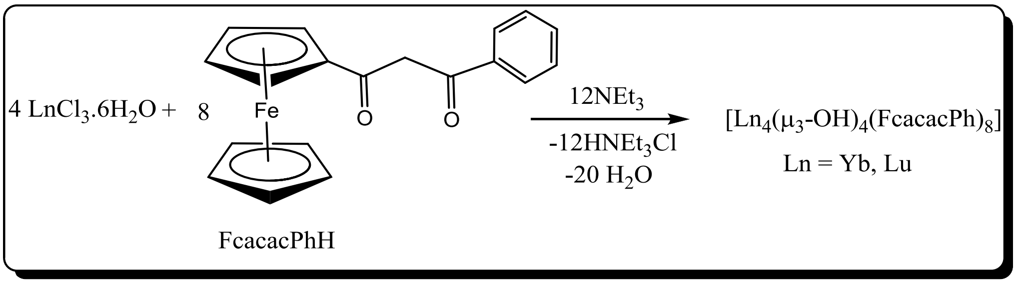


Figure 31: Ball and stick model of $[Ln_2(Fca)_6(CH_3OH)_2(H_2O)_5]$

Although β-Diketonates have been investigated in detail for their ligating ability towards lanthanides and their solid state structures are well understood, the use of ferrocene β-diketonates as ligands towards lanthanides are rare.



Scheme 26

Roesky et al investigated the reactions of lanthanide trichloride hexahydrates $[LnCl_3{\cdot}6H_2O]$ (Ln = Yb, Lu) with two equivalents of benzoylferrocenylmethane, (scheme 26) which resulted in the tetranuclear lanthanide hydroxo clusters $[Ln_4(\mu_3\text{-}OH)_4(FcacacPh)_8]$[48] (Ln = Yb, Lu. FcacacPh = benzoylferrocenoylmethanide). X-ray structural analysis reveals that the compounds were made up of a distorted tetranuclear lanthanide Ln_4O_4 cubane core consisting of four μ_3-oxygen atoms while the eight FcacacPh ligands build up the peripheral part of the cluster (figure 32).

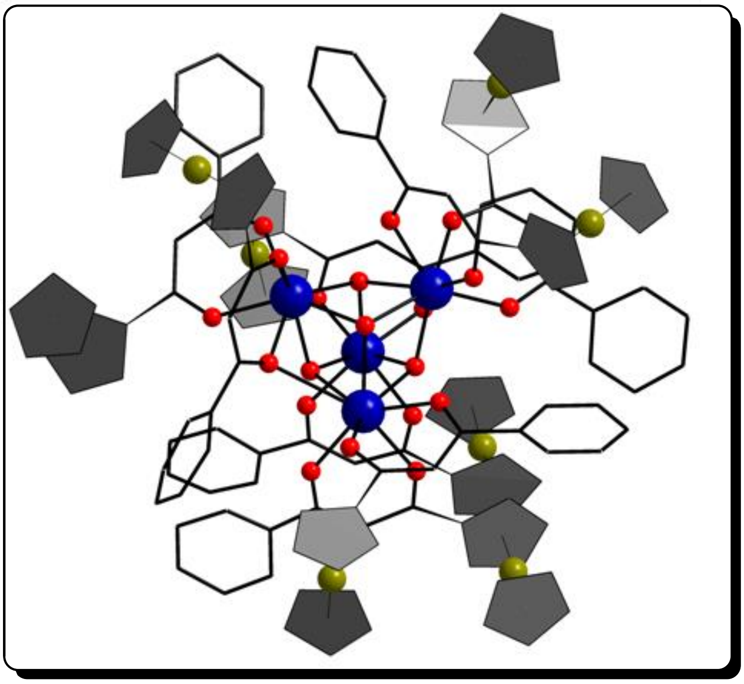


Figure 32: Ball and stick model of [$Ln_4(\mu_3\text{-}OH)_4(FcacacPh)_8$]

The preceeding sections give in detail about what are SMM's and why one prefers lanthanide for synthesizing newer SMM's. The main objective of the work reported in chapter **2** is to synthesize lanthanide based oxo cluster anchoring ferrocenes on the periphery, hence idea being assembling bifunctional molecular architectures. The introduction part clearly shows how by self assembly process metal-oxo cluster frameworks have been used for anchoring ferrocenes. We have utilized the Ln-O cores formed by reaction of Lanthanum halides hydrates with β-diketones for synthesizing newer Ln-O clusters anchoring ferrocenes. The β-diketones used contain ferrocenes as one of the R groups and hence help in anchoring ferrocenes on the Ln-O surface. The details of the work done, the structural characterization, magnetism, CV studies and U.V measurements are detailed in chapter **2**.

1.7 References:

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Redox Shield Enfolding a Magnetic Core

Chapter 2

Abstract: Ferrocenyl betadiketones were reacted with hydrated lanthanide trihalides in presence of a base to yield solids whose single crystal characterization revealed the formation of nona- and tetranuclear lanthanide oxo-hydroxo clusters. Magnetism studies revealed that **2.1** shows slow relaxation of magnetisation at lower temperatures. Cyclic voltammetry studies of **2.1** and **2.2** reveal electrochemically stable quasi reversible oxidation systems whereas **2.3-2.6** showed irreversible nature. Single crystal X-ray structure of **2.1** show the presence of sixteen ferrocenes anchored on a sandglass shaped lanthanide oxo-hydroxo cluster. This is apparently the second largest ferrocene assembly reported till date and the first example wherein redox active ferrocenes are appended on a lanthanide cluster which displays SMM behavior. The dimensions of the isolated discrete molecular clusters fall in the nano range.

2.1 Introduction:

Periphery and core functionalization of macromolecules / nano particles with redox active ferrocene[1] and synthesizing new SMMs[2] are two areas of contemporary research owing to the potential applications of these systems in the field of optics, electronics and in designing new generation magnetic data storage devices.[3] Multiferrocene architectures have been assembled primarily by using coordination driven self assembly approach[4] or by following multi step synthetic pathways for synthesizing dendrimers decorated with ferrocenyl periphery.[5] Recently synthesis and structural characterization of a fascinating molecular cluster built on Ag_2S framework $[Ag_{48}(\mu_4\text{-}S)_6(\mu_{2/3}\text{-}SCH_2Fc)_{36}]$ anchoring thirty six ferrocenes have been reported.[6] In fact till date this is the largest multiferrocene architecture that has been characterized by using single crystal X-ray diffraction technique. By reacting silylated ferrocenyl chalcogenide reagents with metal acetates, it has been shown that twelve and ten ferrocenes can also be anchored on silver sulfide cluster surfaces.[7] Various other metal oxo clusters anchoring multiferrocene assemblies[8] and specifically a cubane lanthanide oxo cluster anchoring ferrocenes are known in the literature.[9] In this chapter, efforts and results obtained thereof towards synthesizing bi-functional / multiferrocene architectures are presented. Synthesis, structure, magnetism (for **2.1**, **2.3**) and cyclic voltammetry studies of $[Dy_9(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_8(\mu\text{-}Fca)_8(Fca)_8][HN(C_2H_5)_3]$ **2.1** $[Lu_4(\mu_3\text{-}OH)_4(\mu\text{-}Fctp)(Fctp)_7]$ **2.2** $[Ln_4(\mu\text{-}OH)_2(\mu\text{-}OCH_3)_4(CH_3OH)_2(Fctfa)_6]$ Ln = Yb (**2.3**), Lu (**2.4**), and $[Ln_4(\mu\text{-}OH)_2(\mu\text{-}OCH_3)_4(CH_3OH)_2(Fcpfa)_6]$ Ln = Yb (**2.5**), Lu (**2.6**) are presented herein.

2.2 Experimental Section

2.2.1 General Information:

A Thermo Finnigan Flash EA1112 series elemental analyzer was used for the microanalyses (C, H, N). The infrared spectra of all the compounds were recorded in KBr pellets on a Jasco-5300 FT-IR spectrophotometer. Transmission electron microscope (TEM) imaging and selected area electron diffraction were carried out on a Tecnai G2FEI F12 TEM at an accelerating voltage of 200 kV. Carbon–coated copper grid loaded with crystalline powder sample have been used to record the TEM images. Mass spectra was recorded on HRMS-ESI-TOF-MAXIS BRUKER instrument. Cyclic voltammetric measurements for compounds (**2.1**-**2.6**) were performed with the help of a CH-Instruments model 620A electrochemical analyzer using dimethylformamide solutions of the complexes containing tetrabutylammonium per chlorate (TBAP) as the supporting electrolyte. A platinum disk working electrode, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode were used in the three electrode measurements at 298 K under dinitrogen atmosphere. NETZSCH STA 409 PC model is used for thermogravimetric analysis (TGA) to examine the thermal stability. Ultraviolet / visible absorption spectra were recorded with a SHIMADZU U.V-3600 UV/VIS spectrometer. Magnetic measurements were carried out on polycrystalline sample (*circa* 30 mg) of **2.1** and **2.3** with a Quantum Design SQUID MPMS-XL magnetometer equipped with a 5 T magnet. Diamagnetic corrections were calculated using Pascal's constants and an experimental correction for the sample holder was applied.

The ferrocene β-diketone ligands were prepared according to the literature procedures[10]

2.2.2 Synthetic methodology:

Hydrated $LnCl_3$ [Ln = Dy (**2.1**), Lu (**2.2**), Yb (**2.3, 2.5**), Lu (**2.4, 2.6**)] and ligands (HFca, HFctp, HFctfa, HFcpfa) were dissolved in 20 ml of methanol; excess triehtylamine was added slowly stirring continued for 12 hrs at room temperature. The precipitate formed was filtered and washed with methanol. The crystals suitable for X-ray diffraction were grown from chloroform/hexane (**2.1**) toluene/hexane diffusion (**2.2**) and methanol/ hexane diffusion (**2.3-2.6**).

Compound 2.1: $DyCl_3.6H_2O$ 0.174g (0.46mmol), HFca 0.25g (0.92mmol), Et_3N 0.18g (1.85mmol). Yield: 0.15g (46%). IR (KBr cm^{-1}) : 3424(b), 3090(w), 1577(s), 1517(m), 1415(m), 1380(s), 1287(w), 1139(s), 1029(w), 958(s), 799(m), 777(s). Decompn temp: 251˚C. Elemental anal.cal. for $C_{230}H_{226}O_{43}NFe_{16}Dy_9$: C, 45.67; H, 3.76; N, 0.23. Found: C, 45.81; H, 3.71; N, 0.28.

Compound 2.2: $LuCl_3.6H_2O$ 0.143g (0.36mmol), HFctp 0.25g (0.73mmol), Et_3N 0.14g (1.47mmol). Yield: 0.12g (39%). IR (KBr cm^{-1}) : 3084(w), 1566(s), 1533(m), 1451(m), 1347(m), 1287(s), 1144(s), 941(s), 788(m), 706(s). Decompn temp: 258˚C. Elemental anal.cal for $C_{136}H_{108}Fe_8Lu_4O_{20}S_8$: C, 47.13; H, 3.14; Found: C, 47.26; H, 3.12.

Compound 2.3: $YbCl_3.6H_2O$ 0.119g (0.30mmol), HFctfa 0.199g (0.61mmol), Et_3N 0.12g (1.23mmol). Yield: 0.12g (54%). IR (KBr cm^{-1}) : 3402(b), 2920(w), 1610 (s), 1523(m), 1430(m), 1375(s), 1254(w), 1134(s), 1024(w), 947(s), 789(m), 663(s). Decompn temp:

240˚C. Elemental anal.cal. for $C_{92}H_{90}F_{18}Fe_6O_{22}Yb_4$: C, 37.88; H, 3.10; Found: C, 37.72; H, 3.06.

Compound 2.4: $LuCl_3.6H_2O$ 0.120g (0.30mmol), HFctfa 0.199g (0.61mmol), Et_3N 0.12g (1.23mmol). Yield: 0.11g (49%). IR (KBr cm^{-1}) : 3339(b), 2925(w), 1621(s), 1528(m), 1435(m), 1380(m), 1293(s), 1134(s), 942(s), 799(m), 663(s). Decompn temp: 244˚C. Elemental anal.cal. for $C_{92}H_{90}F_{18}Fe_6O_{22}Lu_4$: C, 37.78; H, 3.10; Found : C, 37.61; H, 3.16.

Compound 2.5: $YbCl_3.6H_2O$ 0.091g (0.23mmol), HFcpfa 0.175g (0.46mmol), Et_3N 0.095g (0.94mmol). Yield: 0.12g (58.5%). IR (KBr cm^{-1}) : 3433(b), 2921(w), 1602(s), 1521(m), 1428(m), 1374(s), 1292(s), 1145(s), 1041(w), 933(s), 791(m), 666(s). Decompn temp: 249˚C. Elemental anal.cal. for $C_{98}H_{90}F_{30}Fe_6O_{22}Yb_4$: C, 36.58; H, 2.81; C, 36.65; H, 2.91.

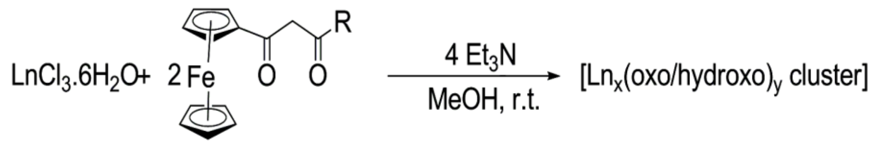
Compound 2.6: $LuCl_3.6H_2O$ 0.091g (0.23mmol), HFcpfa 0.174g (0.46mmol), Et_3N 0.094g (0.94mmol). Yield: 0.13g (69.1%). IR (KBr cm^{-1}) : 3331(b), 3089(w), 1602 (s), 1515(m), 1439(m), 1379(s), 1281(w), 1150(s), 1036(w), 1009(s), 818(m), 671(s). Decompn temp: 256˚C. Elemental anal.cal. for $C_{98}H_{90}F_{30}Fe_6O_{22}Lu_4$: C, 36.50; H, 2.81; C, 36.62; H, 2.75.

2.3 X-ray structure determination:

Single crystal X-ray diffraction studies for (**2.1**, **2.3** - **2.6**) were carried out at 100 K(**2.1** and **2.6**) on a Bruker SMART APEX I CCD single core area detector system equipped with a graphite monochromatic and a MoKα fine-focus sealed tube (λ= 0.71073 Å) operated at 1500 W power (40 kV, 30 mA). Single crystal X-ray diffraction studies for (**2.2**) were carried out at 298 K on an Ox-ford Diffraction Xcalibur Gemini single crystal X-ray diffractometer equipped with graphite monochromated MoKα radiation (λ= 0.71073 Å). All non-hydrogen atoms with full occupancy were refined anisotropically. Hydrogen atoms were included in the structure factor calculations by using a riding model. Structure solution and refinement were performed with the help of SHELX-97 programs available in the WinGX package.

2.4 Results and Discussion

2.4.1 Synthesis. The synthesis of compounds **2.1-2.6** followed the ligand controlled hydrolytic approach. Hydrolysis of the hydrated lanthanide salts supported by suitable ligands was used as general approach to generate lanthanide hydroxo clusters (Scheme **1**). The present study used mixture of one equivalent $LnCl_3.6H_2O$ [Ln = Dy (**2.1**), Lu (**2.2**), Yb (**2.3, 2.5**), Lu (**2.4, 2.6**)] and two equivalents of ferroceneyl β-diketones (HFca, HFctp, HFctfa, HFcpfa) in methanol followed by subsequent addition of triethylamine drop wise. Halfway through the addition of base a yellow precipitate was formed. The reaction mixture was stirred further for a period of 12 h and filtered to isolate the precipitate. Triethylamine scavenges the proton from ferrocene beta-diketones to form $[HEt_3N]Cl$. As a result the ligands readily chelate or bridge the lanthanide ions. The formation of the hydroxido bridges is due to the excess triethylamine used which deprotonates the coordinated water molecules of hydration which could bridge the lanthanide ions and make up cluster core, while the hydrophobic groups of ferrocene beta-diketones ligands took up position in the peripheral part of the resultant cluster.



S.No	R	Abbreviation of ligand	Ln	Clusters formed	Compound No
1	CH_3	HFca	Dy	$[Ln_9(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_8(\mu\text{-}Fca)_8(Fca)_8]^-$ $[HN(CH_2CH_3)_3]^+$	**1**
2		HFctp	Lu	$[Ln_4(\mu_4\text{-}OH)_4(\mu\text{-}Fctp)(Fctp)_7]$	**2**
3	CF_3	HFctfa	Yb, Lu	$[Ln_4(\mu\text{-}OH)_2(\mu\text{-}OCH_3)_4(CH_3OH)_2(Fctfa)_6]$	**3**, **4**
4	CF_2CF_3	HFcpfa	Yb, Lu	$[Ln_4(\mu\text{-}OH)_2(\mu\text{-}OCH_3)_4(CH_3OH)_2(Fcpfa)_6]$	**5**, **6**

Scheme 1

Clusters **2.1-2.6** are soluble in wide range of organic solvents such as dichloromethane, chloroform, acetonitrile, toluene, benzene, xylene, DMF and pyridine. The crystals suitable for X-ray diffraction were grown from chloroform/hexane (**2.1**) toluene/hexane diffusion (**2.2**) and methanol/ hexane diffusion (**2.3-2.6**).

2.5 Description of the crystal structures:

2.5.1 Sand glass type nonanuclear Dy_9 cluster (2.1):

The solid state structure of 2.**1** (figure 1) is similar to a series of Ln_9 clusters reported previously.[11] The anionic metal oxo core resembles a sandglass structure. The cluster can also be described as the one containing a central Dy at the apex position sharing the two square based pyramids containing Dy atoms at the vertices. Further the metal centers are held together by oxo bridges. The exquisiteness of the structure lies in the fact that sixteen ferrocenes decorate the central Dy oxo/hydroxo core which is unprecedented. The approximate molecular dimension of **2.1** is 2.24 x 2.01 x 1.37 nm^3. On analyzing HRTEM image of **2.1** (figure 2), d spacing of 14.40 Å was found which correlated well with the generated powder pattern's d spacing from the single crystal diffraction data. The presence of triethylammonium cation was confirmed by ESI mass spectral measurements by a peak at m/z = 102 which accounts for the charge neutrality. Selected bond lengths bond angles are given in (Table 3**).**

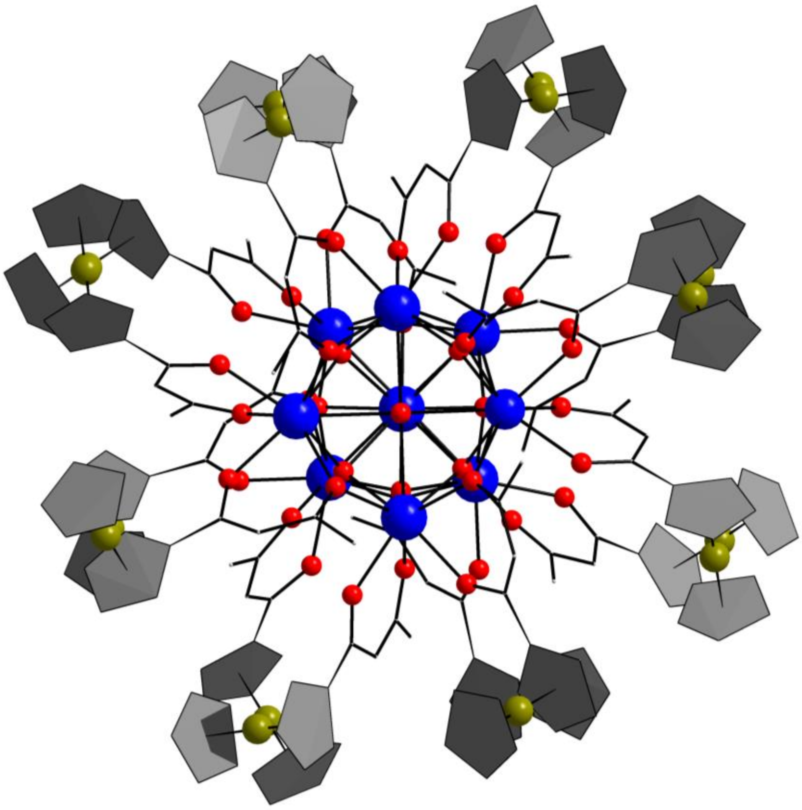


Figure 1: Solid state structure of **2.1** (ball and stick representation) viewed through the z axis. Colour code: blue (Dy), red (O), green (Fe).

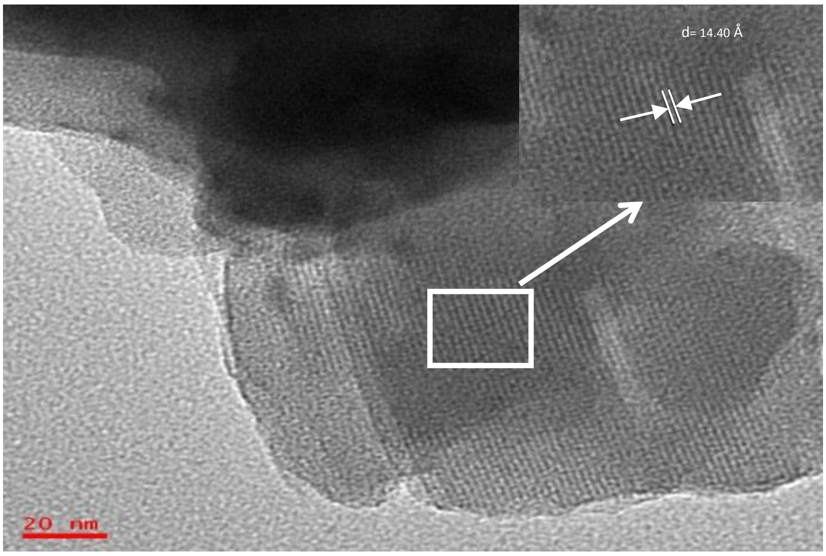


Figure 2: HRTEM image of **2.1**. Insert shows the d spacing

2.5.2 Cubane type tetranuclear Lu_4 cluster (2.2):

Replacing the methyl in beta diketone used in **2.1** with a thiophene leads to a complete change in the structure of the end product obtained on reaction with hydrated lutetium trihalide. The ligand stabilizes a cubane Lu_4O_4 cluster (figure 3) with each metal atom being seven coordinate.

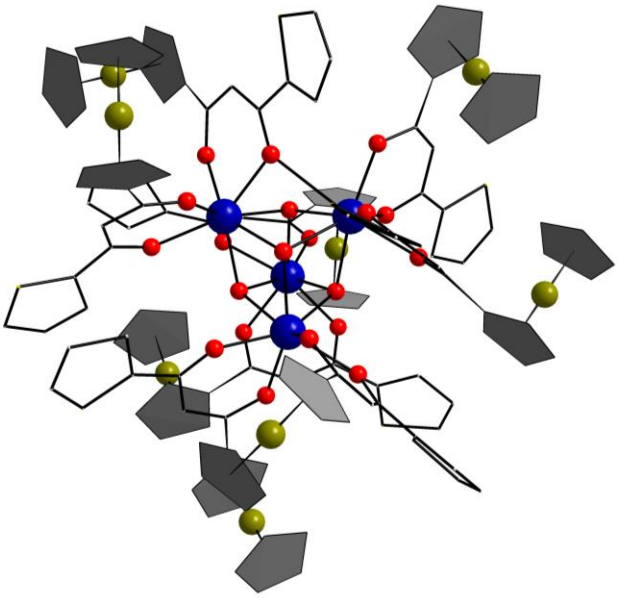


Figure 3: Solid state structure of **2.2** in ball and stick representation. Colour code: blue (Lu), red (O), green (Fe).

Eight ligands are found in the structure and hence results in anchoring eight ferrocenes on the cluster periphery all beta diketones are found to be chelating to lutetium except for one ligand which not only chelates to the metal atom but also is found to be in a long contact (2.874 Å)[12] with a neighbouring lutetium across one of the square faces of the cubane cluster. The approximate molecular dimension of **2.2** is 1.75 x 1.41 x 1.16 nm^3. Selected bond lengths bond angles are given in (Table 3**).**

2.5.3 Butterfly type tetranuclear Lu_4 clusters (2.3 - 2.6):

On further modulation of the organic groups present in the β-diketones to CF_3 / CF_2CF_3 and on reacting with lanthanum hydrate trihalides in presence of excess base leads to the isolation of red colored crystalline products. Single crystals suitable for X-ray diffraction were grown from methanol/hexane diffusion method. Structural analysis reveals the formation of a tetranuclear core[13] in all the four cases. Structure of **2.3** is considered for discussion. The cluster can be described as a butterfly structure with all the metal atoms being 7 coordinate. The metal atoms are present in a planar fashion and are bound together by two μ_3- hydroxide groups and four μ_2-methoxide bridges. The peripheral part of the cluster contains six β-diketone ligands which are bound to the metal atoms in a chelating manner and hence assembling six ferrocenes on the surface of the cluster. The approximate molecular dimensions of compounds **2.3** is 1.44 x 1.84 x 1.98 nm^3.

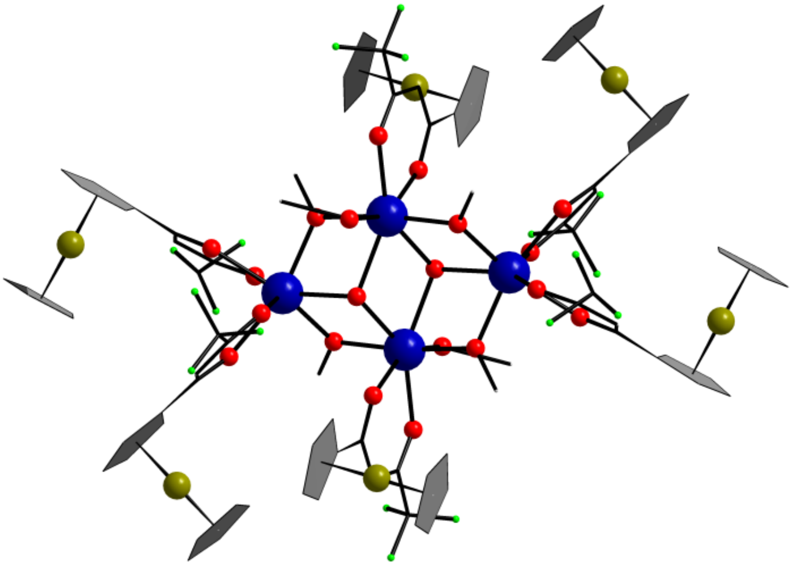
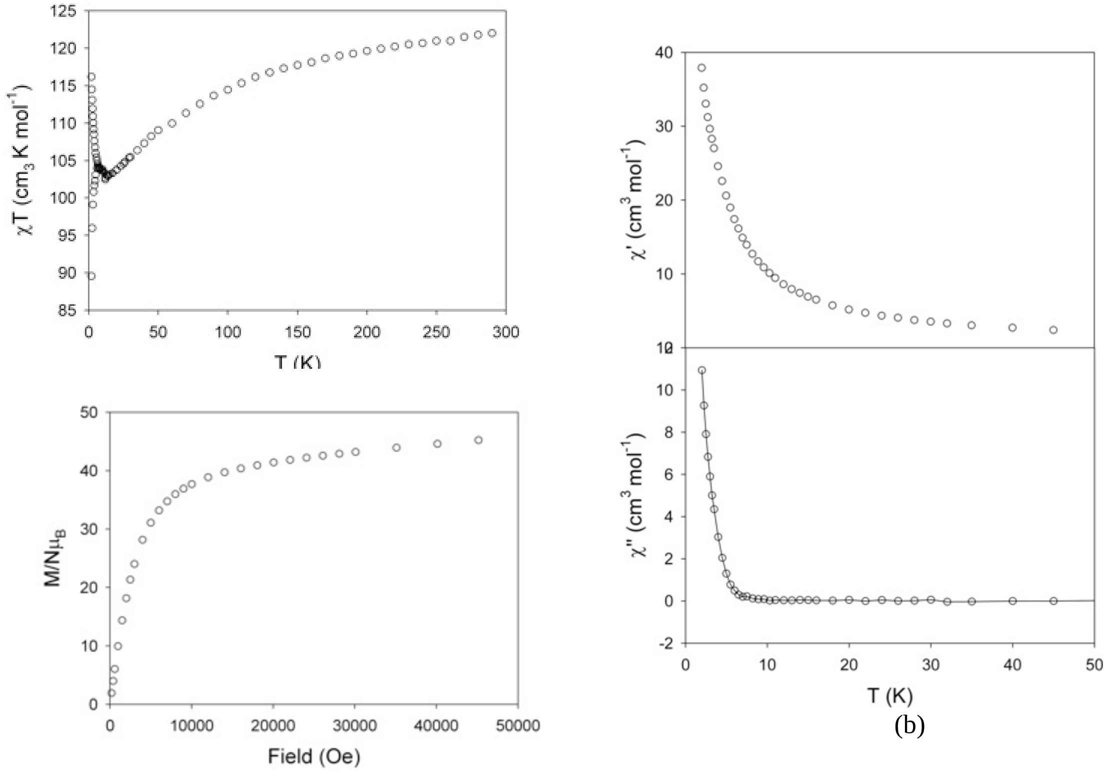


Figure 4: Solid state structure of **2.3** in ball and stick representation. Colour code: blue (Yb), red (O), green (Fe),

2.6 Magnetism studies:

Magnetism studies showed the χT value for **2.1** at 300 K is 122 cm^3 K mol^{-1}, which is in agreement with the expected value of 127 cm^3 K mol^{-1} for nine non-interacting Dy(III) ions (14.16 cm^3 K mol^{-1} per Dy(III) ions ($^6H_{15/2}$, S=5/2, L=5, J=15/2 and gJ= 4/3) (figure 5). As temperature decreases, the χT product decreases until it reaches a minimum at 25 K, and then it rises again. The rise is field dependent and more accentuated with the smaller applied field of 197 Oe due to Zeeman Effect and indicates the population of ferromagnetically coupled ground state. The magnetization versus field plot at 2 K clearly shows saturation at 45 μB, and can be modelled with the software PHI[14] using giant spin model of S = 45/2 and D = -0.030cm^{-1} (figure 5). The AC magnetic susceptibility data for complex **2.1** at 1000 Hz applied frequencies is shown in (figure 5b). Clearly, the tail of an out-of-phase peak can be seen, indicating the onset of a slow relaxation process taking place below 2 K. Further studies investigations to confirm SMM behavior in **2.1** are in progress.



(b)

(a)

Figure 5: (a) χT vs. T plot at 197 and 3000 Oe applied fields and magnetization vs field plot for complex **2.1** (b) AC magnetic susceptibility plot at 1000 Hz for **2.1.**

X’/X’’ AC susceptibilities with Argand plot for **2.1** at 1.8 K (red) and 4.0 K (white) at 1 to 1500 Hz applied frequencies (figure 6,7) are included which are added data for suggesting 1 does show slow relaxation of magnetization.

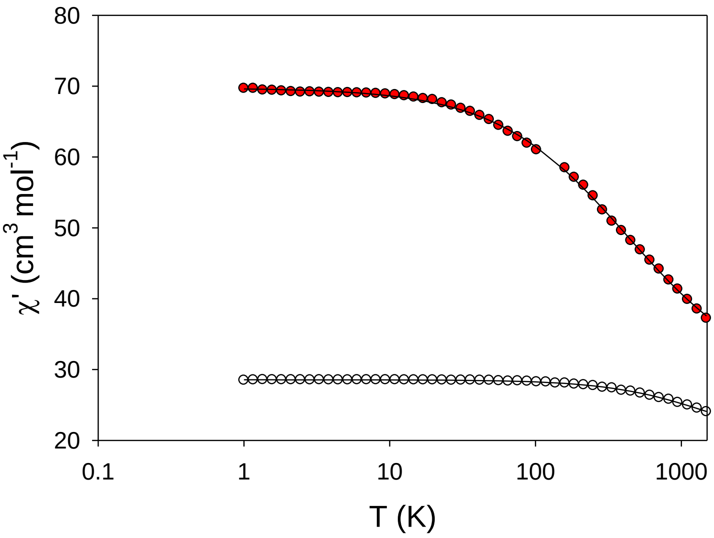


Figure 6: X’ ac susceptibility for Dy9 at 1.8 K (red) and 4.0 K (white) at 1 to 1500 Hz applied frequencies. T was difficult to maintain stable at 1.8 K, the limit of our commercial SQUID, and two data points have been removed due to this.

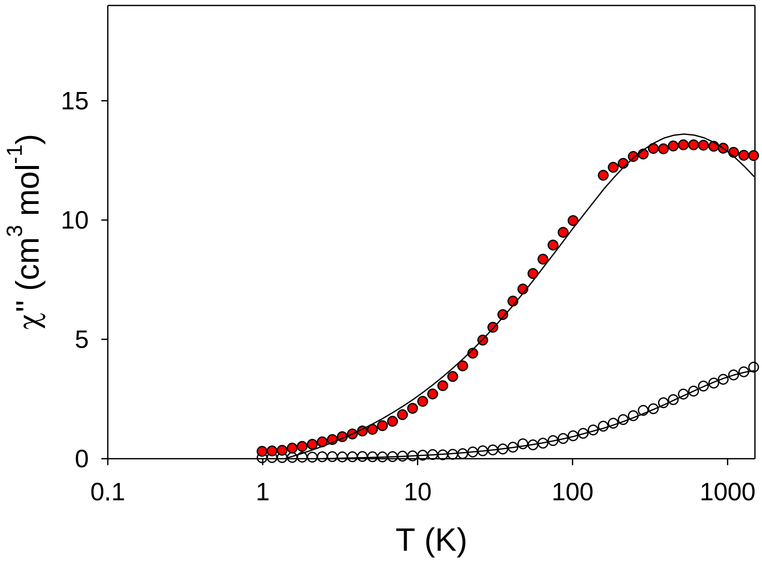


Figure 7: X’’ susceptibility plots for Dy9 at 1-8 K (red) and 4.0 K (white) at 1 to 1500 Hz applied frequencies. T was difficult to maintain stable at 1.8 K, the limit of our commercial SQUID, and two data points have been removed due to this.

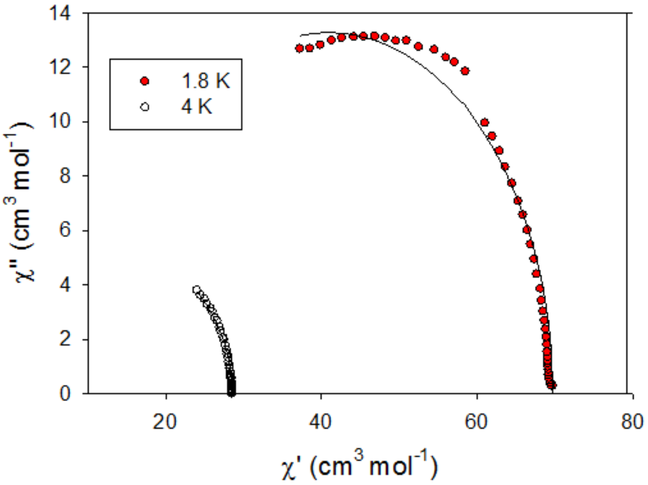


Figure 8: Argand plot for complex Dy9 at 1.8 K and 4.0 K at applied frequencies between 1 and 1500 Hz. T was difficult to maintain stable at 1.8 K, the limit of our commercial SQUID, and two data points have been removed due to this.

Magnetism studies revealed that the χT value for **2.3** at 300 K is 9.6 cm^3 K mol^{-1}, in agreement with the expected value for four non-interacting Yb(III) ions of 10.1 cm^3 K mol^{-1} (Yb(III): $^2F_{7/2}$, S = 1/2, L = 3, J= 7/2 and gJ= 8/7, expected χT for Yb ion is 2.5 cm^3 K mol^{-1}) (Figure 9).[15] As temperature decreases, the χT product smoothly decreases due to the depopulation of Stark sublevels of the Yb(III) ions. The χT product does not go to zero, but around 25 K it reaches a plateau value of 5.2 cm^3 K mol^{-1}, indicating the non-cancellation of the magnetic moments due to ferromagnetic interactions or spin frustration

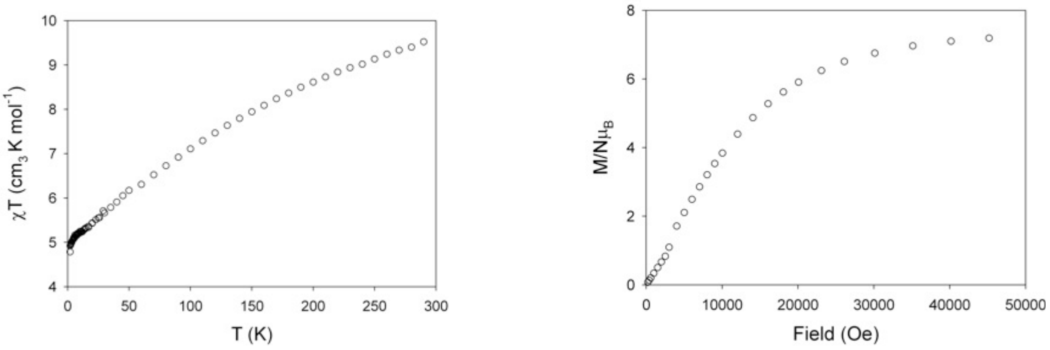


Figure 9: χT vs. T plot for **2.3** at 197 and 3000 Oe applied fields and magnetization vs field plot for complex **2.3.**

This is confirmed by the magnetization vs. field plot for **2.3** at 2 K (Figure 9). The magnetization reaches saturation at a value of nearly 8 μB. The magnetic data of **2.3** seem to indicate an exchange coupled system in which the two central Yb ions are coupled antiferromagnetically, and at the same time coupled ferromagnetically to the wing-tip Yb(III) ions

2.7 Absorption studies:

The UV-Vis absorption of the ligands and compounds **2.1-2.6** were measured in dichloromethane solution (32 x 10^{-6}M), and are shown in Figure 10. The absorption of free ligands HFca, HFctp, HFctfa, HFcpfa shows λ_{max} at 453, 490, 510 nm, 513 nm.

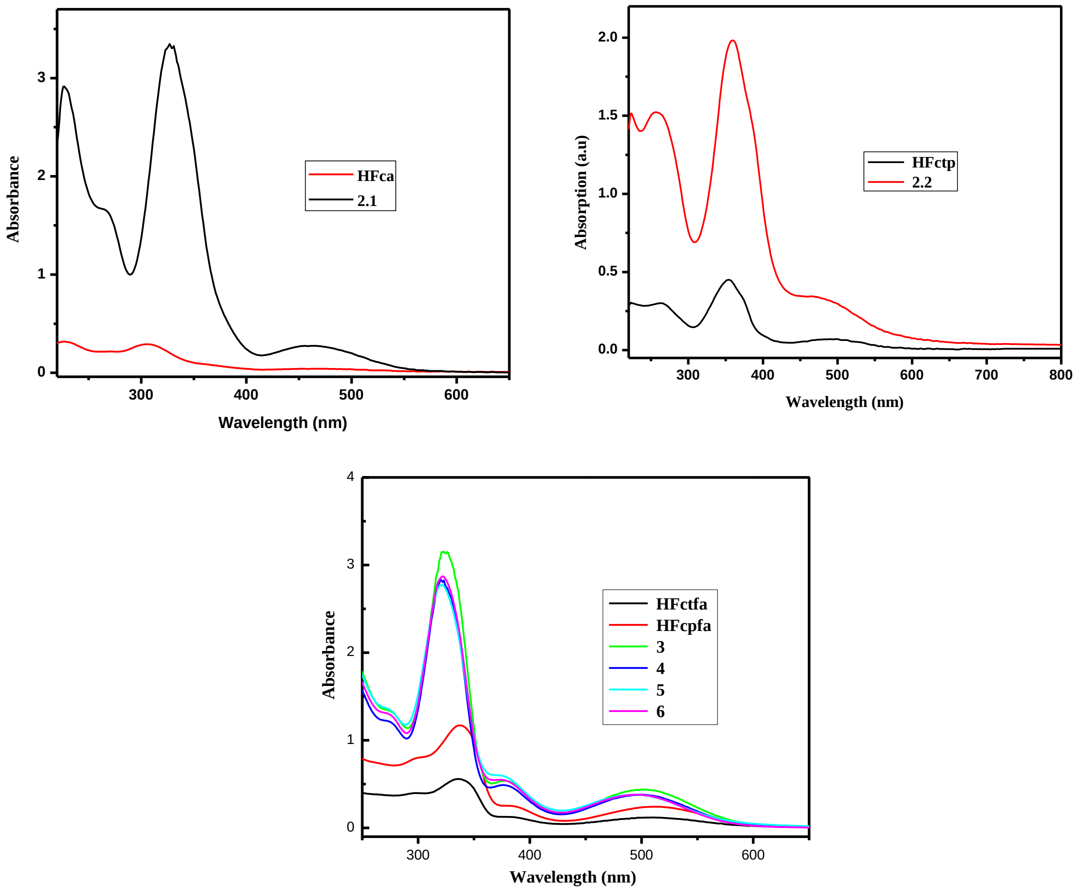


Figure 10: UV-Visible absorption spectra of the ferrocene beta diketone ligands and compounds **2.1-2.6** in Dichloromethane (32 x 10^{-6} M).

The absorptions in the range of 310 and 450 nm and the shoulders are generally attributed to d-d transitions of the ferrocene building blocks[16] The trends in the absorption spectra of complexes (**2.1-2.6**) are almost similar to that of the free ligands with minor shifts being attributed to contributions from the bound β-diketone ligands and also due to electomeric effects of the various substituent's attaching to the diketones. The molar absorption coefficient values for ligands and compounds (**2.1-2.6**) are 1.312 x 10^3 Lmol^{-1}cm^{-1}, 2.187 x 10^3 Lmol^{-1}cm^{-1}, 3.71 x 10^3 Lmol^{-1}cm^{-1}, 7.56 x 10^3 Lmol^{-1}cm^{-1}, 8.593 x 10^3 Lmol^{-1}cm^{-1} (λ =463nm), 10.750 x 10^3 Lmol^{-1}cm^{-1}(λ =465nm), 13.68 x 10^3 Lmol^{-1}cm^{-1}(λ =503nm), 11.81 x 10^3 Lmol^{-1}cm^{-1} (λ =500nm), 11.84 x 10^3 Lmol^{-1}cm^{-1} (λ =493nm), 11.81 x 10^3 Lmol^{-1}cm^{-1}(λ =495nm) respectively.

2.8 Cyclic Volatametry studies:

Cyclic voltagrams of **2.1** and **2.2** reveals quasi reversible oxidation waves at $E_{1/2}$ values 1.12 and 0.967 V with ΔE values being 342 and 257 m.v, which was assigned to Fc^{+2}/Fe^{+3} couple. The oxidation of various ferrocene units at single unique potential indicates that ferrocenes behaves similarly.

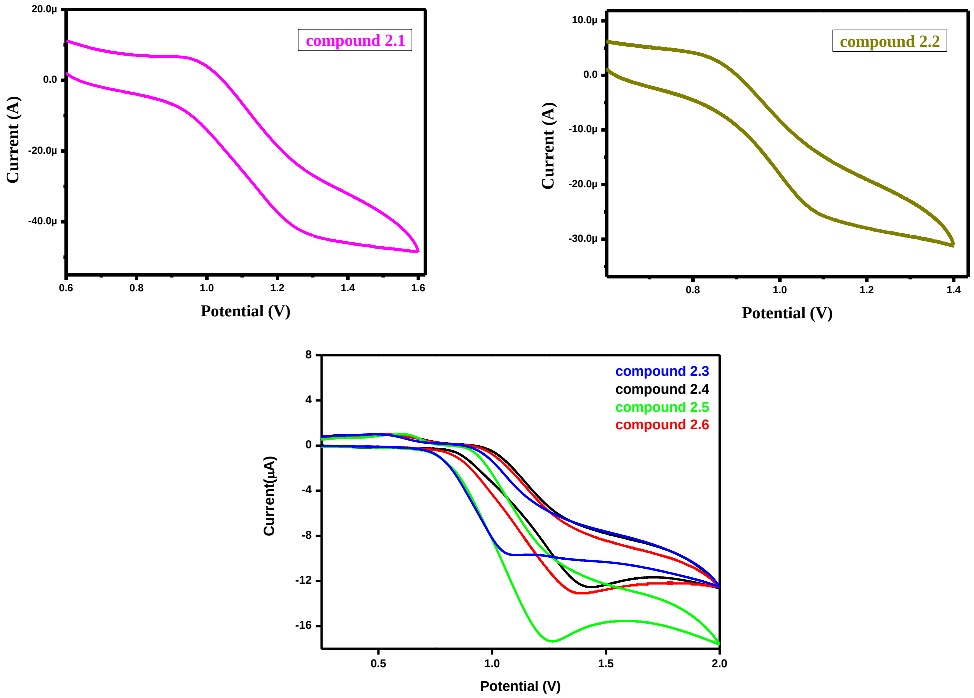


Figure 11: cyclic voltagrams of compounds (**2.1-2.6**)

Another interesting feature is the reversibility of the voltagram even after five continuous cycles which indicates that the cluster does not decompose upon oxidation. Cyclic voltammetric studies shows the appearance of sharp anodic peaks at 1.16, 1.44, 1.28, 1.42 V for compounds (2.3-2.6) respectively. On increasing the number of cycles, the peaks vanishes indicating the irreversible nature and also that (2.3-2.6) decompose up on oxidation.

2.9 Thermogravimetric analysis (TGA):

Thermogravimetric analysis (TGA) studies were performed in N_2 atmosphere with a heating rate of 10˚ C min^{-1} for complexes 2.**1**-2.**6**. The TGA plots (Figure 12) show gradual loss of solvent molecules, methanol (2.**1**, 2.**3**-2.**6**) and toluene (**2.2**) respectively. The clusters are stable up to 270˚C after which decomposition sets in.

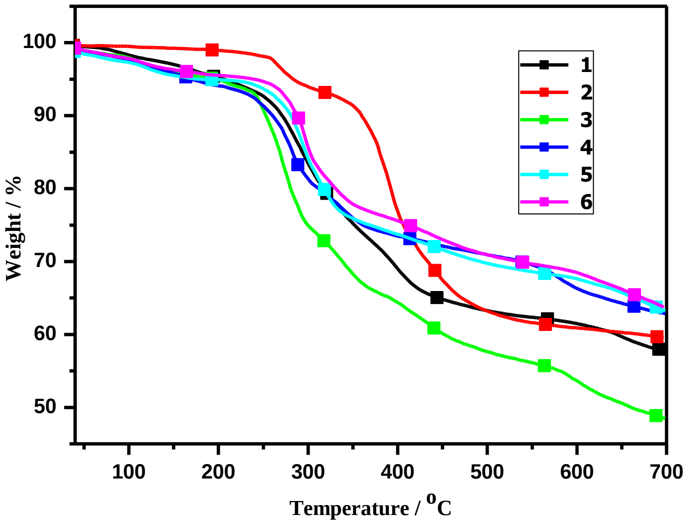


Figure 12: TG curves for the complexes **2.1-2.6**

2.10 Conclusion

To summarize, nano-sized clusters incorporating sixteen (**2.1**) eight ferrocenes (**2.2**) and six (**2.3-2.6**) have been synthesized and structurally characterized. Lanthanide oxo cores displaying interesting magnetic properties can anchor a second / third functionality and hence can act as scaffolds for assembling poly-functional molecular architectures.

Table 1: Crystal and Refinement data for 2.1-2.3

	2.1	**2.2**	**2.3**
Formula	$C_{224}H_{210}Dy_9Fe_{16}O_{43}$	$C_{136}H_{104}Fe_8Lu_4O_{20}S_8$	$C_{92}H_{90}F_{18}Fe_6O_{22}Yb_4$
fw	5946.02	3461.35	2916.90
Temp (K)	100(2)	293(2)	293(2)
Cryst syst	tetragonal	monoclinic	monoclinic
Space group	P4cc	P2(1)/c	P2(1)/c
Cryst size (mm)	0.21 x 0.14 x 0.12	0.18 x 0.14 x 0.12	0.21 x 0.18 x 0.10
a (Å)	20.5320(6)	25.2755(13)	13.371(2)
b (Å)	20.5320(6)	17.1961(5)	18.263(3)
c (Å)	30.7476(19)	35.986(3)	24.302(3)
α (deg)	90.000	90.000	90.000
β (deg)	90.000	112.497(5)	123.381(6)
γ (deg)	90.000	90.000	90.000
V(Å^3)	12962.1(10)	14450.7 (15)	4955.4(13)
Z	2	4	2
d_{calcd} (Mg m^{-3})	1.523	1.591	1.955
μ (mm^{-1})	3.480	3.655	4.686
F(000)	5816	6800	2832
θ range for data collection (deg)	1.30 – 26.11	2.67 to 25.00	1.50 to 25.18
refln collected/unique	119007/11519	51077/25253	46500/8831
R (int)	0.1296	0.1890	0.0418
data/retraints/params	11519 / 1 / 716	25253/0/1585	8831/0/644
GoF on F^2	1.129	0.977	1.045
R_1/wR_2 (I>2σ(I))	0.0862/0.2127	0.1248/ 0.2623	0.0643/0.1417
R_1/wR_2 (all data)	0.0921/0.2168	0.2734/0.3586	0.0856/0.1617
largest diff peak/hole,e Å^{-3}	4.540/-1.720	5.136 /-3.681	4.707 /-3.771

Table 2: Crystal and Refinement data for 2.4-2.6

	2.4	**2.5**	**2.6**
Formula	$C_{92}H_{90}F_{18}Fe_6O_{22}Lu_4$	$C_{98}H_{90}F_{30}Fe_6O_{22}Yb_4$	$C_{98}H_{90}F_{30}Fe_6O_{22}Lu_4$
fw	2924.62	3216.96	3224.68
Temp (K)	293(2)	293(2)	293(2)
Cryst syst	monoclinic	monoclinic	triclinic
Space group	P2(1)/n	P2(1)/n	P2(1)/n
Cryst size (mm)	0.21 x 0.18 x 0.16	0.22 x 0.20 x 0.16	0.18 x 0.14 x 0.10
a (Å)	13.360(3)	16.270(2) (3)	16.013(2)
b (Å)	18.090(4)	19.907(3)	19.834(3)
c (Å)	20.350(4)	17.147(2)	16.742(2)
α (deg)	90.000	90.000	90.000
β (deg)	91.16(3)	97.122(2)	98.218(2)
γ (deg)	90.000	90.000	90.000
V(Å^3)	4917.2(17)	5510.8(14)	5263.0(11)
Z	2	2	2
d_{calcd} (Mg m^{-3})	1.975	1.939	2.035
μ (mm^{-1})	4.934	4.238	4.636
F(000)	2840	3120	3128
θ range for data collection (deg)	1.51 to 25.00	1.57 to 26.10	1.60 to 26.06
refln collected/unique	46011/8655	56565/10907	52884/10358
R (int)	0.0597	0.0929	0.0515
data/retraints/params	8655 / 0 / 644	10907 / 0 / 725	10358 / 0 / 725
GoF on F^2	1.038	1.108	1.073
R_1/wR_2 (I>2σ(I))	0.0502/0.1240	0.0620/0.1521	0.0558/0.1402
R_1/wR_2 (all data)	0.0606/0.1300	0.0982/0.1719	0.0784/0.1625
largest diff peak/hole,eÅ^{-3}	3.105 /-1.557	3.640 /-0.571	4.930/-1.765

Table 3: bond lengh and bond angle parameters for compound 2.1-2.6

Compound 2.1

Dy_1- O_1	2.474(12)	Dy_3- O_4	2.568(3)	O_5-Dy_2-O_{12}	77.5(4)
Dy_1- O_2	2.321(11)	Dy_3- O_6	2.318(12)	O_5-Dy_2-O_3	121.6(3)
Dy_1- O_{12}	2.300(11)	Dy_3- O_9	2.401(10)	O_5-Dy_3-O_6	77.7(4)
Dy_1- O_{10}	2.321(12)	Dy_1- O_3-Dy_2	86.2(5)	O_5-Dy_3-O_7	150.5(4)
Dy_1- O_{11}	2.286(13)	Dy_3- O_4-Dy_2	84.6(7)	Dy_3- O_5-Dy_2	103.9(5)
Dy_2- O_{12}	2.420(11)	O_{11}-Dy_1-O_{12}	149.4(4)		
Dy_2- O_5	2.398(12)	O_{12}-Dy_1-O_{10}	75.8(4)		

Compound 2.2

Lu_1-O_1	2.204(19)	Lu_3-O_4	2.187(19)	Lu_3-O_{18}-Lu_3	103.4(7)
Lu_1-O_2	2.317(17)	Lu_3-O_8	2.259(16)	Lu_2-O_{14}-Lu_3	104.5(6)
Lu_1-O_3	2.265(16)	Lu_4-O_3	2.361(15)	O_2-Lu_1-O_3	78.3(6)
Lu_2-O_3	2.285(15)	Lu_4-O_2	2.291(17)	O_2-Lu_4-O_3	76.9(6)
Lu_2-O_6	2.260(2)	Lu_4-O_3-Lu_1	98.2(6)	O_{14}-Lu_3-O_{18}	72.8(6)
Lu_3-O_2	2.291(16)	Lu_4-O_2-Lu_1	98.7(6)	O_8-Lu_3-O_4	105.2(6)

Compound 2.3

Yb_1-O_7*	2.196(9)	Yb_2-O_2	2.254(11)	O_8-Yb_1-O_9	93.6(5)
Yb_1-O_8	2.344(11)	Yb_2-O_7	2.205(8)	O_8-Yb_1-O_{10}	75.4(3)
Yb_1-O_{10}	2.318(6)	Yb_2-O_{10}	2.328(8)	O_8-Yb_1-O_5	74.5(4)
Yb_1-O_5	2.247(7)	Yb_1*-O_7-Yb_2	110.0(3)	Yb_1*-O_{10}-Yb_2	103.5(3)
Yb_1-O_6	2.280(9)	Yb_1-O_{10}-Yb_1*	103.2(3)		
Yb_2-O_1	2.281(8)	Yb_2-O_9-Yb_1	111.1(4)		
Yb_2-O_9	2.222(7)	O_1-Yb_2-O_2	75.9(4)		

Compound 2.4

Lu$_1$-O$_7$	2.185(6)	Lu$_2$-O$_2$	2.242(5)	Lu$_2$-O$_9$-Lu$_1$*	109.9(2)
Lu$_1$-O$_8$	2.327(7)	Lu$_2$-O$_7$	2.202(5)	O$_1$-Lu$_2$-O2	75.84(19)
Lu$_1$-O$_{10}$	2.267(5)	Lu$_2$-O$_{10}$*	2.325(5)	O$_8$-Lu$_1$-O$_7$	89.9(3)
Lu$_1$-O$_5$	2.250(6)	Lu$_1$-O$_7$-Lu$_2$	111.0(3)	O$_8$-Lu$_1$-O$_{10}$	137.4(2)
Lu$_1$-O$_6$	2.233(6)	Lu$_1$-O$_{10}$-Lu$_1$*	110.5(2)	O$_8$-Lu$_1$-O$_5$	148.2(2)
Lu$_2$-O1	2.234(5)	Lu$_1$-O$_{10}$-Lu$_2$*	103.5(2)	Lu$_2$*-O$_{10}$-Lu$_1$*	102.7(2)
Lu$_2$-O$_9$	2.209(5)				

Compound 2.5

Yb$_1$-O$_7$	2.215(6)	Yb$_2$-O$_9$	2.218(6)	Yb$_1$-O$_{10}$-Yb$_2$*	103.1(2)
Yb$_1$-O$_8$	2.339(8)	Yb$_2$-O$_2$	2.302(6)	Yb$_2$-O$_9$-Yb$_1$	113.0(3)
Yb$_1$-O$_{10}$	2.283(6)	Yb$_2$-O$_7$*	2.196(6)	O$_1$-Yb$_2$-O$_2$	76.1(2)
Yb$_1$-O$_5$	2.297(6)	Yb$_2$-O$_{10}$*	2.387(6)	O$_8$-Yb$_1$-O$_{10}$	132.3(3)
Yb$_1$-O$_6$	2.243(6)	Yb$_1$-O$_7$-Yb$_2^*$	112.0(3)	O$_8$-Yb$_1$-O$_9$	98.1(3)
Yb$_2$-O$_1$	2.278(7)	Yb$_1$-O$_{10}$-Yb$_1$*	109.0(2)	Yb$_2$*-O$_{10}$-Yb$_1$*	103.3(2)

Compound 2.6

Lu$_1$-O$_7$*	2.201(7)	Lu$_2$-O$_9$	2.213(6)	Lu$_1$-O$_{10}$-Lu$_2$*	103.3(2)
Lu$_1$-O$_8$	2.328(7)	Lu$_2$-O$_2$	2.284(6)	Lu$_2$-O$_9$-Lu$_1$	112.2(3)
Lu$_1$-O$_{10}$	2.267(6)	Lu$_2$-O$_7$	2.198(7)	O$_1$-Lu$_2$-O2	76.8(2)
Lu$_1$-O$_5$	2.244(6)	Lu$_2$-O$_{10}$*	2.375(6)	O$_8$-Lu$_1$-O$_9$	95.8(3)
Lu$_1$-O$_6$	2.300(6)	Lu$_1$*-O$_7$-Lu$_2$	111.7(3)	O$_8$-Lu$_1$-O$_{10}$	134.1(2)
Lu$_2$-O1	2.259(7)	Lu$_1$-O$_{10}$-Lu$_1$*	109.5(2)	Lu$_2$*-O$_{10}$-Lu$_1$*	103.2(2)

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PART-B

A brief preview of organoantimony(v) compounds

The chemistry of antimony has both practical and theoretical interest.[1] In early days the Egyptians showed the use of antimony complexes in medicine and cosmetics.[2,3] Until the early 1900's potassium antimony tartrate or tartar emetic was extensively used despite the toxic nature of the material.[4] Antimony complexes, for example sodium antimony(V) gluconate, are still being studied as possible drugs for the treatment of various parasitic diseases.[5-9] In recent years the chemistry of organoantimony(V) complexes has attracted significant attention due to the fascinating structural diversity varying from discrete monomeric molecular species to associated structures and supramolecular assemblies.[10] In addition, organoantimony derivatives also exhibit significant antimicrobial properties as well as antitumor activities[11] which is associated with cytostatic activity[12] similar to that of cis-platin. However, the biological toxicity, is much less than those of Pt and Pd anticancer substances. In addition, organoantimony derivatives also exhibit significant functions as biocides, fungicides, catalyst components and antioxidants. Organoantimony compounds particularly with antimony in the oxidation state of +5 is interesting considering that it can exist in coordination numbers as high as seven or eight due to its hypervalent nature.[13] Very recently the chemistry of monoorganoantimony(V) compounds have started gaining interest since the ability of organostibonic acids to act as inorganic cryptand incorporating d^5 and d^{10} metal ions in their cavity was reported.[14] Further the isolation of the first molecular arylstibonic acids and subsequently the use of mixed arylstibonate/phosphonate clusters as proligands for assembly of multinuclear cobalt clusters have increased the interest in organoantimony(V) compounds in general.[15] Organoantimony(V) compounds have been used in organic synthesis either as reagents or as catalysts for a number of years.[16] However, it is only in the recent years that their application in palladium catalyzed crosscoupling reactions has been shown. In the presence of catalytic amounts of $Pd(PPh_3)_4$ or $Pd(OAc)_2$, pentaphenylantimony reacted with allyl acetate or allyl phenyl ether to afford allylbenzene.[17] Organoantimony(V) derivatives Ar_3SbX_2 (X=/Cl, OAc) gave crosscoupling products with silyloxy alkenes[18] and organotin compounds[19] under palladium catalysis. $Ar_3Sb(OAc)_2$ was used in Pd(0)/Cu(I)-catalyzed cross-coupling reactions with alkynylsilanes.[20] Gushchin et al reported that $Ph_3Sb(OAc)_2$ behaves not only as a phenyl group donor but also as a Pd(0) reoxidant in the Pd catalyzed C-phenylation reaction of methyl acrylate.[21]

Organoantimony halides have been used as starting materials in our investigation. So a brief introduction to organoantimony halides followed by reports of reactions of halides with some O and N donors is given in detail.

Monoorganoantimony(V) halides, because of their unstable nature not much is known about the the structural aspects of mono-alkyl and arylantimony(V) chlorides.[22] For example phenylantimony chloride is unstable and normally tends to disproportionate on standing (scheme 1).

$$2PhSbCl_4 \longrightarrow Ph_2SbCl_3 + SbCl_3 + Cl_2 \quad \dashrightarrow 1$$

Scheme 1

Compounds of monoorganoantimony(v) chlorides with oxo donor ligands are quite stable in ambient temperatures. On the basis of I.R and ^1H NMR spectral studies it was suggested that the antimony atom was hexa coordinated. $MeSbCl_4.L$ (L = PyO or 4-MePyO) exists in cis and trans isomeric forms in the solution (Chart 1).[23]

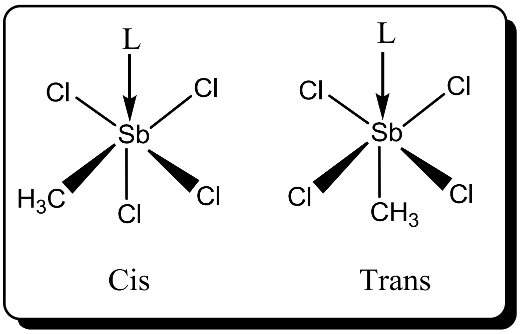
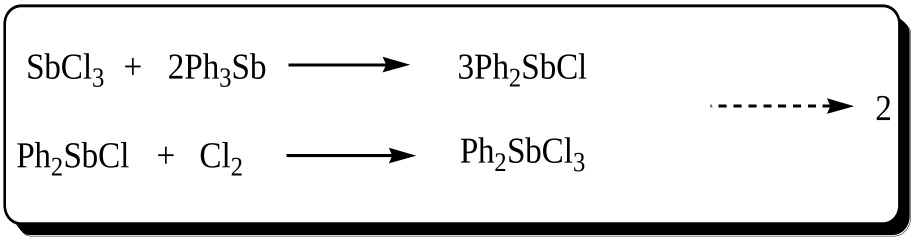


Chart 1: Cis and trans isomeric forms of $MeSbCl_4L$

Diorganoantimony(V) halides have been prepared by the reactions of antimony(III) chlorides with diazonium salts or by halogenations of diorganoantimony(III) halides R_2SbX (scheme 2).[24]



Scheme 2

Diorganoantimony(V) halides can be reduced to diorganoantimony(III) halides by using reducing agents like stannous chloride, sulfurdioxide.[25]

Initially there was an ambiguity regarding the structure of Ph_2SbCl_3. Some groups proposed the compound to be a trigonal pyramidal geometry and some other groups reported the compound as a monohydrate $Ph_2SbCl_3.H_2O$ with octahedral geometry.[26a,b] In order to resolve the above uncertainty Bordner et al. examined the crystal structure analysis of anhydrous Ph_2SbCl_3 and found that it to exist as a dimer[26d] with chlorine bridges (figure 1). Later Bowen and coworkers have also supported an octahedral geometry with small deviation (8˚) for anhydrous Ph_2SbCl_3 and also for other trichloro compounds like Me_2SbCl_3, (p-FC_6H_4)$PhSbCl_3$.

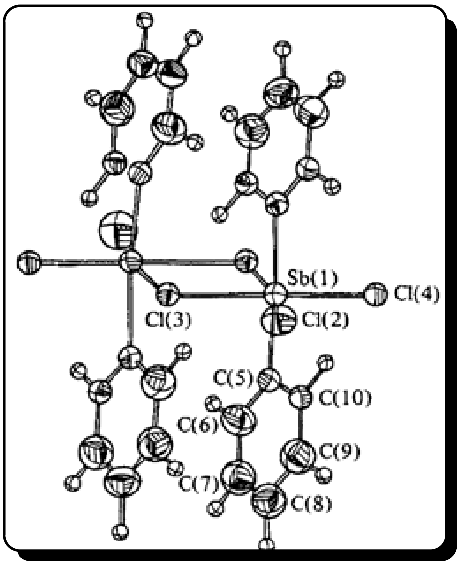


Figure 1: Structure of Ph_2SbCl_3 with chlorine bridges

Bone and Sowerby have prepared Ph_2SbBr_3, Ph_2SbBr_2Cl and $Ph_2SbBrCl_2$.[27] It was determined that in contradiction to octahedral dimeric Ph_2SbCl_3 all the bromine containing compounds are monomeric with distorted trigonal bipyramidal geometry having one Br and two phenyl groups occupying equatorial positions. This was attributed due to the increased elecronegativity of atoms in the axial positions in going from Ph_2SbBr_3 to $Ph_2SbBrCl_2$.

Diorganoantimony(V) halides forms monomeric covalent adducts $R_2SbX_3.L$ with various oxygen donor ligands (e.g DMSO, HMPA, PyO).[28] On the basis of ^1H and NMR spectral data an octahedral geometry has been proposed. Out of the three geometrical isomers, the existence of the isomer shown below has been proposed (chart 2).

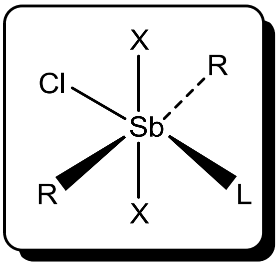


Chart 2: R_2SbX_2Cl. L

Triorganoantimony(V) halides are the best known organoantimony derivatives and have been explored in great detail. Though there are many synthetic routes the most general method for preparation of these compounds is the halogenation of the triorganoantimony (scheme 3).[29]

$$Ph_3Sb + SO_2Cl_2 \longrightarrow Ph_3SbCl_2 \dashrightarrow 3$$

Scheme 3

Triorganoantimony(V) halides can readily be reduced to the corresponding antimony(III) derivatives by various reducing agents. Both trialkyl and aryl antimony(V) halides will undergo elimination reaction, when heated above their melting points in the inert atmosphere (scheme 4).

$$R_3SbX_2 \xrightarrow{\Delta} R_2SbX + RX \dashrightarrow 4$$

Scheme 4

Molecular weight calculations of some triorganoantimony (V) halides show their monomeric behavior. Dipole moments of few of these compounds are also been calculated and correlated with the structures. The diamagnetic susceptibilities of tribenzylantimony(V) halides have been determined by Parab and Desai.[30] In the aryl derivatives, Jaffe and Rao et al has considered the pπ–dπ resonance between the benzene ring and vacant d-orbital's of the antimony atoms.[31]

For triorganoantimony(V) halides a trigonal bipyramidal geometry has been suggested on the basis of I.R and Raman analysis (chart 3).[29a,b] NMR spectroscopy has also been made to elucidate the nature of bonding in trialkyl and triarylantimony(V) halides. In the ^{1}HNMR spectra of trimethylantimony(V) difluoride the appearance of single methyl proton signal and splitting at 32° by two equivalent fluorine's are consistent with trigonal pyramidal geometry.[32a] NMR spectral data of Ph_3SbF_2 and Ph_3SbFCl are also in consistent with the trigonal pyramidal geometry,[32b] there exists some halide exchange reactions have also been investigated by moreland and group.[33]

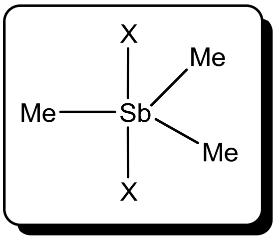


Chart 3: Trigonal pyramidal geometry of Me_3SbX_2

(i) Reactions of organoantimony(V) halides

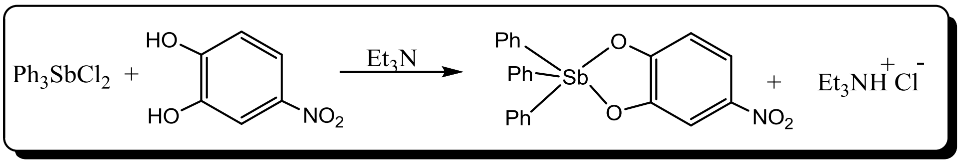
(i.a) with glycols and catechols:

Triorganoantimony(V) glycolates $R_3Sb(OXO)$, have been found to be monomeric in which diol groups appears to chelate antimony through oxygen atoms (scheme 5). These compounds are pentacoordinated probably in trigonal bipyramidal configuration in which oxygen atoms of the ligand occupy axial and one equatorial positions.[34]

$$R_3SbCl_2 + OH(X)OH \longrightarrow R_3SbO(X)O$$

Scheme 5

Interestingly Holmes et al synthesized monocyclic stiborane $Ph_3Sb(O_2C_6H_3\text{-}4\text{-}NO_2)$ by the reaction of Ph_3SbCl_2 with 4-nitrocatechol in the presence of Et_3N, X-ray structure analysis reveals the structure is close to square-pyramidal and not in trigonal bipyramidal configuration (scheme 6).[35] It was suggested that in the solid state it exists as weakly connected dimmers which accounts for its structural displacement towards the square pyramid geometry (figure 2).



Scheme 6

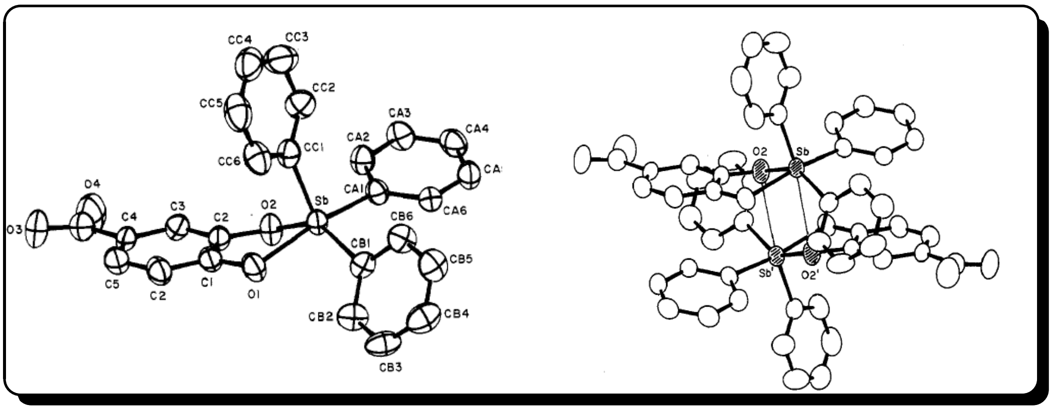


Figure 2 : ORTEP of $Ph_3Sb(O_2C_6H_3\text{-}4\text{-}NO_2)$ and Dimer

(i.b) with β-diketones:

Monoorganoantimony (acetylacetonato) trichlorides have been prepared by the reactions of either arylstibonic acid in HCl or of monoorganoantimony(V) chloride with acetylacetone at low temperatures.[36] All the monoorganoantimony(acetylacetonato) trichlorides are momomeric and behave as non-electrolyte in solution. The I.R spectra of these compounds show that acetylacetone behaves like a bidentate ligand. On the basis of the observed doublet and singlet for acetylacetone-Me in the ^{1}H NMR spectra, Okawara et al have suggested an asymmetric structure for $PhSb(acac)Cl_3$ and a symmetric structure for $MeSb(acac)Cl_3$ (figure 3).

For $MeSb(acac)Cl_3$ the magnitude of the separation between methyl resonance increases in aromatic solvents indicating an enhancement in the non-equivalance of two acetylacetone-Me groups as a result of the aromatic ring current effect on asymmetrically solvated solute molecule. Dipole moment data also supports the asymmetric geometry for these compounds. Later the X-ray analysis of $MeSb(acac)Cl_3$ support the asymmetric structure with distorted octahedral geometry.[37]

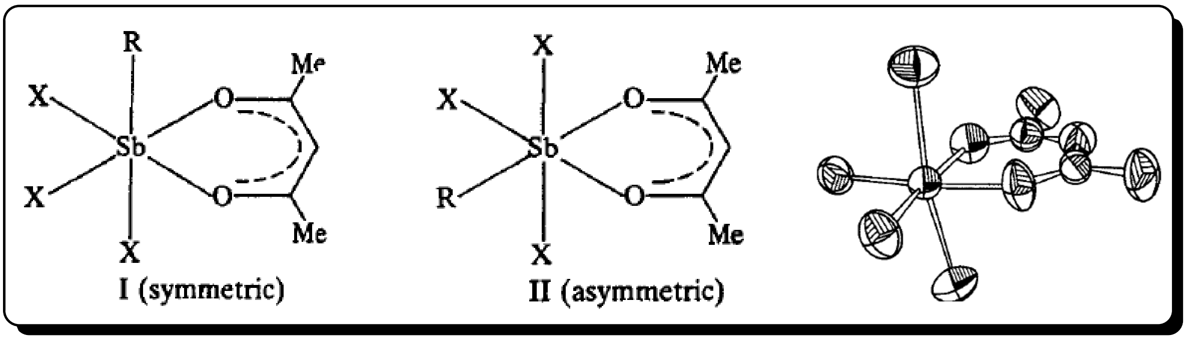
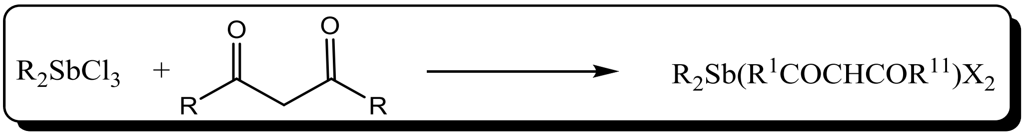


Figure 3: ORTEP of $MeSb(acac)Cl_3$ having asymmetric structure.

Diorganoantimony(V) β-diketones, $R_2Sb(R^1COCHCOR^{11})X_2$, (scheme 7) are monomeric and non conducting in nature.[36b] There are three possible geometric forms have been considered for the compounds of type $R_2Sb(acac)X_2$.



Scheme 7

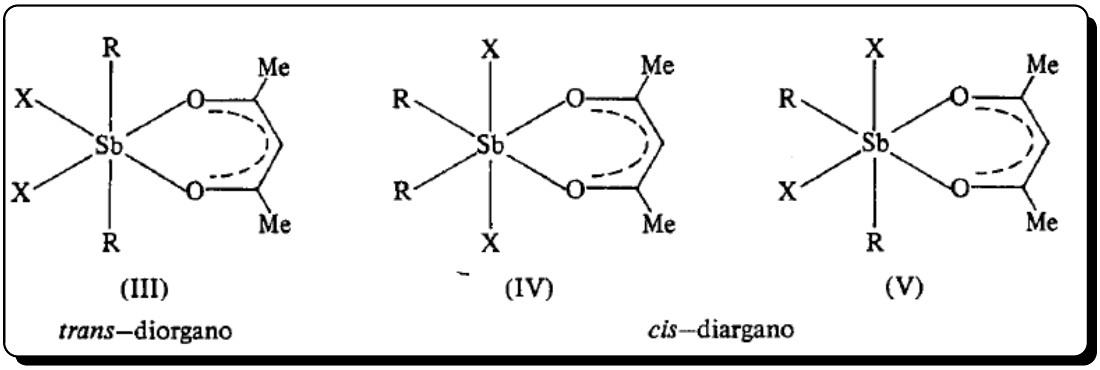


Chart 4: possible geometric forms of $R_2Sb(R^1COCHCOR^{11})X_2$

On the basis of the equivalence of the acetylacetone -Me groups and their peak separations in the ^1H NMR, it has been shown that these exists as a mixture of symmetric forms (III) and (IV) (chart 4). Compounds with R = methyl and ethyl groups and with acetylacetone moieties exists exclusively in trans dialkyl configuration.

The conclusions drawn from ^1H NMR spectral studies have been confirmed by X-ray diffraction studies of $Me_2Sb(acac)Cl_2$ and $Ph_2Sb(acac)Cl_2$.[37b,38] Antimony atom have been found to possess a slightly distorted octahedral geometry in which methyl groups occupy apical positions and are bent towards the planar acetylacetonato group. The compound

$Ph_2Sb(acac)Cl_2$ is also found to have distorted octahedral geometry in which the two phenyl rings occupy the trans positions (figure 4).

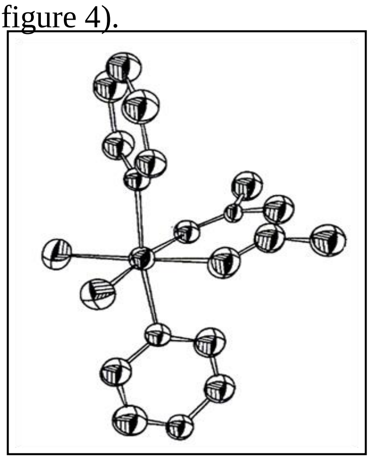


Figure 4: ORTEP of $ph_2Sb(acac)Cl_2$

Triorganoantimony(V) β-diketonates have been prepared by the following reaction route (scheme 8).

$$R_3SbX_2 \; + \; Na(R^1COCHCOR^{11}) \longrightarrow R_3SbX(R^1COCHCOR^{11}) \; + \; NaX$$

Scheme 8

These compounds are monomeric and the infrared spectra show that the ligands moieties are acting as chelating ligands. Their stereochemistry has been elucidated with the help of ^1H NMR spectroscopy. A trans Ph configuration has been proposed for the compounds of the type Ph_3Sb ($R^1COCHCOR^{11}$) (Chart 5).[36c, 39]

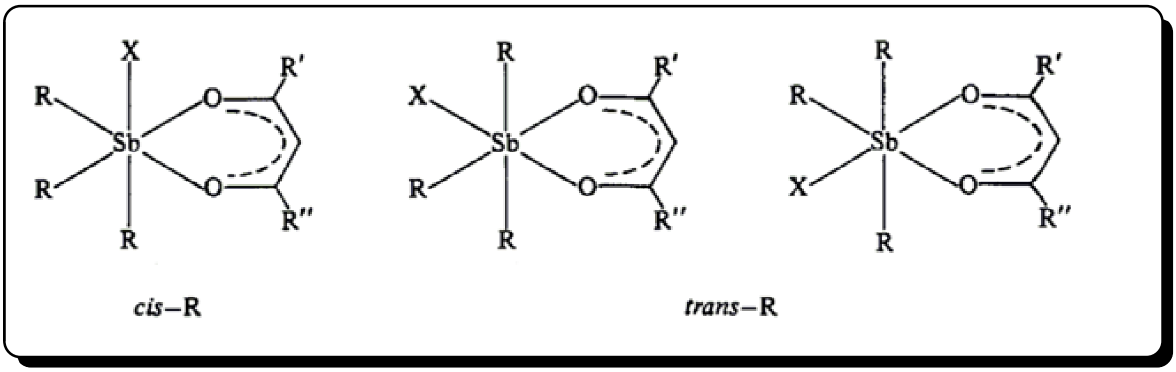
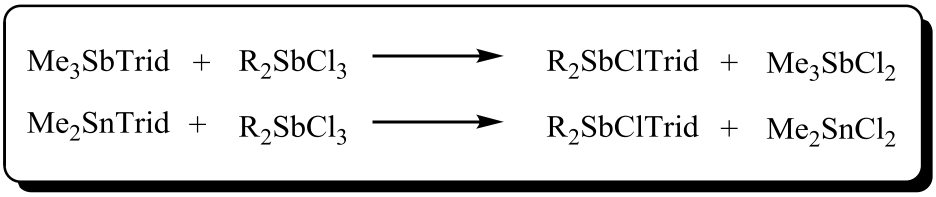


Chart 5: Cis and trans forms of $R_3Sb(R^1COCHCOR^{11})$.

(i.c) with schiff bases:

Diorganoantimony(V) complexes with dianionic tridentate Schiff base ligands (Trid) have been synthesized by the exchange reactions of diorganoantomony(V) chlorides with corresponding Schiff bases of trimethylantimony(V) or dimethyltin(IV) (scheme 9). These reactions proceed to happen as a result of the greater Lewis acidity of $R_2Sb(V)$ than that of $Me_3Sb(V)$ or $Me_2Sn(IV)$.[40]



$$Me_3SbTrid + R_2SbCl_3 \longrightarrow R_2SbClTrid + Me_3SbCl_2$$

$$Me_2SnTrid + R_2SbCl_3 \longrightarrow R_2SbClTrid + Me_2SnCl_2$$

Scheme 9

On the basis of the I.R and ^1H NMR studies, an octahedral coordination environment for the antimony atom with meridionial arrangement of the ONO ligand atoms and a linear C-Sb-C skeleton has been proposed. Further Mossbauer spectra for some complexes $Me_2Sb(sah)Cl$, $Me_2Sb(Bah)Cl$, $Ph_2Sb(Bah)Cl$ and $Ph_2Sb(Aah)Cl$ indicate octahedral geometry with meridionial arrangement (Chart 6).[41]

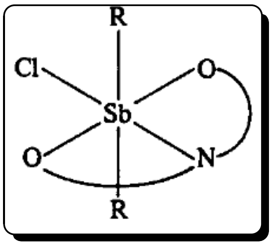
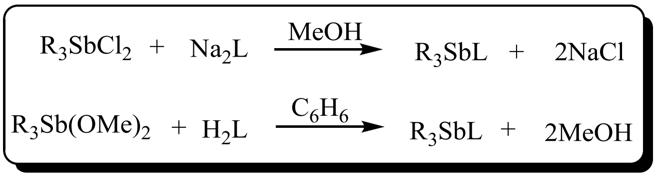


Chart 6: Octahedal arrangement of $R_2SbCl(Trid)$

Triorganoantimony(V) complexes with tridentate Schiff bases (chart 7) can be prepared by the treatment of triorganoantimony dichlorides with the sodium salt of the ligand in anhydrous methanol or reaction of triorgnaoantimony dimethoxides with free ligand in benzene solution (scheme 10).[42]



$$R_3SbCl_2 + Na_2L \xrightarrow{MeOH} R_3SbL + 2NaCl$$

$$R_3Sb(OMe)_2 + H_2L \xrightarrow{C_6H_6} R_3SbL + 2MeOH$$

Scheme 10

Both the U.V and I.R data suggests hexacoordinate molecular structures for the complexes R_3SbL in which the L^{2-} ligand coordinates to the $R_3Sb(V)$ as a planar tridentate ligand. An X ray structure determination has revealed that in the crystalline state the antimony atom in

$Me_3Sb(Sah)$ possesses a distorted octahedral geometry with meridionally disposed tridentate ligand and a T- shaped $R_3Sb(V)$ moiety (figure 5).[41,42b]

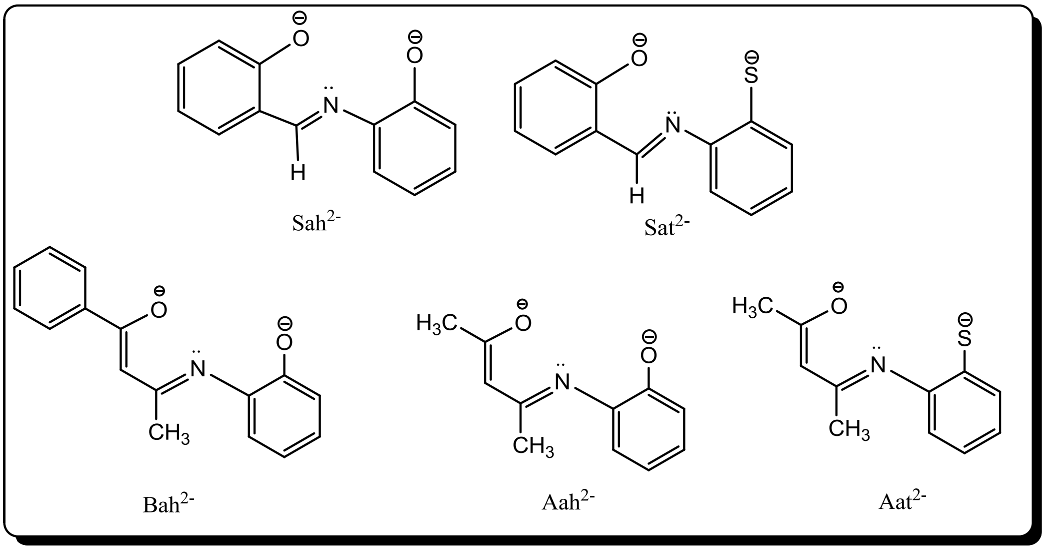


Chart 7: Various Schiff base ligands

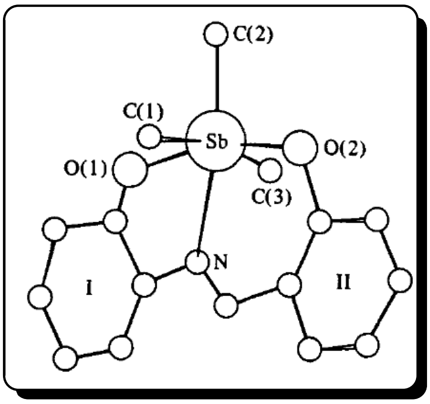


Figure 5: Crystal structure of $Me_3Sb(Sah)$ possesses a distorted octahedral geometry.

(i.d) with oximes :

Trioraganoantimony (V) oximates $[Ph_3Sb(ON{=}C(R)Ar)_2]$ can be synthesized by the reactions of triphenylantimony(V) halides with oximes (chart 8) in the presence of sodium methoxide base in toluene or methanol solutions (scheme 11).[43]

$$Ph_3SbCl_2 + \ Ar(R)C{=}NOH \xrightarrow{NaOMe} [Ph_3Sb\{ON{=}C(R)Ar\}_2] \ + \ NaCl$$

Scheme 11

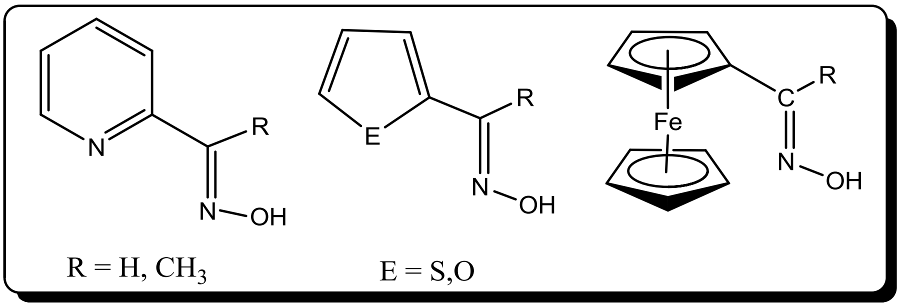


Chart 8: oximes derived from pyridine, thiophene, furan and ferrocene moieties

The structural feature of all the trioraganoantimony(V) oximates have been characterized by I.R, N.M.R spectroscopic and X-ray diffraction studies and it was reported that all the compounds shows slightly distorted trigonal bipyramidal coordination geometry around the antimony center with the carbon atoms of the $SbPh_3$ unit in equatorial positions and the two oxygen atoms of the oxime groups occupy axial positions (figure 6).

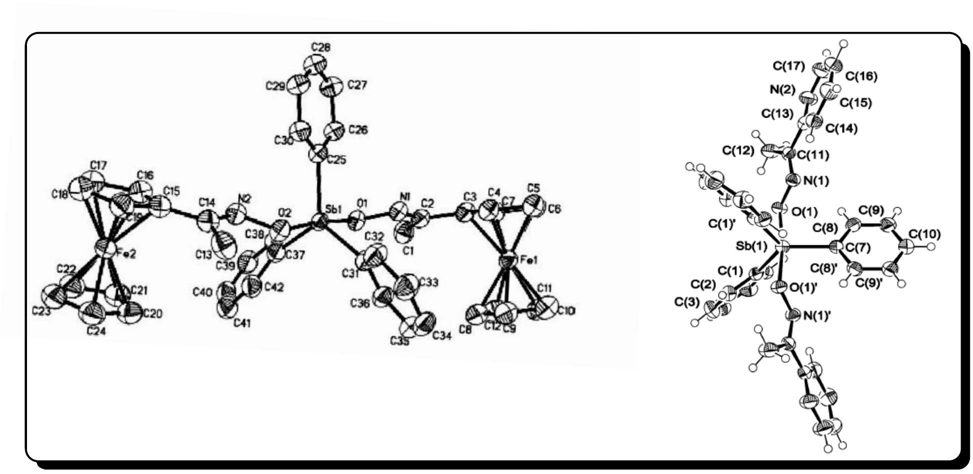


Figure 6: ORTEP of $[(C_5H_5FeC_5H_4C(CH_3)=NO)_2SbPh_3]$ and $[Ph_3Sb\{ON=C(Me)C_5H_4N\text{-}2\}_2]$

(i.e) with phosphinates :

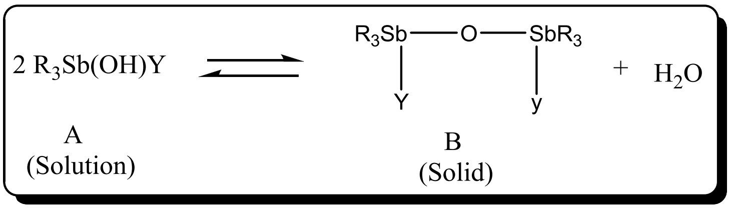
Reactions of triorganoantimony halides with sodium salt of the appropriate dioragnophophinic acids afford bis(diorganophosphinato)triorganoantimony(V) complexes $R_3Sb(O_2PR_2^1)$ (scheme 12).

$$R_3SbCl_2 + 2\,NaO_2PR_2^1 \longrightarrow R_3Sb(O_2PR_2^1)_2 + 2\,NaCl$$

R = Me, Ph $\qquad$ R^1 = Me, Ph

Scheme 12

Silvestru and group investigated these derivatives by I.R and multinuclear (^{1}H, ^{13}C, ^{31}P) NMR spectroscopy. Attempts to crystallize $Me_3Sb(O_2PR_2^1)_2$ has lead to the partially hydrolyzed product $Me_3Sb(OH)[O(O)PPh_2]$.[44] Coordination around the central antimony atom is distorted trigonal bipyramidal with the carbon atoms of the $SbMe_3$ unit in equatorial positions and two oxygen atoms occupying the axial positions (figure 7). There are suggestions that the bulky organic groups on antimony or bulky ligands might stabilize the hydroxo form A in the solid state (scheme 13).



Scheme 13

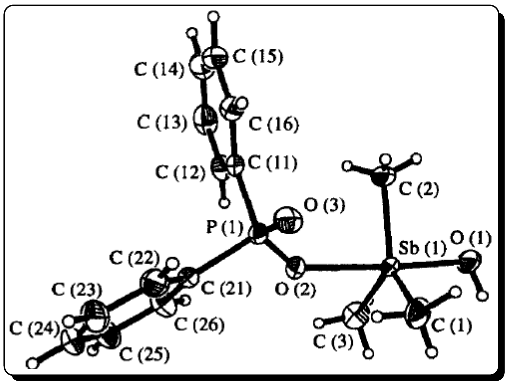


Figure 7: ortep of $Me_3Sb(OH)[O(O)PPh_2]$

Reactions of diphenylantimony trichloride with two equivalents of siver salt of phosphinates leads to the isolation of partially hydrolyzed product $\{SbPh_2Cl[O_2P(C_6H_{11})_2]\}_2O$ (scheme 14).[13a]

$$2Ph_2SbCl_3 + 2AgO_2P(C_6H_{11})_2 \xrightarrow[-2HCl]{H_2O} \{SbPh_2Cl[O_2P(C_6H_{11})_2]\}_2O + 2AgCl$$

Scheme 14

X-ray diffraction reveals that antimony atoms are in octahedral arrangement with bridging phophinates cis to each other. The $\overline{Sb\text{-}O\text{-}P\text{-}O\text{-}Sb\text{-}O}$ rings have a boat conformation with phosphorus at one of the prow positions (chart 9).

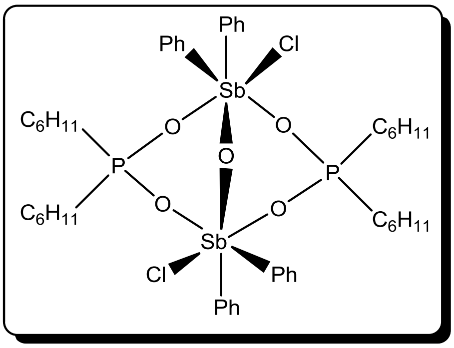
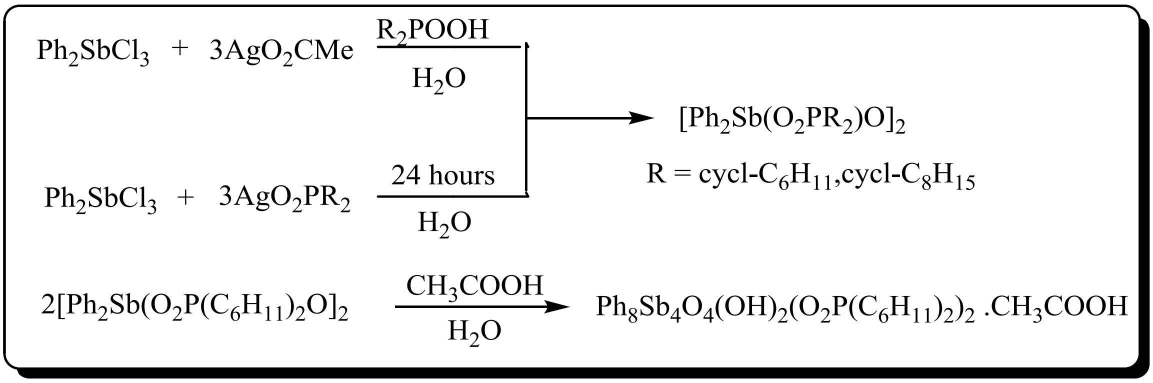


Chart 9: Structure of $\{SbPh_2Cl[O_2P(C_6H_{11})_2]\}_2O$

Kumara swamy et al, reported antimony(V) phosphinates by treating diphenylantimony trichloride with three equivalence of silver acetate followed by one equivalence of phosphinic acid yields dimeric compounds of formula $[Ph_2Sb(O_2PR_2)O]_2$. Interestingly when the dimer was treated with acetic acid / water affords the tetra nuclear cage containing cluster of formula $Ph_8Sb_4O_4(OH)_2(O_2P(C_6H_{11})_2)_2$ are reported (scheme 15).[45]



Scheme 15

All the compounds are structurally characterized by X-ray analysis. In the di and the tetra nuclear clusters the antimony is hexa coordinated with four membered Sb_2O_2 rings. In tetranuclear cluster two Sb_2O_2 rings are connected by oxo bridges on two sides to give an Sb_4O_6 cage (Chart 10).

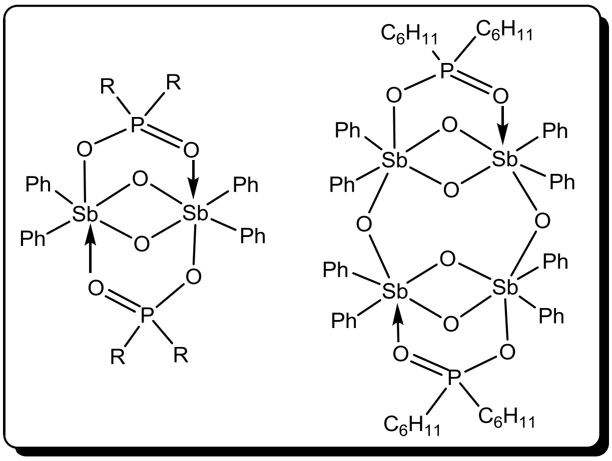
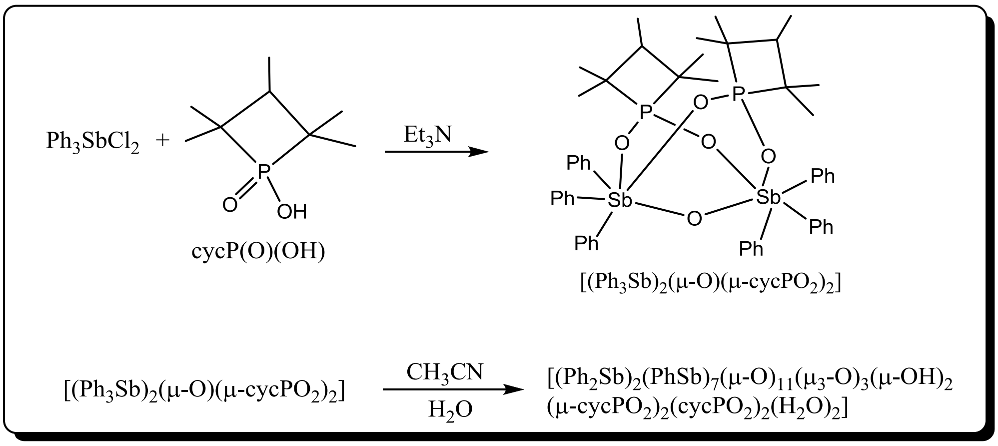


Chart 10: Sb_2O_2 and Sb_4O_6 rings in $[Ph_2Sb(O_2PR_2)O]_2$ and $Ph_8Sb_4O_4(OH)_2(O_2P(C_6H_{11})_2)_2$.

Chahdrasekhar et al reported the first example of a nonanuclear organostiboxane cage by reacting Ph_3SbCl_2 with 2 equivalence of *cyc*-phosphinic acid ($cycPO_2$) 1,1,-2,3,3-pentamethyltrimethylene phosphinate) in the presence of Et_3N which affords a dimer $[(Ph_3Sb)2(\mu\text{-}O)(\mu\text{- }cycPO_2)_2]$ (scheme 16).



Scheme 16

Interestingly this dimer while subjected to mild hydrolysis in a mixture of acetonitrile / water mixture (99:1) at 45˚C affords a nonanuclear organostiboxane cage $[(Ph_2Sb)_2(PhSb)_7(\mu\text{-}O)_{11}(\mu_3\text{-}O)_3(\mu\text{-}OH)_2(\mu\text{-}cycPO_2)_2(cycPO_2)_2(H_2O)_2]$ $2CH_3CN$ H_2O which containing a Sb_9O_{16} core (Chart 11).[46]

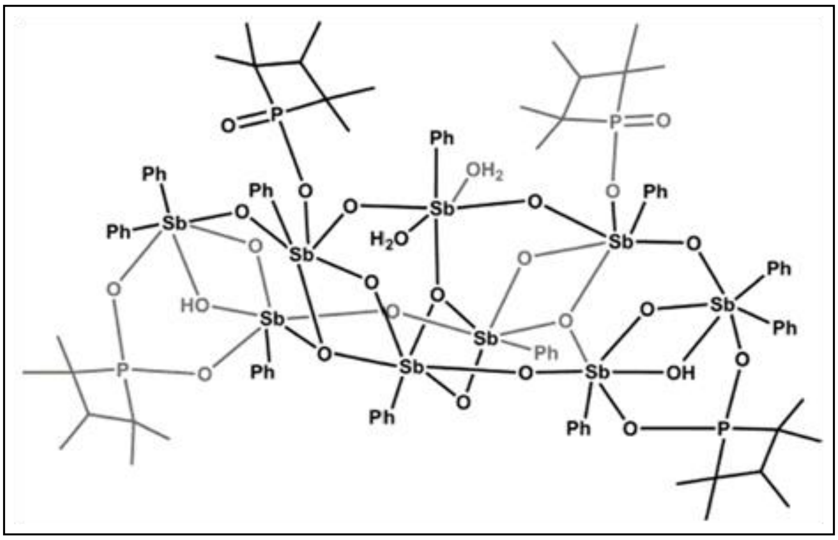
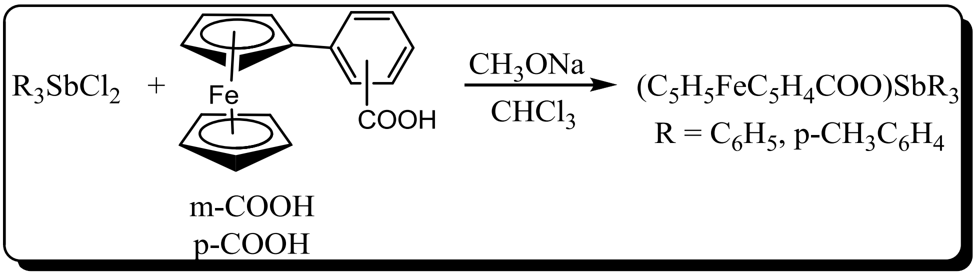


Chart 11 : molecular structure of $[(Ph_2Sb)_2(PhSb)_7(\mu\text{-}O)_{11}(\mu_3\text{-}O)_3(\mu\text{-}OH)_2(\mu\text{-}cycPO_2)_2(cycPO_2)_2(H_2O)_2]$

(i.f) with carboxylic acid groups:

Triarylorganoantimony(V) carboxylates can be prepared by reacting triarylantimony halides with carboxylic acids in the presence of sodium methoxide base (scheme 17). Badshah and group synthesized organoantimony(V) ferrocenyl benzoates[47] by treating triphenylantimony dichloride with (m, p)-ferrocenyl benzoic acids in the presence of base sodium methoxide. The complexes adopt an approximate trigonal bipyramidal Sb coordination environment with unidentate carboxylic acids in the axial positions at trans orientation with respect to ferrocenyl moiety (figure 8). The three aryl groups are in equatorial plane and show a slight distortion towards square base pyramidal with a widening of one of the trigonal angle. Further these complexes show there binding activity towards DNA which was investigated by U.V-Vis spectroscopy and cyclic voltammetry (CV).



Scheme 17

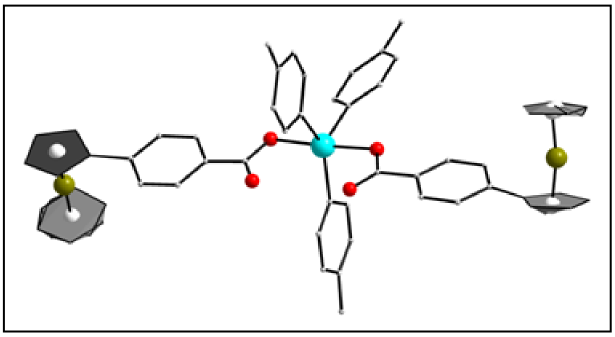
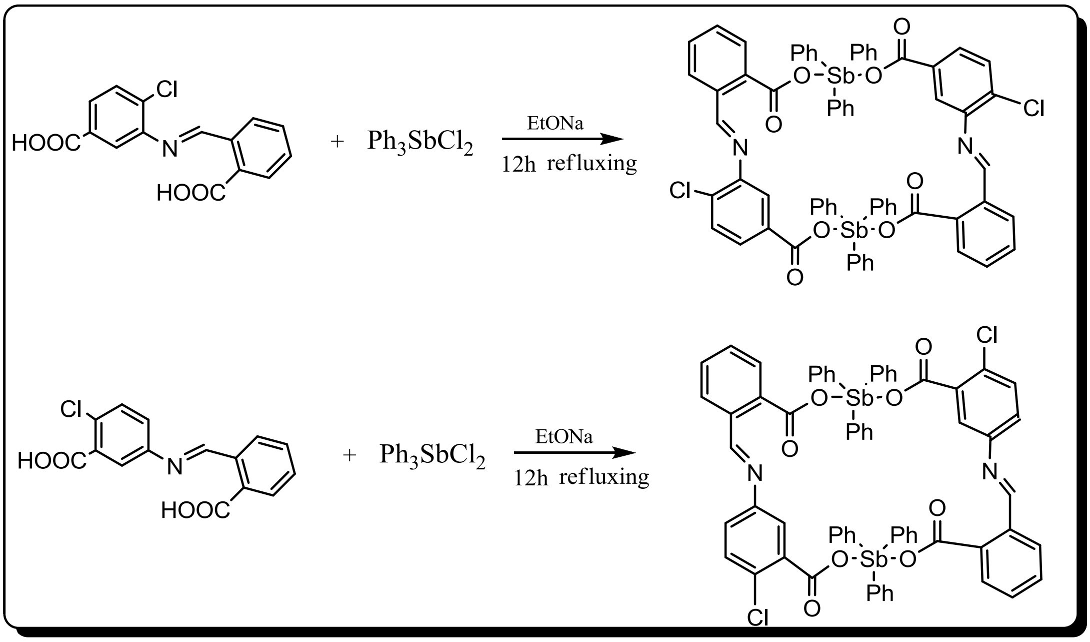


Figure 8: Ball and stick model of $(C_5H_5FeC_5H_4COO)Sb(p\text{-}CH_3C_6H_4)_3$

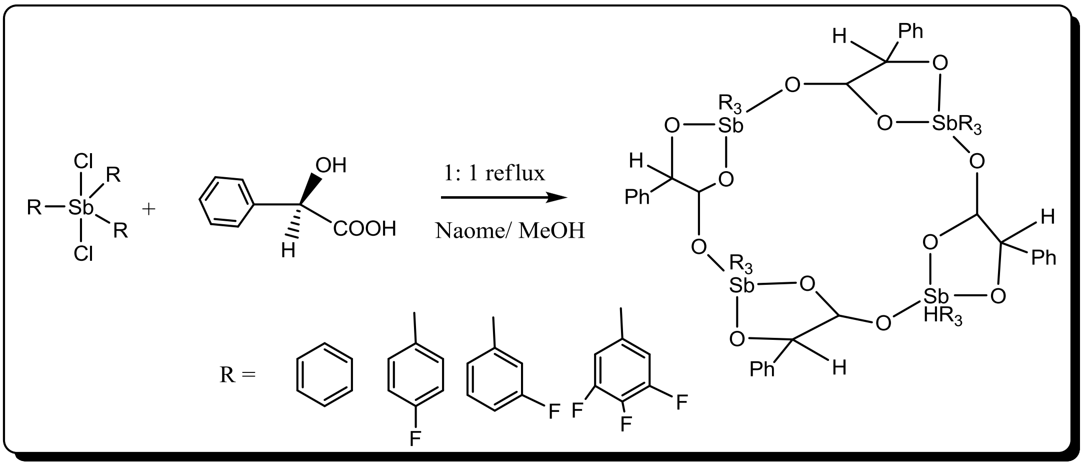
Further synthesis of highly symmetrical 24-membered macrocyclic organoantimony(V) complexes $[Ph_3SbL^a]_2$ and $[Ph_3SbL^b]_2$ (H_2L^a = 5-{[(2-carboxyphenyl)methylene]amino}-4-chloro benzoic acid, and (H_2L^b = 5-{[(2-carboxyphenyl)methylene]amino}-2-chloro benzoic acid) are reported by H-D Yin and group by treating triphenylantimony dichloride with Schiff bases containing carboxylic acids (scheme 18).[48]



Scheme 18

X-ray diffraction studies reveals that antimony atoms are bridged by four terminal carboxylic groups of the Schiff base ligands and antimony atoms exhibit typical five coordinated trigonal bipyramid geometry with two carboxyl atoms occupying the axial positions.

M. Hong group synthesized some novel tetranuclearantimony(V) complexes by reactions of triarylantimonydichlorides and the mandelic acid in the presence of sodium ethoxide base (scheme 19).[49] The structural analysis reveals the cluster is composed of four antimony metal centers in which each one is bounded to three phenyl rings and coordinated to the tridentate $O_2CC(O)(H)Ph$ moiety. Through the 1,3-transannular interaction it forms cyclometallated products. The central part of the structure remains planar but the antimony atoms are slightly bent out of the planes. During the dicarboxy ester interaction it forms a chelate ring which contains 16 atoms, the chelate ring is in boat conformation.

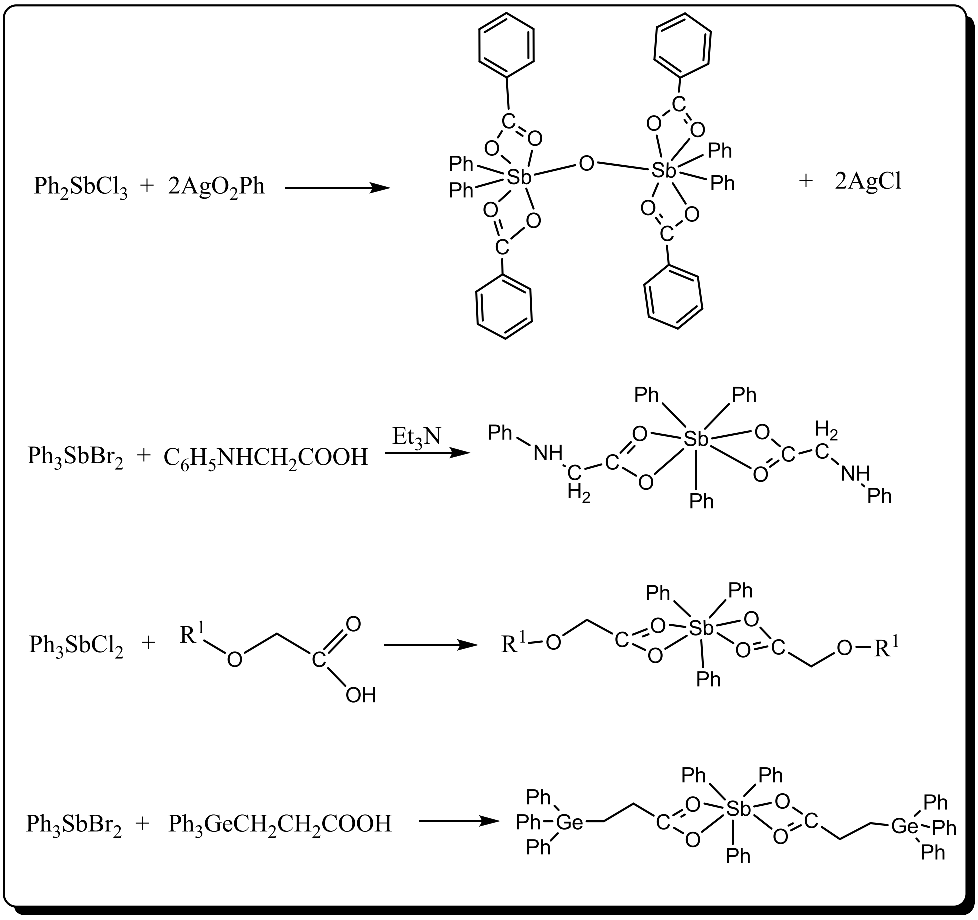


Scheme 19

(ii) Hypervaleny in organoantimony(V) complexes

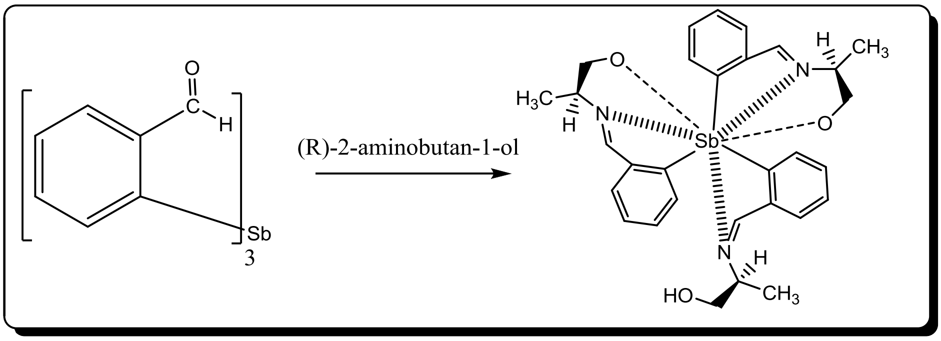
In majority of the organoantimony(V) complexes antimony has coordination number of five. Due to the hypervalent nature of the antimony atom, in some cases it may have a coordination number of six or seven even some times it might reaches to eight.

The coordinate number seven for antimony atoms are reported by various groups by reactions of diorganoantimony(V) trihalides with silver salts of carboxylic acids or treating triorganoantimony(V) halides with N-phenyl glycine, or aryloxyacetic acids or triphenylgermanylpropionic acids (scheme 20).[13]



Scheme 20

P. Sharma etal synthesized tris[(R)-2-benzyliden-2-yl-amino)butan-1-ol]stibine by trating Tris(o-formylphenyl)stibine with (R)-2-aminobutan-1-ol. Xray structure analysis of this antimonated Schiff base shows hypervalent interactions between antimony and SP^2 nitrogen atoms. Further it also shows interestingly intramolecular Sb-O interactions giving eight coordination to antimony (Scheme 21).[13f]



Scheme 21: organoantimony(V) compounds showing eight coordination number.

A brief introduction about the reactions of antimony(v) halides with O and N donors are given in the above sections. In the following chapters our investigations of antimony(v) halides with pyrazolyl phenols and organosilanols will be dealt with in detail.

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Diorganoantimonyl Phenolic Pyrazolates

Chapter 3

Abstract: Reaction of phenolic pyrazoles HRPzR1 (R = phenolic, and naptholic: R1 = phenyl and hydrogen) with tri- and diorganoantimony halides afforded colorless products whose structures were characterized by single crystal X-ray diffraction technique. Structural analysis revealed the formation of mono-, di- and tetranuclear antimony oxo-hydroxo compounds / clusters $[(Ph_2SbCl_2)(HPhPzPh)]$ (**3.1**), $[(Ph_2Sb)_2(O)(PhPz)_2]$ (**3.2**), $[(Ph_2Sb)_2(O)(PhPzPh)_2]$ (**3.3**), $[(Ph_2Sb)_2(O)(NpPz)_2]$ (**3.4**) and $[(Ph_2Sb)_4(HPhPzPh)_2(O)_4(OH)_2]$ (**3.5**). The diorganoantimony dimers (**3.2, 3.3** and**3.4**) have not only been obtained by reaction of diphenylantimony trichloride with phenolic pyrazoles but also by dearylation reactions starting from triphenylantimony dihalides. Structural analysis of the products revealed the presence of interesting four (Sb_2O_2), five- (Sb_2N_2O), six (Sb_2N_4), and eight-membered (Sb_4O_4) ring systems stabilized by phenolic pyrazolyl ligation.

3.1 Introduction:

The applications of organoantimony compounds in catalysis[1] and biology[2] are well documented. Moreover the rich structural variations that organoantimony compounds exhibit has been exploited and several types of organoantimony oxo clusters has been synthesized and structurally characterized.[3-6] Primarily the clusters have been synthesized by reactions of carboxylates, phosphinates, phenols and oximes with organoantimony halides in presence of a base.[7-12] Further due to hypervalent nature of Sb(V), coordination numbers up to seven or even eight around the Sb atom has been achieved.[13-18] Recently, we have been interested in the chemistry of organostibonic acid and phenylboronic acid and have investigated their reactions with phenolic pyrazoles. By varying the steric bulk of the groups present on the pyrazole ring, novel tetra nuclear organoantimony oxo clusters have been synthesized.[19] In the case of reaction of phenolic pyrazoles with phenylboronic acid, again depending on the steric bulk of the groups present on the 3, 5-positions of the pyrazole ring, different modes of coordination of the pyrazole ring nitrogen's have been observed.[20] Since reactions of organoantimony(v) halides with N, N, O -donor ligands are hitherto unknown, we were interested to investigate the reactivity of phenolic pyrazoles with organoantimony halides. In this chapter the synthesis and structural characterization of $[(Ph_2SbCl_2)(HPhPzPh)]$ (**3.1**), $[(Ph_2Sb)_2(O)(PhPz)_2]$ (**3.2**), $[(Ph_2Sb)_2(O)(PhPzPh)_2]$ (**3.3**), $[(Ph_2Sb)_2(O)(NpPz)_2]$ (**3.4**) and $[(Ph_2Sb)_4(HPhPzPh)_2(O)_4(OH)_2]$ (**3.5**) are reported.

3.2 Experimental Section:

3.2.1 General information:

Ph_3SbCl_2, Ph_2SbCl_3 and ligands were synthesized using literature procedures.[21-23] Solvents and other common reagents were purchased from commercial sources. Infrared spectra were recorded on a JASCO-5300FT-IR spectrometer as KBr pellets. The H^1, C^{13}, NMR spectra were recorded on Brucker AVANCE^{III} 400 instrument. Elemental analysis was performed on a Flash EA Series 1112 CHNS analyzer.

3.2.2 Synthetic methodology:

General synthetic method used is as follows. Organoantimony halides (Ph_3SbCl_2 or Ph_2SbCl_3) and pyrazolyl ligands ($H_2PhPzPh$ or H_2PzPh or H_2NpPzH) were taken in 30ml of toluene (**3.2**, **3.3**, **3.4** and **3.5**) and was stirred for ten minutes. Triethylamine was added and the stirring was continued for another six hours at room temperature. The resultant solution was filtered off and the solvent was removed under vacco to form a white crystalline powder. In the case of **3.1** when the organoantimony halide and phenolic pyrazole was stirred in dichloromethane a solid was thrown out which was filtered and crystallized from ethanol to yield the product **3.1**. Block type crystals of **3.2-3.5** were formed from DCM or $CHCl_3$ or toluene in a week's time. The stoichiometry and the amounts of the reagents used in each case are given below.

Compound 3.1: Ph_2SbCl_3 0.3g (0.78 mmol), $H_2PhPzPh$ 0.18g (0.78 mmol). Yield: 0.1g (21.9%). M.P. 210˚C IR (KBr): υ (cm^{-1}) 3248(w), 1612(s), 1581(s), 1462(w), 1435(s), 1342(m), 1304(w), 1257(w), 1047(m), 991(s), 760(s), 738(s), 684(m), 625(m). Elemental anal.cal. for $C_{27}H_{21}N_2SbOCl_2$: C, 55.70; H, 3.63; N, 4.812. Found: C, 55.61, H, 3.58; N, 4.75. ^1H NMR (400MHz $CDCl_3$): δ 8.20 (d, 1H), 8.09 (d, 1H), 8.03 (d, 1H), 7.84 (d, 3H), 7.48 (m, 11H), 7.20 (t, 2H), 6.92 (m, 2H). ^{13}C NMR (400MHz $CDCl_3$): δ 161.65, 132.33, 131.29, 130.97, 130.69, 129.90, 129.40, 129.06, 128.48, 127.92, 127.49, 125.77, 119.74, 116.86.

Compound 3.2: Ph_3SbCl_2 0.4g (0.9 mmol), H_2PhPz 0.15g (0.9 mmol) Et_3N 0.19g (1.8mmol). Yield: 0.18g (43.9 %). M.P. 307˚C, IR (KBr) : υ (cm^{-1}) 3057(m), 1601(s), 1564(s), 1520(m), 1481(s), 1454 (m), 1433 (s), 1356(m), 1286(s) ,1232(s), 1130(s), 1070(s), 1037(w), 979(m), 943(m), 844(s), 756(m), 733(s), 663(m), 617(m), 570(s), 491(s), 449(s), 428(m). Elemental Anal.cal. for $C_{42}H_{32}N_4Sb_2O_3$: C, 57.04; H, 3.64; N, 6.33. Found: C, 57.12; H, 3.68; N, 6.38. ^1H NMR (400 MHz $CDCl_3$): δ 8.27 (d, 4H), 7.59 (s, 2H), 7.49 (d, 10H), 7.26 (d, 2H), 7.23-7.12 (m, 10H), 6.75 (t, 2H), 6.24 (s, 2H). ^{13}C NMR (400 MHz $CDCl_3$): δ 158.41, 146.30, 144.86, 135.70, 135.26, 133.30, 133.05, 130.85, 129.82, 129.67, 129.33, 128.88, 128.34, 127.02, 119.43, 117.85. Compound **3.2** was also synthesized starting from Ph_2SbCl_3. The stoichiometry of the reagents taken are Ph_2SbCl_3 0.3g (0.78 mmol), H2phpz 0.12g (0.78 mmol), Et_3N 0.158g (0.15 mmol). Yield: 0.2g (28.9%). The spectroscopic and analytical data match with that of **3.2**.

Compound 3.3: Ph_3SbCl_2 0.3g (0.70 mmol), H2PhPzPh 0.16g (0.70 mmol), Et_3N 0.143g (1.4 mmol). Yield: 0.15g (40%). M.P. 296˚C, IR (KBr) : υ (cm^{-1}) 3543(w), 3053(w), 1599(m), 1564(m), 1477(s), 1454(s), 1431(s), 1240(m), 1066(m), 1061(m), 846(m), 760(s), 733(s), 694(s), 597(w), 453(m). Elemental Anal.calc. for $C_{54}H_{40}N_4Sb_2O_3$: C, 62.57; H, 3.89; N, 5.40. Found: C, 62.45; H, 3.92; N, 5.51. ^{1}H NMR (400MHz $CDCl_3$): δ 7.94 (d, 3H), 7.63 (t, 2H), 7.53 (d, 3H), 7.51-7.41 (m, 4H), 7.37-7.32 (m, 5H), 7.30-7.19 (m, 10H), 7.06-6.92 (m, 7H), 6.75-6.72 (t, 1H), 6.56 (d, 2H), 6.34 (s, 1H), 6.28 (d, 2H). ^{13}C NMR (400MHz $CDCl_3$): δ 158.29, 151.71, 148.23, 147.24, 146.53, 134.31, 132.87, 129.92, 129.27, 128.51, 127.43, 126.56, 121.46, 119.34, 117.15, 116.09.

Compound 3.4: Ph_2SbCl_3 0.2g (0.52 mmol), H_2NppzH 0.1g (0.52 mmol), Et_3N 0.19g (1.04mmol). Yield 0.12 (41.6 %). M.P. 298˚C, IR (KBr) : υ (cm^{-1}) 3450(m), 1638(s), 1562(s), 1520(m), 1497(s), 1468(m), 1431(s), 1384(m), 1330(s) ,1238(s), 1138(s), 1075(s), 1021(w), 998(m), 954(m), 841(s), 771(m), 734(s), 663(m), 610(m), 580(s), 493(s), 455(s), 428(m). Elemental Anal.cal. for $C_{50}H_{36}N_4Sb_2O_3$: C, 61.01; H, 3.69; N, 5.69. Found: C, 61.12; H, 3.65; N, 5.72. ^{1}H NMR (400 MHz $CDCl_3$): δ 8.66 (br, s, 2H), 8.28 (br, s, 4H), 7.75 (m, 2H), 7.62-7.65 (m, 16H), 7.37-7.34 (m, 2H), 7.24 (m, 2H), 7.18-7.12 (m, 6H) 6.28 (d, 2H). ^{13}C NMR (400MHz $CDCl_3$): δ 154.61, 147.18, 146.91, 144.74 136.31, 134.90, 133.41, 132.95, 130.25, 129.82, 128.98, 128.59, 127.60, 125.49, 119.11, 117.85. Compound **3.4** was also synthesized starting from Ph_3SbCl_2. The stoichiometry of the reagents taken are Ph_3SbCl_2 0.2g (0.47 mmol), H_2NppzH 0.1 g (0.47 mmol), Et_3N 0.1g (0.15 mmol). Yield 0.1gm (38.4%). The spectroscopic and analytical data match with that of **3.4**.

Compound 3.5: Ph_2SbCl_3 0.3g (0.78 mmol), $H_2PhPzPh$ 0.18g (0.78 mmol), Et_3N 0.158g (0.156 mmol). Yield 0.19g (14.5%). M.P. 292 ˚C, IR (KBr) : υ (cm^{-1}) 3053(m), 1601(s), 1568(s), 1537(m), 1475(s), 1431(m), 1300(m), 1234(m), 1122(m), 1070(m), 995(m), 854(s), 692(s), 586(m), 495(w), 459(w). Elemental Anal.cal. for $C_{78}H_{64}N_4Sb_4O_8$: C, 56.08; H, 3.74; N, 3.35. Found: C, 56.25; H, 3.68; N, 3.31. ^{1}H NMR (400MHz $CDCl_3$): δ 7.92 (d, 4H), 7.63 (t, 4H), 7.55-7.43 (m, 11H), 7.37-7.35 (m, 7H), 7.34-7.26 (m, 13H), 6.99-6.92 (m, 14H), 6.73 (t, 3H), 6.56 (d, 4H), 6.29-6.27 (m, 4H). ^{13}C NMR (400MHz $CDCl_3$): δ 156.04, 148.23, 147.23, 134.31, 132.87, 132.87, 129.92, 129.62, 129.20, 128.72, 128.50, 127.43, 125.67, 119.34, 118.82, 117.74.

3.3 X-ray structure determination:

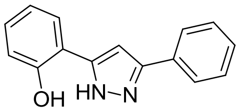
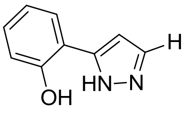
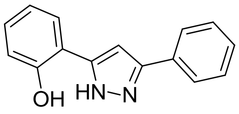
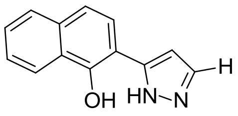
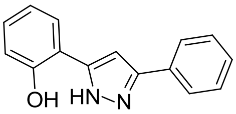
Single-crystal X-ray data collection for compounds **3.1-3.5** were carried out at 100(2) K on Bruker Smart Apex CCD area detector system (λ (Mo Kα) = 0.71073 Å) equipped with Oxford Cryo stream low temperature device and graphite monochromator. The data were reduced using SAINTPLUS and the structures were solved using SHELXS-97[24] and refined using SHELXL-97.[25] The structures were solved by direct methods and refined by full-martix least squares cycles on F^2. All non-hydrogen atoms were refined anisotropically.

3.4 Results and Discussion:

3.4.1 Synthesis:

General synthetic methodology used is as follows; When Ph_2SbCl_3 and $H_2PhPzPh$ (1:1 ration) were stirred in dichloromethane, a white solid (**3.1**) precipitated in good yield. Compounds **3.2**, **3.3**, **3.4** and **3.5** have been prepared by treating corresponding arylantimony halides with phenolic pyrazoles in toluene in the presence of triethylamine as a base (chart 1). Single crystals suitable for X-ray diffraction were grown from ethanol (**3.1**), dichloromethane/hexane (**3.2**), toluene (**3.3**) and chloroform/hexane (**3.4**, **3.5**). The compounds were characterized by standard spectroscopic and analytical methods.

Chart 1

S.No	Organo antimony halides	Phenolic pyrazoles	Base	Products
1	Ph_2SbCl_3		—	$[(Ph_2SbCl_2)(HPhPzPh)]$ (Monomer)
2	Ph_3SbCl_2/Ph_2SbCl_3		Et_3N	$[(Ph_2Sb)_2(O)(PzPh)_2]$ (Dimer)
3	Ph_3SbCl_2		Et_3N	$[(Ph_2Sb)_2(O)(PhPzPh)_2]$ (Dimer)
4	Ph_3SbCl_2/Ph_2SbCl_3		Et_3N	$[(Ph_2Sb)_2(O)(NpPz)_2]$ (Dimer)
5	Ph_2SbCl_3		Et_3N	$[(Ph_2Sb)_4(HPhPzPh)_2(O)_4(OH)_2]$ (Tetramer)

3.5 Description of the Crystal Structure:

Compound **3.1** crystallizes in triclinic space group P-1. The ligand H_2PhPzPh binds to the antimony atom through one of the the pyrazole nitrogen atom (N1) and a phenolic oxygen (O1) while the other nitrogen (N2) of the pyrazole group bearing the hydrogen atom remains a spectator. The remaining four coordinations of the hexa-coordinated antimony comes from the two phenyl carbons and two chlorine atoms. The Sb1-O1 and Sb1-N1 bond distances are 2.025(16), 2.240(19) Å which falls in the range as reported in the literature.[19]

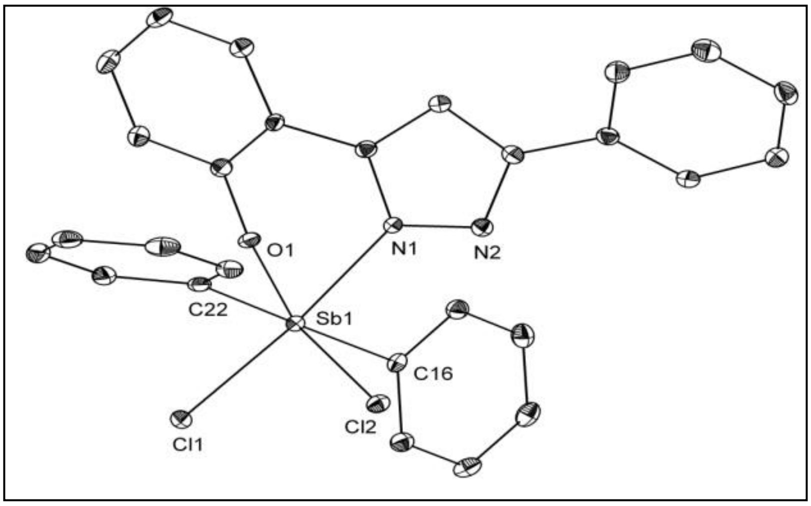
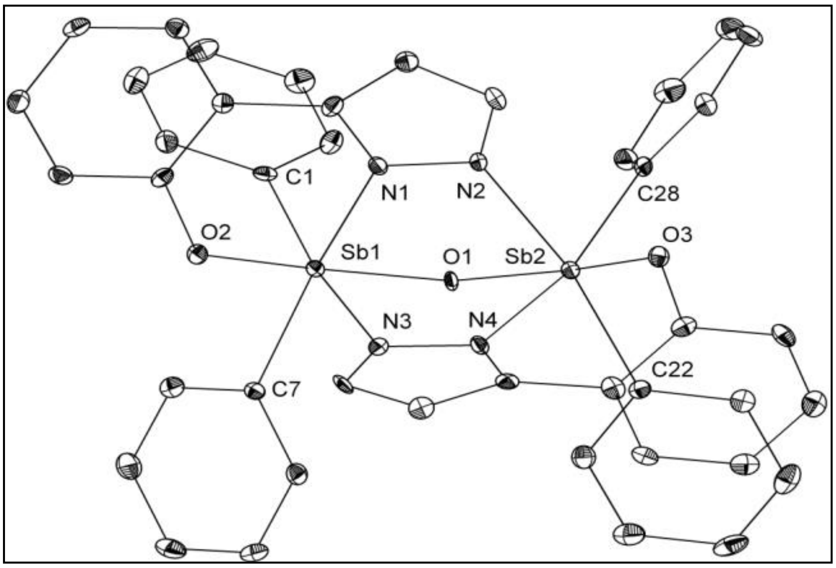
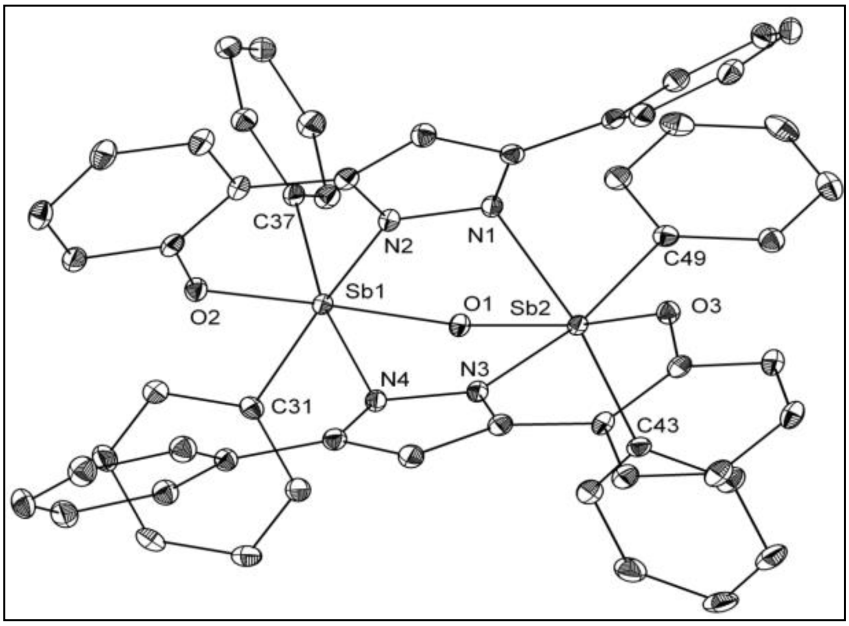


Figure 1: The solid state structure of **3.1**; hydrogen atoms and solvents of crystallization are omitted for clarity

Single Crystal X-ray elucidation studies for **3.2**, **3.3** and **3.4** revealed the formation of dinuclear antimony oxo clusters which are similar in structures but differ in the coordinating ligands present, H_2PhPz, H_2PhPzPh and H_2NpPzH (for **3.2**, **3.3** and **3.4**) respectively. **3.2** crystallizes in monoclinic space group P2(1)/c, **3.3** and **3.4** crystallize in triclinic space group P-1. The ligands (H_2PhPz or H_2PhPzPh or H_2NpPzH) are bound to the Sb atoms through chelating (O, N-) and bridging (N, N-) mode resulting in the formation of antimony dimer. The Sb1-Sb2 metal centers are connected through (μ_2-O) bridge leading to the formation of a five (Sb_2N_2O) and six-membered (Sb_2N_4) membered ring systems. Coordination geometry of each Sb atom is octahedral. The Sb-O and Sb-N bond distances in **3.2-3.4** are in the range as reported in the literature.[19] It should be mentioned here that dearylation of triorganoantimony dihalide was also observed leading to the formation of diorganoantimony derivatives (**3.2**, **3.3** and **3.4**) when the reactions were carrying out with Ph_3SbCl_2 and phenolic pyrazoles in presence of a base.



(a)



(b)

Figure 2: (a, b) The solid state structures of (**3.2-3.3)**; hydrogen atoms and solvents of crystallization are omitted for clarity

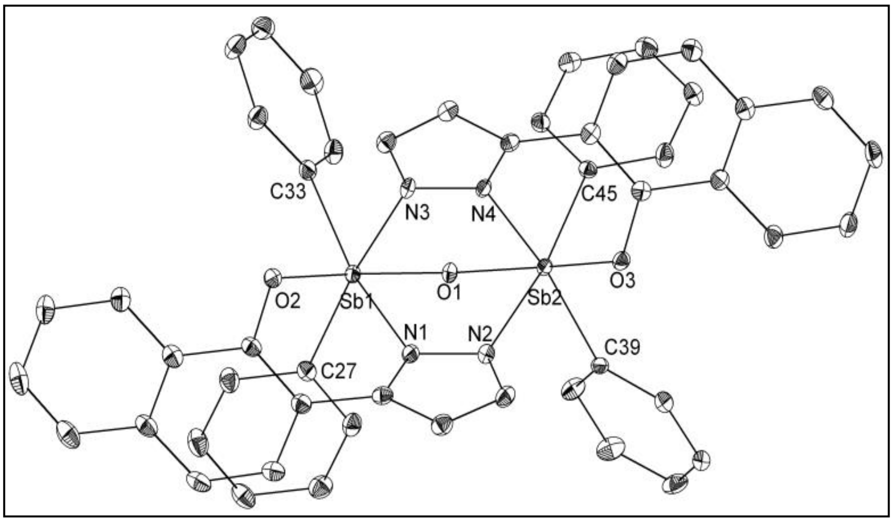


Figure 3: The solid state structures of **3.4**; hydrogen atoms and solvents of crystallization are omitted for clarity

Recently, we have investigated the reactions of phenolic pyrazoles with organostibonic acids.[19] In the presence of bulky groups like phenyl or tert-butyl on the 5th position of the pyrazole ring of the phenolic pyrazole ligand, only the chelating mode of the ligand (O,N) were observed resulting in the formation of a tetra nuclear cluster. On the other hand if the pyrazole ring contains a less bulky atom (like H) on the 5th position, then both chelating (O,N-mode) and bridging (N,N-) mode of ligation were observed leading to the formation of a tetra nuclear cluster structurally different from the one obtained in the earlier case. But in **3.3** even though there is a phenyl group present at the 5th position, both chelating (O,N-) and bridging (N,N-) mode of the ligation is observed. This is probably due to the formation of a different structural end product compared to our earlier report. It results in the formation of a diorganoantimony dimer wherein the steric bulk of the group present on the 5th position of the pyrazole ring does not seem to influence the coordination mode of the ligand. Hence in this case probably the structure of the product obtained drives the coordinating ability of the ligand.

Compound **3.5** is a centrosymmetric tetranuclear antimony cage which crystallizes in triclinic space group P-1. The molecular structure of **3.5** can be described in two ways, 1) Two units of phenolic pyrazolyl chelated SbO_2 units flanking an Sb_2O_2 ring and b) The formation of an eight membered Sb_4O_4 ring with two opposing Sb atoms (Sb1 and Sb1*) being bound together by two μ-2 OH bridges resulting in the formation of a four membered ring which is nearly perpendicular to the Sb_4O_4 ring system while the other two Sb atoms are chelated by the phenolic pyrazolyl ligation. Further all Sb atoms are bound by two phenyl groups each to satisfy the hexa coordinate geometry. IR spectrum shows the presence of a broad peak around 3053 cm^{-1} which confirms the presence of OH group. The Sb1-μ$_2$-OH, Sb1-O2, Sb2-O4, Sb2-N2 and Sb2-O1 bond distances are 1.995(16), 1.966(18), 2.094(17), 2.207(2), 2.041(18) Å which are in good agreement with the earlier reports.[19]

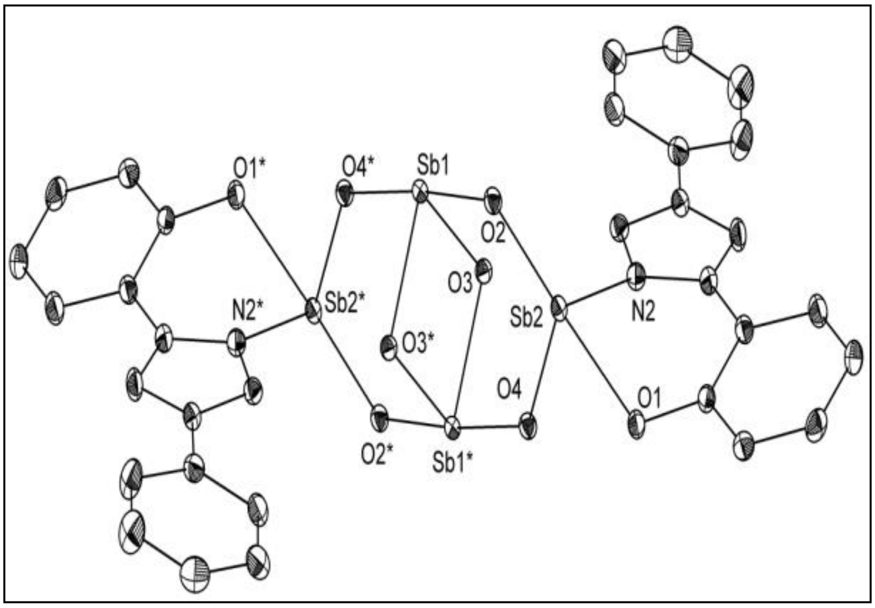


Figure 4: The solid state structures of **3.5**; hydrogen atoms and solvents of crystallization are omitted for clarity

3.6 Supramolecular Interactions:

Crystal packing analysis of **3.1** revealed interesting information. **3.1** is stabilized as a dimer by bifurcated N–H···Cl and C–H···Cl, interactions (Figure 5).[26]

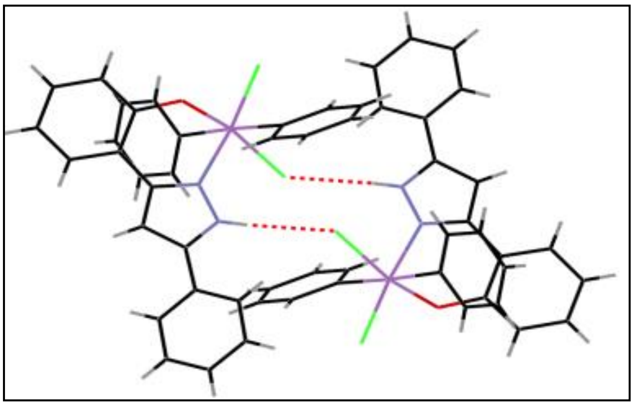


Figure 5: Non-covalent N-H•••Cl interactions observed between two discrete molecules of **3.1**

Compound **3.3** is stabilized by additional π…π weak interactions. There are three different π…π interactions observed in **3.3**. Two π…π interactions are intermolecular present between Sb attached phenyl rings while the third π…π interaction is formed between pyrazole rings to the next neighboring molecule's phenyl ring (Figure 6).

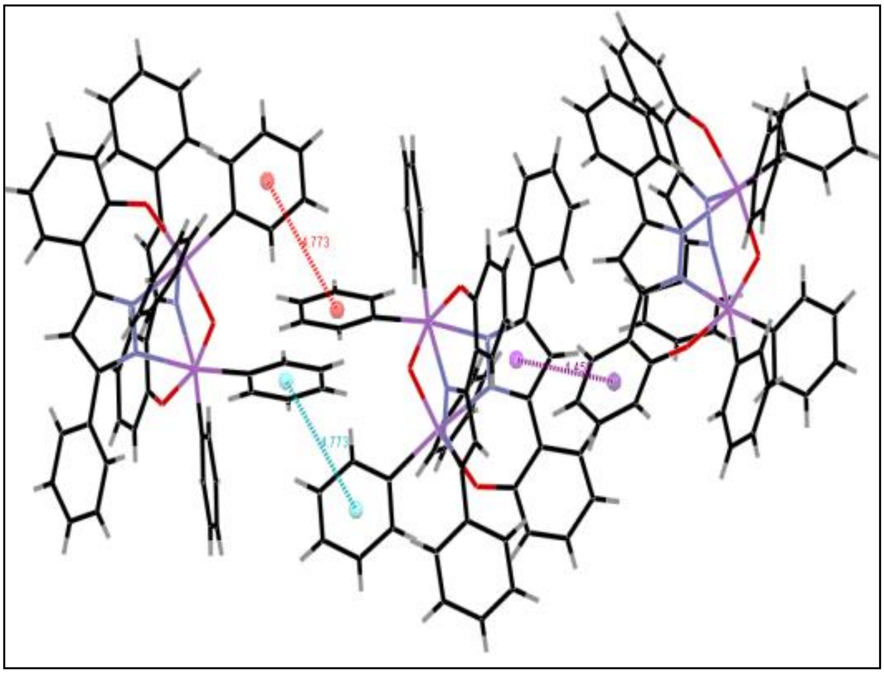


Figure 6: π•••π interactions between two phenyl rings (shown in cyan and red colour) and phenyl to pyrazole rings (shown in violet color) of **3.3**

3.7 Conclusion:

To summarize, using phenolic pyrazoles diorganoantimony compounds/clusters have been synthesized and structurally characterized. Structural analysis of the products revealed the formation of interesting sub units consisting of four (Sb_2O_2), five (Sb_2N_2O), six (Sb_2N_4) and eight (Sb_4O_4) membered ring systems stabilized by phenolic pyrazolyl ligation. Room temperature Sb-C bond cleavage has also been observed leading to the formation of novel diorganoantimony phenolic pyrazolates.

Table 1: Crystal data parameters for compound 3.1-3.3

	3.1	**3.2**	**3.3**
Formula	$C_{27}H_{21}Cl_2N_2OSb$	$C_{43}H_{34}O_3N_4Cl_2Sb_2$	$C_{54}H_{40}O_3N_4Sb_2$
fw	582.11	969.14	1036.40
Temp (K)	298(2)	100(2)	298(2)
Cryst syst	triclinic	monoclinic	triclinic
Space group	P-1	P-2(1)/c	P-1
Cryst size (mm)	0.24 x 0.18 x 0.12	0.24 x 0.18 x 0.12	0.24 x 0.20 x 0.18
a (Å)	10.568(2)	9.5096(5)	12.8653(9)
b (Å)	11.386(2)	15.4868(8)	19.2393(14)
c (Å)	12.291(3)	25.9650(14)	20.0301(14)
α (deg)	110.32(3)	90.0	66.650(10)
β (deg)	92.85(3)	94.0650(10)	79.5680(10)
γ (deg)	117.53(3)	90.0	73.7180(10)
V(Å^3)	1189.9(4)	3814.3(3)	4340.5(15)
Z	2	4	4
d_{calcd} (Mg m^{-3})	1.625	1.688	1.581
μ (mm^{-1})	1.407	1.603	1.291
F(000)	580	1920	2072
θ range for data collection (deg)	1.83 to 24.95	1.53 to 25.02	1.65 to 25.00
refln collected/unique	7149/4138	36142/6714	42080/15292
R (int)	0.0142	0.0535	0.0255
data/restraints/params	4138/0/302	6741/0/487	15292/0/1135
GoF on F^2	1.077	1.173	1.055
R_1/wR_2 ($I>2\sigma(I)$)	0.0218/0.0548	0.0414/0.0759	0.0256/0.0644
R_1/wR_2 (all data)	0.0224/0.0552	0.0474/0.0780	0.0276/0.0655
largest diff peak/hole,e Å^{-3}	0.579 / -0.668	0.923 / -0.576	1.268 / -0.447

	3.4	3.5
Formula	$C_{51}H_{37}Cl_3N_4O_3Sb_2$	$C_{88}H_{66}O_8N_4Cl_6Sb_4$
fw	1103.70	1911.07
Temp (K)	100(2)	100(2)
Cryst syst	triclinic	triclinic
Space group	P-1	P-1
Cryst size (mm)	0.20 x 0.14 x 0.12	0.24 x 0.18 x 0.12
a (Å)	12.7596(10)	12.5822(10)
b (Å)	13.1480(11)	13.9248(11)
c (Å)	13.5524(11)	14.1608(11)
α (deg)	85.7600(10)	114.4270(10)
β (deg)	83.4990(10)	90.3770(10)
γ (deg)	77.0770(10)	116.2490(10)
V(Å^3)	2199.0(3)	1970.7(3)
Z	2	1
d_{calcd} (Mg m^{-3})	1.667	1.610
μ (mm^{-1})	1.461	1.616
F(000)	1096	944
θ range for data collection (deg)	1.51 to 25.97	1.62 to 25.02
refln collected/unique	22674/8541	12742/6870
R (int)	0.0380	0.0220
data/restraints/params	8541/0/568	6870 / 6 / 503
GoF on F^2	1.052	1.039
R_1/wR_2 (I>2σ(I))	0.0388/0.1002	0.0254/0.0647
R_1/wR_2 (all data)	0.0426/0.1026	0.0269/0.0657

Table 4: bond lengh and bond angle parameters for compound 3.1, 3.2 and 3.3

Compound 3.1

Sb_1-O_1	2.025(16)	C_{22}-Sb_1- O_1	91.69(8)	C_{22}-Sb_1-C_{16}	176.87(8)
Sb_1-N_1	2.240(19)	O_1-Sb_1-N_1	80.45(7)	O_1-Sb_1-Cl_2	167.55(4)
Sb_1-C_{16}	2.125(2)	N_1-Sb_1-C_{16}	90.01(8)	N_1-Sb_1-Cl_1	173.83(5)
Sb_1-Cl_2	2.485(8)	C_{16}-Sb_1- Cl_2	88.62(7)		
Sb1-Cl_1	2.420(9)	Cl_2-Sb_1- Cl_1	98.99(4)		
Sb_1-C_{22}	2.131(2)	Cl_1-Sb_1- C_{22}	91.19(7))		

Compound 3.2

Sb_1- O_1	2.504(7)	Sb_2 -N_4	2171(3)	N_2- Sb_2-N_4	77.00(13)
Sb_2- O_1	1.963(3)	Sb_1 -C_1	2.124(4)	N_2- Sb_2-N_4	77.00(13)
Sb_1- O_2	2.021(3)	Sb_2 - C_{28}	2.115(4)	O_2-Sb_1- N_1	82.68(12)
Sb_2- O_3	2.016(3)	Sb_2 -C_{22}	2.114(4)	O_2- Sb_1 -N_3	82.64(12)
Sb_1- N_1	2.137(3)	Sb_1 - C_7	2.112(4)	O_3 - Sb_2 -N_2	84.12(12)
Sb_2 -N_2	2.249(3)	Sb_1-O_1-Sb_2	122.93(14)	O_3 - Sb_2 - N_4	81.66(12)
Sb_1-N_3	2.253(4)	N_1 - Sb_1 -N_3	76.75(13)	C_1 - Sb_1 -C_7	102.06(16)
				C_{22}-Sb_2-C_{28}	103.83(16)

Compound 3.3

Sb_1- O_1	1.949(16)	Sb_2-N_3	2.153(2)	N_1 - Sb_2 -N_3	78.64(7)
Sb_2 -O_1	1.943(16)	Sb_1-C_{31}	2.115(2)	O_2 -Sb_1 - N_2	84.53(7)
Sb_1 - O_2	1.997(16)	Sb_2-C_{49}	2.112(2)	O_2 -Sb_1 - N_4	86.59(7)
Sb_2 - O_3	1.998(16)	Sb_2-C_{43}	2.129(2)	O_3 - Sb_2 - N_1	83.61(7)
Sb_1 -N_2	2.134(2)	Sb_1-C_{37}	2.123(2)	O_3 -Sb_2 - N_3	84.36(7)
Sb2 -N_1	2.329(2)	Sb_1-O_1-Sb_2	122.36(2)	O_3 -Sb_2 - N_4	81.66(12)
Sb_1-N_4	2.310(2)	N_2 -Sb_1-N_4	76.29(7)	C_{31}-Sb_1- C_{37}	101.59(9)
				C_{49}- Sb_2-C_{43}	100.02(9)

Table 4: bond lengh and bond angle parameters for compound 3.4 and 3.5

Compound 3.4

Sb_1-O_1	1.948(3)	Sb_2-N_4	2.153(3)	$N_1-Sb_1-N_3$	77.04(12)
Sb_2-O_1	1.952(3)	Sb_1-C_{33}	2.125(3)	$O_2-Sb_1-N_3$	83.52(11)
Sb_1-O_2	2.006(3)	Sb_2-C_{45}	2.118(4)	$O_2-Sb_1-N_1$	82.68(12)
Sb_2-O_3	2.012(3)	Sb_2-C_{39}	2.122(4)	$O_2-Sb_1-N_1$	82.99(12)
Sb_1-N_1	2.174(3)	Sb_1-C_{27}	2.121(4)	$O_3-Sb_2-N_2$	84.44(12)
Sb_2-N_2	2.330(3)	$Sb_1-O_1-Sb_2$	122.68(13)	$O_3-Sb_2-N_4$	81.90(11)
Sb_1-N_3	2.232(3)	$N_2-Sb_2-N_4$	76.96(12)	$C_{33}-Sb_1-C_{27}$	102.46(15)
				$C_{45}-Sb_2-C_{39}$	99.72(14)

Compound 3.5

Sb_2-O_1	2.041(18)	$Sb_1-O_3^*$	2.012(18)	$O_2-Sb_1-O_3^*$	92.31(7)
Sb_2-O_2	1.937(18)	$Sb_1-O_4^*$	2.227(18)	$O_3-Sb_1-O_3^*$	78.61(7)
Sb_1-O_2	1.966(18)	Sb_2-N_2	2.207(2)	$O_2-Sb_1-O_4^*$	173.85(7)
Sb_1-O_3	1.995(16)	$Sb_1-O_3-Sb_1^*$	101.39(7)	$O_3-Sb_1-O_4^*$	82.56(7)
$Sb_1^*-O_3$	2.012(17)	$Sb_2-O_2-Sb_1$	138.69(10)	$O_3^*-Sb_1-O_4^*$	85.34(7)
Sb_2-O_4	2.094(17)	$Sb_2-O_4-Sb_1^*$	134.94(9)	$O_2-Sb_2-N_2$	90.63(8)
$Sb_1^*-O_4$	2.227(17)	$O_2-Sb_1-O_3$	91.40(7)	$O_1-Sb_2-N_2$	77.80(8)

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Hexa- and Trinuclear Organoantimony Oxo Clusters Stabilized by Organosilanols

Chapter 4

Abstract: Reactions of Ph_2SbCl_3 were investigated with $RSi(OH)_3$ [where R = *tert*-Bu, *cyclo*-C_6H_{11}] and $Ph_2Si(OH)_2$ in toluene in the presence of triethylamine as a base. Single crystal X-ray structural elucidation of the products revealed the formation of hexanuclear antimony(V) and mixed valent antimony(III/V) oxo-hydroxo clusters built up of incomplete cubane sub units. Interestingly in all the reactions, at least one Sb-C bond cleavage has been observed leading to the formation of novel cluster assembly $[(Ph_2Sb)_4(PhSb)_2(C_4H_9SiO_3)_2(O)_6(OH)_2]$ (**4.1**), $[(Ph_2Sb)_4(PhSb)_2(C_6H_{11}SiO_3)_2(O)_6(OH)_2]$ (**4.2**), $[(Ph_2Sb)_4(Sb)_2(Ph_2SiO_2)_2(O)_6(OH)_2]$ (**4.3**) and $[(Ph_2Sb)(PhSb)_2(Ph_2SiO_2)_2(O)_3(OH)_2]^-Et_3NH^+$ (**4.4**) respectively.

4.1 Introduction:

Molecular clusters constructed from organoantimonates[1-5]/organosilanols are a rarity despite potential applications in biology, catalysis[6,7] and in synthesizing model compounds for zeolites.[8] Recently assembly of an Sb_4O_4 cubane cluster by reacting organostibonic acid with diorganosilane diol have been reported.[9] Continuing our interest in synthesizing molecular architectures consists of organoantimonates/organosilanols, investigations on reactions of diorganoantimony trihalides with organosilanetriols {where R= *tert*-Bu (**4.1**) and *cyclo*-C_6H_{11} (**4.2**)} and diphenylsilane diol were carried out. Further isolation of a nonanuclear antimony phosphinate cluster involving Sb-C bond cleavage has been reported.[10] Diorgano/triorgano antimony halides have been reacted with silver salts of acids leading to the isolation of interesting diorgano antimony based molecular clusters.[11] Considering the facile cleavage of Sb-C bonds reported in the literature[12,10] and the rarity of molecular clusters containing Sb-O-Si the reactions of diphenylantimony(V) trichlorides with organosilane triols and diols were investigated. Further an interesting report wherein the promotion of phosphaalkyne cyclooligomerisation by a Sb(V) to Sb(III) redox system caught our attention.[13] Recently, Beckmann et al reported the synthesis and structural characterisation of Sb(V)/Sb(III) mixed valent cluster starting from a Sb(III) precursor.[14] In this chapter to the best of our knowledge for the first time the synthesis of a mixed valent cluster where in a Sb(V)/Sb(III) redox process has lead to isolation of a mixed valent cluster assembly is reported.

4.2 Experimental Section:

4.2.1 General information:

Ph_2SbCl_3, *tert*-butylsilane triol and *cyclo*-hexylsilane triol were synthesized using literature procedures.[15] Solvents and other common reagents were purchased from commercial sources. Infrared spectra were recorded on a JASCO-5300 FT-IR spectrometer as KBr pellets. Elemental analysis was performed on a Flash EA series 1112 CHNS analyzer.

4.2.2 Synthetic methodology:

The stoichiometric amounts of Ph_2SbCl_3 and organosilanol compounds [*t*-Bu or *cyclo*-C_6H_{11} or $Ph_2Si(OH)_2$] were dissolved in 50ml toluene in course of twenty minutes.

Triethylamine was added and the stirring was continued for another six hours at room temperature. The resultant solution was filtered and the solution was evaporated under reduced pressure to yield a white crystalline powder. Block type crystals were formed from slow diffusion of hexane in to toluene solution after several days. The crystals for the compounds **4.3** and **4.4** are obtained from the same reaction. The stoichiometry and the amounts of the reagents used in each case are given below.

Compound 4.1: Ph_2SbCl_3 (0.421g, 1.1 mmol), *tert*-$BuSi(OH)_3$ (0.05g, 0.36 mmol), Et_3N (0.11g, 1.1mmol). Yield: 0.21g (60.0%). M.P. >300˚C. Elemental anal.cal. for $C_{68}H_{68}O_{14}Sb_6Si_2$: C, 43.07; H, 3.61. Found: C, 43.16, H, 3.65. IR (cm^{-1}, KBr pellet): υ(cm^{-1}) 3419(b), 3051(w), 2925(m), 2848(s), 1577(m), 1473(s), 1435(m), 969(s), 936(s), 804(s), 733(m), 684(m).

Compound 4.2: Ph_2SbCl_3 (0.353g, 0.92mmol), *cyclo*$C_6H_{11}(OH)_3$ (0.05g, 0.30 mmol), Et_3N (0.09g, 0.92mmol). Yield: 0.12g (40.0%). M.P. >300˚C. Elemental anal.cal. for $C_{72}H_{72}O_{14}Sb_6Si_2$: C, 44.39; H, 3.72. Found: C, 44.21, H, 3.74. IR (cm^{-1}, KBr pellet): 3325(b), 3051(m) 2903(m), 2843(s), 1478(m), 1429(s), 1067(m), 996(s), 941(s), 881(s), 728(m), 689(m), 481(S).

Compound 4.3: Ph_2SbCl_3 (0.30g, 0.78 mmol), $Ph_2Si(OH)_2$ (0.169g, 0.78mmol), Et_3N 0.238g (2.3mmol). Yield: 0.21g, (34.4%). M.P. >300˚C. Elemental anal.cal. for $C_{115}H_{118}N_2Sb_6O_{18}Si_4$: C, 51.94; H, 4.47; N, 1.053. Found: C, 51.49, H, 4.36; N, 1.17. IR (cm^{-1}, KBr pellet): 3430(b), 3046(w), 3002(m), 1478(s), 1429(m), 1111(s), 958(s), 903(s), 739(m), 700(m).

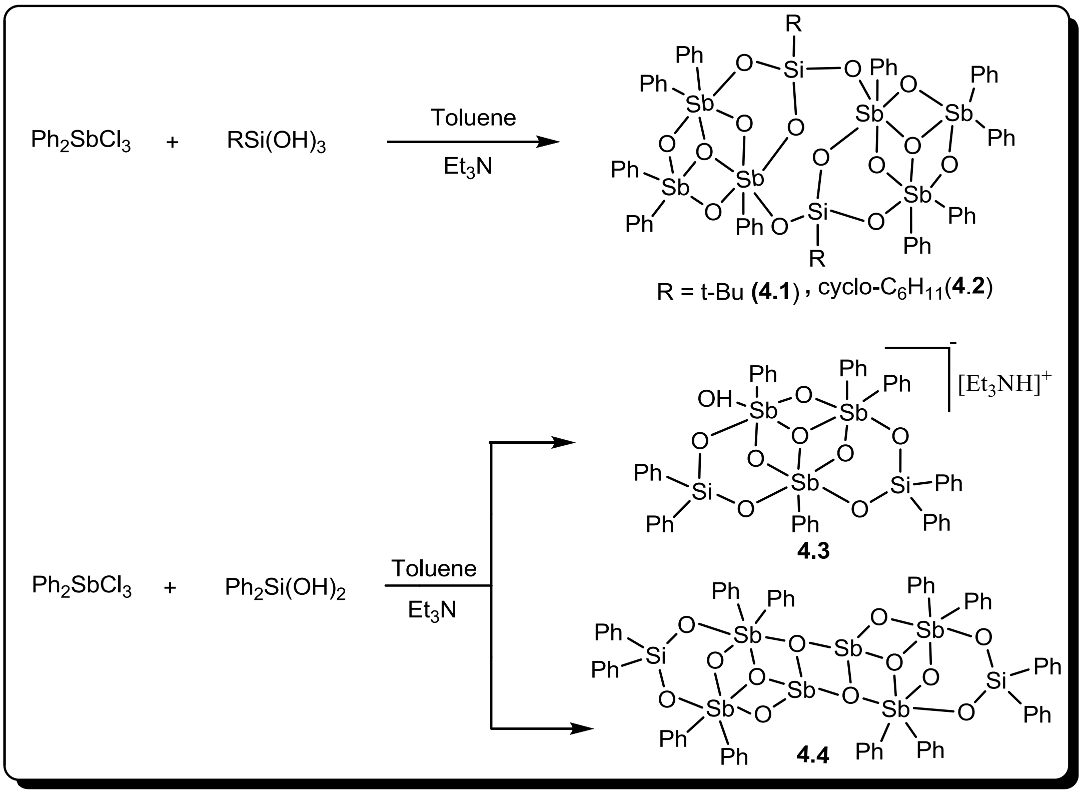
Compound 4.4: Yield 0.015g, (1.9%). M.P. >300˚C. Elemental anal.cal. for $C_{79}H_{70}O_{12}Sb_6Si_2$: C, 47.48; H, 3.53;. Found: C, 47.38, H, 3.56. IR (cm^{-1}, KBr pellet): 3414(b), 3041(w), 2997(m), 1589(m) 1479(s), 1430(m), 1112(s), 1073(s), 953(s), 904(s), 728(m), 690(m).

4.3 X-ray structure determination:

Single crystal X-ray data collection for compounds **4.1**-**4.4** were carried out at 298(2) K on Bruker Smart Apex CCD area detector system (λ (Mo Kα) = 0.71073Å) equipped with Oxford Cryo stream low temperature device and graphite monochromator. The data were reduced using SAINTPLUS and the structures were solved using SHELXS-97[16a] and refined using SHELXL-97.[16b] The structures were solved by direct methods and refined by full-martix least squares cycles on F^2. All non-hydrogen atoms were refined anisotropically.

4.4 Results and discussion:

4.4.1 Synthesis: The synthesis of **4.1-4.4** were carried out in toluene by reaction of Ph_2SbCl_3 with $RSi(OH)_3$(R = *tert*-Bu/*cyclo*-hexyl) or with $Ph_2Si(OH)_2$ in presence of triethylamine as a base. The compounds were analyzed using standard spectroscopic and analytical methods. Isolated crystals of **4.1-4.4** show poor solubility in common organic solvents and hence solution NMR studies could not be performed.



Scheme 1

4.5 Description of the Crystal Structure:

Single crystal X-ray diffraction studies revealed **4.1** and **4.2** are structurally similar. Hence **4.1** is considered for discussion. **4.1** crystallize in triclinic space group p-1. The structure of **4.1** can be described as follows: Two Sb_3O_4 units linked together by a organosilanol, binding in [3.111] mode. Each Sb_3O_4 unit can be described as a cube with a vertex missing. The three metal atoms are connected to each other by a μ$_2$-O group and further a μ$_3$-O bridges all the three metal atoms hence making up the Sb_3O_4 unit (figure 2). Within each Sb_3O_4 unit two Sb atoms are present as diorgano forms where as the third metal atom is present as a monoorgano unit, which is obtained due to cleavage of an Sb-C bond from the diorganoantimony based starting material. Such cleavage and formation of an insitu generated R-SbO_3^{2-} unit are known in a recently reported organophosphinate based nonanuclear cluster.[10] Two silanols bind the two trimers in a [3.111] mode of binding leading to the formation of a hexanuclear cluster in solid state (figure 1). For charge balance considerations the μ$_2$-O is consider as oxo and the μ$_3$-O are hydroxyl. Effect of changing the R group on the silanol from *tert*-butyl to *cyclo*-hexyl did not have any effect on the structure of the end product obtained (figure 3). Structural elucidation reveals the formation of a hexanuclear organoantimony silanolate in the case of **4.2** which is structurally similar to **4.1**. The Sb–O bond distances and Sb–O–Sb bond angles of the core are in the range 1.91(18)–2.31(18) Å and 93.77(7)–109.90(8) Å respectively. Similarly the Si–O and the silicon-bound O---Sb distances falls in the range 1.62(19)–1.65(18) Å and 1.93(18) – 1.97(18) Å which are in close agreements with the literature values.

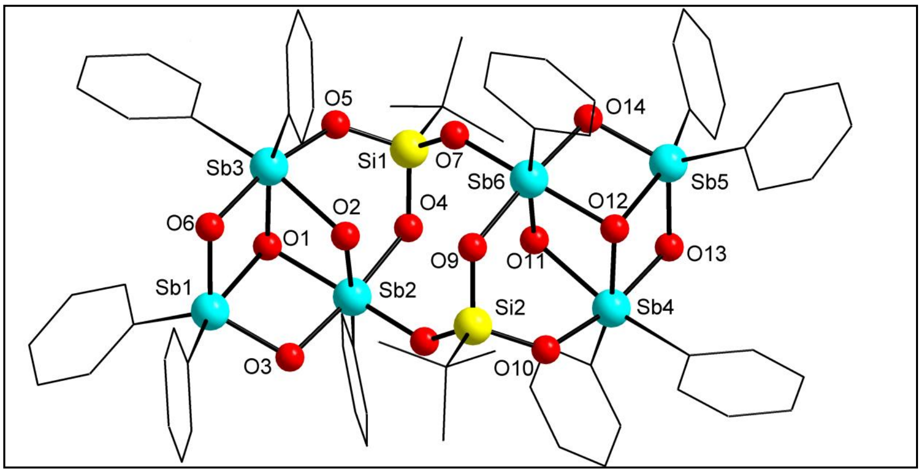


Figure 1: The solid state structure of compound **4.1**

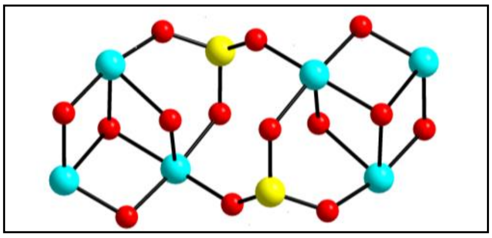


Figure 2: (b) metal–oxo core of the compound **4.1**

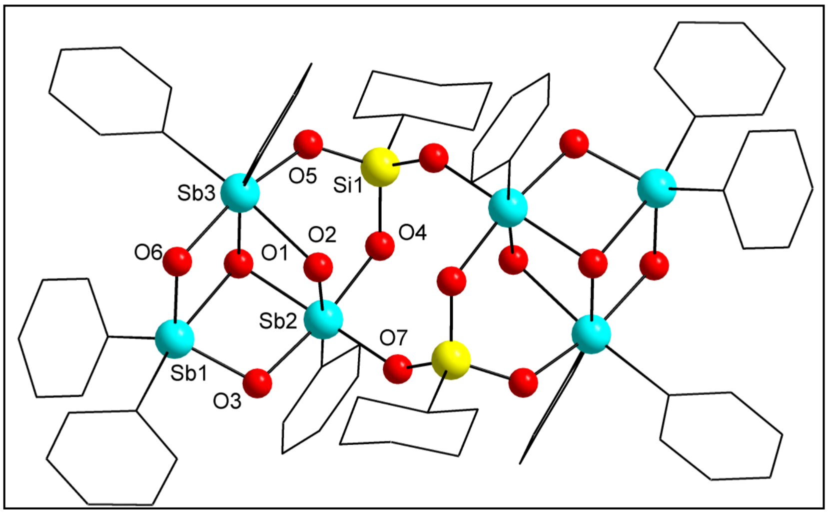


Figure 3: The solid state structure of compound **4.2**

Sb-O-Si containing compounds and clusters are a rarity in literature except for few instances reported in earlier studies. The isolation of a antimony(III) bicyclic siloxane and a cubic Sb(III) containing Sb^{III}-O-Si^{IV} are known.[17-18] We have recently reported the isolation of a cubane Sb_4O_4 cluster stabilized by diphenylsilane diol.[9] The clusters reported herein are the first reports of organoantimonyl/organosilanolates in literature.

4.3 crystallizes in monoclinic space group p2(1)/n. Structural elucidation reveals the formation of trinuclear anionic cluster $[(Ph_2Sb)(PhSb)_2(Ph_2SiO_2)_2(O)_3(OH)_2]^-$ whose charge is balanced by the presence of $[Et_3NH]^+$ cation. Interestingly literature reports of reactions of diorganosilane diols with main group metals like gallium and aluminum in the presence of Et_3N/ pyridine leads to isolation of two different products; on being anionic siloxane and the other being a neutral cluster.[19] Similar observation has been seen in this reaction also. Wherein a Sb(V) state cluster and a mixed valent Sb(V)/Sb(III) cluster has been isolated.

The structural description of **4.3** is as follows: Sb_3O_4 core stabilized by two diorganosilane diol binding in [2.11] mode (figure 4a). The Sb_3O_4 unit in **4.3** is similar to the unit found in **4.1**, the formation of a broken cubane with a vertex missing. The three Sb metal atoms are bridged by μ_2-O and a μ_3-O further binds to all the three metal centers keeping the Sb_3O_4 motif intact. The interesting aspect about the structure is the presence of two monorganoantimony groups formed by dearylation and one Sb atom present in the diorgano form. Infact this cluster represents a state wherein insitu generated R-SbO_3^{2-} unit and $RSb(OH)O_2^-$ (which could be a fore runner to $RSbO_3^{2-}$) being present. The overall anionic trinuclear organoantimony cluster is charge balanced by the presence of a triethylammonium cation. Further analysis of the solid state packing revealed the presence of strong O-H···O interactions with 2.586 Å bond length ($O_6 \cdots O_7$) hence stabilizing the trinuclear cluster in to a hexa nuclear unit. The structure is shown in fig 4(c).

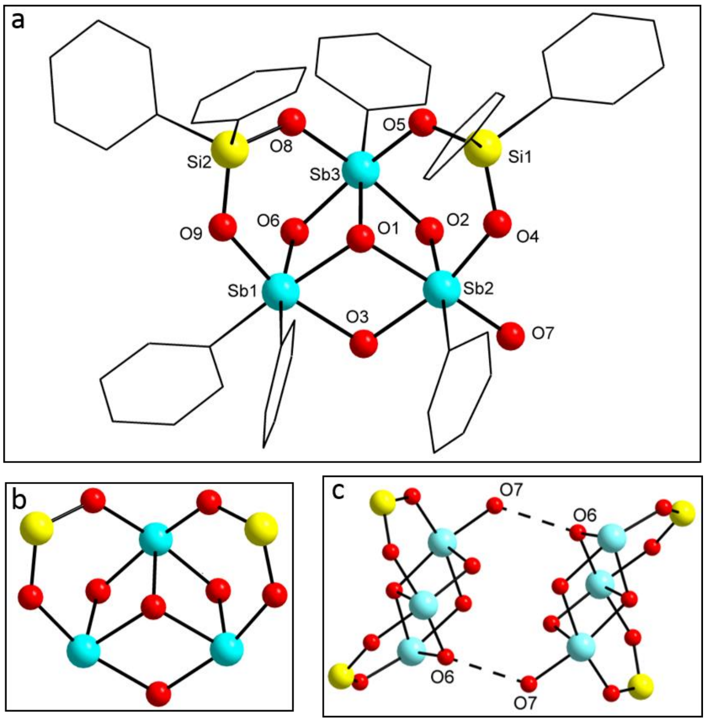
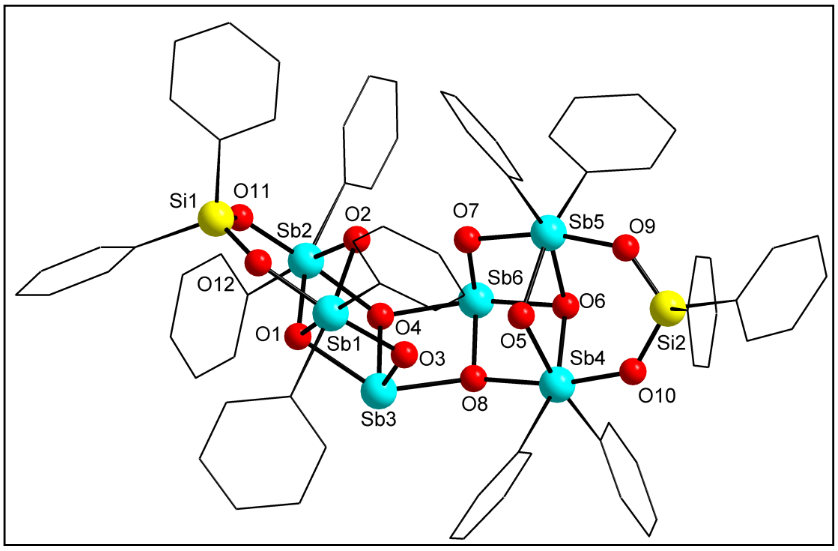
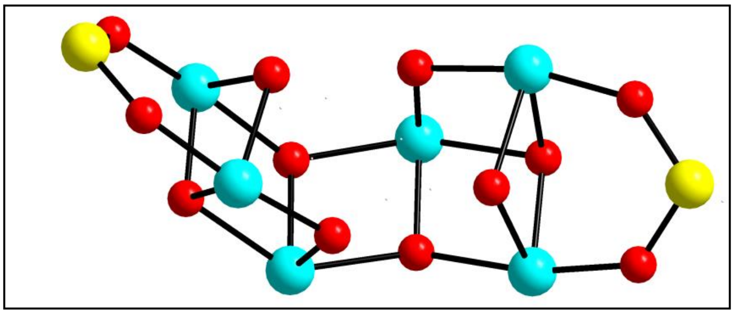


Figure 4: (a) The solid state structure of compound **4.3** (b) metal–oxo core of the compound **4.3**. (c) Intermolecular O-H····O interaction

Along with **4.3** a crystal of different morphology in small amounts were seen and structural elucidation of the compound was carried out. **4.4** crystallizes in monoclinic space group p2(1)/c. Structural characterization revealed the formation of a mixed valent hexanuclear organoantimony cluster (figure 5a). Structure of **4.4** can be described as follows. Again the cluster consists of two Sb_3O_4 units connected along a Sb-O edge. The Sb metal atoms which are connected are Sb(III) centers and hence two Sb(III) metal atoms are present in the cluster. The Sb(III) centers are 4 coordinate. The two other Sb metals in each Sb_3O_4 unit are Sb (V) and are held together by diphenylsilanediol by a [2.11] mode of binding. Over all the cluster has four μ_2-O and four μ_3-O making up the cluster core. Of the four μ_3-O, two μ_3-O connect the three metal atoms in a Sb_3O_4 unit while the other two μ_3-O are present in the edge that links the two Sb_3O_4 units (figure 5b).



(a)



(b)

Figure 5: (a) The solid state structure of compound **4.4.** (b) metal-oxo core of the compound **4.4**

This isolation of a mixed valent compound starting from an Sb(V) precursor is very interesting. Considering the fact that Beckmann et al recently reported the synthesis and structural characterization of a mixed valent Sb clusters by carrying out controlled hydrolytic cleavage of highly soluble and bulky 2,6-$Mes_2C_6H_3SbCl_2$ where in Sb atoms are present in +3 oxidation state.[14] Herein we present for the first time the formation of mixed valent organoantimony cluster obtained by starting from antimony(V) starting material and reduction followed by cleavage or vice versa has resulted in this unique molecular cluster. Recently such reduction of Sb(V) to Sb(III) has been shown to catalyze promotion of phosphaalkyne cycloligomerization.[13] For the first time we have seen Sb(V) to Sb(III) reduction in the formation of the reported molecular cluster. The average Sb^{V}–O and Sb^{III}–O bond distances of **4.4** falls in the range 1.955(2)–2.159(2) Å and1.966(2)–2.207(2) Å respectively. These values are in good agreement with the mixed valent cluster bond lengths reported recently by Beckmann et al.

To summarize, reaction of monoorganostibonic acid with diorganosilane diol has lead to the isolation of a cubane cluster which has been reported recently. Herein the investigation of reactions of diorganoantimony trihalides with silanediols / triols has lead to the isolation of crystal structures whose basic core is built up of a cubane with a vertex missing. The basic structural units are summarized in chart 1.

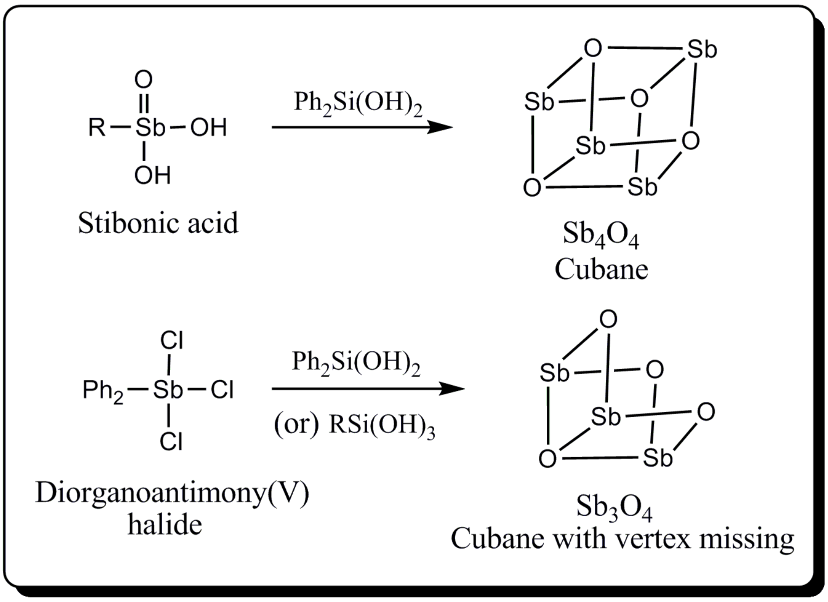


Chart 1

4.6 Conclusion:

Novel hexa- and trinuclear organoantimony oxo-hydroxo clusters have been assembled by reaction of organoantimony halides with silanols. To the best of our knowledge, synthesis of a mixed valent cluster through reduction of the Sb(V) starting material is reported herein for the first time in organoantimony literature.

Table 1: Crystal data parameters for compound 4.1-4.4

	4.1	**4.2**	**4.3**	**4.4**
Formula	$C_{68}H_{68}O_{14}$ Sb_6Si_2	$C_{72}H_{72}O_{14}$ Sb_6Si_2	$C_{115}H_{118}N_2O_{18}Sb_6Si_4$	$C_{79}H_{70}O_{12}Sb_6Si_2$
fw	1895.90	1947.98	2658.97	1998.09
Temp (K)	298(2)	298 (2)	298(2)	298(2)
Cryst syst	triclinic	triclinic	Monoclinic	Monoclinic
Space group	P-1	P-1	P2(1)/n	P2(1)/c
Cryst size (mm)	0.18 x 0.16 x 0.12	0.18 x0.16 x 0.14	0.22 x 0.18 x 0.12	0.22 x 0.16 x 0.10
a (Å)	11.1250(8)	12.728(4)	18.9322(15)	11.3751(10)
b (Å)	12.0487(9)	13.015(4)	28.524(2)	35.748(3)
c (Å)	26.136(2)	13.544(4) (12)	24.7911(19)	19.2299(14)
α (deg)	85.4960(10)	108.884(4)	90.00	90.00
β (deg)	79.7310(10	116.854(4)	102.7550(10)	110.493
γ (deg)	78.7210(10)	95.664(4)	90.00	90.00
V(Å^3)	3377.1(4)	1812.4(9)	13057.4(18)	7324.7(10)
Z	2	1	4	4
d_{calcd} (Mg m^{-3})	1.864	1.785	1.353	1.812
μ (mm^{-1})	2.465	2.299	1.317	2.276
F(000)	1844	950	5312	3896
θ range for data collection (deg)	1.59 to 26.05	11.73 to 24.98	1.10 to 25.09	1.14 to 28.28
refln collected/unique	35100/13221	17302/6338	125092/23117	84932/17576
R (int)	0.0211	0.0568	0.0745	0.0369
data/retraints/params	13221 / 0 / 817	6338 / 0 / 424	23117 / 0 / 1313	17576 / 0 / 893
GoF on F^2	1.035	1.055	1.029	1.148
R_1/wR_2 (I>2σ(I))	0.0245/0.0614	0.0624/0.1358	0.0833/0.2389	0.0353/0.0745
R_1/wR_2 (all data)	0.0286/0.0636	0.0849/0.1464	0.0981/0.2527	0.0392/0.0761
largest diff peak/hole,e Å^{-3}	1.038 / -0.625	2.328 / -0.656	5.021 / -1.075	1.601 / -0.599

Table 2: Bond length and bond angle parameters for compound 4.1-4.4

4.1	**4.2**	**4.3**	**4.4**
Sb1-O6 1.9107 (18)	Sb1-O6 1.9000(6)	Sb1-O6 1.991(7)	Sb1-O1 2.124(2)
Sb3-O2 2.2185 (18)	Sb3-O2 2.205(5)	Sb3-O2 2.026(7)	Sb1-O12 1.955(2)
Sb2-O3 2.0043(17)	Sb2-O3 2.005(5)	Sb2-O3 2.129(7)	Sb1-O2 2.159(2)
Sb1-O1 2.3132(18)	Sb1-O1 2.293(6)	Sb1-O1 2.18(7)	Sb1-O3 2.010(2)
Sb2-O1 2.0447(18)	Sb2-O1 2.042(5)	Sb2-O1 2.099(7)	Sb3-O3 1.966(2)
Sb3-O1 2.0515(17)	Sb3-O1 2.031(6)	Sb3-O1 2.089(7)	Sb3-O8 2.153(2)
Sb2-O8 1.9374(18)	Sb2-O7* 1.938(5)	Sb2-O7 1.949(7)	Sb3-O1 2.207(2)
Sb3-O5 1.9758(18)	Sb3-O5 1.959(5)	Sb3-O5 1.963(7)	Sb3-O4 2.027(2)
Sb2-O4 1.9890(17)	Sb2-O4 1.971(5)	Sb2-O4 1.967(7)	Sb2-O1 2.025(2)
Si1-O4 1.6527(18)	Si1-O4 1.646(6)	Si1-O4 1.627(7)	Sb2-O2 2.142(2)
Si1-O5 1.6253(19)	Si1-O5 1.610(6)	Si1-O5 1.619(8)	Sb2-O4 2.116(2)
Si1-O7 1.6373(19)	Si1-O7 1.627(6)	Sb1-O6-Sb3 104.6(3)	Sb2-O11 1.958(2)
Sb1-O6-Sb3 109.90(8)	Sb1-O6-Sb3 109.8(3)	Sb2-O2-Sb3 103.1(3)	Sb1-O1-Sb2 107.16(10)
Sb2-O2-Sb3 101.97(7)	Sb2-O2-Sb3 101.8(2)	Sb1-O3-Sb2 102.9(3)	Sb1-O2-Sb2 101.87(9)
Sb1-O3-Sb2 108.51(8)	Sb1-O3-Sb2 109.6(2)	Sb1-O1-Sb2 106.0(3)	Sb1-O3-Sb3 107.45(11)
Sb1-O1-Sb2 93.77(7)	Sb1-O1-Sb2 94.9(2)	Sb1-O1-Sb3 97.5(3)	Sb2-O1-Sb3 102.93(10)
Sb1-O1-Sb3 95.08(7)	Sb1-O1-Sb3 96.0 (2)	Sb2-O1-Sb3 97.0(3)	Sb2-O4-Sb3 106.17(10)
Sb2-O1-Sb3 109.04(8)	Sb2-O1-Sb3 109.6(3)	Sb2-O2-Sb3 103.1(3)	Sb3-O8-Sb6 105.43(10)
Sb2-O2-Sb3 101.97(7)	Sb2-O2-Sb3 101.8(2)	O4-Si1-O5 112.2(4)	O8-Sb3-O4 74.58(9)

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Organoboron based rings and macrocycles – a perspective

Boronic acids are boron-containing trivalent organic compounds which are surrounded by an alkyl or aryl substituent and two hydroxyl groups. The sp^2 hybridized boron atom is in trigonal planar arrangement with only 6 valence electrons and possess a vacant p orbital perpendicular to the trigonal planar geometry. The first boronic acid was reported by Frankland in 1860.[1] On treating diethyl zinc with triethyl borate an extremely moisture sensitive triethylborane was obtained which up on slow oxidation in air produces ethylboronic acid. All the boronic acids are less toxic in nature, can easily handle and eventually undergoes degradation in to the environmentally friendly boric acid. So boronic acids can be considered as green compounds. Various oxygenated organoboron compounds were shown in chart 1.

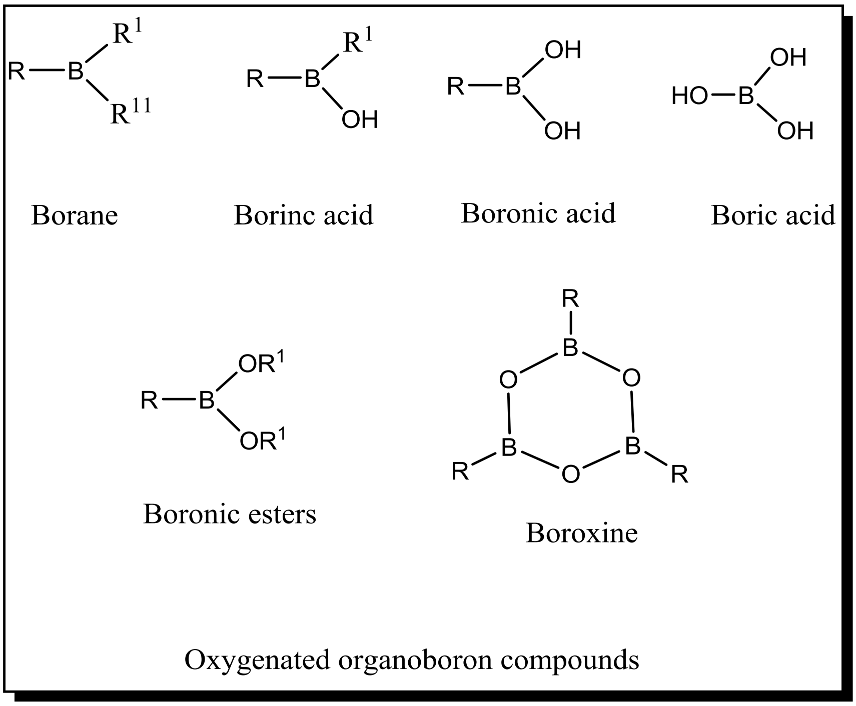
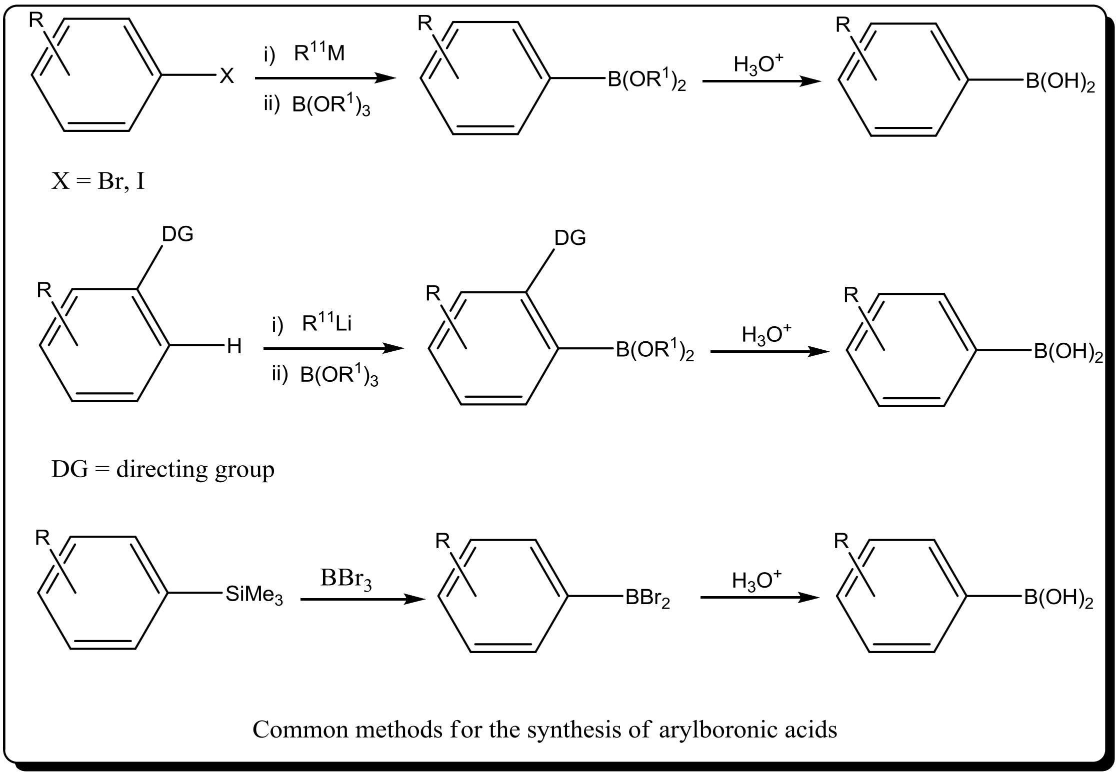


Chart 1: Various oxygenated organoboron compounds

(I) Synthesis of Boronic aicds :

Boronic acids can be obtained in several ways, the most common way is reaction of organometallic compounds based on magnesium (Gignard)[2] or lithium[3] with borate esters followed by hydrolysis. Another method is reaction of aryl silanes ($RSiR_3$) with (BBr_3) in a transmetallation $RBBr_2$ followed by acid hydrolysis (scheme 1).[4]



Common methods for the synthesis of arylboronic acids

Scheme 1

(II) Lewis Acidity of Boron and Calculation of Tetrahedral character of B→N bond in Boron complexes :

Trisubstitued boron derivatives are electron deficient in order to attain its octet they may coordinate to basic molecules and usually exhibits their Lewis acidic nature. The borane-based Lewis acids play an important roles as catalysts in organic synthesis,[5] promoters for olefin polymerization organometallic precatalysts[6] and components of frustrated Lewis pairs (FLP) that promote activation of dihydrogen and other small molecules.[7] The change in Lewis acidity of boron compounds is the origin for the design of fluorescent sensors for detection and recognition of carbohydrates and medications[8] as well as sensors for detection of fluoride and cyanide anions.[9] The Lewis acidity of boron compounds plays an important role in mechanism of pharmacological action of various boron containing pharmaceuticals[10] and determines the structures of boron-based coordination polymers and supramolecular materials.[11]

Perspective

Boron compounds have the strong tendency to react with nucleophiles like amines, phosphines, and other lewis bases which forms strong adduct and give rise to more or less stable species possessing a tetrahedral boron atom (chart 2).[12]

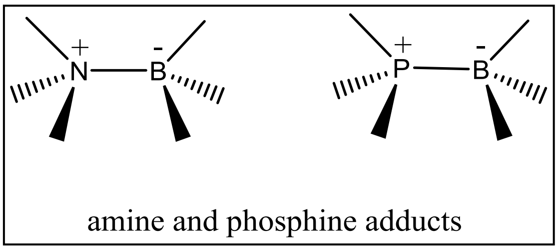


Chart 2: amine and phosphine adducts of boron

The strength of the dative $N \rightarrow B$ depends on the different substituent's of both the atoms, electron withdrawing substituent's on the boron atoms increases the Lewis acidity at boron atoms whereas electron donating atoms increases the Lewis basicity of the nitrogen atoms. The $N \rightarrow B$ bond length varies from 1.57Å, the value for the covalent boron nitrogen bond in cubic boron nitride[13] to 2.91 Å, the sum of the vanderwalls radii of the nitrogen and the boron (chart 4).[14] With increasing $N \rightarrow B$ bond length the geometry of boron complexes changes from tetrahedral to trigonal planar (chart 3).

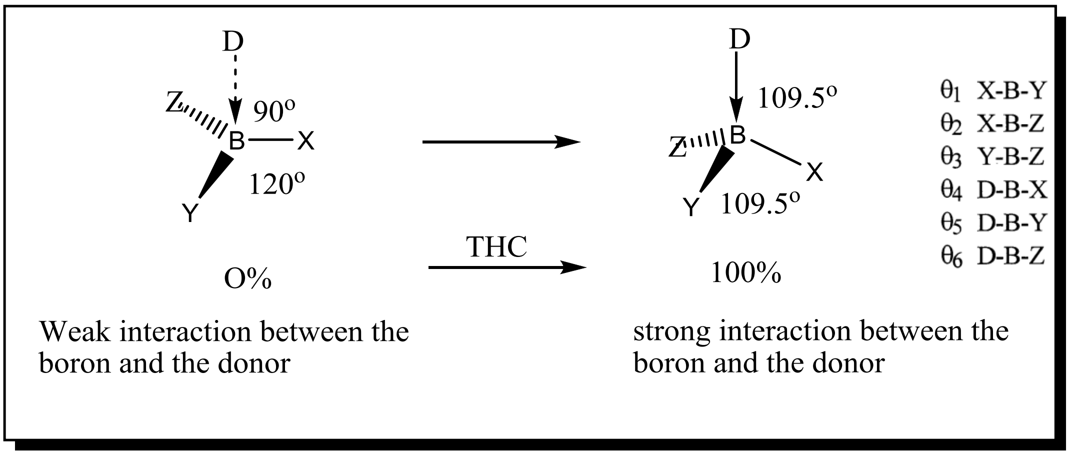


Chart 3: Change of bond angles on the approximation of a donor to three-coordinated boron atoms.

Boron nitrides

Compound	Structure	$d(\mathrm{N}\longrightarrow\mathrm{B})$ (Å)	$\mathrm{THC}_{\mathrm{DA}}$ (%)
α-BN	Cubic	1.57	100
β-BN	Hexagonal	3.33	0

Chart 4

M. Oki introduced a new parameter so called tetrahedral character (THC) for the calculation of the geometry of boron complexes with dative N⟶B bond.[15] This parameter is calculated form the bond angles around boron atoms, if the molecular structure of the compound to be studied is known. The bond angles θ_1- θ_3 used for the calculation of this parameter are all related to covalent bonds. It is supposed that the interaction between the boron and the donor changes the geometry at the boron atom from trigonal planar to tetrahedral. In the presence of a weak interaction the corresponding tetrahedral character is close to 0%, while a strong donor–acceptor interaction provides a value near 100%. The disadvantage of this formula is that sometimes the tetrahedral character even goes beyond 100% because only the three bond angles at the boron atoms with the covalent bonds are considered

$$\mathrm{THC}\,[\%] = \frac{120 - \frac{(\theta 1+\theta 2+\theta 3)^\circ}{3}}{120-109.5^\circ}\times 100$$

$$= \frac{\sum_{n=1-3}(120-\theta n)}{31.5^\circ}\times 100$$

Under the condition $\theta_n \geq 109.5^\circ$the THC can be caliculated by using the formula

$$\mathrm{THC}\,[\%] = \left[1-\sum_{n=1-3}\frac{||109.5-\theta n|^\circ|}{31.5^\circ}\right]\times 100$$

The tetrahedral character at the boron atom with all six bond angles around the central atom can be calculated by considering that bond angles θ_1–θ_3 normally range from 109.5–120˚ and bond angles θ_4–θ_6 from 90–109.5˚. With this assumption the following equation can be proposed.

$$\text{THC}\,[\%] = \left[1 - \sum_{n=1-6} \frac{\left| |109.5 - \theta n|^{\circ} \right|}{3(120-109.5)^{\circ} + 3(109.5-90)^{\circ}}\right] \times 100$$

$$= \left[1 - \sum_{n=1-6} \frac{\left| |109.5 - \theta n|^{\circ} \right|}{90^{\circ}}\right] \times 100$$

(III) Hypervalent nature of Boron atoms :

In general small sized boron atom preferentially forms tetra coordinated species up on interaction with inter or intra molecular coordinating groups, in very rare instances the geometrical factors allow the boron atoms to become hypervalent. In 1984, Martin's group succeeded in synthesizing the first example of a pentacoordinate organoboron compound.[16] The vacant p orbital of boron atom interacts with two sets of alkoxylate lone-pair electrons at the axial positions of the TBP geometry. This axial interaction forms a three-center four electron (3c−4e) bond. Later different groups synthesized new family of pentacoordinate boranes (chart 5).[17]

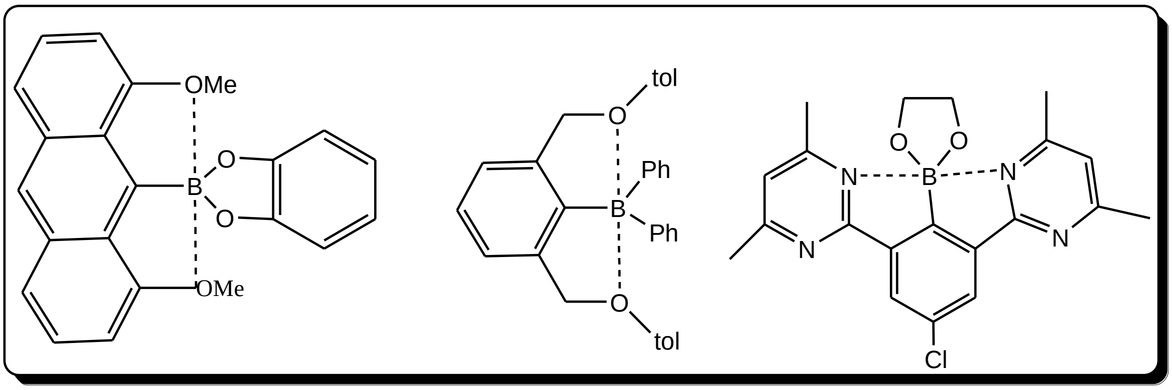


Chart 5: penta coordinate organoboron compounds

(IV) Spectroscopic Methods for Boronic Acid Derivatives :

(IV.1) Mass Spectrometry

One useful analytical information in the mass spectrometric analysis of boronic acid derivatives is the study of boron's isotopic pattern, which is constituted of ^{10}B (20% distribution) and ^{11}B (80%). However, unless other functionalities help increase the sensitivity of a boronic acid containing compound, it is frequently hard to see intense signals with most ionization methods due to the low volatility of these compounds. This problem even goes worse by the facile occurrence of gas-phase dehydration and anhydride (boroxine) formation in the ion source. To minimize these thermal reactions and improve volatility, cyclic boronates are employed.[18]

(IV.2) Nuclear Magnetic Resonance Spectroscopy

Boron compounds, including boronic acid derivatives, can be easily analyzed by NMR spectroscopy.[19] Of the two isotopes, ^{11}B spin state (3/2) is the most abundant (80%) and and its quadrupole moment are more attractive towards NMR. When analyzing boronic acids in non-hydroxylic solvents by NMR spectroscopy, it is often essential to add a small amount of deuterated water (e.g. one or two drops) to the sample in order to break up the oligomeric anhydrides. Observation of the ^{11}B nucleus against a reference compound (e.g. BF_3) is straightforward with modern instruments, and can be especially revealing of the electronic characteristics[20] and coordination state of the boronate moiety. The boron resonance of free boronic acids and tricoordinate ester derivatives is generally detected in the 25–35 ppm range, and tetra coordinate derivatives such as diethanolamine esters resonate at around 10 ppm.[21] In 13C analysis, carbons next to the ^{11}B atom tend to be broadened often beyond detection limits. As a result, with aromatic boronic acids the signal of the quaternary carbon bearing the boron atom, which is already reduced by a long relaxation time, is very hard to watch over the background noise.

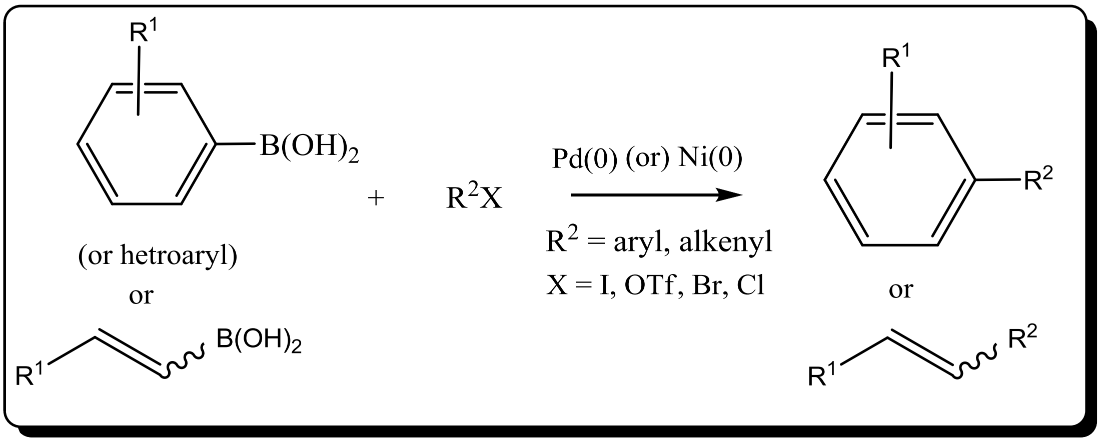
(IV.4) I.R Spectroscopy :

IR absorptions shows strong H-bonded OH stretch (3300–3200 cm^{-1}), and a very strong band attributed to B–O stretch (1380–1310 cm^{-1}). IR is particularly indicative of the presence of boronic anhydrides. Upon anhydride (boroxine) formation, the OH stretch disappears and a new strong absorption appears at 680–705 cm^{-1}.[22]

(V) Applications of Boronic acids :

(V.1) Palladium-catalyzed cross-coupling with carbon halides (Suzuki Coupling):

The most important discovery in the recent history of boronic acid chemistry was reported in 1979 by Miyaura and Suzuki describing a Pd(0)-catalyzed coupling between alkenyl boranes or catecholates and aryl halides, in the presence of a base, providing arylated alkene products in high yields.[23] Soon after that a seminal paper on the synthesis of biaryls by coupling of phenylboronic acid with aryl bromides and halides was reported[24] (scheme 2). Since then, significant development have been made through an optimization of the different reaction factors such as catalyst, ligands, base, solvent, and additives. These advances have been reviewed frequently.[25]



Scheme 2: Transition metal catalyzed coupling of boronic acids with carbon halides/ triflates

The accepted mechanism involves oxidative addition of the halide substrate to give a Pd(II) intermediate, followed by a transmetallation, and a final reductive elimination that regenerates the catalyst (chart 6).[26] The two key catalytic intermediates have been identified by electrospray mass spectrometry. Although the correct role and influence of the base remains ambiguous, the transmetallation is thought to be assisted by base-mediated formation of the tetracoordinate boronate anion, which is more electrophilic than the free boronic acid.

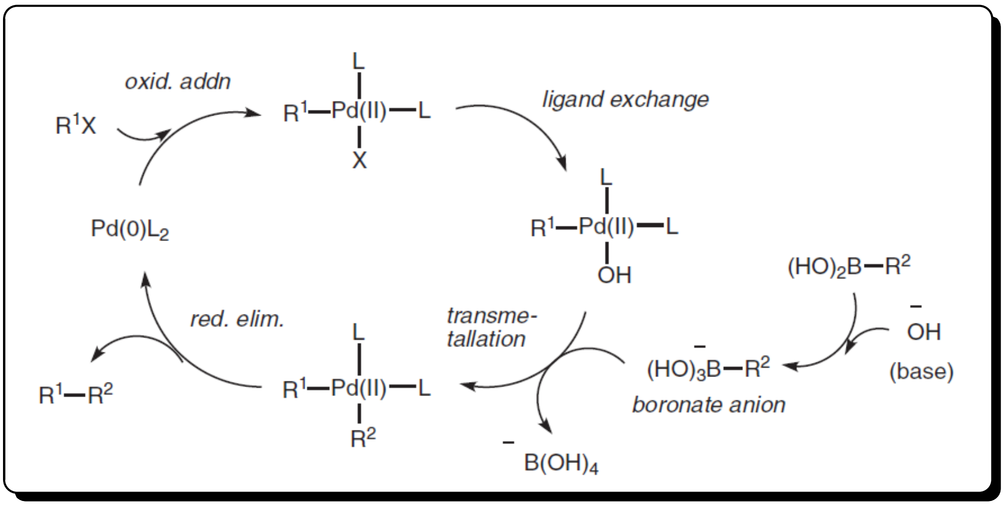
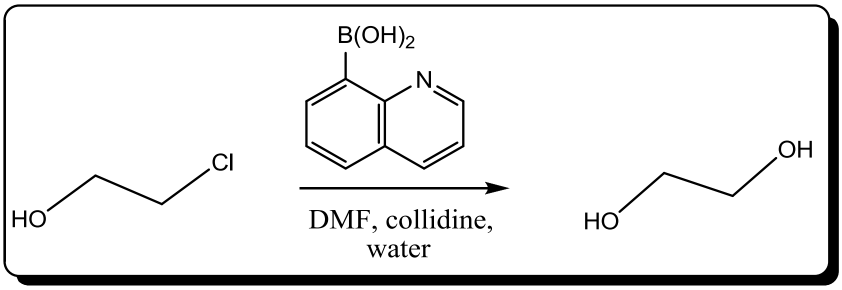


Chart : 6 Mechanism of Suzuki cross coupling reaction under aqueous conditions.

(V.2) Use as reaction promoters and catalysts

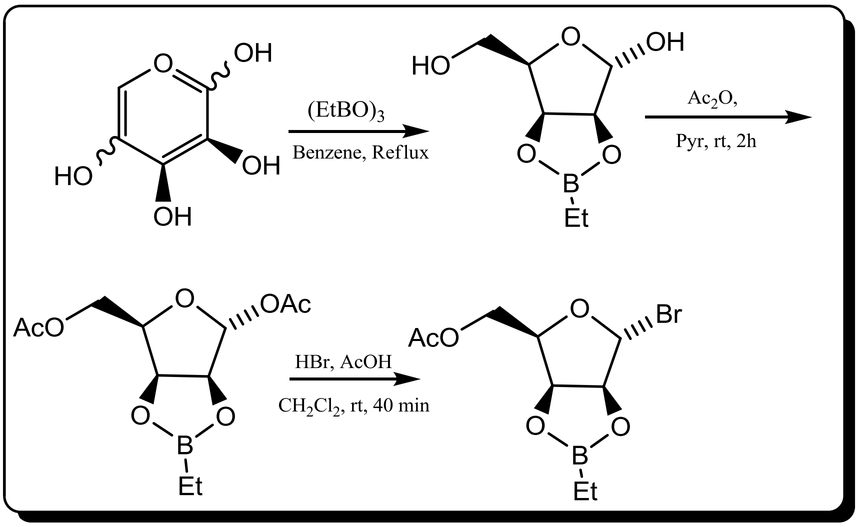
By forming temporary esters with alcohols, boronic acids can act as catalysts or templates for directed reactions. In the early 1960s, Letsinger established that a bifunctional boronic acid, 8-quinolineboronic acid, accelerates the hydrolysis of certain chloroalkanols[27](Scheme 3) and that boronoarylbenzimidazole serves as catalyst for the etherification of chloroethanol.[28] It was suggested that the mechanisms involving covalent hemiester formation between the boronic acid in the catalyst and the alcohol substrate, which then combined with a basic or nucleophilic participation of the nitrogen, were invoked.



Scheme 3: Selected example showing boronic acid as a catalyst

(V.3) Use as protecting groups for diols.

Ferrier and Köster established the use of boronic acids to protect diol units in carbohydrate chemistry more than a few decades ago.[29,30] For example, where as an excess of ethylboronic acid (as the boroxine) leads to a bisboronate furanose derivative of D-lyxose, equimolar amounts provided 2,3-O-ethylboranediyl-D-lyxofuranose (scheme 4). From the latter, a regioselective diacetylation reaction followed by treatment with HBr led to the desired α-Dlyxofuranosyl bromide in a very high yield. Simple Phenylboronic acid has also been employed as a protecting group for 1,2- and 1,3-diol units of other natural products[31], such as terpenes,[32] macrolides,[33] prostaglandins,[34] quinic acid derivatives,[35] anthracyclines[36] macrocyclic polyamines[37] and polyether antibiotics.[38] Normally, phenylboronates are made by a simple condensation with a diol which can be finally deprotected by exchange with another diol or by a destructive oxidation with hydrogen peroxide.



Scheme: 4 Selected example showing boronic acid as a protecting group for carbohydrates

(V.4) Use as sensors for carbohydrates

Carbohydrates are one of the richest organic substances in nature, which plays an important role in metabolic pathways in living organisms.[39] Consequently, the design of chemosensors which detect biologically important sugars (e.g. glucose, fructose, galactose) in a variety of medicinal and industrial contexts and particularly in aqueous environments, is extremely a significant attempt. The pKa of phenylboronic acid is 8.70 in water at 25˚C.[40] The relatively weak Lewis acidity of the boron center in this substance is accountable for complex formation with molecules that contain heteroatom's. Although it has been known for almost 50 years that boronic acid has a high affinity for diol-containing compounds such as carbohydrates, boronic acid-based fluorescent carbohydrate probes were first described in the 1990s. In 1992 Yoon and Czarnik reported the first example in which 2-anthrylboronic acid serves as a fluorescent chemosensor (chart 7).[41] This sensor, which displays polyol chelation promoted quenching of the emission band at 416 nm, shows strongest binding to fructose in aqueous solutions among the tested polyols but it also binds more weakly to 1,1,1-tris-(hydroxymethyl)ethane, glucose and ethylene glycol. After the first report by Yoon and Czarnik, research groups headed by Shinkai and James have extensively explored boronic acid-based fluorescent probes for sugars.

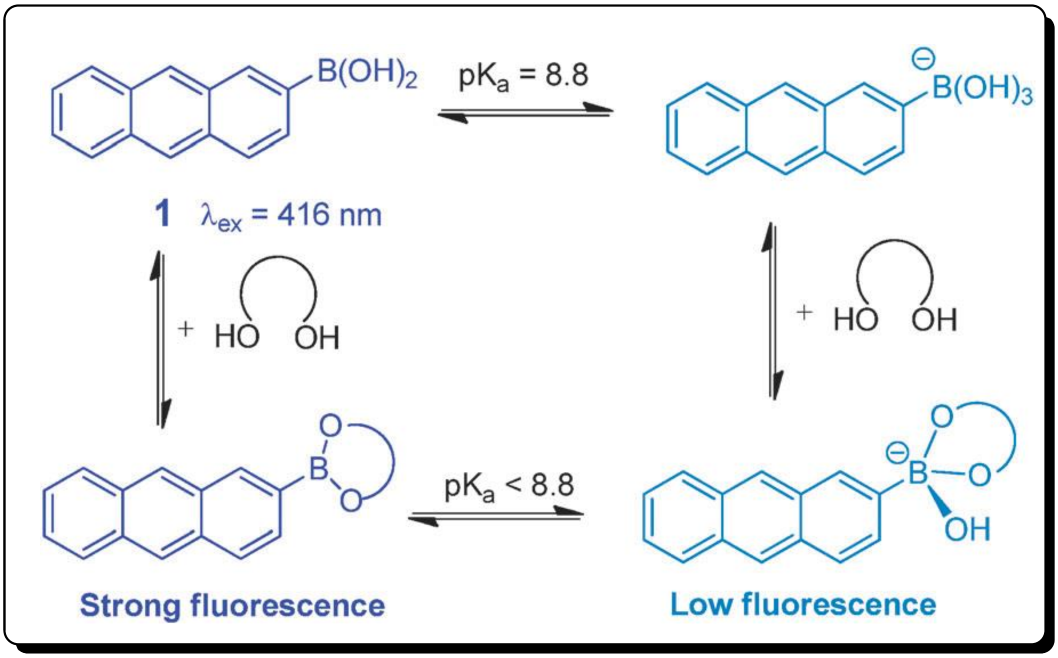


Chart 7: Response of 2-anthrylboronic acid to polyols

(V.5) Use as antimicrobial agents

Michaelis and Becker identified the toxicity of phenylboronic acid against microorganisms and its relative harmlessness against higher animals more than a century ago.[42] In 1930s the antimicrobial properties of simple arylboronic acid derivatives were further inspected.[43] Interestingly, the activity of arylboronic acids in plants has been investigated thoroughly, and several were found to support root growth.[44,45] Several boronic acids and their benzodiaza- and benzodioxaborole derivatives were evaluated as sterilants of house flies.[46] Several boronic acids and esters display potent antifungal activity.[47]

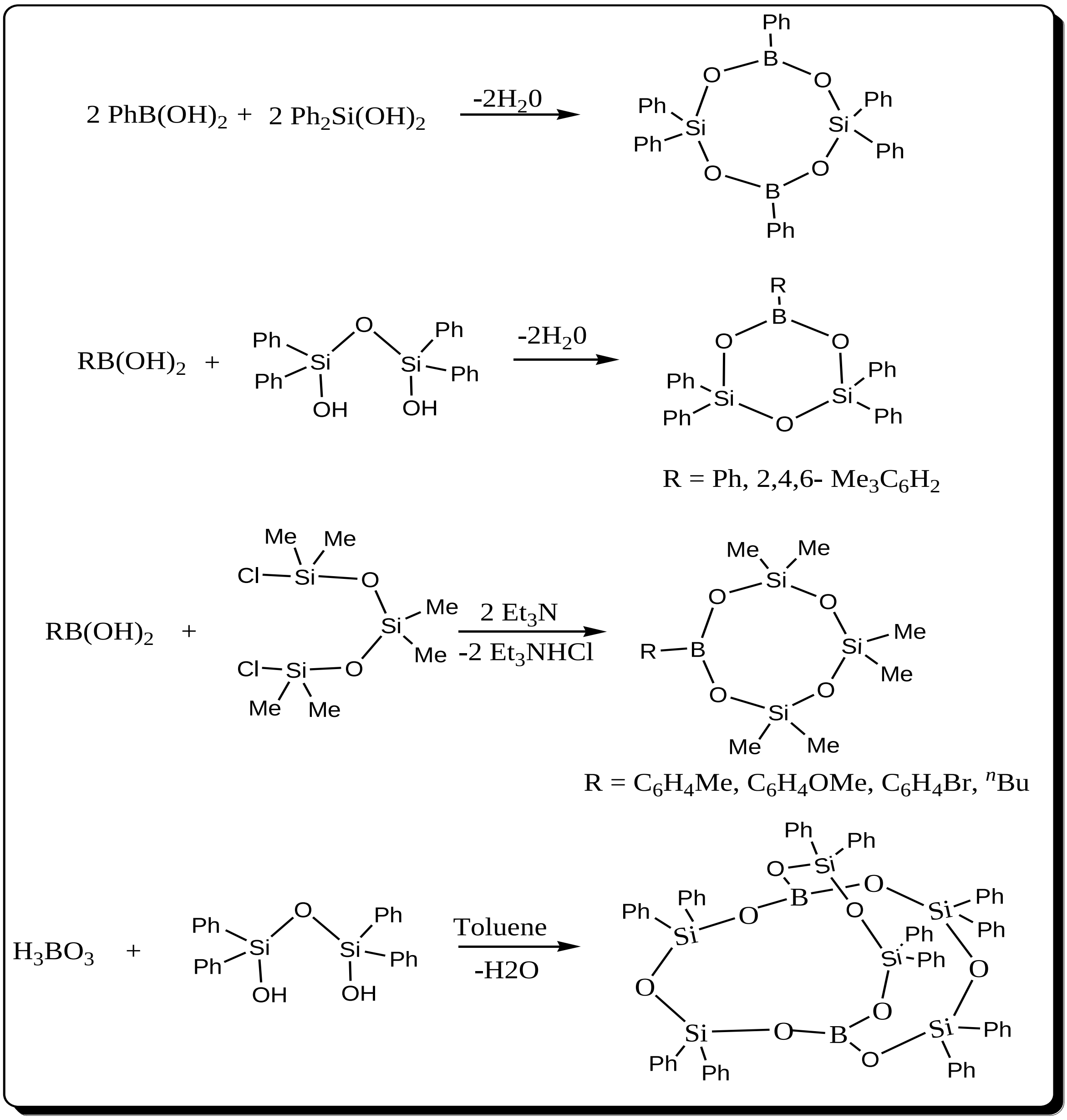
(V.6) Use in Neutron Capture Therapy for cancer

Several boronic acids such as 4-boronophenylalanine have been estimated as sources of boron for their potential use in a form of brain cancer therapy based on the technology of soft neutron capture.[48]

(VI) Borosiloxanes

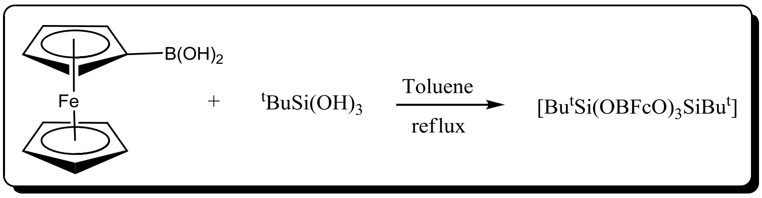
Cyclic species containing B–O–Si linkages are represented in the literature by a number of 6-, 8- and 10- membered cyclo-borasiloxane ring systems.[49] There synthesis is outlined in scheme 5 below Cyclo-borasiloxane ring systems are synthetically available by cyclocondensation reactions of appropriate B and Si containing precursors. Reported syntheses of borasiloxane rings have involved cyclocondensation reactions from either (i) Ph-$B(OH)_2$ and an α,ω-dichlorosiloxane in the presence of NEt_3 (ii) $PhB(OH)_2$ and a dihydroxysilane or α,ω-dihydroxysiloxane (iii) $PhBCl_2$ and a dihydroxysilane; or (iv) $PhB(OH)_2$ and a diethoxysilane or α,ω-diethoxysiloxane.

Borosiloxane cage compounds that have been structurally characterized in the reports include $[^tBuSi\{O(4\text{-}BrC_6H_4B)O\}_3SiBu^t]$ which contains the 11-atom ‘‘spherical’’ B_3Si_2O6 core,[49(j,s)] $[B(OSiPh_2SiPh_2O)_3B]$ with a ‘‘cylindrical’’ $B_2Si_6O_6$ core,[49k] ‘‘cube-based’’ $[(^tBuSi)_4(4\text{-}RC_6H_4B)_4O_{10}]$[49m] species where R = $(CH_2{=}CH)$ or Br which have $B_4Si_4O_{10}$ cores, and silesesquioxane-based species which contain ‘‘cube based’’ BSi_7O_{12} units.[49l]



Scheme 5: preparations of borosiloxanes

Spalding et al synthesized several spherical cage borosiloxanes $[^{t}BuSi(OBRO)_3SiBu^{t}]$ with a wide variety of R groups by adopting water elimination reactions in a Dean-Stark apparatus between $^{t}BuSi(OH)_3$ and boronic acids $RB(OH)_2$ in a 2:3 molar ratio in toluene solution heated at the reflux temperature (scheme 6).[49s] One interesting example is the reaction of ferroceneboronic acid with ^{t}Butyl silanetriol which gives a ‘‘spherical’’ B_3Si_2O6 core with three ferrocene units (figure 1).



Scheme 6

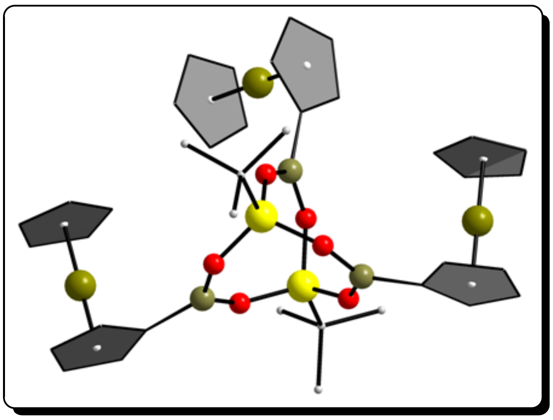


Figure 1: Ball and stick model of [^{t}BuSi(OBFcO)$_3$SiBu^t]

The applications of borosiloxane based conjugated polymer sensors were constructed by simple 2 + 2 cyclocondensation with dihydroxysilane and arylboronic acids to serve as bifunctional cage molecules which were subsequently electropolymerized to provide thin film materials responding to volatile amines were reported by Dongwhan Lee (chart 8).[50]

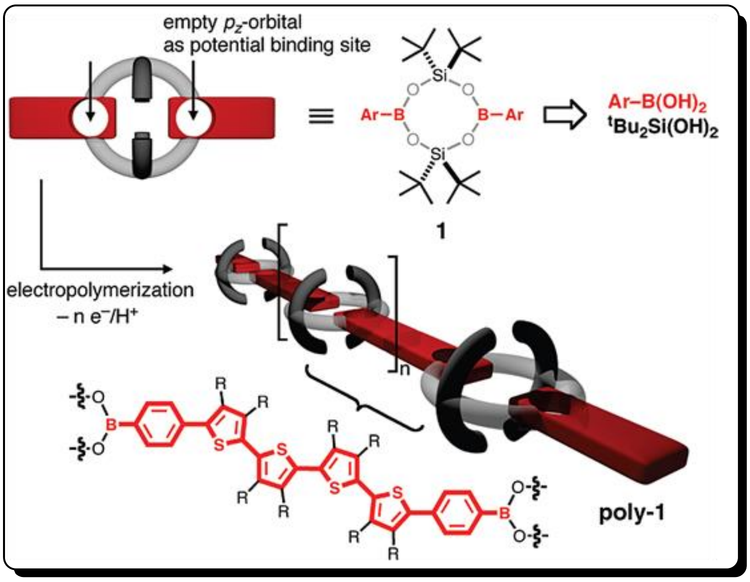
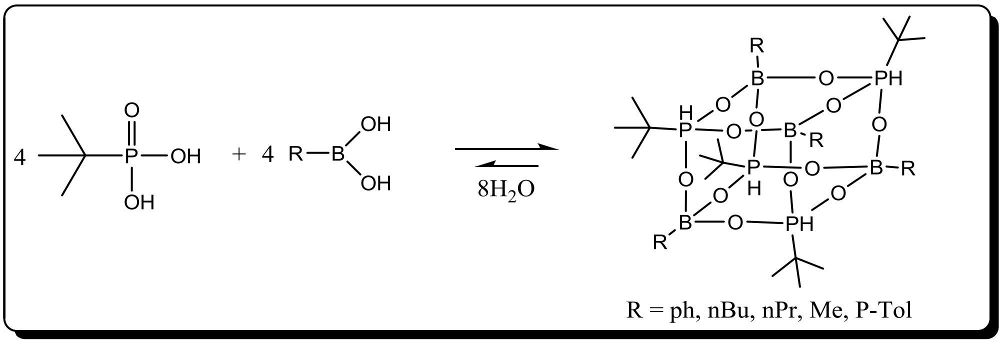


Chart 8: {$B_2Si_2O_4$} core serves as a rigid junction that connects two extended π-segments in a linear fashion for subsequent electropolymerization

(VII) Borophosphonates

Kay Severin and group explained that borophosphonates of the general formula $[^tBuPO_3BR']_4$ can be synthesized by condensation of tert-butylphosphonic acid with boronic acids (scheme 7).[51]



Scheme 7: Borophosphonate cages by [4+4] condensation of phosphonic and boronic acids.

Further they provide clear evidences for the dynamic behavior of the borophosphonate cage compounds through various experiments, and explains the possibility to use simple condensation reactions substantially facilitates the synthesis of borophosphonates, because boronic acids are easily available and easy to handle.

(VIII) Boronic acids in supramolecular chemistry :

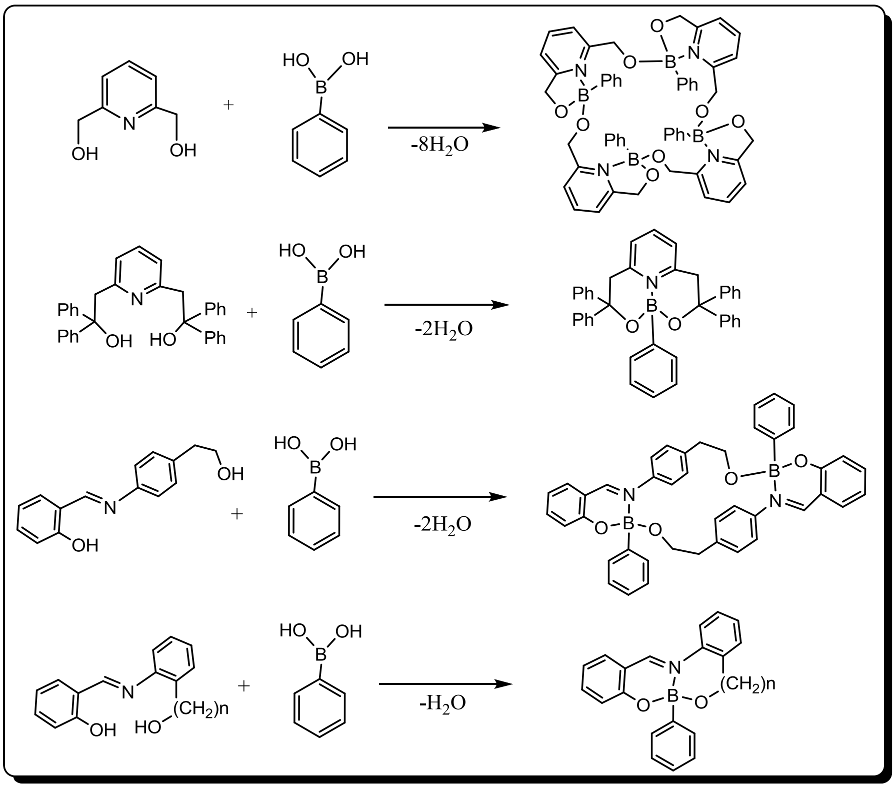
Boronic acids being Lewis acids, they are capable to form bonds with donor atoms such as oxygen, nitrogen, sulfur or phosphorus. Another possible reaction of boronic acids is the condensation with diols, such as catechol, a set of ligands commonly use in supramolecular chemistry. Further these reactions are reversible, although bond energies are usually high. This feature ensures the formation of the thermodynamically most stable product, through the "error correction" mechanism. Thus, boronic acids are potentially good candidates for self assembly reactions. Boronic acids are also highly directional elements, and their geometry can either be trigonal planar, for the Lewis acidic boronic acid/ester, or tetrahedral, for the acid-base adduct. This characteristic feature facilitates the incorporation of this building block in supramolecular assemblies

(VIII.1) Macrocycles and cages :

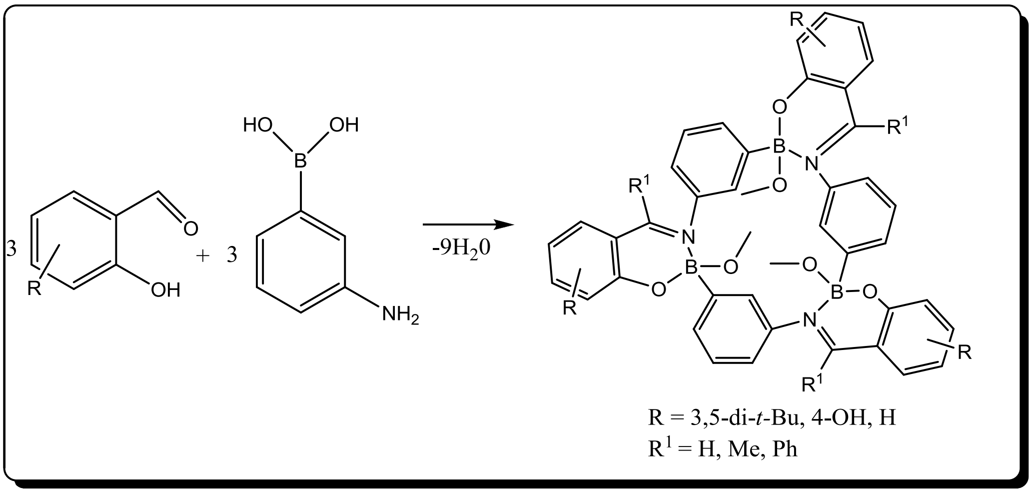
In 1997 boron-based self-assembly were reported by the group of Farfàn and Höpfl., they reported the synthesis of the tetrameric macrocycle from phenyl boronic acid and 2,6-

pyridinedimethanol.[52] Though this ligand was reported to be a tridentate chelating ligand with metal ions interestingly with the smaller boron atoms it was observed that only chelate ring was formed. Thus pendent methanol arm is compelled to condense with another fragment, initiating macrocyclization. Latter the same group reported that monochelation can also be attained using a ligand with longer and more flexible arms (scheme 8).[53] The same researchers in addition investigated the condensation of boronic acids with other tridentate amino dialcohols ligands obtained from salicylaldehyde and aliphatic[54] or aromatic aminoalcohols.[55] The goal was to achieve cyclophanes type of dimeric macrocycles. In their study, Farfàn and Höpfl noticed that, although dimers can be synthesized, electronic effects, steric and transannular strains greatly influence the geometry of the assembly.

More recently, the same groups have studied the reactions of 3-aminophenylboronic acid with substituted salicylaldehydes, 2-hydroxyacetophenone or 2-hydroxybenzophenone.[56,57] These condensation reactions gave trimeric macrocycles in good yield (scheme 9). Some of these macrocycles have a calix[3]arene-like shape. As observed for calixarenes, several conformations are possible depending on the relative orientation of the arene groups. Interestingly, some of these macrocycles are able to act as hosts for primary amines and ammonium chlorides with binding constants in the range of 10^2–10^3 M^{-1} in methanol.[56a]



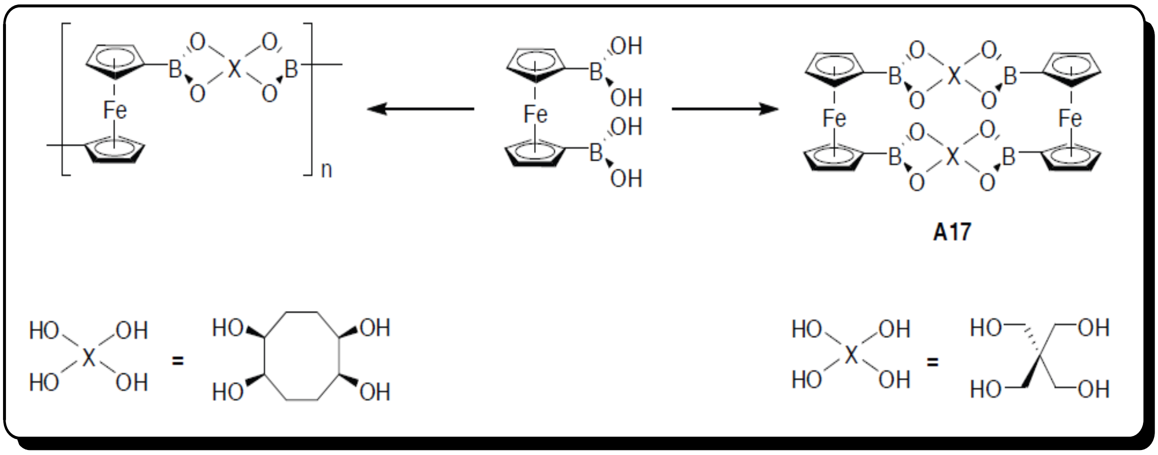
Scheme 8: condensation reactions between phenyl boronic acid and different tridentate ligands



Scheme 9: Formation of boron containing calix[3]arenas.

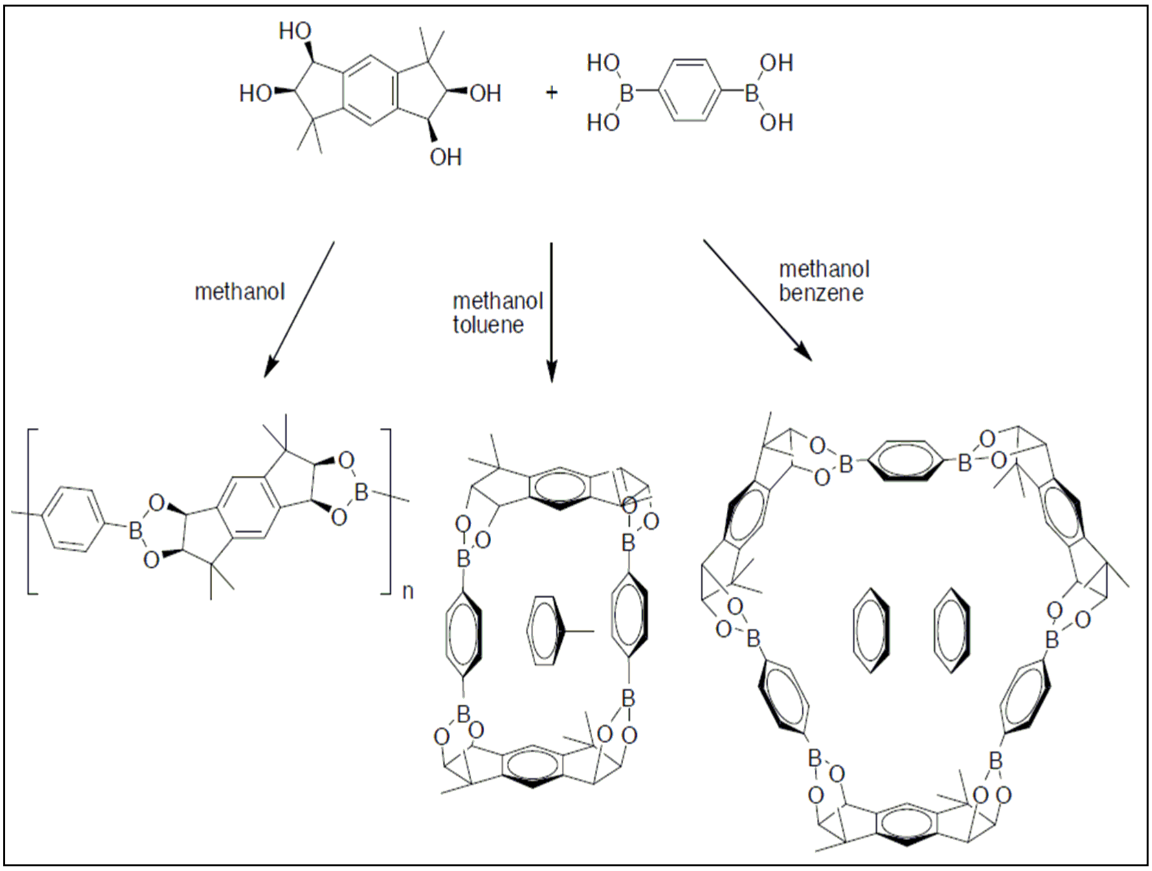
(VIII.2) Reactions with catechols :

Aldridge and co-workers prepared dimeric macrocycle from 1,1'- ferrocenediboronic acid and pentaerythritol (scheme 10). When using(1R,2S,5R,6S)-tetrahydroxycyclooctane as bridging ligand, only oligomers were formed. MALDI-mass spectrometry allowed for the detection of oligomers containing up to seventeen identical units.[58]



Scheme 10: Aggregation of 1,1'-ferrocenediboronic acid with two different tetraols.

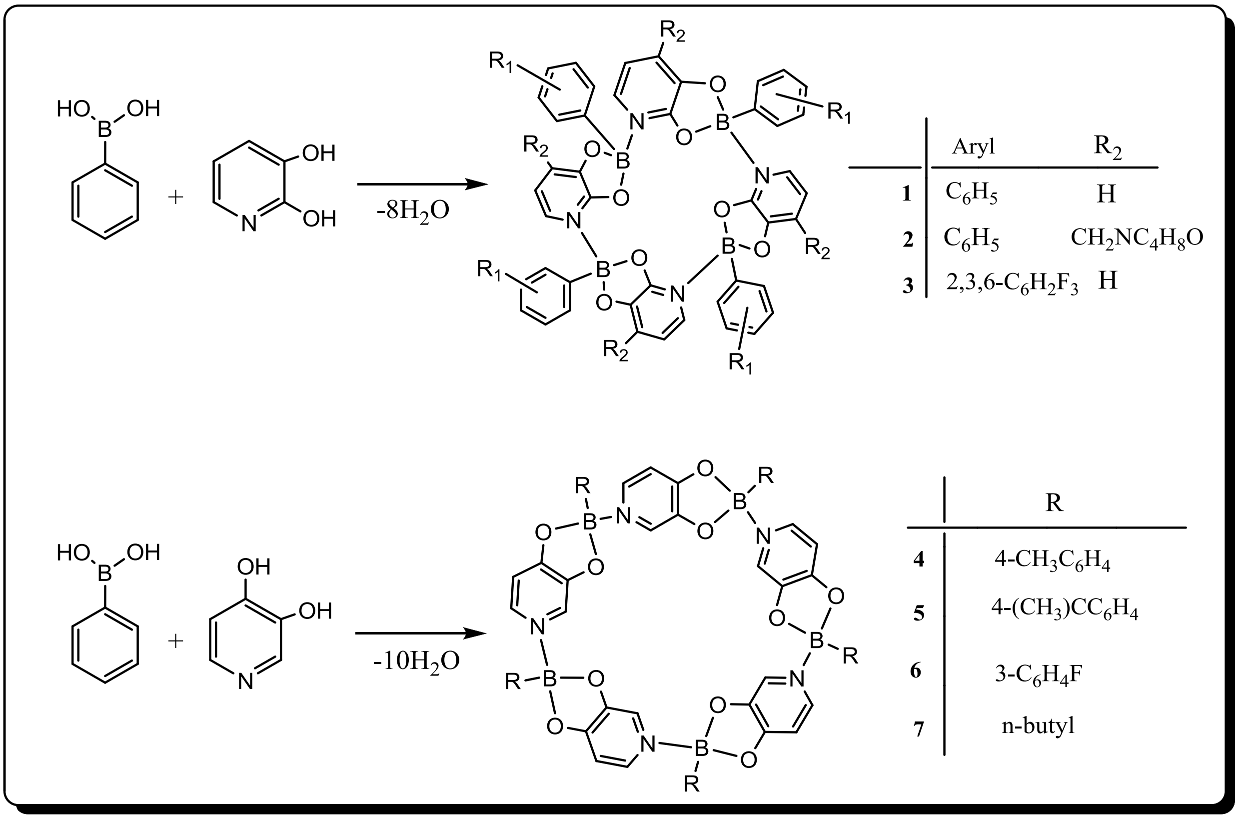
Similarly, the 2 : 1 reaction of 1,4-benzenediboronic acid with an indacene-based tetraol in a mixture of methanol and toluene yielded a macrocycle of [2 + 2] condensation product with four boron centers. On the other hand, when a 2 : 1 mixture of methanol and benzene was used as the solvent, a [3 + 3] condensation product was formed exclusively (Scheme 11). From this it was concluded that the aromatic solvents can act as templates to control the ring size. X-ray analyses reveals the presence of a toluene / benzene molecule in the cavity, suggesting that π - π interactions between toluene/benzene and the phenyl ring of the boronic acid might be the possible reason for the formation of the closed structure. Naphthalene also supports the [2 + 2] condensation but1-methylnaphthalene did not. It was therefore possible to separate these aromatic molecules by selective co-precipitation with the host.[59]



Scheme 11: Templated synthesis of boronate macrocycles.

(VIII.3) Reactions with dihydroxypyridine ligands :

The reactions between various aryl- and alkyl-boronic acids and dihydroxypyridine ligands have been investigated. When 2,3-dihydroxypyridine was used, four-membered macrocycles were attained. The isomeric 3,4-dihydroxypyridine led to the formation of pentameric macrocycles (Scheme 12). In these reactions, first the boronic acid condenses with the two adjacent hydroxyl groups of the ligand to form a boronate ester. The monomeric units then self-assemble into a macrocycle via formation of intermolecular dative B-N bonds.[60, 61]



	Aryl	R$_2$
1	C_6H_5	H
2	C_6H_5	$CH_2NC_4H_8O$
3	2,3,6-$C_6H_2F_3$	H

	R
4	4-$CH_3C_6H_4$
5	4-$(CH_3)CC_6H_4$
6	3-C_6H_4F
7	n-butyl

Scheme 12: Formation of tetrameric and pentameric macrocycles

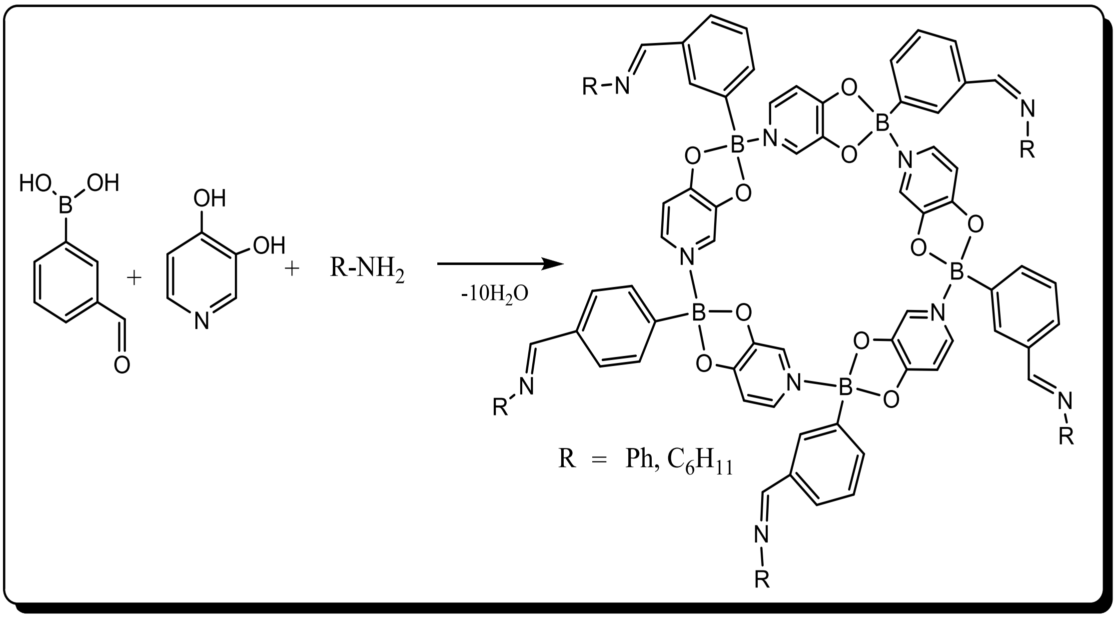
(IX) Multicomponent assembly of boron based Dendrimers

The generation of dendrimers via multi step path route typically involves substantial synthetic efforts and often yields very poor yields. An interesting alternative is the self-assembly of appropriate building blocks. Most of the times these reactions provide dendrimers in one-pot synthesis with high yields and purity. The self assembly process generally avails of Hydrogen bonds or metal–ligand interactions to generate dendrimeric structures. Kay Severin et al demonstrated that reversible covalent and dative bonds involving boronic acids for the first time.

The above reactions of boronic acids with 2,3- or 3,4- dihydroxypyridines to give four or five -membered macrocycles, have been used as scaffolds to build dendritic structures.[61] The origin for this study was the observation that aldehyde-amine condensation reactions do not interfere with the macrocyclization.

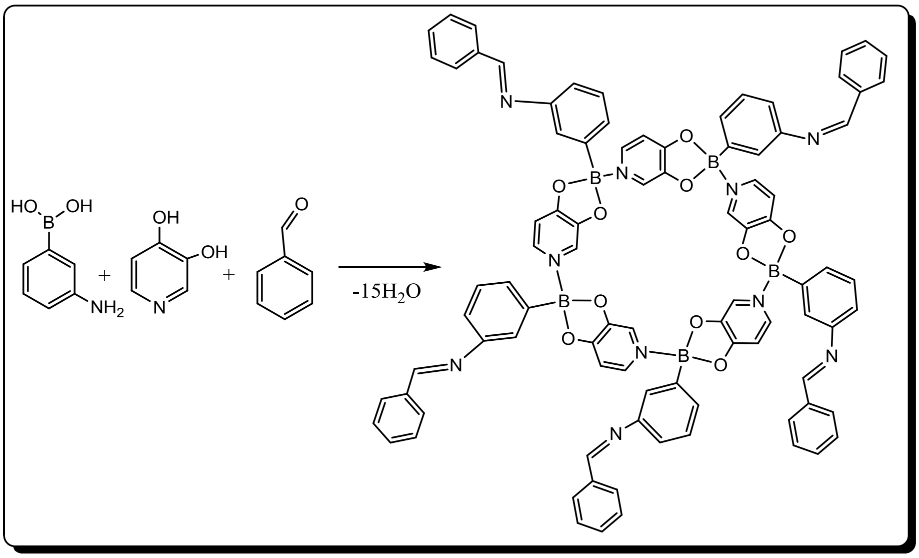
In a first set of experiments, 3-formylphenyl boronic acid, 3,4-dihydroxypyridine and primary amines such as aniline and cyclohexylamine were condensed. Again, the ^{1}H NMR spectra of the compounds were in agreement with the formation of a pentameric macrocycle with five imine-based side-chains. In addition, the aldehyde signal at 9.99 ppm had disappeared and a new one corresponding to the CH=NR proton had appeared at 8.42 (ph) and 8.29 (C_6H_{11}) ppm.

X ray structure analysis of the macrocyclics reveals that the cores are structurally very similar as previously observed which are formed by five identical boronate ester subunits connected via B-N bonds. At its periphery, five benzylideaniline side chains are dandling out, forming a star shape complex (Scheme 13).

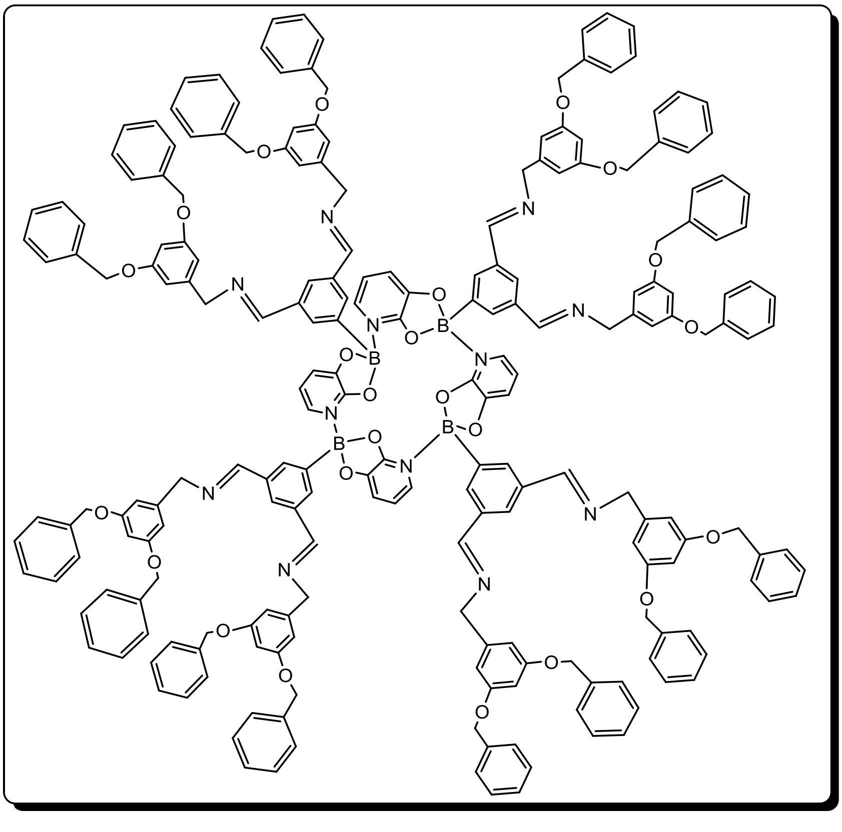


Scheme 13: Three-component reactions of 3-formylphenyl boronic acid, 3,4- dihydroxypyridine and an amine to form functionalized macrocycles

The group successfully reverse the connectivities and condensate 3-aminophenyl boronic acid, 3,4-dihydroxypyridine and an aldehyde to obtain a dendrimeric macrocycles (scheme 14). The successful formation of complexes proves that it is possible to perform imine condensation in parallel to the assembly of boronate macrocycles. The largest structure that was synthesized by this methodology is shown in Scheme 15. It was obtained by using the dendron 3,5-(benzyloxy)benzylamine as the amine building block.



Scheme 14: Three-component reaction of 3-aminophenyl boronic acid, 3,4- dihydroxypyridine and benzaldehyde to form functionalized macrocycles.

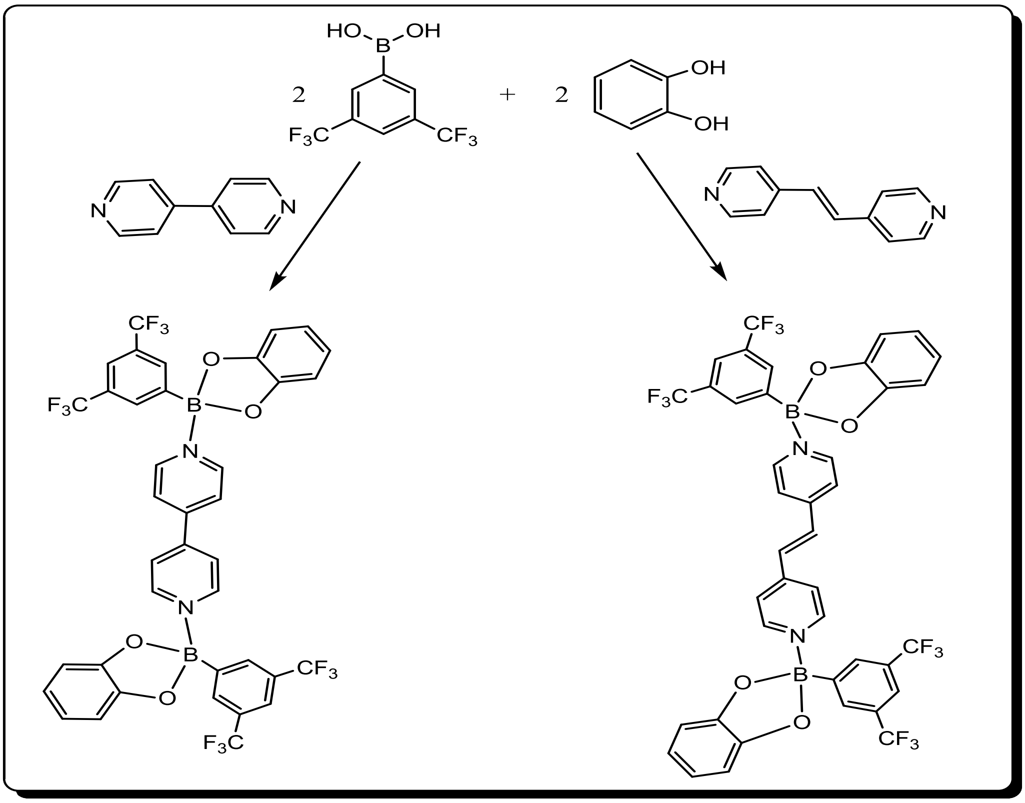


Scheme 15: Macrocycle constructed using 3,5-(benzyloxy)benzylamine as the amine building block.

(X) Boronic acids in Rotaxanes :

Rotaxanes are interlocked compounds, the synthetic strategies of rotaxane in general obtained by pre-organized building blocks, which are locked by covalent capture under kinetic control. An alternative for this approach is the formation of rotaxanes under thermodynamic control using reversible bonds. The advantage of the latter approach is being its good organization, which allows for the generation of complex structures in high yield.[62] First examples of boronic acid based rotaxanes have been described recently,[63,64] and are obtained by thermodynamically controlled condensation reactions as mentioned below (scheme 16).

Kay Severin and group, studied the multicomponent reaction of 1,2-di(4-pyridyl)ethylene, catechol, 3,5-bis(trifluoromethyl)-phenylboronic acid, and 1,5-dinaphto-38-crown-10. The compounds were dissolved in a 1: 2: 2: 1 ratio in toluene and then heated with a Dean–Stark trap. After cooling to room temperature, the rotaxane was isolated in 67% yield (figure 2).



Scheme 16: One-pot synthesis of adducts with bipyridyl linkers

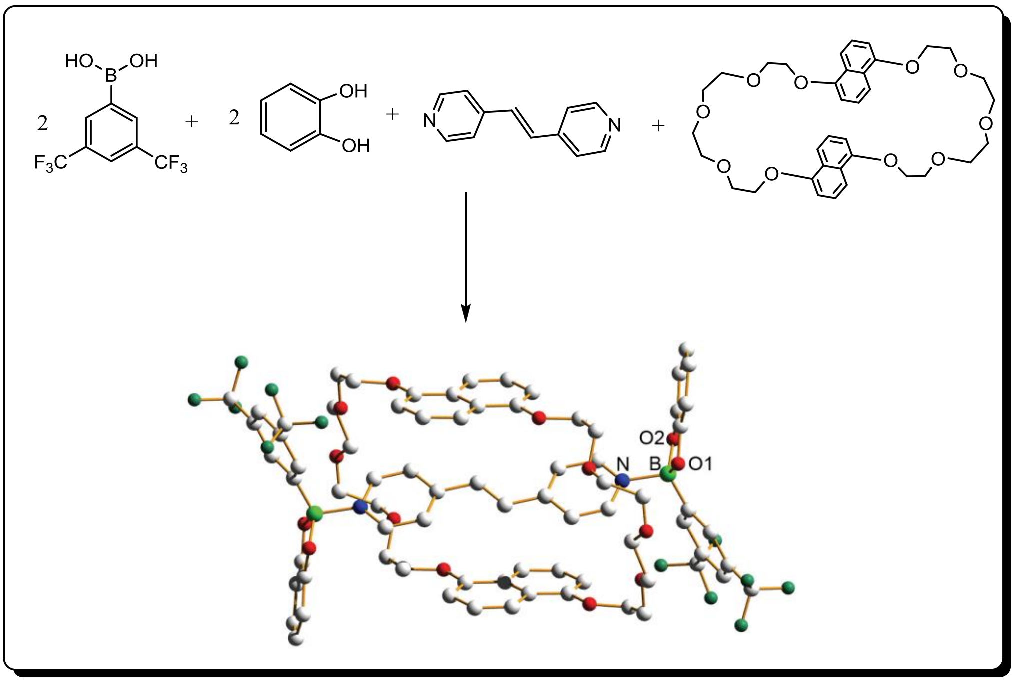


Figure 2: One-pot synthesis of rotaxane

Here, in the following chapter's reaction of phenyl boronic acid with pyrazolyl phenols and a three component reactions involving boric acid, silanol and pyrazolyl phenol leading to isolation of interesting twelve membered macrocycles will be dealt with in detail.

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Investigations on the Reactivity of Arylboronic Acid with Phenolic Pyrazole

Chapter 5

Abstract: Reaction of phenylboronic acid with phenolic pyrazole was carried out in 1:1 stochiometry using toluene as a solvent. Depending on the steric bulk of the group present on the pyrazole ring, PhB (HPhPzPh)(OEt) **5.1**, [(PhB)(PhPzHt-Bu)(OH)][$(PhB)_2$(PhPzt-Bu)$_2$(O)] **5.2** and $(PhBPhPz)_2$ **5.3** were isolated. Compound **5.3** is an example of cis-isomer of pyrazabole crystallized in a boat conformation for the B_2N_4 heterocycle.

5.1 Introduction:

Organoboron compounds have been an area of active research for several decades now due to the innumerable applications of organoboron compounds in the fields ranging from organic synthesis[1], organometallic and inorganic coordination chemistry[2] to materials chemistry.[3] The coordination chemistry of poly(pyrazolyl)borates have been investigated in detail and several reviews have appeared describing the rich coordination chemistry arising out of these systems.[4,2a] The ease with which boron forms coordinate bonds with donor atoms like N and O have been exploited and a series of interesting organoboron complexes and macrocycles have been isolated by reaction of arylboronic acids with salen-type ligands and aminophenols.[5] Another interesting class of boron compound is the pyrazabole, a boron nitrogen containing heterocycle.[6] Ever since the isolation of pyrazabole was reported in 1966 by Trofimenko along with the poly(pyrazolyl)borate ion and their free acids, several pyrazaboles with substitution both at the boron atoms and the carbon atoms have been reported.[7,6b] Pyrazaboles are relatively more air and moisture stable compared to other boron-nitrogen heterocycle and hence a variety of organic transformations have been carried out resulting in a large number of derivatives bearing various functional groups. Importantly, pyrazaboles have been shown to be useful as building block for discotic liquid crystals[8], linkers of ansa ferrocenes to form active container molecules for supramolecular applications[9] and for synthesizing luminescent polymers.[10] Though pyrazaboles mainly crystallize with the boat conformation for the B2N4 ring, planar and chair like conformers have also been reported.[11,7b,7d] In general, pyrazaboles with symmetrical 4,8-disubstitutions at the boron atom have been synthesized by the reaction of amine complexes of borane or organoborane reagents with pyrazole under reflux conditions in toluene.[6] The other synthetic route employed is by functionalizing the hydrogen coordinated to boron of pyrazabole by other groups.[12] In the case of gem boron disubstituted or asymmetrically boron monosubstituted materials, the synthesis is challenging due to unpredictable reaction of the bis(pyrazolyl)borate salt with the amine complexes of the boranes bearing good leaving group.[13]

On the other hand, phenolic pyrazoles (N2O-type ligand) have been used as ligands for synthesizing multinuclear transition metal clusters; some of which possess interesting magnetic properties.[14] But the ligating ability of phenolic pyrazoles (O,N,N-donors) towards main group metals were not known. Recently we have shown the utility of phenolic pyrazoles as ligands for synthesizing organoantimony oxo clusters by carrying out reactions with organostibonic acids.[15] Depending on the steric bulk of the group present in the pyrazole ring, either one or two nitrogen atoms coordinate to the antimony metal leading to the formation of novel tetranuclear clusters. Considering the various applications of organoboron complexes the complexing ability of phenolic pyrazoles towards organoboronic acids have been investigated. The syntheses and structural elucidation of the products are presented in this chapter.

5.2 Experimental Section:

5.2.1 General information:

Phenylboronic acid, solvents and other common reagents were purchased from commercial sources. Ligands were synthesized using literature procedures. Infrared spectra were recorded on a JASCO-5300 FT-IR spectrometer as KBr pellets. The ^{1}H, ^{13}C, and ^{11}B solution NMR spectra were recorded on a Bruker DRX 400 instrument. Elemental analysis was performed on a Flash EA series 1112 CHNS analyzer.

5.2.2 Synthetic methodology:

Compound 5.1: Phenylboronic acid (0.15 g, 1.26 mmol), H_2PhPzPh (0.30 g, 1.26 mmol) were taken in 50ml of toluene and the solution was stirred for 6 h. The white solid which precipitated was filtered and dissolved in ethanol for crystallization. White crystals suitable for X-ray studies were grown over night by slow evaporation. Yield : 0.40 g, (44%, based on weight of phenylboronic acid). m.p: 260˚ C. Elemental anal.cal. for **5.1**: $C_{23}H_{21}O_2BN_2$, calc : C, 75.01; H, 5.74; N, 7.60. Found C, 75.12; H, 5.89; N, 7.75. IR (KBr, cm^{-1}) 2964(w), 1614(s), 1574(s), 1485(m), 1460(w), 1431(w), 1319(s), 1267(m), 1167(w), 1107(s), 974(w), 835(w), 748(m), 692(m). ^{1}H NMR ($CDCl_3$): δ 7.65 (t, 3H), 7.39 (q, 6H), 6.9 (d, 5H), 6.86 (d, 2H), 3.68 (q, 2H), 1.14 (t, 3H). ^{13}C NMR ($CDCl_3$): δ 146.89, 145.82, 133.23, 131.74, 131.40, 130.72, 130.06, 129.49, 128.98, 127.87, 127.38, 126.73, 125.73, 125.15, 119.44, 118.78, 97.54 .^{11}B NMR (DMSO): δ 5.0 ppm.

Compound 5.2: Phenylboronic acid (0.20 g, 1.64 mmol), H_2PhPztBu (0.35 g, 1.64 mmol) were taken in toluene (50ml). The solution was refluxed for 6 h using a Dean stark apparatus to remove the water eliminated in the reaction as an azeotropic mixture. The clear solution then formed was cooled to room temperature, filtered and evaporated under reduced pressure to yield a colorless solid. Crystals suitable for X-ray studies were grown from chloroform solution by direct evaporation after a week time. Yield : 0.45g, (29.6%, based on the weight of phenylboronic acid). m.p: 192˚C. Elemental anal.cal. for **5.2**:

$C_{57}H_{61}N_6B_3O_5$, calc : C, 72.63; H, 6.52; N, 8.91. Found C, 72.45; H, 6.59; N, 9.03. I.R (KBr, cm^{-1}): 3460(w), 3136(w), 2964(w), 1616(s), 1564(m), 1491(s), 1369(m), 1311(m), 1259(w), 1192(m), 1105(m), 951(m), 856(w), 810(w), 754(s), 704(s), 667(w), 553(w). ^1H NMR ($CDCl_3$): δ 7.32 (d, 1H), 7.17 (d, 5H), 7.06 (d, 2H), 6.98 (d, 1H), 6.73 (t, 3H), 0.92 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.60, 155.95, 144.86, 134.22, 132.21, 130.95, 127.58, 126.96, 126.70, 125.00, 119.72, 118.59, 114.31, 96.64, 31.48, 30.94, 29.47. ^{11}B NMR ($CDCl_3$): δ 4.8 ppm.

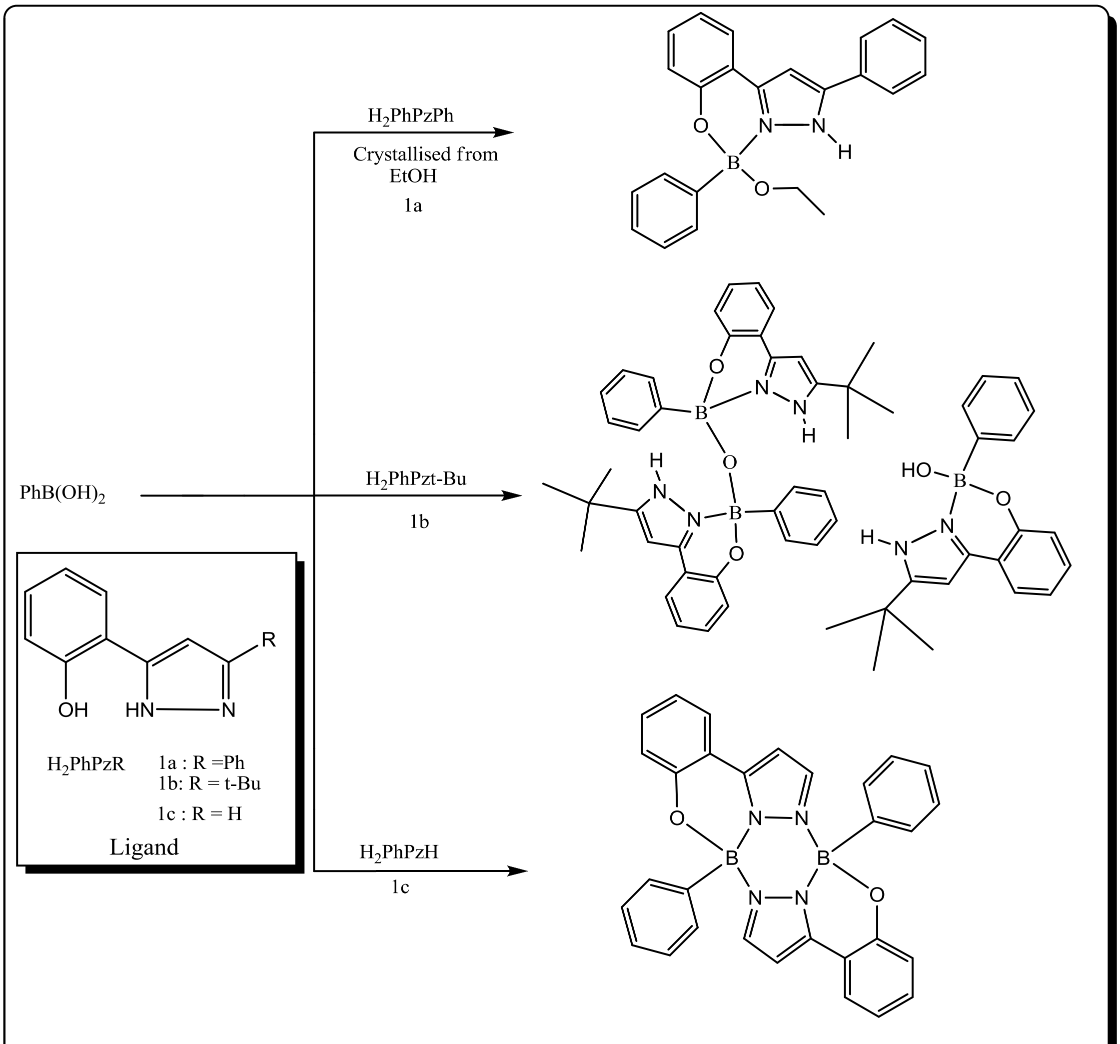
Compound 5.3: Synthetic procedure is similar to 2. Amount and stochiometry of the reactants taken are phenylboronic acid (0.15 g, 1.24 mmol), H_2PhPzH (0.20 g, 1.24 mmol). Yield: 0.25g (41%, based on the weight of phenylboronic acid). m.p: 270˚C. Elemental anal.cal. for **5.3** $C_{30}H_{22}N_4B_2O_2$, calc : C, 73.21; H, 4.50; N, 11.38. Found: C, 73.11; H, 4.55; N, 11.45. I.R (KBr, cm^{-1}): 3117(w), 3067(w), 2964(w), 1614(s), 1574(s), 1537(m), 1502(m), 1448(m), 1412(m), 1365(w), 1313(s), 1249(s), 1205(m), 1124(w), 1051(m), 908(w), 856(w), 835(w), 744(m), 692(m), 646(m), 488(w). ^1H NMR ($CDCl_3$): δ 8.28 (d, 2H), 7.60 (d, 2H), 7.27 (t, 2H), 7.02 (d, 2H), 6.92 (m, 4H), 6.78 (d, 6H), 6.70 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 153.65, 143.39, 134.58, 131.73, 130.79, 126.87, 126.81, 125.27, 120.06, 119.65, 115.69, 101.19. ^{11}B NMR ($CDCl_3$): δ 3.6 ppm.

5.3 X-ray structure determination:

Single-crystal X-ray data collection for compounds **5.1-5.3** were carried out at 100(2) K on Bruker Smart Apex CCD area detector system (λ (Mo Kα) = 0.71073Å) equipped with Oxford Cryo stream low temperature device and graphite monochromator. The data were reduced using SAINTPLUS and the structures were solved using SHELXS-97 and refined using SHELXL-97. The structures were solved by direct methods and refined by full-martix least squares cycles on F^2. All non-hydrogen atoms were refined anisotropically.

5.4 Results and Discussion:

5.4.1 Synthesis: General synthetic method used is as follows. Phenylboronic acid and phenolic pyrazole (H_2PhPzR, where R = Ph **5.1**, t-Bu **5.2**, H **5.3**) were either stirred at room temperature (for **5.1**) or refluxed in toluene for 6 h (**2** and **3**) until a clear solution was obtained. When reflux condition was employed, the water formed during the reaction was removed as an azeotropic mixture using a Dean Stark apparatus. Compound **5.1** dissolved in high polar solvents like ethanol and methanol whereas **5.2** and **5.3** dissolved in a wide range of solvents like dichloromethane, chloroform and toluene. Compounds **5.1-5.3** were characterized using standard spectroscopic and analytical techniques. IR spectrum of **5.2** shows the presence of a broad peak around 3067 cm^{-1} which can be attributed to the presence of OH group. ^{11}B NMR for **5.1-5.3** (in DMSO for **5.1**, $CDCl_3$ for **5.2** and **5.3**) shows single resonance at 5.0, 4.8 and 3.6 ppm respectively which is in similar range as reported in literature for analogous organoboron compounds.



Scheme 1

The products were crystallized in ethanol (**5.1**) and chloroform (**5.2** and **5.3**) to isolate crystals suitable for single crystal X-ray diffraction analysis. Crystallographic data and refinement details for **5.1**, **5.2** and **5.3** are provided in table 1. Structural elucidation revealed the formation of PhB(HPhPzPh)(OEt) **5.1**, [(PhB)(PhPzHt-Bu)(OH)][$(PhB)_2(PhPzt\text{-}Bu)_2(O)$] **5.2** and $(PhBPhPz)_2$ **5.3** (Scheme 1).

5.5 Description of crystal structures:

Compound **5.1** crystallizes in monoclinic space group p2(1)/n (Figure 1). The ligand H_2PhPzPh binds to the boron atom through the pyrazole N atom and the phenolic oxygen while the other nitrogen of the pyrazole group bearing the hydrogen atom remains a spectator. The remaining two coordinations of the tetrahedral boron atom come from the phenyl carbon and oxygen of ethoxy group. Since ethanol was used for crystallization, the initially present OH group from the phenylboronic acid is present as the ethoxy derivative in **5.1**. Selected bond lengths (Å) and angles (deg) for **5.1** are given in the table 2. The B-O bond distances in **5.1** are 1.477(3) Å (B1-O1) and 1.459(3) Å (B1-O2). The phenolic oxygen to boron is slightly longer than the B-O_{ethoxy} group. The B-N bond distance is 1.590(3) Å, which falls in the range as reported in literature for tetrahedral boron atoms containing B-N bonds.[16] The % THC[17] of boron in **5.1** was found to be 99.73 which confirm that the boron atom is in a perfect tetrahedral site.

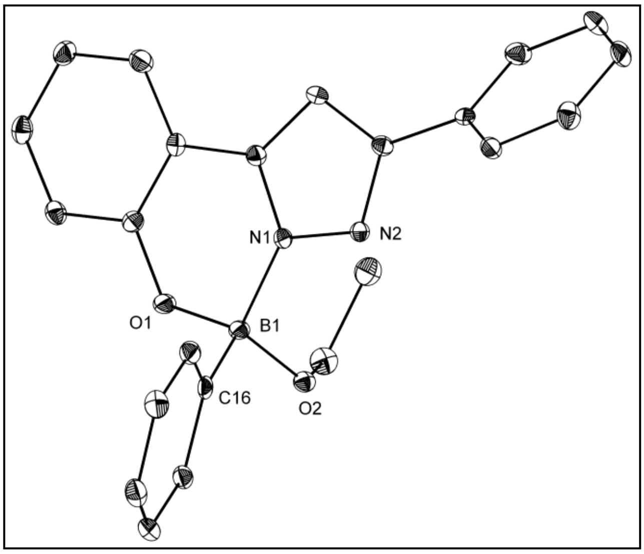


Figure 1: ORTEP view of compound **5.1** (30% probability)

It is of interest to mention here that monometallic boron compounds are a rarity when compared to the other elements of group 13 like aluminum, gallium and indium which readily forms monometallic complexes even with flexible salen-type N_2O_2 ligands. The isolation of a monometallic near perfect tetrahedral organoboron complex is probably due to the chelating O, N-donor atoms of the phenolic pyrazole.

Organoboron compound **5.2** crystallizes in orthorhombic space group pbca (Figure 2). Despite several attempts the structure refinement for **5.2** was poor due to the inferior quality of the crystals obtained. However the data was sufficiently good to arrive at the core structure. The asymmetric unit consists of an oxo bridged boron dimer and a organoboron monomer. The mode of binding of the ligand H_2PhPzt-Bu in **5.2** is similar to that of H_2PhPzPh in **5.1**. The only difference observed is that the fourth coordination of boron in **5.1** was from an ethoxy group whereas in **5.2** it is from a μ_2-bridging oxo group. Since the compound was crystallized from chloroform, the B-OH group combines with a similar moiety of a neighboring boron atom forming an oxo bridged dimer eliminating a water molecule in the process. Similar observations have been reported earlier for organoboron compounds involving other ligand systems wherein crystallization from chlorinated solvents or acetonitrile have led to the formation of oxo-bridged dimers. Moreover in the crystal lattice of **5.2**, a organoboron phenolic pyrazolyl complex similar to **5.1** co-crystallizes with the dimer. Hence we propose that a monometallic compound is formed initially which subsequently dimerises by water elimination leading to the formation of an oxo bridged dimer. The dimer and monomer are held together by hydrogen bonds. Selected bond lengths and angles for **5.2** are given in the table 2. The B-O distances are similar to that of **5.1**. The phenolic oxygen to the boron atom bond distances are slightly longer than the boron to oxygen atoms of the μ_2-bridging oxo and the terminal OH groups. The B-O (phenolic) distances fall in the range 1.493(6) to 1.504(6) Å; the B- O(μ_2-bridging) being 1.427(6) and 1.446(6) Å and B-O (terminal OH) distance being 1.439(6) Å respectively. The B-N bond distances fall in the range 1.591(6) to 1.612(7) Å, which is in the range as reported in literature for monometallic tetrahedral organoboron compounds containing B-N bonds indicating the coordinative nature of the bond.[16] The % THC of boron in **5.2** are 99.11 (B1), 98.67 (B2) and 99.50 (B3) which confirms that the boron atoms in **5.2** are also in a near perfect tetrahedral site. The B2-O2-B3 bond angle is 128.6(4)° which again falls in the range as reported earlier in literature for oxo-bridged boron dimmers.[5e]

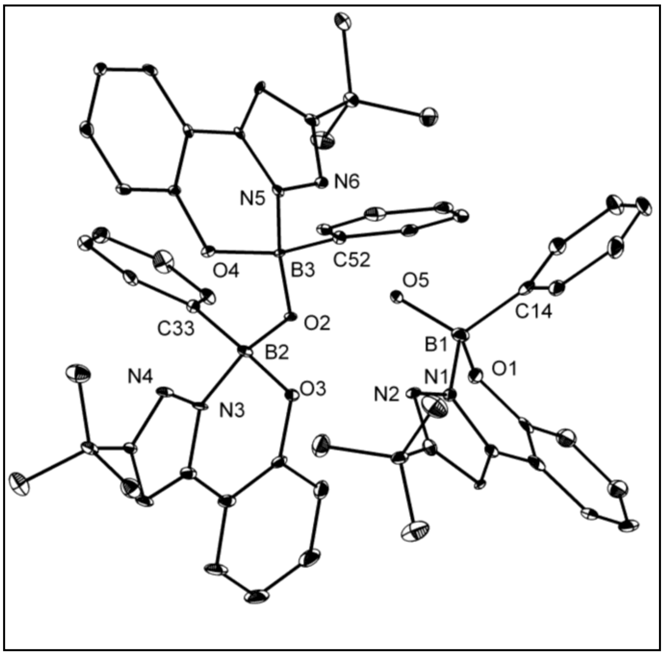


Figure 2: ORTEP view of compound **5.2** (30% probability)

Compound **5.3** crystallizes in monoclinic space group p2(1)/n (Figure 3). Structural elucidation reveals the stabilization of the B_2N_4 heterocycle, pyrazabole. The ligand chelates to the boron atom through the O, N-end while the other nitrogen of the pyrazole coordinates to the second boron atom and subsequent dimerization leads to the formation of the *cis*-pyrabazole with the boat conformation for the B_2N_4 ring. The B-O distances for B1-O1 and B2-O2 are 1.458(2) and 1.449(2) Å respectively and the B-N distances fall in the range 1.570(1) to 1.575(2) Å. Selected bond lengths and angles for **5.3** are given in the table 2. The isolation of pyrazabole by reaction of arylboronic acid with phenolic pyrazole is interesting since it provides an easy access to this heterocycle bearing substitutions at both the boron and carbon atoms. Compared to earlier reports where pyrazabole has been synthesized either by reactions of the highly reactive amine complexes of borane or air and moisture sensitive organoborane reagents with pyrazole, our method of assembling this B_2N_4 heterocycle is more facile. Moreover in the present case we exclusively get the cis-isomer probably due to the nature of the substituents present on both boron and carbon atoms. By varying the groups on boron and carbon atoms isolation of the *trans* isomer could be possible and work in that direction is currently under progress.

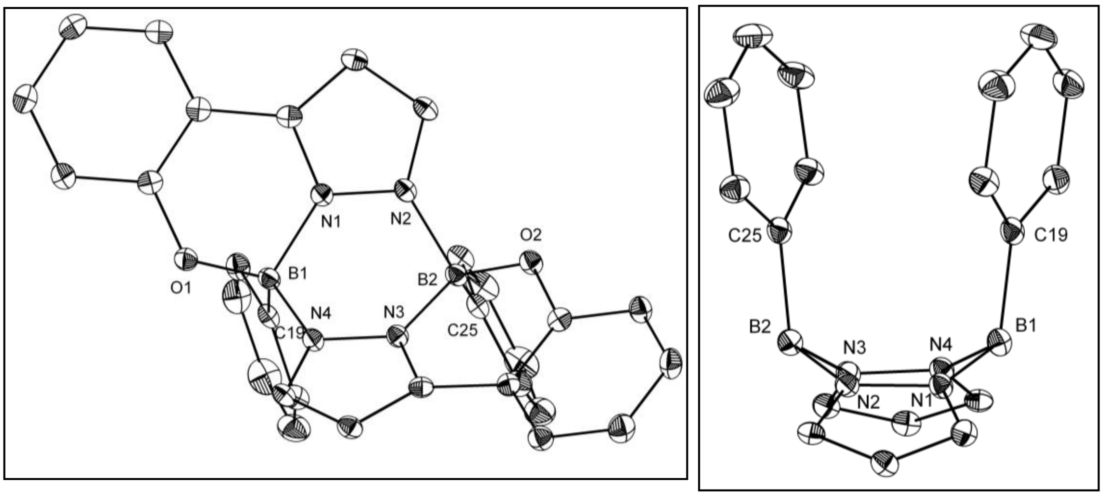


Figure 3: (a) ORTEP view of compound **5.3**(30% probability) (b) boat view of compound **5.3**

Recently, we have investigated the reactions of phenolic pyrazoles with organostibonic acids wherein the presence of phenyl or *tert*-butyl groups on the 5-position of the pyrazole ring led to the formation of isostructural tetranuclear organoantimony oxo clusters wherein the pyrazoles chelated to the metal atoms through the O,N-end while the other N atom of the pyrazole is noncoordinating.[15] But when arylstibonic acids were reacted with phenolic pyrazoles with hydrogen on the 5-position of the pyrazole ring the ligand bound to the Sb atoms through both chelating (O,N-mode) and bridging (N,N-) mode. Herein, when phenolic pyrazole is reacted with phenylboronic acid the substitution on the pyrazole ring directs the structure of the products. When phenyl or *tert*-butyl substituents are present the ligand binding mode is purely chelating (O,N-atoms) while the presence of hydrogen on the 5th position of the pyrazole encourages both the chelating (O,N-mode) and bridging (N,N-) mode. In the case of organoantimony oxo clusters both phenyl and *tert*-butyl substituents on the pyrazole led to the isolation of isostructural compounds whereas in the present case it varies due to the difference in the solvent of crystallization employed for **5.1** and **5.2**. Earlier reports[18] on organoboron complexes suggest that crystallization in chlorinated solvents or acetonitrile may lead to isolation of oxo bridged boron dimers which is probably the reason why despite similar mode of ligand binding in **5.1** and **5.2**, products with different nuclearity have been isolated. When the 5-position of the pyrazole ring bears a less bulky group like hydrogen, the phenolic pyrazolyl ligand binds to the metal centre through both the O,N-mode and N,N-bridging mode and subsequent dimerization leads to the formation of pyrazabole.

5.6 Conclusion:

To summarize, the reactions of phenylboronic acid with phenolic pyrazoles (H_2PhPzR, where R = Ph **5.1**, t-Bu **5.2**, H **5.3**) have been investigated. Single crystal X-ray analysis shows the formation of a monometallic organoboron complex, an oxo bridged dimer and pyrazabole, a B_2N_4 heterocycle. It is of interest to mention that by modifying the groups present on the pyrazole ring interesting organoboron compounds have been isolated in good yield. In particular, the formation of a rare monometallic organoboron monomer and pyrazabole by this simple and straight forward reaction methodology is significant considering the recent interest in the applications of organoboron reagents and pyrazabole.

Table 1: Crystal data parameters for compound 5.1-5.3:

	5.1	**5.2**	**5.3**
Formulae	$C_{23}H_{21}BN_2O_2$	$C_{59}H_{63}B_3Cl_6N_6O_5$	$C_{30}H_{22}B_2N_4O_2$
Fw.g mol^{-1}	368.23	1181.28	492.14
Cryst syst	Monoclinic	Orthorhombic	Monoclinic
Cryst size.mm	0.22 x 0.16 x 0.10	0.24 x 0.18 x 0.12	0.24 x 0.18 x 0.16
Space group	P2(1)/n	Pbca	P2(1)/n
a, Å	12.2483(9)	17.9703(17)	12.3020(7)
b, Å	11.8804(9)	24.943(2)	10.2432(6)
c, Å	12.8447(9)	26.735(2)	19.8982(12)
α, deg	90.0	90.0	90.0
β, deg	95.4520(10)	90.0	104.8120(10)
γ, deg	90.0	90.0	90.0
V, Å^3	1860.6(2)	11983.5(17)	2424.1(2)
Z	4	8	4
Dcacld.Mgm^{-3}	1.315	1.310	1.348
Temp(K)	100	100	100
μ, mm^{-1}	0.084	0.340	0.085
F(000)	776	4928	1024
θ range,deg	2.20 to 24.99	1.52 to 25.00	1.77 to 25.09
no.of.refln colled/unique	16900/3266	109242/10552	22718/4308
data/restraints/params	3266 / 0 / 254	10552 / 0 / 720	4308 / 0 / 343
R_{int}	0.0713	0.1733	0.0271
GooF(F^2)	1.076	1.113	1.044
R_1/wR_2 ($I>2\sigma(I)$)	0.0556/0.1110	0.1019/0.1867	0.0364/0.0882
R_1/wR_2 (all data)	0.0812/0.1211	0.1530/0.2070	0.0406/0.0912
largest diff peak/hole,e Å^{-3}	0.288 / -0.202	0.742 / -0.583	0.247/ -0.239

Table 2: Bond length and bond angle parameters for compound 5.1-5.3:

Compound 5.1

B_1-O_1	1.477(3)	N_1-N_2	1.348(2)	$O_1-B_1-O_2$	110.05(19),
B_1-O_2	1.459(3)	$O_1-B_1-C_{16}$	111.42(19)	$O_2-B_1-C_{16}$	109.27(18)
B_1-N_1	1.590(3)	$O_1-B_1-N_1$	104.76(18)	$B_1-N_1-N_2$	124.40(17)
B_1-C_{16}	1.600(4)	$O_2-B_1-N_1$	109.40(18)		

Compound 5.2

B_1-O_1	1.493(6)	B_3-O_4	1.504(6)	$O_2-B_2-O_3$	105.2(4)
B_1-O_5	1.439(6)	B_3-N_5	1.591(6)	$O_3-B_2-N_3$	103.6(3)
B_1-N_1	1.612(7)	B_3-C_{52}	1.628(7)	$N_3-B_2-C_{33}$	108.9(4)
B_1-C_{14}	1.615(7),	$O_1-B_1-N_1$	102.2(4)	$O_2-B_2-C_{33}$	110.5(4)
B_2-O_2	1.446(6)	$O_5-B_1-N_1$	110.6(4)	$C_{33}-B_2-O_3$	110.5(4)
B_2-O_3	1.495(6)	$O_5-B_1-C_{14}$	114.2(4)	$O_2-B_3-O_4$	110.9(4)
B_2-N_3	1.591(6)	$O_1-B_1-C_{14}$	110.6(4)	$O_4-B_3-N_5$	104.0(3)
B_2-C_{33}	1.622(7)	$O_1-B_1-O_5$	109.3(4)	$N_5-B_3-C_{52}$	108.5(3)
B_3-O_2	1.427(6)	$O_2-B_2-O_3$	105.2(4)	$B_2-O_2-B_3$	128.6(4)

Compound 5.3

O_1-B_1	1.458(18)	B_2-N_3	1.571(17)	$N_2-B_2-N_3$	102.51(10)
B_1-N_1	1.575(18)	B_2-C_{25}	1.607(2)	$O_2-B_2-C_{25}$	112.52(11)
B_1-N_4	1.570(18)	$O_1-B_1-N_4$	108.06(11)	$N_2-B_2-C_{25}$	111.31(11)
B_1-C_{19}	1.609(2)	$N_4-B_1-C_{19}$	112.11(11)	$N_3-B_2-C_{25}$	114.15(11)
O_2-B_2	1.449(17)	$O_1-B_1-C_{19}$	113.54(11)	$N_1-B_1-C_{19}$	113.16(11)
B_2-N_2	1.570(18)	$O_1-B_1-N_4$	108.06(11)	$O_2-B_2-N_3$	107.23(10)

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Twelve-Membered $B_2Si_4O_6$ BoraSiloxane Macrocycles

Chapter 6

Abstract: A one pot three component reaction of boric acid, diphenylsilane diol and functionalized alcoholic pyrazole in 1:1:1 stochiometry using toluene as a solvent under reflux conditions afforded twelve-membered borasiloxane macrocycle $[(Ph_2Si)_4(O)_6(BR^1PzR)_2]$ in moderate yields. Single crystal X-ray elucidation revealed the formation of a puckered twelve-membered ring system. ESI-MS studies indicate the stability of these macrocyclic systems in solution.

6.1 Introduction:

Inorganic rings systems have attracted considerable attention not only owing to their aesthetic appeal but also due to potential application arising out of their interesting magnetic[1-6] and optical properties.[7] Of particular interest to us were the recent reports on conjugated polymer sensors built on π-extended borasiloxane cages assembled by electrode polymerization of eight-membered borasiloxane rings.[8] By adopting a similar methodology metal containing conducting polymers have also been assembled by starting from N,N-bidentate dioximate ligands and π-extended boronic acids, wherein the N-atoms have been shown to coordinate to metal ions like Fe, Co and Ru.[9] Hence synthesizing novel borasiloxane rings containing a pendent N-atom for further coordination to metal ions would be crucial for assembling frameworks possessing interesting properties. Borosilicate rings and cages reported in literature have been primarily synthesized by condensation reactions between diorganosilane diols/triorganosilanols with phenylboronic acids /boric acids in refluxing toluene as solvent.[10-14] Single crystal X-ray structural elucidation has revealed the formation of six and eight membered borasiloxane rings while a twelve-membered borasiloxane ring has been proposed to be formed by analysing mass spectral data of the reaction mixture.[15] Hence the aim of the present study is to synthesize novel borasiloxane rings containing pendant N-atoms which can be further employed for coordination to metal ions.

6.2 Experimental section:

6.2.1 General information: Diphenylsilanediol, boric acid, solvents, and other common reagents were used as purchased from commercial sources. Pyrazolyl ligands were synthesized using literature procedures.[16, 17] Infrared spectra were recorded on a JASCO-5300FT-IR spectrometer as KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX 400 instrument. Elemental analysis was performed on Flash EA Series 1112 CHNS analyser.

6.2.2 Synthetic methodology: General synthetic method used is as follows. Boric acid, phenolic pyrazole (H_2PhPzR, where R = H **6.1**, Me **6.2**, and H_2NpPhPz **6.3**) and diphenylsilane diol were refluxed in toluene for 12 hours until a clear solution was obtained. When reflux condition was employed, the water formed during the reaction was removed as an azeotropic mixture using a Dean Stark apparatus. The clear solution then formed was cooled to room temperature, filtered and evaporated under reduced pressure to yield a colorless solid. Colorless crystals suitable for single crystal X-ray studies were grown from chloroform/hexane in 4days. Molar ratios and weights of reactants used along with the standard spectroscopic and analytical data are as follows.

Compound 6.1: Boric acid (0.077 g, 1.24 mmol), H_2PhPzH (0.2 g, 1.24 mmol) and $Ph_2Si(OH)_2$ (0.27 g, 1.24 mmol). Yield: 0.25g (34.7%, based on the weight of Boric acid). M.P: 232˚ C. Elemental. anal.calc. for $C_{66}H_{54}B_2Si_4O_8N_4$: C, 68.03; H, 4.67; N, 4.8. Found: C, 68.15; H, 4.78; N, 4.73. I.R (cm^{-1}, KBr pellet): 3136(w), 3067(w), 3045(w), 3007(w), 1618(m), 1581(m), 1550(m), 1462(m), 1429(m), 1315(m), 1060(m), 981(w), 844(w), 738(s), 698(s), 522(s), 497(m). ^1H NMR in $CDCl_3$: δ 14.57 (s, 2H), 7.94 (d, 8H), 7.48-7.40 (m, 13H), 7.10-7.06 (m, 4H), 6.85 (d, 2H), 6.79-6.75 (m, 13H), 6.55 (d, 2H), 6.51-6.46 (m, 10H). ^{13}C NMR in $CDCl_3$: δ 154.52, 144.27, 136.49, 134.81, 134.02, 133.72, 130.73, 129.72, 128.60, 127.57, 126.44, 124.49, 118.27, 117.38, 112.21, 99.01 ppm. ^{11}B NMR in $CDCl_3$: δ -0.104 ppm. ^{29}Si NMR in DMSO: δ -36.04 ppm.

Compound 6.2: Boric acid (0.053 g, 0.86 mmol), $H_2PhPzMe$ (0.15 g, 0.86 mmol) and $Ph_2Si(OH)_2$ (0.186 g, 0.86 mmol) Yield: 0.15 g (29.4%, based on the weight of Boric acid). M.P: 248˚C. Elemental. anal.calc. for $C_{68}H_{58}B_2Si_4O_8N_4$: C, 68.45; H, 4.9; N, 4.69. Found: C, 68.32; H, 4.96; N, 4.75. I.R (cm^{-1}, KBr pellet): 3192(w), 3142(w), 3063(w), 3043(w), 1618(m), 1591(m), 1574(m), 1462(m), 1429(m), 1315(m), 1271(m), 981(s), 852(m), 698(s), 522(s), 499(m). ^1H NMR in $CDCl_3$: δ 14.15 (s, 2H), 7.98 (d, 8H), 7.45 (d, 13H), 7.26 (s, 1H), 7.07 (t, 2H), 6.88 (d, 2H), 6.76-6.74 (m, 12H), 6.45-6.40 (m, 12H), 2.07 (s, 6H). ^{13}C NMR in $CDCl_3$: δ 154.63, 144.61, 142.28, 136.50, 134.97, 134.17, 133.65, 130.39, 129.65, 128.45, 127.47, 126.33, 124.43, 118.88, 117.13, 112.49, 98.24, 10.46 ppm. ^{11}B NMR in $CDCl_3$: δ -0.354 ppm. ^{29}Si NMR in DMSO: δ -36.15 ppm. HRMS (ESI) *m/z* calcd for $C_{68}H_{58}B_2Si_4O_8N_4$: $[M + H]^+$ 1193.36; $[M+Na]^+$ 1215.33 ; $[M+K]^+$ 1231.44; Found: 1193.34; 1215. 32; 1231.29.

Compound 6.3: Boric acid (0.058 g, 0.95 mmol), $H_2NpPhPz$ (0.20 g, 0.95 mmol) and $Ph_2Si(OH)_2$ (0.205 g, 0.95 mmol). Yield: 0.21g (35.0%, based on the weight of Boric acid). M.P: 260˚C. Elemental. anal.calc. for $C_{74}H_{58}B_2Si_4O_8N_4$: C, 70.24; H, 4.62; N, 4.42.

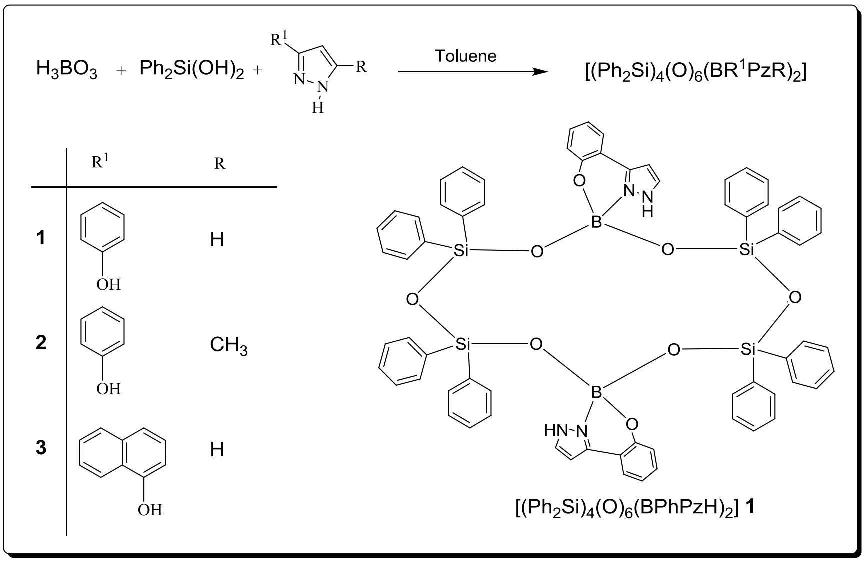
Found: C, 70.32; H, 4.55; N, 4.38. I.R (cm^{-1}, KBr pellet): 3128(w), 3067(w), 2912(w), 1624 (m), 1579(m), 1556(m), 1508(m), 1487(m), 1429(s), 1408(s), 1267(s), 1217(m), 1128(m), 968(m), 941(m), 885(m), 821(m), 748(m), 715(m), 698(s), 572(m), 516(m); HRMS (ESI, *m/z*) calcd for $C_{74}H_{58}B_2Si_4O_8N_4$: $[M + H]^+$ 1265.36; $[M+Na]^+$ 1287.33; Found: 1265.1; 1287.03

6.3 X-ray structure determination

Single Crystal X-ray data collection for **6.1- 6.3** were carried out at 100(2) K on a Bruker Smart Apex CCD area detector system [(λ(MoKα) = 0.71073Å)] with a graphite monochrometer. The data were reduced using SAINTPLUS. The structures were solved using SHELXS-97 and refined using SHELXS-97.[18-19] All non-hydrogen atoms were refined anisotropically.

6.4 Results and Discussion

6.4.1. Synthesis: General synthetic methodology used is as follows; boric acid, phenolic pyrazole (H_2PhPzR, where R = H **6.1**, Me **6.2**, and H_2NpPhPz **6.3**) and diphenylsilanediol were refluxed in toluene for 12 h until a clear solution was obtained (Scheme 1). When reflux conditions were employed, the water formed during the reaction was removed as an azeotropic mixture using a Dean Stark apparatus. The clear solution then formed was cooled to room temperature, filtered and evaporated under reduced pressure to yield a colorless solid. Colourless crystals suitable for X-ray studies were grown from chloroform/hexane in 4 days. Macrocycles **6.1**-**6.3** were characterized by spectroscopic



Scheme 1

and analytical techniques.

Macrocycles **6.1** and **6.2** were soluble in a wide range of organic solvents like dichloromethane, chloroform, toluene and acetonitrile but the napthyl pyrazole containing macrocycle **3** was poorly soluble in common organic solvents. ^{11}B NMR (in $CDCl_3$) gave single resonances at – 0.104 ppm for **6.1** and at – 0.354 ppm for **6.2**. The ^{11}B NMR values are comparable to the literature values for a tetra-coordinate boron atom.[20,21] Similarly, ^{29}Si NMR (in DMSO) gave a single resonance at – 36.04 ppm and – 36.15 ppm for **6.1** and **6.2** respectively. Due to the poor solubility of **6.3**, solution NMR studies could not be carried out as the concentration was not sufficient to measure solution ^{29}Si and ^{11}B NMR. The ESI-MS studies (positive ion mode, ESI) on **6.1**, **6.2** and **6.3** were carried out in a solvent mixture of dichloromethane and methanol. For **1**, *m/z* peak at 851.1 can be assigned to the macrocycle where the two ligand moieties have detached from the boron atoms and has been replaced by two hydrogen's per boron and hence a total of four hydrogen's for the macrocycle. For **6.2** and **6.3** *m/z* peaks at 1193.3 and 1265.1 were obtained which can be assigned to the molecular ion peak [M + H]$^+$ suggesting the stability of the twelve-membered macrocycles in solution. Further for **6.2**, *m/z* peaks at 1215.3 and 1231.2 can be assigned to [M + Na]$^+$ and [M + K]$^+$ ions respectively (Figure 1). For macrocycle **6.3** an *m/z* peak at 1287.0 was seen which can be assigned to [M + Na]$^+$.

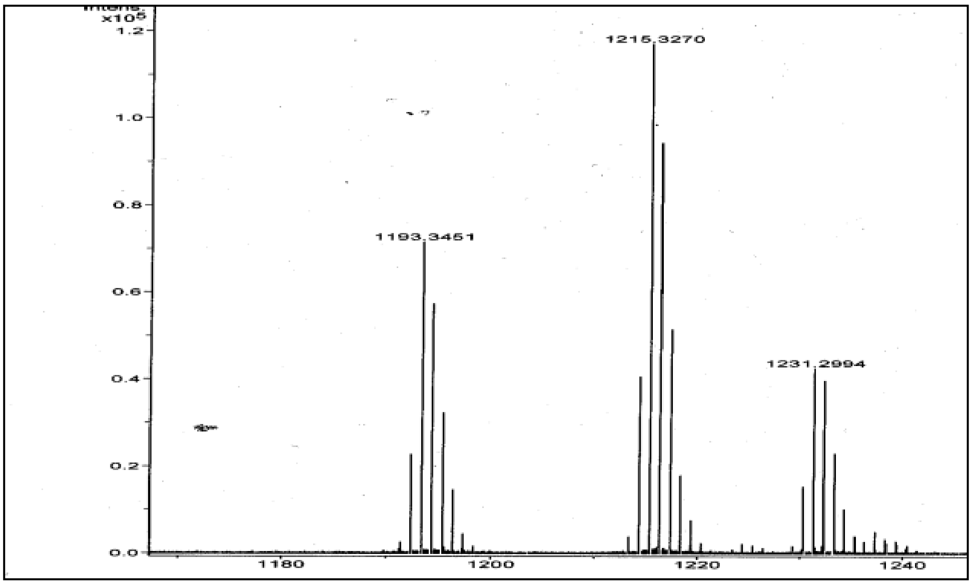


Figure 1: The ESI-MS of **6.2** in MeOH/DCM mixture.

6.5 Crystal structure description:

Macrocycles **6.1-6.3** crystallized in triclinic space group P-1. Since the compounds are isostructural solid state structure of **1** is considered for discussion. Structural elucidation revealed the formation of a twelve-membered macrocyclic borasiloxane frame work (Figure 2). The boron atoms are tetrahedrally coordinated in a O_3N mode of binding. Diphenysilanediol self condensed *insitu* leading to the formation of tetraphenyldisiloxanediol which then coordinates to the two boron atom through each of its residual oxygen atom. The self condensation of silanols leading to the formation of siloxane framework in presence of Lewis acids or bases is well known. The pyrazolyl phenolic ligand chelates to the boron atom satisfying its coordination sphere. The important metric parameters found in **6.1-6.3** are given in the ESI. It is interesting to note that the non coordinated N---N distance between the two phenolic pyrazolyl ligand present on top and bottom of the macrocyclic plane is approximately 3.8 Å, hence potentially they can be used to bind metal ions.

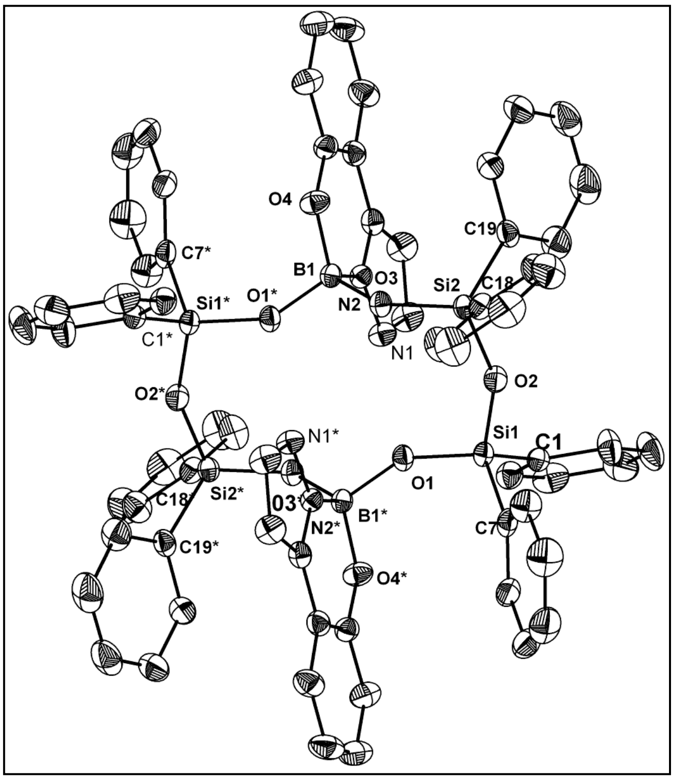


Figure 2: Molecular structure of **6.1** with thermal ellipsoids shown at 30% probability.

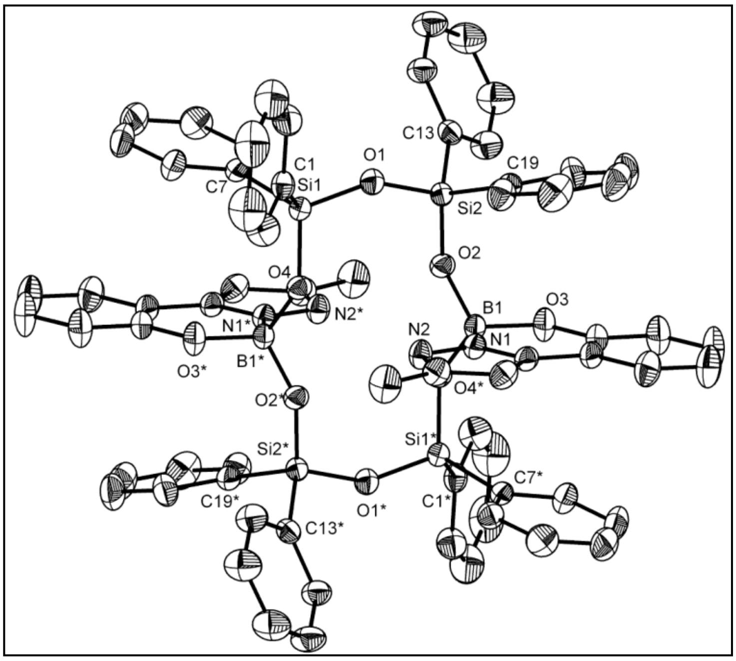


Figure 3: (a) Molecular structure of **6.2** with thermal ellipsoids shown at 30% probability.

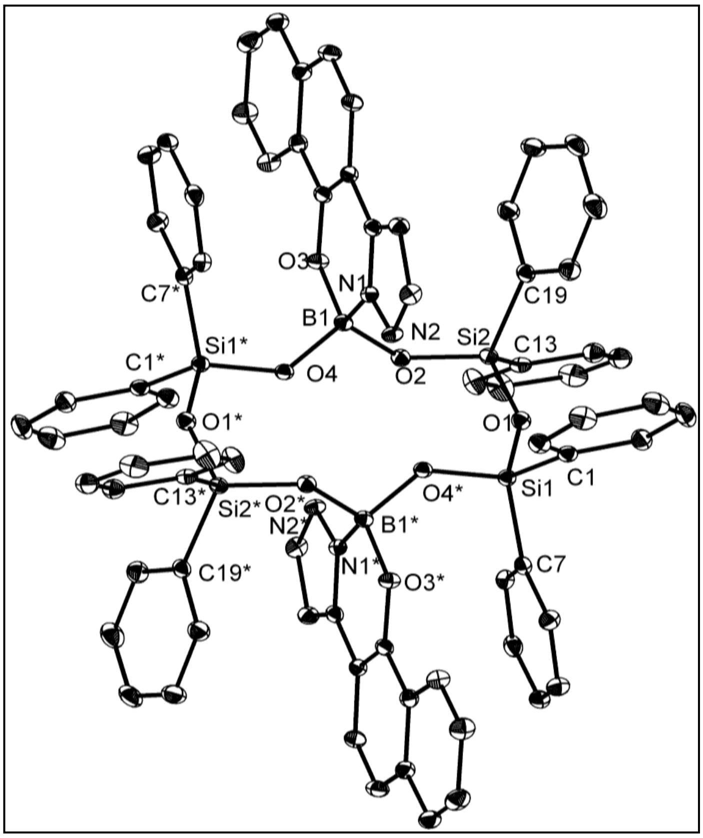


Figure 4: Molecular structure of **6.3** with thermal ellipsoids shown at 30% probability.

Literature reports reveal that the reaction of phenylboronic acid with diphenylsilanediol in 1:1 ratio leads to the formation of an eight-membered $B_2Si_2O_4$ borasiloxane ring while the reaction of phenylboronic acid with tetraphenyldisiloxanediol leads to the formation of a six-membered ring.[22]

Interestingly when tetraphenyldisiloxanediol is reacted with boric acid the product isolated had an intriguing "*cage type*" structure wherein two fused twelve-membered rings were present.[23] But when phenylboronic acid was reacted with 1,3-dichlorotetramethyldisiloxane in presence of a base, six, eight, ten and twelve- membered borasiloxane ring systems have been isolated of which the six and eight-membered rings has been structurally characterized. Though the formation of a twelve-membered ring has been proposed structural evidence was found lacking.[15]

6.6 Conclusion:

A simple one pot three component synthetic method has been utilized to synthesize twelve-membered borasiloxane macrocycles **6.1**-**6.3**. Structural characterization reveals the formation of a puckered macrocyclic ring system. ESI-MS studies show that these macrocycles **6.1**-**6.3** are stable in solution. Metallation studies of these macrocycles are currently underway in our laboratory.

Table 1: Crystal data table for compound 6.1-6.3

	6.1	**6.2**	**6.3**
Formulae	$C_{66}H_{54}B_2N_4O_8Si_4$	$C_{70}H_{60}Cl_6B_2N_4O_8Si_4$	$C_{76}H_{60}B_2Cl_6N_4O_8Si_4$
Fw.g mol^{-1}	1165.11	1431.90	1503.96
Cryst syst	triclinic	Triclinic	Triclinic
Cryst size.mm	0.16 x 0.14 x 0.12	0.24 x 0.18 x 0.12	0.20 x 0.16 x 0.10
Space group	p-1	p-1	P-1
a, Å	11.344(5)	13.6338(18)	12.5384(11)
b, Å	11.928(5)	15.0670(19)	12.8423(12)
c, Å	12.365(5)	18.881(2)	13.2190(12)
α, deg	86.357(7)	75.862(2)	90.222(2)
β, deg	74.113(7)	89.823(2)	117.9000(10)
γ, deg	66.935(6)	69.782(2)	105.453(2)
V, Å^3	1478.8(11)	3515.2(8)	1792.4(3)
Z	1	2	1
Dcacld.Mgm^{-3}	1.308	1.353	1.393
Temp(K)	100	100	100
μ, mm^{-1}	0.161	0.370	0.367
F(000)	608	1480	776
θ range,deg	1.71 to 26.13	1.49 to 26.50	1.66 to 25.00
no. of.refln colled/unique	15138/5764	38156/14395	17366/6292
data/restraints/params	5764 / 0 / 379	14395 / 0 / 895	6292 / 0 / 455
R_{int}	0.0573	0.0390	0.0363
GooF(F^2)	1.038	1.033	1.016
R_1/wR_2 ($I>2\sigma(I)$)	0.0547/0.1367	0.0883/0.2306	0.0506/0.1188
R_1/wR_2 (all data)	0.0692/0.1482	0.1156/0.2533	0.0585/0.1236
largest diff peak/hole,e Å^{-3}	0.407 / -0.286	0.772 / -1.149	0.754 /-0.749

Table 2: Bond length and bond angle parameters for compounds 6.1-6.3

Compound 6.1

B_1-N_2	1.586(3)	Si_1-O_2	1.614(18)	Si_2-O_2-Si_1	150.02(11)
B_1-O_4	1.456(3)	Si_1-O_1	1.615(17)	O_2-Si_1-O_1	107.93(8)
B_1-O_3	1.424(3)	Si_1-C_1	1.855(2)	O_1-Sb_1-N_1	84.40(10)
B_1-O_1*	1.431(3)	Si_1-C_7	1.858(2)	B_1-O_3-Si_2	139.08(14)
Si_2-O_3	1.608(17)	O_3-B_1-O_1*	107.40(18)	B_1*-O_1-Si_1	142.02(15)
Si_2-C_{19}	1.844(2)	N_2-B_1-O_4	105.28(17)	C_{19}-Si_2-C_{18}	111.74(11)
Si_2-C_{18}	1.858(2)	N_2-B_1-O_3	110.28(17)	C_1-Si_1-C_7	111.69(11)
Si_2-O_2	1.620(18)	O_2-Si_2-O_3	110.50(8)		

Compound 6.2

B_1-N_1	1.584(5)	Si_2-O_1	1.625(3)	O_1-Si_1-O_4	109.10(13)
B_1-O_4*	1.443(5)	O_3-B_1-O_4*	111.80(3)	B_1-O_2-Si_2	137.60(2)
B_1-O_3	1.460(4)	N_1-B_1-O_3	105.40(18)	O_3-B_1-O_2	112.60(3)
B_1-O_2	1.424(5)	N_1-B_1-O_4*	109.60(3)	O_2-B_1-O_4*	107.0(3)
Si_2-O_2	1.610(3)	O_2-Si_1	110.25(9)	Si_2-O_1-Si_1	148.49(18)
Si_1-O_1	1.616(3)				

Compound 6.3

B_1-N_1	1.586(3)	Si_1-O_4*	1.630(17)	N_1-B_1-O_2	111.53(19)
B_1-O_4	1.450(3)	Si_2-O_1	1.626(17)	O_2-Si_2-O_1	109.84(9)
B_1-O_3	1.463(3)	Si_1-O_1	1.623(17)	Si_2-O_1-Si_1	147.57(11)
B_1-O_2	1.423(3)	Si_1-C_1	1.860(2)	O_1-Si_1-O_4*	108.76(9)
Si_2-O_2	1.609(17)	Si_1-C_7	1.851(2)	B_1-O_2-Si_2	137.52(15)
Si_2-C_{19}	1.865(2)	O_3-B_1-O_4	110.95(19)	O_4-B_1-O_2	108.08(19)
Si_2-C_{13}	1.859(2)	N_1-B_1-O_4	108.84(18)	C_{19}-Si_2-C_{13}	108.37(11)

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Future Scope of the Present Thesis

Part A of the thesis demonstrated the isolation of ferrocene anchored lanthanide oxo-hydroxo clusters by employing ferrocenyl beta diketone ligands. Single molecule magnet behavior exhibited by the compound **2.1** of chapter 2 reconfirms that lanthanide hydroxo clusters are suitable candidates for the preparation of new single molecule magnets. Further improvements have to be made to improve the effective energy barriers and blocking temperatures of the SMMs.The compound **2.1** contain sixteen redox active ferrocene units anchored on lanthanide oxo-hydroxo cluster which proves that these inorganic cores can be used for making multi ferrocene assemblies alternative to the organic, dendrimeric, and aromatic cores. It is clear that there is still a larger scope to develop the present work by synthesizing ferrocene anchored Lanthanide oxo core molecules which displaying interesting magnetic properties can bring to anchor a second and third functionality and hence act as scaffolds for assembling polyfunctional molecular architectures.

In the chapter 3 and 4 Sb-C bond cleavages reactions of arylantimony(V) halides with phenolicpyrazoles and organo silanols have been discussed and these investigations lead to the isolation of novel diorganoantimonyl(V) phenolic pyrazolates (**3.1**-**3.5**) and organoantimony(V)-oxo siloxide clusters with Sb-O-Si frameworks (**4.1**-**4.4**). Still this chemistry can be developed, by introducing some polymerizable groups (vinyl, allyl) on to the organoantimony precursors or organosilanols, and thus making organoantimony clusters with polymerizable groups which can be used as precursors for synthesizing new inorganic-organic hybrid framework materials.

In the chapters 5 the reactions of organoboronic acids with phenolic pyrazoles have been discussed, which leads to the isolation of novel organoboron compounds. For instance the compound **5.3** is a B2N4 heterocycle, pyrazabole which is relatively stable compared to other boron-nitrogen heterocycles, so a variety of organic transformations can be carried out on the pyrazabole ring resulting in a large number of derivatives bearing various functional groups and hence can show various potential applications.

In the chapter 6 a simple one pot three component synthetic method has been utilized to synthesize twelve-membered borasiloxane macrocycles. The compounds **6.1-6.3** can potentially act as novel macrocyclic ligand systems to bind metal ions as they have a non-coordinated N-atom above and below the plane of the macrocycle. Hence these macrocyclic systems can open up new avenues in coordination chemistry and probably can act as sensors to variety of metal ions.

List of Publications

1. Functionalized β–diketone Assisted Self - Assembly of a Hexa nuclear Yttrium Hydroxo Cluster
   Ananda Kumar Jami, **Pilli.V.V.N Kishore** and V. Baskar, ***Polyhedron*. 2009**, 28, 2284.

2. Investigations of on the Reactivity of Arylboronic acid with Phenolic pyrazoles
   Pilli.V.V.N Kishore, Ananda Kumar Jami and V. Baskar, ***Inorg.Chim.Acta.* 2011**, 372, 321.

3. Twelve-membered $B_2Si_4O_6$ Borasiloxane macrocycles.
   Pilli.V.V.N Kishore and V. Baskar. ***J.Organomet.Chem.* 2013**, 743, 83.

4. Redox shield enfolding magnetic core.
   Pilli.V.V.N Kishore, V. Baskar and E.C.Sañudo. *(Manuscript under revision)*

5. Hexa- and Trinuclear organoantimony oxo clusters Stabilized by Organosilanols.
   Pilli.V.V.N Kishore and V. Baskar. *(Manuscript under revision)*

6. Diorganoantimonyl Phenolic Pyrazolates
   Pilli.V.V.N Kishore and V. Baskar. *(Manuscript under revision)*

Poster and Oral Presentations

1. Phenolic pyrazolyl ligands and silanols for assembling organoantimony oxo-hydroxo clusters. **Frontiers in Chemical Sciences (FICS – 2010),** Department of Chemistry, Indian Institute of Technology Guwahati on Dec 3-4, **2010**.

2. Phenolic pyrazolyl ligands and silanols for making pyrazabole and Borasiloxane rings. **Asian Conference on Coordination Chemistry (ACCC-3)**, India Habitat Centre, New Delhi on October 17-20, **2011**.

3. Phenolic pyrazolyl ligands and silanols for making pyrazabole and Borasiloxane rings. **Modern Trends in Inorganic Chemistry (MTIC- XIV)**, University of Hyderabad, on Feb 13-14, **2012**.

4. Presented oral and poster presentation on "Lanthanide oxo-hydroxo clusters anchoring ferrocenes" at In house symposium, **"Chemfest-2013"** University of Hyderabad, Hyderabad, March **2013**.