



Review

Lanthanide-Based Single-Molecule Magnets Derived from Schiff Base Ligands of Salicylaldehyde Derivatives

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Abstract: The breakthrough in Ln(III)-based SMMs with Schiff base ligands have been occurred for the last decade on account of their magnetic behavior, anisotropy and relaxation pathways. Herein, we review the synthetic strategy, from a structural point of view and magnetic properties of mono, di, tri and polynuclear Ln(III)-based single-molecule magnets mainly with Schiff bases of Salicylaldehyde origin. Special attention has been given to some important breakthroughs that are changing the perspective of this field with a special emphasis on slow magnetic relaxation. An overview of 50 Ln(III)-Schiff base complexes with SMM behavior, covering the period 2008–2020, which have been critical in understanding the magnetic interactions between the Ln(III)-centers, are presented and discussed in detail.

Keywords: lanthanides; Schiff base; synthetic strategies; single-molecule magnets

1. Introduction

1.1. General Introduction to Single-Molecule Magnets (SMMs)

SMMs are subunits of metal-organic compounds that show superparamagnetic behavior below a certain blocking temperature (T_B), purely of molecular origin [1]. Since the discovery of the manganese coordination cluster, $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$ [2], behaving as a single-domain magnet, numerous discoveries have been devoted to the “hot” area of molecular magnetism [3–5]. Because of the large magnetic moment and single-ion anisotropy, lanthanides(III) (Ln(III)) have entered into this area. Among them, some of the mononuclear complexes of Ln(III) have drawn maximum attention compared to the polynuclear ones, owing to their small size and bistable nature and so could be ideal candidates for high-density storage and quantum computing [6–9].

After the report of the first SMM, $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$, a tremendous amount of SMMs were investigated with 3d transition metals on account of their strong coupling while less interest was with Ln(III) systems due to their weak exchange interaction when they are in their most stable trivalent oxidation state. Furthermore, much work has been done on a single-ion magnet (SIM)/SMMs with 4d and 5d transition metal, owing to their magnetic anisotropy, which received much attention in the area

of high T_B molecular magnets. However, due to the synthetic difficulties, the SMMs/SIM based on 4d and 5d are still very limited compared to 3d analog [10,11].

However, in recent years SMMs with f-block elements are commonly based on the interaction between the electron density of the 4f-ions and the crystal field environment in which they are placed. For example, dysprosium (III)(Dy(III)) has a spin-orbit coupled ground state, $^6H_{15/2}$, that is more informative in understanding how 4f-ions are useful in constructing SMM than simply representing the electronic structure by the number of valence electron ($4f^9$) (Figure 1) [12,13].

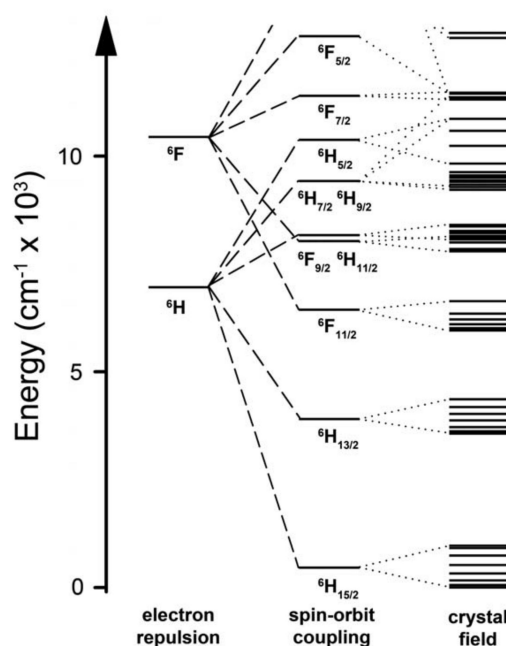


Figure 1. Low energy electronic structure of Dy(III) ions, with the crystal field-splitting modeled on the $\text{Dy}[\text{Me}_3\text{Si})_2\text{N}]_3$ complexes. Reproduced with permission from [13]; Published by Royal Society of Chemistry, 2011.

1.2. The Anisotropy of Lanthanide Ions-Oblate/Prolate Model

In Ln(III) systems, the magnetic anisotropy typically arises from the extensive splitting of M_J ground state caused by the ligand field [14] and is quantified by a g-factor, which characterizes the shape of the ions and the amplitude of anisotropy. In most of the SMM's, there is an anisotropic axis in a “hard plane” (Figure 2d). When the magnetic axis of the metal ion is in line with the anisotropic axis, and the value of g_z will be maximized [15]. This anisotropy is also can be called an Ising type anisotropy, which is an ideal condition for an SMM. The higher the “pure” excited state, the bigger the effective energy barrier will be obtained [16]. In some cases, the easy axis can be a plane, where it is possible to find magnetization, which can be called “easy plane”, where $g_z < g_x \approx g_y$.

In other words, there is a way to maximize the single-ion anisotropy by modifying the coordination environment of the Ln(III)-ion. Rinehart and Long suggested simple rules in order to optimize 4f-SMMs, simply by exploiting their single-ion anisotropy [13]. For increasing the anisotropy of the oblate ions which are equatorially expanded (Figure 2a), we should place it in a ligand field for which the ligand electron density is located above and below the xy plane (“sandwich” type ligand geometry), which means donor atoms should be on the axial position (Figure 2b). It is not a coincidence that most of the geometries of mononuclear Tb(III) and/or Dy(III) SMMs with the highest energy barriers are square-antiprismatic (SARP-8) [15]. However, for prolate ions, which are axially expanded (Figure 2a), equatorial coordination geometry is preferred (Figure 2c), and here, the donor atoms should be on the equatorial plane.

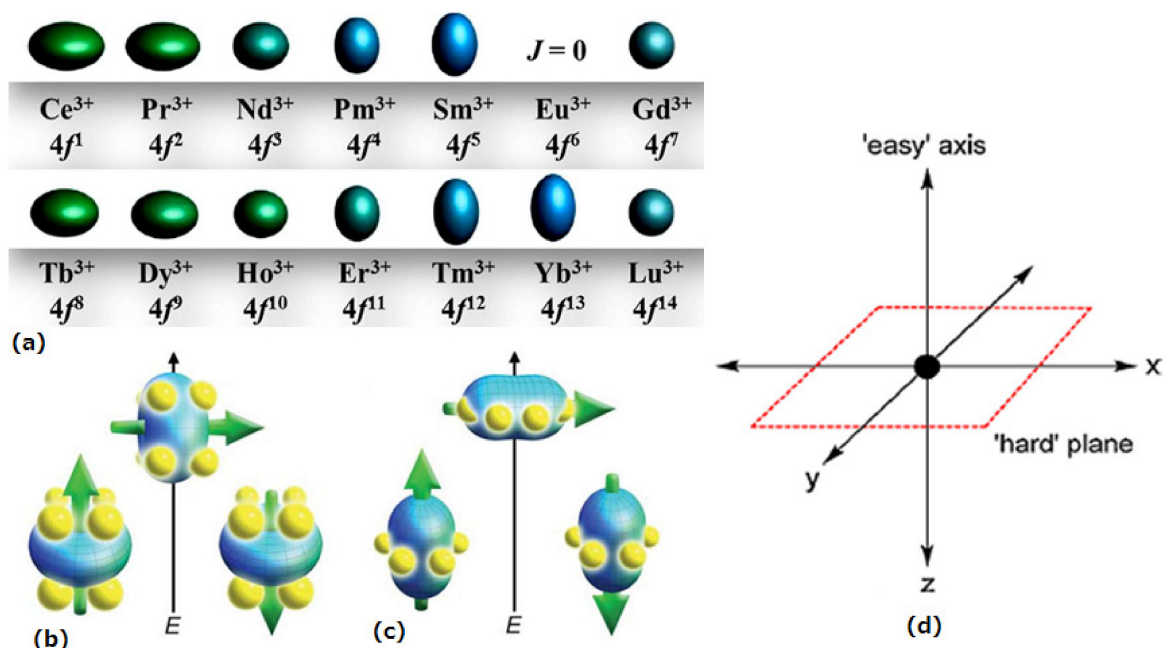


Figure 2. (a) Shapes of 4f electron densities in Ln(III). Europium is not shown as it has a $J = 0$ ground state; low and high energy configurations of the f-orbital electron coupled to the orbital moment (J): density with respect to the crystal field environment for an oblate (left) (b) and a prolate (right) (c) electron density of Ln(III) ions. The green arrow represents the orientation of the spin angular momentum (L), (d) the representation of the easy axis and hard plane in three-dimensional space. Reproduced with permission from [13,15]; Published by Royal Society of Chemistry, 2011 and Elsevier, 2014.

For Dy(III) single-ion magnet (SIM) with ground state $J = 15/2$ under extremely axial crystal field, the energy landscape of the magnetic microstates could resemble the time-reversal symmetric double-well potential as depicted in Figure 3a. It is important mentioning the difference between the height of the double-well potential and the effective energy barrier (U_{eff}) for magnetization reversal. Provided all, but Orbach mechanisms of relaxation (vide infra, Figure 3a) are prohibited, the molecules in principle can revert their magnetization moment (i.e., jumping from one potential well to other in the double-well potential) via climbing through all the possible M_J states as shown by dashed green arrows in Figure 3a. The energy required for such a magnetization reversal equals the height of the double-well potential ($U = U_{eff}$). However, in practice, spin-lattice relaxations (direct/Raman) and quantum tunneling of magnetization accompany the Orbach process. The former processes are more prone in the excited states. Therefore, it is not needed for the system to climb all the possible M_J states for magnetization reversal. In most of the Ln(III) based SIMs/SMMs, magnetization reversal takes place through first (e.g., $M_J = +15/2 \rightarrow M_J = +13/2 \rightarrow M_J = 13/2 \rightarrow M_J = 15/2$; Figure 3a) or second (e.g., $M_J = +15/2 \rightarrow M_J = +13/2 \rightarrow M_J = +11/2 \rightarrow M_J = 11/2 \rightarrow M_J = 13/2 \rightarrow M_J = 15/2$; Figure 3a) excited state [13,17–20]. Therefore, the effective energy (U_{eff}) required for the magnetization reversal is the energy between the ground state and first excited state where $M_J = +15/2$ and $+13/2$, respectively or the ground state ($M_J = +15/2$) and the second excited state ($M_J = +11/2$), respectively in the above cases.

It is worthwhile to note that the eigenstates are not necessarily organized following the decreasing/increasing order of the M_J values. As shown in Figure 3b, the ground, the first- and second excited states for Tb analog are associated with $M_J = \pm 6, \pm 5$ and 0 , respectively. On the other hand, those states for Dy analog correspond to $M_J = \pm 13/2, \pm 11/2$ and $\pm 9/2$, respectively. However, the best performing SMMs are indeed those for which magnetization relaxes via the third [21], fourth [22] and even fifth [23] excited states since this provides a larger anisotropy barrier.

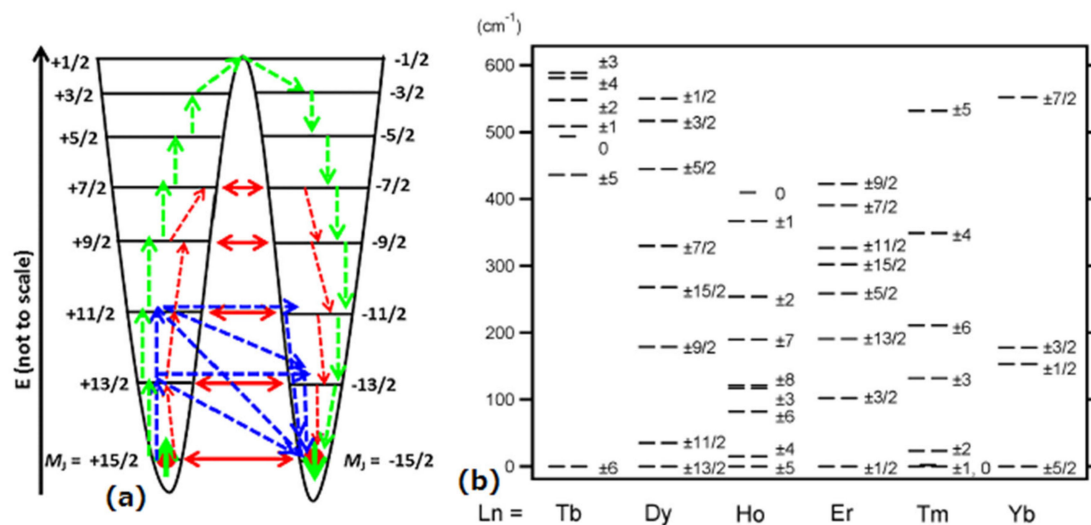


Figure 3. (a) The most common mechanisms involved in the magnetization relaxation of magnetically bi-stable systems. Color codes: green = thermally activated (Orbach) process; red = quantum tunneling of magnetization (QTM) or thermally assisted (TA) QTM; blue = phonon-triggered direct (Raman) spin-lattice relaxation. (b) calculated angular dependence (approximate) of every lanthanide magnetic state. Reproduced with permission from [5,24,25]; Published by Elsevier, 2018, American Chemical Society, 2003 and 2004.

1.3. Phthalocyanine Double-Decker SIM and Dy(III) Triangular SIM/SMM

In 2003, Ishikawa et al. [26] (Figure 4b) reported the first example of SIM comprising Ln(III)-ions ($[\text{Pc}_2\text{Ln}]^- \cdot \text{TBA}^+$; Pc = phthalocyanine (Figure 4a); Ln = Dy, Tb; $\text{TBA}^+ = \text{N}(\text{C}_4\text{H}_9)_4^+$). The arrangement of the Pc ligands around the Ln(III) induces a sandwich structure in which the Ln(III) ions are in a D_{4d} symmetrical environment. Their energy barriers for spin reversal are reported to be 28 and 230 cm^{-1} for the Dy(III) and Tb(III) compounds, respectively. Solution ^1H NMR studies of the electronic spin dynamics of $[\text{Pc}_2\text{Tb}]^-$ molecules produced a much larger barrier of $U_{\text{eff}} = 584 \text{ cm}^{-1}$, and solid samples diluted with the diamagnetic salt $(\text{Bu}_4\text{N})\text{Br}$ also indicated considerably high barriers of 641 cm^{-1} [26]. The radical analog $[\text{TbPc}_2]$ has shown a strong frequency dependence of out-of-phase signal, with a peak maximum observed at 50 K. The resulting Arrhenius analysis revealed a remarkable $U_{\text{eff}} = 410 \text{ cm}^{-1}$, which is considerably higher than any analogous value extracted for $[\text{Pc}_2\text{Ln}]^-$ from ac susceptibility data [27].

Furthermore, in 2006, Powell et al. reported the discovery of the exotic Dy(III) triangular clusters having the formulae $[\text{Dy}_3(\mu_3\text{-OH})_2\text{L}_3\text{Cl}_2(\text{H}_2\text{O})_4]$ $[\text{Dy}_3(\mu_3\text{-OH})_2\text{L}_3\text{Cl}(\text{H}_2\text{O})_5]\text{Cl}_5 \cdot 19\text{H}_2\text{O}$ (1) and $[\text{Dy}_3(\mu_3\text{-OH})_2\text{L}_3\text{Cl}(\text{H}_2\text{O})_5]\text{Cl}_3 \cdot 4\text{H}_2\text{O} \cdot 2\text{MeOH} \cdot 0.7\text{MeCN}$ (2) in Figure 4c using *o*-vanillin as a ligand (Figure 4d). Ever since, pure Dy(III) based SMMs have drawn the attention of many investigators, as evident by the plethora of contributions with Dy(III) to this interesting field of molecular magnetism. In the Dy_3 triangle, despite an almost nonmagnetic ground state, all the characteristics of SMM have been observed with an effective energy barrier of 61.7 K, possibly derived from the thermally populated excited state. Antiferromagnetic linking of two Dy_3 triangles to form Dy_6 gave an increase in the temperature at which the magnetization is observed from 8 to 25 K, suggesting a promising strategy to increase the blocking temperature of lanthanide-based SMMs [28]. The above pioneering investigations shed light on the further development of lanthanide-based mononuclear and cluster-based SIMs and SMMs.

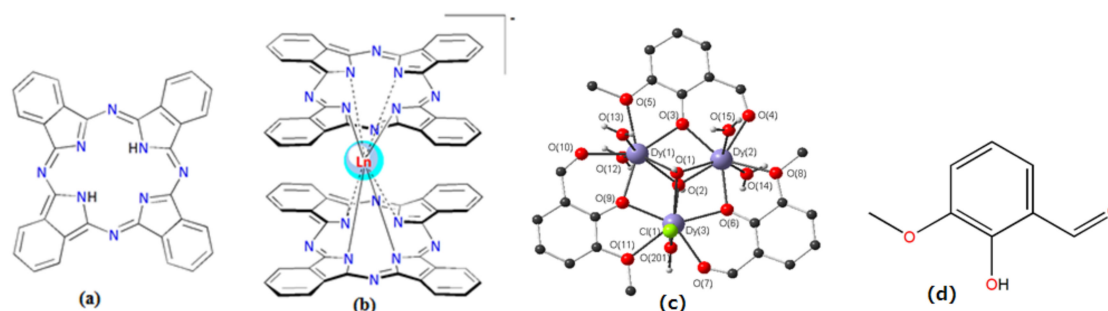


Figure 4. (a) The structure of the phthalocyanine molecule, and (b) structure of $[Pc_2Ln]-TBA^+$ (Pc = dianion of phthalocyanine, where $TBA^+ = N(C_4H_9)_4^+$ and $Ln = Tb, Dy, Ho, Er, Tm$ and Yb). (c) structure of the triangular units in **1** and **2**, (d) the structure of *o*-vanillin. Reproduced with permission from [26,29]; Published by American Chemical Society, 2003 and Wiley, 2006.

1.4. The Current Progresses in Ln(III)-Based SMMs

After the published work of Ishikawa [26], a number of Ln(III)-SMMs have been reported. Two main features are continuously optimized, namely, the energy barrier value (U_{eff}) and T_B . Before 2016, the largest record of energy barrier was 938 K [30], and the highest T_B was 14 K [31]. In 2016, a striking development of the value of the energy barrier was pushed forward. Here the complex $[Dy(bbpen)Br]$ ($H_2bbpen = N,N'$ -bis(2-hydroxybenzyl)- N,N' -bis(2-methylpyridyl)ethylenediamine) synthesized by Liu et al. [32], breaks the record of the energy barrier, surpassing 1000 K. The Dy(III) ions are in a pseudo- D_{5h} symmetry, surrounded by four neutral atoms and one bromide ion in the equatorial plane, and two oxygens occupying the capping positions. The spin flips from the ground state to the third excited doublet, which increases the effective energy barrier dramatically to 1025 K, accompanied by a magnetic hysteresis of up to 14 K.

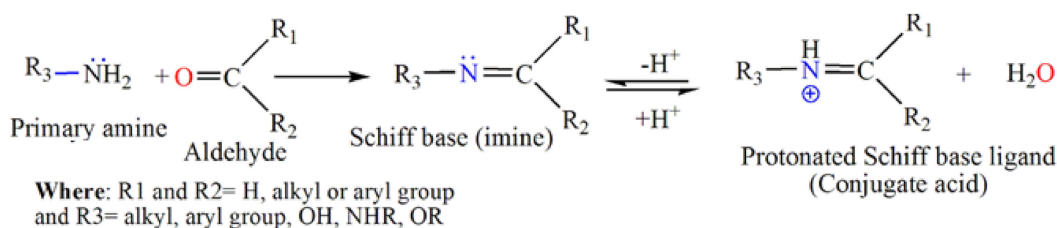
In 2018 Guo et al. also reported a dysprosium metallocene cation $[(Cp^iPr_5)Dy(Cp^*)]^+$ (Cp^iPr_5 , penta-iso-propylcyclopentadienyl; Cp^* , pentamethylcyclopentadienyl), which displays magnetic hysteresis above liquid-nitrogen temperatures with an effective energy barrier to a reversal of the magnetization of $U_{eff} = 1541 \text{ cm}^{-1}$ and having magnetic blocking temperature of $T_B = 80 \text{ K}$. In the same year, McClain and coworkers have synthesized and reported dysprosium metallocenium SMMs, $[Dy(Cp^iPr_4R)_2][B(C_6F_5)_4]$, where $R = H$ (**3**), Me (**4**), Et (**5**), iPr (**6**) [33]. A slight variation of the cyclopentadienyl ring substituents resulted in large changes of the molecular structures and in an increase of 45 K in the operating temperature for **3–6** and also led to the manifestation of the highest 100 s blocking temperatures reported for an SMM till now. Complex **3** has the highest operating temperature along the series, having a 100 s T_B at 62 K. It is interesting to note that **4** displays an energy barrier of 1468 cm^{-1} with hysteresis at 72 K [33].

By comparing the success of different SMMs, the bigger the magnitude of the anisotropic barrier, the more prominent the SMM properties at higher temperatures. A breakthrough in SMM based technology can only be achieved when these two major problems get addressed. One of the imposing challenges in this field is to design and synthesis well-organized SMMs, that operating at ambient temperature for practical uses [6,34].

2. Schiff Base Ligands

Schiff bases are prepared from amines and aldehyde precursors by condensation reaction [35] (Scheme 1). The ligand designs can be tailored by incorporating new functionalities to either the aldehyde or the amine precursor component. This makes them ideal candidates for the development of a library of ligands for metal aggregate synthesis. The number of amino and keto precursors that can be selected for condensation reactions, leading to azomethine compounds, are numerous and practically limitless [35]. The careful selection of both aldehydic and amino precursors enables us to perfectly switch the donating ability of the resulting ligands, the nature of the donor atoms and the

number of the chelating motif. Moreover, one or both precursors can be decorated with bulky groups that can further influence the stereochemistry of the metal ions.



Scheme 1. The condensation mechanism of carbonyl compounds with primary amines. Reproduced from [35]; Published by Wiley, 1864.

3. Designing Schiff Bases in Ln(III)-Based SMM Systems

Schiff base ligands have been widely used for the purpose of synthesizing Ln(III)-based SMMs [36–39]. The growing interest in Ln(III)-SMMs leads to a great demand for ligand architecture since the coordination environment is the main factor in the properties of metal aggregates. Usually, Schiff base ligands are derived from aldehydes and primary amines, reactions commonly taking place in alcohol through condensation [40]. The straightforward synthesis could be one of the reasons that Schiff base ligands are so popular, and also the basic imine nitrogen, which exhibits pi-acceptor property, shows affinity to Ln(III) ions, making it the preferred choice.

Additionally, Schiff base ligands can be easily modified by controlling the amines and aldehydes of different sizes, flexibilities and basicities [41,42], which provides different “pockets” for Ln(III) ions to occupy the resulting dinuclear, trinuclear, tetranuclear and even more polynuclear structures [43–46]. Additionally, the flexibility of the diamines or the linkers potentially introduces chirality to the complex by increasing the chances of forming helicate or mesocate structures [47]. Schiff base ligands derived from *o*-vanillin have proven to be particularly suitable for the synthesis of Ln-SMMs [37–39,45,46,48]. In his recent review, Andruh has discussed several relevant structural types of heterobinuclear 3d–3d' and 3d–4f complexes obtained from *o*-vanillin-based Schiff ligands, which show interesting magnetic, luminescence, catalytic, cytotoxic, and ferroelectric properties [49].

The ligands can be designed to provide a coordination environment favored by a 3d metal such as Mn(III) or Cu(II) (relatively N rich) as well as a site (relatively O rich) more favored by a “hard” metal ion such as Fe(III) or any Ln(III). For example, combining *o*-vanillin and tris(hydroxymethyl) aminomethane to give the ligand (H₄L, Chart 1) provides a system that captures two Ln(III) and transition metal ions [50]. While this ligand had been previously employed to prepare homometallic clusters [51], it seemed reasonable to expect that the oxygen donor rich tripodaltris(hydroxymethyl) aminoethane derived group would capture the oxophilic Ln(III), while the transition metal in +2 oxidation state like ions would be coordinated by both the imine nitrogen and oxygen donors [51]. Schiff base ligands can also be designed with the aim of getting spin-crossover (SCO) materials [52].

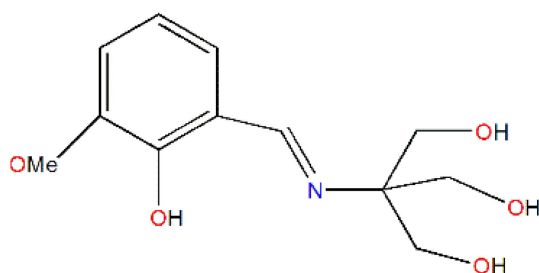


Chart 1. The Schiff base ligand derived from *o*-vanillin H₄L.

Some important theoretical and experimental studies on Ln(III)-based Schiff base complexes, namely Dy-(trenovan), have been done by Lucaccini et al. The studies reached the conclusion that the crucial parameter in determining the slow relaxation of the magnetization is the number of unpaired electrons (only Kramers ions showing in-field slow relaxation) than the shape of the charge distribution for different Ln(III) ions when the complex exhibits trigonal symmetry and the Ln(III) ion is heptacoordinated [53].

With respect to the scope of the review, we have attempted an overview on the synthesis, structural and magnetic properties of Ln(III)-based complexes with the following list of Schiff base ligands (HL1–H₂L20), mainly of salicylaldehyde origin (Chart 2).

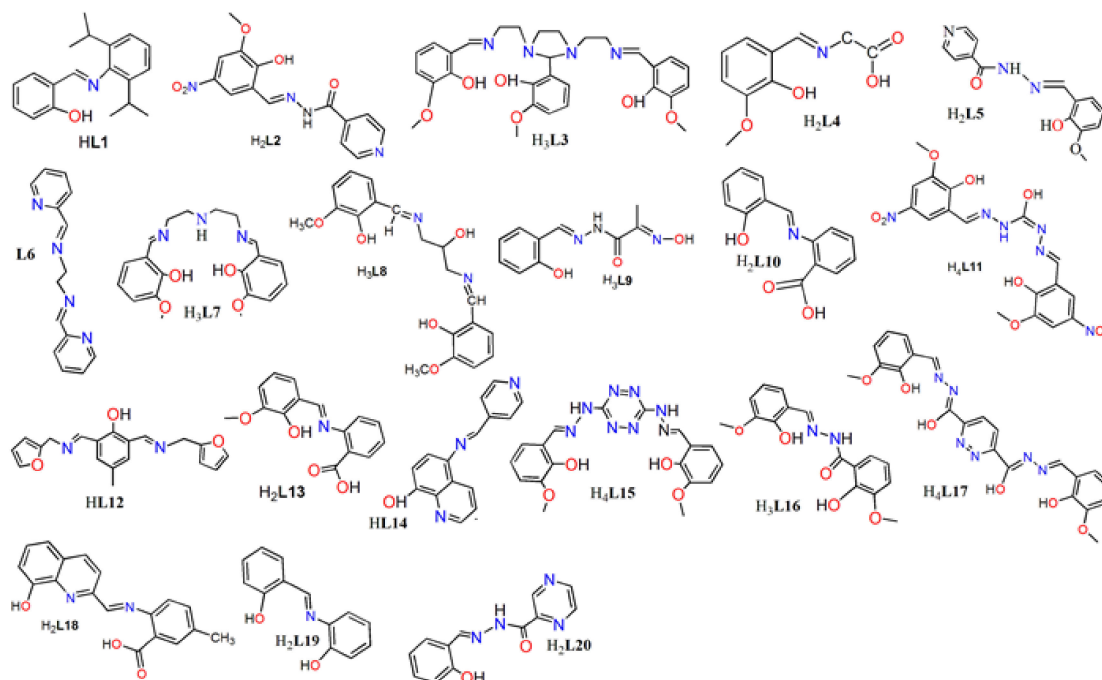


Chart 2. List of selected Schiff base ligands mainly of salicylaldehyde origin in the present review.

4. Ln(III)-Based Schiff Base SMMs of Different Nuclearities

In the following sections, we are discussing the lanthanide complexes of Schiff base ligands listed in Chart 2 of different nuclearity varying from mononuclear to hexanuclear, with a special reference to their synthetic strategy, structure and magnetic behavior.

4.1. Mononuclear Schiff Base Ln(III)-Complexes of SMMs

Gou and Tang have reported six coordinate Ln(III) complexes with the general formula [Ln(L1)₃] (Ln = Dy (7) and Er (8), having isostructure with the metal ion in distorted trigonal-prismatic coordination geometry, Where HL1 = 2-(((2,6-diisopropylphenyl)imino)methyl)-phenol) (Figure 5a). Complexes 7 and 8 are isostructural (Figure 5b) with an RT; the $\chi_M T$ values (Figure 5c) of 7 and 8 are 13.77 and 11.38 cm³ K mol^{−1}, respectively. For 7, $\chi_M T$ gradually decreases on decreasing T till 2 K, reaching the value of 11.60 cm³ K mol^{−1} for 7 [54]. The τ vs. T^{-1} plots the presence of more than one relaxation pathway with a crossover from a linear increase of thermally activated to a temperature-independent regime of QTM (Figure 5d) [54].

Both in-phase (χ') and out-of-phase (χ'') ac susceptibilities for complex 7 show frequency and temperature dependence (Figure 6a). However, no maximum peaks of the temperature dependence of the out-of-phase (χ'') signal are observed in the range of 1–1488 Hz, which may be caused by the quantum tunneling of the magnetization (QTM), as indicated by strong temperature-independent peaks below 9 K (Figure 6a) [54]. For 8, there are no out-of-phase (χ'') signals observed above 1.9 K at

997 Hz, attributed to the quick quantum tunneling of the magnetization at zero dc field. The rather different magnetic properties of **7** and **8** are correlated with the axial ligand field of trigonal-prismatic coordination geometry, as Dy(III) is oblate and Er(III) is prolate [13].

Both **7** and **8** show frequency and temperature-dependent and temperature-dependent χ' and χ'' signals (Figure 6a) at low-temperature [54], proving its field-induced SMM behavior. The Cole–Cole plots (Figure 6b) of both **7** and **8** are asymmetrical semicircular in shape and can be well fitted by the generalized Debye model, with a series of α parameters below 0.11 from 1.9 to 13 K and 0.13 from 1.9 to 3.7 K, respectively, which shows a narrow distribution of the relaxation time for both complexes [54]. Complex **7** shows the features of SMMs under zero dc field with an effective energy barrier of 31.4 K while **8** shows SMM characteristic under an external field of 400 Oe with an effective energy barrier of 23.96 K.

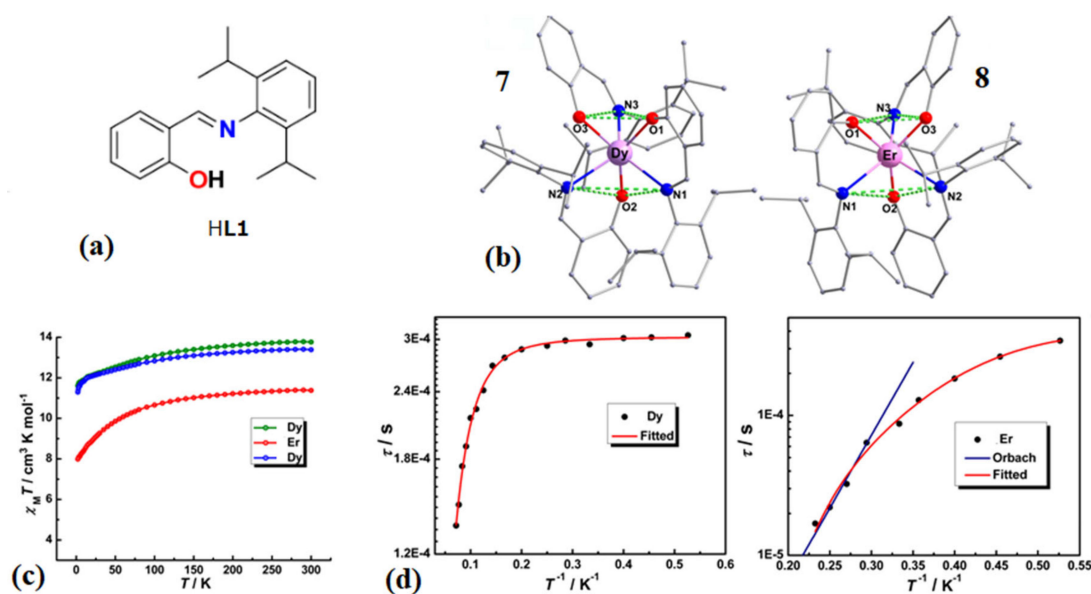


Figure 5. (a) The structure of HL1, (b) the molecular structures of complexes **7** (left) and **8** (right), (c) plots of the $\chi_M T$ vs. T for **7** and **8** in an applied field of 1 kOe, (d) plots of τ vs. T^{-1} for **7** (left) and **8** (right), respectively. Reproduced from [54]; Published by MDPI, 2018.

Cheng and coworkers synthesized and characterized two mononuclear complexes with the general formula, $[\text{Ln}(\text{L3})(\text{NO}_3)(\text{DMF})_2] \cdot \text{DMF}$ (**9**·DMF) and $[\text{Ln}(\text{L2})_2(\text{H}_2\text{O})_2] \cdot \text{NO}_3 \cdot \text{EtOH}$ (**10**·NO₃·EtOH) [55], where Ln = Dy, with two Schiff bases with an electron-withdrawing group NO₂ where ($\text{H}_2\text{L2}$ = 2-(hydroxyl-3-methoxy-5 nitrophenyl)methylene(isonictino)hydrazine (Figure 7d).

Complex **9** (Figure 7a) is a nine coordinated species having a spherical tricapped trigonal prism geometry with one $\text{H}_2\text{L2}$, two nitrates and two DMF molecules in the coordination sphere. The Schiff base ligand $\text{H}_2\text{L2}$ coordinates through both oxygen atoms (O1 and O2) and one N atom (N3) to the central metal ion. Upon comparing with the earlier report, $[\text{Dy}(\text{hmb})(\text{NO}_3)_2(\text{DMF})_2]$ (Hhmb: N' -(2-hydroxy-3-methoxybenzylidene)benzohydrazide) [56], it is interesting to note that the electron-withdrawing nature of the nitro group para to the phenoxide group in $\text{H}_2\text{L2}$ has a pronounced effect on the coordination nature of the ligand. Complex **10** is 8 coordinated species with a spherical triangular dodecahedron geometry with two ligands as well as two water molecules. The ligands are coordinated in keto form and NO_3^- are also present in the crystal lattice as a counter anion (Figure 7b) [55].

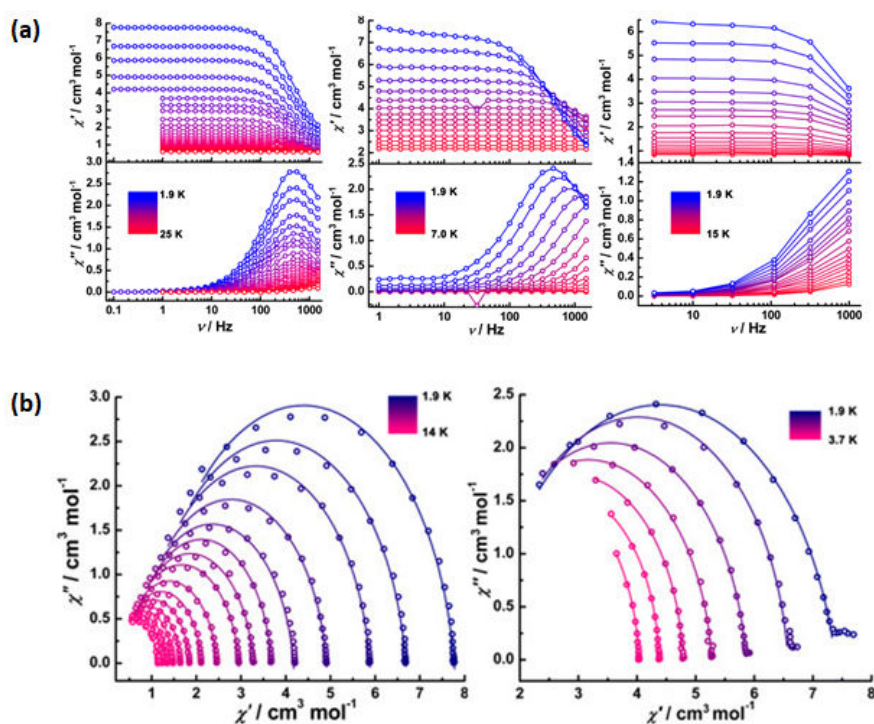


Figure 6. (a) Frequency-dependent in-phase χ' (top) and out-of-phase χ'' (bottom) AC susceptibilities for **7** (left) under 0 Oe DC field and **8** (right) under 400 Oe DC field, (b) Cole–Cole plots for **7** (left) and **8** (right) at the indicated temperature. Reproduced from [54]; Published by MDPI, 2018.

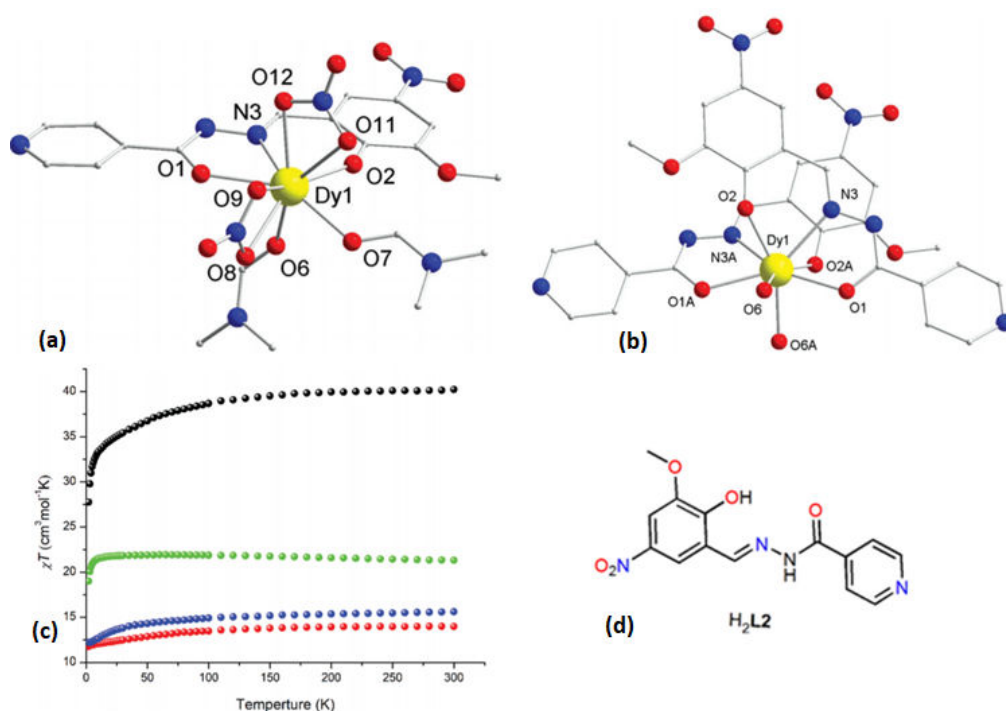


Figure 7. (a) Molecular structures of complex **9**, (b) molecular structure of complex **10**, (c) χT product of complexes **9** (red) and **10** (blue) at 1000 Oe, (d) the structures of H₂L2. Reproduced with permission from [55]; Published by Royal Society of Chemistry, 2019.

The RT value of χT for complexes **9** and **10** are 13.96 and 14.69, $\text{cm}^3 \text{K mol}^{-1}$, respectively (Figure 7c), and a gradual decrease with temperature for both complexes may be due to inherent magnetic anisotropy from the Dy(III) ion, the stark level depopulation and/or occurring of SMM behavior [55]. The AC measurements show out of phase signal χ'' below 11 K for **9** indicate low-temperature SMM behavior (Figure 8a,b). Compound **9** exhibits an anisotropic energy barrier of $U_{\text{eff}} = 34 \text{ K}$ [55].

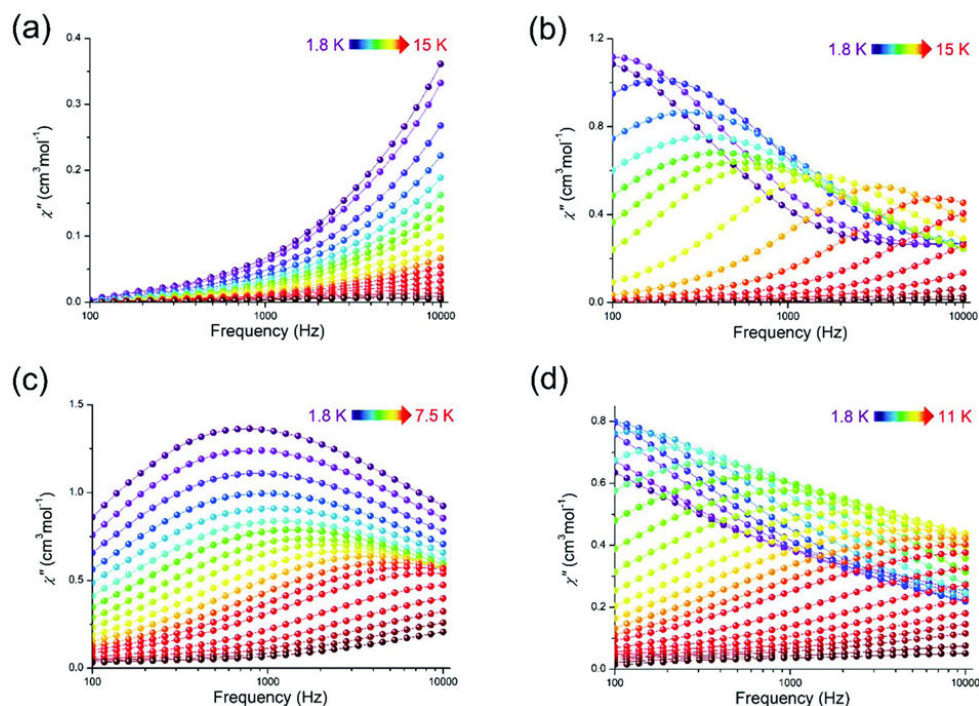


Figure 8. AC measurement showing out of phase signal (χ'') under zero DC field for complex **9** (a,b) (400 Oe) and **10** (c,d (800 Oe)). Reproduced with permission from [55]; Published by Royal Society of Chemistry, 2019.

For **10**, the dynamics of magnetization shows a frequency χ'' in the absence of DC field (Figure 8c). The effective energy barrier and relaxation time are $U_{\text{eff}} = 19 \text{ K}$ and $\tau_0 = 3.8 \times 10^{-7} \text{ s}$, respectively, which is larger than that of complex **9**. The AC measurements of various DC fields show that the broad peaks under 200 and 400 Oe, is an indication of multiple exchange interactions with tunneling electrons [55]. For further investigation of QTM, the AC measurements were done under the magnetic field of 800 Oe. However, the relaxation got slower with a higher energy barrier of $U_{\text{eff}} = 41 \text{ k}$ [55].

4.2. Dinuclear and Trinuclear Schiff Base Ln(III) SMM Complexes

The investigations on multinuclear Ln(II) systems were very crucial with respect to the advancement of T_B , and these types of compounds generated showed significant progress to quench QT effects. Hence, designing ligands with appropriate symmetry, and incorporating Ln(III) centers, may enhance exchange coupling and quench the QT effects. Controlling intermolecular interactions using bulky counter anions/ligands and then utilizing enriched lanthanides to avoid hyperfine couplings is a hot research area in molecular magnetism in general and Ln(III) based Schiff base SMMs in particular. Here we are attempting to show how these different multinuclear Schiff base Ln(III) compounds derived from salicylaldehyde derivatives will have an effect on quenching QT and thereby generating SMMs with improved T_B .

Tang and coworkers have prepared isomorphous dinuclear Ln(III)-complexes [57] having the formula of $[\text{Ln}_2(\text{HL}_3)_2] \cdot n\text{CH}_3\text{CN}$, where Ln = Gd (**11**), Tb (**12**) with $n = 0$ and Ln = Dy (**13**) with $n = 4$ and $\text{H}_3\text{L}_3 = \text{N}1, \text{N}2, \text{N}3, \text{N}4$ -tri(3-methoxysalicylidene)triethylenetetraamine) (Figure 9d). H_3L_3 behaves as a heptadentate ligand coordinating through three phenoxide oxygens and four azomethine nitrogen. It is interesting to note that the three methoxy oxygen of H_3L_3 is not coordinated in the complex [57].

The Ln(III)-coordination sphere of **11–13** are slightly longitudinally compressed with comparable parameters of skew angles (φ) 56.03, 56.12 and 55.64°, respectively. As shown in Figure 9a, the ligand binds to the central metal ion through the N_4O_4 coordination environment generating a square-antiprismatic geometry (SAP). The α angles shown in Figure 9c corresponds to the magic angle, 54.74° for **13** using H_3L_3 [57]. Here the obtuse and acute angles are in accordance with the compression and elongation along the tetragonal axis [12]. However, the φ values, 42.9, 36.9 and 42.9° of **11–13** show that in **12**, the coordination sphere deviates from the ideal square-antiprismatic than **11** and **13** (Figure 9b). The shortest intermolecular distance between Dy(III)-ions (from different dinuclear units) is 9.142 Å, and this shows that there are no significant intermolecular interactions [57].

For **11**, the $\chi_M T$ remains constant till 50 K, then shows a sharp decrease to a minimum value of 10.64 cm³ K mol^{−1} at 2 K, suggesting dominant intramolecular antiferromagnetic interaction between Gd(III) ions (Figure 10b). The RT DC magnetic susceptibilities of **11–13** in a magnetic field of 1000 Oe are 14.98, 21.82 and 26.99 cm³ K mol^{−1}, respectively (Figure 10a). The variation in these values from the expected theoretical values is due to the weak magnetic exchange interaction between the metal centers through the bridging phenoxy group. The magnetization (M) data for **11–13** in 0–70 kOe field below 5 K shows the occurrence of weak antiferromagnetic coupling for **11** (Figure 10b). The AC measurement of **13** exhibits a frequency-dependent out-of-phase signal under 800 Oe DC field, showing slow relaxation of magnetization having an energy barrier of 18.9 K (Figure 10c) [57]. For **13**, above 3.5 k, the magnetic relaxation follows a thermally activated Orbach mechanism having an energy gap of 18.9 k (Figure 10d).

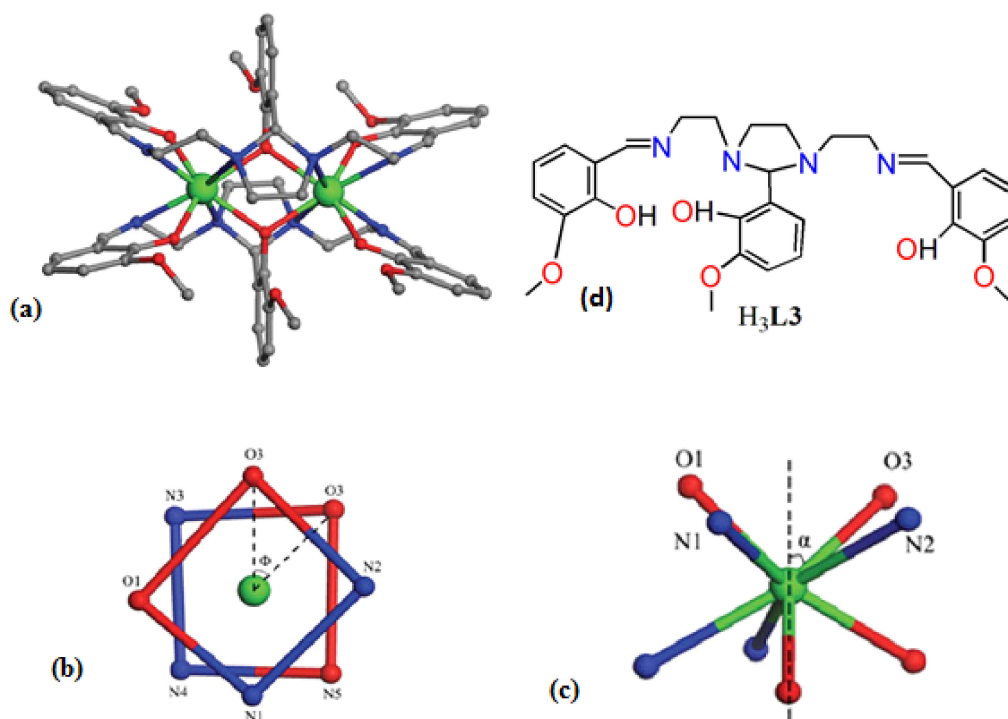


Figure 9. (a) Molecular structure of **13**, (b) SAP environment with skew angle φ between the diagonals of the two squares of **11**, (c) angle between the S_8 axis and Dy-L vector (α) of **13**, (d) the structure of H_3L_3 . Reproduced with permission from [57]; Published by Royal Society of Chemistry, 2013.

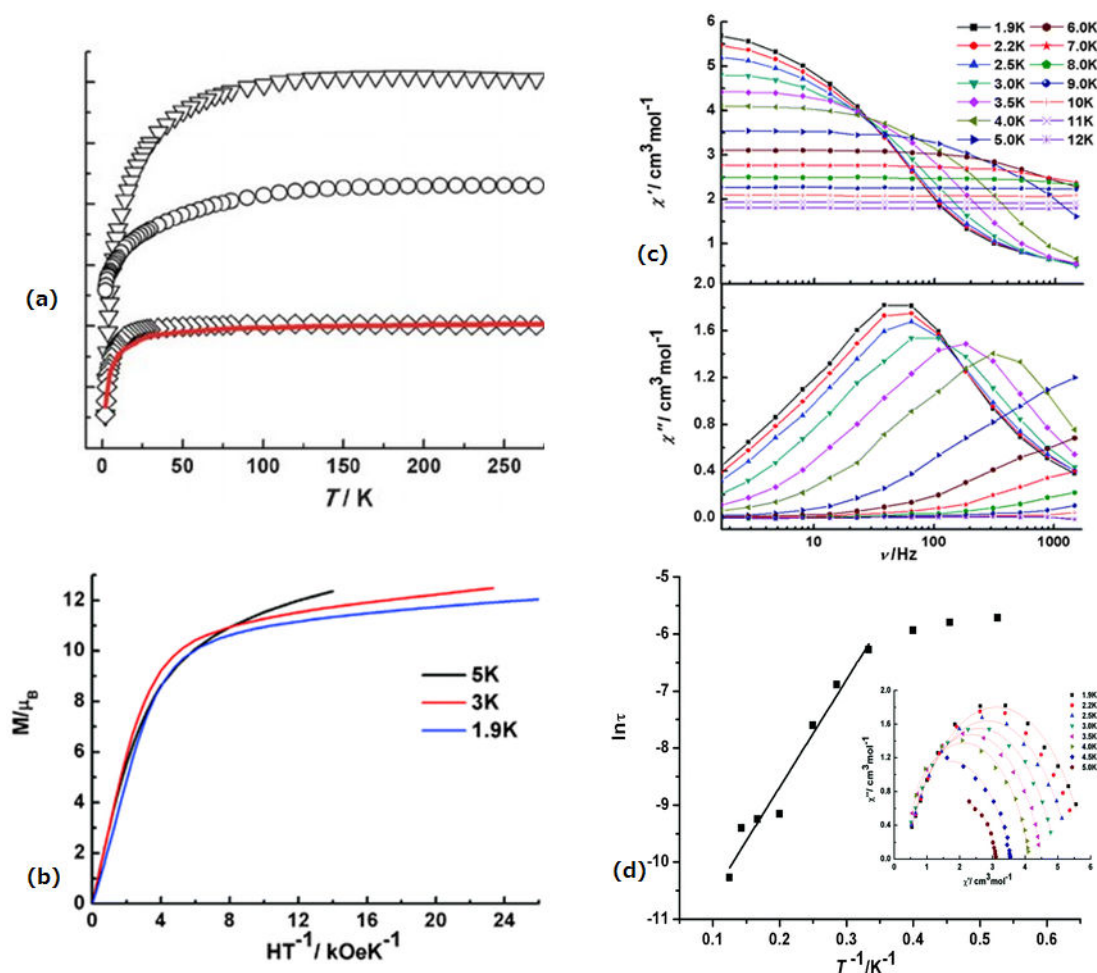
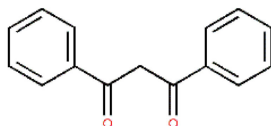


Figure 10. (a) $\chi_M T$ vs. T for 11–13 (b) M vs. H/T plots for 13 at indicated temperatures, (c) AC susceptibility measurement of 13 (d) $\ln \tau$ vs. T^{-1} plot for 13. Reproduced with permission from [57]; Published by Royal Society of Chemistry, 2013.

In this class of compounds, another dinuclear mixed ligand complex, $[\text{Dy}_2(\text{L4})_2(\text{DBM})_2(\text{DMF})_2] \cdot 3\text{CH}_3\text{OH}$ (**14**), (Figure 11b), has been synthesized by Zhang et al. (Where $\text{H}_2\text{L4}$ = 2-((2-hydroxy-3-methoxybenzylidene)amino)acetic acid, HDBM = dibenzoylmethane) (Chart 3). The structure of **14** consists of two crystallographically independent units of neutral centrosymmetric dinuclear complex, with two Dy(III), two dianionic (L4^{2-}) (Figure 11a), two bidentate monoanionic DBM^- ligands and two terminal DMF by generating a NO_7 coordination environment with a square-antiprismatic coordination geometry [58].



HDBM

Chart 3. The structures of HDBM.

The M vs. H plots for **14** below 5 K (Figure 11c) gives a relatively fast increase of the magnetization at low fields followed by a slow linear increase at high fields reaching the values of $10.7 N_\beta$ up to 70 kOe at 2 K, which is supported by the observation that the M vs. HT^{-1} curves at different fields (Figure 11c, bottom), are not superimposed on a single master-curve [59]. The complex **14** shows a frequency-dependent χ' and χ'' , exhibiting slow relaxation. The maximum value of χ'' for 1488 Hz is

observed approximately at 3 K [59]. From the χ'' vs. χ' , (Figure 11d), an effective energy barrier of 11 K is obtained for **14** (Figure 11e) [60].

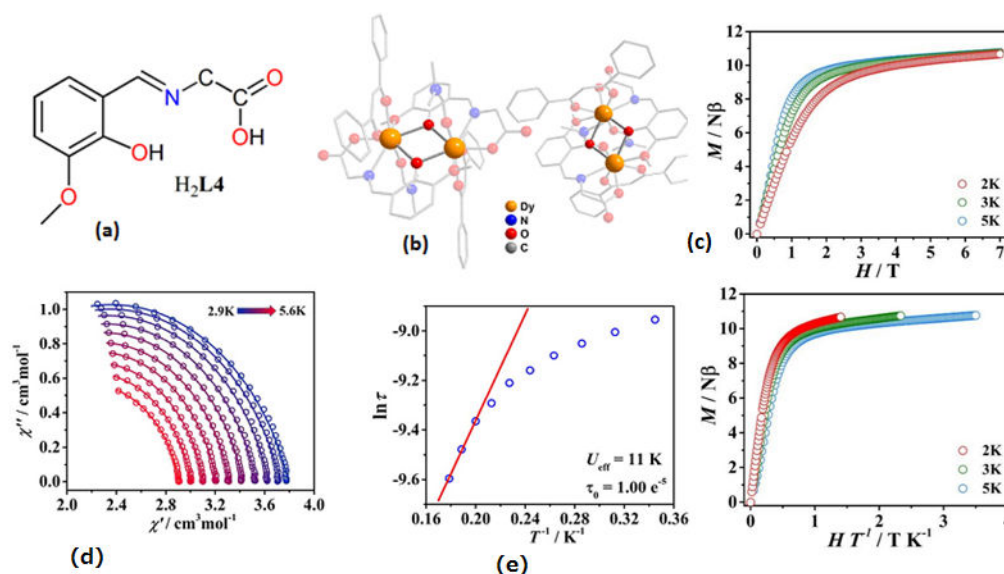


Figure 11. (a) The structure of H_2L4 , (b) molecular structure of complex **14**, (c) field dependence of the magnetization (M) at 2, 3 and 5 K for complex **14** plotted as M vs. H (left) and M vs. HT^{-1} (right), (d) the Cole–Cole plot for complex **14** (e) plot of $\ln \tau$ vs. $1/T$ plot for **14**. Reproduced with permission from [58]; Published by American Chemical Society, 2003.

Murugesu et al. have discussed the use of the pro-ligand (2-hydroxy-3-methoxyphenyl) methylene(isonicotino)hydrazine (H_2L5) (Figure 12c), in reactions with Dy(III), because of its ability to act as a rigid chelate [38]. By reacting penta-aqua Dy-nitrate, $Dy(NO_3)_3 \cdot 5H_2O$, with H_2L5 in methanol (with the presence of triethylamine) in a 3:1 mixture of acetonitrile and methanol (in the presence of pyridine), pale orange crystals of $[Dy_2(HL5)_2(NO_3)_2(MeOH)_2](15)$ and $[Dy_2(HL5)_2(NO_3)_2(MeOH)_2]_{\infty}(MeCN) \cdot (2MeCN)(16)$ were obtained (Figure 12a,b). Phenoxide-bridged Dy-dimers resulted from this reaction, where the positioning of the pyridyl groups helps the formation of an extended network that can control the arrangement of the SMM units in a three-dimensional way. However, with regard to complex **16**, the pyridyl N atoms further coordinate to the Dy atoms of the adjacent complexes forming a two-dimensional network of the dimetallic Dy complexes. Dy(III) is eight coordinated in **15** and **16**, and a square-antiprismatic geometry may be assigned in both cases [38].

The magnetic properties of **15** and **16** are somewhat similar as they possess the same coordination environment (Figure 12d). At RT, the $\chi_M T$ values of 30.4 and 30.0 $cm^3 K mol^{-1}$ for **15** and **16**, respectively and they are in accordance with the expected value of 28.34 $cm^3 K mol^{-1}$ for two Dy(III) ions [61,62]. For both complexes, the $\chi_M T$ product remains roughly constant before reaching a minimum value of 29.3 $cm^3 K mol^{-1}$ at 23 K. The $\chi_M T$ then sharply increases to a maximum value of 38.4 $cm^3 K mol^{-1}$ for **15** and 36.6 $cm^3 K mol^{-1}$ for **16** at 1.8 K, which confirms the presence of intramolecular ferromagnetic interactions between metal centers [38].

Repeated magnetic measurements on **16** showed that this compound possessed one of the largest energy barriers, at 71 K, reported for an Ln(III)-complex at that time with Schiff base ligands. The magnetization curve below 10 K exhibits a rapid increase at low field, which is expected for ferromagnetically coupled spins. Magnetization increases linearly up to 11.9 μ_B (**15**) and 11.6 μ_B (**16**) at 1.8 K and 7 T without clear saturation. From the M vs. H/T data inset (Figure 12d), we can reach a conclusion that there is a significant magnetic anisotropy and/or low-lying excited states in these compounds. It is interesting to note that the M vs. H data does not exhibit a hysteresis effect above 1.8 K, but below 12 K (at about 1500 Hz), the indication of out-of-phase AC signal reveals a slow relaxation of the magnetization (Figure 12e) [38].

From the frequency dependence measurement, the relaxation time (τ) is derived and is plotted as a function of $1/T$ (in the range 1.8–10 K) (Figure 12e). The dynamics of **15** and **16** below 2 K are temperature-independent as expected in a pure quantum regime with a τ value of 0.3×10^{-2} s and 1.2×10^{-2} s for **15** and **16**, respectively and above 2 K, the relaxation becomes thermally activated. Above 8 K, remarkably big energy barriers are observed at 56 K and 71 K, and the pre-exponential factors of the Arrhenius laws (τ_0) are 3×10^{-7} s and 7×10^{-8} s for **15** and **16**, respectively.

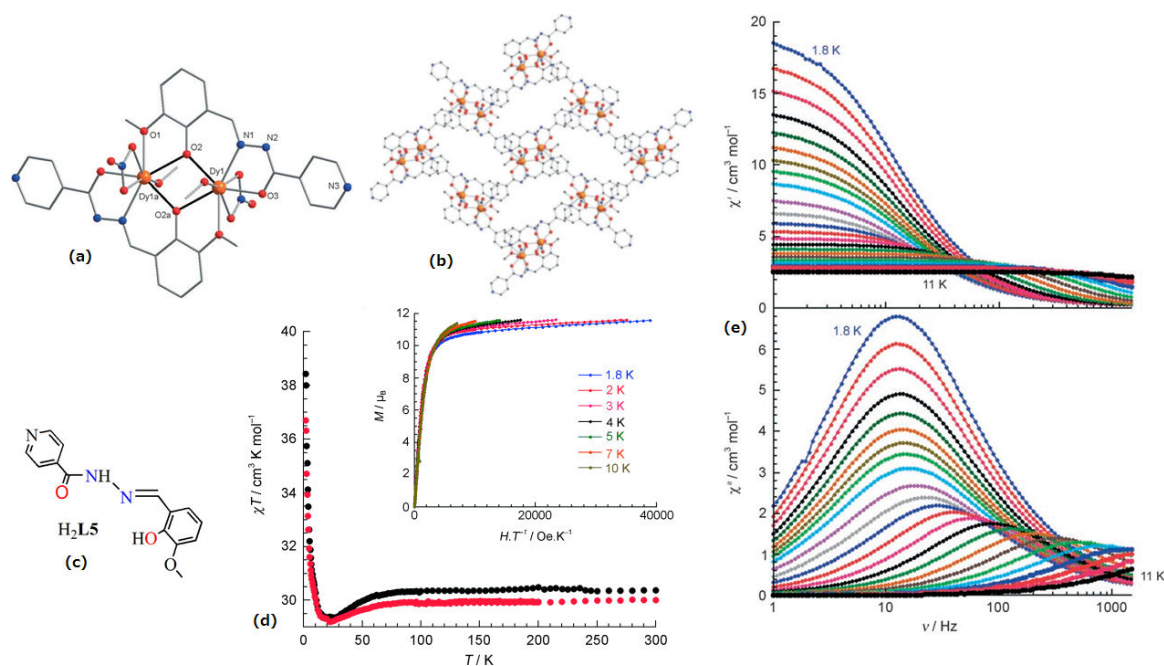


Figure 12. (a) the molecular structure of the centrosymmetric complex **15**, (b) 2D network of complex **16** as viewed along the c axis, (c) the structure of H_2L5 , (d) temperature dependence of the χT product at 1000 Oe for **15** (black) and **16** (red) (with $\chi = M/H$ normalized per mol): Inset M vs. H/T plot at low-temperatures for **16**, (e) frequency dependence of the in-phase (χ') and out-of-phase (χ'') AC susceptibility from 1.8 to 3.2 K at an interval of 0.2 K and from 3.5 to 11 K at an interval of 0.5 K under zero DC field for **16**. Reproduced with permission from [38]; Published by Wiley, 2008.

In 2016 a new family of five new isostructural Ln(III)-complexes with the general formula $[Ln_2(DBM)_6(L6)]$ (where Ln = Sm, Eu, Gd, Dy, Yb; **L6** = N,N' -bis(pyridin-2-ylmethylene)ethane-1,2-diamine (Figure 13a), DBM = dibenzoylmethane have been reported by Sun et al. (Chart 3). Based on the single-crystal analysis, all the complexes are isomorphic and for discussion, let us take the example of Dy(**17**) and Yb(**18**) complexes. (Figure 13b,c) which have one ligand (**L6**), two Yb(III) ions and six DBM molecules, generating a distorted square antiprismatic geometry [63].

Compound **17** and **18** have the RT $\chi_M T$ values of 28.21 and 5.53 cm³ K mol⁻¹, respectively (Figure 13d). For **17**, there is the first drop of $\chi_M T$ vs. T occurring due to the thermal depopulation of the magnetic energy levels split by the crystal field. Below 60 K, a second drop occurs may be because of intramolecular antiferromagnetic coupling. The $\chi_M T$ for **18** declined along with the temperature and went down to 1.85 cm³ K mol⁻¹ at 2 K. For **17** and **18**, the magnetization curves show a saturation value of 11.1 μ_B (top) and 3.5 μ_B (bottom), respectively at 2 K and 70 kOe, which is lower than the expected saturation value. This may be due to the anisotropy and important crystal field effects at the Dy(III)-ion that eliminate the 16-fold degeneracy of the $^6H_{15/2}$ ground state [63]. The energy barriers for **17** and **18** are 46.8 K and 23.0 K, respectively (Figure 13e) [63].

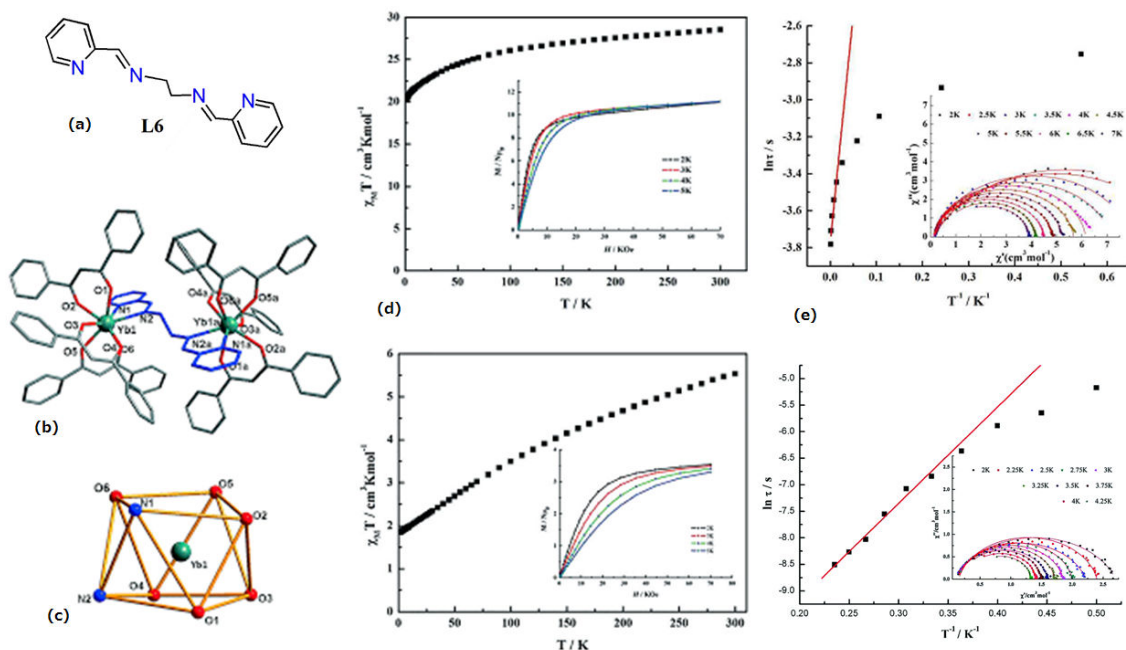


Figure 13. (a) The structure of **L6**, (b) the molecular structure of **18**, (c) coordination polyhedron for **18**, (d) $\chi_M T$ vs. T at 1000 Oe field for **17** (top) and **18** (bottom): the field dependence of magnetization for **17** (top) and **18** (bottom) at 2.0–5.0 K (insets), (e) magnetization relaxation time, $\ln \tau$ vs. T^{-1} for **17** (top) and **18** (bottom) under a DC field of 2000 Oe. Reproduced with permission from [63]; Published by Royal Society of Chemistry, 2016.

In 2011 a family of five dinuclear Ln(III)-complexes having the general formula $[\text{Ln(III)}_2(\text{L7})_2(\text{NO}_3)_2]$, where ($\text{H}_3\text{L7} = \text{N1,N3-bis(3-methoxy salicylidene) diethylene triamine}$) and $\text{Ln(III)} = \text{Eu(III)}$ (**19**), Gd(III) (**20**), Tb(III) (**21**), Dy(III) (**22**), and Ho(III) (**23**) were reported by Murugesu et al. having an intermediate coordination geometry between square antiprism (D_{4d}) and dodecahedron (D_{2d}) for all complexes [37]. The Ligand $\text{H}_3\text{L7}$ (Figure 14a), with a large inner compartment having N_3O_2 coordination sites, is particularly appropriate to accommodate a sizable 4f-ion. While in a previous study of 2007, Dou et al. structurally characterized two mononuclear complexes with the same ligand $\text{H}_3\text{L7}$ with large La(III) and Nd(III) ions where the outer donor O_4 set of $\text{H}_3\text{L7}$ was involved in the coordination [64], but in Murugesu's report, the synthetic methods they promptly employed the functionality to promote coordination in both compartments of $\text{H}_3\text{L7}$. For a matter of discussion, the structure of the Dy-analog, compound **22**, was described as in-depth as a representative of the other families (Figure 14b).

For all compounds **19–23** (Figure 14c) at RT, the χT values are in good agreement with the expected theoretical values for two non-interacting Ln(III)-ions. For the europium analog **19**, the nonmagnetic ground state ($^7\text{F}_0$) is observed at low-temperatures as indicated by the χT value of $0.04 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K [2]. While in the gadolinium analog **20**, the decrease of the χT when lowering the temperature reveals the presence of antiferromagnetic interaction between the Gd(III) ions. For complexes, **21–23**, the χT vs. T curves for complexes **21–23** reach a value of 10.2, 5.2, and $7.1 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K, respectively (Figure 14c). The frequency dependence of the maximum of **22** related only with a single relaxation process and which appears clearly on a tridimensional plot of the variation of χ'' vs. the temperature and the frequency of the oscillating field between 1 and 1500 Hz (Figure 14e), confirming the slow magnetic relaxation. Here, the existence of a single relaxation process agrees with the presence of a unique crystallographic Dy(III) ion in the dinuclear structure. The relaxation process in the tridimensional plot gives two regimes of relaxation, as indicated in Figure 14e. The χ'' vs. χ' in the temperature range 2–12 K additionally confirms the single relaxation process (Figure 14d). The effective energy barrier obtained from fitting, for **22** (Figure 14f), is $U_{\text{eff}} = 76 \text{ K}$ [37].

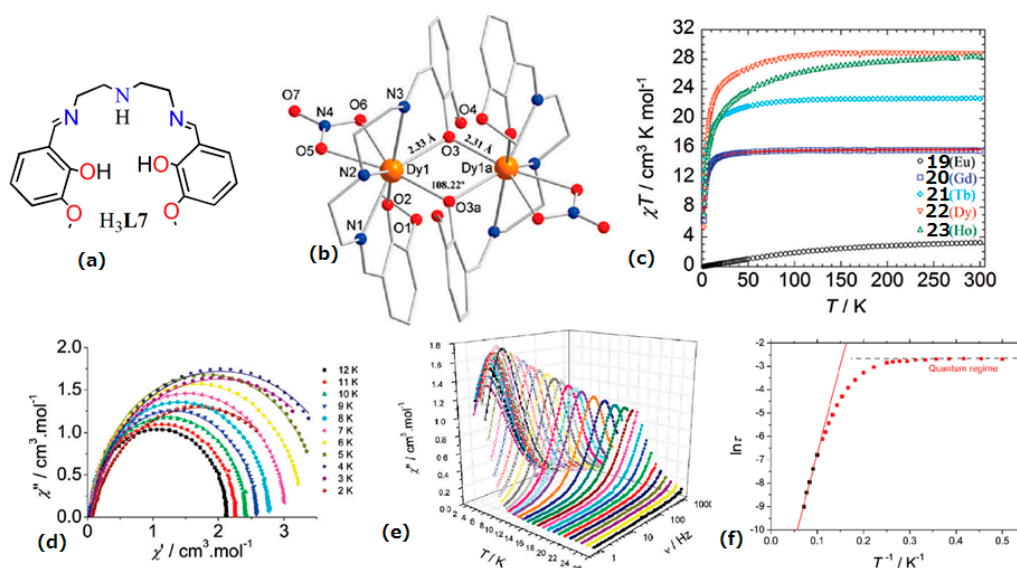


Figure 14. (a) The structure of H_3L7 , (b) the molecular structure of **22**, (c) temperature dependence of the χT product at 1000 Oe for complexes **21–23**, (d) Cole–Cole plot for **22** obtained using the AC susceptibility data, (e) out-of-phase susceptibility χ'' vs. frequency ν (logarithmic scale) in the temperature range 2–25 K for **22**, (f) relaxation time of the magnetization $\ln \tau$ vs. T^{-1} (Arrhenius plot using AC data) for **22**. Reproduced with permission from [37]; Published by American Chemical Society, 2011.

Zhang and coworkers have prepared two new mixed ligand dinuclear Ln(III)-complexes, $[Ln_2(HL8)(DBM)_4] \cdot 2CH_3OH$ ($Ln = Gd$ (**24**) and Dy (**25**) [65], $H_3L8 = N,N'$ -bis(3-methoxysalicylidene)-1,3-diamino-2-propanol (Figure 15a), and $Hdbm = 1,3$ -diphenyl-1,3-propanedione) (Chart 3). As a representative, complex **24** is discussed, and its crystal structure is depicted in Figure 15b. The asymmetric unit consists of two $Gd(III)$ -ions, one $HL8^{2-}$, four dbm^- ligands and two free methanol molecules. The two $Gd(III)$ ions in the Gd_2 dimeric unit are bridged by three μ_2-O atoms from two $HL8^{2-}$ (O2 and O4) and one dbm^- (O8), respectively (Figure 15c) [65]. The $Gd1$ located in an N_2O_6 pocket (N1, N2, O2, O4, O6, O7, O8 and O9), is eight coordinated with a distorted dodecahedron coordination geometry, and $Gd2$ has a nine coordination environment with O9 set (O1, O2, O4, O5, O8, O10, O11, O12 and O13), exhibiting a three-capped trigonal prism [65].

Variable temperature DC magnetic susceptibility for **24** and **25** was done under an applied magnetic field of 1 kOe and in between 2–300 K (Figure 15d). The $RT, \chi_M T$ values for **24** and **25** are 15.70(3) and 28.28(4) $cm^3 K mol^{-1}$, respectively. For **24**, on decreasing the temperature, the $\chi_M T$ values almost keep constant up to 25 K, then decrease to a minimum of 6.78 $cm^3 K mol^{-1}$ at 2 K, proving the existence of weak antiferromagnetic exchange between the gadolinium ions. While in **25**, the $\chi_M T$ values drop gradually over the temperature range from 300 to about 50 K, then drop abruptly to the minimum value 8.63(0) $cm^3 K mol^{-1}$ at 2 K, which may be due to either the depopulation of excited Stark sublevels and/or a weak antiferromagnetic interaction of $Dy(III)$ ions [66]. The magnetization data of **24** is collected in the temperature range from 2.0 to 10.0 K under the external magnetic field of 0–80 kOe. The M vs. H plots in Figure 15e show a continuous increase with the increasing of the magnetic field and reach the saturation value of 14.05(1) $N\beta$ at 80 kOe and 2.0 K, which is in good agreement with the expected value of 14.0 $N\beta$ for two isolated $Gd(III)$ ($g = 2$, $^8S_{7/2}$) ions [65]. Further to investigate the dynamics of the magnetization, the AC-susceptibility measurements for **25** were performed as a function of temperature and frequency under zero DC field with an oscillation of 3.0 Oe. On increasing the frequency (111–2311 Hz), the frequency dependence below 20 K cannot be clearly observed from the (χ') vs. T plots (Figure 15f (top)). The frequency dependence of out-of-phase AC signal below 12 K suggests slow magnetization relaxation, indicating the presence of QTM (Figure 15f (bottom)).

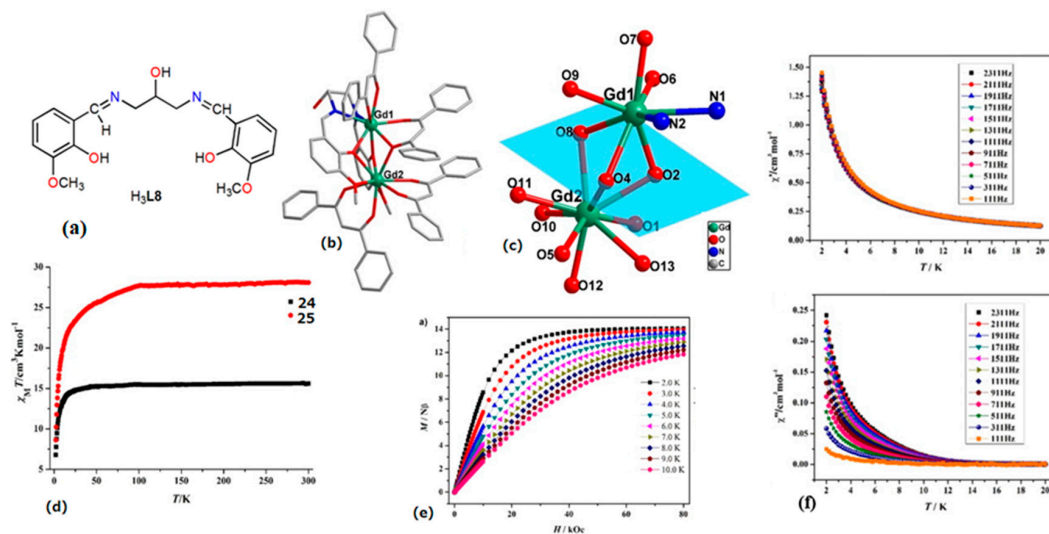


Figure 15. (a) The structure of H_3L8 , (b) the molecular structure for **24** (c) the $[Gd_2]$ cluster bridged by three μ_2 -O atoms, (d) the plots of $\chi_M T$ vs. T for **24** and **25** under an applied field of 1 kOe between 2 and 300 K, (e) M vs. H curves for **24**, where $T = 2.0$ – 10.0 K and $H = 0$ – 80 kOe (f) χ' (top) vs. χ'' AC-susceptibility for **25** under zero DC field with an oscillation of 3.0 Oe (bottom). Reproduced with permission from [65]; Published by Elsevier, 2019.

Most recently, Li and coworkers have prepared and characterized three dinuclear mixed ligand Dy(III)-compounds, $[Dy_2(dbm)_2(HL9)_2(H_2O)_2] \cdot CH_3CN$ (**26**), $[Dy_2(dbm)_3(HL9)(H_2L9)(CH_3OH)] \cdot CH_3OH$ (**27**) and $[Dy_2(dbm)_2(HL9)_2(C_2H_5OH)_2]$ (**28**) [67] ($H_3L9 = N'$ -(2-hydroxybenzylidene)-2-(hydroxyimino)-propanohydrazide (Figure 16d), and HDBM = 1,3-diphenyl-1,3-propanedione) (Chart 3). The compound **26** is centro-symmetric, with two Dy(III), two doubly deprotonated $HL9^{2-}$, two singly deprotonated co-ligands dbm^- , two water molecule and one free acetonitrile molecule (Figure 16a) [67]. Each independent Dy(III) ion is eight-coordinated with an N_2O_6 coordination environment displaying a distorted bicapped trigonal-prismatic geometry. Compound **27** (Figure 16b) has a structure different from that of **26** and **28**. The asymmetric unit is composed of two Dy(III) ions, with singly deprotonated Schiff base ligand H_2L9^- , doubly deprotonated Schiff base ligand $HL9^{2-}$, three singly deprotonated DBM^- , one coordinated MeOH molecule and one free methanol molecule [67].

The coordination sphere of N_2O_6 for Dy1 ion is constructed by two oxygen atoms O5 and O6 from dbm^- , two phenoxide oxygen atoms from O7 and O12, two carbonyl oxygen atoms O8 and O11 also two imidogen nitrogen atoms N1 and N4 from H_2L9^- and $HL9^{2-}$. Dy2 has a different coordination environment compared with Dy1. It is located in O_7N set completed by four oxygen atoms O1, O2, O3 and O4 of two dbm^- , one oximido nitrogen atom N6, one carbonyl oxygen atom O11 of $HL9^{2-}$, phenoxide oxygen atom O7 of H_2L9^- ligand as well as the oxygen atom O13 of methanol molecule. The coordination geometries of Dy1 and Dy2 show a distorted bicapped trigonal-prismatic geometry [67].

The variable temperature DC magnetic susceptibility for **26**–**28** was collected between 2–300 K under 1000 Oe (Figure 16c) [67] and their $\chi_M T$ values at RT are 28.15 (**26**), 28.08 (**27**), 28.11 (**28**) $cm^3 K mol^{-1}$ [67], which are in accordance with the expected values of two isolated Dy(II) ions. On lowering the temperature, the $\chi_M T$ values for **26**–**28** are almost unchanged from 300 to 150 K, then drop abruptly to the minimum values of 15.08 (**26**), 14.25 (**27**), and 14.50 (**28**) $cm^3 K mol^{-1}$ at 2.0 K, respectively. The decreasing trend points to weak antiferromagnetic coupling between the neighboring Dy(III)-ions in **26**–**28** [67]. The plots of χ_M^{-1} vs. T for **26**–**28** obey the Curie-Weiss law, with a Weiss constants $\theta = -3.96 \pm 0.59$ (**26**), -5.09 ± 0.92 (**27**) and -8.26 ± 1.12 (**28**) [67]. The negative values of the parameter θ further suggesting the presence of the antiferromagnetic interaction between the Dy(III) in **26**–**28**, respectively [68].

The $\ln\tau$ vs. T^{-1} plot for **28** is shown in Figure 16e, with spin-reversal energy barrier ($\Delta E/k_B$) of (45.6 ± 3.24) K having pre-exponential factor $\tau_0 = (5.14 \pm 1.61) \times 10^{-8}$. However, the values of $\Delta E/k_B$ for **26** and **27** cannot be extracted by the Arrhenius law due to the lack of χ'' maxima. It is assumed that only one relaxation exists in **26** and **27**, thus their susceptibilities could be fitted to the Debye function $\ln(\chi''/\chi') = \ln(\omega\tau_0) + Ea/k_B T$ (Figure 16g,h) [38], resulting in the energy barrier $\Delta E/k_B$ of (2.29 ± 1.17) K for **26** and 1.31 ± 1.05 K for **27**, and the pre-exponential factor τ_0 of $(0.31 \pm 0.21) \times 10^{-5}$ s for **26** and $(0.20 \pm 0.09) \times 10^{-5}$ s for **27** [67]. The Cole–Cole plots of **28** having a semicircular shape (Figure 16f) were fitted by the generalized Debye function between 2.0–16.0 K [69], and the obtained parameter α fall in the range of 0.06–0.27. The small α values suggest a narrow distribution of magnetic relaxation time under a 5 kOe DC field.

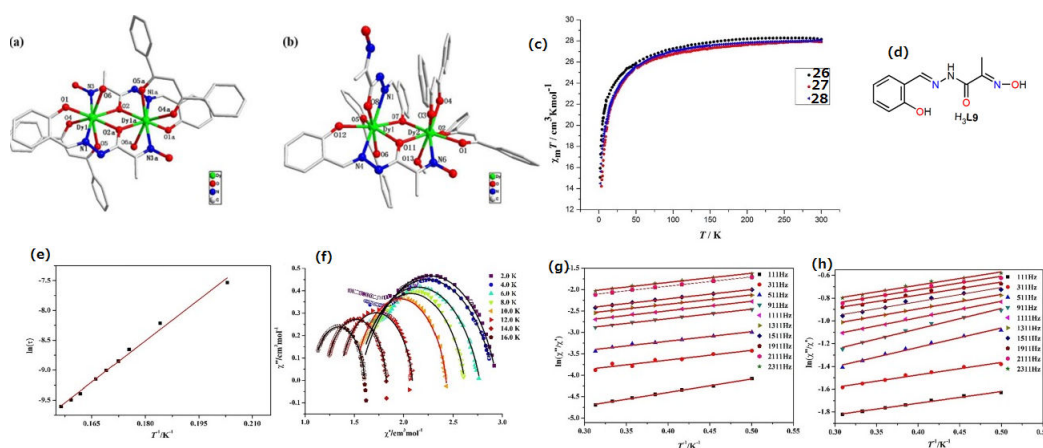


Figure 16. Molecular structures for **26** (a), and **27** (b), (c) temperature dependence of $\chi_M T$ for compounds **26–28** under 1000 Oe, (d) the structure of H_3L9 , (e) the plots of $\ln\tau$ vs. T^{-1} for **28**: the solid red line corresponds to the fitting of the experimental data to the Arrhenius equation, (f) the Cole–Cole plots of **28** measured from 2.0 to 16.0 K in $H_{dc} = 5$ kOe, plots of the natural logarithm of χ''/χ' vs. T^{-1} for **26** (g) and **27** (h). Reproduced with permission from [67]; Published by Elsevier, 2020.

Very recently, Ln(III) based dinuclear SMMs with the Schiff base ligand, H_2L10 (Figure 17a), were reported by Anastasiadis et al. The complexes are of the formulae $[Ln_2(NO_3)_4(HL10)_2(MeOH)_4] \cdot MeOH$, $Ln = Gd$ (**29**·MeOH) and $[Ln_2(NO_3)_2(HL10)_4] \cdot 6MeCN$, $Ln = Dy$ (**30**·6MeCN) [70] having interesting magnetic optical, and catalytic properties [70]. Complex **29**·MeOH contains two crystallographically independent, centrosymmetric molecules (Figure 17b). The two Gd(III) atoms are bridged by the syn, syn-carboxylate groups of two $\eta^1:\eta^1\eta^1\mu_2$ of $HL10^-$ ligands. Two bidentate chelating nitrato groups, two-terminal MeOH molecules, and one terminal phenolate O atom complete 9-coordination at each metal ion. The H atom of the phenol –OH group of $HL10^-$ has “emigrated” to the imine N atom, and the latter is thus protonated without coordination.

The two Dy(III) atoms in the representative centrosymmetric molecule **30** (Figure 17c) are bridged by the syn, syn-carboxylate groups of the four $\eta^1:\eta^1\eta^1\mu_2$ $HL10^-$ ligands. In addition to this, there is a bidentate chelating nitrato group and two terminal phenolate O atoms, which complete 8-coordination, resulting in a square-antiprismatic geometry for the metal ion [70]. The DC molar magnetic susceptibility (χ_M) data on **29** and **30** were collected at 0.03 T in the temperature range 300–2.0 K and plotted as $\chi_M T$ vs. T in Figure 17d, left; The Ln(III) center in **29**, which is bridged by two carboxylate groups, is not interacting. A weak intramolecular ferromagnetic interaction is observed in **30**, where the two Dy(III) centers are bridged by four carboxylate groups. The AC magnetic susceptibility studies performed on a polycrystalline sample of **30** measured in the 2.0–12 K range in a 4.0 G AC field oscillating at 1490–10 Hz. The χ_M'' signals are observed at low-temperatures under a DC field of 1500 G only for **30** (Figure 17d, right), providing evidence of field-induced slow magnetic relaxation for **30**. Analysis of the experimental data afforded an effective barrier for the magnetization reversal (U_{eff}) of 8.0 cm^{-1} and a τ_0 value of 3.5×10^{-6} s [70].

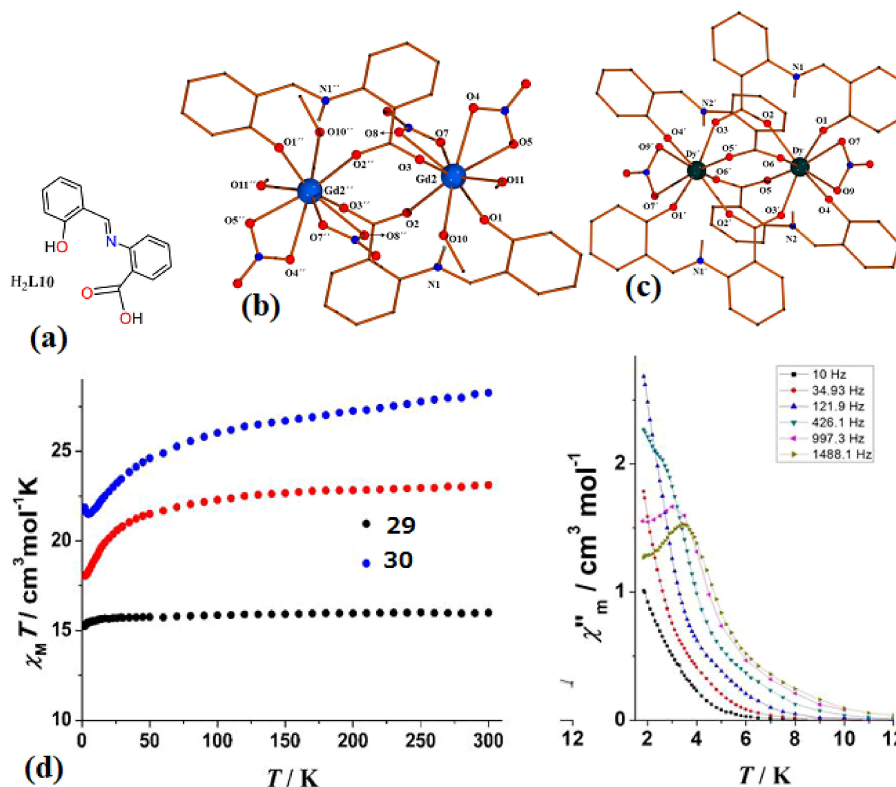


Figure 17. (a) The structure of H_2L10 , (b) structure of the $Gd_2/2''$ —containing dinuclear molecule, **29**·MeOH. (c) structure of the dinuclear molecule, **30**·6MeCN. (d) (Left) $\chi_M T$ vs. T plots for complexes **29** (black) and **30** (blue). (Right) out-of-phase (χ_M'') vs. T AC susceptibility signals for **30** in a 4.0 G AC field oscillating between 1488 and 10 Hz, under a DC field of 1500 G. Reproduced with permission from [70]; Published by American Chemical Society, 2019.

Cheng and coworkers synthesized and characterized two trinuclear complexes with the general formulae $Dy_3(HL11)_3(DMF)_6$ (**31**), and $[Gd_3(HL11)_3(DMF)_6]$ (**32**) [55], with Schiff base ligands containing an electron-withdrawing group (NO_2), H_4L11 (Where $H_4L11 = 1,5$ -bis(2-hydroxy-3-methoxy-5-nitrobenzylidene)carbonohydrazide (Figure 18f). Complexes **31** and **32** are isostructural. A perspective view of the molecular structure of **31** is represented in Figure 18a. Dy(III) in **31** was bonded to two H_4L11 and two DMF terminal solvents, leading to an eight coordinated triangular dodecahedron [55]. The coordination modes of the three ligands between any two Dy(III) ions are similar, where the two Dy(III) ions are held together by $\mu-\kappa^3:\kappa^3-HL11^{3-}$.

In contrast to the report of similar ligands [71], the trans-trans conformations were switched to cis-trans conformation in **31**, leading to the $N-N$ pathway (Figure 18b) ($N2-N3$, $N2a-N3a$ and $N2b-N3b$ between $Dy1-Dy1a$, $Dy1a-Dy1b$ and $Dy1b-Dy1$, respectively) [55]. On account of this, the three intramolecular Dy–Dy distances are 5.862 Å (Figure 18c), which are longer than other literature triangular complexes with Schiff base ligands [72] with Dy–Dy–Dy angles close to 60.0° , giving a nearly perfect equilateral triangle. In addition to this, $N3$, $N3a$ and $N3b$ are also settled on the triangular plane, where the three O, N coordination environments of the 3 ligands are all above the plane, as shown in Figure 18d [55].

The RT χT of **31** and **32** are 40.23 and 21.89 $cm^3 K mol^{-1}$, respectively (Figure 18e). The χT product shows weak antiferromagnetic interactions between the Dy(III) ions. The gradual decrease with temperature for **31** till 100 K, then a rapid decrease to a value of 27.73 $cm^3 K mol^{-1}$ at 1.8 K can be due to weak antiferromagnetic interactions between the Dy(III) ions. In Gd(III) analog **32**, the χT value reach of a minimum of 18.99 $cm^3 K mol^{-1}$ at 1.8 K shows the presence of weak antiferromagnetic coupling between the metal centers [55].

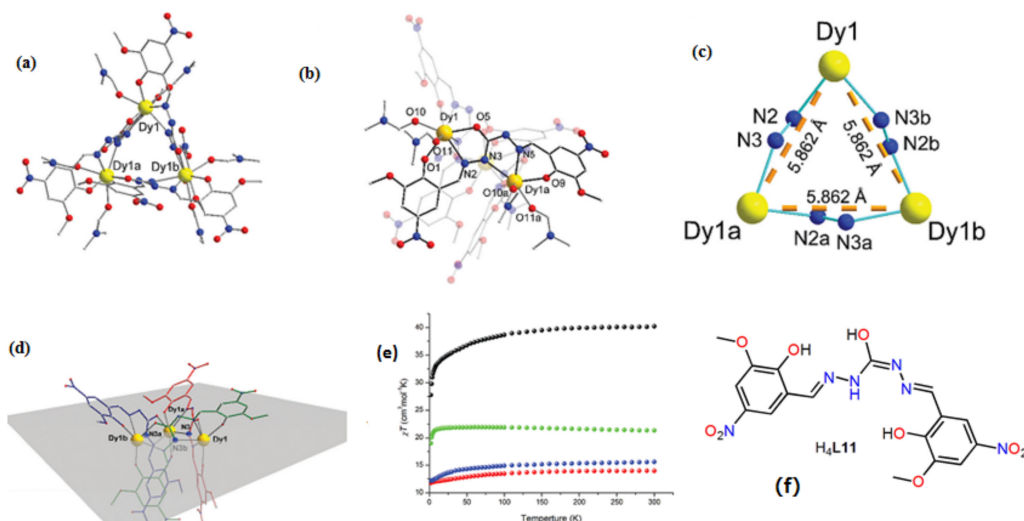


Figure 18. (a) Molecular structure of **31**, (b) the structure of $[Dy_3]$ (c) the core **31** with Dy–Dy distances, (d) side view of **31**, (e) temperature dependence of the χT product of complexes **31** (black) and **32** (green) at 1000 Oe, (f) the structures of H_4L11 . Reproduced with permission from [55]; Published by Royal Society of Chemistry, 2019.

The dynamics of magnetization for **31** between 30 and 1.8 K show frequency-dependent χ'' above 6 K, indicating SMM properties (Figure 19a) [55]. The ac susceptibility at 10 K in an applied field of 5000 Oe was done to investigate the feasibility of lowering the relaxation probability via the quantum pathway. At 1.8 K, the relaxation dynamics of **31** was affected by a static field with a shift of the peaks towards the left and having the tail of the peak in the 100–10,000 Hz range. Above 7 K out-of-phase signal was observed having a shift of the peak maxima with an energy barrier of 81 K (Figure 19a). The χ'' vs. χ' plot of **31** 6–13 K and 5–15 K also supports the relaxation process (Figure 19b) [55]. The longer Dy(III)–Dy(III) distances and Dy_3 plane of **31** are shown in Figure 19c,d [55].

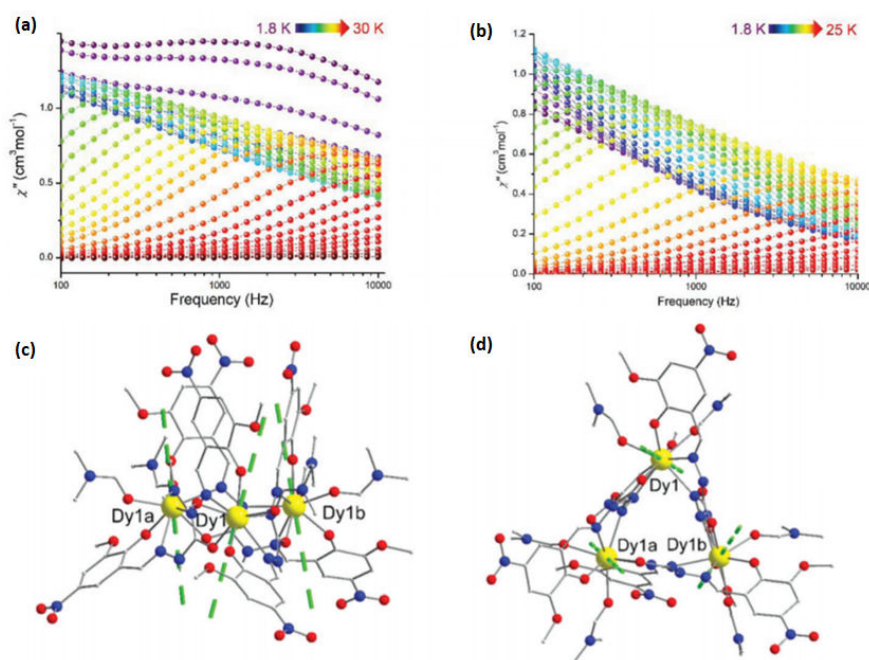


Figure 19. (a) The χ'' under zero, (b) the χ'' under 2600 Oe: DC field for complex **31** exhibiting anisotropy axes, (green dashed line) for all Dy(III) ions (side view: left (c), top view: right (d)). Reproduced with permission from [55]; Published by Royal Society of Chemistry, 2019.

4.3. Tetranuclear Schiff Base Ln(III)-Complexes of SMMs

In the construction of tetranuclear complexes, Tang and coworkers have successfully isolated two discrete linear Ln_4 isostructural complexes $[\text{Dy}_4(\text{L12})_2(\text{C}_6\text{H}_5\text{COO})_{12}(\text{MeOH})_4]$ (**33**) and $[\text{Gd}_4(\text{L12})_2(\text{C}_6\text{H}_5\text{COO})_{12}(\text{MeOH})_4]$ (**34**), by introducing steric, potentially pentadentate Schiff base ligand HL12. The ligand HL12 (Figure 20a) may provide effective hindrances to prevent the formation of extended structures and result in tetranuclear complexes. The structural description of Dy analog is taken as a phototype [73].

Complex **34** is nearly linear with Dy1–Dy2 and Dy1–Dy1A distances of 4.241 and 4.055 Å, respectively. Two different coordinating modes were observed for the benzoate ligands in its syn-syn $\eta^1:\eta^1-\mu_2$ and non-bridging chelating forms. Two central Dy atoms of Dy1 and Dy1A are coordinated by one non-bridging chelating benzoate ligand, while two peripheral Dy2 and Dy2A are coordinated by two benzoates. Every two neighboring Dy ions (Dy2 and Dy1; Dy1 and Dy1A) are bridged by syn-syn $\eta^1:\eta^1-\mu_2$ -benzoate in pairs (by $\mu_2\text{-O8-C41-O9}$ and $\mu_2\text{-O10-C34-O11}$; $\mu_2\text{-O14-C48-O17A}$ and $\mu_2\text{-O14A-C48A-O17}$) by generating a linear array. There are two methanol molecules in the coordination sphere generating eight-coordinate centers with a distorted bicapped trigonal- prismatic geometry [73].

Magnetization dynamics also reveal mainly one thermally-activated discrete linear Ln_4 complexes, instead of 1D Ln(III) chains (Figure 20b). The temperature-dependent magnetic susceptibility measurements (Figure 20d) were performed on the polycrystalline samples in the range of 300–2 K under 1000 Oe of the external field. For compound **34**, $\chi_M T$ of $32.58 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K is consistent with the spin-only value based on Gd(III) [73] ions ($^8\text{S}_{7/2}$, $S = 7/2$; $L = 0$, $g = 2$) and almost remains constant till 14 K. Upon cooling, the $\chi_M T$ value shows small decrease below 10 K, reaching a minimum value of $30.63 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K, showing the existence of antiferromagnetic coupling between Gd(III) ions (Figure 20c) for **34**. The $\chi_M T$ product of **33** at RT is $57.5 \text{ cm}^3 \text{ K mol}^{-1}$, and it decreases gradually over the operating temperature range to reach a minimum of $47.8 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K (Figure 20c). This behavior can be related to the thermal depopulation of the Dy(III) excited states because the Dy–Dy exchange interactions are insignificant by comparison [73]. The χ'' vs. χ' plots of **33** (Figure 20e) show multiple relaxations associated with distinct anisotropic centers indicating the Dy(III) complex exhibits SMM characteristics.

The relaxation times of **33** at different temperatures were obtained from frequency-dependent out-of-phase AC susceptibility measurements and plotted as a function of $\ln\tau$ vs. $1/T$ between 1.9 and 5.0 K (Figure 20f). Above 4 K, the relaxation follows a thermally activated mechanism and can be determined by the Arrhenius law ($\ln\tau = \ln\tau_0 + \Delta/k_B T$) with an energy barrier of 17.2 K and a pre-exponential factor of $\tau_0 = 6.7 \times 10^{-6} \text{ s}$, which is consistent with the expected τ_0 of 10^{-6} – 10^{-11} for an SMM [74]. At lower temperatures, a gradual crossover to a temperature-independent regime is observed, while below 2.5 K, a dominant temperature-independent quantum regime is observed with a characteristic time of 0.005 s. This behavior is predictable for an SMM when the quantum tunneling of the magnetization becomes dominant [38].

Other tetranuclear and octanuclear Dy clusters having the formulae $[\text{Dy}_4(\text{HL13})_4(\text{C}_6\text{H}_4\text{NH}_2\text{COO})_2(\mu_3\text{-OH})_4(\text{OH})_2(\text{H}_2\text{O})_4] \cdot 4\text{CH}_3\text{CN} \cdot 12\text{H}_2\text{O}$ (**35**) and $[\text{Dy}_8(\text{HL13})_{10}(\text{C}_6\text{H}_4\text{NH}_2\text{COO})_2(\mu_3\text{-OH})_8(\text{OH})_2(\text{NO}_3)_2(\text{H}_2\text{O})_4]$ (**36**), where $\text{H}_2\text{L13} = 2\text{-}[[2\text{-hydroxy-3-methoxyphenyl)methylidene]amino}]\text{benzoic acid}$ (Figure 21d) have also been reported by Tang et al. [75].

The single-crystal X-ray diffraction studies reveal that compound **35** exhibits a tetranuclear cubane-like structure (Figure 21a) and that **36** is a dimerized version of the tetranuclear analog resulting in octanuclear, bis-cubane complex (Figure 21b). The $[\text{Dy}_4(\mu_3\text{-OH})_4]$ cubane cores of **35** and **36** are structurally related. For compound **36**, the two cubane units are doubly bridged by $\mu\text{-O,O'}$ -carboxylato ligands (oxygen atoms O26, O26a, O24, and O24a; orange bonds). The blue bonds symbolize the μ_3 -hydroxido ligands [75].

As shown in Figure 21c, the $\chi_M T$ value at 300 K is $53.6 \text{ cm}^3 \text{ K mol}^{-1}$ for **35** and $50.2 \text{ cm}^3 \text{ K mol}^{-1}$ for **36**. $\chi_M T$ slowly decreases until 50 K and then additionally decreases, reaching a minimum of

23.1 cm³ K mol^{−1} for **35** and 23.8 cm³ K mol^{−1} for **36** at 2 K, indicating a progressive depopulation of excited Stark sublevels [75]. The non-superimposition of the M vs. H/T data on a single master curve (Figure 21e,f) suggests the presence of a significant magnetic anisotropy and/or low-lying excited states. The magnetization eventually reaches the value of 24.4 μ_B for **35** and 22.2 μ_B for **36** at 2 K and 70 kOe without clear saturation. This value is much smaller than the expected saturation value of 40 μ_B for four non-interacting Dy(III) ions, which may be due to the crystal-field effect of Dy(III), which cancels the 16-fold degeneracy of the ⁶H_{15/2} ground state.

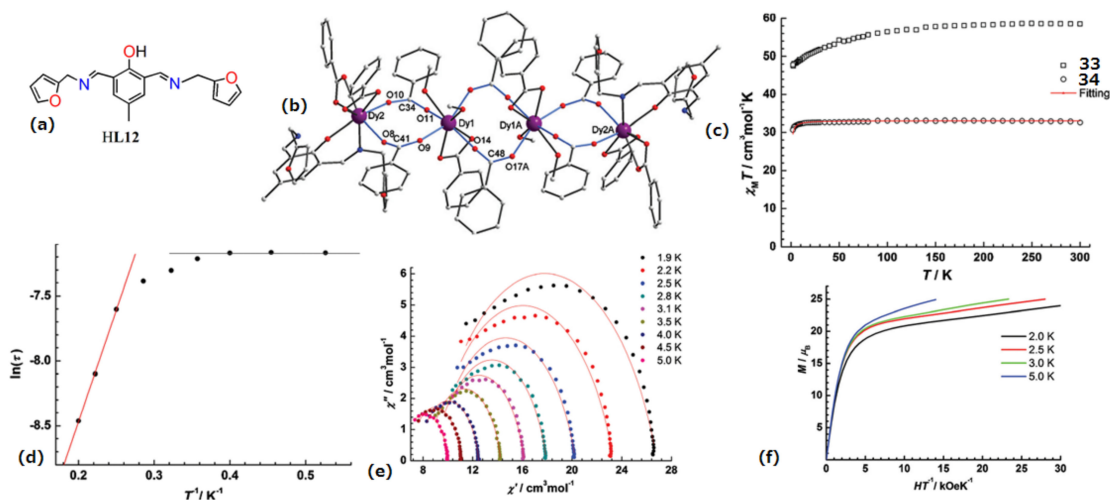


Figure 20. (a) The structure of HL12, (b) tetranuclear unit of **33** with the central core highlighted by blue bonds, (c) $\chi_M T$ vs. T products at 1 kOe for **33** (open square) and **34** (open cycle) and fitting of data for **34** (red line), (d) magnetization relaxation time, $\ln \tau$ vs. T^{-1} plot for **34** in zero DC field, (e) χ'' vs. χ' plots measured below 9 K and zero-DC field (right side) for **33**, (f) the plot of the reduced magnetization vs. H/T for **33** in the field range 0–7 T and temperature range 2.0–5.0 K. Reproduced with permission from [73]; Published by Royal Society of Chemistry, 2012.

The AC susceptibility measurements were performed for **35** and **36** under a zero-DC field to investigate the dynamics of the magnetization. Checking the bond distances and angles of the respective [Dy₄(μ₃-OH)₄] cores reveal small but apparently important disparities in the M–O–M angles. These angle differences (induced by the presence of additional μ-OH- bridges in **35**) clearly affect the orbital overlaps between the metal centers and the μ₃-hydroxido ligands, as well as the local tensor of anisotropy on each Dy(III) site and their relative orientations, generating dissimilar dynamic magnetic behavior [75].

More recently in 2018, Hong-Ling and coworkers have reported five tetranuclear Ln(III)-complexes represented by the following chemical formulae [76], [Ln₄(dbm)₄(L14)₆(μ₃-OH)₂]·5CH₃CN (**37**), [Ln₄(dbm)₄(L14)₆(μ₃-OH)₂]·2CH₃CH₂OH·4CH₃CN (**38**), [Ln₄(dbm)₄(L14)₆(μ₃-OH)₂]·4CH₃CN·2H₂O (**39**), [Ln₄(dbm)₄(L14)₆(μ₃-OH)₂]·CH₃CH₂OH·4CH₃CN·2H₂O (**40**) and [Ln₄(dbm)₄(L9)₆(μ₃-OH)₂] (**41**), where Ln = Gd(**37**), Tb(**38**), Dy(**39**), Ho(**40**), Er(**41**) and HL14 = 5-(4-pyridinecarboxaldehyde)amino-8-hydroxyquinoline (Figure 22d).

In **39**, there are four Dy(III) centers with L14[−] and four DBM[−] ligands with crystallographic inversion symmetry. The complexes **37–41** adopt a typical butterfly topology and have a distorted square-antiprismatic geometry (Figure 22b).

The $\chi_M T$ values of **37–41** at RT are 33.58, 47.20, 56.52, 57.16 and 44.37 cm³ K mol^{−1}, respectively (Figure 22c). For **37**, the $\chi_M T$ value remains nearly constant between 300 and 60 K and decreases sharply, reaching a minimum of 17.36 cm³ K mol^{−1} at 2 K showing weak intramolecular antiferromagnetic interaction between the Gd(III) centers. For **39**, the $\chi_M T$ increase as temperature decreases to 70 K to a value of 58.96 cm³ K mol^{−1} is an indication of weak ferromagnetic interaction between metal ions. On further cooling of **39** to 2 K, the $\chi_M T$ reaches a value of 35.91 cm³ K mol^{−1}. For **38**, **40**, and

41, the $\chi_M T$ product slowly decreases from 300 to 60 K, and then reaches minima of 39.61, 30.05 and 18.90 cm³ K mol^{−1}, respectively, at 2 K [76].

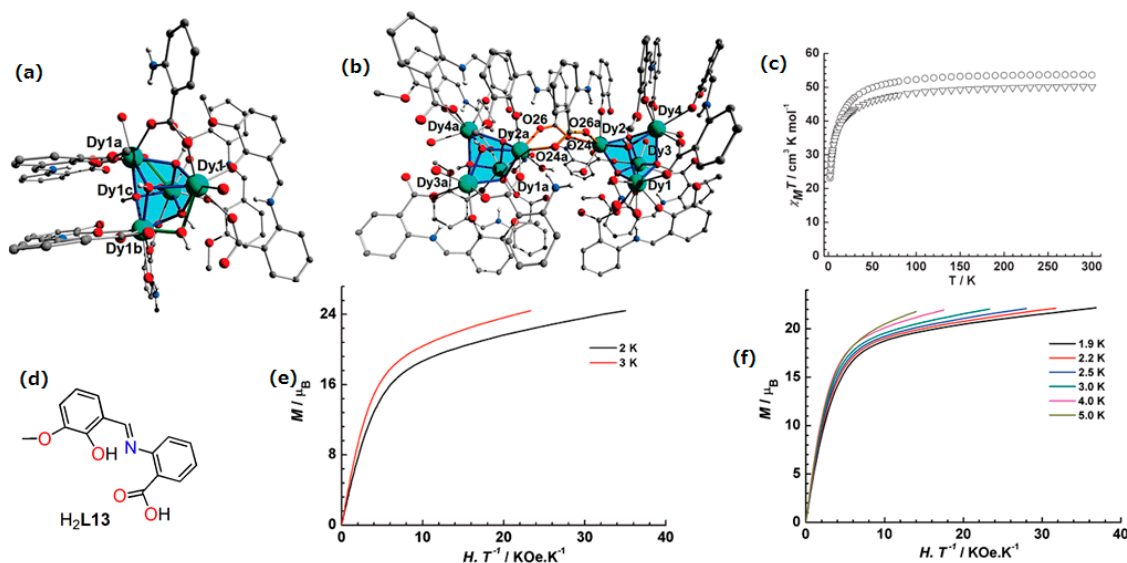


Figure 21. (a) Molecular structure of **35**, illustrating the Dy₄ cubane core, (b) molecular structure of octanuclear **36**, (c) temperature dependence of the $\chi_M T$ products at one kOe for **35** (open circle) and **36** (open triangle) (d) structure of the ligand H₂L13, (e) M vs. H/T plots for **35** at 2 and 3 K, (f) M vs. H/T plots for **36** at different temperatures below 5 K, by normalizing the data per Dy₄ unit. Reproduced with permission from [75]; Published by American Chemical Society, 2010.

The dynamics of the magnetization of **39** were investigated in both temperature and frequency-dependent AC fields under a zero DC field. Here the relaxation parameters from $\ln\tau$ vs. $1/T$ plots came out with an energy barrier of 89.38 K (Figure 22f) [77]. From (Figure 22e), complex **39** shows the presence of strong frequency-dependent in-phase (χ') and out-of-phase (χ'') signals, with slow magnetic relaxation at a lower temperature, proving its SMM nature [76].

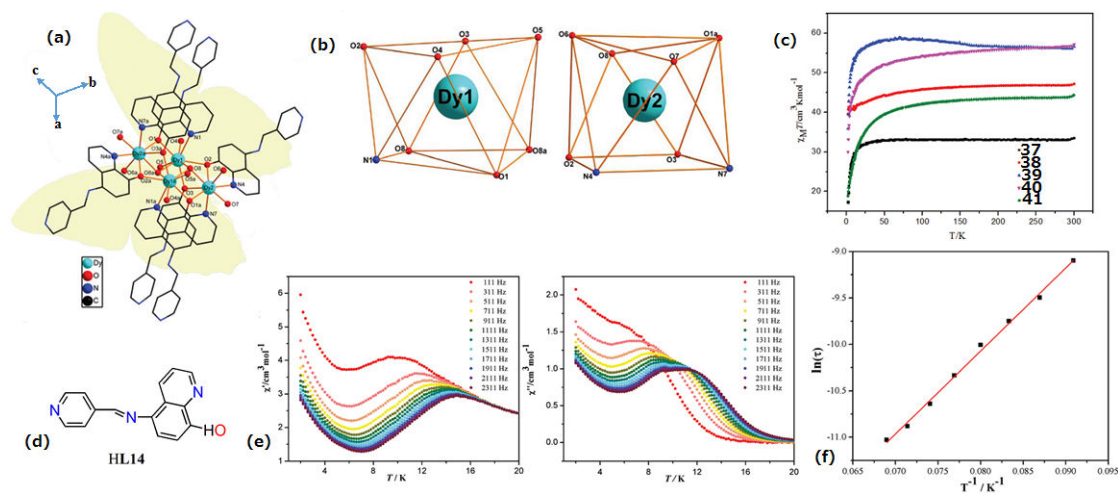


Figure 22. (a) Molecular structure of **39**, (b) geometrical representation of Dy1 and Dy2 ions in **39**, (c) $\chi_M T$ vs. T plots for complexes **37–41** between 2 and 300 K, (d) the structure of HL14, (e) temperature dependence of the χ' (left) and χ'' (right) components of the AC magnetic susceptibility for **39** (f) Plot of $\ln\tau$ vs. T^{-1} fitted to the Arrhenius law for complex **39**. Reproduced with permission from [76]; Published by Royal Society of Chemistry, 2018.

Two analogous tetranuclear Ln(III)-complexes with Dy(III) (**42**), Gd(III) (**43**) with tetrazine-centered hydrazone Schiff base ligand having the general formula, $[\text{Ln}_4(\text{H}_2\text{L15})_4(\text{MeOH})_8](\text{NO}_3)_4 \cdot a\text{MeOH} \cdot b\text{H}_2\text{O}$, were reported by Murugesu et al. [78], where $\text{H}_4\text{L15} = (3,6\text{-bis}(\text{vanillidenehydrazinyl})\text{-}1,2,4,5\text{-tetrazine})$ (Figure 23c) and $a = 8.07$ and $b = 0.65$ for **42** and $a = 8.19$ and $b = 0.91$ for **43**. The ligand $\text{H}_4\text{L15}$ has a tetrazine ring at the center and two identical hydrazone moieties [78]. The ligand has four coordination pockets comprising of N1, N4a and O1 tridentate coordination sites, and a bidentate pocket consists of O1 and O2 coordination sites. A distorted spherical capped square antiprism geometry is assigned for Dy1 and a spherical tricapped trigonal prism for Dy2 in **42** (Figure 23a).

The χT vs. T product exhibits the presence of non-negligible ferromagnetic coupling between spin carriers (Figure 23b). On lowering from RT, the χT values of **42** and **43** remain unchanged till 12 K and abruptly increased to a value of $69.86 \text{ cm}^3 \text{ K mol}^{-1}$ for **42** and $33.73 \text{ cm}^3 \text{ K mol}^{-1}$ for **43** at 1.9 K, showing an indication of intramolecular ferromagnetic exchange [78]. The AC susceptibility of **42** under zero applied DC field (Figure 23d) shows both the in-phase (χ') and out-of-phase (χ'') signals, and the shifting of peak maxima shows slow relaxation of the magnetization with an energy barrier of 158 K. The micro-SQUID measurement of **42** at below 0.5 K with a sweep rate of 14 T s^{-1} shows hysteretic behavior (Figure 23e). The width of the magnetic hysteresis loop of complex **42** indicates a strong dependence on temperature and moderate dependence on sweep rate [78].

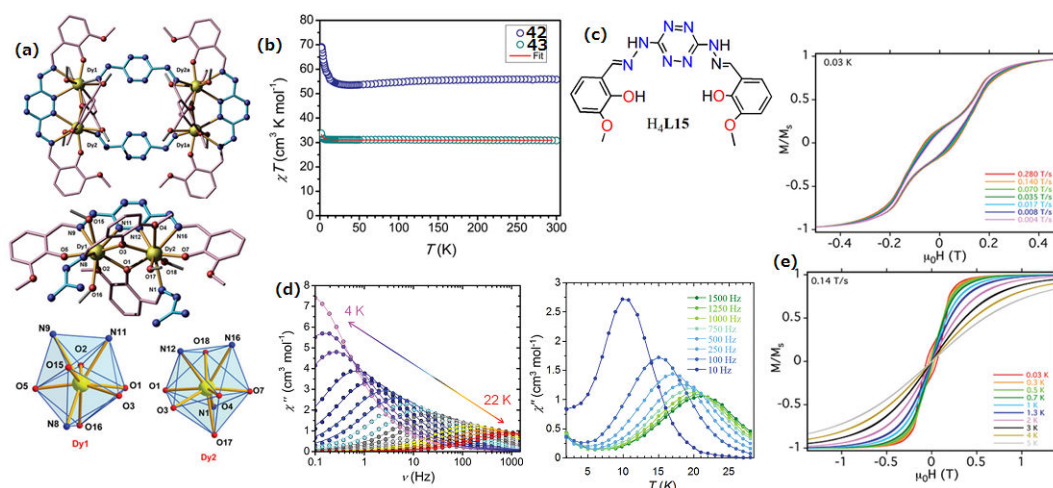


Figure 23. (a) Molecular structures (top), dinuclear complex (middle) and coordination polyhedra of **42** (bottom), (b) Temperature dependence of χT for **42** and **43**, (c) the structure of $\text{H}_4\text{L15}$, (d) χ'' vs. ν (Hz) (left) and χ'' vs. T (right) for **43**, (e) magnetic hysteresis measurements of a single crystal of **43** on a micro-SQUID **43** (top) and temperatures (bottom). Reproduced with permission from [78]; Published by Royal Society of Chemistry, 2017.

A tetranuclear Dy-cluster having the structural formula, $[\text{Dy}_4(\text{HL16})_4(\text{MeOH})_6] \cdot 2\text{MeOH}$ (**44**) was reported by Tang et al., whose molecular structure is depicted in Figure 24a, where $\text{H}_3\text{L16} = 2\text{-hydroxy-3-methoxybenzoic acid [2-hydroxy-3-methoxyphenyl] methylene] hydrazide}$ (Figure 24d) [44]. The central Dy(III) ions of the Dy₄ core are connected by two $\mu\text{-O}$ units. Strong inter- and intramolecular hydrogen bonding interactions give a two-dimensional supramolecular array with a zigzag arrangement of the molecules. The Dy₄ compound derived from a rigid hydrazone ligand shows a nearly linear Dy₄ core, one being in a distorted bicapped trigonal-prismatic geometry and the other in a nearly perfect mono-capped square-antiprismatic environment [44].

Direct-current magnetic susceptibility studies of **44** were carried out in an applied magnetic field of 1 kOe in the temperature range 300–2 K (Figure 24e). The $\chi_M T$ value of $54.9 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K observed is slightly lower than the value of $56.7 \text{ cm}^3 \text{ K mol}^{-1}$. The value of $\chi_M T$ gradually decreases until $\sim 30 \text{ K}$, where it drops abruptly to a minimum of $31.3 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K, indicating a progressive depopulation of excited Stark sublevels. Magnetization data are shown in the inset of (Figure 24e,f).

The non-super position of the $\chi_M T$ vs. H/T data on a single master curve suggests the existence of significant magnetic anisotropy or/and low-lying excited states [44].

It is interesting to note that more than one peak is seen in the temperature-dependent ac magnetic susceptibility curves (Figure 24b), showing an unusual multiple relaxation mechanism operating in **44**. Additionally, in terms of the χ'' vs. frequency plots characterized by two clear maxima, two effective energy barriers identified are 19.7 and 173 K corresponding to fast and slow relaxation phases, respectively [44], which was confirmed by the Cole–Cole plots, that clearly indicate the evolution from fast relaxation to slow relaxation phases with the changing of temperature observed at 7 and 8 K (Figure 24b). The two different relaxation processes might be associated with distinct anisotropic centers, that is, two Dy(III) ions with different geometries [44]. The (χ'') vs. frequency plot of **44** at 7 K (Figure 24c) exhibiting two peaks centered at 1.2 and 1200 Hz, respectively, could be because of the spin noncollinearity of two types of Dy(III) ions in the weakly coupled molecular system. It is interesting to note that the peaks in the frequency-dependent AC susceptibility are quite distorted, exhibiting a unique double-ridge structure (Figure 24c) as opposed to the shoulder structure in the Dy₃ system [29].

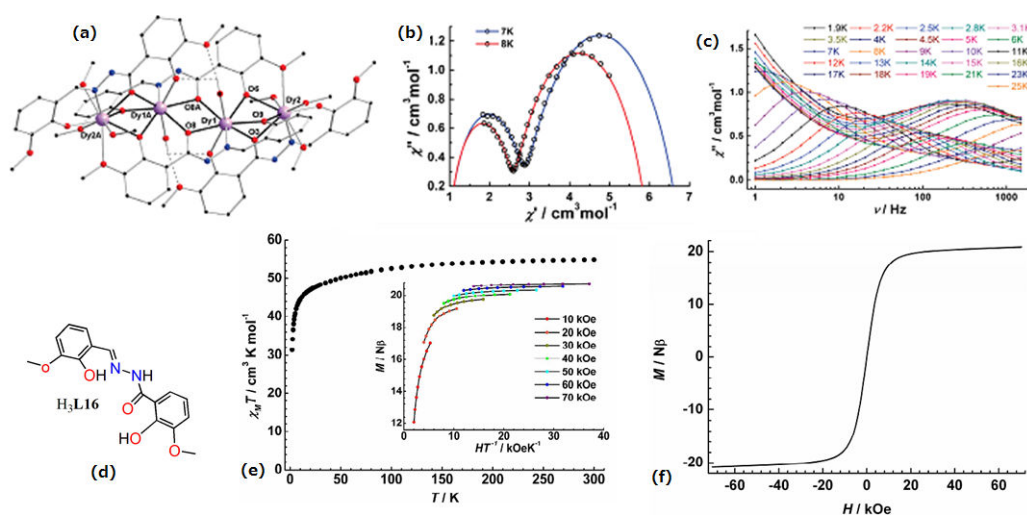


Figure 24. (a) Molecular structure of **44**, (b) dynamical susceptibility (ω) at 7 and 8 K for **44**, (c) out-of-phase AC-susceptibility χ'' vs. frequency ν on a logarithmic scale for **44** over the temperature range 1.9–25 K, (d) the structure of H₃L16, (e) plot of $\chi_M T$ vs. T for **44**. The inset is a plot of the reduced magnetization ($M/N\beta$) vs. H/T for **44** in the field range 1–7 T and temperature range 1.9–4 K, (f) $\chi_M T$ vs. H data of **44** at 1.9 K. Reproduced with permission from [44]; Published by American Chemical Society, 2010.

In another communication, Tang and coworkers have reported a tetranuclear Dy cluster having the formula $[\text{Dy}_4(\text{L10})_4(\text{HL10})_2(\text{C}_6\text{H}_4\text{NH}_2\text{COO})_2(\text{CH}_3\text{OH})_4] \cdot 5\text{CH}_3\text{OH}$ (**45**) where H₂L10 = *N*-(2-carboxyphenyl) salicylaldimine (Figure 25d), whose molecular structure is in Figure 25a [79]. Here H₂L10 has three different binding modes (Chart 4). Two full deprotonated tetradentate L10²⁻ wrap Dy atoms in $\eta^1:\eta^1:\eta^2:\eta^2:\mu_3$ - fashion and two peripheral fully deprotonated L10²⁻ ligands bind in a $\eta^1:\eta^1:\eta^2:\eta^1:\mu_2$ - way. Furthermore, two peripheral zwitterionic ligands coordinate in $\eta^1:\eta^1:\eta^1:\mu_2$ way generating a linear metal array. Lastly, two peripheral zwitterionic-tridentate ligands bind in a $\eta^1:\eta^1:\eta^1:\mu_2$ - condition, and a linear metal array is generated. The peripheral zwitterionic ionic HL10⁻ ligands block the *N*-coordination to the metal ions.

A molecule of methanol is also coordinated to Dy1, generating an 8-coordinated species with a square-antiprismatic geometry, while for Dy2, a molecule of methanol and an anthranilate ligand is also coordinated for an 8-coordination around Dy2 in between a bi-capped trigonal prism and a square antiprism.

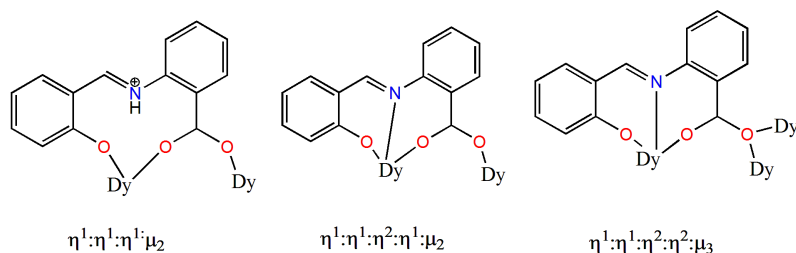


Chart 4. Coordination modes of HL10^- ($\eta^1:\eta^1:\eta^1:\mu_2$) and L10^{2-} ($\eta^1:\eta^1:\eta^2:\eta^1:\mu_2$ and $\eta^1:\eta^1:\eta^2:\eta^2:\mu_3$) in compound **45**. Reproduced with permission from [79]; Published by Royal Society of Chemistry, 2010.

The $\chi_M T$ vs. T curve of **45** shows a value of $56.3 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K, and it decreases gradually to reach a minimum of $31.7 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K (Figure 25b) [80]. The magnetization data collected in the 0–70 kOe shows significant magnetic anisotropy, which rapidly increases and reaches $27.0 \mu\text{B}$ at 1.9 K and 70 kOe without clear saturation (Figure 25b), which is lower than the expected saturation value for four non-interacting Dy(III) ions [81]. The relaxation time was extracted from the frequency-dependent data between 1.9 and 9 K (Figure 25c). Below 3 K, a temperature-independent relaxation regime is observed with a characteristic time of 0.00068 s. Such behavior is expected for an SMM when the quantum tunneling of the magnetization becomes dominant [38,82].

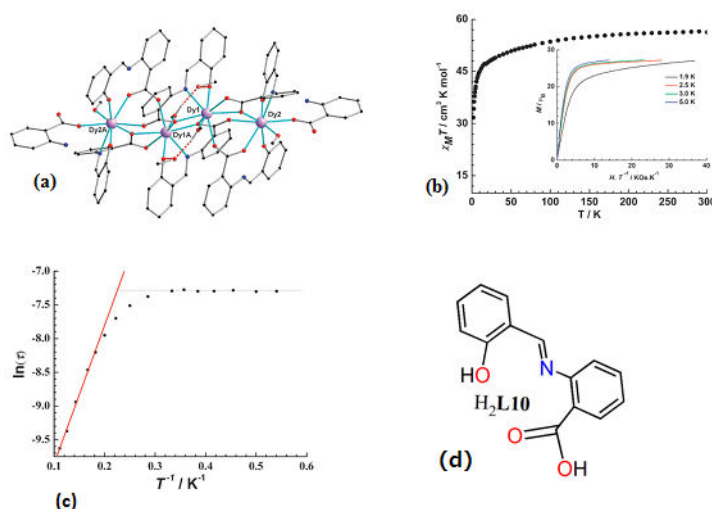


Figure 25. (a) The molecular structure of compound **45**, (b) $\chi_M T$ vs. T plot at 1 kOe; inset: M vs. H/T plots at different temperatures below 5 K for **45**, (c) relaxation time, $\ln \tau$ vs. T^{-1} plot for **45** under zero-DC field; the solid line is fitted with the Arrhenius law, (d) the structure of $\text{H}_2\text{L10}$. Reproduced with permission from [79]; Published by Royal Society of Chemistry, 2010.

In 2019 Tang and coworkers prepared and characterized a Dy-based linear helicate cluster, $[\text{Dy}_4(\text{HL17})_2\text{L17}(\text{DMF})_8] \cdot 2\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2 \cdot 4\text{DMF} \cdot (\text{CH}_3\text{CH}_2)_2\text{H}_2\text{O}$ (**46**), with pyridazine-based Schiff base, ([3,6-bis(2-hydroxy-3-methoxybenzylidene)hydrazinecarbonyl]-pyridazine), $\text{H}_4\text{L17}$, (Figure 26a), was synthesized by the condensation of pyridazine-3,6-dicarbohydrazide and *o*-vanillin [83,84] and it exhibits flexible coordination modes (Chart 5), owing to structural tautomerism. It is interesting to note that the coordination centers always reside on the same side of $\text{H}_4\text{L17}$, which favors the formation of polynuclear clusters [85]. With respect to the scope of this review, the pure Ln(III) compound, $[\text{Dy}_4(\text{HL17})_2\text{L17}(\text{DMF})_8] \cdot 2\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2 \cdot 4\text{DMF} \cdot (\text{CH}_3\text{CH}_2)_2\text{O} \cdot \text{H}_2\text{O}$ (**46**) is discussed.

The compound **46** is a linear array of Dy_4 core (Figure 26b). In **46**, among the three ligands, one is completely deprotonated and connects with four Dy(III) ions with the binding mode indicated in Chart 5 (left) by utilizing NO-bidentate and ONO-tridentate coordination nature. The other two are tri-deprotonated and coordinate to four Dy(III) ions, as shown in Chart 5 (right) using three kinds

of coordination pockets [86]. For compound **46**, the smallest intermolecular Dy–Dy distance is 9.495, indicating relatively weak intermolecular magnetic interactions [86].

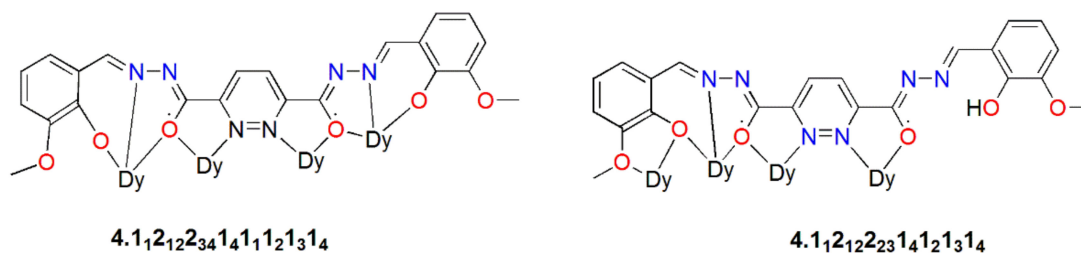


Chart 5. Coordination nature of the H_4L17 with different deprotonated conditions in **46** (Harris notation). Reproduced with permission from [86]; Published by Royal Society of Chemistry, 2020.

The DC susceptibility measurement was carried out for compound **46** from 2 to 300 K in an applied field of 1 kOe (Figure 26c). The $\chi_M T$ products at 300 K, for compound **46** is $57.31 \text{ cm}^3 \text{ K mol}^{-1}$. When the temperature is lowered, the $\chi_M T$ product of **46** progressively decreases and reaches a value of $48.37 \text{ cm}^3 \text{ K mol}^{-1}$ at 12 K, and then sharply increases to a value of $63.36 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K, suggesting dominant ferromagnetic interactions [39,87,88].

The field-dependent magnetization measurements were done for compound **46** between 0–70 kOe at 1.9, 3 and 5 K, respectively (Figure 26e). For compound **46**, the magnetizations quickly rise to 10 kOe and reach the value of $20.96 \mu_B$, at 70 kOe at 1.9 K, which is much lower than the expected saturation value of $40 \mu_B$ for four independent Dy(III) ions [86], which may be due to the significant crystal-field effect [29,89]. The non-superposition of magnetization plots over a single master curve proves the presence of considerable magnetic anisotropy and/or low-lying excited states [31,90]. In order to investigate the dynamics of magnetization of **46**, the AC measurements were conducted under a zero DC field (Figure 26d). The χ'' signals of **46** show frequency dependence below 20 K, indicating the slow relaxation of magnetization. On cooling, a remarkable increase without well-defined peaks indicates a fast QTM effect at low-temperatures, as observed in most of the early reports [89–94]. The U_{eff} of **46** is reported as $\sim 4 \text{ k}$ [86].

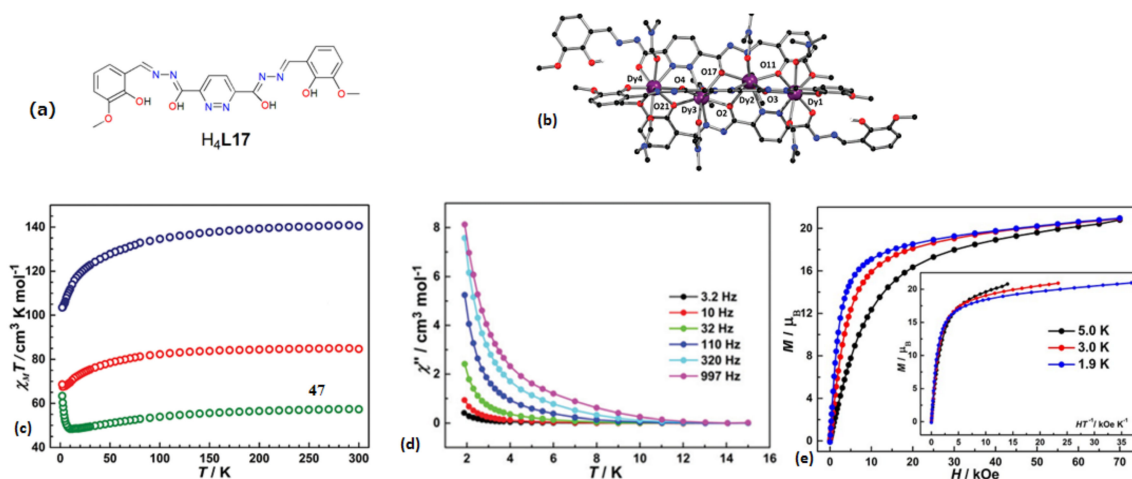


Figure 26. (a) The structure of H_4L17 (b) crystal structure of **46**, (c) $\chi_M T$ vs. T of **46** (blue) under a 1 kOe DC field, (d) temperature dependences of out-of-phase (χ'') signals for **46** under zero DC field, (e) field dependences of magnetization between 0 and 70 kOe and at temperatures of 1.9 and 3.0 K. Insets: plots of the reduced magnetization M vs. HT^{-1} for **46**. Reproduced with permission from [86]; Published by Royal Society of Chemistry, 2020.

In the search for tetranuclear aggregates, another Dy(III)₄ aggregate has been reported by Hou et al. having the formula [Dy₄(TTA)₄(L18)₄(H₂O)₂·4CH₃OH (**47**) [95], with the multidentate 8 hydroxyquinoline-based Schiff base ligand (H₂L18) (Figure 27a), where H₂L18 is 2-[(4-methoxyphenyl)imino] methyl]-8-hydroxy-quinolone and TTA is 2-thenoyltrifluoroacetone (Chart 6). The ligand H₂L18, having flexible coordination modes of N and O atoms, acts as a good candidate to construct Ln(III)-based high nuclearity clusters. On reacting Dy(TTA)₃·2H₂O, with H₂L18 compound **47** was obtained.

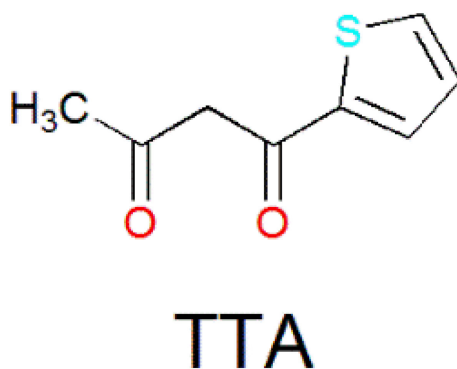


Chart 6. The structures of TTA.

The coordination modes of H₂L18 and TTA in cluster **47** are shown in Figure 27c. As shown in Figure 27b, the molecular structure of **47** mainly consists of four Dy(III) ions, four TTA[−], four L18^{2−} and two coordinated waters. Six oxygen atoms (O1, O2, O4, O7, O8 and O11) and two nitrogen atoms (N1 and N2) are coordinated to the central Dy(III) ion with the N₂O₆ coordination environment. The four Dy(III) ions are bridged by two carboxyl oxygen atoms and four μ₂-O atoms from four L18^{2−}, resulting in a Dy₄ parallelogram core. The coordination polyhedrons for both 8-coordinate Dy1 and Dy2 central ions are described as a distorted square-antiprismatic geometry with a quasi-D_{4d} symmetry, which was calculated using Shape 2.0 software [96].

As shown in Figure 27d, for **47**, at RT $\chi_M T$ value is 56.64 cm³ K mol^{−1} [95], which is in conformity with the expected value of four non-interacting Dy(III) ions. On decreasing the temperature, the $\chi_M T$ values decrease slowly between 300–50 K, and then rapidly falls to a minimum of 38.15 cm³ K mol^{−1} at 2.0 K [95]. This behavior generally can be attributed to the weak antiferromagnetic exchange between the adjacent Dy(III) ions in the system and/or the thermal depopulation of the Dy(III) Stark sub-levels [92]. In the 0–80 kOe magnetic field range and at $T = 2.0$ K, the M vs. H curve for **47** was investigated [95]. M value increases quickly at low field and then increases slowly without complete saturation till H = 80 kOe. The M value of **47** is 23.05 Nβ at 80 kOe, which is much lower than the theoretical saturated value of 40 Nβ for four free Dy(III) ions. Furthermore, like shown in Figure 27e, the M vs. HT^{−1} curves at 2.0–8.0 K show non-superimposed magnetization curves for cluster **47**, which also suggests the existence of significant anisotropy and/or low-lying excited states of Dy(III) ions [97].

In order to understand the magnetic relaxation dynamics of **47**, AC susceptibility measurement was done at zero DC magnetic field in the temperature range 2.0–15.0 K and frequency 111–3111 Hz. As shown in Figure 27f [95], there is no obvious frequency dependence below 15.0 K in the in-of-phase (χ') component susceptibility for **47**, however, the out-of-phase susceptibility (χ'') clearly displays frequency-dependent signals below 10 K, but no well-defined peaks are seen till the temperature drops to 2.0 K, which may be due to quantum tunneling of the magnetization (QTM) [98].

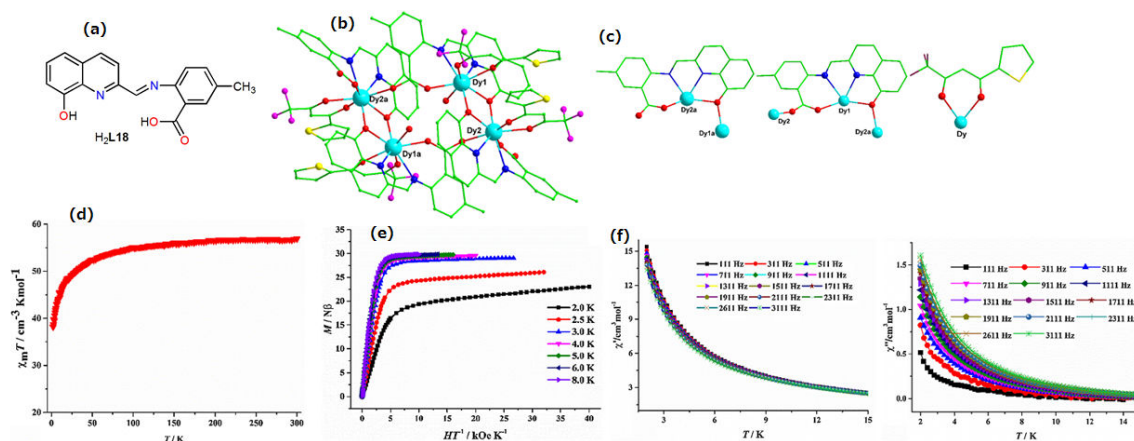


Figure 27. (a) The structure of H_2L18 , (b) molecular structure for 47, (c) coordination modes of H_2L18 and TTA in 47, (d) $\chi_M T$ vs. T for 47 under an applied DC field of 1000 Oe, (e) M vs. HT^{-1} for 47 in the field range 0–80 kOe, (f) χ' (left) and χ'' (right) components of the AC magnetic susceptibility measurement for 47. Reproduced with permission from [95]; Published by Elsevier, 2020.

4.4. Hexanuclear Schiff Base Ln(III)-Complexes of SMMs

Ghosh and coworkers have reported a hexanuclear Dy(III) cluster $[Dy_6(L19)_7(HL19)(MeOH)_2(H_2O)(OH)_2(OAc)]$ (**48**) [99], where (H_2L19) are *o*-phenolsalicylimine (comprising of two similar coordination pockets for Dy encapsulation) (Figure 28a). This unique Dy(III)₆ cluster, formed by the exclusive combination of two vertex-sharing and one edge-sharing high-anisotropy Dy₃ triangles (Figure 28b), gives rise to an unprecedentedly asymmetric Dy(III)₆ homometallic core. The crystal packing reveals that the molecules of **48** are in contact through π - π interactions, generating an infinite supramolecular array, where there is a strong π - π interaction ($d = 3.268 \text{ \AA}$) between two ligands of the two closely situated molecules, generating intermolecular π - π interactions. The hexanuclear Dy(III) complex is represented in Figure 28b. Each Dy(III) in the hexanuclear aggregate is 8-coordinated, and a square-antiprismatic geometry may be assigned around the metal ion [99].

The dynamics of the magnetization measurements operating in a 3.0 Oe AC field oscillating at frequencies of 3–1200 Hz and with a zero DC field for Dy₆ is shown in Figure 28d, as the plots of χ' vs. T and χ'' vs. T . The DC magnetic susceptibility studies of a polycrystalline sample (Figure 28c) gives a room-temperature $\chi_M T$ value equal to $82.39 \text{ cm}^3 \text{ K mol}^{-1}$. The $\chi_M T$ values decrease gradually with decreasing the temperature. The M vs. H data at different temperatures show a swift rise in the magnetization at low fields, reaching values of $32.09 \mu_B$ at 1.9 K and 7 T for Dy₆ (Figure 28f). The non-superimposed curves validate the existence of anisotropy and/or low-lying excited states [99]. Linear fitting of the experimental $\ln(\chi''/\chi')$ data to the equation $\ln(\chi''/\chi') = \ln(\omega\tau) + U_{eff}/kT$ generating the parameters $U_{eff} \approx 3.0 \text{ K}$ and $\tau_0 \approx 8.3 \times 10^{-6} \text{ s}$ can be seen in Figure 28e. The frequency-dependent out-of-phase signals signify the onset of slow magnetization relaxation. The nonexistence of frequency-dependent peaks in the out-of-phase susceptibility signals for this Dy₆ system is most probably attributed to the fast quantum tunneling of the magnetization [99].

Continuing the search for hexanuclear aggregates, a distinctive hexanuclear Dy(III) compound having the formula $[Dy_6(\mu_3-OH)_3(\mu_3-CO_3)(\mu-OMe)(L20)_6(MeOH)_4(H_2O)_2] \cdot 3MeOH \cdot 2H_2O$ (**49**), Figure 29a, was reported by Tang et al. with the polydentate Schiff base ligand (H_2L20) (Figure 29d). The hexanuclear core of complex **49** contains six Dy(III) ions, which can be considered as the amalgamation of three capped triangular Dy₃ units [100]. The structure of **49** consists of two crystallographically unique but structurally same, Dy₆ units in the unit cell, as shown in Figure 29a. A total of six polydentate Schiff-base ligands surround the Dy₆ cluster core and exhibit three different binding modes in its di-deprotonated forms. Four methanol molecules, two water molecules, and one CO_3^{2-} anion occupy the remaining coordination sites of Dy(III) ions. Importantly, the CO_3^{2-} anion coordinated to the three Dy(III) ions in a $\eta^2:\eta^2-\mu_3$ bidentate fashion. Each metal center in **49** is

8-coordinated, and a square-antiprismatic geometry may be assigned around the Dy(III) ions in the aggregate [100].

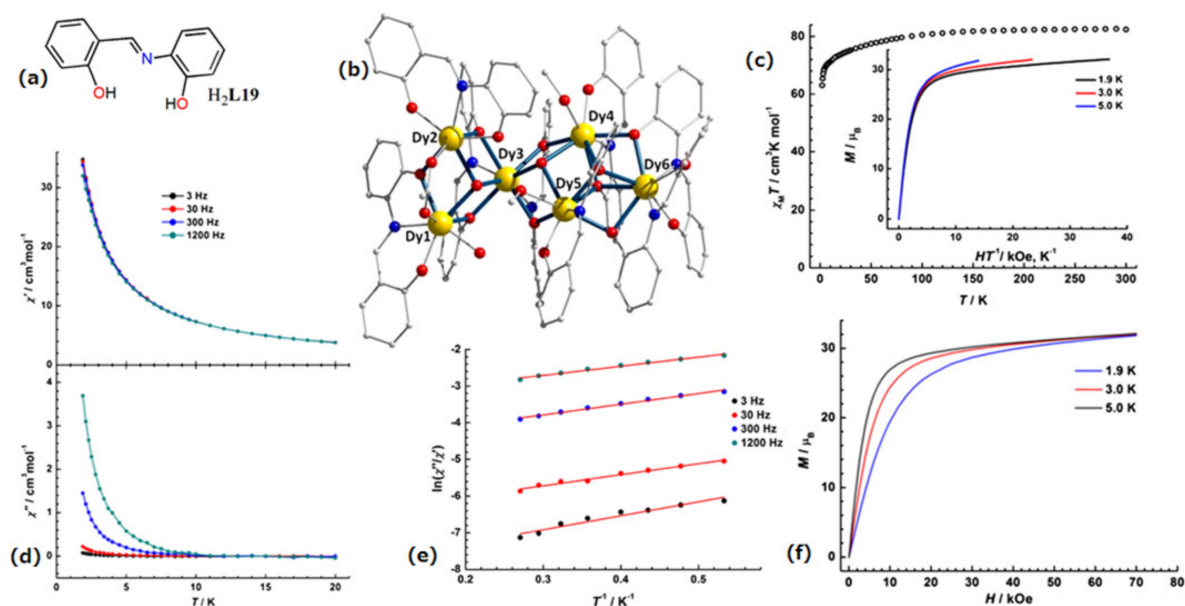


Figure 28. (a) The structure of H2L19, (b) hexanuclear unit of **48** with the central core highlighted by blue bonds, (c) $\chi_M T$ vs. T for **48** at 1 kOe (with $\chi = M/H$ normalized per mol). Inset: M vs. H/T plot at various temperatures between 1.9 and 5 K for **48**, (d) temperature-dependent AC susceptibility data for compound **48**, obtained under zero DC field at the indicated frequency, (e) natural logarithm of the ratio of χ'' over χ' vs. $1/T$ of the data for **48**, (f) field dependence of the magnetization at various temperatures between 1.9 and 5 K. Reproduced with permission from [99]; Published by Elsevier, 2013.

The DC magnetic susceptibility studies for complex **49** was performed in a magnetic field of 1000 Oe in the temperature range 300–2 K (Figure 29b). The room temperature $\chi_M T$ value of **49** is $84.8 \text{ cm}^3 \text{ K mol}^{-1}$, which corresponds to the anticipated value of $85.02 \text{ cm}^3 \text{ K mol}^{-1}$ for six uncoupled Dy(III)-ions. The $\chi_M T$ values decrease up to 50 K with an additional drop at 2 K and reach a minimum of $68.6 \text{ cm}^3 \text{ K mol}^{-1}$ probably due to the progressive depopulation of excited Stark sub-levels and the additional drop at 2 K may be due to the competition between the ligand field effect and the ferromagnetic interaction between the Dy (III) ions. The M vs. H/T (Figure 29b), inset data at different temperatures disclose a prompt surge of the magnetization at low magnetic fields, which finally reaches a value of $30.9 \mu_B$ at 1.9 K and 7 T without the saturation value of $60 \mu_B$ (six no-interacting Dy(III) ions). This could be due to the anisotropy and the crystal field effects of Dy(III) ions.

The non-superposition of the M vs. H/T data on a single master curve refers to the existence of noteworthy magnetic anisotropy and/or low-lying excited states in compound **49** [100]. The dynamics of the magnetization by AC susceptibility measurements at zero static fields and a 3.0 Oe AC field oscillating from 1 to 1500 Hz are shown in Figure 29c. At temperatures below ~ 30 K, a frequency-dependent out-of-phase (χ'') AC signal reveals the onset of slow relaxation of the magnetization. The relaxation time was calculated from the frequency-dependent data between 1.9 and 17 K, with the Arrhenius plot (Figure 29c). It is important to note that the two relaxation processes, which are clearly observed, may be due to the single-ion interaction of individual Dy(III) ions and the weak coupling at high and low-temperatures, respectively [100]. It is interesting to note the energy gap (Δ) between the two relaxation regimes are 5.6 and 37.9 K with pre-exponential factors (τ_0) of 4.2×10^{-5} and 3.8×10^{-6} s for the low- and high-temperature domain, respectively [100].

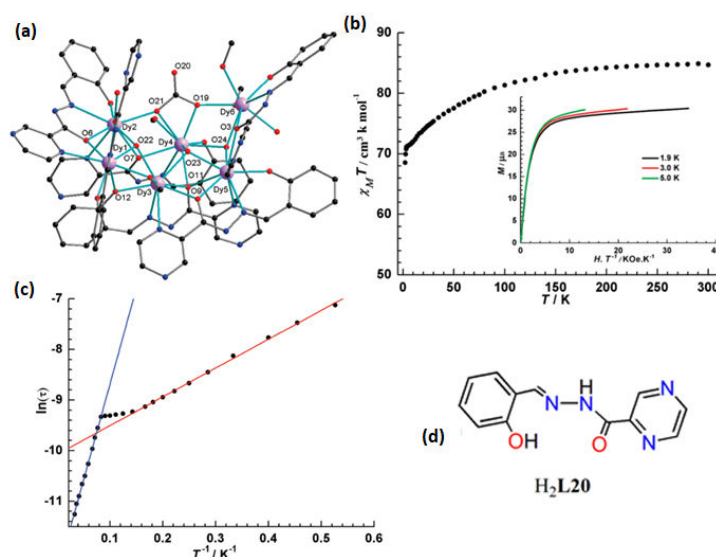


Figure 29. (a) Molecular structure of complex **49**, (b) $\chi_M T$ vs. T plot at 1 kOe. Inset: M vs. H/T plots at different temperatures below 5 K for complex **49**, (c) magnetization relaxation time, $\ln \tau$ vs. T^{-1} plot under zero DC field, (d) the structure of H_2L20 . Reproduced with permission from [100]; Published by American Chemical Society, 2011.

Another Dy-based linear helicate Dy_6 cluster with H_4L17 have been prepared and characterized by Tang et al. The compound is of the formula $[Dy_6(L17)_3(PhCOO)_6(CH_3OH)_6] \cdot 11CH_3OH \cdot H_2O$ (**50**), where the ligand, H_4L17 , is ([3,6-bis(2-hydroxy-3-methoxybenzylidene)hydrazinecarbonyl]-pyridazine) (Figure 30a).

In compound **50**, three H_4L17 wrap around six-Dy(III), generating a linear hexanuclear triple helical structure (Figure 30b) [86]. The asymmetric unit of **50** consists of three fully deprotonated H_4L17 , six-coordinated benzoate and methanol molecules also having solvent molecules in the lattice. H_4L17 coordinated with six Dy(III), as shown in Chart 7 [86].

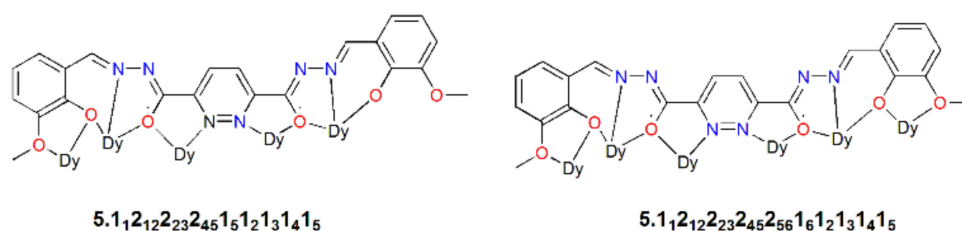


Chart 7. Coordination nature of the H_4L17 with various deprotonated forms in compound **50** (Harris notation). Reproduced with permission from [86]; Published by Royal Society of Chemistry, 2020.

The DC susceptibility was done on **50**, between 2 and 300 K in an applied field of 1 kOe (Figure 30c). The $\chi_M T$ products at 300 K, for **50** is $84.77 \text{ cm}^3 \text{ K mol}^{-1}$, which slightly decreases on decreasing temperature to a value of $78.44 \text{ cm}^3 \text{ K mol}^{-1}$ at 50 K, and then decreases rapidly to a value of $68.61 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The lowering of $\chi_M T$ products can be attributed to the thermal depopulation of excited Stark sub-levels, with the possibility of weak antiferromagnetic interactions between the Dy(III) ions at low-temperatures [86].

The AC measurements were done on **50** under a zero DC field (Figure 30d). It has been observed that the out-of-phase (χ'') signals for **50** at 11 K indicate the slow magnetic relaxation behavior. χ'' component shows a significant increase in cooling without well-defined peaks, probably induced by the fast QTM effect at low-temperatures. The field-dependent magnetization measurements were done in the range of 0–70 kOe and at 1.9, 3 and 5 K, respectively, for **50** (Figure 30e). It has been observed that up to 10 kOe, the magnetization rises quickly and reaches a maximum value of 33.14 μ_B with 70 kOe at 1.9 K, which is less than the expected saturation value of six non-interacting DY(III) ions is 60 μ_B [86]. Further, the non-superposition of the M vs. H/T plots over a single master curve shows the presence of magnetic anisotropy and **50** exhibits an effective energy barrier around 2 K [86].

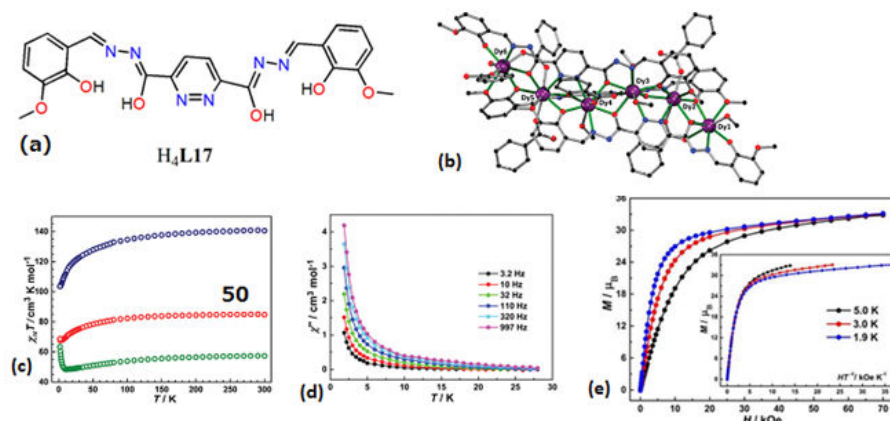


Figure 30. (a) The structure of H_4L17 (b) crystal structure of **50**, (c) $\chi_M T$ vs. T curve for **50** (red), (d) temperature dependence of out-of-phase (χ'') signals for **50** under zero DC field, (e) field dependences of magnetization between 0 and 70 kOe and at temperatures of 1.9 and 3.0 K. Insets: plots of the reduced magnetization M vs. HT^{-1} for **50**. Reproduced with permission from [86]; Published by Royal Society of Chemistry, 2020.

The above discussed Ln(III)-based Schiff base complexes are categorized in Table 1 according to their nuclearities, coordination environment and polyhedra, as well as their indicative SMMs characteristics like energy barrier (U_{eff}).

Table 1. The coordination environment and energy barriers of Ln(III)-based Schiff base single-molecule magnets (SSMMs) of different nuclearities.

Complex Formula and Number	Nuclearity	Coordination Environments	Coordination Polyhedra	Energy Barrier (U_{eff}/K)	Ref.
[Ln(L1) ₃](7) (Ln = Dy)	Mononuclear	N ₃ O ₃	Distorted trigonal-prismatic	31.4 K	[54]
[Ln(L1) ₃](8) (Ln = Er)	Mononuclear	N ₃ O ₃	Distorted trigonal-prismatic	24 K	[54]
[Dy(L2)(NO ₃)(DMF) ₂]·DMF(9·DMF)	Mononuclear	N ₂ O ₇	Spherical triangular dodecahedron	34 K	[55]
[Dy(L2) ₂ (H ₂ O) ₂]·NO ₃ ·EtOH (10·NO ₃ ·EtOH)	Mononuclear	N ₂ O ₆	Spherical triangular dodecahedron	19 K	[55]
[Ln ₂ (HL3) ₂]·nCH ₃ CN (Ln = Gd) (11)	Dinuclear	N ₄ O ₄	Square-antiprismatic	N/A	[57]
[Ln ₂ (HL3) ₂]·nCH ₃ CN (Ln = Tb) (12)	Dinuclear	N ₄ O ₄	Square-anti-prismatic	N/A	[57]
[Ln ₂ (HL3) ₂]·nCH ₃ CN (Ln = Dy) (13)	Dinuclear	N ₄ O ₄	Square-antiprismatic	19 K	[57]
[Dy ₂ (L4) ₂ (DBM) ₂ (DMF) ₂]·3CH ₃ OH(14)	Dinuclear	NO ₇	Square-antiprismatic	11 K	[58]
[Dy ₂ (HL5) ₂ (NO ₃) ₂ (MeOH) ₂](15)	Dinuclear	NO ₇	Square-antiprismatic	56 K	[38]
[Dy ₂ (HL5) ₂ (NO ₃) ₂ (MeOH) ₂] _∞ (MeCN)·(2MeCN)(16)	Dinuclear	NO ₇	Square-antiprismatic	71 K	[38]
Ln ₂ (DBM) ₆ (L6) (Ln = Dy(17) and Ln = Yb(18))	Dinuclear	N ₂ O ₆	Distorted square antiprism	47 (Dy)	[63]
[Ln(III) ₂ (L7) ₂ (NO ₃) ₂] (Ln(III) = Dy(III) (22))	Dinuclear	N ₃ O ₅	Square antiprism or/and dodecahedron	76 K	[37]
[Ln ₂ (HL8)(dbm) ₄]·2CH ₃ OH (Ln = Dy (25),	Dinuclear	N ₂ O ₆	Distorted dodecahedron	0.73 K	[65]
[Dy ₂ (dbm) ₂ (HL9) ₂ (C ₂ H ₅ OH) ₂] (28)	Dinuclear	N ₂ O ₆	Distorted bicapped trigonal-prismatic	46 ± 3.2 K	[67]
[Ln ₂ (NO ₃) ₄ (HL10) ₂ (MeOH) ₄]·MeOH, Ln = Gd (29·MeOH) and [Ln ₂ (NO ₃) ₂ (HL10) ₄]·6MeCN, Ln = Dy (30·6MeCN)	Dinuclear	N ₂ O ₇	Square-antiprismatic	N/A	[70]
[Dy ₃ (HL11) ₃ (DMF) ₆] (31)	Trinuclear	N ₂ O ₄	Triangular dodecahedron	80 K	[55]

Table 1. Cont.

Complex Formula and Number	Nuclearity	Coordination Environments	Coordination Polyhedra	Energy Barrier (U_{eff}/K)	Ref.
[Dy ₄ (L12) ₂ (C ₆ H ₅ COO) ₁₂ (MeOH) ₄](33) and [Gd ₄ (L12) ₂ ·(C ₆ H ₅ COO) ₁₂ (MeOH) ₄](34)	Tetranuclear	NO ₇	Distorted bicapped trigonal-prismatic	17 K	[73]
[Dy ₄ (HL13) ₄ (C ₆ H ₄ NH ₂ COO) ₂ (μ ₃ -OH) ₄ (μ-OH) ₂ (H ₂ O) ₄]·4CH ₃ CN ₃ ·12H ₂ O(35)	Tetranuclear	O ₈	Tetranuclear cubane for 35 and octanuclear, bis-cubane for 36	N/A	[75]
[Dy ₄ (dbm) ₄ (L14) ₆ (μ ₃ -OH) ₂]·4CH ₃ CN·2H ₂ O (39)	Tetranuclear	N ₂ O ₆	Square-antiprismatic	89 K	[76]
[Ln ₄ (H ₂ L15) ₄ (MeOH) ₈](NO ₃) ₄ ·aMeOH·bH ₂ O, (Ln = Dy(III) (42))	Tetranuclear	N ₃ O ₆	Distorted spherical capped square antiprism	158 K	[78]
[Dy ₄ (HL16) ₄ (MeOH) ₆]·2MeOH (44)	Tetranuclear	NO ₇	Distorted bicapped trigonal-prismatic	173 K	[44]
[Dy ₄ (L10) ₄ (HL10) ₂ (C ₆ H ₄ NH ₂ COO) ₂ (CH ₃ OH) ₄]·5CH ₃ OH (45)	Tetranuclear	NO ₇	Bi-capped trigonal prism or/and a square antiprism	20 K	[79]
[Dy ₄ (HL17) ₂ (L17)(DMF) ₈]·2ClO ₄ ·CH ₂ Cl ₂ ·4DMF·(CH ₃ CH ₂)·2H ₂ O(46)	Tetranuclear	O ₇ N ₂ /O ₆ N ₃	Distorted spherical tricapped trigonal prism/spherical capped square antiprism	~4 K	[86]
[Dy ₄ (TTA) ₄ (L18) ₄ (H ₂ O) ₂]·4CH ₃ OH (47)	Tetranuclear	N ₂ O ₆	Distorted square-antiprismatic	1.5 K	[95]
[Dy ₆ (L19) ₇ (HL19)(MeOH) ₂ (H ₂ O)(OH) ₂ (OAc)] (48)	Hexanuclear	N ₂ O ₆	square-antiprismatic	3.0 K	[99]
[Dy ₆ (μ ₃ -OH) ₃ (μ ₃ -CO ₃)(μ-OMe)(L20) ₆ (MeOH) ₄ ·(H ₂ O) ₂]·3MeOH·2H ₂ O (49)	Hexanuclear	NO ₇	square-antiprismatic	5.6 and 38 K	[100]
[Dy ₆ (L17) ₃ (PhCOO) ₆ (CH ₃ OH) ₆]·11CH ₃ OH·H ₂ O (50)	Hexanuclear	N ₅ O ₃ /O ₇ N ₂ /O ₆ N ₃	Triple-stranded helical structure	2 K	[86]

N/A = Not applicable.

5. Conclusions

To summarize, we have done a brief up to date review of important, notable work on pure Ln(III) based SMMs, mainly with Schiff bases of salicylaldehyde. There is a remarkable interest in Ln(III)-based SMMs in the quest to synthesize SMMs with higher effective energy barriers and blocking temperatures, whereby the synthetic strategies can play an important role. However, custom tuning of the SMM properties still remains a big challenge. Emphasis has been given for Dy(III) SMMs in the present discussions as it shows superiority in magnetism, resulting from high anisotropy of the Dy(III)-ions so as to reach the limit of the effective energy barrier.

The great potential of Schiff base ligands was used to achieve this goal by incorporating new functionalities in both amines as well as aldehydic precursors in the ligand synthesis. It was inferred from the structures discussed that by varying precursors of Schiff base condensation, we could create coordination pockets or compartments that can be used for a particular lanthanide ion to occupy, facilitating suitable magnetic exchange interactions in the clusters so generated with SMM behavior. In spite of the numerous complexes synthesized to date, the Schiff base chemistry is far from being exhausted. Among the various Schiff bases and the lanthanide (III) SMMs discussed, the Dy₄ cluster reported by Tang et al. from 2-hydroxy-3-methoxybenzoic acid (2-hydroxy-3-methoxyphenyl) methylene) hydrazide H₃L16 exhibits the highest energy barrier ($U_{eff} = 173$ K). While not having exhaustively reviewed the results of the past twelve years from various research groups, what we have discussed will give an insight into the very promising field of SMMs based on Ln(III)-ions with Schiff base ligands, mainly from salicylaldehyde derivatives.

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