



Review

High-Coordinate Mononuclear Ln(III) Complexes: Synthetic Strategies and Magnetic Properties

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Abstract: Single-molecule magnets involving monometallic 4f complexes have been investigated extensively in last two decades to understand the factors that govern the slow magnetization relaxation behavior in these complexes and to establish a magneto-structural correlation. The prime goal in this direction is to suppress the temperature independent quantum tunneling of magnetization (QTM) effect via fine-tuning the coordination geometry/microenvironment. Among the various coordination geometries that have been pursued, complexes containing high coordination number around Ln(III) are sparse. Herein, we present a summary of the various synthetic strategies that were used for the assembly of 10- and 12-coordinated Ln(III) complexes. The magnetic properties of such complexes are also described.

Keywords: high-coordinate Ln(III) complexes; multi-dentate ligands; single-ion magnets; quantum tunneling of magnetization



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1. Introduction

The seminal discovery by Sessoli et al. that a Mn_{12} cluster can show slow relaxation of magnetization reversal at very low temperatures has ignited the interest of both theoretical and experimental researchers from disciplines such as coordination chemistry, molecular magnetism and molecular materials [1]. This area of work, which is now very active, includes different systems such as single-molecule magnets (SMMs), single-ion magnets (SIMs) and single-chain magnets (SCMs). These systems are receiving attention due to the possibility of their potential to be utilized in various areas including data storage, quantum computation and spintronics [2–6]. In addition, the field of molecular magnetic refrigerants based on the principle of magneto caloric effect (MCE) also has been receiving wide research interest [7].

Single-molecule magnets (SMMs), of which SIMs are a sub-set, are characterized by a well-defined magnetically bi-stable ground electronic state and can remain magnetized below certain temperatures showing a slow relaxation of magnetization. Through experimental and theoretical work carried out over several years it has now been established that one of the characteristics of SMMs is the effective energy barrier (U_{eff}) that separates the two lowest energy spin states. This is the energy required to flip the direction of the magnetization and has been shown in polynuclear transition metal complexes to be dependent on the *Ising* type magnetic anisotropy as characterized by the zero-field splitting parameter, D and the total spin: $U_{eff} = |D|S^2$ for integer spin and $|D|(S^2 - \frac{1}{4})$ for half-integer spin. In contrast to what this relationship suggests—that increasing the total spin would continuously cause an increase of U_{eff} —it has been shown that the magnetic anisotropy, in fact, is more important. This has led to a focus on 4f metal complexes [8–10]. The 4f orbitals of the lanthanide ions are deeply buried and therefore do not interact strongly with an external ligand field. Thus, even in their complexes, lanthanide ions can possess large

spin-orbit coupling due to the unquenched orbital angular momentum and therefore these systems can be good candidates for molecular magnets. Ishikawa and co-workers were the first to demonstrate slow relaxation of magnetization in Ln(III) sandwich complexes [11]. This has led to considerable research interest in Ln(III) complexes and tailoring of magnetic anisotropy through chemical and geometric modification around the paramagnetic metal ion, particularly in mononuclear complexes, has become an important focus area. These mononuclear complexes showing SMM properties are termed as single ion magnets (SIMs) or mononuclear SMMs (MSMMs). All the lanthanides, except Gd(III) which is completely isotropic, and Eu(III) which has a non-magnetic ground state (angular momentum quantum number $J = 0$), are potential candidates in the assembly of SMMs. Again among them, complexes of Dy(III) have been the most widely studied because Dy(III) has a high J value of 15/2 and g value of 4/3 [12–17]. In addition, Dy(III) is a Kramers ion, having an odd J value which results in a time-reversal symmetric degenerate M_J states. On the other hand, for the non-Kramers ions, having an even J value, the M_J states are not degenerate [18]. For a ligand electron, i , this crystal field (CF) perturbation can be expressed by the following one electron operator, $u_{CF}(i)$ as: [19]

$$u_{CF}(i) = -e \int \frac{\rho(R)}{|R-r_i|} dv \quad (1)$$

In this equation (R) is the potential generated by means of the charge distribution and r_i is the radial distance. Thus, the overall perturbation can be calculated by summation of the one electron operators acting on all the electrons. However, the following Hamiltonian best describes the overall crystal field perturbation through Wybourne formalism as: [20]

$$\widehat{H_{CF}} = \sum_{i,k,q} B_k^q C(i)_k^q \quad (2)$$

In the above equation, B_k^q is the crystal field (CF) coefficient and $C(i)_k^q$ represents a one-electron operator acting on i th electron. For Ln(III) ions, the k and q values are limited as: $k \leq 7$ and $-k \leq q \leq k$ and the even value of k are responsible for CF splitting, while the odd k values are responsible for various spectroscopic transitions. These parameters can be useful to understand the nature of the magnetic anisotropy of the lanthanide ions in a certain ligand field (*easy plane* or *easy axis*) [21]. Rinehart et al. [22] and Jiang et al. [23] have employed quadruple approximation and electrostatic models respectively for calculating basic shapes of the charge density distributions corresponding to various M_J states for all Ln(III) ions. These studies allowed lanthanide ions to be classified into three types: prolate ions having axially elongated 4f electron density, oblate ions having equatorially expanded 4f electron density and isotropic ions of spherical electron density (see Figure 1).

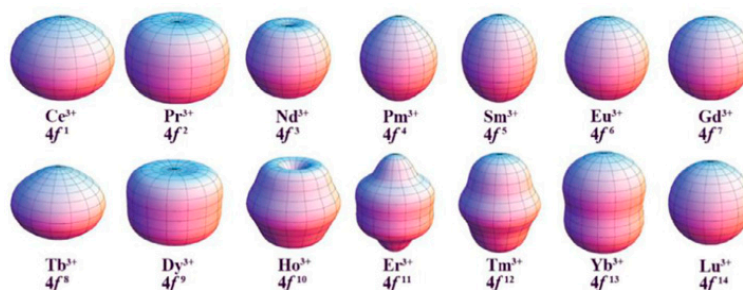


Figure 1. Electrostatic potential surfaces corresponding to the eigen states with different M_J values for each Ln(III) ion. In the absence of a crystal-field all the eigen states with different M_J values are degenerate for a particular Ln(III) ion. The shapes are evaluated with respect to the local reference frame for the electrostatic potential surfaces corresponding to the eigen states with the maximum M_J values. The figure and caption are reproduced from Reference [23] with permission from the Royal Society of Chemistry.

However, the M_J state with highest J value needs to be ground state, and at the same time there should be a sufficiently large separation from its excited states to have a large effective energy barrier. Ideally, in these situations, when the relaxations processes such as Raman, direct (these promote relaxation of magnetization by the reversal of magnetization orientation through virtual electronic states) and quantum tunneling of magnetization (that enhance the rate of magnetization reversal through ground states without any energy barrier)—which undercut the energy barrier (see Figure 2)—are absent in the system and there is a sizable separation between the ground and the excited electronic states, the maximum energy barrier for magnetization reversal can be observed.

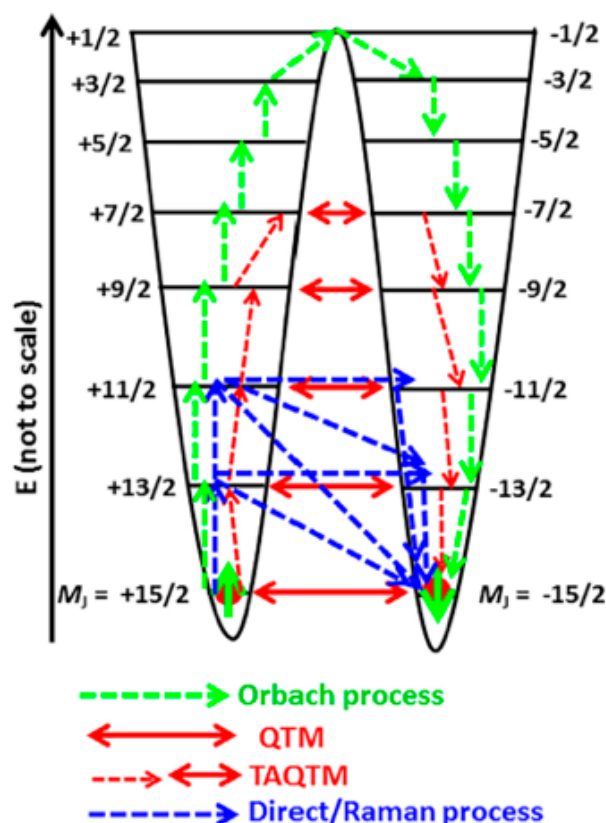


Figure 2. All possible magnetic relaxation processes involved in single-molecule magnets (SMMs). The figure is reproduced from Reference [24] with permission from the Elsevier Ltd.

This maximum separation between the M_J states can be achieved by employing an axially strong crystal field for an oblate ion and an equatorially strong ligand field for prolate ions. In practice, Ln(III) ions have a very rich coordination chemistry with a large coordination number variation that ranges from 3 to 14 [25]. In order to estimate the effect of coordination geometry on the magnetic anisotropy for Dy(III) an extensive calculation was carried out by Ungur et al. on a series of empirical complexes of the common formula $[\text{DyF}_n]^{3-n}$ (Figure 3). This study revealed that a maximum effective energy barrier can be achieved for very low coordinated Dy(III) complexes [26]. In spite of this theoretical insight, several lanthanide complexes of varying coordination geometry have been studied. This article will review those complexes where the coordination number around the lanthanide ions is greater than 9.

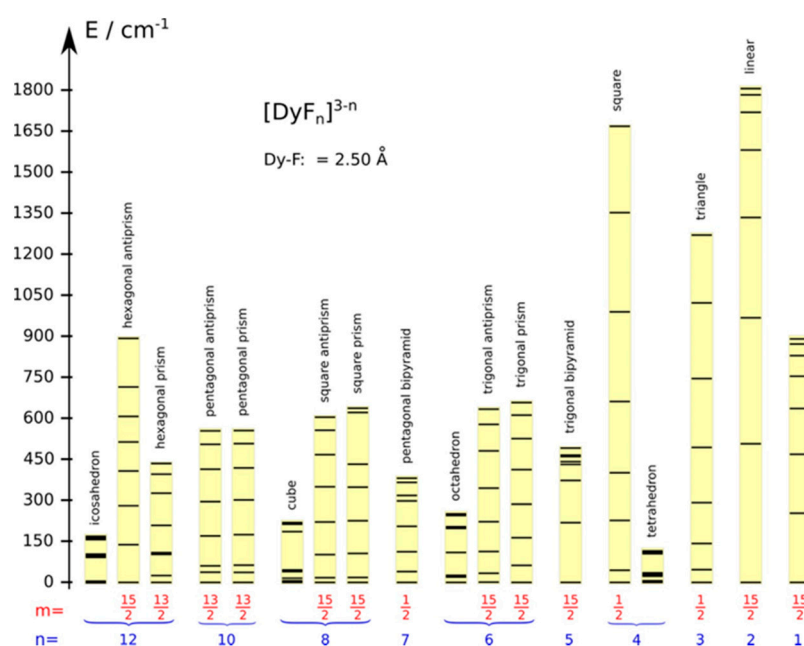


Figure 3. Energy level splitting of M_J multiplets in a different coordination number in the hypothetical complex $[\text{DyF}_n]^{3-n}$. The figure is reproduced from Reference [26] with permission from the American Chemical Society copyright © 2015.

2. High-Coordinate Ln(III) Complexes

The coordination chemistry of Ln(III) ions is dominated by coordination numbers 8 or 9 although the range of coordination numbers can be from 3–14 (see Figure 4). Among the high-coordinate (C.N. > 9) Ln(III) complexes coordination number 10 is the most commonly observed (see Figure 4) [27]. The second commonly observed high coordination numbers are 11 and 12 [28] whereas the coordination numbers 13 and 14 are extremely rare [29]. Due to the inter-ligand repulsions (“first-order” effects), monodentate ligands could lead to coordination numbers of only up to 8 and 9. Therefore, to synthesize high coordinate (C.N. > 9) Ln(III) complexes, two different synthetic strategies are employed. The first one is a multi-dentate ligand approach and the second one is a mixed ligand approach utilizing a combination of multi-dentate ligand(s) and bidentate ligand(s). It is worth noting that bidentate ligands such as the nitrate anion, have a small “bite angle” and therefore can minimize the inter-ligand repulsions. Broadly, the mixed ligand approach appears to be the more promising synthetic strategy for assembling high-coordinate lanthanide complexes.

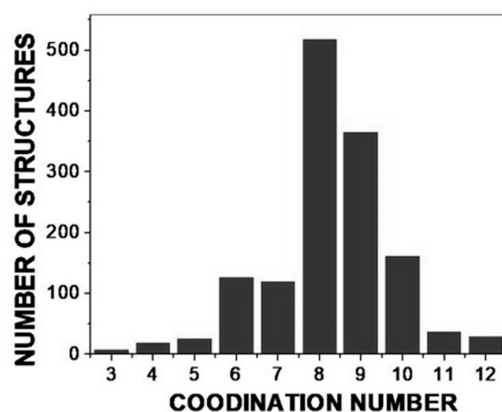


Figure 4. Abundance of coordination numbers in Ln-complexes (La–Nd, Sm–Lu, Y) based on the analysis of 1389 crystal structures published between 1935 and 1995. The figure and captions were reproduced from Reference [24] with permission from the Elsevier Ltd.

Unlike the reviews that have already been published, [8,24,30–34] herein, we review the magnetic properties of high-coordinate (C.N. > 9) Ln(III) complexes. Only those that have exhibited at least a field-dependent SMM behavior are discussed. Unfortunately, there seem to be no examples of zero-field SMM behavior among high-coordinate lanthanide complexes.

2.1. Ten-Coordinate Ln(III) Complexes

Both the multi-dentate ligand approach and the mixed ligand approach have been used to generate ten-coordinate Ln(III) complexes. In addition, the use of just the nitrate ligands has also allowed the assembly of ten-coordinate Ln(III) complexes. These approaches are discussed below.

2.1.1. Multi-Dentate Ligand Approach

Pentadentate chelating ligands are known to generate ten-coordinate Ln(III) complexes [35–37]. Diacetylpyridine bishydrazone ligands can provide a rigid pentagonal planar structure to Ln(III) ions and therefore coordination of two such ligands orthogonally towards the Ln(III) metal center could result in a ten-coordinate structure. A bicapped square antiprism (BSA) geometry is the preferred polyhedron for a mononuclear Ln(III) complex chelated by two pentadentate ligands.

Mallah and co-workers synthesized two Dy(III) compounds, $[\text{Dy}(\text{H}_2\text{dapbh})_2](\text{NO}_3)_3$ (**1**) and $[\text{Dy}(\text{H}_2\text{dapbh})(\text{Hdapbh})](\text{NO}_3)_2$ (**2**) utilizing a pentadentate hydrazone ligand (Figure 5a,b), H_2dapbh (H_2dapbh = 2,6-diacetylpyridinebis(benzoic acid hydrazone)) to study the effect of chemical tuning on slow magnetic relaxation [38]. These complexes were isolated by the reaction of two equivalents of H_2dapbh with hydrated $\text{Dy}(\text{NO}_3)_3$ in EtOH (for **1**) and in EtOH- H_2O (for **2**). The molecular structures of the two complexes were found to be similar although the formation of **2** involves a deprotonation of an amino nitrogen in one of the dapbh ligands. Therefore, the tripositive charge of the Dy(III) ion is balanced by three NO_3^- counter anions in **1** while it is balanced by two NO_3^- counter anions in **2**. In both cases, each multi-dentate ligand coordinates via the pyridyl nitrogen, two hydrazone nitrogens, and two carbonyl oxygen atoms in an interlocked fashion resulting in a ten-coordinate geometry. A C–O distance in the range 1.242–1.250 Å further confirmed the carbonyl assignment. SHAPE [39] analysis confirmed a distorted bicapped square antiprismatic geometry around the Dy(III) center with the pyridyl nitrogens being the capping atoms. The “skew angles” for the two complexes are remarkably similar: 27° for **1** and 29° for **2** (for a perfect D_4 symmetry it is 45°). Both AC and DC magnetic measurements were performed to probe the differences in the magnetic properties of **1** and **2**. The dynamic alternating current (AC) magnetic measurements at zero applied field did not reveal well-resolved maxima in the out-of-phase (χ''_M) susceptibility component for **1** and **2** even at low temperatures. After the application of an optimum DC field of 1000 Oe strong frequency-dependent signals and maxima in both the in-phase (χ'_M) and out-of-phase (χ''_M) components were observed (Figure 5c,d). Both the complexes followed a thermally activated relaxation mechanism at temperatures above 4 K. Therefore, the anisotropic barrier and the pre-exponential parameter was extracted from the $\ln(\tau)$ vs. $1/T$ plot by fitting the Arrhenius equation ($\tau = \tau_0 \exp(U_{\text{eff}}/k_B T)$) which resulted in $U_{\text{eff}} = 32.4$ K for **1** and ~ 19 K for **2**, respectively. Below 4 K, the relaxation behavior was dominated by the temperature independent QTM process. Micro-SQUID studies confirmed the presence of an easy axis of magnetization in both **1** and **2**. Both the complexes also showed hysteresis loops confirming slow relaxation of magnetization although **2** showed much faster relaxation. A larger structural distortion in **2** due to deprotonation was found to be responsible for the faster relaxation of magnetization. To gain further insight, ab initio calculations of the CASSCF/RASSI/SINGLE_ANISO type were carried out. The transverse components of the g tensor (g_x and g_y) were found to be greater in **2** than in **1** in the ground Kramer Doublet. This resulted in a large tunneling gap in **2** and therefore the complex showed faster relaxation in the magnetic measurements. The ab initio calculated main

magnetic axis (g_z) of **1** was found to be oriented along the Dy–N(pyridyl) coordination bonds which is linked to the idealized four-fold symmetry axis. On the other hand, deprotonation in **2** causes a rotation of the main magnetic axis at an angle of 60° towards the Dy–O(carbonyl) bonds. The ab initio calculated crystal field parameters were also found to be significantly different for the two complexes. This study revealed the sensitivity of the magnetic anisotropy on the ligand field around the Dy(III) sites.

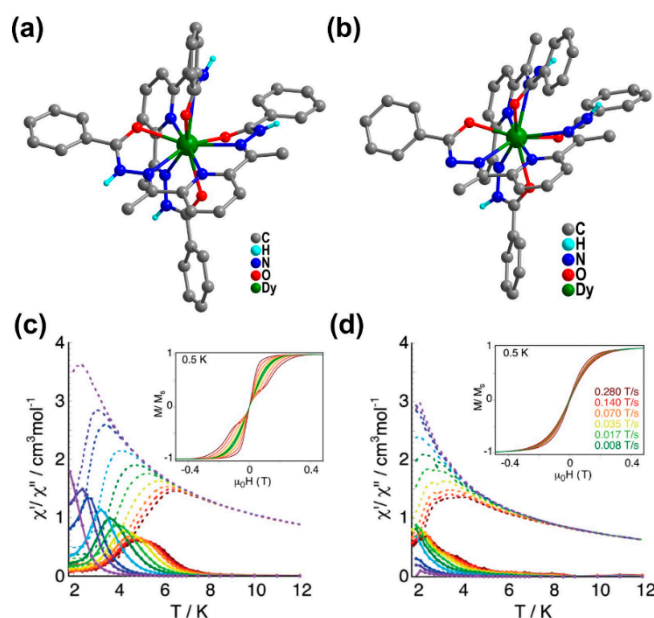


Figure 5. (a,b) Structures of the cationic part of **1** and **2**; (c,d) Temperature dependence of χ'_M (dotted lines) and χ''_M (solid lines) of **1** and **2** under 1000 Oe applied DC field at frequencies from 1 to 1200 Hz (Inset: hysteresis loops taken at 0.5 K and at variable scan rates). Figures and captions are reproduced from Reference [38] with permission from the Royal Society of Chemistry.

Recently Vasiliev and co-workers isolated a series of neutral ten-coordinate mononuclear lanthanide complexes, $[\text{Ln}(\text{Hdapbh})(\text{dapbh})]$ (Ln = Dy(III), **3**; Ho(III), **4**; Er(III), **5** and Tb(III), **7**) by the reaction of H_2dapbh (2 equiv.) with hydrated $\text{LnCl}_3/\text{Er}(\text{HCO}_3)_3$ salts in the presence of 2 equivalents of NEt_3 [40]. Following the same synthetic protocol, they isolated another neutral ten-coordinate mononuclear Dy(III) derivative, $[\text{Dy}(\text{Hdapmbh})(\text{dapmbh})]$ (**6**) that involved a methoxy-substituted H_2dapmbh ligand ($\text{H}_2\text{dapmbh} = 1,1'$ -(pyridine-2,6-diyl)bis(ethan-1-yl-1-ylidene))di-4-methoxybenzohydrazine) [40]. All these complexes are isostructural with **1** and **2** (Figure 6). Compared to **1** and **2** (vide supra), the multi-dentate ligand in **3–7** acted both in a dianionic and a monoanionic manner. The free N–H group of the monoanionic ligand was involved in hydrogen-bonding interactions with lattice solvent molecules (H_2O , MeOH and EtOH). The dihedral angles ($\text{N}_{\text{imine}}\text{--N}_{\text{pyridyl}}\text{--N}_{\text{imine}}$) of the Dy(III) derivatives were found to be similar (58.7° for **3** and 58.36° for **6**) and lie between the dihedral angles of non-deprotonated (57.17° for **1**) and singly deprotonated structures (59.43° for **2**). The coordination polyhedra of the Ln(III) ions in **3–7** was found to be a bicapped square antiprism with N(pyridyl) atoms at the capping positions.

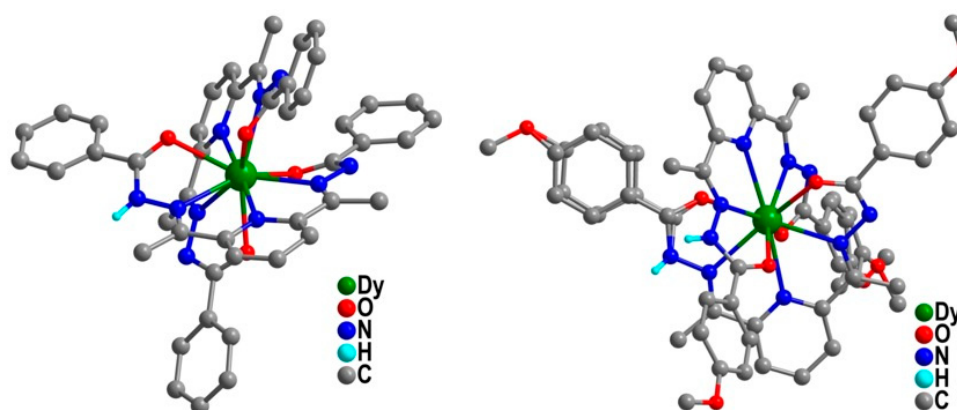


Figure 6. Molecular structure of **3** (left) and **6** (the two H's at N are disordered with 50% occupancy: (right)). The structures are re-drawn from Reference [40] with permission from MDPI.

DC magnetic measurements on **3–6** revealed the χ_{MT} products to be close to the respective free-ion approximation values, i.e., 14.17 (Dy(III), $^6H_{15/2}$), 14.07 (Ho(III), 5I_8) and 11.48 (Er(III), $^4I_{15/2}$) $\text{cm}^3 \text{ K mol}^{-1}$ at 300 K. The temperature-dependent DC data was analyzed to extract the crystal field parameters. All the complexes showed less than 400 cm^{-1} of crystal field splitting energy in the calculated crystal field energy spectrum for the lowest J -multiplets. In addition, the calculated g -tensors in the ground and the first excited Kramer doublets in **6** exhibited stronger *Ising*-type magnetic anisotropy with $g_z = 19.000$ (ground state) and $g_z = 17.310$ (first excited state) respectively. The transverse g components, $g_x = 0.082$ and $g_y = 0.581$ for **6** were also found to be smaller among all. The first excited CF state of **6** was found lying at 39 cm^{-1} from the ground state which is the highest among all the complexes. To probe the slow relaxation behavior in **3–6**, dynamic AC magnetic measurements were performed (Figure 7). At zero DC field, none of the complexes showed signals in the frequency-dependent out-of-phase (χ'') susceptibility. Upon application of an external biased field **3** ($H_{DC} = 800 \text{ Oe}$), **5** ($H_{DC} = 1500 \text{ Oe}$) and **6** ($H_{DC} = 300 \text{ Oe}$) showed frequency-dependent AC signals in both the in-phase (χ') and out-of-phase (χ'') susceptibility components due to the suppression of QTM. The SMM-silent behavior of the non-Kramer Ho(III) derivative (**4**) is primarily due to the non-magnetic character of the ground state. The temperature dependence of relaxation times in case of **4** was analyzed considering the equation, $\tau^{-1} = \tau_{QTM}^{-1} + AT + BT^n + \tau_0^{-1} \exp(-U_{eff}/k_B T)$ corresponding to the contributions from quantum tunneling of magnetization (QTM) effects (first term), direct relaxation (second term), Raman process (third term) and the Orbach process (fourth term). The best fit yielded $C = 1.2 \cdot \text{s}^{-1}$, $n = 6.1$, $U_{eff} = 87 \text{ K}$ and $\tau_0 = 4 \times 10^{-12} \text{ s}$, $\tau_{QTM} = 4.4 \times 10^{-3} \text{ s}$ and $A = 0$. The experimental $U_{eff} = 87 \text{ K}$ was found to be considerably higher than that of the first excited CF state at 23 cm^{-1} (33 K) which is close to the second excited CF state at 75 cm^{-1} (108 K) as extracted from the DC data of **5**. The $\chi''(\nu)$ and Cole–Cole plots ($\alpha_1 = 0.6\text{--}0.45$ and $\alpha_2 = 0.41\text{--}0.56$) revealed two distinct maxima at 2–2.45 K representing two different relaxation processes that could be resulting from two independent molecules present in the unit cell of **3**. Fitting $\ln(\tau)$ vs. T plot with the Arrhenius equation in the temperature range 4.4–5 K afforded the values of the effective energy barrier and the time constant: $U_{eff} = 29 \text{ K}$ and $\tau_0 = 8.3 \times 10^{-8} \text{ s}$. The experimental value of U_{eff} nicely co-related to the theoretical value ($U_{cal} = 23 \text{ cm}^{-1}$ (first excited state)). On the other hand, the temperature dependence of relaxation times in the case of **6** was analyzed considering combined Orbach and Raman processes and the best fit yielded $C = 4.2 \text{ s}^{-1}$, $n = 4.8$ (for Raman process), $U_{eff} = 70 \text{ K}$, $\tau_0 = 2.2 \times 10^{-11} \text{ s}$ (for Orbach process).

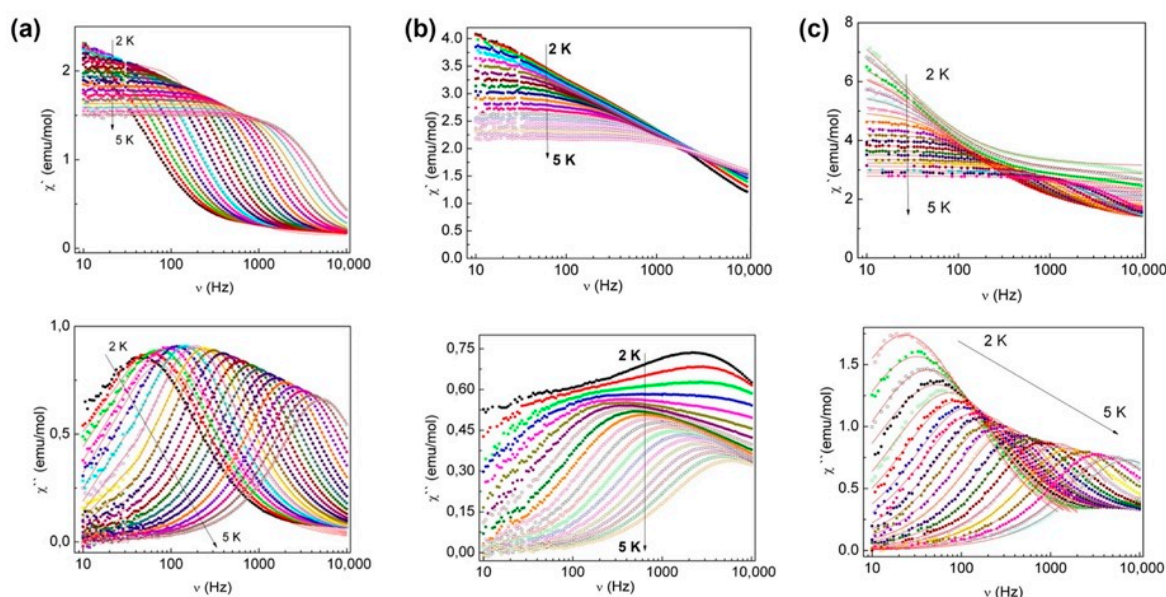


Figure 7. The frequency-dependence of the $\chi'(\nu)$ (top) and $\chi''(\nu)$ (bottom) for **4** (a) under $H_{DC} = 1500$ Oe, **3** (b) under $H_{DC} = 800$ Oe, and **6** (c) under $H_{DC} = 300$ Oe. The figures are reproduced from Reference [40] with permission from MDPI.

Unlike the $(3N2O)_2$ coordination environment discussed above, a flexible $(N5)_2$ coordination resulted in a spherical $LnN10$ coordination geometry. Tong and co-workers synthesized two $Ln(III)$ complexes of the formula, $[Ln(N5)_2](CF_3SO_3)_3$ ($Ln = Dy$ (**8**) and Er (**9**)) by the reaction of $Ln(CF_3SO_3)_3$ with two equivalents of **N5** (2,6-diacetylpyridinebis(2'-pyridyl)hydrazone) in CH_3CN [41]. The ten-coordinate low symmetry polyhedron in these complexes resulted from the coordination of two **N5** ligands interlocked by the central metal ion (Figure 8). The average $Ln-N$ distances in **8** and **9** differed only slightly (2.566 Å for **8** and 2.543 Å for **9**). SHAPE analysis revealed a very close resemblance between the bi-capped square antiprism geometry (D_{4d}) and the sphenocorona (C_{2v}) geometry confirming a spherical coordination environment in both cases. Quantitative information on energy-levels and eigenstates was extracted from the DC magnetic measurements. The ground eigen doublet state of **8** was found to be mixed with the components being $\pm 1/2$ (79%), $\pm 3/2$ (17%) and $\pm 5/2$ (3%) m_J states, respectively. On the other hand, for the prolate $Er(III)$ ion in **9** the ground doublet state was found to be mixed with the components being $\pm 15/2$ (46%), $\pm 11/2$ (44%) and $\pm 7/2$ (10%) m_J states respectively. To probe the dynamics of magnetization, AC magnetic measurements were performed under the zero DC field (Figure 8). None of these complexes showed a clear maximum in the out-of-phase (χ''_M) AC component in the temperature range of 2–10 K (1.8–7 K for **9**). This behavior has been explained as due to the QTM effects resulting from the admixture of the different m_J states in the ground state. However, for both the complexes, at an optimum field of 1200 Oe QTM was suppressed and a set of strong frequency-dependent peaks in the χ''_M AC component indicative of the slow magnetic relaxation was observed. Cole–Cole plots with quasi-semi-circular features also revealed a narrow-to-moderate distribution of relaxation times with $\alpha = 0.04$ –0.25 (for **8**) and 0.04–0.18 (for **9**) respectively (the generalized Debye function was used for fitting). The $\ln(\tau)$ vs. T^{-1} plot was fitted considering the equation, $\tau^{-1} = AT + BT^n + \tau_0^{-1} \exp(-U_{eff}/k_B T)$ where the first, second, and third terms represent direct, Raman, and Orbach relaxation process, respectively. In the high temperature regime, the Arrhenius law fit resulted in an effective anisotropic barrier of magnitude $U_{eff} = 79(4)$ K ($\tau_0 = 2.9 \times 10^{-8}$ s) for **8** and $59(4)$ K ($\tau_0 = 6.9 \times 10^{-11}$ s) for **9** which are comparable to each other. To gain further insight, a $\log(\tau)$ vs. $\log(T)$ was plotted which showed that τ obeys the T^{-n} behavior with $n = 6$ for **8** and 9.2 for **9**. In addition, consideration of both the direct and Raman processes to fit the τ versus T plot also verified the admixture of these two types of spin-lattice interaction mechanisms. The magnetic properties of the above

two complexes revealed that a spherically symmetric coordination geometry could be an effective strategy to develop SIMs with mixed m_J states.

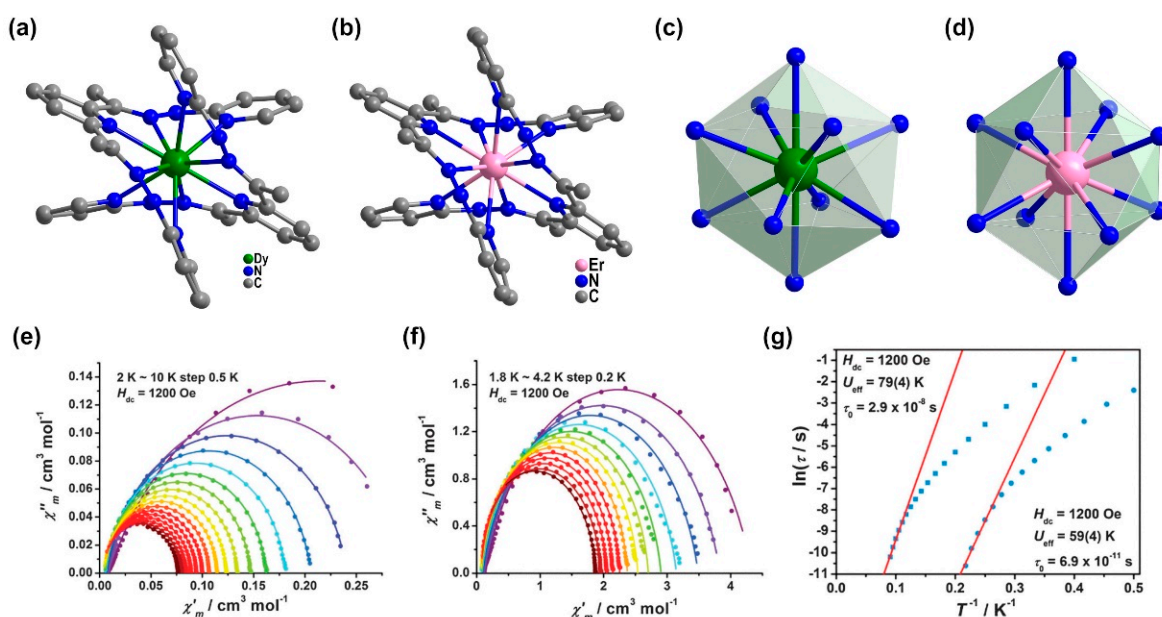


Figure 8. (a,b) Molecular structures of the cationic part of **8** and **9**, (c,d) coordination geometry of the Ln(III) ions, (e,f) Cole–Cole plots for **8** and **9** obtained from the AC susceptibility data (external DC field 1200 Oe). The solid lines correspond to the best fit obtained from the generalized Debye equation, and (g) Temperature-dependence of relaxation time (the red solid lines represent the Arrhenius law fit). Figures and captions are reproduced from Reference [41] with permission from the Royal Society of Chemistry.

2.1.2. Mixed Ligand Approach Crown Ether Ligands

Multi-dentate crown ether ligands provide an excellent opportunity to produce mononuclear ten-coordinate Ln(III) complexes in association with the coordinating nitrate anions. Crown ether ligands having small cavity size such as 12-crown-4-ether (12-crown-4 = 1,4,7,10-tetraoxacyclododecane) could form half-sandwich type mononuclear lanthanide complexes of the formula $[\text{Ln}(12\text{-crown-4})(\text{NO}_3)_3]$ (Ln = Dy(III) (**10**), Tb(III) (**11**), Ho(III) (**12**) Er(III) (**13**)) [42]. These highly crystalline complexes were easily prepared by the reaction of an equimolar mixture of the hydrated lanthanide nitrate salts and 12-crown-4 ether in acetonitrile solvent. The half-sandwich structure around the Ln(III) ion comprise of one 12-crown-4 ether ligand on one side and three bidentate NO_3^- ligands on the other side giving rise to a ten-coordinate sphenocorona (SPC, C_{2v}) geometry (Figure 9). It is important to note that the reaction of an equimolar mixture of 12-crown-4 ether and 15-crown-5 ether with hydrated lanthanide perchlorate in acetonitrile resulted in a sandwich-type complex of the formula, $[\text{Dy}(12\text{-crown-4})(15\text{-crown-5})(\text{CH}_3\text{CN})][\text{Dy}(12\text{-crown-4})(15\text{-crown-5})_2(\text{CH}_3\text{CN})_2(\text{ClO}_4)_9]$ having mixed coordination numbers (10 and 9). Dynamic AC magnetic measurements were performed on **10–13** to assess the SIM properties. None of these complexes showed well-resolved peaks in the frequency-dependent out-of-phase (χ'') AC susceptibility measurements at zero biased field. However, the application of a DC biased field to suppress the QTM partially or fully resulted in strong signals in the frequency-dependent out-of-phase (χ'') AC susceptibility only in the case of the Dy(III) derivative confirming the presence of slow relaxation of magnetization (Figure 9). From the $\ln(\tau)$ vs. T^{-1} plot at high temperature the following parameters could be extracted: $U_{eff} = 76$ K ($\tau_0 = 6.8 \times 10^{-11}$ s) at $H_{DC} = 500$ Oe [42] and $U_{eff} = 68$ K ($\tau_0 = 2.07 \times 10^{-10}$) at $H_{DC} = 1000$ Oe [43] respectively. The non-Kramer Tb(III) and Ho(III)

ions did not show this behavior because of the large energy gap between the ground and first excited states and the presence of low symmetry ligand field (sphenocorona, C_{2v}) around the metal ion. On the other hand, the Kramer ion, Er(III) did not show non-zero AC signals probably due to the existence of strong QTM or a non *Ising* ground state.

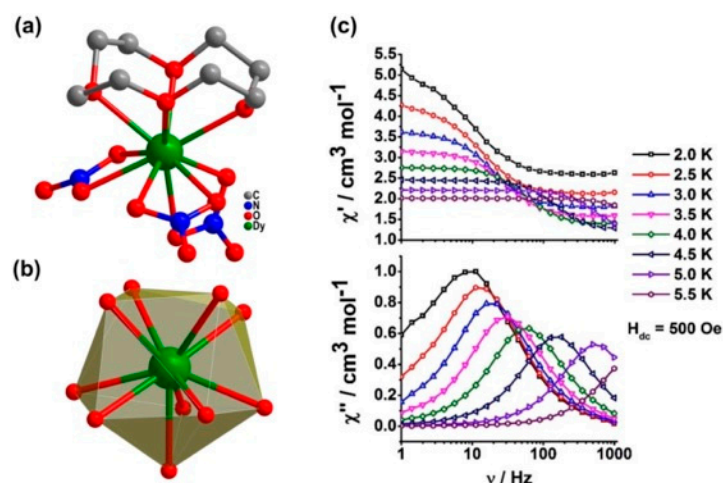


Figure 9. (a) Molecular structure of **10**, (b) sphenocorona coordination geometry around the central Dy(III) ion, and (c) frequency-dependent in-phase (χ') and out-of-phase (χ'') AC susceptibilities from 2.0 to 5.5 K for **10** under $H_{DC} = 500$ Oe. Figures and captions are reproduced from Reference [42] with permission from the Royal Society of Chemistry.

A larger cavity sized crown ether ligand such as 18-crown-6 ether can accommodate only one Ln(III) ion inside its cavity and therefore serves as a flexible equatorial ligand. Zheng and co-workers synthesized two isostructural ten-coordinate complexes of the formula $[Dy(18\text{-crown-6})(NO_3)_2]ClO_4$ (**14**) and $[Dy(18\text{-crown-6})(NO_3)_2]BPh_4$ (**15**) by employing two different charge balancing counter anions [43]. The cationic unit in both the complexes, i.e., $[Dy(18\text{-C-6})(NO_3)_2]^+$ were similar (Figure 10). The Dy–O bond lengths arising from the two nitrate ligands are comparatively shorter (Dy–O range 2.402(3)–2.439(3) Å) than the Dy–O bond lengths of the 18-crown-6 ligand (Dy–O range 2.450(5)–2.562(3) Å) in both the complexes. The crown ether ligand in **15** was found to be more distorted than that in **14**. All these structural differences resulted in different coordination polyhedra in **14** and **15** namely sphenocorona (CShM = 2.28) for **14** and bicapped square antiprism (CShM = 3.10) for **15**. None of the two complexes showed out-of-phase (χ'') AC magnetic susceptibility signals in the dynamic AC magnetic measurements under zero field. However, at an optimum external DC field of 1000 Oe, both the complexes showed strong frequency-dependent in-phase (χ') and out-of-phase (χ'') AC susceptibility signals. The analysis of this data afforded the following parameters: $U_{eff} = 63$ K ($H_{DC} = 1000$ Oe) and $\tau_0 = 1.02 \times 10^{-8}$ s for **14** and $U_{eff} = 43$ K ($H_{DC} = 1000$ Oe) and $\tau_0 = 1.37 \times 10^{-6}$ s for **15** respectively (Figure 10). Irrespective of the structural similarity in the cationic part of **14** and **15**, the significant difference in the anisotropic barriers solely resulted from the geometrical perturbations around the Dy(III) center. In the low temperature regime, the Raman relaxation process was found to be the dominant relaxation process. This study concludes that 18-crown-6 crown ether ligand could play an important role as a ligand for designing axially tuned high-performance SMMs in the future.

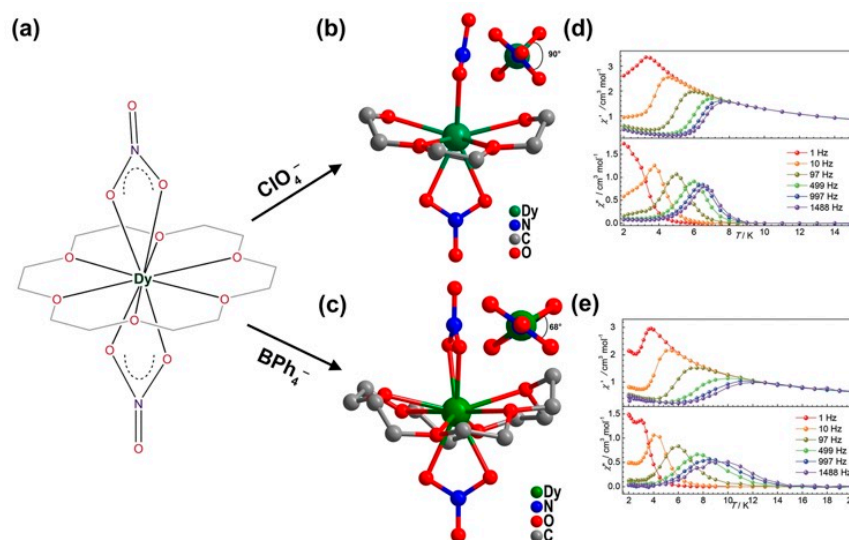


Figure 10. Scheme sketch (a), for side view (b) for **14** and (c) for **15** of $[\text{Dy}(\text{18-crown-6})(\text{NO}_3)_2]^+$ cation. Inset: dihedral angles for apical bidentate nitrate anions, (d) and (e) Temperature-dependence of the in-phase (χ') and out-of-phase (χ'') AC susceptibility signals under 1000 Oe DC field at the indicated frequencies for complexes **14** and **15**. Lines are visual guides only. Figures and captions are reproduced from Reference [43] with permission from the Royal Society of Chemistry.

Bidentate N,N-Donor Ligands

Bidentate N,N-donor ligands such as phenanthroline (phen) and bipyridine (bipy) in combination with chelating nitrate ligands are known to produce mononuclear ten-coordinate Ln(III) complexes of the formula $[\text{Ln}(\text{L})_2(\text{NO}_3)_3]$ (where L is phen and bipy). Liang and co-workers synthesized a mononuclear ten-coordination complex $[\text{Dy}(\text{phen})_2(\text{NO}_3)_3]$ (**16**) by the reaction of 1,10-phenanthroline and $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ under solvothermal conditions [44]. A perspective view of **16** is shown in Figure 11. The coordination of two phen and three NO_3^- ligands resulted in two symmetrical 5-membered rings (DyN_2C_2) and three 4-membered rings (DyO_2N) in **16**. This complex did not show any peaks in the dynamic AC magnetic measurements performed under the zero DC field. Under an applied DC field of 1500 Oe **16** showed significant dependence on both frequency and temperature in the out-of-phase (χ'') AC susceptibility components in the temperature range 2–10 K revealing its field-induced slow magnetic relaxation characteristics (Figure 11). The complex **16** also exhibited a red emission (~ 630 nm) corresponding to the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ transition. Investigation of such dual properties in a single complex is currently in vogue in the field of molecular magnetism.

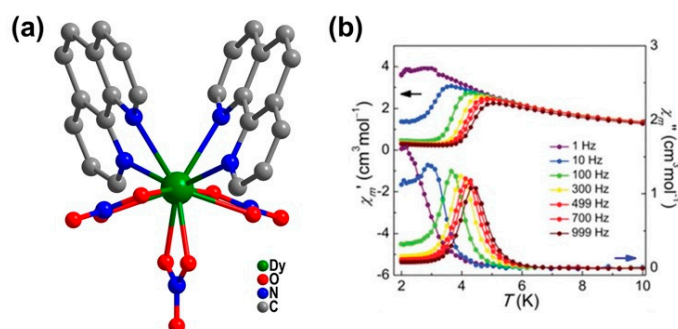


Figure 11. (a) Molecular structure and (b) temperature dependence of the in-phase (χ') and out-of-phase (χ'') AC susceptibilities for different frequencies at a DC field of 1500 Oe of **16**. Figures and captions are reproduced from Reference [44] with permission from the Royal Society of Chemistry.

Korolkov and co-workers introduced a chiral (–)-menthol fragment in the ortho position of phenanthroline resulting in a new chiral ligand, 2-((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl)-1,10-phenanthroline (**L1**). Further, **L1** was utilized to synthesize a series of mononuclear ten-coordinate Ln(III) complexes, $[\text{Ln}(\text{L1})_2(\text{NO}_3)_3]$ (Ln = Eu; (**17**), Gd; (**18**), Tb; (**19**), Dy; (**20**)) [45]. The molecular structure analysis revealed the presence of a 2-fold rotational axis passing through the metal center and the N–O bond of a coordinated nitrate ligand (Figure 12). It is to be noted that the chair conformation of the 6-membered carbocycle belonging to the menthol moiety did not change upon coordination by **L1**. A comparison of the crystal parameters of the Tb(III) derivative with its achiral analogue, $[\text{Tb}(\text{phen})_2(\text{NO}_3)_3]$ (**21**) [46] revealed that the presence of the chiral ligand changes the unit cell parameters and the space group (centrosymmetric ($C2/c$) in **21** to non-centrosymmetric ($P4_12_12$) in **19**). The temperature-dependent μ_{eff} (effective magnetic moment) values for **17**–**20** agree well with the achiral analogue $[\text{Ln}(\text{phen})_2(\text{NO}_3)_3]$ [47] which suggests that the high temperature μ_{eff} values are not affected by the replacement of phen by **L1**. None of these complexes showed any peaks in the frequency-dependent out-of-phase (χ'') AC magnetic measurements at 2 K even at high frequency.

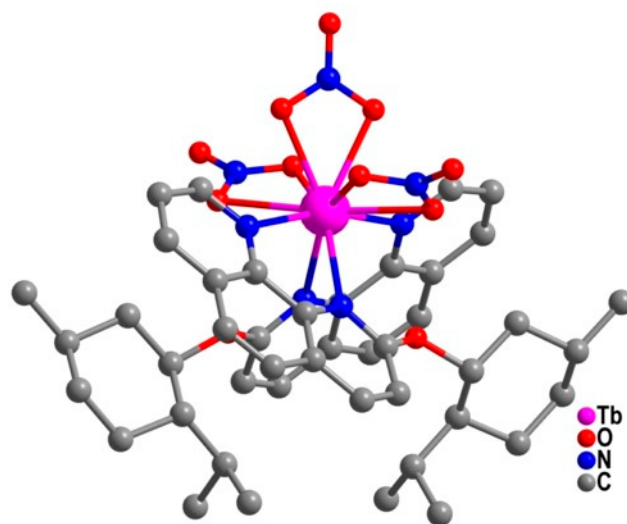


Figure 12. Molecular structure of **19**. Hydrogen atoms are omitted for clarity. The figure is reproduced from Reference [45] with permission from the Royal Society of Chemistry.

Modifying the phenanthroline backbone Lau and co-workers synthesized a phenanthroline-amide ligand, N^2,N^9 -dibutyl-1,10-phenanthroline-2,9-dicarboxamide (**L2**) [48]. In comparison to the ligands discussed above, **L2** is now a tetradentate ligand symmetrically substituted by amide functionalities at the 2 and 9 positions of the phenanthroline moiety. The reaction of **L2** with $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in MeOH in the presence of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ afforded three isostructural mononuclear complexes, $[\text{Ln}(\text{L2})_2(\text{NO}_3)](\text{ClO}_4)_2$ (Ln = Eu (**22**), Sm (**23**), Tb (**24**) and Dy (**25**)) [48]. The ten-coordinate geometry of Ln(III) in **22**–**25** resulted from the coordination of four N atoms and four O atoms from two **L2** ligands, and two O atoms from a $\kappa^2\text{O}$ -nitrate (Figure 13). All the complexes exhibited sphenocorona coordination geometries with an approximate C_{2v} symmetry. The presence of bulky ClO_4^- anions and the butyl groups ensured well-separated magnetic centers with large $\text{M} \cdots \text{M}$ separations in the range of 10.8–11.1 Å. Dynamic AC magnetic measurements were performed to probe the SIM behavior in the Tb(III) and Dy(III) derivatives. Both did not show peaks in the out-of-phase(χ'') susceptibility under a zero biased DC field revealing significant QTM in the ground state. Application of an external DC field (1500 Oe for **24** and 1000 Oe for **25**) caused the QTM to be suppressed and a clear maxima in the frequency-dependent in-phase and out-of-phase AC components to be observed (Figure 13). It was surprising that complex **24** showed two maxima in the out-of-phase(χ'') susceptibility component below 3 K while only one maximum was observed in the temperature range 3 to 5.5 K. The double relaxation

behavior was further confirmed in the Cole-Cole plots with two obvious semicircles. The complex relaxation behavior of **24** was analyzed considering three relaxation processes namely Raman, Orbach, and quantum tunneling, following the equation, $\tau^{-1} = CT^n + \tau_0^{-1}\exp(-U_{\text{eff}}/k_B T) + \tau_{\text{QTM}}$ which resulted in $U_{\text{eff}} = 76.0$ K, $\tau_0 = 1.35 \times 10^{-11}$ s, $C = 3.27 \text{ K}^{-4.72} \text{ s}^{-1}$, $n = 4.72$, and $\tau_{\text{QTM}} = 3.93 \times 10^{-4}$ s respectively. Although the Dy(III) derivative is isostructural with the Tb(III) derivative only one relaxation process was observed in this case as confirmed by the Cole-Cole plots. The temperature-dependent relaxation times of **25** were analyzed considering the Raman and Orbach relaxation mechanisms (first two terms in the previous equation) and an energy barrier $U_{\text{eff}} = 44.3$ K and pre-exponential parameter $\tau_0 = 5.17 \times 10^{-7}$ s, respectively was extracted. Also, the Raman relaxation parameters C and n were found to be $0.475 \text{ K}^{-4.29} \text{ s}^{-1}$ and 4.29 , respectively.

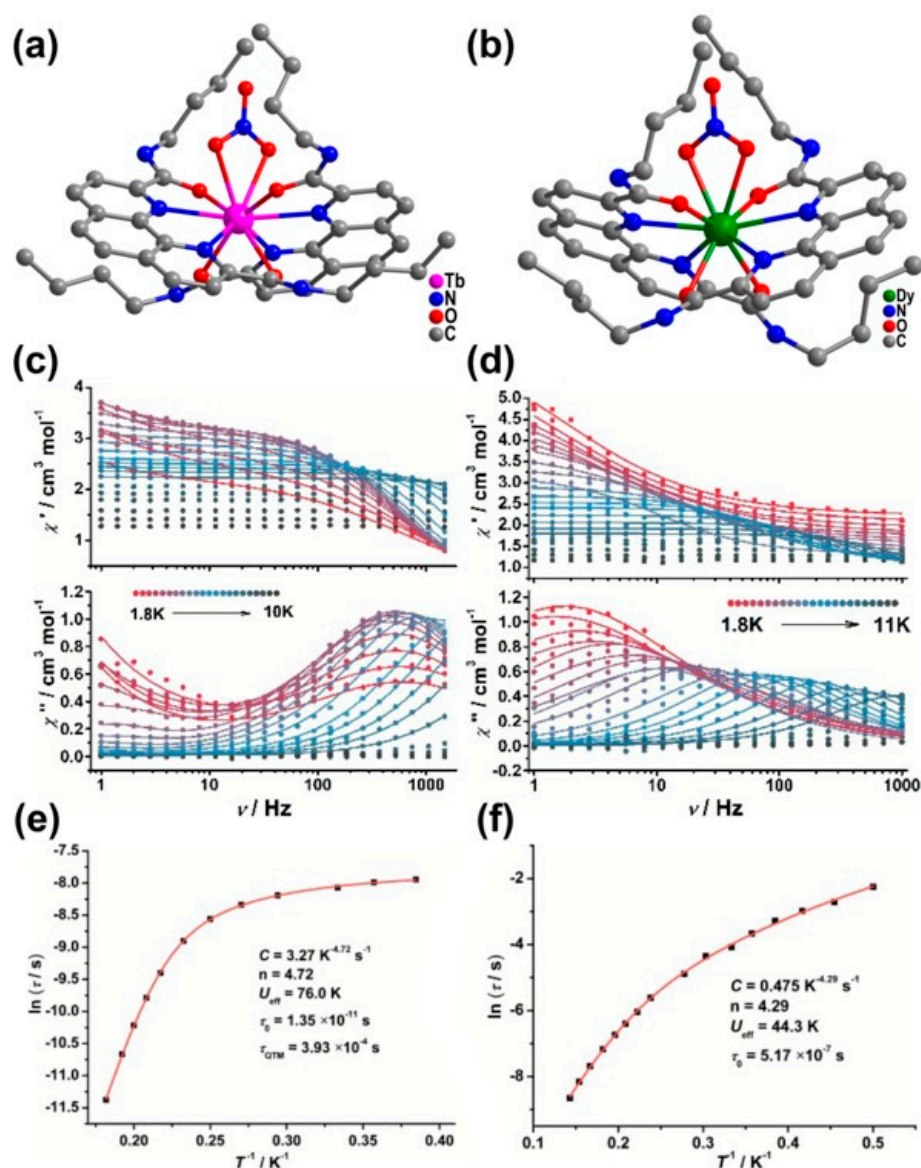


Figure 13. (a,b) Perspective viewings for the cationic structures of **24** and **25**, (c,d) frequency dependence of in-phase (χ') and out-of-phase (χ'') AC magnetic susceptibility for **24** and **25** under a 1.5 kOe (for **24**) and 1.0 kOe (for **25**) DC field, and (e,f) the $\ln(\tau)$ vs. T^{-1} plots for **24** and **25** (red lines are the best fits). Figures and captions are reproduced from Reference [48] with permission from the Royal Society of Chemistry.

Terpyridyl Ligand

Terpyridine ligands are known to produce stable mononuclear complexes with 4f ions. Wand and co-workers synthesized a ten-coordinate Ce(III) complex, $[\text{Ce}(\text{Fcterpy})(\text{NO}_3)_3(\text{H}_2\text{O})]$ (**26**) with a ferrocene-based terpyridine ligand (Figure 14), 4'-ferrocenyl-2,2':6',2''-terpyridine (Fcterpy) [49]. The deca-coordination around the Ce(III) ion resulted from the coordination of one Fcterpy, three bidentate nitrate ligands and one water molecule. The polyhedral geometry could be described as distorted bicapped square antiprism with two nitrate O atoms in the capping positions. Static magnetic susceptibility measurement revealed a $\chi_M T$ value of $0.55 \text{ emu K mol}^{-1}$ at room temperature which is slightly lower than the theoretical value of $0.80 \text{ emu K mol}^{-1}$ for a Ce(III) ($^2F_{5/2}$, $S = 1/2$; $L = 3$, $g = 0.857$) for the monomeric structure. Field-dependent magnetization measurements with the non-saturation of magnetization even at high fields revealed the presence of magnetic anisotropy in **26**. The experimental susceptibility data was modelled [50] and $g_{\text{Ce}} = 0.686$ and $D = 0.04 \text{ cm}^{-1}$ was extracted from the best fit. The lower value of the obtained zero-field splitting parameter (D) represents a small magnetic anisotropy in **26**. AC magnetic measurements did not show peaks in the out-of-phase (χ''_M) susceptibility component under zero biased field. Under an applied DC field of 2000 Oe, strong frequency-dependent maxima in the out-of-phase (χ''_M) susceptibility with peak maxima shifting towards lower frequencies verified the slow relaxation of the magnetization in **26**. The Cole-Cole plots also revealed a narrow distribution of relaxation times with $\alpha = 0.05$ – 0.11 (2–3 K) (Figure 14).

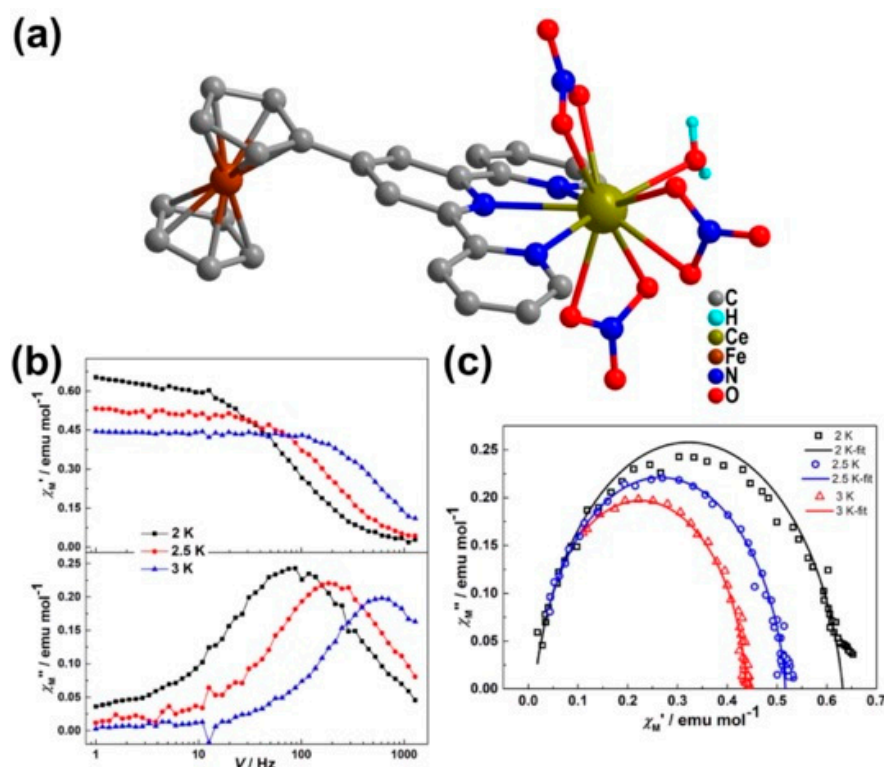


Figure 14. (a) Molecular structure of **26**, (b) frequency dependence of the in-phase (χ') (top) and out-of-phase (χ''_M) (bottom) magnetic susceptibility of **26** between 2 and 3 K under 2 kOe, (c) Cole–Cole plots of **26** between 2 K (black) and 3 K (red) (the solid lines represent the best fits as calculated with an extended Debye model). Figures and captions are reproduced from Reference [49] with permission from Elsevier Ltd.

Schiff Base and Semicarbazone Ligands

Hetero donor Schiff base ligands are widely used as compartmental ligands to assemble a variety of homo- and heterometallic complexes with different nuclearity [51–53]. Shanmugam and co-workers synthesized a couple of ten-coordinated Ln(III) complexes of

the common formula $[\text{Ln}(\text{HL}_3)_2(\text{NO}_3)_3]$ (where Ln is Dy(III) (**27**); Pr(III) (**28**) and HL_3 = 2-methoxy-6-[(E)-phenyliminomethyl]phenol) (Figure 15) [54]. The central Ln(III) in both the complexes is present in a distorted bicapped square anti-prism geometry. Interestingly, in these complexes the donor N atom of the ligand does not take part in coordination. Rather, it accepts the acidic proton from the phenolic -OH group of the ligand. This deprotonated phenolic group with another -OMe group of two participating ligands provides four coordinating atoms to the Ln(III) ion. The remaining coordination sites are occupied by three chelating nitrate ions which also provide charge neutrality to the complex. Interestingly, complex **27** (Dy(III) analogue) has been found to be co-crystallized with another geometric isomer with the same molecular formula with a different orientation of the coordinated nitrate groups. The room temperature $\chi_M T$ values for Dy(III) analogue ($14.06 \text{ cm}^3 \text{ K mol}^{-1}$) and the Pr(III) analogue ($1.61 \text{ cm}^3 \text{ K mol}^{-1}$) are consistent with the theoretically expected values. Dynamic magnetization studies revealed that the Dy(III) analogue was a field-induced SMM at an optimum field of 2 kOe. From the Cole-Cole plot (Figure 16), two types of closely spaced relaxation dynamics were detected. These were rationalized as occurring due to the presence of two geometrical isomers in the crystal structure of **27**. The extracted effective energy barriers from Arrhenius equation were found as 16.6 cm^{-1} ($\tau_0 = 2.47 \times 10^{-6} \text{ s}$) and 15.8 cm^{-1} ($\tau_0 = 3.6 \times 10^{-7} \text{ s}$).

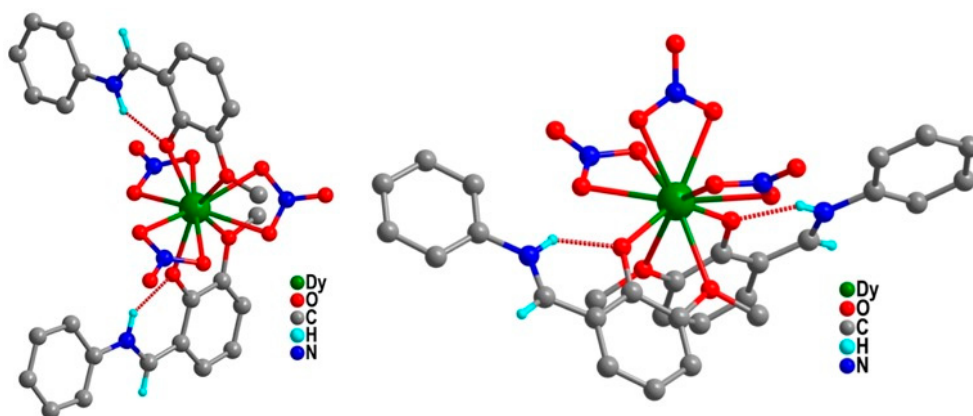


Figure 15. Molecular structures of the two geometrical isomers **27** (left) and **27'** (right). Figures and captions are reproduced from Reference [54] with permission from the Wiley-VCH.

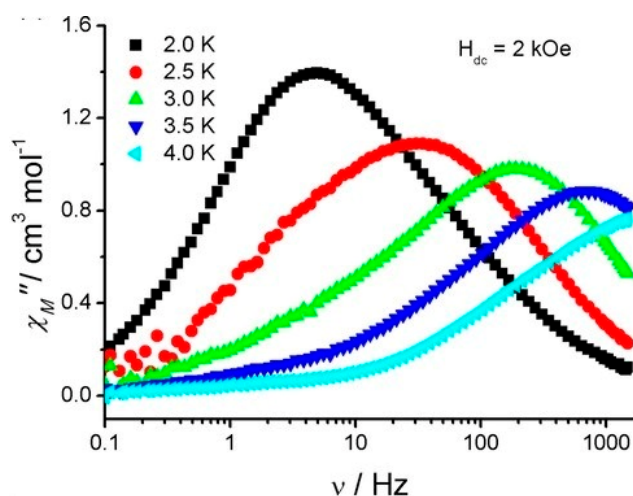


Figure 16. Frequency-dependent out-of-phase susceptibility data measured for polycrystalline sample of **27**. Figures and captions are reproduced from Reference [54] with permission from the Wiley-VCH.

Ab initio CASSCF SINGLE_ANISO calculations on the Dy(III) analogue were performed by taking the two distinct geometrical isomers separately to ascertain the origin of the magnetic relaxation (Figure 17). In both the isomers, although the ground Kramer's doublet is computed to be $\pm 15/2$ a significant multiconfigurational wave nature of the ground state was observed which opened the channel for ground state QTM which accounted for the absence of SMM behavior in zero field.

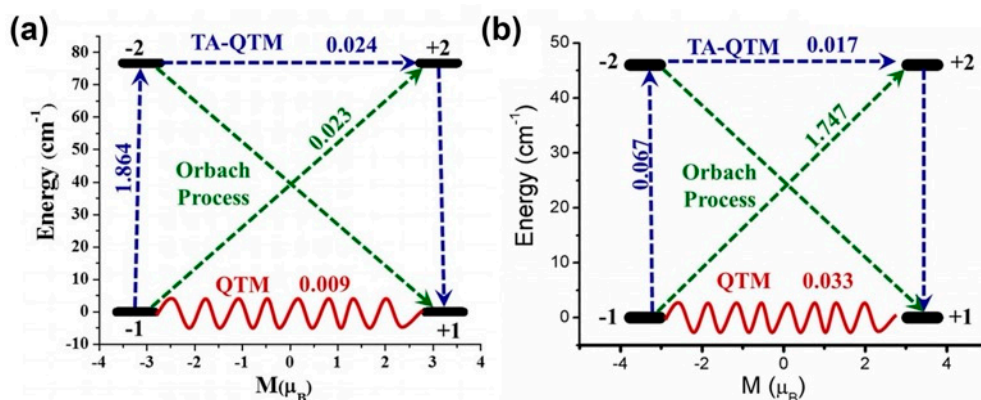


Figure 17. Ab initio computed matrix elements between the connecting pairs (ground state and first excited state) in complexes **27** (a) and **27'** (b). The thick black line indicates the Kramer's doublets (KDs) as a function of magnetic moment. The dotted green lines show the possible pathway of the Orbach process. The zigzag lines connecting the ground state KDs represent the QTM. The dotted blue lines show the thermally activated-QTM through the first excited state. Figures and captions are reproduced from Reference [54] with permission from the Wiley-VCH.

A subcomponent self-assembly strategy was employed by Mallah and co-workers to synthesize a series of mononuclear ten-coordinate complexes, $[\text{Ln}(\text{L4})(\text{NO}_3)_2](\text{NO}_3)$ where $\text{Ln}(\text{III}) = \text{Dy}$, (**29**); Tb , (**30**); Ho , (**31**); Er , (**32**); Y , (**33**) and $\text{L4} = \text{N,N}'\text{-bis-pyridin-2-yl-methylene-1,8-diamino-3,6-dioxaoctane}$ (Figure 18) [55]. The $\text{Ln}(\text{III})$ ion in these complexes served as a template around which the ligands were organized. The deca-coordination around the $\text{Ln}(\text{III})$ ions resulted from the coordination of L4 with N_4O_2 coordination sites in an equatorial plane and four O atoms from two NO_3^- ligands from above and below this plane. The equatorial plane comprising the L4 ligand was highly distorted due to the steric bulk of the pyridine rings. The LnN_4O_6 polyhedron in these complexes has been described as *very* distorted bicapped square antiprism. To probe the SMM properties in **29**–**32**, dynamic AC magnetic measurements were performed. Under zero DC field, only the complexes **29** (Dy) and **30** (Tb) showed frequency-dependent out-of-phase (χ'') susceptibility signals, but without any clear maxima. This behavior was attributed to a fast QTM. Upon application of an optimal biased field of 1000 Oe both frequency-dependent AC signals (in-phase and out-of-phase) were observed for **29** and **30** below 10 K though only **29** (Dy) showed a clear maxima (Figure 18). The $\ln(\tau)$ vs. $1/T$ plots were fitted with the Arrhenius law which resulted in $U_{\text{eff}} = 50$ K and $\tau_0 = 6.80 \times 10^{-7}$ s. The Cole-Cole plots with semi-circular curves confirmed a single relaxation time with α parameter close to zero though at low temperature the appearance of a second semicircle can be seen. Both the complexes revealed hysteresis loops in the micro-SQUID measurements at varying sweep rates. The Dy(III) derivative showed step-like features signifying QTM at the level crossing while the Tb derivative did not.

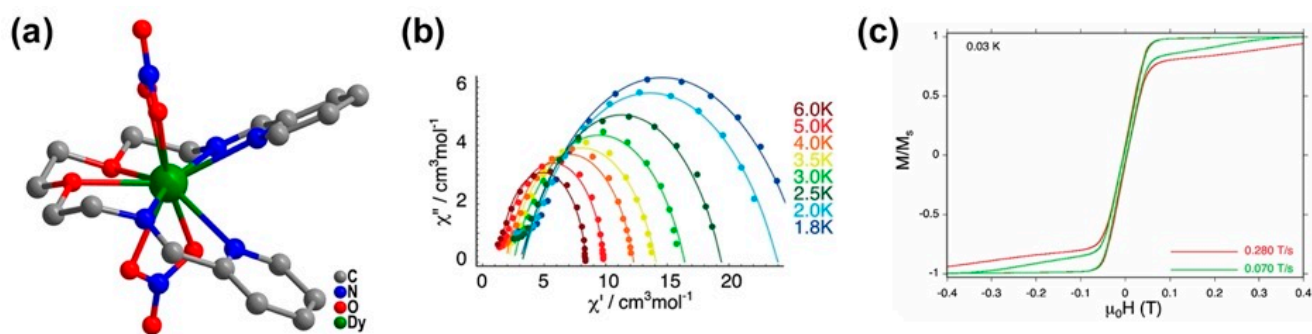


Figure 18. (a) Molecular structure of **29**, (b) Cole-Cole plots for **29** obtained from the magnetic susceptibility data. The solid lines represent the fit obtained with a generalized Debye model with $\alpha = 0.36, 0.35, 0.29, 0.28, 0.26, 0.21, 0.12$, and 0.08 sorted by increasing temperatures, and (c) Full sweep hysteresis loops for **29** at the indicated sweep rates and temperature. Figures and cations are reproduced with permission from Reference [55] copyright @ American Chemical Society.

Semicarbazone based ligands have been widely used in coordination chemistry including in the formation of lanthanide complexes. Nunes and co-workers used a semicarbazone based Schiff base ligand 1-((E)-2-pyridinylmethylidene)semicarbazone, Hscpy, to prepare mononuclear complexes, $[\text{Ln}(\text{Hscpy})_2(\text{NO}_3)_2]\text{NO}_3 \cdot \text{MeOH}$ ($\text{Ln}(\text{III}) = \text{Gd}$ (**34**) and Tb (**35**)) (Figure 19) [56].

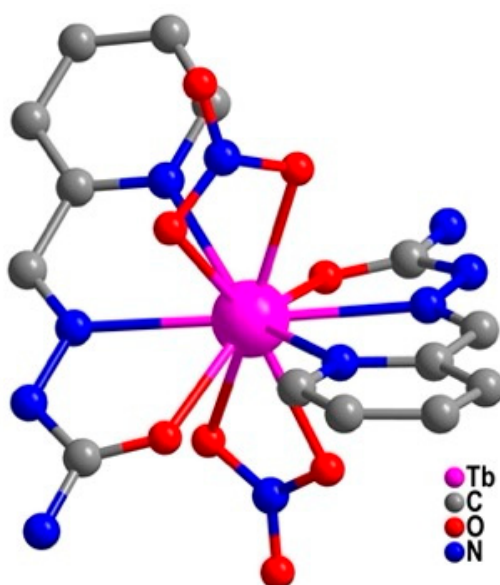


Figure 19. Molecular structure of complex **35**. The figure is reproduced from Reference [56] with permission from the Elsevier Ltd.

The two ligands provided a 4N,2O coordination environment while the remaining four sites were occupied by the nitrate ions. In the AC susceptibility measurements, the complex **35** ($\text{Tb}(\text{III})$ derivative) did not show any out-of-phase susceptibility peak maxima. However, upon applying a static field of 1 kOe and then further 1.5 kOe, fast relaxation was stopped which allowed a peak maxima to be observed (Figure 20). The extraction of the data by fitting the extended Debye model followed by utilizing the Arrhenius equation produced the following parameters, $\tau_0 = 2.6(1) \times 10^{-6} \text{ s}$, $\Delta = 7.6(2) \text{ cm}^{-1}$ and $\tau_{\text{QTM}} = 2.60(3) \times 10^4 \text{ Hz}$ for the applied field of 1 kOe and $\tau_0 = 8.3(5) \times 10^{-7} \text{ s}$, $\Delta = 21.9(4) \text{ cm}^{-1}$ and $\tau_{\text{QTM}} = 1.92(1) \times 10^4 \text{ Hz}$ for applied of 1.5 kOe.

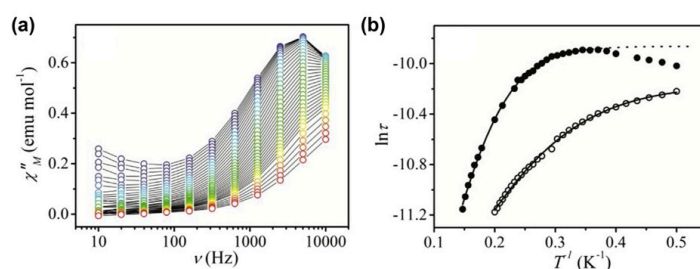


Figure 20. (a) Frequency dependence of the out-of-phase magnetic susceptibility of **35**, measured for different temperatures ranging from 2.0 K (blue points) to 6.0 K (red points) measured with an applied magnetic field of 1 kOe; (b) Temperature dependence of the relaxation times measured with a static applied magnetic field of 1 kOe (empty circles) and 1.5 kOe (full circles) along with the corresponding best fitting lines. Figures and captions are reproduced from Reference [56] with permission from the Elsevier Ltd.

Tripodal Ligands

Konar and co-workers utilized a tripodal ligand, tris(2-benzimidazolymethyl)amine (ntbi) having bulky benzimidazole arms to capture a single Ln(III) ion into its cavity [57]. Therefore, the reaction of ntbi with hydrated Ln(III) nitrate salts afforded mononuclear ten-coordinate complexes of the formula $[\text{Ln}(\text{ntbi})(\text{NO}_3)_3]$ (Ln = Dy (**36**) and Ho (**37**)) (Figure 21). It is to be noted that changing the metal precursor to Ln(III) chlorides resulted in eight-coordinate mononuclear complexes where two ntbi ligands chelate one Ln(III) ion. The ten-coordinate sphenocorona polyhedron (CShM = 3.655) around the Ln(III) ions resulted from the coordination of four N atoms from the ntbi ligand and six O atoms from the three NO_3^- ligands. The three free NH groups corresponding to the benzimidazole ligands of the ntbi ligand were further involved in H-bonding interactions with a nitrate group of neighboring $[\text{Ln}(\text{ntbi})(\text{NO}_3)_3]$ molecule resulting in undulating 1D chains along the crystallographic *c* axis. Further, the N–H...O hydrogen-bonding links could be arranged in 2D grid-like layers and 3D supramolecular cubic framework structures. Dynamic AC magnetic measurements were performed to assess the SIM properties in these complexes (Figure 21). Under zero applied DC field none of them showed clear maxima in the out-of-phase AC susceptibility above 2 K due to fast QTM. However, under an optimum biased field of 1200 Oe distinct peaks were observed ($U_{\text{eff}} = 53.4$ K and $\tau_0 = 1.6 \times 10^{-12}$ s).

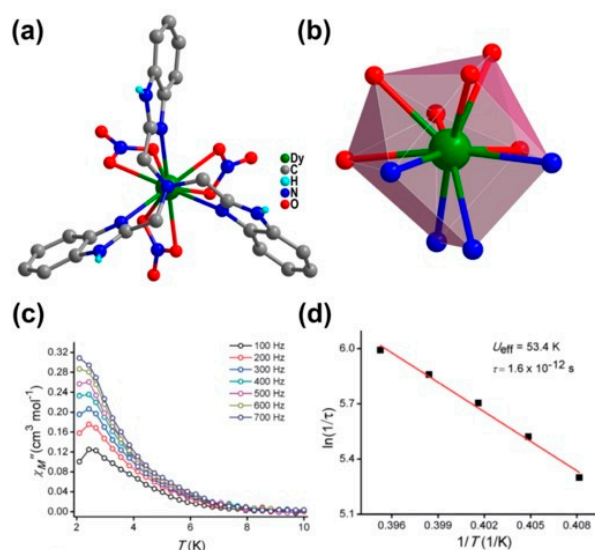


Figure 21. (a) Molecular structure of the complex **36**, (b) illustration of the “sphenocorona” coordination geometry of the Dy(III) center, and (c) out-of-phase (χ''_M) vs. *T* AC susceptibility plots, (d) plot of relaxation time (τ) as a function of temperature (*T*) for **36** at 1200 Oe. Figures and captions are reproduced from Reference [57] with permission from the Wiley-VCH.

Glycol Ligand

Triethylene glycol (H₂TEG) ligands are rich in O donor atoms and therefore exhibit high affinity towards the Ln(III) ions. Li and co-workers synthesized a ten-coordinate mononuclear Dy(III) complex, [Dy(H₂TEG)(NO₃)₃].[18-crown-6] (**37**) utilizing the H₂TEG ligand in combination with a 18-crown-6 ligand (Figure 22) [58]. Here the crown ether ligand does not coordinate to the metal center but merely acts as a promoter in crystallizing the complex. The ten-coordinate tetradecahedron geometry of the Dy(III) ion resulted from the cumulative coordination of one H₂TEG ligand and three NO₃[−] anions. The field dependence of magnetization measurements using a sweeping magnetic field (sweep rate of 50 Oe/s) at 2 K did not reveal any hysteresis loops confirming fast magnetization relaxation in **37**. To probe the relaxation dynamics, AC magnetic measurements were performed. At zero field no maximum was observed in the out-of-phase (χ''_M) AC susceptibility component above 2 K. Upon application of an optimum DC field of 1000 Oe, strong χ''_M signals with clear maxima were observed (Figure 22c). The frequency-dependent χ''_M AC component showed two maxima indicating the possibility of two relaxation processes in **37**. This was further confirmed in the Cole-Cole plots which showed two semi-circular shapes with $\alpha_1 = 0.21$ – 0.42 and $\alpha_2 = 0.11$ – 0.38 . The temperature dependence of relaxation times was fitted with the Arrhenius equation and an energy barrier, $U_{\text{eff}} = 28$ K with $\tau_0 = 2.49 \times 10^{-9}$ s was obtained.

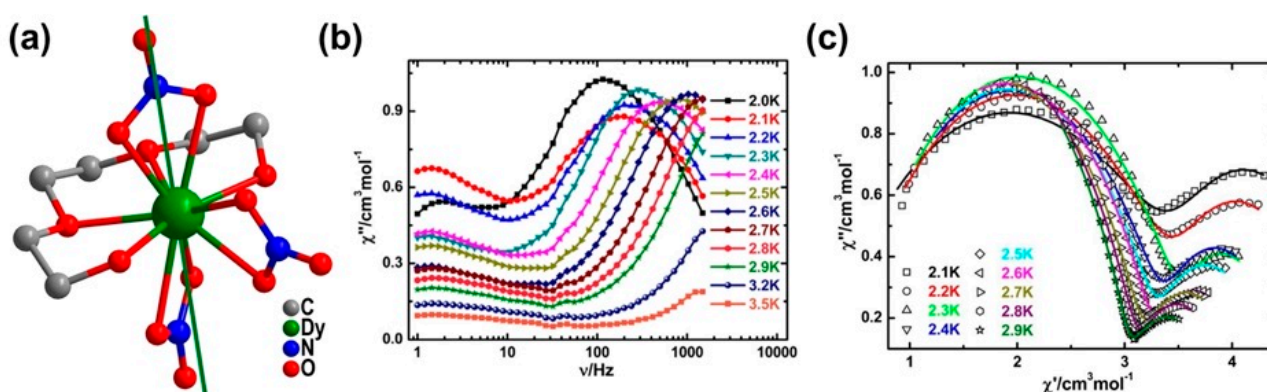


Figure 22. (a) Molecular structure of **37** with the magnetic easy axes, (b) Frequency dependence of χ''_M signals under 1000 Oe DC field, and (c) Cole-Cole plots with the best fits corresponding to the sum of two modified Debye functions. Figures and captions are reproduced from Reference [58] with permission from the Elsevier Ltd.

Radical Ligand

A ten-coordinate Pr(III) complex of the formula [Pr(NIT₂Py)₂(NO₃)₃] (**38**; NIT₂Py = 2-(2'-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) was synthesized utilizing a chelating nitronyl nitroxide radical ligand (Figure 23) [59]. The Pr(III) was coordinated by two N,O-chelating NIT₂Py radicals and six O atoms from the three nitrato groups in a κ_2O chelating coordination mode. The ONCNO fragment of the nitronyl nitroxide moiety was found to be almost planar indicating the delocalization of the free electron in this fragment. The dihedral angles between the pyridyl and the nitronyl nitroxide moieties were found to be 38.2° and 35.2° for the two NIT₂Py ligands. Static magnetic measurements revealed a $\chi_M T$ value of 1.99 cm³ mol^{−1} K at 300 K which is lower than the expected theoretical $\chi_M T = 2.36$ cm³ mol^{−1} K for two radical and one Pr(III) ion (³H₄ ground state ($g_J = 4/5$)). Upon cooling the system to 77 K, the $\chi_M T$ value slowly decreased which has been attributed as resulting from the magnetic anisotropy of the Pr(III) ion. Dynamic magnetization studies were not carried out on this system.

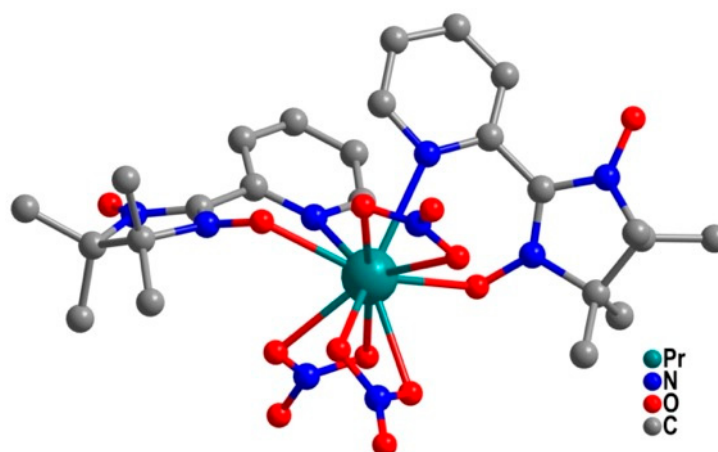


Figure 23. Molecular structure of complex **38**. The structure was re-drawn from Reference [59] with permission from the Elsevier Ltd.

2.1.3. Penta-Nitrate Ln(III) Complexes

In addition to the synthetic approaches discussed above, Song and co-workers pursued a spherical ligand field around the Ln(III) ions and in this pursuit they synthesized two isostructural ten-coordinate mononuclear complexes of the formula, $(^n\text{Bu}_4\text{N})_2[\text{Ln}(\text{NO}_3)_5]$ (Ln = Dy (**39**) and Er (**40**)) (Figure 24) [60]. As discussed previously, a spherical ligand field could stabilize the magnetic anisotropy of both Dy(III) (oblate) and Er(III) (prolate) ions simultaneously. The complexes were synthesized by the reactions of hydrated $\text{Ln}(\text{NO}_3)_3$ with appropriate equivalents of AgNO_3 and $^n\text{Bu}_4\text{NBr}$ in ethanolic medium. The small “bite angle” of the NO_3^- anion resulted in the high coordinate geometry with a 100 coordination [61,62]. The tetradehedron (C_{2v} symmetry) geometry around the Ln(III) ions resulted from the simultaneous coordination of five nitrate ligands of which three nitrates formed an equatorial plane while the other two nitrates coordinated perpendicularly from above and below this equatorial plane. The Dy–O distances in the (DyO_{10}) coordination geometry differs only slightly ($0.03 \text{ \AA}$) suggesting symmetrical binding nature of the NO_3^- ligands. The presence of bulky $[^n\text{Bu}_4\text{N}]^+$ cations ensured large distances between the Ln(III) ions. Both DC and AC magnetic measurements were performed on **39** and **40**. The crystal field parameters were obtained from the static magnetic measurements which revealed impure eigenstates in both ground and the excited states of **39**. Accordingly, the latter does not exhibit the typical *Ising* behavior. On the other hand, the ground doublet of **40** was found to be the $m_J = \pm 11/2$ state while the first excited state was found to be an admixture of $m_J = \pm 9/2$ and $m_J = \pm 13/2$ doublet states representing a typical *Ising* type anisotropy in **40**. The relatively larger electron density in the equatorial plane provided by the three NO_3^- ligands is particularly suited for the prolate Er(III) ion and is responsible for the *Ising* behavior in **40**. To probe the relaxation dynamics, AC magnetic measurements were performed under zero biased field. None of the complexes showed peaks in the out-of-phase AC susceptibility (χ''_M)—even at low temperature—presumably because of significant QTM in the ground state. Upon application of an optimum DC field, both the complexes showed clear maxima in the temperature- and frequency-dependent in-phase (χ'_M) and out-of-phase (χ''_M) susceptibilities (Figure 24). The Cole-Cole plots with small values of α parameters (0.15–0.22 for **39** and 0.08–0.22 for **40**) implied a narrow distribution of relaxation times in both the complexes. The temperature dependence of relaxation times were fitted by the Arrhenius equation and the effective energy barriers, $U_{\text{eff}} = 24.3 \text{ K}$ ($C = 3.40 \times 10^{-9} \text{ s}$; $H_{\text{DC}} = 500 \text{ Oe}$) for **39** and $U_{\text{eff}} = 22.3 \text{ K}$ ($\tau_0 = 3.06 \times 10^{-7} \text{ s}$; $H_{\text{DC}} = 1000 \text{ Oe}$) for **40** were obtained. An analysis of the experimental data supported by theoretical calculations suggested that magnetization relaxation occurred through an intermediate state between the ground and first excited states.

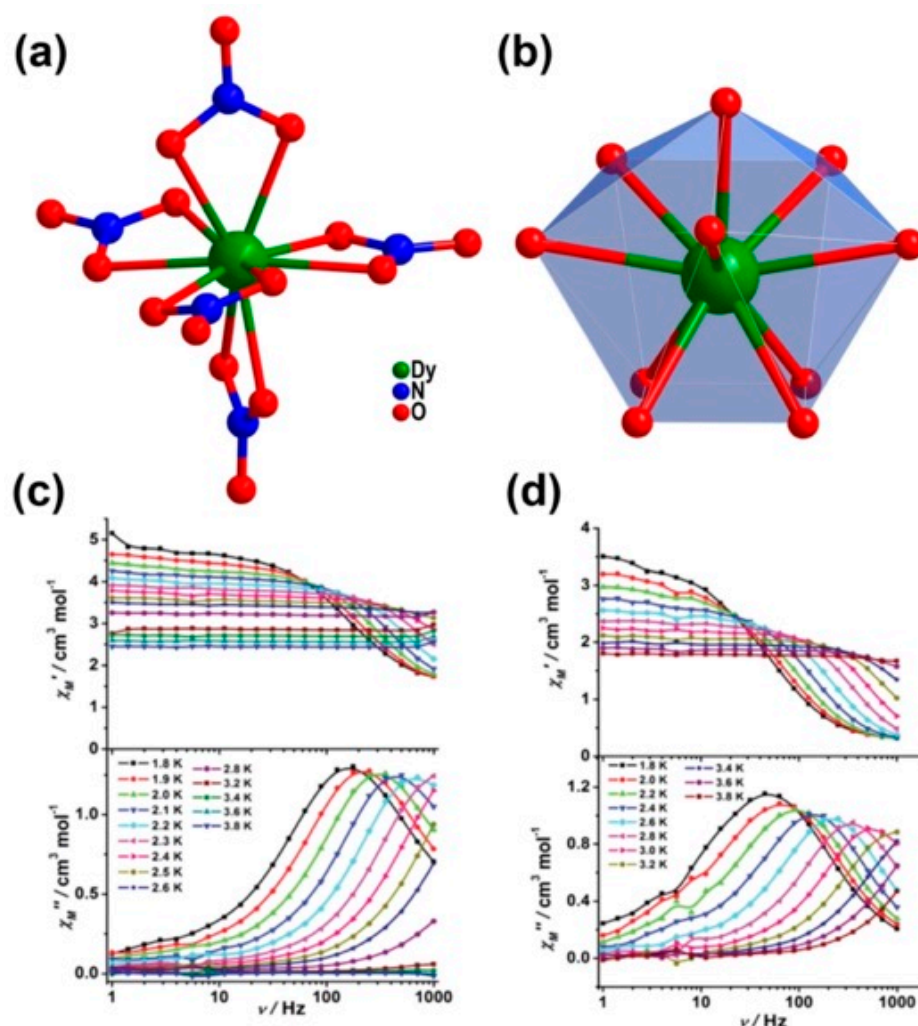


Figure 24. Molecular structure of the anionic part of (a) and the corresponding coordination geometry (b) of **39**; Frequency dependence of the AC susceptibility under a DC field of 500 Oe for **39** (c) and 1000 Oe for **40** (d). Figures and captions are reproduced from Reference [60] with permission from the Royal Society of Chemistry.

3. Twelve-Coordinate Ln(III) Complexes

Although twelve-coordination is known for lanthanide ions in a few heterometallic 3d-4f complexes, such a behavior among mono nuclear Ln(III) complexes is quite sparse.

Mixed Ligand Approach

Kajiwarra and co-workers reported a series of mononuclear Ln(III) systems having dodeca coordination by following the mixed ligand approach [63]. The complexes, [Ln(NO₃)₃(18-crown-6)] (Ln = Ce (**41**), Pr (**42**), and Nd (**43**)) and [Ln(NO₃)₃(1,10-diaza-18-crown-6)] (Ln = Ce (**44**), Pr (**45**), and Nd (**46**)) were synthesized by employing 18-crown-6 and 1,10-diaza-18-crown-6 systems respectively along with chelating nitrate ligands (Figure 25). For the first set of complexes having 18-crown-6 as the main ligand, the six O donor atoms of the ligand coordinates to the metal ion equatorially while the three nitrate ions chelating the metal ion from above and below complete the coordination environment as well as provide charge neutrality to the system. On the other hand, for the other set of molecules consisting 1,10-diaza-18-crown-6 as the ligand, the coordination action of the ligand remains similar but the overall chemical environment around the Ln(III) changes to 10O,2N. The geometry around the Ln(III) ion is found to be distorted icosahedron but the

magnitude of distortion from the ideal geometry is found to be more for the case of 12O coordination (*vide infra*).

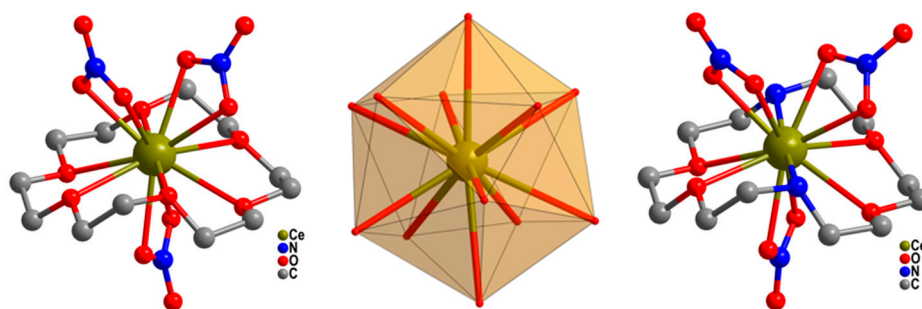


Figure 25. Molecular structure of **41** (left); Icosahedron coordination geometry around the Ce(III) ion (middle); and molecular structure of **44** (right). The structures are re-drawn from Reference [63] with permission from the American Chemical Society © 2016.

DC susceptibility measurements revealed that the room temperature $\chi_M T$ values for the complexes **41** to **46** were found to be 0.76, 1.52, 1.41, 0.68, 1.48, and 1.60 emu K mol^{−1} respectively which are in good agreement with the theoretical values. However, unlike the other complexes, at lower temperatures the $\chi_M T$ values for the two Pr(III) analogues sharply decreased and reached almost to the diamagnetic limit. This has been attributed to the rapid depopulation of the low lying J_z sublevels.

In the AC susceptibility measurements, none of the complexes were found to be showing out-of-phase susceptibility peak maxima. But in the presence of 1000 Oe of applied magnetic field complexes **41**, **43**, **44**, **46** showed both distinct in-phase and out-of-phase peak maxima (Figure 26).

An analysis of the data suggested the presence of multiple relaxation pathways (Figure 27). The best fit parameters were extracted considering Raman and Orbach process which are summarized in Table 1.

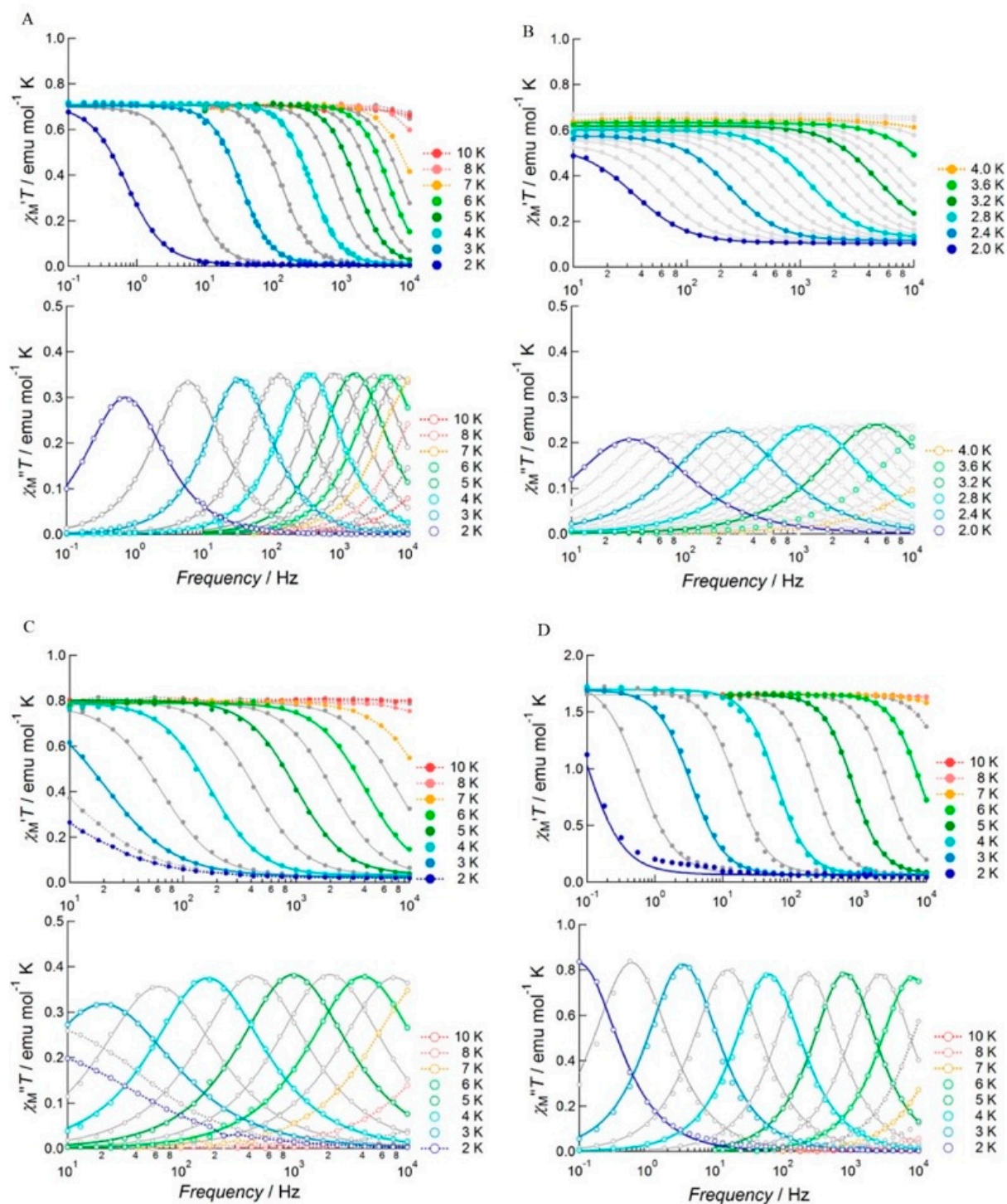


Figure 26. In-phase and out-of-phase susceptibility peak maxima for **41** (A); **43** (B); **44** (C); and **46** (D) at an applied field of 1000 Oe. Figures are reproduced from Reference [63] with permission from the American Chemical Society © 2016.

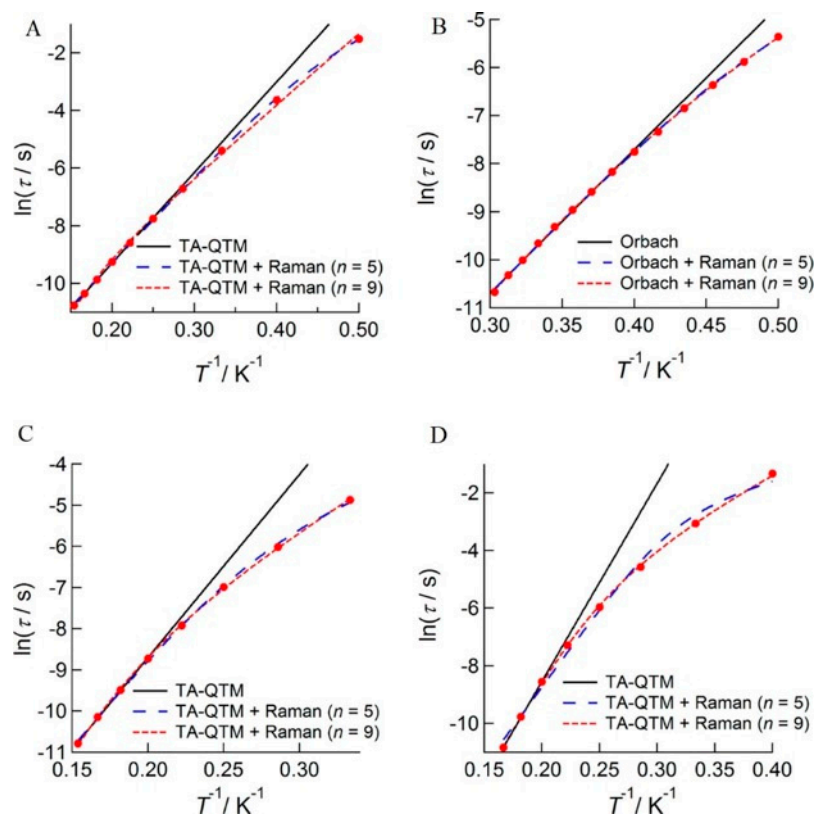


Figure 27. (A–D) Arrhenius plots for complexes **41**, **43**, **44**, and **46** respectively measured under a 1000 Oe bias field. Solid lines and dotted curves represent theoretical fitting taking into account the TA-QTM process (black), the TA-QTM and the Raman processes with $n = 5$ (blue), and the TA-QTM and the Raman processes with $n = 9$ (red). Figures and caption are reproduced from Reference [63] with permission from the American Chemical Society © 2016.

Table 1. Best fitted parameters of Arrhenius equation.

Relaxation Parameters	41	43	44	46
n is fixed at 5				
$\Delta E k_B^{-1} / K$	30.3(3)	30.9(4)	45(2)	55(4)
τ_0 / ns	220(17)	2.2(3)	26(7)	2.6(1.9)
$C / s^{-1} K^{-5}$	0.108(10)	4.1(3)	0.52(4)	0.050(12)
n is fixed at 9				
$\Delta E k_B^{-1} / K$	25.6(7)	33.4(5)	23(1)	73(2)
τ_0 / ns	$9(2) \times 10^2$	1.6(2)	$6(2) \times 10^3$	0.14(6)
$C / s^{-1} K^{-5}$	16(4)	0.350(11)	22(9)	10.7(4)

4. Magneto-Structural Correlation

As is evident from the above survey that ten-coordination is the most abundant among the higher coordinated Dy(III) complexes with three possible geometries: sphenocorona, tetradecahedron and bicapped square antiprism (see Table 2). A variety of synthetic approaches involving different types of ligands have been employed to synthesize high coordinated complexes. Although none of the high coordinated complexes exhibited zero field SMM behavior, many revealed a field-induced SMM behavior. The highest effective energy barrier was found when the coordination environment around the Dy(III) was either 10N or 10O rather than the mixed 6N4O or 4N6O environments. The 10N coordination was achieved only from the multidentate Schiff base ligands whereas the 10O coordination could be achieved by many ligand systems. However, the mixed ligand approach involving the crown ether ligand appeared to be most effective in generating

complexes that possessed high effective energy barriers. Further, it has been observed that the effective energy barrier is not only dependent on the coordination environment but also seems to be dependent on the extent of distortion from *regular* geometry. In Figure 28 a correlation of observed effective energy barrier (U_{eff}) with geometry and the magnitude of distortion from ideal geometry has been plotted. It is evident from this plot that in [DyO10] systems high U_{eff} is possible when the geometry is bicapped square antiprism with high distortion. But when the geometry is sphenocorona the distortion should be low for getting high U_{eff} .

Table 2. A summary of the magnetic properties of all ten-coordinate Dy(III) and two dodeca-coordinated Ce(III) complexes.

Sl. No.	Formula (Complex Number)	Co-Ordination Environment	Geometry Around Metal *	ChSM Value	U_{eff}, τ_0 (H_{dc})	Ref
1	[Dy(H ₂ dapbh) ₂](NO ₃) ₃ (1)	4O6N	BSA	2.840	32.4 K (1000 Oe)	[38]
2	[Dy(N5) ₂](CF ₃ SO ₃) ₃ (8)	10N	BSA	3.335	79 K, 2.9×10^{-8} s, 1200 Oe	[36]
3	[Dy(12-crown-4)(NO ₃) ₃] (10)	10O	SPC BSA	2.837 20.899	68 K, 2.07×10^{-10} s (1000 Oe) 75.92 K, 6.8×10^{-11} s (500 Oe)	[37]
4	[Dy(18-crown-6)(NO ₃) ₂](ClO ₄) (14)	10O	BSA	3.101	63 K, 1.02×10^{-8} s (1000 Oe)	[38]
5	[Dy(L2) ₂ (NO ₃)](ClO ₄) ₂ (25)	6O4N	SPC	3.223	44.3 K, 5.17×10^{-7} s (1000 Oe)	[42]
6	[Dy(HL3) ₂ (NO ₃) ₃] (27)	10O	BSA	3.148	23.9 K, 2.47×10^{-6} s (2000 Oe)	[48]
7	[Dy(L4)(NO ₃) ₂](NO ₃) (29)	6O4N	SPC	21.104	50 K, 6.80×10^{-7} s, (1000 Oe)	[49]
8	[Dy(ntlbi)(NO ₃) ₃] (36)	4O6N	SPC	3.655	53.4 K, 1.6×10^{-12} s (1200 Oe)	[51]
9	[Dy(H ₂ TEG)(NO ₃) ₃]·[18-crown-6] (37)	10O	TDH	3.292	28 K, 2.49×10^{-9} s (1000 Oe)	[52]
10	(ⁿ Bu ₄ N) ₂ [Dy(NO ₃) ₅] (39)	10O	TDH	1.513	24.3 K, 3.40×10^{-9} s, (500 Oe)	[54]
11	[Ce(NO ₃) ₃ (18-crown-6)] (41)	12O	IC	1.862	30.3 K, 2.20×10^{-7} s (1000 Oe)	[57]
12	[Ce(NO ₃) ₃ (1,10-diaza-18-crown-6)] (44)	10O2N	IC	1.765	44 K, 2.3×10^{-8} s (1000 Oe)	[57]

* BSA = bicapped square antiprism; TDH = tetradecahedron; SPC = sphenocorona; IC = icosahedron.

On the other hand, when the decacoordination is fulfilled by mixed donor atoms (O and N) only two types of geometries are observed, sphenocorona and bicapped square antiprism (Figure 28). However, for (DyO6N4) systems only sphenocorona geometry is reported and the higher U_{eff} is seen when distortion is higher while for (DyO4N6) systems higher U_{eff} is found in sphenocorona geometry.

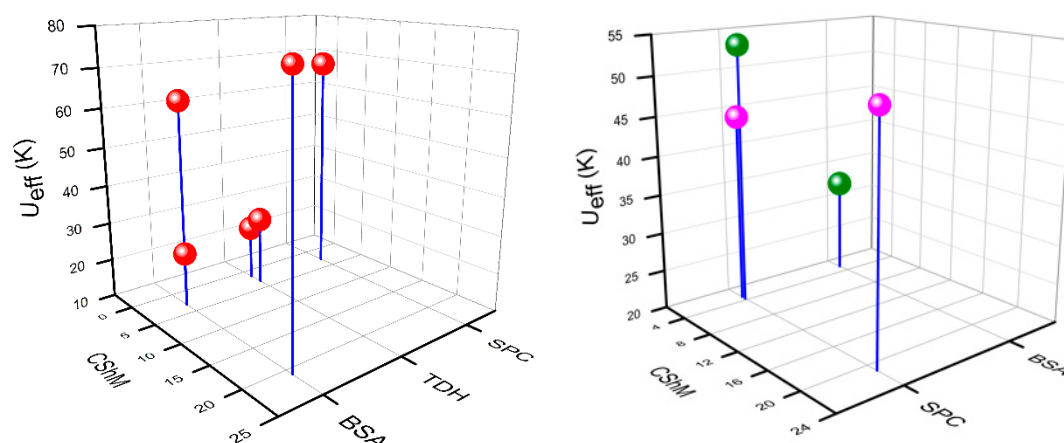


Figure 28. (left) Geometry and magnitude dependent experimentally found effective energy barrier for (DyO10) systems; (right) for (DyO6N4) systems (magenta color spheres), and for (DyO4N6) systems (green color spheres).

5. Summary

In this article we have tried to summarize the status on high-coordinate lanthanide complexes that show a field-dependent single-molecule magnet behavior. We considered coordination numbers above nine for this purpose. Although, coordination numbers 10–14 are possible for lanthanide ions, our survey indicated that given the constraint that such complexes should show slow relaxation of magnetization, only those possessing coordination numbers 10 and 12 are of interest. Such complexes have been assembled by utilizing a variety of synthetic methodologies involving an array of ligand systems including mixed ligands. Our review of such high-coordinate complexes reveals that they display very low site symmetry which enables quantum tunneling of magnetization. Because of this none of the complexes discussed in this review have been found to show zero-field SMM behavior. On the other hand, application of appropriate small DC field seems to alleviate some of these problems with the realization of slow relaxation of magnetization under such conditions. A qualitative structure-property correlation reveals the dependence of local coordination geometry and the magnitude of distortion from regular geometry on the magnetic properties including the effective energy barrier for the reversal of magnetization.

6. Future Direction

There are several examples of heterometallic 3d-4f complexes featuring ten- and twelve-coordinate lanthanide sites where good exchange interaction (between the 3d and 4f metal ions) could play a crucial role to suppress QTM. Thus, while it appears from the above survey that high-coordinate lanthanide complexes by themselves might not be attractive candidates for assembling molecular magnets, incorporating such sites in heterometallic complexes might be a fruitful endeavor.

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