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$_2$S framework [Ag$_{48}$(µ$_4$-S)$_6$(µ$_{2/3}$-SCH$_2$Fc)$_{36}$] 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 bifunctional / multiferrocene architectures are presented. Synthesis, structure, magnetism (for 2.1, 2.3) and cyclic voltammetry studies of [Dy$_9$(µ$_4$-O)$_2$(µ$_3$-OH)$_8$(µ-Fca)$_8$(Fca)$_8$][HN(C$_2$H$_5$)$_3$] 2.1 [Lu$_4$(µ$_3$-OH)$_4$(µ-Fctp)(Fctp)$_7$] 2.2 [Ln$_4$(µ-OH)$_2$(µ-OCH$_3$)$_4$(CH$_3$OH)$_2$(Fctp)$_6$] Ln = Yb (2.3), Lu (2.4), and [Ln$_4$(µ-OH)$_2$(µ-OCH$_3$)$_4$(CH$_3$OH)$_2$(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 procedures10

2.2.2 Synthetic methodology:

Hydrated LnCl₃ [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 triethylamine 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:** DyCl₃.6H₂O 0.174g (0.46mmol), HFca 0.25g (0.92mmol), Et₃N 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 C₂₃₀H₂₂₆O₄₃NFe₁₆Dy₉: C, 45.67; H, 3.76; N, 0.23. Found: C, 45.81; H, 3.71; N, 0.28.

**Compound 2.2:** LuCl₃.6H₂O 0.143g (0.36mmol), HFctp 0.25g (0.73mmol), Et₃N 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 C₁₃₆H₁₀₈Fe₈Lu₄O₃₈S₄: C, 47.13; H, 3.14; Found: C, 47.26; H, 3.12.

**Compound 2.3:** YbCl₃.6H₂O 0.119g (0.30mmol), HFctfa 0.199g (0.61mmol), Et₃N 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$_6$O$_{22}$Yb$_4$: C, 37.88; H, 3.10; Found: C, 37.72; H, 3.06.

**Compound 2.4:** LuCl$_3$.6H$_2$O 0.120g (0.30mmol), HFctfa 0.199g (0.61mmol), Et$_3$N 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$_6$O$_{22}$Lu$_4$: C, 37.78; H, 3.10; Found: C, 37.61; H, 3.16. **Compound 2.5:** YbCl$_3$.6H$_2$O 0.091g (0.23mmol), HFcpfa 0.175g (0.46mmol), Et$_3$N 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$_6$O$_{22}$Yb$_4$: C, 36.58; H, 2.81; C, 36.65; H, 2.91. **Compound 2.6:** LuCl$_3$.6H$_2$O 0.091g (0.23mmol), HFcpfa 0.174g (0.46mmol), Et$_3$N 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$_6$O$_{22}$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 Oxford 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$_2$O [$\text{Ln} = \text{Dy (2.1), Lu (2.2), Yb (2.3, 2.5), Lu (2.4, 2.6)}$] and two equivalents of ferrocenyl $\beta$-diketones (HFca, HFctp, HFcfa, 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 $[\text{HEt}_3\text{N}]\text{Cl}$. 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.

![Scheme 1](image)

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 Dy₉ cluster (2.1):

The solid state structure of 2.1 (figure 1) is similar to a series of Ln₉ clusters reported previously. 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 nm³. 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](image_url)

**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 Lu4 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 Lu₄O₄ 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) 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 nm³. Selected bond lengths bond angles are given in (Table 3).

2.5.3 Butterfly type tetranuclear Lu₄ clusters (2.3 - 2.6):

On further modulation of the organic groups present in the β-diketones to CF₃ / CF₂CF₃ 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 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 µ₃- hydroxide groups and four µ₂-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 nm³.

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 $\chi T$ 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 ($^6$H$_{15/2}$, S=$5/2$, L=5, J=15/2 and gJ= 4/3) (figure 5). As temperature decreases, the $\chi T$ 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 $\mu$B, 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.

![Graphs](image)

**Figure 5:** (a) $\chi T$ 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.
Chapter 2

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 $\chi T$ 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 $g_J= 8/7$, expected $\chi T$ for Yb ion is 2.5 cm$^3$ K mol$^{-1}$) (Figure 9). As temperature decreases, the $\chi T$ product smoothly decreases due to the depopulation of Stark sublevels of the Yb(III) ions. The $\chi T$ 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: $\chi T$ 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.

![Absorption spectra](image)

**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. The trends in the absorption spectra of
Redox shield

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⁻¹cm⁻¹, 2.187 x 10^3 Lmol⁻¹cm⁻¹, 3.71 x 10^3 Lmol⁻¹cm⁻¹, 7.56 x 10^3 Lmol⁻¹cm⁻¹, 8.593 x 10^3 Lmol⁻¹cm⁻¹ (λ =463nm), 10.750 x 10^3 Lmol⁻¹cm⁻¹(λ =465nm), 13.68 x 10^3 Lmol⁻¹cm⁻¹(λ =503nm), 11.81 x 10^3 Lmol⁻¹cm⁻¹ (λ =500nm), 11.84 x 10^3 Lmol⁻¹cm⁻¹ (λ =493nm), 11.81 x 10^3 Lmol⁻¹cm⁻¹(λ =495nm) respectively.

2.8 Cyclic Voltammetry 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.

![Cyclic Voltammetry Studies](image)

**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 N₂ 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](image)

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

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

#### Compound 2.1

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#### Compound 2.2

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#### Compound 2.3

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63
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2.11 References:


Chapter 2


(9) Baskar V.; and Roesky, P. W. *Dalton Trans.* **2006**, *676*.


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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 cisplatin. 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\(_3\)SbX\(_2\) (X=Cl, OAc) gave crosscoupling products with silyloxy alkenes\(^18\) and organotin compounds\(^19\) under palladium catalysis. Ar\(_3\)Sb(OAc)\(_2\) was
used in Pd(0)/Cu(I)-catalyzed cross-coupling reactions with alkynylsilanes.$^{20}$ Gushchin et al reported that Ph$_3$Sb(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).

![Scheme 1](image)

Compounds of monoorganoantimony(v) chlorides with oxo donor ligands are quite stable in ambient temperatures. On the basis of IR and $^1$H 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](image)

Diorganoantimony(V) halides have been prepared by the reactions of antimony(III) chlorides with diazonium salts or by halogenations of diorganoantimony(III) halides R$_2$SbX (scheme 2).$^{24}$
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 Ph₂SbCl₃. Some groups proposed the compound to be a trigonal pyramidal geometry and some other groups reported the compound as a monohydrate Ph₂SbCl₃.H₂O with octahedral geometry.²⁶a,b In order to resolve the above uncertainty Bordner et al. examined the crystal structure analysis of anhydrous Ph₂SbCl₃ and found that it to exist as a dimer²⁶d with chlorine bridges (figure 1). Later Bowen and coworkers have also supported an octahedral geometry with small deviation (8°) for anhydrous Ph₂SbCl₃ and also for other trichloro compounds like Me₂SbCl₃, (p-FC₆H₄)PhSbCl₃.

Bone and Sowerby have prepared Ph₂SbBr₃, Ph₂SbBr₂Cl and Ph₂SbBrCl₂.²⁷ It was determined that in contradiction to octahedral dimeric Ph₂SbCl₃ all the bromine containing compounds are monomeric with distorted trigonal bipyramidal geometry having one Br and

\[
\text{SbCl}_3 + 2\text{Ph}_3\text{Sb} \quad \rightarrow \quad 3\text{Ph}_2\text{SbCl} \\
\text{Ph}_2\text{SbCl} + \text{Cl}_2 \quad \rightarrow \quad \text{Ph}_2\text{SbCl}_3
\]
two phenyl groups occupying equatorial positions. This was attributed due to the increased electronegativity of atoms in the axial positions in going from Ph$_2$SbBr$_3$ to Ph$_2$SbBrCl$_2$.

Diorganoantimony(V) halides forms monomeric covalent adducts R$_2$SbX$_3$.L with various oxygen donor ligands (e.g DMSO, HMPA, PyO). On the basis of $^1$H 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$_2$SbX$_3$.L](image)

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).

![Scheme 3](image)

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).

![Scheme 4](image)

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. In the aryl derivatives, Jaffe and Rao et al has
considered the π–dπ resonance between the benzene ring and vacant d-orbital’s of the antimony atoms.\textsuperscript{31}

For triorganoantimony(V) halides a trigonal bipyramidal geometry has been suggested on the basis of I.R and Raman analysis (chart 3).\textsuperscript{29a,b} NMR spectroscopy has also been made to elucidate the nature of bonding in trialkyl and triarylmantimony(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.\textsuperscript{32a} NMR spectral data of Ph$_3$SbF$_2$ and Ph$_3$SbFCl are also in consistent with the trigonal pyramidal geometry,\textsuperscript{32b} there exists some halide exchange reactions have also been investigated by moreland and group.\textsuperscript{33}

\textbf{Chart 3:} Trigonal pyramidal geometry of Me$_3$SbX$_2$

(i) \textbf{Reactions of organoantimony(V) halides}

(i.a) \textbf{with glycols and catechols:}

Triorganoantimony(V) glycolates R$_3$Sb(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.\textsuperscript{34}

\[
\text{Scheme 5}
\]

Interestingly Holmes et al synthesized monocyclic stiborane Ph$_3$Sb(O$_2$C$_6$H$_3$-4-NO$_2$) by the reaction of Ph$_3$SbCl$_2$ with 4-nitrocatechol in the presence of Et$_3$N, X-ray structure analysis reveals the structure is close to square-pyramidal and not in trigonal bipyramidal configuration (scheme 6).\textsuperscript{35} It was suggested that in the solid state it exists as weakly
connected dimers which accounts for its structural displacement towards the square pyramid geometry (figure 2).

![Scheme 6](image)

**Figure 2**: ORTEP of Ph₃Sb(O₂C₆H₅-4-NO₂) and Dimer

(i.b) with β-diketones:

Monoorganoantimony (acetylaconato) trichlorides have been prepared by the reactions of either arylstibonic acid in HCl or of monoorganoantimony(V) chloride with acetylacetone at low temperatures. All the monoorganoantimony(acetylaconato) 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 ¹H NMR spectra, Okawara et al have suggested an asymmetric structure for PhSb(acac)Cl₃ and a symmetric structure for MeSb(acac)Cl₃ (figure 3).

For MeSb(acac)Cl₃ the magnitude of the separation between methyl resonance increases in aromatic solvents indicating an enhancement in the non-equivalence 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)Cl₃ support the asymmetric structure with distorted octahedral geometry.
Diorganoantimony(V) \( \beta \)-diketones, \( R_2\text{Sb}(R^1\text{COCHCOR}^{11})X_2 \), (scheme 7) are monomeric and non conducting in nature.\(^{36b}\) There are three possible geometric forms have been considered for the compounds of type \( R_2\text{Sb}(\text{acac})X_2 \).

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

The conclusions drawn from \( ^1\text{H} \) NMR spectral studies have been confirmed by X-ray diffraction studies of \( \text{Me}_2\text{Sb}(\text{acac})\text{Cl}_2 \) and \( \text{Ph}_2\text{Sb}(\text{acac})\text{Cl}_2 \).\(^{37b,38}\) 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
Ph₂Sb(acac)Cl₂ is also found to have distorted octahedral geometry in which the two phenyl rings occupy the trans positions (figure 4).

Figure 4: ORTEP of ph₂Sb(acac)Cl₂

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

\[
R_3SbX_2 + Na(R^1COCHCOR^{11}) \rightarrow R_3SbX(R^1COCHCOR^{11}) + NaX
\]

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 Ph₃Sb (R¹COCHCOR¹¹) (Chart 5).³⁶c,³⁹

Chart 5: Cis and trans forms of R₃Sb(R¹COCHCOR¹¹).

(i.e.) with Schiff bases:
Diorganoantimony(V) complexes with dianionic tridentate Schiff base ligands (Trid) have been synthesized by the exchange reactions of diorganoantimony(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 $\text{R}_2\text{Sb(V)}$ than that of $\text{Me}_3\text{Sb(V)}$ or $\text{Me}_2\text{Sn(IV)}$.\textsuperscript{40}

![Scheme 9](image)

On the basis of the I.R and $^1$H NMR studies, an octahedral coordination environment for the antimony atom with meridional arrangement of the ONO ligand atoms and a linear C-Sb-C skeleton has been proposed. Further Mossbauer spectra for some complexes $\text{Me}_2\text{Sb(sah)Cl}$, $\text{Me}_2\text{Sb(Bah)Cl}$, $\text{Ph}_2\text{Sb(Bah)Cl}$ and $\text{Ph}_2\text{Sb(Aah)Cl}$ indicate octahedral geometry with meridional arrangement (Chart 6).\textsuperscript{41}

![Chart 6: Octahedral arrangement of $\text{R}_2\text{SbCl(Trid)}$](image)

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 triorgnanoantimony dimethoxides with free ligand in benzene solution (scheme 10).\textsuperscript{42}

![Scheme 10](image)

Both the U.V and I.R data suggests hexacoordinate molecular structures for the complexes $\text{R}_3\text{SbL}$ in which the $\text{L}^2$ ligand coordinates to the $\text{R}_3\text{Sb(V)}$ as a planar tridentate ligand. An X ray structure determination has revealed that in the crystalline state the antimony atom in
Me$_3$Sb(Sah) possesses a distorted octahedral geometry with meridionally disposed tridentate ligand and a T-shaped R$_3$Sb(V) moiety (figure 5).$^{41,42}$

![Chart 7: Various Schiff base ligands](image)

**Figure 5:** Crystal structure of Me$_3$Sb(Sah) possesses a distorted octahedral geometry.

(i.d) with oximes:

Trioraganontimony (V) oximates [Ph$_3$Sb(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$_3$SbCl$_2$ + Ar(R)C=NOH $\xrightarrow{\text{NaOMe}}$ [Ph$_3$Sb{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 triorganogantimony(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$_5$H$_5$FeC$_5$H$_4$C(CH$_3$)=NO)$_2$SbPh$_3$] and [Ph$_3$Sb{ON=C(Me)C$_5$H$_4$N-2}]$_2$

( i.e) with phosphinates:

Reactions of triorganogantimony halides with sodium salt of the appropriate diorganophosphinic acids afford bis(diorganophosphinato)triorganogantimony(V) complexes R$_3$Sb(O$_2$PR$_2$)$^\text{1}$ (scheme 12).

\[
\text{R}_3\text{SbCl}_2 + 2 \text{NaO}_2\text{PR}_2^\text{1} \rightarrow \text{R}_3\text{Sb(O}_2\text{PR}_2^\text{1})_2 + 2 \text{NaCl}
\]

R = Me, Ph  
R$^\text{1}$ = 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$_3$Sb(O$_2$PR$_2$)$_2$ has lead to the partially hydrolyzed product Me$_3$Sb(OH)[O(O)PPh$_2$]. 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](image)

**Figure 7:** ortep of Me$_3$Sb(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$_2$Cl[O$_2$P(C$_6$H$_{11}$)$_2$]}$_2$O (scheme 14).$^{13a}$

![Scheme 14](image)

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

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Kumar 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 [Ph₂Sb(O₂PR₂)O]₂. Interestingly when the dimer was treated with acetic acid / water affords the tetra nuclear cage containing cluster of formula Ph₈Sb₄O₈(OH)₂(O₂P(C₆H₁₁)₂)₂ are reported (scheme 15).⁴⁵

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 Sb₂O₂ rings. In tetranuclear cluster two Sb₂O₂ rings are connected by oxo bridges on two sides to give an Sb₄O₆ cage (Chart 10).
Chahdrasekhar et al reported the first example of a nonanuclear organostiboxane cage by reacting Ph₃SbCl₂ with 2 equivalence of cyc-phosphinic acid (cycPO₂) 1,1,-2,3,3-pentamethyltrimethylene phosphinate) in the presence of Et₃N which affords a dimer [(Ph₃Sb)₂(μ-O)(μ-cycPO₂)]₂ (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 [(Ph₂Sb)₂(PhSb)₇(μ-O)₁₁(μ₃-O)₃(μ-OH)ₒ(μ-cycPO₂)₂(cycPO₂)₂(H₂O)₂] 2CH₃CN H₂O which containing a Sb₉O₁₆ core (Chart 11).
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 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).
Further synthesis of highly symmetrical 24-membered macrocyclic organoantimony(V) complexes [Ph$_3$Sb$L^a$]$_2$ and [Ph$_3$Sb$L^b$]$_2$ (H$_2$L$^a$ = 5-[(2-carboxyphenyl)methylene]amino]-4-chloro benzoic acid, and (H$_2$L$^b$ = 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 triarylanthimonydichlorides 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$_2$CC(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) Hypervalency 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 triphenylgermanylpropiolic acids (scheme 20).
P. Sharma et al. synthesized tris[(R)-2-benzyliden-2-yl-amino]butan-1-ol]stibine by treating Tris(o-formylphenyl)stibine with (R)-2-aminobutan-1-ol. X-ray structure analysis of this antimonated Schiff base shows hypervalent interactions between antimony and SP² nitrogen atoms. Further, it also shows interestingly intramolecular Sb-O interactions giving eight coordination to antimony (Scheme 21).
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 organosilanol will be dealt with in detail.

(iii) References:


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