

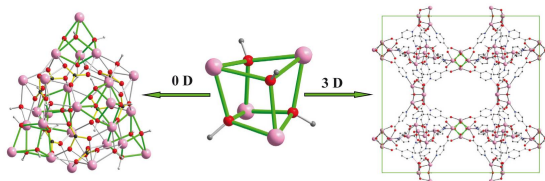


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Employing Crystal Engineering Principles to Fabricate Zero to Three-Dimensional 4f-based Metal Aggregates using O-Donor Ligands

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Chapter 1: Introduction

Rare earth elements, owing to their unique properties such as hard Lewis acid character, sharp, wide-range (from near IR to UV) long-lived luminescence, and high magnetic moment with long electron-spin relaxation time, etc. coupled with a variety of potential applications of their complexes, have established reasonable grounds for the development of rare earth coordination chemistry. The large ionic radii of rare earth elements allow for many interactions, typically between 7 to 10 coordinate, with a decrease often observed across the period due to the lanthanide contraction.^[1-4] The large coordination spheres typically lead towards oligomeric or polymeric complexes, or those with a high degree of solvation. After the observation of slow magnetic relaxation in mononuclear Ln-phthalocyanine complexes by Ishikawa et al in 2003,^[5a] Ln ions have acquired special attention in the field of molecule based magnets leading to an outburst of research in this area. Further developments led to Ln-polyoxometalate single molecule magnets,^[6a] liquid crystalline single molecule magnets^[6b] and single ion magnets based on mononuclear Ln ions.^[6c] However, studies on the structural and magnetic properties of polynuclear Ln complexes, with an object to understand magneto-structural relationships, are of continuing interest for synthetic chemists aiming to develop new molecular materials with improved magnetic properties.^[7]

Due to the highly oxophilic nature of Ln ions, carboxylate ligands are one of the most frequently employed class of ligands in *4f* coordination chemistry. With few exceptions,^[8] interaction of simple monocarboxylate ligands with *4f* ions leads almost exclusively to dimeric or one dimensional (1D) polymeric species^[9-11] whereas polycarboxylate ligands generally result in more complicated two dimensional (2D) and three dimensional (3D) network structures.^[12] The key feature of carboxylate ligands is their ability to adopt a variety of possible coordination modes. They can undergo self assembly reactions as well as simultaneously bridge many metals ions to produce zero to three dimensional (3D) metal aggregates. Therefore, research studies on polynuclear lanthanide-carboxylate complexes may provide information concerning exchange and magnetic interaction mechanisms.

Another important class of ligands is alkoxy ligands, which, owing to their good bridging as well as chelating abilities, have been extensively employed in metal coordination



chemistry. In addition, alkoxide bridges often result in ferromagnetic coupling between the bridging metal centers, thus leading to high-spin molecules. Adequate examples are available in the literature where alkoxy ligands have been successfully utilized in the synthesis of high nuclearity homometallic $3d$ and heterometallic $3d/4f$ clusters.^[13] All such efforts for the synthesis of polynuclear coordination complexes have given birth to a closely allied subject of crystal engineering which helps in pre-designing molecular architectures with desired properties. In this context much work has been done using $3d$ metals while the analogous chemistry based upon pure lanthanides is still far less explored and hence there is scarcity of information documented in this particular area, which is a part of the motivation behind this research work.

1.1 Crystal engineering: A vital tool in modern coordination chemistry

Crystal engineering (CE) is an emerging area of modern science encompassing various domains of chemistry, physics, biology, materials science, engineering, and pharmaceuticals.^[14] It seeks to understand the aptitude of molecules to pack in certain particular fashions and to use this knowledge to deliberately engineer the arrangement of molecules, hence leading to new materials with controlled structures and properties.^[15] Crystal engineering with metal and organic building blocks (generally called “*tectons*”) deals primarily with strong coordination bonds (the main “*synthons*”) in addition to all other weak interactions (the weak “*synthons*”) and is called inorganic crystal engineering (ICE).^[16] The field involves engineering discrete species [e.g. metal-organic polygons/polyhedra (MOPs) or metal-organic containers/cages (MOCs)] to polymeric crystalline materials [e.g., coordination polymers (CPs) or metal-organic frameworks (MOFs)].^[17]

A coordination polymer is an infinite array of metal ions, serving as directional nodes, and organic linkers providing bridging between these nodes in the form of coordination bonds culminating in a network structure.^[18] Among these polymeric materials, 3D coordination polymers, generally called MOFs, have gained special attention in recent years mainly because of their applications in luminescent materials,^[19] magnetism and data storage devices^[20,21] and as separation materials for various gases and guest molecules.^[22] MOFs, are fundamentally interesting because of their regular structure and the positioning of components in three dimensional space. It is these key features that are



responsible for determining the material properties of MOFs and in turn, dictate their applications in so many diversified fields of modern science. Although the range of potential MOF materials is vast, the subject of controlling framework structure in these materials is still very much in its infancy and notably in the area of understanding chirality in such materials,^[23] prompting the scientific community for more exploration in this diversified field.

1.2 Introduction to magnetochemistry

Magnetochemistry is a branch of physical chemistry that examines the interrelationship between the chemical structure and magnetic properties of a material. Magnetic studies can help deduce information about the electronic structure and magnetic exchange interactions in metal complexes.

1.2.1 Magnetic susceptibility

The magnetic moment of a free atom arises from three principal origins: the electronic spins, the electronic orbital angular momentum and the change in the orbital moment induced by an applied magnetic field. The first two factors lead to paramagnetic contributions while the last one gives rise to a diamagnetic contribution.

Magnetic susceptibility is the degree to which a material can be magnetized in an external magnetic field and the magnetization, M , is defined as the magnetic moment per unit volume. The magnetic susceptibility per unit volume then comes out to be:

$$\chi = M/H \text{ (cgs)} \quad \text{or} \quad \chi = \mu_0 M/H \text{ (SI)} \quad \text{Eq.1}$$

where H is the macroscopic magnetic field intensity in Oersted, Gauss or Tesla. Susceptibility is often defined as per mole or per unit mass of the substance, hence the molar susceptibility is designated as χ_M , and the magnetic moment per gram is sometimes written as σ .^[24-26]

1.2.2 Types of magnetic states

The phenomenon of magnetism originates from the orbital and spin motion of the electrons and their interaction with one another. The best way to differentiate among different magnetic states is to observe the response of the susceptibility in the presence of an applied magnetic field. In some materials there is no collective interaction of atomic magnetic moments, whereas in other materials there is a very strong interaction between atomic moments.

Diamagnetism

Diamagnetism is a fundamental property of matter and usually arises from the interaction of magnetic field with the motion of the electrons in their orbitals. A diamagnetic compound has all of its electron spins paired giving a net spin of zero and negative magnetization. Diamagnetic compounds are weakly repelled by a magnet.

Paramagnetism

A paramagnetic substance has one or more unpaired electrons and possesses a net magnetic moment. These compounds are attracted to the magnetic field due to partial alignment of the atomic magnetic moments in the direction of the field, resulting in a net positive magnetization and positive susceptibility.

Ferromagnetism

Substances having magnetic interaction between the neighboring paramagnetic centers, commonly known as “ferromagnetic coupling”, lead to an increase in the magnetic moment and are referred to as ferromagnets. In this case, the individual moments are perfectly aligned parallel to each other. Ferromagnetic compounds are strongly attracted to external magnetic fields.

Antiferromagnetism

A substance having unpaired electrons in antiparallel alignment with an equal number of spins in each direction is referred to as antiferromagnetic. Such substances are repelled by an external magnetic field.

Ferrimagnetism

A ferrimagnetic substance has unpaired electron spins which tend to align antiparallel to each other, as in case of antiferromagnets, but there is incomplete cancellation of the spins, leading to spontaneous magnetization as is observed in ferromagnetic compounds. A ferrimagnetic compound is attracted to a magnet.

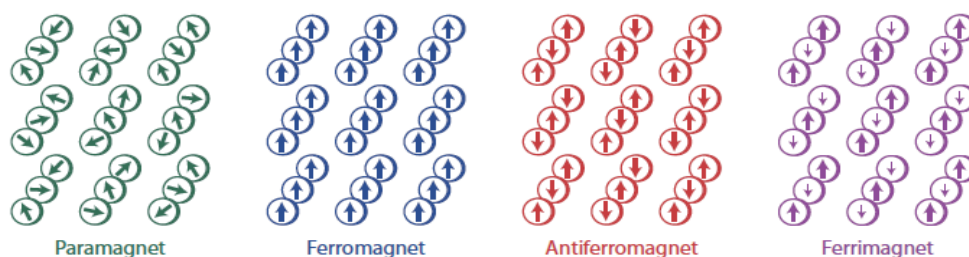


Fig. 1.1 The different alignments of magnetic moments.

1.2.3 Determination of magnetic behavior : Curie and Curie-Weiss laws.

Pierre Curie showed that for most paramagnetic substances with isolated magnetic sites, the magnetization is directly proportional to the applied magnetic field and is inversely proportional to the temperature. This is known as Curie law which can be expressed as:

$$M = C \cdot H / T \quad \text{Eq. 3}$$

where M is the resulting magnetization, H is the applied field and C is the Curie constant. Since the magnetic susceptibility is $\chi = M/H$, in this case:

$$\chi = C/T \quad \text{Eq. 4}$$

The Curie law is obeyed in materials when there is no exchange interaction among neighboring spin centers. However, in case of spontaneous interactions between adjacent spins, a better fit to the high-temperature, paramagnetic behavior is often provided by the Curie-Weiss law:

$$\chi = C/T - \theta \quad \text{Eq. 5}$$

where θ is the Weiss constant. The temperature dependence of the susceptibility can be expressed graphically in three ways as shown in Fig. 1.2 below. From these plots the nature of magnetic interactions in a particular compound can be easily deduced.

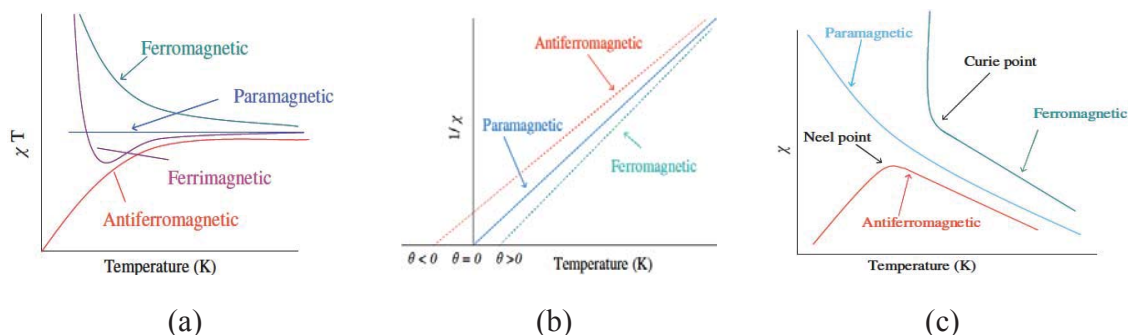


Fig.1.2 (a) The plot of χT (b) plot of $1/\chi$ and (c) plot of χ as a function of T for paramagnetic, ferromagnetic, antiferromagnetic and ferrimagnetic materials.

Depending on the ferro- or antiferromagnetism, θ is either positive or negative respectively, which is accompanied by increase or decrease in the χT product at low temperatures (Fig. 1.2 (a)). The value of θ can be obtained by plotting $1/\chi$ vs T (Fig. 1.2 (b)). A *ferromagnet* has a characteristic temperature called the *Curie temperature* (T_C) above which it behaves like a paramagnet that obeys the Curie-Weiss law,^[27] but below this temperature, its magnetic susceptibility increases rapidly. An *antiferromagnet* has a characteristic *Néel temperature* (T_N) above which it behaves like a paramagnet, but below



this temperature, its magnetic susceptibility decreases with decreasing temperature (Fig. 1.2 (c)).

1.2.4 Molecule-based magnets (MBMs).

Molecule-based magnets are a broad, emerging class of magnetic materials that expand the materials properties typically associated with magnets to include low density, transparency, electrical insulation, and low-temperature fabrication, as well as combine magnetic ordering with other properties such as photo responsiveness. They are constructed of paramagnetic precursors which are molecular in nature. These precursor units are frequently embedded with transition or Ln metal ions having unpaired electrons, which are the source of magnetic moment, and organic ligands to mediate magnetic interactions between these spin centers.

MBMs exhibit a wide variety of bonding and structural motifs. These include isolated molecules (zero-dimensional, 0D), and those with extended bonding within chains (1D), within layers (2D), and within 3D network structures. The two main types of MBMs are: single molecule magnets (SMMs) and single chain magnets (SCMs).

1.2.4.1 Single molecule magnets (SMMs)

SMMs are discrete molecular clusters which act as nanomagnets below a certain blocking temperature (T_B). SMM behavior was first observed in Mn_{12} -Ac which showed a $S=10$ ground state and slow relaxation of the magnetization.^[28] Thus, the field of single molecule magnets was born and Mn_{12} -acetate became a classical SMM material. For a compound to act as a SMM, it should have negative uni-axial magnetic anisotropy (D) and non zero spin ground state (S). The uni-axial anisotropy removes the degeneracy of the ground spin state splitting into $M_S = -S$ to $+S$. These two parameters combine to give rise to a significant energy barrier towards the reversal of spin reorientation with the result that the relaxation of magnetization becomes slower. The energy barrier is given by $\Delta E = |D| S^2$ or $|D| (S^2 - 1/4)$ for integral or half integral spin respectively. A positive D value would result in $M_S = 0$ level being lowest in energy, such that there is no energy cost for losing direction of the spin (i.e. in going from $M_S = +S$ to $M_S = 0$). This means that for a molecule to behave as SMM, it should have a negative D value.

After the initial discovery of SMM behavior in Mn_{12} -Ac, high-spin transition metal clusters acquired enormous popularity in this area. Later on in 2003, with the discovery



of unprecedented relaxation behavior in Ln-phthalocyanine complexes,^[5a] Ln ions gained gradual acceptance in the field of molecular magnetism. The distinguishing feature of 4f elements as spin carriers for SMMs is their unparalleled single-ion anisotropy.

Among the lanthanide family, the dysprosium (Dy^{III}) ion has become the bull's eye for making magnetic materials mainly because of its high magnetic moment and the high anisotropy of the spin-orbit coupled Kramers doublet ground state ($S = 5/2$, $L = 5$, $J = 15/2$). Consequently, homometallic polynuclear Dy^{III} SMMs have become of increasing interest since the observation of the unusual slow relaxation behavior in a triangular Dy₃ cluster in spite of its almost nonmagnetic ground state.^[7a] Although recent research in this area has yielded many interesting SMMs incorporating Dy^{III} ions,^[29] the science of making 4f-based SMMs is still in its infancy and hence there is dire need to explore this rich area of coordination chemistry.

1.2.4.2 Single chain magnets (SCMs)

Recent years have witnessed one of the most fascinating developments in the field of molecule-based magnets in the form of one-dimensional (1D) magnetic chains. As an analogue to SMMs, these 1D magnetically isolated chains also exhibit slow relaxation of magnetization and magnetic hysteresis of molecular origin^[28] and are known as single chain magnets (SCMs). The motivation behind SCM construction was to increase the blocking temperature of SMMs so as to fulfill the dream of their future application as molecular memory devices or recording media. The first prediction for SCM behavior was made by Glauber in 1963.^[30] In light of Glauber's theory, the main requirements for observing SCM behavior are large Ising-type magnetic anisotropy and weak or negligible interchain interactions that hamper the transition to 3D magnetic ordering. Therefore the synthetic strategies used to construct SCMs include: (i) linking uniaxial, anisotropic spin carriers, such as Co²⁺, Ni²⁺, Mn³⁺, Fe²⁺ and lanthanide ions, into 1D chains (ii) to utilize appropriate bridging ligands as effective magnetic couplers and (iii) to employ suitable diamagnetic separators so as to minimize interchain interactions.

From the point of view of magnetism, there are three possible approaches for the construction of 1D ordered magnets with spontaneous magnetization. These are ferromagnetic, ferrimagnetic and spin-canted antiferromagnetic approaches, depending on the type of magnetic exchange interactions among the spin carriers (Scheme 1.1).



Scheme 1.1 Three strategies towards single-chain magnets.

In contrast to ferrimagnetic and spin-canted antiferromagnetic systems, ferromagnetic systems are relatively rare due to the fact that ferromagnetic interactions rely on the orthogonality of the magnetic orbitals of the interacting spin carriers and hence are significantly less common.^[25-26,31]

In 2001, Gatteschi and co-workers reported the first observation of slow relaxation of magnetization in a cobalt(II)-organic radical alternating chain.^[32] This solid, a radical-bridged compound of formula $\text{Co}(\text{hfac})_2(\text{NITPhOMe})$, displayed a high relaxation barrier of 107 cm^{-1} . Despite the modest net spin generated through antiferromagnetic coupling between anisotropic Co^{II} ions (effective $S = 1/2$) and nitroxide radical ligands ($S = 1/2$), this remarkable energy barrier spurred a breakthrough in the field of molecule-based magnets, prompting many researchers to target other one-dimensional systems. Consequently a number of SCMs have been structurally and magnetically characterized over the years including $3d$,^[33] $3d$ -radical,^[34] $3d$ - $3d$,^[35] $3d$ - $5d$ ^[36] and $3d$ - $4f$ systems.^[37]

Rare-earth based chains are very appealing candidates for SCMs due to the large Ising anisotropy of their metallic centers and the first example was documented in 2005-06, when the Gatteschi group characterized the lanthanide analogues of $[\text{Co}(\text{hfac})_2(\text{NITPhOMe})]_n$, $[\text{Ln}(\text{hfac})_3(\text{NITPhOPh})]_n$ where $\text{Ln} = \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}$ and Yb . Out of this series only the Dy, Tb and Ho analogues exhibited slow relaxation of the magnetization (with energy barriers of 69, 45 and 34 K, respectively) (Fig. 1.3). This was the first rare-earth-radical to behave as a SCM.^[38] Lanthanides are advantageous over other paramagnetic spin centers owing to their very similar chemical properties. This allows an easy substitution of the metal center and hence the magnetic anisotropy can be tuned. A couple of Ln-based SCMs have been isolated and characterized in the recent years.^[39] However, in order to gain a deep insight into the

rational design of such fascinating SCM materials with improved blocking temperature and higher energy barriers, this area of MBMs still needs to be nurtured.

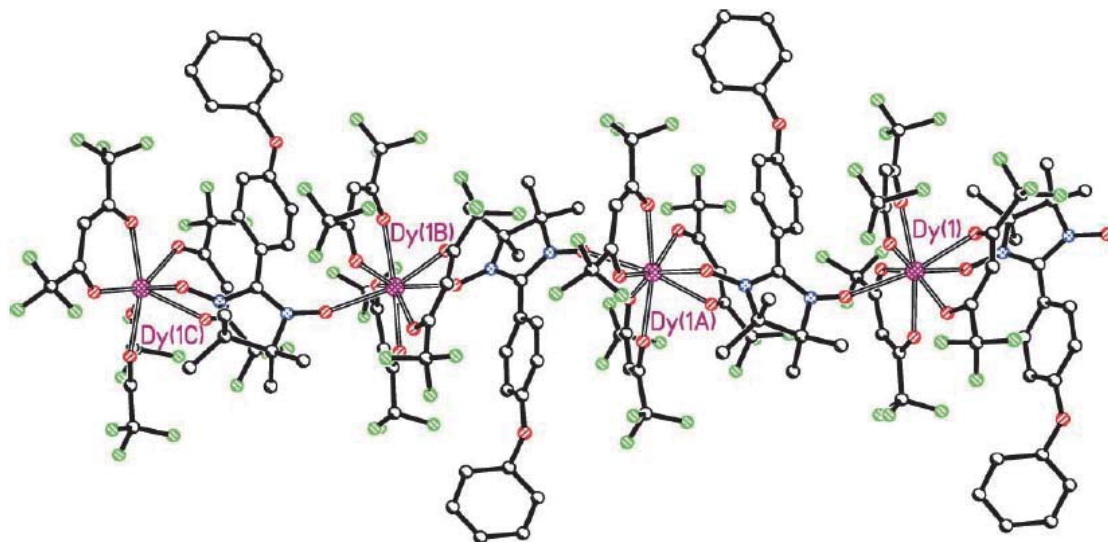


Fig.1.3 The molecular structure of the 1D chain complex $[\text{Dy}(\text{hfac})_3(\text{NITPhOPh})]_n$ ^[38a]

1.3 Introduction to Ln chemistry

Lanthanide elements (commonly abbreviated as Ln) have atomic numbers ranging from 57 (Lanthanum, La) to 71 (Lutetium, Lu). Together with scandium (Sc) and yttrium (Y), this series of 17 elements is generally referred to as rare earth elements (RE). The main sources of lanthanides are Bastnasite LnFCO_3 , Monazite $(\text{Ln-Th})\text{PO}_4$ (richer in earlier lanthanides) and Xenotime $(\text{Y-Ln})\text{PO}_4$ (richer in later lanthanides).

Lanthanides exist almost exclusively in the trivalent oxidation state Ln^{3+} having the electronic configuration $[\text{Xe}]4f^n$, ($n = 0-14$) in their coordination complexes. However, some divalent and tetravalent states are also stable which attain an f^0 , f^7 or f^{14} configuration. The majority of the Ln ions contain unpaired electrons and are therefore paramagnetic; the exceptions being La^{3+} , Ce^{4+} and Lu^{3+} having no unpaired electrons and are therefore diamagnetic.

As the series from La-Lu is traversed, there is a decrease in both the atomic and ionic radii of lanthanide elements. This is because as the atomic number increases, the effective attraction between the nucleus and the outer $5s$ and $5p$ electrons increases due to poor shielding of $4f$ electrons, causing shrinkage in the atomic or ionic radius. This phenomenon is commonly referred to as “Lanthanide Contraction” (Fig. 1.4).

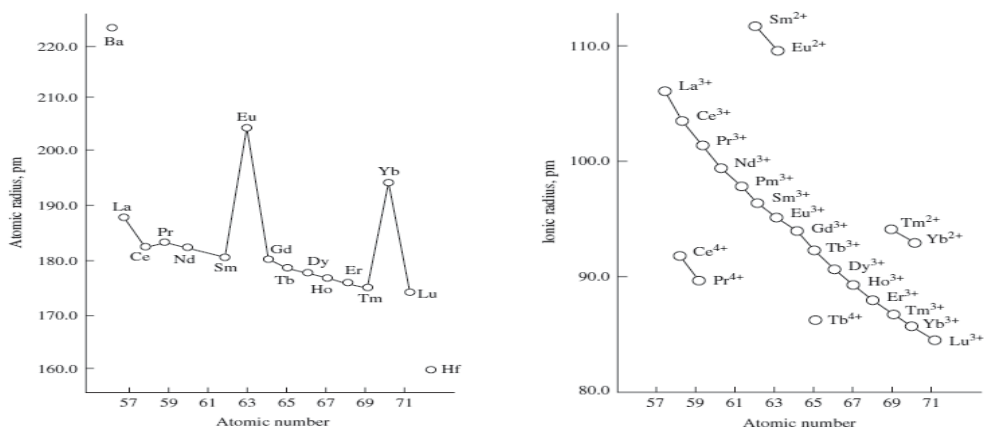


Fig. 1.4 Relationship between atomic number and atomic radii (left) / ionic radii (right).

This gradual decrease in the radius of Ln ions with increase in atomic number results in regular changes in the properties of lanthanide elements. For example, the stability constant of lanthanide complexes usually increases; the alkalinity of lanthanide ions decreases and the pH at which hydroxides start to precipitate from an aqueous solution decreases gradually as the atomic number increases.

Lanthanide ions have large radii and therefore offer high and variable coordination numbers ranging from 6 to typically found 8 and 9 but as high as 12 have also been documented. Lanthanides are also considered to be hard acids due to their preference for F- and O-donor ligands.

Many Ln compounds show strong luminescence in the infra-red, UV and visible regions. As a result Ln compounds have found applications in TV tubes, sensory probes, lasers and so on. At the same time, lanthanides have a large number of unpaired *f*-electrons and considerable single ion anisotropy, rendering them an ideal candidate for making molecule based magnetic materials. Some recent examples from literature, relevant to the work presented here, are briefly described below.

1.3.1 The Ln₄ cubane cluster

A tetranuclear Dy complex of the formula [Dy₄(μ₃-OH)₄(isonicotinate)₆(pyridine)(CH₃OH)₇·(ClO₄)₂ · pyridine · 4CH₃OH has been reported in 2009.^[40] The compound was synthesized in 25% yield by the reaction of Dy(ClO₄)₃ with isonicotinic acid in the presence of pyridine and a Schiff base. It shows a cubane structure in which four Dy^{III} ions are bridged by four μ₃-OH groups (Fig. 1.5, left). Terminal capping is provided by six isonicotinate ligands.

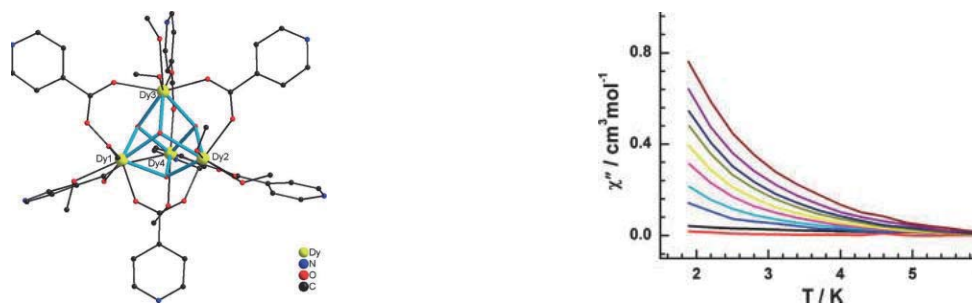


Fig. 1.5 (left) $[\text{Dy}_4(\mu_3\text{-OH})_4]$ cubane cluster (right) Plot of χ'' vs T for $[\text{Dy}_4(\text{OH})_4]$ cluster

Static (*dc*) measurements have indicated that the interactions between Dy centers are largely antiferromagnetic while *ac* studies showed slow relaxation of magnetisation (Fig. 1.5, right) which is a characteristic of SMM behavior.

1.3.2 Dy_{30} cluster containing Dy_{26} cage and Dy_4 cubane unit

This compound was synthesized in 42% yield by the reaction of Dy_2O_3 , isonicotinic acid, AgI, HNO_3 and H_2O under hydrothermal conditions at 150°C for 10 days.^[41] The $\{\text{Dy}_{26}\}$ cage is constructed by twenty six Dy^{III} ions and one Γ^- ion. Nine NO_3^- ligands provide additional ligation to the cluster core backbone by Dy-O coordination bonds (Fig1.6, left). This cage is further connected through terminal isonicotinate ligands to a $\text{Dy}_4(\mu_3\text{-OH})_4$ cubane unit (Fig1.6, right). A similar analogue with Er has also been reported.^[41b]

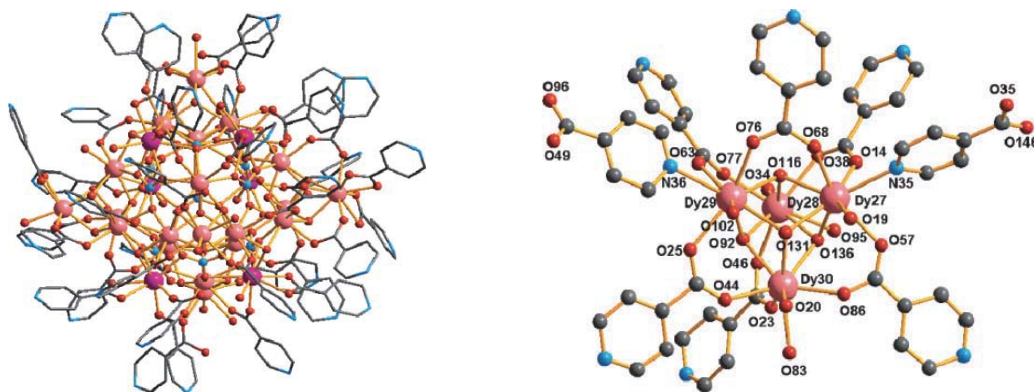


Fig. 1.6 (left) $[\text{Dy}_{26}(\mu_3\text{-OH})_{20}(\mu_3\text{-O})_6(\text{NO}_3)_9]^{36+}$ cluster (right) $[\text{Dy}_4(\mu_3\text{-OH})_4]^{8+}$ cluster

Static (*dc*) magnetic studies indicated the presence of dominating antiferromagnetic interactions among Dy_{26} and Er_{26} clusters (Fig1.7, left) while *ac* magnetic measurements showed slow relaxation of magnetization in the Dy analogue (Fig1.7, right). This is the first example of a high nuclearity Ln cluster showing SMM behavior which has triggered enormous research over the years in this area.

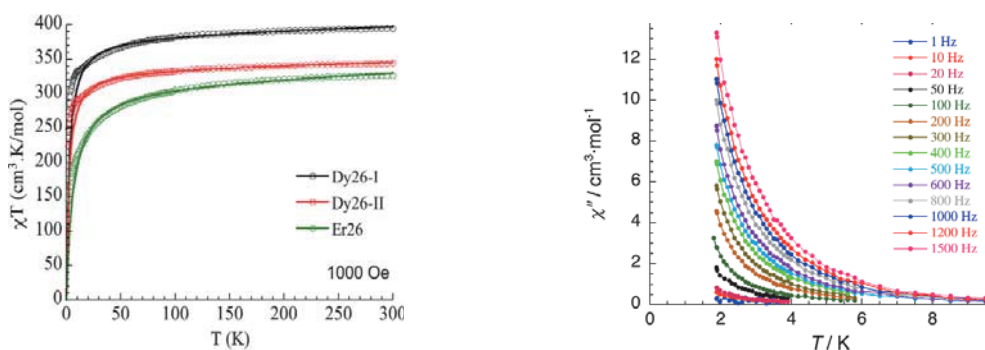


Fig. 1.7 (left) Plots of χT vs T for Ln_{26} clusters (right) Plots of χ'' vs T for Dy_{26}

1.3.3 The dysprosium 1D coordination polymer $[\text{Dy}^{\text{III}}(\text{OAc})_3(\text{MeOH})]_n$

The compound was reported in 2009.^[39a] It was synthesized by the polymerization of basic dimeric unit $[\text{Dy}_2(\text{OAc})_6(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ in methanol under refluxing conditions for 24 hrs leading to about 32% product yield. The structure seems to be derived from the dimeric unit (Fig1.8, left) in such a way that one chelating acetate on each Dy in one dimer bridges to a Dy in the next dimeric unit with concomitant displacement of an aqua ligand. The second chelating acetate in the dimer unit opens up further to provide additional *syn,syn*-bridging between neighboring dimers, thus leading to a zigzag chain running parallel to the *c*-axis (Fig1.8, right).

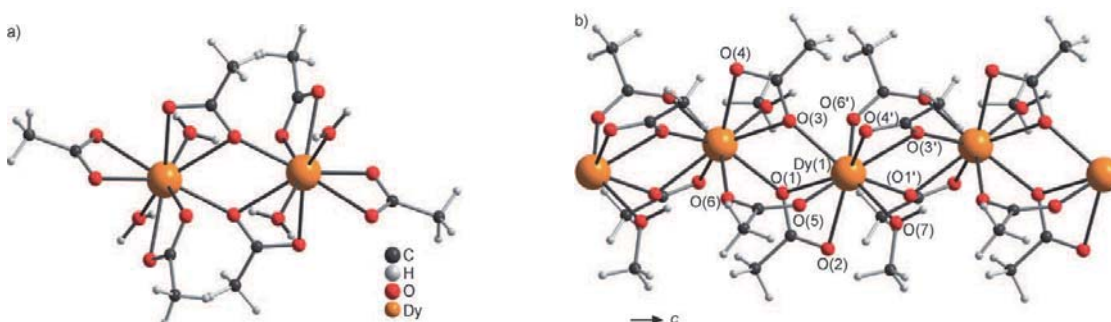


Fig. 1.8 (left) Structure of $[\text{Dy}_2(\text{OAc})_6(\text{H}_2\text{O})_4]$ (right) Structure of $[\text{Dy}(\text{OAc})_3(\text{MeOH})]_n$ ^{1D}

Static (*dc*) magnetic susceptibility measurements indicated antiferromagnetic interactions among the paramagnetic spin centers in the chain polymer at high temperatures up to about 5K. Below 5K, the χT product increases indicating the presence of ferromagnetic coupling among the Dy ions at low temperatures. The *ac* susceptibility measurements indicated the presence of slow relaxation of magnetisation (Fig1.9, left). Also hysteresis loops were observed at around 0.5 K using micro squid technique (Fig1.9, right). These observations suggested that the compound behaves as a single chain magnet (SCM).

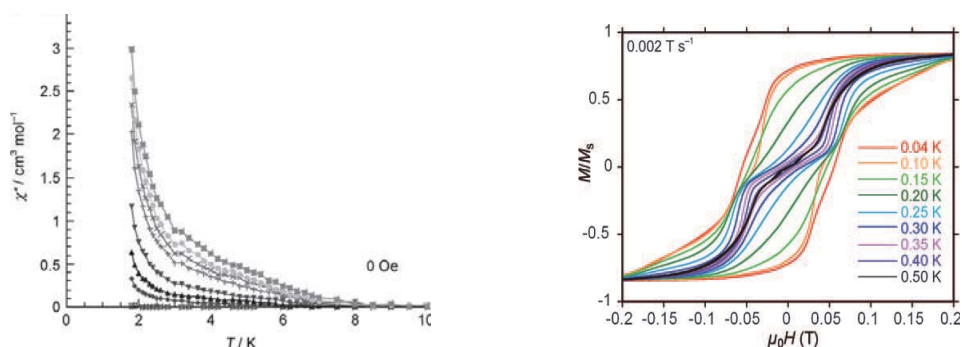


Fig. 1.9 (left) Plots of χ'' vs T (right) Hysteresis loops for $[\text{Dy}(\text{OAc})_3(\text{MeOH})]_n$ ^{1D}

1.3.4 The 3D lanthanide metal organic framework $[\text{Ln}_2(\text{N-BDC})_3(\text{DMF})_4]_n$

Lanthanide containing MOFs have gained special attention during recent years mainly because of their versatile applications like photoluminescence, magnetism and so on, thus rendering them ideal candidates for making multifunctional materials. One such example is quoted here.^[42] The compound was obtained by reacting Ln salt with 2-amino-1,4-benzene dicarboxylic acid in DMF under solvothermal conditions at 120°C for 20 hrs. The structure is described as a dinuclear edge-sharing Ln cluster bridged by four carboxylate groups from four ligands. Four DMF molecules provide additional coordination. These dinuclear units having octahedral geometry act as secondary building units (SBUs) and are further connected in three dimensions to make a cubic network having large cavities occupied by the coordinated solvent molecules (Fig. 1.10, left). The Eu and Tb analogues showed characteristic red and green photoluminescence upon excitation with UV light. The compounds were also measured magnetically and *dc* measurements indicated the presence of antiferromagnetic interactions among the metal centers which is in accordance with theoretical calculations (Fig1.10, right).

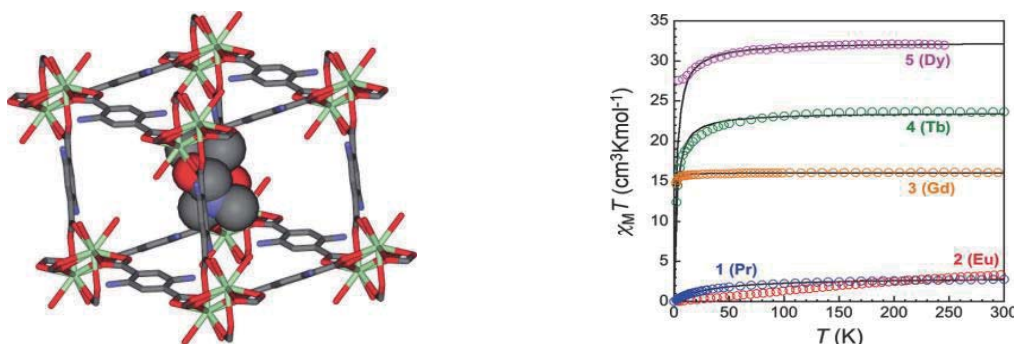


Fig. 1.10 (left) View of the repeating cubic unit (right) Plots of χT vs T for different lanthanides in $[\text{Ln}_2(\text{N-BDC})_3(\text{DMF})_4]_n$



1.4 Introduction to Ln–Mn chemistry

The synthesis and characterization of polynuclear clusters of paramagnetic metal ions have attracted intense study since the discovery that such molecules can display the phenomenon of single-molecule magnetism (SMM).^[28a] In these molecules there exists an energy barrier to the relaxation of the magnetization due to the combination of a large ground state spin multiplicity and a significant negative zero-field splitting of that ground state. This imparts a molecular magnetic memory effect that can be observed as temperature and sweep rate dependent hysteresis loops in single crystal M vs. H studies.^[28b] There are now several species displaying such behavior—the majority of which are transition metal clusters containing Mn ions,^[43] since Mn clusters often display large spin ground states and large and negative magneto-anisotropies associated with the presence of Jahn–Teller distorted Mn^{III} ions.

As the search for new SMMs expanded, several groups explored mixed metal compounds, and particularly Ln–Mn ones, as an attractive area. These efforts were greatly stimulated by the Cu₂Tb₂ SMM reported by Matsumoto and co-workers.^[44] The strategy is obviously to take advantage of the lanthanide ion's significant spin, and/or its large anisotropy, as reflected in a large D value, to generate SMMs distinctly different from the homometallic ones. Indeed, there are now several Ln–Mn polynuclear SMMs, including Dy₆Mn₆,^[45] Ln₄Mn₁₁,^[46] Gd₂Mn₁₁,^[47] Ln₄Mn₅,^[48] Ln₆Mn₅,^[49] and DyMn₂₁.^[50] However, more systematic and in-depth studies are inevitable in order to synthesize complexes having higher energy barriers, so that they could be used in future electronic devices.

1.4.1 The first Ln–Mn SMM (Ln₆Mn₆)

The dodecanuclear cluster [Dy₆Mn₆(H₂shi)₄(Hshi)₂(shi)₁₀(CH₃OH)₁₀(H₂O)₂]·9CH₃OH is the first example of a Ln–Mn cluster that shows SMM property.^[45] Its structure consists of a hexagonal ring of six Dy ions that is capped on each end by the Mn^{III}₂Mn^{IV} trimer unit.

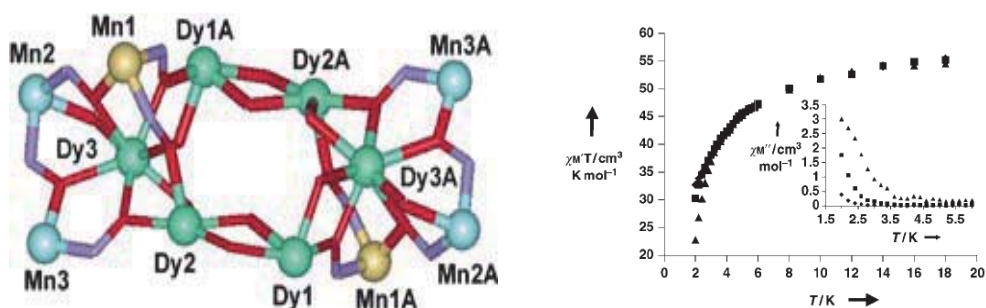


Fig. 1.11 (left) Dy_6Mn_6 core topology (right) Plot of χT vs T ; (inset) χ'' vs T for Dy_6Mn_6 . Static (*dc*) magnetic susceptibility measurements indicated the presence of dominating antiferromagnetic interactions among different spin carriers (Fig. 1.11, outside), while *ac* measurements revealed an out of phase *ac* signal showing slow relaxation of magnetization but without a maximum (Fig. 1.11, inset).

1.4.2 Ln_2Mn_6 SMM with highest energy barrier

Clérac et al. have recently reported two multi-nuclear Ln–Mn clusters having formula $[\text{Mn}^{\text{III}}_6\text{O}_3(\text{saO})_6(\text{OCH}_3)_6\text{Ln}_2(\text{MeOH})_4(\text{H}_2\text{O})_2]$ where (Ln = La(**1**), Tb(**2**)).^[51] These complexes contain a $\{(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})\text{Ln}\}-(\mu_4\text{-O})_3\text{-Ln}(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})\}$ linear motif with a synperiplanar conformation. This central Ln–O₃–Ln “axis” is attached through the three μ_4 -oxo ligands to a surrounding Mn^{III}_6 wheel on an equatorial position of the Mn sites.

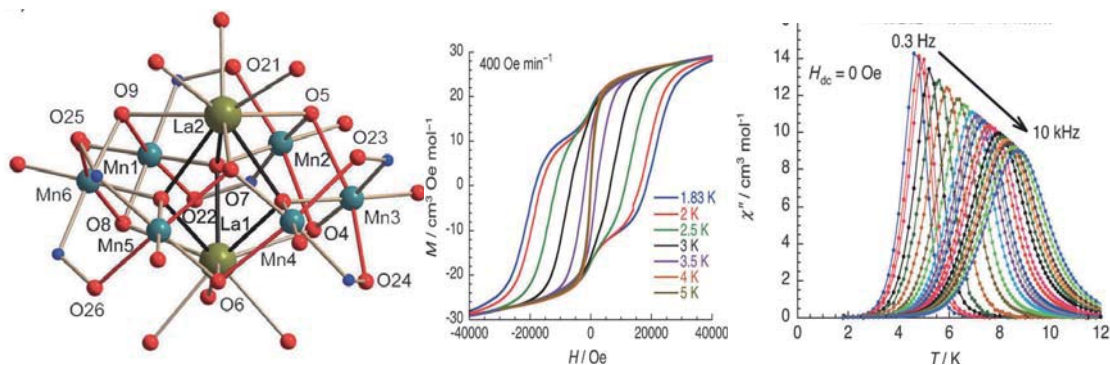


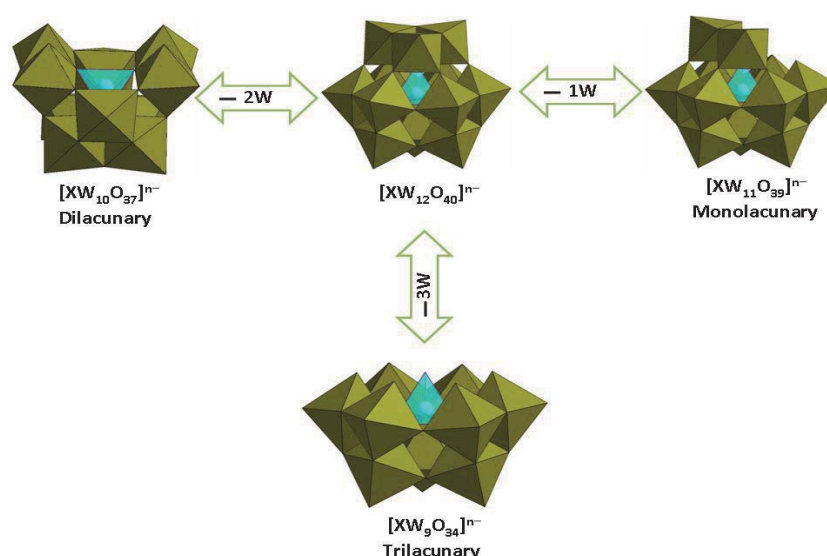
Fig. 1.12 (left) Metal core in **1** (middle) Hysteresis loops for **2** (right) χ'' vs T plot for **2**.

Solid-state *dc* susceptibility measurements for **1** and **2** indicated an increase in the χT product at high temperatures, suggesting dominant ferromagnetic interactions among the spin centers. While at low temperatures the χT product follows a decrease, as expected due to the magnetic anisotropy and/or weak inter-complex antiferromagnetic interactions. Below 1.8 and 4.5 K for **1** and **2** respectively, hysteresis effects are observed on the field

dependence of the magnetization highlighting a magnet type behavior of the two compounds. At 5K, as in the case of compound **2**, the hysteresis loop disappears because the blocking temperature is not high enough to observe the loop at this sweep rate. The *ac* susceptibility measurements indicated a prominent out of phase signal which confirms the SMM property of both La(**1**) and Tb(**2**) analogues. A fit of the thermally activated region gave $\Delta E = 32.8$ K and 103 K, for **1** and **2** respectively. The SMM energy barrier of 103 K found in **2** is one of the highest that have ever been reported and the largest measured among the *3d* and *3d/4f* SMMs, thus prompting the scientific community to explore this rich area of Ln–Mn chemistry.

1.5 Introduction to Ln–POM chemistry

Polyoxometalates (POMs) or polyoxoanions is an emerging field of inorganic chemistry since the first compound was documented by Berzelius in 1826.^[52a] POMs constitute a large family of oxo-bridged discrete anionic metal clusters composed of edge and corner shared $\{MO_6\}$ octahedra with early transition metals in high oxidation states [for example, W(VI), Mo(VI), V(V)] etc.^[52b, 52c] Plenary POMs with closed shell structures are chemically inert towards reaction with electrophiles due to the low basicity of the terminal oxygen atoms. However, their reactivity can be dramatically increased by preparing vacant (“lacunary”) derivatives through controlled hydrolysis in basic aqueous medium, leading to mono-, di-, tri-, or even hexa-vacant derivatives as in case of heteropolytungstates (Fig. 1.13).



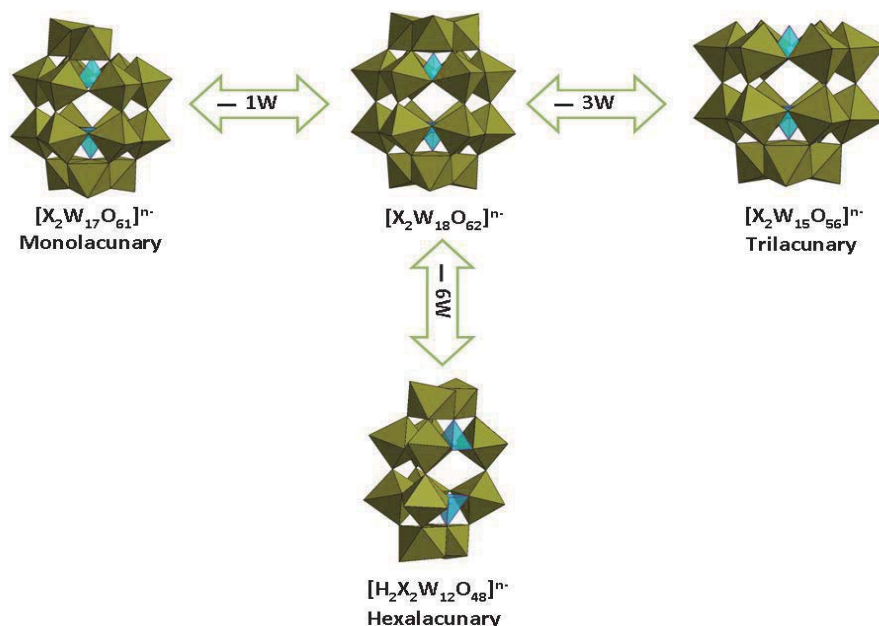


Fig. 1.13 Common lacunary heteropolyanions of the Keggin (upper) and Wells–Dawson type (lower) {Green polyhedra: WO_6 , Blue polyhedra: heteroatom X}.

These lacunary POMs offer useful features as inorganic ligands, such as solubility, diamagnetic nature, arrangement of coordination sites, flexibility of coordination modes, and ability to rearrange.^[53] Their oxygen rich compositions are particularly suitable to bind highly oxophilic Ln ions thus giving rise to a new subclass of Ln–POM complexes having applications in areas as diverse as photoluminescence, Lewis acid catalysis, electrochemistry and magnetism.^[54]

In contrast to $3d$ metal ions, Ln ions have better potential to link two or more lacunary POM units due to their large size and high coordination numbers. This area is dominated by tungsten based POMs, due to the availability of a large number of lacunary polyoxotungstates (as opposed to molybdates or vanadates). Many instances of Ln–POM complexes containing one or more Ln ions are available in the literature.^[52d, 55] However, complexes where both organic and inorganic POM ligands are simultaneously bound to the Ln centers are indeed scarce,^[56] despite the fact that it can lead to novel hybrid materials. A couple of representative examples are briefly described below.

1.5.1 The Di- and Octanuclear Tb-polyoxotungstates.

The two Tb complexes having formulas $[Tb_2(pic)(H_2O)_2(B-\beta-AsW_8O_{30})_2(WO_2(pic))_3]^{10-}$ (**1**) and $[Tb_8(pic)_6(H_2O)_{22}(B-\beta-AsW_8O_{30})_4(WO_2(pic))_6]^{12-}$ (**2**) were obtained in 31 and

18% yield respectively by reacting Ln salt (OAc for **1** / NO₃ for **2**) with picolinic acid (picH) and the dilacunary polyoxotungstate [As₂W₁₉O₆₇(H₂O)]¹⁴⁻ under acidic conditions.^[57]

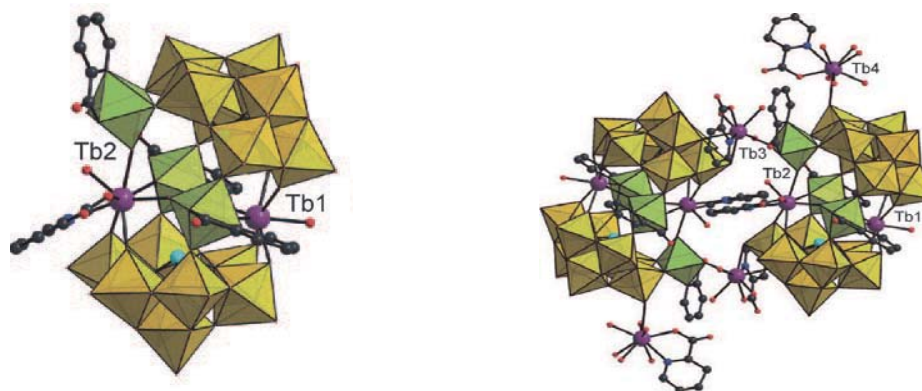


Fig. 1.14 (left) Structure of complex **1**

(right) Structure of complex **2**

The structure of complex **1** consists of two [B-β-AsW₈O₃₀]⁹⁻ units oriented at 180° to each other with three {WO₂(pic)} moieties and two Tb^{III} centers sandwiched between them. Complex **2** is considered to be made up of two molecules of **1** linked together through two {Tb(pic)(H₂O)₃} moieties. Luminescence studies showed intense green light for **2** upon excitation with UV radiation (λ_{ex} = 254nm) with characteristic transitions of Tb ion in the emission spectrum. The *dc* magnetic susceptibility measurements for **1** and **2** suggested weak antiferromagnetic interactions among Tb^{III} centers while in the *ac* susceptibility measurements, no out-of-phase signal was observed indicating the absence of SMM property in both the complexes.

1.5.2 The 3D Dy-POM network

The Ln-POM framework, K₅Na[K₂{Dy(H₂O)₃]₂{As₂W₁₉O₆₈}{WO₂(pic)}₂·27H₂O was obtained by reacting Dy(NO₃)₃, picolinic acid (picH) and [As₂W₁₉O₆₇(H₂O)]¹⁴⁻ at pH 3.4.^[58] The structure is described as a 3D framework comprised of constituent {Dy(H₂O)₃]₂{As₂W₁₉O₆₈}{WO₂(pic)}₂ Ln-POM units and {K₄O₄} distorted cubane units serving as a template (Fig. 1.15, left /middle). The tungsten center of each {WO₂(pic)} fragment, formed by the dissociation of the dilacunary POM, makes a 5-membered chelate ring with N- and carboxyl O- of the picolinate ligand. The other product of dissociation i.e. {B-α-AsW₉O₃₃} anions reassemble to make the dilacunary {As₂W₁₉O₆₈} unit which further binds two Dy^{III} ions on its vacant sites.

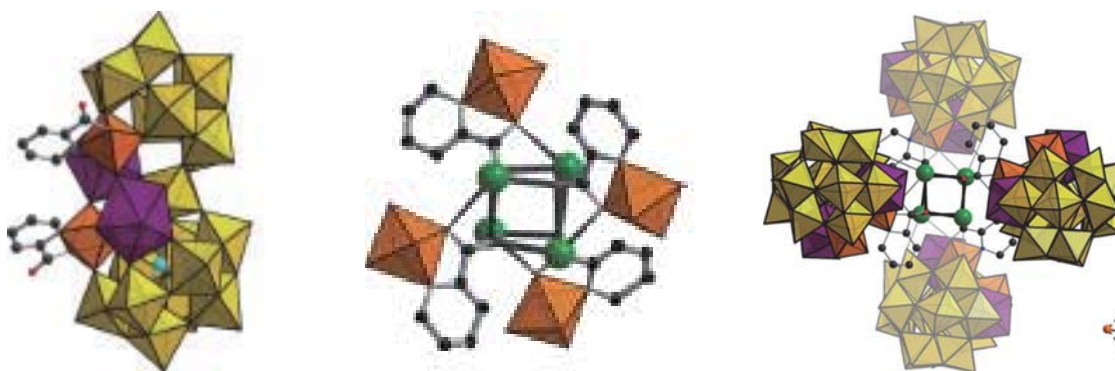


Fig. 1.15 (left) POM building block, (middle) $\{K_4O_4\}$ cubane unit, (right) The tetrahedral arrangement of POM units around the templating $\{K_4O_4\}$ cubane

This POM building block acts as a 2-connecting node and is further connected to the other building block of the 3D structure, the $\{K_4O_4\}$ distorted cubane units through K-O-W connection to the $\{WO_2(pic)\}$ fragments. In this way each $\{K_4O_4\}$ unit acts a 4-connecting node leading to a tetrahedral arrangement of POMs around the central cubane template (Fig. 1.15, right), hence resulting in a diamondoid network topology.

1.6 Synthetic strategy

With an object to construct polynuclear molecule-based magnetic materials, ranging from zero dimensional clusters to three dimensional MOFs, various synthetic methodologies adopted during the course of this research work are briefly described below.

The first approach was the synthesis and characterization of Ln-based coordination polymers using simple aliphatic as well as aromatic monocarboxylate ligands:

(a) To systematically study the effect of varying steric hindrance of R-groups on the structure and properties of the resulting products.

(b) To develop a rational synthetic approach for synthesizing multidimensional networks based on Ln^{III} ions.

A second approach was the use of a binary ligand system containing an additional polyol ligand in combination with a carboxylate. The object was to synthesize high nuclearity Ln aggregates as well as Ln-based networks containing carboxy as well as alkoxy bridges which could provide us further understanding of the kind of interactions mediated through this hybrid ligand system.

As a third approach, a 3d metal such as Mn was introduced into the Ln-polyol-carboxylate system. The presence of two types of metal centers can give rise to



interesting magnetic properties and can allow further investigation of the exchange interaction between two different metal ions.

Another strategy adopted was to replace the organic polyol ligand by a polyoxometalate (POM) cluster which can serve as purely inorganic polyoxo ligand. This study employing inorganic (POM) and organic (carboxylate) ligands not only helped to probe further into the structural variations accompanied by a change of the polyol ligand but also provided a sound comparison of the properties of the resulting products under the influence of organic/inorganic hybrid ligand systems.

Last but not the least, the key point of this whole research work was to establish a simple, convenient and efficient synthetic procedure for the development of polynuclear Ln-based coordination compounds. Since 4*f* metals are not so reactive compared to their 3*d* rivals, in the majority of the literature where 4*f*-based polynuclear aggregates or coordination networks are reported, the use of stringent synthetic conditions like hydro(solvo)thermal techniques^[42,59] employing high pressures and temperatures and longer reactions times is reported. Yet in many cases the yields are not so impressive. Contrarily, all compounds presented in this study were synthesized under open heating or refluxing conditions in a time span of just 1-2 hours along with product yields of 50-60% or even higher.

Another salient feature of this synthetic strategy is the controlled metal-hydrolysis which was achieved by manipulating pH of the reaction medium. Lanthanides have a normal working pH range of around 4-6 beyond which metal-hydroxides start to precipitate out of the solution. Even this pH range gradually decreases while moving along the period from left to right hence making the chemistry of later lanthanides a bit more difficult. This problem was addressed firstly by using NaN₃ as a mild base to deprotonate the ligands, while at the same time allowing only partial metal-hydrolysis and secondly, in some cases, by using small amounts of polyols as buffering agents to optimize the solution pH. All these efforts have provided a deep insight into the self-assembly process of polynuclear Ln-based aggregates.

1.7 Ligand selection strategy

Carboxylate ligands are highly complementary towards Ln ions due to the oxophilic nature of the latter. Their ability to adopt many different coordination modes (Fig. 1.16) caters well for the metals' lack of defined coordination geometry. Thus carboxylate moieties are one of the best candidates to synthesize discrete as well as polymeric metal aggregates and hence to study various factors governing electronic exchange coupling interactions among adjacent metal centers. Various carboxylate ligands used in this study are described in Table 1.1 along with their formulas.

Table 1.1 Formulas of carboxylate ligands used.

Ligand	R-Group	Structure	Ligand	R-Group	Structure
Acetic Acid	CH ₃		Butyric Acid	CH ₃ (CH ₂) ₂	
Propionic Acid	CH ₃ CH ₂		3-substituted-Propionic Acid	XCH ₂ CH ₂ (X = Cl, NH ₂)	
Pivalic Acid	(CH ₃) ₃ C		Benzoic Acid	C ₆ H ₅	
3-Cl-Benzoic Acid	ClC ₆ H ₄		Isonicotinic Acid	C ₅ H ₄ N	

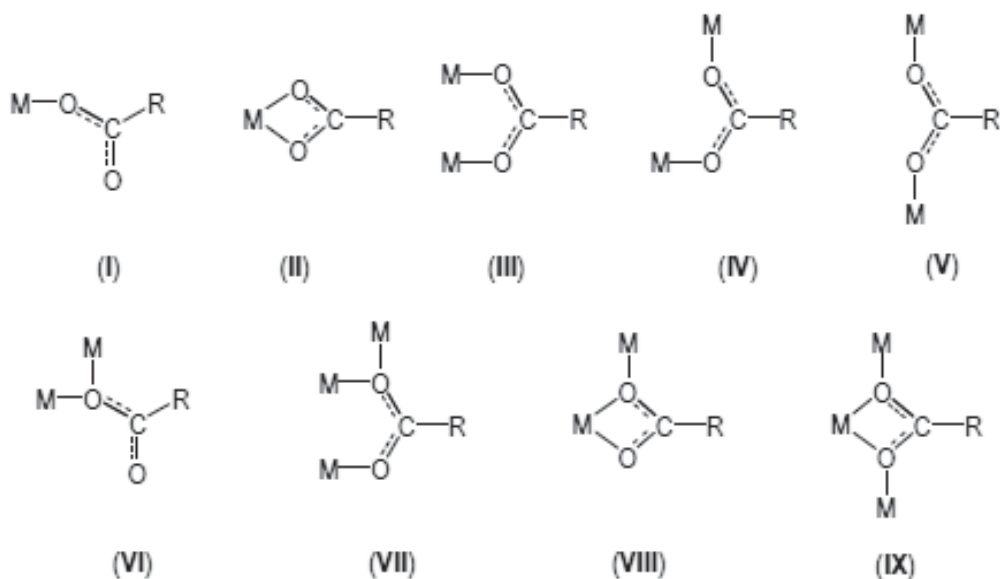


Fig. 1.16 Common coordination modes of carboxylate ligands.

Another successful approach for making polynuclear coordination compounds involves the use of alkoxide-based chelating ligands. Polyol ligands have been frequently employed in $3d$ and $3d/4f$ mixed-metal chemistry; however the analogous lanthanide chemistry is still far less explored. Based on these observations, two tritopic polyol ligands, namely glycerol (H_3Gly) and diethylene glycol (H_2DEG) have been selected, which in combination with carboxylate ligands have been used to synthesize pure Ln-based polynuclear coordination compounds.



Fig. 1.17 (left) Glycerol (H_3Gly)

(right) Diethylene Glycol (H_2DEG)

These ligands were chosen on the following grounds:

(a) Glycerol is a highly flexible ligand, containing three hydrophilic OH-groups, and is capable of forming both intra- and intermolecular hydrogen bonds.^[60] It exhibits various coordination modes such as chelating and chelating/bridging modes (Fig. 1.18), and hence can bind up to 3 or even more metal centers.

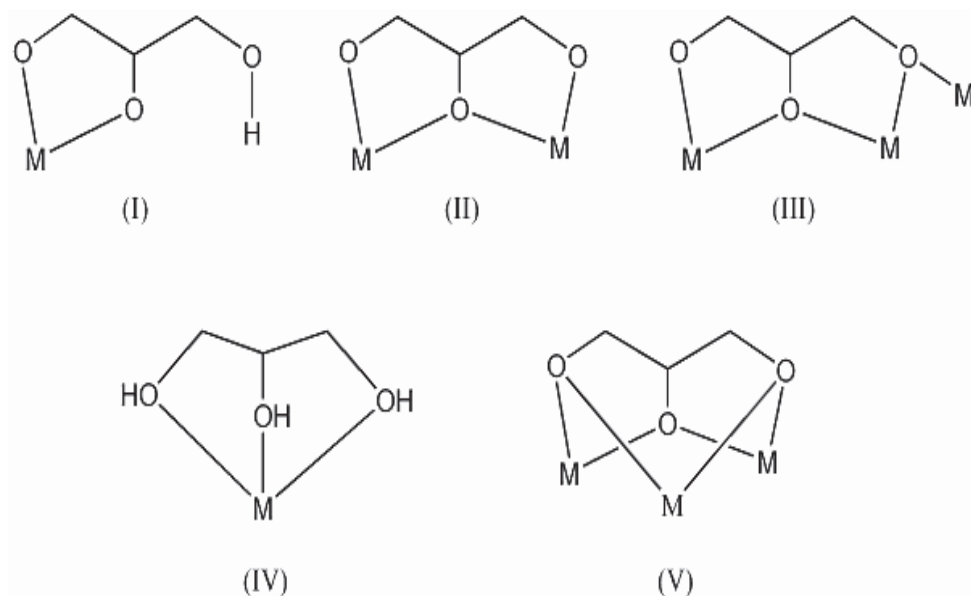


Fig. 1.18 Different coordination modes of glycerol ^[61-64]

The fact that glycerol can lead to chiral magnets, depending upon its versatile coordination modes, provides enormous motivation to explore its role in coordination chemistry for the synthesis of high nuclearity Ln aggregates.

(b) Glycerol (H_3Gly) is a very promising ligand and some reports are available where it has been successfully employed for the synthesis of polynuclear $3d$ metal aggregates.^[62-63] With $4f$ metals there is only one report documented so far containing a series of dimeric Ln clusters^[64], while in case of $3d/4f$ chemistry this ligand has not been used until now.

(c) In contrast to a plethora of literature available where structurally related diethanolamine ligands have been extensively employed for synthesizing polynuclear $3d$, $3d/4f$ and some $4f$ aggregates with interesting magnetic properties,^[65-67] much less attention has been paid to the use of diethylene glycol (DEG),^[68,69] and hence there is still plenty of room available for exploring the role of DEG in coordination chemistry.

(d) Compared with diethanolamine (N,O,O-donor) ligands, which are especially suitable for binding $3d$ or $3d/4f$ metals ions, DEG is an (O,O,O-donor) alkoxy ligand with highly flexible pendant arms, and is anticipated to be adequate for building up polynuclear $4f$ -based metal aggregates. Fig. 1.19 depicts all known coordination modes of DEG.

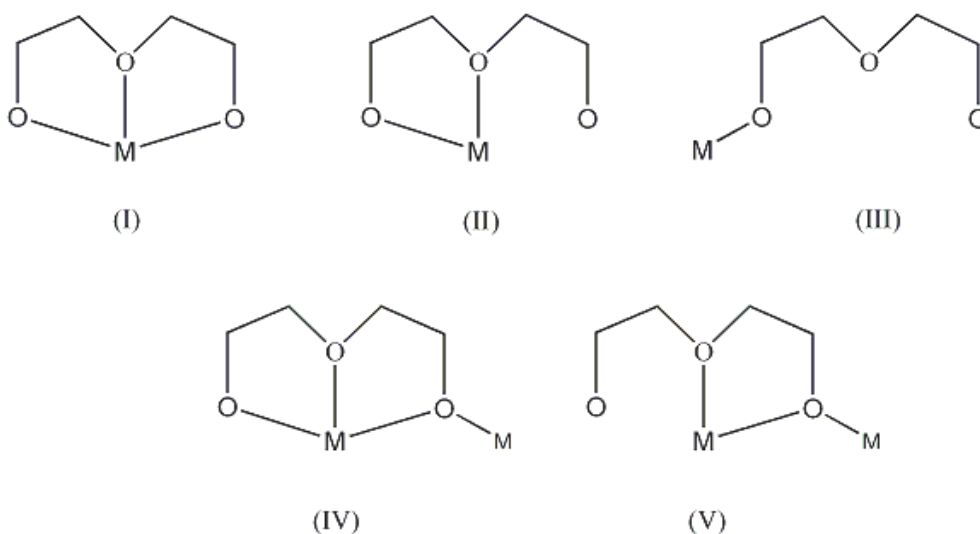


Fig. 1.19 Different coordination modes of DEG.^[68,69]

Finally, the organic polyol ligand in the Ln-polyol-carboxylate system is replaced with an inorganic polyoxometalate (POM) moiety, with an object to obtain new POM-encapsulated polynuclear lanthanide complexes. As starting material, a trilacunary lone-pair containing heteropolytungstate $[XW_9O_{33}]^{9-}$ $\{X = As^{III}\}$ has been selected (Fig. 1.20). This trivacant Keggin POM is an excellent supporting ligand, mainly because of the large number of reactive oxygens on the lacunary sites that are available for coordination to the highly oxophilic lanthanide ions. Secondly, the lone-pair of electrons on the POM heteroatom (X) prevents the formation of closed plenary Keggin units, providing a more open space to accommodate the Ln centers.

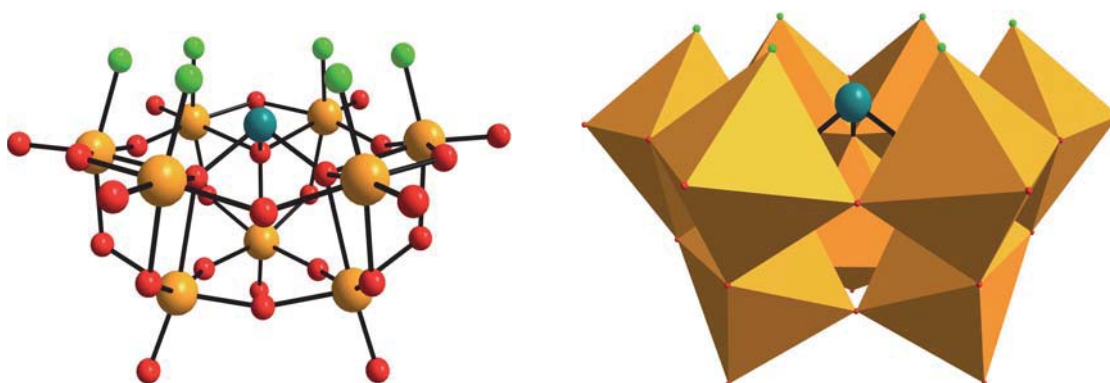


Fig. 1.20 Molecular structure of trilacunary POM precursor $[AsW_9O_{33}]^{9-}$ in ball-and-stick mode (left), combined polyhedral/ball-and-stick representation (right). Color code: W/ WO_6 octahedra = orange, As = sea green balls, Reactive O sites = bright green balls, O = red balls.



1.8 Thesis overview

This dissertation describes the synthesis and characterization of homometallic Ln, heterometallic Ln–Mn and Ln–POM zero to three dimensional polynuclear coordination complexes using O-donor ligands. In total, there are 16 isostructural series containing 75 compounds which are described in three different chapters. In lanthanide chemistry, it is possible to obtain isostructural analogues with different lanthanides. Therefore, it is not necessary to characterize each analogue by single crystal X-ray diffraction. Alternatively, such compounds are characterized either by comparing the unit cell parameters or the powder diffraction patterns. As a result, in each series described here, the Dy analogue has been structurally characterized by single crystal X-ray diffraction and described as the reference compound, since it is usually the most magnetically interesting lanthanide. Chapter 3 describes a systematic and comprehensive study performed on the synthesis and characterization of various Ln-based coordination polymers using simple monocarboxylate ligands. In chapter 4, a binary ligand approach is introduced using additional polyol ligands, to study the synergic effect on the magneto-structural properties of various Ln-based coordination polymers as well as high nuclearity metal aggregates. Chapter 5 extends the Ln-polyol-carboxylate chemistry further where firstly a second metal Mn is introduced to study heterometallic Ln–Mn polynuclear aggregates. Secondly, the organic polyol ligand in the Ln-polyol-carboxylate system is replaced with a purely inorganic polyoxometalate moiety (inorganic polyoxo ligand), with the aim of synthesizing novel organic/inorganic hybrid materials. Afterwards, the whole research effort is concluded in chapter 6. A brief summary of the dissertation is described as “Zusammenfassung” in chapter 7. Chapter 8 contains detailed experimental synthetic procedures as well as characterization techniques employed while the crystallographic data and bibliographies are reported in subsequent chapters 9 and 10 respectively.