

IRON–LANTHANIDE SINGLE MOLECULE MAGNET COMPOUNDS

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Abstract

Over the last decades, interest of researchers in the preparation and study of heterometallic Fe–Ln organometallic compounds has increased due to their intriguing architectures and promising applications as single molecule magnets (SMMs) that exhibit magnetic hysteresis of purely molecular origin. SMMs are fundamentally different from conventional bulk magnets because a collective long-range magnetic ordering of magnetic moments is not necessary. It is expected that SMMs can be employed in the future as the smallest magnetic memory units or in quantum computational devices. This review examines synthetic strategies and magnetic properties of Fe–Ln SMM compounds published till July 2016.

1. Introduction

Single molecule magnets (SMMs) are coordination compounds with slow relaxation of their magnetisation at low temperatures. The first SMMs represent a dodecanuclear $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$ manganese compound (Fig. 1a), which was first prepared by Lis in 1980 [1] and then studied in more detail by several research teams [2–5]. This Mn_{12} –Ac complex with an $S = 10$ ground state shows magnetization hysteresis and quantum tunnelling of magnetization (QTM). The term "single molecule magnet" was first employed by Christou in 1996, when his team studied the magnetic properties of distorted $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_3\text{O}_3\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}$) cubane complexes [6].

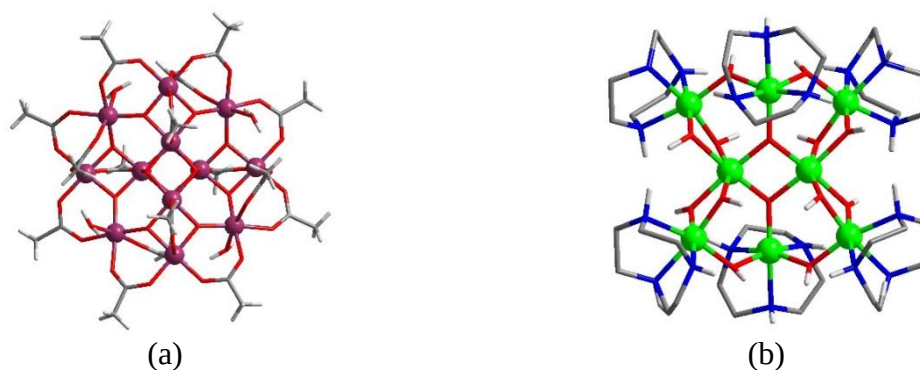


Fig. 1. Structure of (a) $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$ and (b) $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]^{8+}$. Color definition: Mn, plum; Fe, green balls; N, blue; O, red; C, grey; and H, light grey sticks.

In 1984 Weighardt et al. prepared a $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]\text{Br}_8(\text{H}_2\text{O}) \cdot 8\text{H}_2\text{O}$ (tacn = 1,4,7-triazacyclononane) cluster [7] based on a $\{\text{Fe}_8\}$ core (Fig. 1b), which was characterized as an SMM by Wernsdorfer in 2000 [8]. The Weighardt's $\{\text{Fe}_8\}$ compound showed a high spin ground state ($S = 10$), low anisotropy, and a hysteresis loop. This finding has given rise to intense development in this area of research. Since then, a large number of coordination compounds based on Mn [9–12], Fe [13–15] and, to a lesser extent, Ni [16–17] or Co [18–20] exhibiting an SMM behavior have been discovered. Hexanuclear $[\text{Mn}_6\text{O}_2(\text{L})_6(\text{O}_2\text{CPh}(\text{Me})_2)_2(\text{EtOH})_6]$ (L = 2-hydroxyphenylpropanone oxime) reported by Brechin showed a blocking temperature of ~ 4.5 K; this is the highest value of this parameter known to date [21].

Starting from the development of homometallic polynuclear d-block transition systems, the research moved to the discovery of f-based polynuclear complexes as promising candidates with SMM properties. The lanthanide centers have large magnetic moments and—what is most important—extremely high magnetic anisotropy owing to the orbital contribution that made them good candidates for construction of SMM materials. A contribution to this area was made by Kirin and his colleagues, when they first described the synthesis of phthalocyanine double-decker of lanthanides $[\text{Pc}_2\text{Ln}]$ in 1965 [22]. In 1979, the structures of double-decker complexes of lanthanides were reported by Moskalev et al. [23]. Later, in 2003 [24] Ishikawa et al. studied the magnetic properties of the double-decker phthalocyanine (Pc) mononuclear complexes with Tb^{3+} or Dy^{3+} and composition $[\text{Pc}_2\text{Tb}]$ and $[\text{Pc}_2\text{Dy}]$ (Fig. 2) and showed slow magnetization relaxation as a single-molecular property; the temperature ranges in which the behavior was observed were higher than that in the 3d-cluster SMMs. Among lanthanide SMM systems that showed different magnetic behavior, some Ln complexes gave the highest energy barrier [25–28] or a prominent QTM effect in relaxation behavior below 3 K [29]; others showed a better single molecule behavior than that of the compounds of the same nuclearity [30–33]. Long and his colleagues reported a radical bridged dimeric complex exhibiting a magnetic hysteresis curve at 14 K. This hysteretic behavior occurs at the highest temperature recorded for any previous molecule known to date [34].

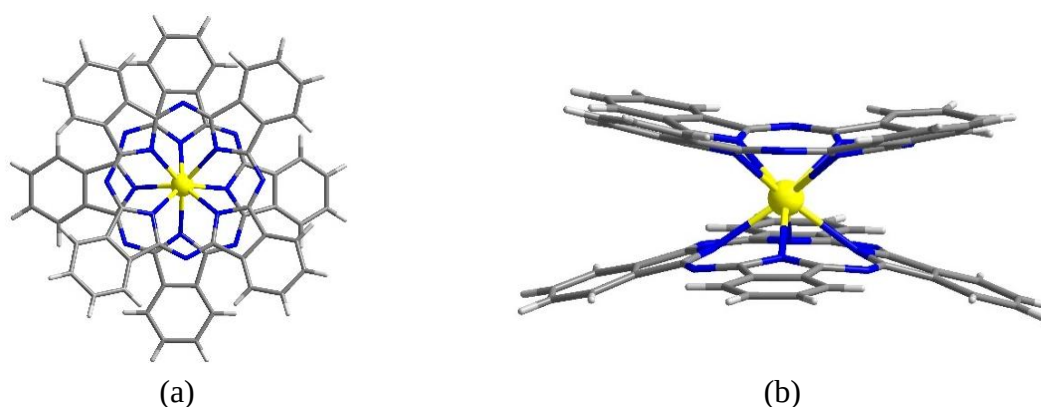


Fig. 2. Structure of $[\text{Pc}_2\text{Ln}]^+$. Color definition: Ln, yellow balls; N, blue; C, gray; and H, light gray sticks.

Another advantageous approach to SMMs is based on the combination of different spin carriers as d-block metals with lanthanide ions into polyheterometallic assemblies. The

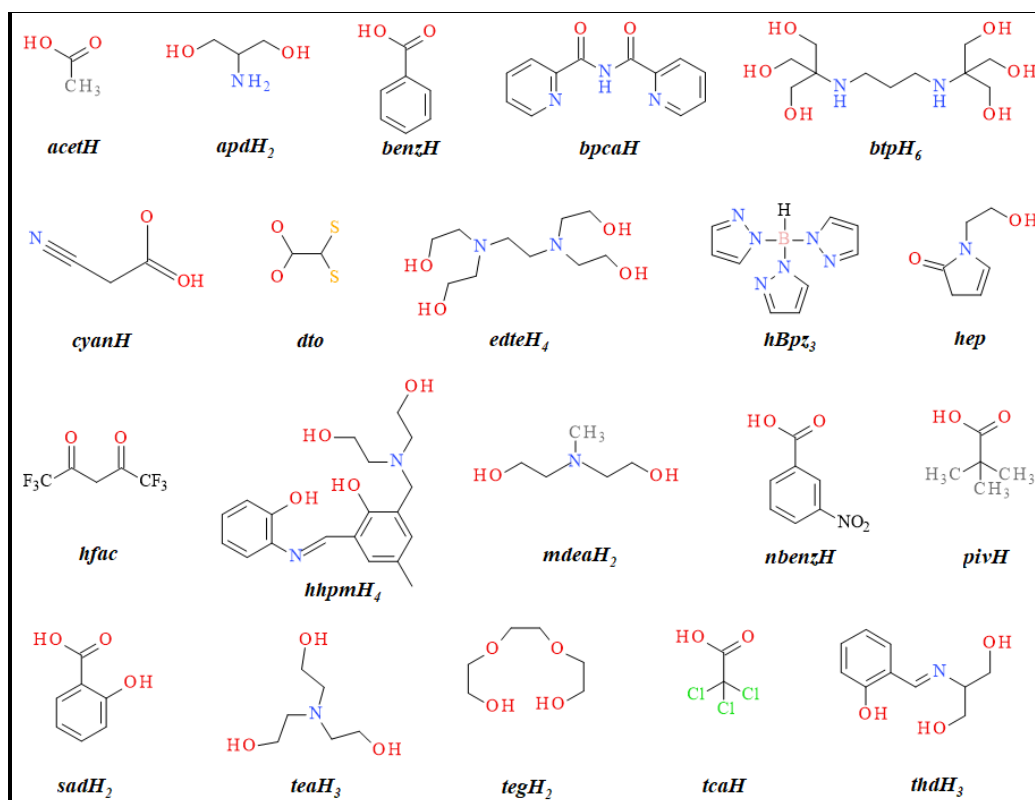
high spin-states of transition metals and the large predominately anisotropic—magnetic moment of some trivalent lanthanide ions can give 3d-4f SMM clusters with properties that differ from those of homometallic compounds. Furthermore, cluster that comprises a 3d-4f core can exhibit strong magnetic coupling of mixed-metals; there are possibilities of achieving a ferromagnetic interaction between these two types of metal ions. The development of the chemistry of d-f complexes originates in the early of 20th century, when a series of $\text{Ln}[\text{Co}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ [35] was reported. Since then, many transition metal-lanthanide compounds have been synthesized by various synthetic routes [36, 37]. Studies of SMM properties of 3d-Ln complexes began much later. The preparation of SMM complexes with high blocking temperatures has attracted much attention; many efforts have been made to find new approaches for obtaining these materials [38] after reporting the first 3d-Ln mixed SMM compound with a $[\text{Cu}_2\text{Tb}_2]$ core by Matsumoto et al. in 2004 [39]. A survey of the literature shows that the researchers were mainly focused on Mn-Ln [40–47], Cu-Ln [48–61], Co-Ln [62], and Ni-Ln complexes [63–66] because integration of a high Ln^{III} spin into 3d systems with a high-spin ground state can stimulate sufficient magnetic anisotropy to exhibit an SMM behavior. Fe-Ln clusters have also been documented, mainly for Dy and Tb [67–74]. Over the last decades, 417 structures of Fe-Ln compounds have been synthesized; however, only several of them have been characterized as SMMs [75–96]. This review reports a class of magnetic compounds based on Fe-Ln metals exhibiting single-molecule magnet properties. X-ray data of the described $\text{Fe}^{\text{II/III}}\text{-Ln}^{\text{III}}$ SMM compounds have been searched in the CCDC database up to 2016 (version 5.37, updated on July 2016) [97].

2. Design and Preparation of Fe-Ln SMMs

To date, several approaches for the design and preparation of SMMs have been introduced; the most efficient and most widely used approach is the preparation of these materials via “serendipitous self-assembly.” The term “serendipitous self-assembly” in the chemistry literature was first introduced by Winpenny in “Serendipitous assembly of polynuclear cage compounds” [98]. A review of the methods of preparation of heterometallic clusters possessing SMMs has revealed that one of the frequently used techniques is “step-by-step” strategy, including preliminary preparation of a precursor, such as μ_3 -oxo trinuclear transition metal carboxylates ($[\text{Fe}_3\text{O}(\text{benz})_6(\text{H}_2\text{O})_3](\text{benz})$ [99], $[\text{Fe}^{\text{III}}(\text{bpca})_2]^+$ [100], $[\text{Fe}_2\text{BaO}(\text{tca})_6(\text{thf})_6]$ [101], $[\text{Fe}_3\text{O}(\text{acet})_6(\text{H}_2\text{O})_3]\text{NO}_3$ [102], $[\text{Fe}_3\text{O}(\text{piv})_3(\text{H}_2\text{O})_3](\text{piv})$ [103], and $[\text{Fe}_3\text{O}(\text{cyan})_6(\text{H}_2\text{O})_3](\text{NO}_3) \cdot 5\text{H}_2\text{O}$ [104] compounds (where benzH = benzoic acid, bpca = bis(2-pyridylcarbonylamine, tcaH = trichloroacetic acid, acetH = acetic acid, pivH = pivalic acid, cyanH = cyanoacetic acid) and salts of metals: $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$, and $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$). The reported Fe-Ln SMM compounds have been synthesized by several synthesis methods: reflux, microwave irradiation, liquid-liquid diffusion, hydro(solvo)thermal methods, stirring at room temperature, and recrystallization.

The N- and O-containing donor ligands have been frequently used to combine iron and a lanthanide ions in the same heterometallic cluster, because nitrogen atoms exhibits a strong tendency to coordinate with transition metal ions, while the oxygen atoms prefer to bond to the lanthanide metal ions.

Ligand selection strategy is an important stage in the design and preparation of SMMs. Carboxylate ligands are commonly involved in synthesis due to their ability to adopt many different coordination modes. Thus, carboxylate moieties are great candidates to synthesize heterometallic systems. The organic ligands used in the preparation of heterometallic SMMs are shown in Scheme 1.

Scheme 1. Ligands for the preparation of SMM compounds.

3. Fe^{II/III}–Ln^{III} SMMs

The Fe–Ln SMMs era began in 2005 due to the paper of Christou et al. [75], who reported the $[\text{Fe}_2\text{Ho}_2(\mu_3\text{-OH})_2(\text{teaH})_2(\text{benz})_4(\text{NO}_3)_2] \cdot 4(\text{MeCN}) \cdot 3(\text{H}_2\text{O})$ (**1**) and $[\text{Fe}_2\text{Dy}_2(\text{OH})_2(\text{teaH})_2(\text{benz})_6]$ (**2**) clusters (where teaH_3 = triethanolamine) (Fig. 3a). Clusters **1** and **2** having an incomplete double cuban metallic core were prepared by the liquid–liquid diffusion method: two solutions $[\text{Fe}_3\text{O}(\text{benz})_6(\text{H}_2\text{O})_3](\text{benz})$ in acetonitrile and $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Ho}, \text{Dy}$) with teaH_3 in methanol/acetonitrile were mixed together and layered with diethyl ether. Single crystal X-ray diffraction analysis showed that **1** and **2** are isostructural, only two chelating NO_3^- groups were replaced by chelating benzoate groups. Structure of **1** consists of a Fe_2Ho_2 core (Fig. 3a), in which $\mu_3\text{-OH}^-$ ligands bind two Fe^{III} ions and one Dy^{III} ion in a trinuclear $\{\text{Fe}_2\text{Ho}\}$ sub-unit. The teaH^{2-} and benz^- ligands additionally bind the metal atoms in a Fe_2Ho sub unit to form three types of different O-bridges between the metal heteroatoms. The $\text{Fe} \dots \text{Ln}$ distances are 3.3936(6) and 3.4026(8) Å; the $\text{Fe} \dots \text{Fe}$ distance is 3.2430(8) Å. The temperature-dependent magnetic susceptibility data for **1** and **2** suggest predominantly antiferromagnetic exchange interactions within two complexes. The out-of-phase AC (alternating current) measurements displayed a hysteresis loop for **2** at 4 K and 1.1 K, whereas a hysteresis loop for **1** was observed with a very small coercivity at 0.3 K. In 2011, Powell et al. reported related $[\text{Fe}_2\text{Dy}_2(\text{OH})_2(\text{teaH})_2(\text{R-benz})_6]$ (**3**) (where R = para-CN (**3a**) and meta-CN (**3b**)) [76] compounds; both displayed out-of-phase (χ'') signals establishing their SMM behavior.

In 2006, was reported a dinuclear $[\text{FeDy}(\text{bpca})(\mu\text{-bpca})(\text{NO}_3)_4]$ (**4**) SMM compound [77] synthesized from the reaction of the $[\text{Fe}^{\text{III}}(\text{bpca})_2]^+$ building block (bpcaH = bis(2-pyridylcarbonylamine) with dysprosium(III) nitrate hydrate, where the bpca^-

acts as tridentate chelate N,N,N-ligand toward the *d*-ion and as a bidentate O,O-chelate towards the *f*-site. Cluster **4** crystallizes in the triclinic *P*-1 space group and comprises the Fe^{III} and Dy^{III} ions linked by a central bridging bpca[−] ligand (Fig. 3b). The second bpca[−] ligand coordinates in *NNN*-chelating manner to the Fe^{III} ion and completes the coordination environment of Fe^{III} ion up to octahedron. The coordination environment of Dy is completed by four NO₃[−] anions. The intra-cluster distance Fe...Dy is 5.730(2) Å. The AC measurements for **4** reveal a frequency-dependent signal χ'' giving an energy barrier (U_{eff}) of 8.98 cm^{−1} and relaxation time (τ_0) of 7.77×10^{-8} s.

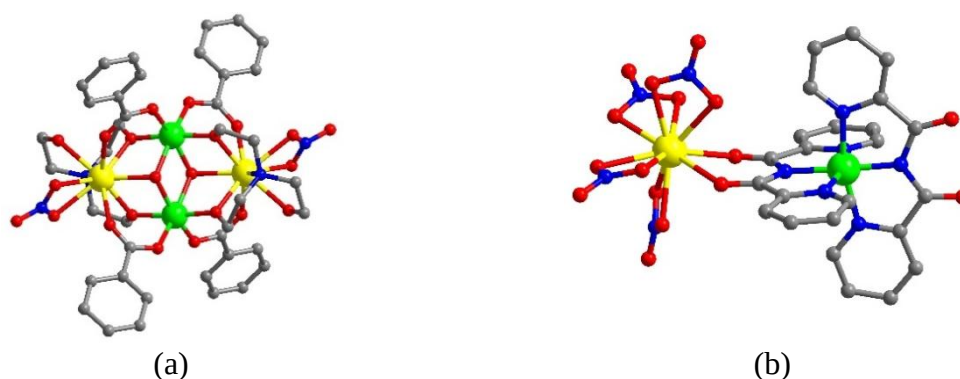


Fig. 3. Structure of (a) [Fe₂Ho₂(OH)₂(teaH)₂(benz)₄(NO₃)₃] (**1**) and (b) [Fe(bpca)(μ-bpca)Dy(NO₃)₄] (**4**).

A year later, was reported a linear trinuclear [$\{\text{Fe}^{\text{II}}(\text{bpca})_2\}\{\text{Dy}^{\text{III}}(\text{hfac})_3\}_2\cdot\text{CHCl}_3$ (**5**) (hfac[−] = 1,1,1,5,5,5-hexafluoroacetylacetonate, see Scheme 1) cluster [78] obtained by interaction of [Dy(hfac)₃·2(H₂O)] and [Fe^{III}(bpca)₂]⁺ precursors (Fig. 4a). Cluster **5** comprises two peripheral Dy^{III} ions and one central Fe^{II} ion. Two bpca ligands complete the N₆ octahedral environment of Fe^{II} ion and bridge Dy^{III} ions via O,O-chelate mode coordination. Three hfac[−] ligand coordinate chelating to each of the Dy centers. The Fe...Dy distances are 5.653(3) and 5.654(3) Å. The Dy centers have an O₈ coordination environment. In-phase (χ') and out-of-phase (χ'') components of AC susceptibility of **5** were measured in a temperature range of 1.5–3.5 K. An energy barrier of **5** is $U_{\text{eff}} = 9.7$ K with a relaxation time of $\tau_0 = 8.71 \times 10^{-8}$ s.

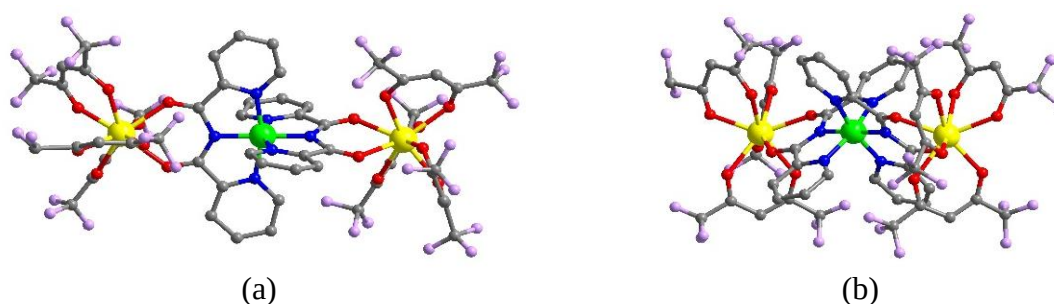


Fig. 4. (a) Structure of [$\{\text{Fe}(\text{bpca})_2\}\{\text{Dy}(\text{hfac})_3\}_2$] (**5**) and (b) view of the structure of **5** under the different angles. Color definition: Fe, bright green; Ln, yellow; N, blue; O, red; F, violet; and C, grey spheres. H-atoms are omitted.

In 2009, decanuclear [Fe₇Dy₃(μ₄-O)₂(μ₃-OH)₂(mdea)₇(benz)₄(N₃)₆]·7(MeOH)·2(H₂O) (**6**) [79], tetranuclear [Fe₃Tb(μ₃-O)₂(tca)₈(H₂O)(THF)₃]·THF (**7**) [80] and hexanuclear [Fe₄Dy₂(μ₄-O)₂(NO₃)₂(piv)₆(Hedte)₂]·x(CH₃CN)·y(CH₂Cl₂)·z(C₆H₅OH) (**8**) clusters [81] with SMM behavior were reported. The reaction of FeCl₃, DyCl₃·6H₂O, benzoic acid, and sodium azide in the presence of methyldiethanolamine (mdeaH₂) yielded SMM cluster

[Fe₇Dy₃(μ₄-O)₂(μ₃-OH)₂(mdea)₇(benz)₄(N₃)₆]·7(MeOH)·2(H₂O) (**6**). The core of cluster **6** consists of seven Fe^{III} and three Dy^{III} ions bridged by two (μ₄-O)²⁻ and two (μ₃-OH)⁻ ligands (Fig. 5a). Each (μ₄-O)²⁻ ligand bridges two iron and two dysprosium ions to form {Fe₂Dy₂(μ₄-O)} units. Each (μ₃-OH)⁻ ligand links one Fe^{III} center and two Dy^{III} centers. Each of the seven mdea²⁻ ligands coordinates in tridentate η¹:η²:η²-μ₃ chelate-bringing mode. Six azides coordinate to Fe ions and four benzoates bridge to the metal ions. The coordination sphere of the Fe center is a distorted *cis*-N₂O₄ octahedral environment, except for one (in the top of Fig. 5a) that has a NO₄ coordination environment. Three Dy centers are eight-coordinated and adopt a square-antiprismatic geometry. Magnetic susceptibility studies revealed dominant antiferromagnetic interactions between Fe^{III} (*S* = 5/2) and Dy^{III} (*S* = 5/2) ions. AC susceptibility data displayed the maximum in χ'' at 4.4 K at a frequency of 1500 Hz. An effective energy barrier (*U*_{eff}) is 33.4 K at a relaxation time (τ₀) of 6.6 × 10⁻⁸ s. Magnetic measurements below a temperature of 1.8 K gave a hysteresis loop with a field sweep rate of 0.035 T/s. Later, this team reported a related dodecanuclear SMM compound with a Tb ion [Fe₇Tb₃(μ₄-O)₂(μ₃-OH)₂(N₃)₆(mdea)₇(benz)₄]·4(MeCN)·H₂O (**13**) [86]. Clusters **6** and **13** are isostructural; however, they differ in solvate molecules in the outer sphere. Magnetic studies revealed that antiferromagnetic interactions within **13** are dominant. AC measurements of **13** showed a clear out-of-phase signal indicating that the cluster exhibits a slow relaxation of magnetization.

The interaction of iron–barium [Fe₂BaO(tca)₆(thf)₆] (tcaH=trichloroacetic acid, thf=tetrahydrofuran, see Scheme 1) with Tb(NO₃)₃·6H₂O resulted in a [Fe₃Tb(μ₃-O)₂(tca)₈(H₂O)(thf)₃]·thf (**7**) cluster [80], which comprises a tetranuclear "butterfly"-type metallic core with two triangles sharing the Tb...Fe edge (Fig. 5b). The Tb³⁺ ion resides in the O₈ coordination environment, while three Fe centers adopt distorted O₆ octahedral geometries. The compound exhibits strong an intramolecular antiferromagnetic exchange between Fe ions. AC measurements revealed a weak out-of-phase signal.

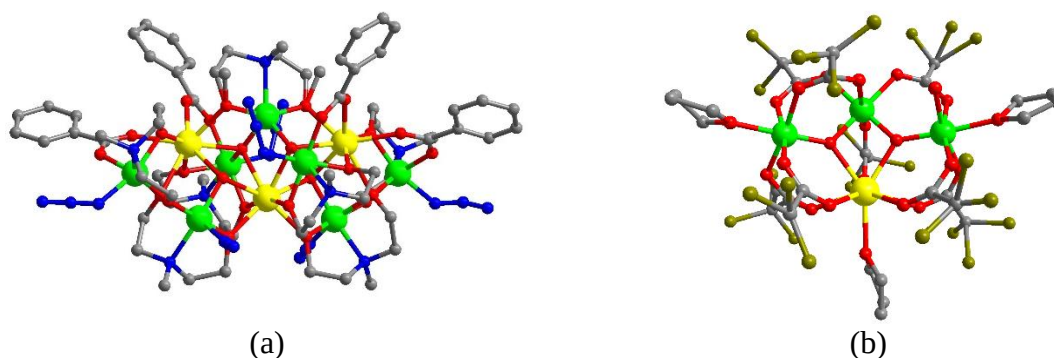


Fig. 5. Structure of [Ln₃Fe₇O₂(OH)₂(mdea)₇(benz)₄(N₃)₆] (Ln=Dy(**6**) and Tb (**13**)) (a) and [Fe₃TbO₂(tca)₈(H₂O)(thf)₃] (**7**) (b). Color definition: Fe, bright green; Ln, yellow; N, blue; O, red; Cl, green-yellow; and C, grey spheres.

The [Fe₄Dy₂O₂(NO₃)₂(piv)₆(edteH)₂]·x(CH₃CN)·y(CH₂Cl₂)·z(C₆H₅OH) (**8**) heterocluster (edteH₄=N,N,N',N'-tetrakis-(2-hydroxyethyl)ethylenediamine; pivH= pivalic acid) was obtained from the reaction of FeCl₃·4H₂O, Ln(NO₃)₃·H₂O, pivalic acid, edteH₄, and phenol in a mixture of acetonitrile and dichloromethane [81]. The central core of **8** consists of [Fe^{III}₄Dy₂(μ₄-O)₂]¹⁴⁺ with the four Fe^{III} centers arranged in a butterfly shape (Fig. 6a). Three Fe ions and one Dy ion are connected via μ₄-O bridges to form one wing and two body-iron atoms. Fe...Dy distances in each of the Fe₃Dy wingtips are 3.3973(8)–3.8273(7) Å. Each of the Dy centers is coordinated by one NO₃⁻ and one pivalate group; the remaining four pivalic ligands coordinate in a *syn,syn* bridging fashion. The edteH⁻ ligand is triply coordinated and

chelating to the iron center via two nitrogen and three μ -alkoxo oxygen atoms and bridges two metal ions that are two iron metals and iron–dysprosium metals. The $\text{Fe}_4\text{Dy}_2\text{O}_2$ core characterized by antiferromagnetic $\text{Fe}^{\text{III}}(\text{wingtip})\text{--Fe}^{\text{III}}(\text{body})$ and weaker $\text{Fe}^{\text{III}}(\text{body})\text{--Fe}^{\text{III}}(\text{body})$ ferromagnetic interactions. AC magnetic susceptibility data showed the temperature dependence of AC susceptibility significantly depends on frequency below 6 K. The estimated energy barrier was $U_{\text{eff}} = 30.85$ K with a relaxation time of $\tau_0 = 3.7 \times 10^{-8}$ s for **8**.

The octanuclear $[\text{Fe}_4\text{Dy}_4(\text{teaH})_8(\text{N}_3)_8(\text{H}_2\text{O})]\cdot 4(\text{CH}_3\text{CN})\cdot (\text{H}_2\text{O})$ (**9**) compound is the first Fe–Ln cluster possessing a wheel-type architecture characterized as an SMM. It was prepared by the reaction of iron(III) chloride and dysprosium(III) chloride with the triethanolamine ligand and sodium azide in methanol and acetonitrile [82]. The structure of **9** revealed the alternation of Fe^{III} and Dy^{III} centers (Fig. 6b) along the ring. Each of the Dy centers is chelated by two doubly-deprotonate teaH^{2-} ligand, and four oxygens also bridge the Dy^{III} ion with the two neighboring Fe^{III} ions. The couple of monocoordination of azide groups completes the coordination environment of each of the iron centers up to N_2O_4 octahedron. The Dy^{III} center has a distorted square antiprismatic N_2O_6 coordination environment, except for one that additionally coordinates the aqua ligand giving a capped square antiprismatic N_2O_7 coordination environment. The Fe...Dy distances vary between 3.4572(6) and 3.512(1) Å. Comprehensive magnetic studies revealed dominant ferromagnetic interactions in **9** (Dy^{III} and Fe^{III} of $S = 5/2$). AC measurements showed that the octanuclear wheel is frequency dependent in-phase and out-of-phase. The energy barrier was calculated by the Arrhenius law and resulted in 30.5 K with a relaxation time of 2.0×10^{-9} s. The authors reported a hysteresis loop for **9** at 1.4 K; at 6.8 K, the hysteresis disappears.

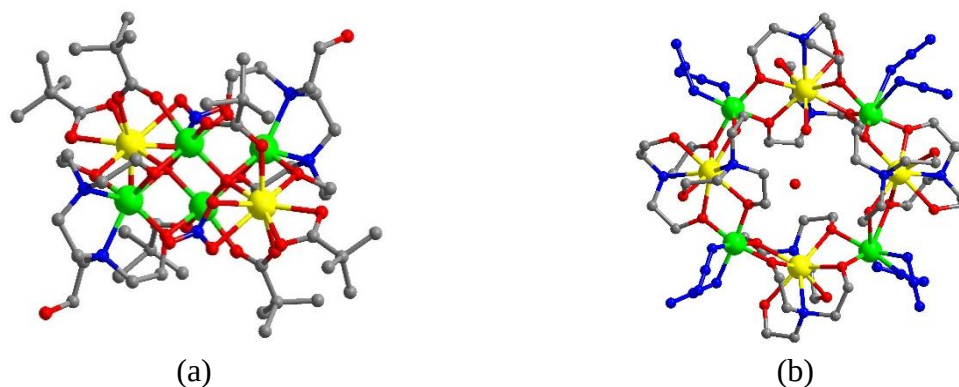


Fig. 6. Structure of (a) $[\text{Fe}_4\text{Ln}_2(\mu_4\text{-O})_2(\text{NO}_3)_2(\text{piv})_6(\text{edteH})_2]$ (**8**) and (b) $[\text{Fe}_4\text{Dy}_4(\text{teaH})_8(\text{N}_3)_8(\text{H}_2\text{O})]$ (**9**).

A hexanuclear $[\text{Fe}_4\text{Dy}_2(\text{thdH}_2)_2(\text{thdH}_2)_2\text{thd}_2(\text{CH}_3\text{OH})_2(\text{piv})_2(\text{NO}_3)_2][\text{Dy}(\text{NO}_3)_4(\text{thdH}_3)(\text{CH}_3\text{OH})]\cdot (\text{NO}_3)\cdot \text{H}_2\text{O}$ (**10**) SMM cluster (thdH_3 = trihydroxy Schiff-base ligand, see Scheme 1) was obtained from the interaction of thdH_3 ligand, which was prepared by the reaction of apdH_2 (2-amino-1,3-propanediol) with sadH_2 ligand (salicylaldehyde) in a methanol/acetonitrile solution, with $\text{Ln}(\text{NO}_3)_3\cdot \text{H}_2\text{O}$ and $[\text{Fe}_3(\mu_3\text{-O})(\text{H}_2\text{O})_3(\text{piv})_2](\text{piv})$ resulted in **10**. The compound is composed of a $[\text{Fe}_4\text{Dy}_2]^{2+}$ cation and a mononuclear $[\text{Dy}]^-$ anion (Figs. 7a, 7b). The metallic atoms in the core are organized in an “S” shape and coordinated by the μ -pivalato ligands and μ -phenoxide and μ -alkoxide groups of the Schiff-based ligand. Dy^{III} ions are located at the terminal positions and Fe^{III} ions occupy the central position of the

core. Each of the Dy ions is nine-coordinated with one chelating nitrate, one methanol molecule, one μ -pivalate, and two Schiff-based ligands. The Fe...Dy distances are 3.3918(9) Å; the Fe...Fe distances are 3.074(1) and 3.192(1) Å. The mononuclear anion consists of a Dy center coordinated with four chelating nitrates, one thdH₃ ligand, and a monodentate methanol molecule. Reported magnetic studies revealed the presence of both strong antiferromagnetic and weak ferromagnetic interactions between the Fe^{III} ions in **10**. Cluster **10** showed a frequency-dependent out-of-phase signal, which suggests that **10** really acts as an SMM at low temperatures.

Sanudo et al. [84] synthesized the first largest at that time Fe₁₂Sm₄ cluster with composition [Fe₁₂Sm₄(μ_4 -O)₆(μ_3 -O)₄(μ_3 OH)₄(benz)₂₄] (**11**) and an SMM behavior, prepared by the solvothermal reaction of [Fe₃O(benz)₆(H₂O)₃](benz) with Sm(NO₃)₃·9H₂O in acetonitrile under autogenous pressure. The structure of **11** consists of two [Fe₄O₂(OH)₂] cuban sub-units, where four Fe^{III} ions bridged by two μ_3 -OH⁻ and two μ -O²⁻ ligands. These two cuban sub-units sandwich four Fe^{III} centers via four μ_3 -O²⁻ bridges. Four Sm^{III} ions are linked with two [Fe₄O₂(OH)₂] cuban sub-units through six μ_4 -O²⁻ bridges to form the {Fe₁₂Sm₄} core (Fig. 7c). The Sm^{III}...Fe^{III} distances vary between 3.980(2) and 4.092(2) Å. The Fe...Fe distances in each of the [Fe₄O₂(OH)₂] cuban sub-units are in a range of 3.393(2)–3.432(2) Å. Twenty μ_2 -PhCO²⁻ and four μ_3 -PhCO²⁻ carboxylate groups of benz ligands on the periphery of the cluster complete the environment around the {Fe₁₂Sm₄} core. Direct current (DC) susceptibility data indicated an antiferromagnetic coupling between the Sm^{III} and Fe^{III} ions in **11**. AC susceptibility of **11** showed a strong frequency dependent χ'' signal at 1.5 K. A hysteresis loop was observed at 0.5 K. High-nuclearity complex **11** has an energy barrier of $U_{\text{eff}} = 16$ K with a relaxation time of $\tau_0 = 2 \times 10^{-8}$ s.

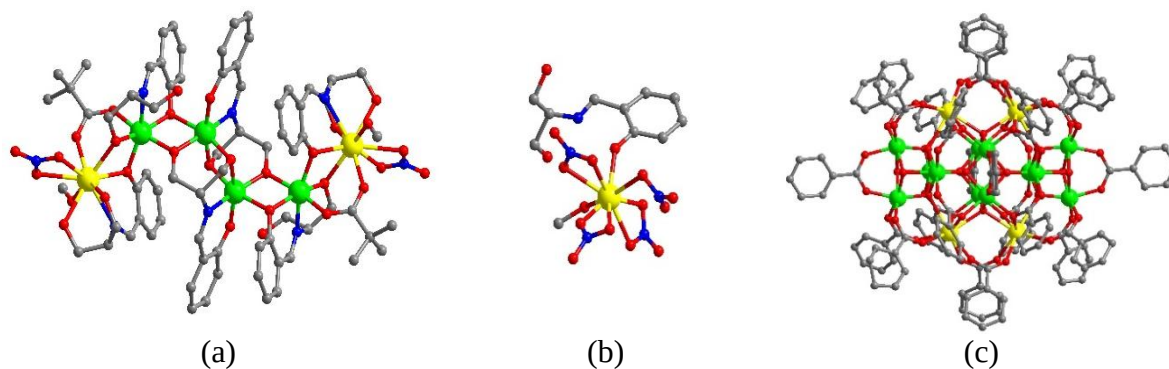


Fig. 7. Structure of (a) [Fe₄Dy₂(thdH₂)₂(thdH₂)₂thd₂(CH₃OH)₂(piv)₂(NO₃)₂]²⁺ cation (**10**), (b) [Dy(NO₃)₄(thdH₃)(CH₃OH)]⁻ anion (**10**), and (c) Fe₁₂Sm₄(μ_4 -O)₆(μ_3 -O)₄(μ_3 -OH)₄(benz)₂₄] (**11**).

In 2013, was published another example of the tetranuclear SMM complex [FeDy₃(Bpz₃H)₆(dto)₃] · 4(MeCN) · 2(CH₂Cl₂) (**12**) (Bpz₃H=hydrotris(pyrazolyl)borate, dto=dithiooxalato dianion ligand) (Fig. 8a) [85]. The tetranuclear FeDy₃ cluster has a propeller-like geometry and consists of three [Dy(HBpz₃)₂] units that coordinate to the central iron ion via three dto ligands. Each of the Dy centers has a square antiprismatic N₆O₂ coordination environment, while the Fe center comprises an S₆ coordination sphere. The bond lengths are in a range of 2.260–2.277 Å for Fe–S, 2.356(5)–2.395(1) Å for Dy–O, and 2.413(4)–2.520(6) Å for Dy–N. Magnetic susceptibility measurements revealed very weak intramolecular magnetic interaction because the Fe...Dy distances are 6.156 and 6.188 Å. The

authors reported a frequency-dependent out-of-phase signal of complex **12** that exhibits maxima above 1.8 K. The energy barrier is 15 K and the relaxation time is 1.5×10^{-6} s.

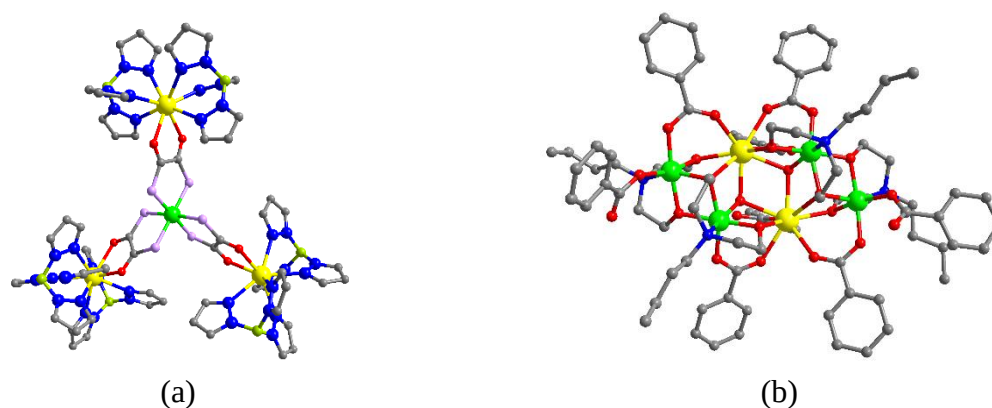


Fig. 8. Structure of (a) $[\text{FeDy}_3(\text{HBpz}_3)_6(\text{dto})_3]$ (**12**) and (b) $[\text{Fe}_4\text{Dy}_2(\mu_3\text{-OH})_2(\text{n-bdea})_4(\text{benz})_8]$ (**14**). Color definition: Fe, bright green; Dy, yellow; N, blue; O, red; Cl, green-yellow; S, lavender; B, lime; and C, grey spheres.

Two more SMM compounds were reported, namely, hexanuclear $[\text{Fe}_4\text{Dy}_2(\text{OH})_2(\text{bdea})_4(\text{benz})_8] \cdot (\text{MeCN})$ (**13**) [86] and nonanuclear $[\text{Fe}_6\text{Dy}_3(\text{C}_2\text{H}_2\text{O}_4)(\text{tea})_2(\text{teaH})_4(\text{N}_3)_2(\text{N}_3)_6(\text{NO}_3)] \cdot 2(\text{EtOH})$ (**14**) [87]. The reaction of $[\text{Fe}_3\text{O}(\text{benz})_6(\text{H}_2\text{O})_3](\text{benz})$ with $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and butyldiethanolamine (bdeaH_2) resulted in $[\text{Fe}_4\text{Dy}_2(\text{OH})_2(\text{bdea})_4(\text{benz})_8] \cdot \text{MeCN}$ (**14**) (Fig. 8b). In **14**, two peripheral dimeric $[\text{Fe}_2(\text{n-bdea})_2]^{2+}$ units are bridged by the $[\text{Dy}_2(\mu_3\text{-OH})_2]^{4+}$ dimer to form a hexanuclear core. Four Fe^{III} ions have an octahedral NO_5 environment; two Dy^{III} centers are eight-coordinated to form an almost ideal square antiprism O_8 coordination environment. The Dy–O distances vary in a range of 2.272(2)–2.617(4) Å; the Fe–O bonds are 1.929(4) and 2.068(4) Å; the Fe–N bond lengths are 2.199(5) and 2.206(5) Å. DC magnetic susceptibility studies of **14** revealed dominant antiferromagnetic interactions between spin carriers. According to the Arrhenius law, the anisotropy barrier in **14** is $U_{\text{eff}} = 21.4$ K with a relaxation time of 2.7×10^{-8} s.

The nonanuclear $\text{Fe}_6\text{Dy}_3(\text{C}_2\text{H}_2\text{O}_4)(\text{tea})_2(\text{teaH})_4(\text{N}_3)_2(\text{N}_3)_6(\text{NO}_3)] \cdot 2(\text{EtOH})$ ($\text{C}_2\text{H}_2\text{O}_4^{4-}$ = tetraanion of 1,1,2,2-tetrahydroxyethane) (**15**) cluster was obtained by the reaction of $[\text{Fe}_3\text{O}(\text{acet})_6(\text{H}_2\text{O})_3]\text{NO}_3$ (acetH = acetic acid) and $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with triethanolamine and sodium azide in the presence of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ [88]. The compound consists of six Fe^{III} and three Dy^{III} centers to form a cone-like metallic core (Fig. 9a). The metal centers of iron and dysprosium are linked through tetraanion of 1,1,2,2-tetrahydroxyethane, bi- and tridentate triethanolamine ligands, and two bidentate azides. The structure is completed by six monodentate azides which cupped the iron ions and nitrate anion coordinated to the Dy center on the top of the cone. The Dy centers are eight-coordinated to adopt a square antiprismatic and dodecahedral geometry. The Fe centers are six-coordinated to adopt a distorted octahedral geometry. Magnetic susceptibility studies showed a dominant ferromagnetic behavior in **15**. The AC susceptibility data were analyzed according to the Arrhenius law and gave an estimate for the energy barrier at 65.1 K with a relaxation time of 1.64×10^{-12} s. Cluster **15** displayed the highest energy barrier known to date among Fe–Ln SMM complexes.

In 2014, a tetranuclear $[\text{Fe}_2\text{Tb}_2(\text{hhpmH}_2)_4(\eta_2\text{-NO}_3)_2] \cdot 2(\text{ClO}_4) \cdot 2(\text{CH}_3\text{OH}) \cdot 2(\text{H}_2\text{O})$ (**16**) SMM complex ($\text{hhpmH}_4 = (\text{E})$ -2,2'-(2-hydroxy-3-((2-hydroxyphenylimino)methyl)-5-

methylbenzyl-azanediy)-diethanol) was obtained by the reaction of iron(III) perchlorate with triethylamine in the presence of an hhp mH_4 ligand, $\text{Tb}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, and trimethylamine (Figure 9b) [89]. This cluster contains two Fe^{III} ions at the periphery and two Dy^{III} ions in the center. The entire structure is held by four doubly deprotonated $[\text{hhpmH}_2]^{2-}$ ligands possessing an overall Z-type topology. The two iron centers are hexa-coordinated adopting a N_2O_4 distorted octahedral geometry, while the dysprosium centers are octa-coordinated with a NO_7 trigonal dodecahedral geometry. The $\text{Fe} \dots \text{Tb}$ distances are 3.552(2) Å; the distance between two Dy ions is 3.749(1) Å. Magnetic data revealed the presence of predominant ferromagnetic coupling at low temperatures; Tb(III) has an effective spin of $S = 3$. AC susceptibility analysis showed a frequency dependent out-of-phase signal; no maxima were observed.

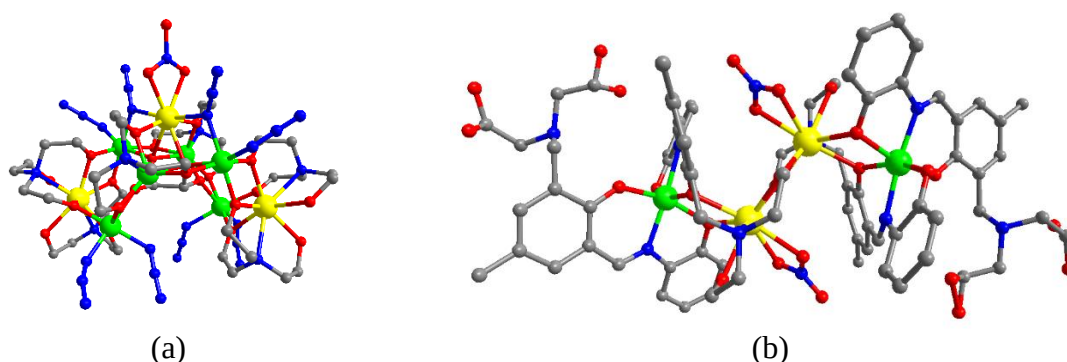


Fig. 9. (a) Structure of the cone-type $\text{Fe}_6\text{Dy}_3(\text{C}_2\text{H}_2\text{O}_4)(\text{tea})_2(\text{teaH})_4(\text{N}_3)_8(\text{NO}_3)]$ (**15**) cluster and (b) Z-type topology of the cationic $[\text{Fe}_2\text{Tb}_2(\text{hhpmH}_2)_4(\eta^2\text{-NO}_3)_2]^{2+}$ (**16**) cluster.

Powell et al. [90] synthesized a tetranuclear $[\text{Fe}_2\text{Dy}_2(\mu_3\text{-OH})_2(\text{teg})_2(\text{N}_3)_2(\text{benz})_4]$ cluster (**17**), where tegH_2 =triethylene glycol, and studied the magnetic properties of the compound. The central core of the compound represents a Fe_2Dy_2 butterfly topology, where Fe^{III} and Dy^{III} ions are held together by two $\mu_3\text{-OH}$ groups (Fig. 10a). Two teg^{2-} anionic ligands coordinate to Dy centers in a tetradentate coordinate mode and bridge to two Fe centers with two deprotonated alkoxide arms. Azides and benzoate groups complete the coordination sphere of the Dy and Fe centers. The Fe centers are six-coordinated and have a slightly distorted NO_5 octahedral coordination geometry, whereas Dy centers are eight-coordinated with an O_8 trigonal dodecahedral coordination geometry. The $\text{Dy} \dots \text{Fe}$ distances are 3.3557(6) and 3.3952(6) Å; the $\text{Dy} \dots \text{Dy}$ distance is 3.9347(5) Å. The Dy-O distances are in a range of 2.280(2)–2.417(2) Å. Magnetic studies revealed dominant antiferromagnetic interactions between the metal ions in **17**. AC magnetic susceptibility measurements of $[\text{FeDy}_2\text{Fe}(\mu_3\text{-OH})_2(\text{teg})_2(\text{N}_3)_2(\text{benz})_4]$ (**17**) showed frequency-dependent χ'' signals; however, there was no maxima above 1.8 K.

2015 was a year marked by achievements in the preparation of five heterometallic SMM clusters with terbium and dysprosium. Two hexanuclear SMM clusters $[\text{Fe}_6\text{Ln}_2(\mu_3\text{-O})_2(\text{btpH}_4)_2(\text{Piv})_{12}] \cdot 0.5(\text{DMF}) \cdot (\text{EtOH}) \cdot 2.5(\text{H}_2\text{O})$ ($\text{Ln}=\text{Dy}$ (**18**) and Tb (**19**), btpH_6 =bis-tri propane) were formed using the solvothermal reaction of trinuclear $[\text{Fe}_3\text{O}(\text{piv})_6(\text{H}_2\text{O})_3](\text{piv})$, $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ($\text{Ln}=\text{Dy}$ (**18**), Tb (**19**)), bis-tris propane, and $\text{Li}(\text{OH}) \cdot \text{H}_2\text{O}$ in a mixed solvent of EtOH and DMF [91]. Clusters **18** and **19** are isostructural; their structures include six Fe^{III} and two Dy^{III} ions linked via 2 $\mu_3\text{-OH}^-$ groups, 2 btpH_4^{2-} ligands, and 12 pivalates (Fig. 9b). Four iron sites are hexa-coordinated to adopt an O_6 octahedral geometry; two in the center have an N_2O_4 environment. The Fe-N bond distances

vary in a range of 2.152(5)–2.187(5) Å, while the Fe–O bond distances are from 1.852(3) to 2.177(4) Å. The Dy–O distances lie in a range of 2.259(4)–2.615(3) Å. Magnetic measurements indicated that the complexes exhibit a ferrimagnetic behavior. AC measurements suggest that these compounds exhibit a slow magnetic relaxation.

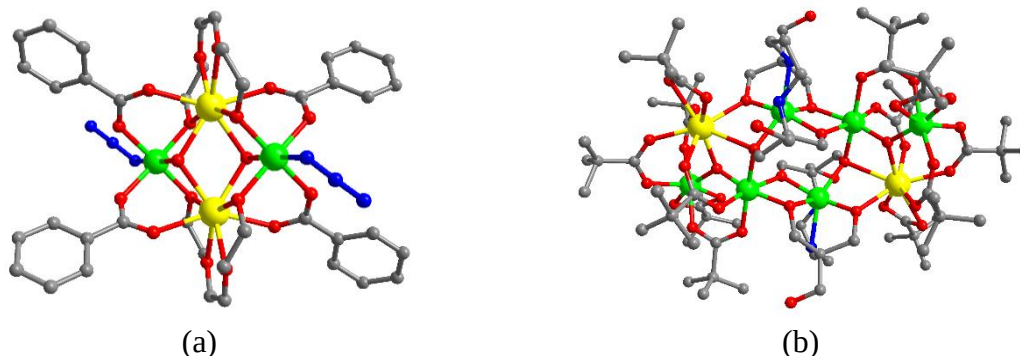


Fig. 10. Structure of (a) $[\text{FeDy}_2\text{Fe}(\mu_3\text{-OH})_2(\text{tec})_2(\text{N}_3)_2(\text{benz})_4]$ (**17**) and (b) $[\text{Fe}_6\text{Ln}_2(\mu_3\text{-O})_2(\text{btpH}_4)_2(\text{Piv})_{12}]$ ($\text{Ln}=\text{Dy}$ (**18**) and Tb (**19**)).

A heteronuclear complex $[\text{Fe}_2\text{Dy}_3(\mu_5\text{-O})(\text{edteH})_2(\text{NO}_3)_5(\text{H}_2\text{O})(\text{MeOH})]\cdot 0.5(\text{MeOH})$ (**20**) ($\text{edteH}_4=\text{N,N,N,N}$ -tetrakis(2-hydroxyethyl) ethylenediamine)) is the first example of pentanuclear Fe–Ln SMM. Cluster **20** was prepared by the reaction of $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, $\text{Dy}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ and edteH_4 in the presence of triethylamine in a solvent mixture of MeOH and MeCN [92]. The cluster core consists of three Dy^{III} and two Fe^{III} ions, which reside in the vertexes of a square pyramid. All metal ions are held by the central $\mu_5\text{-O}$ bridge (Fig. 11a). Two Fe^{III} and two Dy^{III} ions form the base of the pyramid, while one Dy^{III} ion occupies the vertex. It is of interest that each of the Fe^{III} ions is seven-coordinated and adopts an N_2O_5 capped octahedral polyhedron, whereas Dy^{III} ions are nine-coordinated and surrounded by O_9 donor atoms. The Fe–O, Fe–N, and Dy–O bond lengths are in a range of 1.965(5)–2.264(4) Å, 2.258(5)–2.240(6), and 2.283(4)–2.626(4) Å, respectively. The static magnetic susceptibilities of **20** revealed that the cluster undergoes strong antiferromagnetic interactions. The out-of-phase AC magnetic susceptibilities of **20** exhibit frequency dependence below 6 K, which indicates a slow relaxation of magnetization, with an energy barrier of $U_{\text{eff}} = 6.78$ K and a relaxation time of $\tau_0 = 2.01 \times 10^{-5}$ s.

Reaction of $\text{Dy}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ and 1-(2-hydroxyethyl)-2-pyrrolidone in the presence of $\text{K}_3[\text{Fe}(\text{CN})_6]$ in an aqueous solution produces the dinuclear SMM complex $[\text{FeDy}(\text{CN})_6(\text{hep})_2(\text{H}_2\text{O})_4]$ (**21**) ($\text{hep}=1$ -(2-hydroxyethyl)-2-pyrrolidone) [93]. The structure consists of the $[\text{Fe}(\text{CN})_6]^{3-}$ entity which acts as a bridging ligand toward a Dy^{III} ion to form a heterodinuclear structure (Fig. 11b). The Dy ion has a distorted pentagonal-bipyramidal geometry with a NO_6 donor set, whereas Fe^{III} ion resides in a C_6 octahedral environment. The DC magnetic measurements showed an antiferromagnetic coupling between the intradimer Dy^{III} and Fe^{III} ions. Under an external field, the compound shows an AC magnetic relaxation dynamics, which gives rise to antiferromagnetic interaction in **21**. Fitting the data to the Arrhenius law, the characteristic SMM energy gap, U_{eff} was estimated at 63 K and the relaxation time was 7.1×10^{-11} s.

Another hexanuclear SMM cluster $[\text{Fe}_2\text{Dy}_4(\mu_4\text{-O})_2(\mu_3\text{-OH})_{2.36}(\mu_3\text{-OMe})_{1.64}(\text{cyan})_{10}(\text{MeOH})_5(\text{H}_2\text{O})]\cdot 3(\text{MeOH})\cdot 0.36(\text{H}_2\text{O})$ ($\text{cyanH}=\text{cyanoacetic acid}$) (**22**) was reported by Powell et al. [94]; it was derived from the

reaction of trinuclear $[\text{Fe}_3\text{O}(\text{cyan})_6(\text{H}_2\text{O})_3](\text{NO}_3)\cdot 5\text{H}_2\text{O}$ and $\text{Dy}(\text{NO}_3)_3\cdot x\text{H}_2\text{O}$ in the presence of $(\pm)$ -3-diisopropylamino-1,2-propanediol in methanol. Compound $(\pm)$ -3-diisopropylamino-1,2-propanediol does not coordinate to complex **22**; however, the presence of it in the reaction is mandatory for growing orange crystals of **22**. The structure consists of four Dy^{III} and two Fe^{III} ions linked via two $\mu_4\text{-O}^{2-}$ and $\mu_3\text{-OH}^-$ ligands in the vertexes of square pyramid, while iron ions occupy the axial positions (Fig. 11b). The metal atoms in the core is additionally linked by ten cyanoacetate groups; eight of them coordinate in a $\text{syn},\text{syn-}\eta^1:\eta^1:\mu_2$ -bridging mode, while the remaining two coordinate in a $\eta^1:\mu$ -bridging mode. The peripheral environment of the Dy ions is provided by one aqua and five MeOH ligands. Each of the Dy^{III} ions has an eight-coordinated oxygen atoms environment with a nearly square antiprismatic geometry, whereas each of the Fe^{III} ions coordinates six oxygen atoms to adopt a slightly distorted octahedral geometry. Magnetic studies displayed that antiferromagnetic coupling in the squashed octahedral topology core are dominant. In **22**, the anisotropy barrier was estimated at 34 K ($\tau_0 = 2.0 \times 10^{-11}$ s).

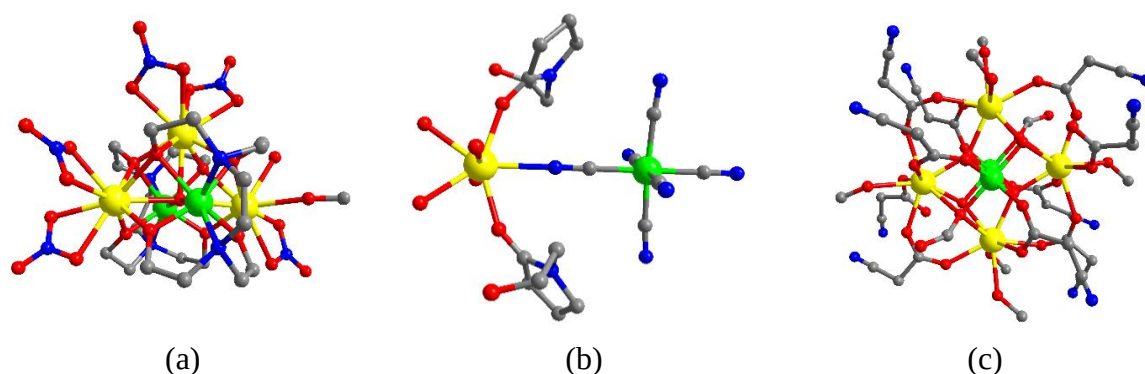


Fig. 11. Structure of (a) $[\text{Fe}_2\text{Dy}_3\text{O}(\text{edteH})_2(\text{NO}_3)_5(\text{H}_2\text{O})(\text{MeOH})]$ (**20**), (b) $[\text{FeDy}(\text{CN})_6(\text{hep})_2(\text{H}_2\text{O})_4]$ (**21**), and (c) $[\text{Fe}_2\text{Dy}_4\text{O}_2(\text{OH})_{2.36}(\text{OMe})_{1.64}(\text{O}_2\text{CCH}_2\text{CN})_{10}(\text{MeOH})_5(\text{H}_2\text{O})]$ (**22**).

In the beginning of 2016, Powell et al. [95] increased the number of Fe–Ln SMM complexes by publishing hexanuclear cluster $[\text{Fe}_4\text{Dy}_2(\mu_3\text{-OH})_2(\text{mdea})_4(\mu\text{-nbenz})_8]\cdot 3(\text{MeCN})$ (**23**) ($\text{nbenzH}_2=\text{m-NO}_2\text{C}_6\text{H}_4\text{COOH}$) and nonanuclear cluster $[\text{Fe}_6\text{Dy}_3(\mu_4\text{-O})_3(\mu_3\text{-O})(\text{mdea})_5(\text{nbenz})_9]\cdot 3(\text{MeCN})$ (**24**). Cluster **23** was derived from the interaction of $[\text{Fe}_3\text{O}(\text{nbenz})_6(\text{H}_2\text{O})_3]\cdot (\text{nbenz})$, $\text{Ln}(\text{NO}_3)_3\cdot x\text{H}_2\text{O}$ with a methyldiethanolamine ligand; it contains a $\{\text{Fe}_4\text{Dy}_2\}$ core with a butterfly-shaped central $\{\text{Fe}_2\text{Dy}_2\}$ unit, where each of the two $\{\text{FeDy}_2\}$ triangles is bridged by a $(\mu_3\text{-OH})^-$ ligand, a syn,syn μ -benzoate ligand, and a doubly-deprotonated mdea^{2-} ligand (Fig. 12a). The remaining two Fe^{III} ions coordinate to the butterfly-like core through the oxygens that arrive from the double deprotonated mdea^{2-} ligand and bridging benzoate. The Fe...Fe distance is 5.1884 Å; Dy...Dy is 3.8750 Å, while Fe...Dy distances are 3.3583 and 3.5546 Å. Compound **23** was used as a precursor to prepare a higher nuclearity cluster $[\text{Fe}_6\text{Dy}_3(\mu_4\text{-O})_3(\mu_3\text{-O})(\text{mdea})_5(\text{nbenz})_9]\cdot 3(\text{MeCN})$ (**24**). The molecular structure of **24** consists of six Fe^{III} ions and three Dy^{III} ions that are linked via three $\mu_4\text{-O}^{2-}$ and one $\mu_3\text{-O}^{2-}$ to form the metallic core of **24** (Fig. 12b). Five mdea and nine benzoate ligands complete the peripheral ligation of the metal core. The Dy...Dy distances are 3.7412(6), 3.7635(7), and 3.8347(7) Å. Temperature dependent magnetic measurements indicated dominant antiferromagnetic interactions between Fe^{III} ions and weakly ferromagnetic interactions between Dy^{III} ions in **23**. In **24**, the $\text{Fe}^{\text{III}}\text{--Fe}^{\text{III}}$ interactions are antiferromagnetic and $\text{Dy}^{\text{III}}\text{--Dy}^{\text{III}}$ interactions are weakly antiferromagnetic. Magnetic AC measurements of the $\{\text{Fe}_4\text{Dy}_2\}$ (**23**) cluster revealed the slow relaxation of magnetization.

Fitting the frequency-dependent AC susceptibility data of **23** with the Arrhenius law gives a characteristic SMM effective energy barrier of $U_{\text{eff}} = 7.1$ K with a relaxation time of $\tau_0 = 6.4 \times 10^{-6}$ s. The AC susceptibility measurements for **24** in a zero DC field showed an extremely weak χ'' signal. However, a DC field of 1000 Oe provides a clear out-of-phase signal. Calculations for the data with the Arrhenius law yield an effective energy barrier of 17.1 K and a relaxation time of 7.4×10^{-8} s.

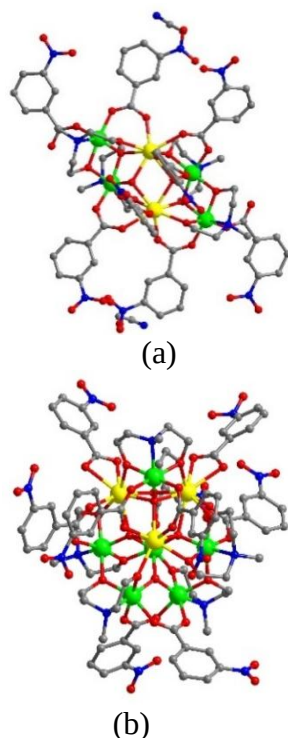


Fig. 12. Structure of (a) $[\text{Fe}_4\text{Dy}_2(\mu_3\text{-OH})_2(\text{mdea})_4(\text{nbenz})_8]$ (**23**) and (b) $[\text{Fe}_6\text{Dy}_3(\mu_4\text{-O})_3(\mu_3\text{-O})(\text{mdea})_5(\text{nbenz})]$ (**24**).

Recently, Baca et al. [96] have contributed to this area by reporting two hexanuclear carboxylate wheels $\{\text{Fe}_4\text{Tb}_2\}$ (**25**) and $\{\text{Fe}_4\text{Ho}_2\}$ (**26**) and the two largest Fe-4f SMM wheels to date $\{\text{Fe}_{18}\text{Dy}_6\}$ (**27**) and $\{\text{Fe}_{18}\text{Tb}_6\}$ (**28**) to display slow magnetic relaxation. Clusters $[\text{Fe}_4\text{Ln}_2(\text{piv})_6(\text{N}_3)_4(\text{teaH})_4]$ ($\text{Ln}=\text{Tb}$ (**25**) and Ho (**26**)) $\cdot 2(\text{EtOH})$ (pivH=pivalic acid; teaH₃=triethanolamine) were synthesized by the interaction of $[\text{Fe}_6\text{O}_2(\text{OH})_2(\text{piv})_{12}]$ with terbium(III) nitrate or holmium(III) nitrate in the presence of sodium azide and triethanolamine in an ethanol solution. Clusters **25** and **26** composed of four Fe^{III} and two Ln^{III} ions linked by an array of bridging carboxylate, azide, and aminopolyalcoholato-based ligands into a cyclic structure with a cavity and ethanol solvents for **26** (Fig. 13a). Each of the Fe^{III} atoms has a distorted octahedral N_2O_4 coordination environment, whereas each of the Ln^{III} atoms is eight-coordinated with an N_2O_6 donor set. The reported temperature-dependent magnetic susceptibility data are consistent with dominant ferromagnetic exchange interactions within the complexes. AC susceptibility data of **25** and **26** showed an energy barrier of $U_{\text{eff}} = 31.68$ K and $\tau_0 = 1.2 \times 10^{-9}$ s.

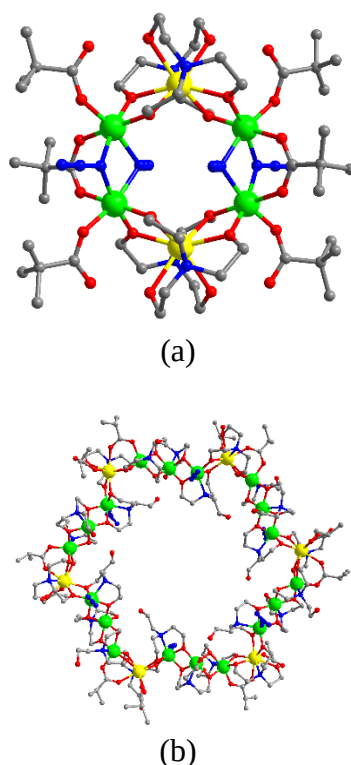


Fig. 13. Structure of (a) $[\text{Fe}_4\text{Ln}_2(\text{piv})_6(\text{N}_3)_4(\text{teaH})_4]$ ($\text{Ln}=\text{Tb}$ (**25**) and Ho (**26**)) and (b) $[\text{Fe}_{18}\text{Ln}_6(\text{is})_{12}(\text{teaH})_{18}(\text{tea})_6(\text{N}_3)_6]$ ($\text{Ln}=\text{Tb}$ (**27**) and Ho (**28**)).

Large wheels $[\text{Fe}_{18}\text{Ln}_6(\text{is})_{12}(\text{teaH})_{18}(\text{tea})_6(\text{N}_3)_6] \cdot n(\text{solvent})$ ($\text{Ln}=\text{Dy}$ (**27**) and Tb (**28**); isH =isobutyric acid) were derived from the reaction of $[\text{Fe}_3\text{O}(\text{is})_6(\text{H}_2\text{O})_3]\text{NO}_3 \cdot 2(\text{MeCN}) \cdot 2(\text{H}_2\text{O})$ with dysprosium(III) nitrate or terbium(III) nitrate in the presence of sodium azide and triethanolamine in a MeOH/MeCN solution. The molecular core structures in **27** and **28** involve 18 Fe^{III} and six Ln^{III} ions interconnected by 6 isobutyrate and 24 amino alcohol ligands into a ring with alternating three Fe^{III} ions and one Ln^{III} ion (Fig. 13b). All Fe centers are six-coordinated in a distorted octahedral environment: 12 of them have a NO_5 donor set, and the remaining 6 Fe atoms have a N_2O_4 donor set. All Ln atoms are eight-coordinated having a distorted square antiprismatic NO_7 environment. Temperature magnetic measurements of **27** and **28** indicated predominant antiferromagnetic exchange interactions within each of the Fe_3 units ($S = 5/2$) and ferromagnetic interactions within the ring structure. The magnetic AC measurements revealed out-of-phase signals of the compounds and, thus, slow relaxation above 2.0 K and below 1500 Hz.

The Table 1 lists the heterometallic Fe–Ln SMMs published in a period of 2005–2016, along with relevant parameters used to characterize their SMM properties. Specifically, the table shows the range in which the hysteresis loops of the compounds were observed, the effective energy barrier (U_{eff}), and the relaxation time (τ_0) of the obtained Fe–Ln SMM compounds.

#	Fe-Ln SMM's	U_{eff} (K)	τ (s) (rel. time)	Hysteresis (K)	Ref
1.	$[\text{Fe}^{\text{III}}\text{Ho}^{\text{III}}_2(\mu_3\text{-OH})_2(\text{teaH})_2(\text{benz})_4(\text{NO}_3)_2] \cdot 4(\text{MeCN}) \cdot 3(\text{H}_2\text{O})$			<0.3	[75]
2.	$[\text{Fe}^{\text{III}}_2\text{Dy}^{\text{III}}_2(\mu_3\text{-OH})_2(\text{teaH})_2(\text{benz})_6]$			4 - 1.1	[75]
3.	$[\text{Fe}^{\text{III}}_2\text{Dy}^{\text{III}}_2(\mu_3\text{-OH})_2(\text{teaH})_2(\text{R-benz})_6]$				[76]
4.	$[\text{Fe}^{\text{III}}\text{Dy}^{\text{III}}(\text{bpca})(\mu\text{-bpca})(\text{NO}_3)_4]$	8.98	7.77×10^{-8}	0.4	[77]
5.	$[\{\text{Fe}^{\text{III}}(\text{bpca})_3\} \{\text{Dy}^{\text{III}}(\text{hfac})_3\}_2] \cdot \text{CHCl}_3$	9.7	8.71×10^{-8}		[78]
6.	$[\text{Fe}^{\text{III}}_7\text{Dy}^{\text{III}}_3(\mu_4\text{-O})_2(\mu_3\text{-OH})_2(\text{mdea})_7(\text{benz})_4(\text{N}_3)_6] \cdot 7(\text{MeOH}) \cdot 2(\text{H}_2\text{O})$	33.4	6.6×10^{-8}	<1.8	[79]
7.	$[\text{Fe}^{\text{III}}_3\text{Tb}^{\text{III}}(\mu_3\text{-O})_2(\text{tea})_8(\text{H}_2\text{O})(\text{THF})_3] \cdot \text{THF}$				[80]
8.	$[\text{Fe}^{\text{III}}_4\text{Ln}^{\text{III}}_2(\mu_4\text{-O})_2(\text{NO}_3)_2(\text{piv})(\text{Hedte})] \cdot x(\text{CH}_3\text{CN}) \cdot y(\text{CH}_2\text{Cl}_2) \cdot z(\text{C}_6\text{H}_5\text{OH})$	30.85	3.7×10^{-8}		[81]
9.	$[\text{Fe}^{\text{III}}_4\text{Dy}^{\text{III}}_4(\text{teaH})_8(\text{N}_3)_8(\text{H}_2\text{O})] \cdot 4(\text{CH}_3\text{CN}) \cdot (\text{H}_2\text{O})$	30.5	2.0×10^{-9}	1.4	[82]
10.	$[\text{Fe}^{\text{III}}_4\text{Dy}^{\text{III}}_2(\text{piv})_2(\text{thdH})_2(\text{thdH})_2 \cdot \text{thd}_2(\text{CH}_3\text{OH})_2(\text{NO}_3)_2][\text{Dy}^{\text{III}}(\text{NO}_3)_4(\text{thdH}_3(\text{MeOH})) \cdot \text{NO}_3 \cdot \text{H}_2\text{O}]$				[83]
11.	$[\text{Fe}^{\text{III}}_{12}\text{Sm}^{\text{III}}_4(\mu_4\text{-O})_6(\mu_3\text{-O})_4(\text{OH})_4(\text{benz})_{24}]$	16	2.0×10^{-8}	0.5	[84]
12.	$[\text{Fe}^{\text{III}}\text{Dy}^{\text{III}}_3(\text{HBpz}_3)_6(\text{dto})_3] \cdot 4(\text{MeCN}) \cdot 2(\text{CH}_2\text{Cl}_2)$	15	1.5×10^{-6}		[85]
13.	$[\text{Fe}^{\text{III}}_7\text{Tb}^{\text{III}}_3(\mu_4\text{-O})_2(\mu_3\text{-OH})_2(\text{PhCO}_2)_4(\text{N}_3)_6(\text{mdea})_7] \cdot 4(\text{MeCN}) \cdot \text{H}_2\text{O}$				[86]
14.	$[\text{Fe}^{\text{III}}_4\text{Dy}^{\text{III}}_2(\mu_3\text{-OH})_2(\text{benz})_8(\text{n-bdea})_4] \cdot \text{MeCN}$	21.4	2.7×10^{-8}		[87]
15.	$[\text{Fe}^{\text{III}}_6\text{Dy}^{\text{III}}_3(\mu_7\text{-C}_2\text{H}_2\text{O}_4)(\mu_4\text{-tea})_2(\mu_3\text{-teaH})_4(\mu_2\text{-N}_3)_2(\text{N}_3)_6(\text{NO}_3)] \cdot 2(\text{EtOH})$	65.1	1.64×10^{-12}	1.4	[88]
16.	$[\text{Fe}^{\text{III}}_2\text{Tb}^{\text{III}}_2(\text{H}_2\text{L})_4(\eta_2\text{-NO}_3)_2] \cdot 2(\text{ClO}_4) \cdot 2(\text{CH}_3\text{OH}) \cdot 2(\text{H}_2\text{O})$				[89]
17.	$[\text{Fe}^{\text{III}}_2\text{Dy}^{\text{III}}_2(\mu_3\text{-OH})_2(\text{benz})_4(\text{teg})_2(\text{N}_3)_2]$				[90]
18.	$[\text{Fe}^{\text{III}}_6\text{Dy}^{\text{III}}_2(\mu_3\text{-O})_2(\text{Piv})_{12}(\text{btpH}_4)_2] \cdot 0.5(\text{DMF}) \cdot (\text{EtOH}) \cdot 2.5(\text{H}_2\text{O})$	2.5	7.8×10^{-7}		[91]
19.	$[\text{Fe}^{\text{III}}_6\text{Tb}^{\text{III}}_2(\mu_3\text{-O})_2(\text{Piv})_{12}(\text{btpH}_4)_2] \cdot 0.5(\text{DMF}) \cdot (\text{EtOH}) \cdot 2.5(\text{H}_2\text{O})$	2.4	6.0×10^{-7}		[91]
20.	$[\text{Fe}^{\text{III}}_2\text{Dy}^{\text{III}}_3(\mu_5\text{-O})(\text{Hedte})_2(\text{NO}_3)_5(\text{H}_2\text{O})(\text{MeOH})] \cdot 0.5(\text{MeOH})$	6.78	2.01×10^{-5}		[92]
21.	$[\text{Fe}^{\text{III}}\text{Dy}^{\text{III}}(\text{CN})_6(\text{hep})_2(\text{H}_2\text{O})_4]$	63	7.1×10^{-11}		[93]
22.	$[\text{Fe}^{\text{III}}_2\text{Dy}^{\text{III}}_4(\mu_4\text{-O})_2(\mu_3\text{-OH})_2(\mu_3\text{-OMe})_{1.64}(\text{cyan})_{10}(\text{MeOH})_5(\text{H}_2\text{O})] \cdot 3(\text{MeOH}) \cdot 0.36(\text{H}_2\text{O})$	34	2.0×10^{-11}		[94]
23.	$[\text{Fe}^{\text{III}}_4\text{Dy}^{\text{III}}_2(\mu_3\text{-OH})_2(\mu\text{-nbenz})_8(\text{mdea})_4] \cdot 3(\text{MeCN})$	7.1	6.4×10^{-6}		[95]
24.	$[\text{Fe}^{\text{III}}_6\text{Dy}^{\text{III}}_3(\mu_4\text{-O})_3(\mu_3\text{-O})(\text{nbenz})_9(\text{mdea})_5] \cdot 3(\text{MeCN})$	17.1	7.4×10^{-8}		[95]
25.	$[\text{Fe}^{\text{III}}_4\text{Tb}^{\text{III}}_2(\text{piv})_6(\text{N}_3)_4(\text{teaH})_4]$	31.68	1.2×10^{-9}		[96]
26.	$[\text{Fe}^{\text{III}}_4\text{Ho}^{\text{III}}_2(\text{piv})_6(\text{N}_3)_4(\text{teaH})_4] \cdot 2(\text{EtOH})$	31.68	1.2×10^{-9}		[96]
27.	$[\text{Fe}^{\text{III}}_{18}\text{Dy}^{\text{III}}_6(\text{is})_{12}(\text{teaH})_{18}(\text{tea})_6(\text{N}_3)_6] \cdot n(\text{solvent})$				[96]
28.	$[\text{Fe}^{\text{III}}_{18}\text{Tb}^{\text{III}}_6(\text{is})_{12}(\text{teaH})_{18}(\text{tea})_6(\text{N}_3)_6] \cdot n(\text{solvent})$				[96]

4. Conclusions

The review shows the advances that have been achieved in the preparation of SMM compounds based on a Fe–Ln core. Over the last decade, the field of iron–lanthanide SMMs has been rapidly developed by synthesizing more and more interesting SMM compounds. Chemists and researchers have synthesized and studied a number of SMMs to understand the properties of these materials. A rational design involving N-/O-containing donor ligands gives glorious architectures exhibiting properties required to be SMMs. This review describes SMM species possessing different architecture topologies: linear, s-shaped, propeller-, ring-, Z-, butterfly-, wheel-type cores, and others structures. Over the last decade, 28 Fe–Ln heteronuclear coordination clusters have revealed an SMM behavior. The effective preparation of SMM compounds depends on the types of structures and on basic and complementary ligands binding metal ions. A huge number of various types of ligands could be employed in different combinations for assembling other Fe–Ln complexes exhibiting better magnetic behavior.

There are two main criteria that determine 3d–4f compounds as an SMM; one of them is a hysteresis loop, which can be observed at extremely low temperatures; the other criterion is frequency-dependent signals of out-of-phase susceptibility of AC measurements, which enable calculations of energy barriers with relaxation times.

References

- [1] T. Lis, *Acta Crystallogr., Sect. B* 36, 2042 (1980).
- [2] A. Caneschi, D. Gatteschi, Je. Laugier, P. Rey, R. Sessoli, and C. Zanchini, *J. Am. Chem. Soc.* 110 (9), 2795 (1988).
- [3] J. P. Richard, T. L. Amyes, and T. Vontor, *J. Am. Chem. Soc.* 113 (15), 5871 (1991).
- [4] R. Sessoli, D. Gatteschi, A. Caneschi, and M. A. Novak, *Nature* 365, 141 (1993).
- [5] R. Sessoli, H. L. Tsai, A. R. Schake, Sh. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, and D. N. Hendrickson, *J. Am. Chem. Soc.* 115 (5), 1804 (1993).
- [6] Sh. M. J. Aubin, M. W. Wemple, D. M. Adams, H. L. Tsai, G. Christou, and D. N. Hendrickson, *J. Am. Chem. Soc.* 118, 7746 (1996).
- [7] K. Weighardt, K. Pohl, I. Jibril, and G. Huttner, *Angew. Chem. Int. Ed.* 23, 77 (1984).
- [8] W. Wernsdorfer, R. Sessoli, A. Caneschi, D. Gatteschi, and A. Cornia, *Europh. Lett.* 50 (4), 552 (2000).
- [9] A. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K. A. Abboud, and G. Christou, *Angew. Chem. Int. Ed.* 43, 2117 (2004).
- [10] C. Boskovic, E. K. Brechin, W. E. Streib, K. Folting, J. C. Bollinger, D. N. Hendrickson, and G. Christou, *J. Am. Chem. Soc.* 124 (14), 3725 (2002).
- [11] St. Piligkos, G. Rajaraman, M. Soler, N. Kirchner, J. van. Slageren, R. Bircher, S. Parsons, H. U. Güdel, J. Kortus, W. Wernsdorfer, G. Christou, and E. K. Brechin, *J. Am. Chem. Soc.* 127 (15), 5572 (2005).
- [12] C. J. Milios, C. P. Raptopoulou, A. Terzis, F. Lloret, R. Vicente, S. P. Perlepes, and A. Escuer, *Angew. Chem. Int. Ed.* 43, 210 (2004).
- [13] A. Cornia, A. C. Fabretti, P. Garrisi, C. Mortal, D. Bonacchi, D. Gatteschi, R. Sessoli, L. Sorace, W. Wernsdorfer, and A.L. Barra, *Angew. Chem. Int. Ed.* 43, 1136 (2004).
- [14] L. F. Jones, E. K. Brechin, D. Collison, M. Helliwell, T. Mallah, S. Piligkos, G. Rajaraman, and W. Wernsdorfer, *Inorg. Chem.* 42 (21), 6601 (2003).
- [15] A. K. Boudalis, B. Donnadieu, V. Nastopoulos, J. M. Clemente-Juan, A. Mari, Y. Sanakis, J. P. Tuchagues, and S. P. Perlepes, *Angew. Chem. Int. Ed.* 43, 2266 (2004).
- [16] M. Moragues-Canovas, M. Helliwell, L. Ricard, E. Riviere, W. Wernsdorfer, E. Brechin,

- and T. Mallah, *Eur. J. Inorg. Chem.* 2219 (2004).
- [17] S. T. Ochsenbein, M. Murrie, E. Rusanov, H. Stoeckli-Evans, Ch. Sekine, and H. U. Güdel, *Inorg. Chem.* 41 (20), 5133 (2002).
- [18] E. Ch. Yang, D. N. Hendrickson, W. Wernsdorfer, M. Nakano, L. N. Zakharov, and R. D. Sommer, *J. Appl. Phys.* 91, 7382 (2002).
- [19] M. Murrie, S. J. Teat, H. Stoeckli-Evans, and H. U. Güdel, *Angew. Chem. Int. Ed.* 42, 4653 (2003).
- [20] R. Ruamps, L. J. Batchelor, R. Guillot, G. Zakhia, A. L. Barra, W. Wernsdorfer, N. Guihéry, and T. Mallah, *Chem. Science* 5, 3418 (2014).
- [21] C. J. Milios, A. Vinslava, W. Wernsdorfer, S. Moggach, S. Parsons, S. P. Perlepes, G. Christou, and E. K. Brechin, *J. Am. Chem. Soc.* 129 (10), 2754 (2007).
- [22] I. S. Kirin, P. N. Moskalev, and Y. A. Makashev, *Russ. J. Inorg. Chem.* 10, 1065 (1965).
- [23] P. N. Moskalev, G. N. Shapkin, and A. N. Darovskikh, *Russ. J. Inorg. Chem.* 24, 340 (1979).
- [24] N. Ishikawa, M. Sugita, T. Ishikawa, Sh.-ya. Koshihara, and Y. Kaizu, *J. Am. Chem. Soc.* 125, 8694 (2003).
- [25] K. Bernot, J. Luzon, L. Bogani, M. Etienne, C. Sangreggiorio, M. Shanmugam, A. Caneschi, R. Sessoli, and D. Gatteschi, *J. Am. Chem. Soc.* 131 (15), 5573 (2009).
- [26] K. Katoh, T. Kajiwara, M. Nakano, Y. Nakazawa, W. Wernsdorfer, N. Ishikawa, B. K. Breedlove, and M. Yamashita, *Chem. Eur. J.* 17, 117 (2011).
- [27] K. Katoh, Y. Horii, N. Yasuda, W. Wernsdorfer, K. Toriumi, B. K. Breedlove, and M. Yamashita, *Dalt. Trans.* 41, 13582 (2012).
- [28] F. Tuna, C. A. Smith, M. Bodensteiner, L. Ungur, L. F. Chibotaru, E. J. L. McInnes, R. E. P. Winpenny, D. Collison, and R. A. Layfield, *Angew. Chem. Int. Ed.* 51, 6976 (2012).
- [29] G. F. Xu, Q. L. Wang, P. Gamez, Y. Ma, R. Clérac, J. Tang, S. P. Yan, P. Cheng, and D. Z. Liao, *Chem. Commun.* 46, 1506 (2010).
- [30] Y. N. Guo, G. F. Xu, P. Gamez, L. Zhao, S. Y. Lin, R. Deng, J. Tang, and H. J. Zhang, *J. Am. Chem. Soc.* 132, 8538 (2010).
- [31] P. H. Lin, T. J. Burchell, L. Ungur, L. F. Chibotaru, W. Wernsdorfer, and M. Murugesu, *Angew. Chem. Int. Ed.* 48, 9489 (2009).
- [32] R. J. Blagg, F. Tuna, E. J. L. McInnes, and R. E. P. Winpenny, *Chem. Commun.* 47, 10587 (2011).
- [33] R. J. Blagg, C. A. Muryn, E. J. L. McInnes, F. Tuna, and R. E. P. Winpenny, *Angew. Chem. Int. Ed.* 50, 6530 (2011).
- [34] J. D. Rinehart, M. Fang, W. J. Evans, and J. R. J. Long, *Am. Chem. Soc.* 133 (36), 14236 (2011).
- [35] C. James and P. S. Willand, *J. Am. Chem. Soc.* 38 (8), 1497 (1916).
- [36] W. E. Bayley, R. J. Williams, and W. O. Milligan, *Acta Crystallogr., Sect. B*, B29, 1365 (1973).
- [37] J. M. Boncella and R. A. Andersen, *Inorg. Chem.* 23 (4), 432 (1984).
- [38] G. Christou, D. Gatteschi, D. N. Hendrickson, and R. Sessoli, *MRS Bull.* 25, 66 (2000).
- [39] S. Osa, T. Kido, N. Matsumoto, N. Re, A. Pochaba, and J. Mrozinski, *J. Am. Chem. Soc.* 126 (2), 420 (2004).
- [40] C. Benelli, M. Murrie, S. Parsons, and R. Winpenny, *J. Chem. Soc., Dalt. Trans.* 4125, (1999).
- [41] C. Zaleski, E. Depperman, J. Kampf, M. Kirk, and V. Pecoraro, *Angew. Chem. Int. Ed.* 43, 3912 (2004).
- [42] A. Mishra, W. Wernsdorfer, K. Abboud, and G. Christou, *J. Am. Chem. Soc.* 126 (48), 15648 (2004).
- [43] A. Mishra, W. Wernsdorfer, S. Parsons, G. Christou, and E. Brechin, *Chem. Commun.*

- 2086 (2005).
- [44] V. Mereacre, A. M. Ako, R. Clerac, W. Wernsdorfer, G. Filoti, J. Bartolome, C. E. Anson, and A. K. Powell, *J. Am. Chem. Soc.* 129 (30), 9248 (2007).
- [45] V. Mereacre, A. M. Ako, R. Clerac, W. Wernsdorfer, I. J. Hewitt, C. E. Anson, and A. K. Powell, *Chem. Eur. J.* 14, 3577 (2008).
- [46] T. C. Stamatatos, S. J. Teat, W. Wernsdorfer, and G. Christou, *Angew. Chem. Int. Ed.* 48, 521 (2009).
- [47] A. M. Ako, V. Mereacre, R. Clerac, W. Wernsdorfer, I. J. Hewitt, C. E. Anson, and A. K. Powell, *Chem. Commun.* 544 (2009).
- [48] Z. Zhang, W. Wernsdorfer, F. Pan, Z.-M. Wang, and S. Gao, *Chem. Commun.* 31, 3302 (2006).
- [49] J.-P. Costes, M. Auchel, F. Dahan, S. Shova, and W. Wernsdorfer, *Inorg. Chem.* 45 (5), 1924 (2006).
- [50] F. Mori, T. Nyui, T. Ishida, T. Nogami, K.-Y. Choi, and H. J. Nojiri, *J. Am. Chem. Soc.* 128 (5), 1440 (2006).
- [51] C. Aronica, G. Pilet, G. Chastanet, W. Wernsdorfer, J.-F. Jacquot, and D. Luneau, *Angew. Chem. Int. Ed.* 45 (28), 4659 (2006).
- [52] G. Novitchi, J.-P. Costes, J.-P. Tuchagues, L. Vendier, and W. Wernsdorfer, *New J. Chem.* 32, 197 (2008).
- [53] Gh. Novitchi, W. Wernsdorfer, L. Chibotaru, J.-P. Costes, C. E. Anson, and A. K. Powell, *Angew. Chem. Int. Ed.* 48, 1614 (2009).
- [54] A. Bencini, C. Benelli, A. Caneschi, R. L. Carlin, A. Dei, and D. Gatteschi, *J. Am. Chem. Soc.* 107 (26), 8128 (1985).
- [55] M. Andruh, I. Ramade, E. Codjovi, O. Guillou, O. Kahn, and J. C. Trombe, *J. Am. Chem. Soc.* 115 (5), 1822 (1993).
- [56] M. Andruh, J.-P. Costes, C. Diaz, and S. Gao, *Inorg. Chem.* 48 (8), 3342 (2009).
- [57] M. L. Kahn, C. Mathoniere, and O. Kahn, *Inorg. Chem.* 38, 3692 (1999).
- [58] J.-P. Sutter, M. L. Kahn, and O. Kahn, *Adv. Mat.* 11 (10), 863 (1999).
- [59] M. L. Kahn, J.-P. Sutter, S. Golhen, P. Guionneau, L. Ouahab, O. Kahn, and D. Chasseau, *J. Am. Chem. Soc.* 122 (14), 3413 (2000).
- [60] M. L. Kahn, P. Lecante, M. Verelst, C. Mathoniere, and O. Kahn, *Chem. Mat.* 12 (10), 3073 (2000).
- [61] M. L. Kahn, R. Ballou, P. Porcher, O. Kahn, and J.-P. Sutter, *Chem. Eur. J.* 8 (2), 525 (2002).
- [62] V. Chandrasekhar, B. M. Pandian, R. Azhakar, J. J. Vittal, and R. Clerac, *Inorg. Chem.* 46 (13), 5140 (2007).
- [63] E. Brechin, S. Harris, S. Parsons, and R. Winpenney, *J. Chem. Soc., Dalt. Trans.* 1665 (1997).
- [64] J.-P. Costes, F. Dahan, A. Dupuis, and J.-P. Laurent, *Inorg. Chem.* 36 (19), 4284 (1997).
- [65] T. Shiga, N. Ito, A. Hidaka, H. Okawa, S. Kitagawa, and M. Ohba, *Inorg. Chem.* 46 (9), 3492 (2007).
- [66] A. M. Madalan, N. Avarvari, M. Fourmigue, R. Clerac, L. F. Chibotaru, S. Clima, and M. Andruh, *Inorg. Chem.* 47 (3), 940 (2008).
- [67] V. Mereacre, D. Prodius, Y. H. Lan, C. Turta, C. E. Anson, and A. K. Powell, *Chem. Eur. J.* 17 (1), 123 (2011).
- [68] S. Mukherjee, M. R. Daniels, R. Bagai, K. A. Abboud, G. Christou, and C. Lampropoulos, *Polyhed.* 29 (1), 54 (2010).
- [69] J. P. Costes, F. Dahan, F. Dumestre, J. M. Clemente-Juan, J. Garcia Tojal, and J. P. Tuchagues, *Dalt. Trans.* 464 (2003).
- [70] A. M. Ako, V. Mereacre, R. Clerac, I. J. Hewitt, Y.-H. Lan, C. E. Anson, and A. K.

- Powell, *Dalt. Trans.* 5245 (2007).
- [71] J. P. Costes, A. Dupuis, and J. P. Laurent, *Eur. J. Inorg. Chem.* (10), 1543 (1998).
- [72] A. Figuerola, C. Diaz, J. Ribas, V. Tangoulis, J. Granell, F. Lloret, J. Mahia, and M. Maestro, *Inorg. Chem.* 42 (2), 641 (2003).
- [73] S. Gao, B.-Q. Ma, H.-L. Sun, and J.-R. Li, *J. Solid State Chem.* 171, 201 (2003).
- [74] C. I. Turta, D. N. Prodius, V. M. Mereacre, S. G. Shova, M. Gdaniec, Yu. A. Simonov, V. Kuncser, G. Filoti, A. Caneschi, and L. Sorace, *Inorg. Chem. Commun.* 7, 576 (2004).
- [75] M. Murugesu, A. Mishra, W. Wernsdorfer, K. A. Abboud, and G. Christou, *Polyhed.* 25, 613 (2006).
- [76] A. Baniodeh, V. Mereacre, N. Magnani, Y. Lan, J. A. Wolny, V. Schünemann, C. E. Anson, and A. K. Powell, *Chem. Commun.* 49, 9666 (2013).
- [77] M. Ferbinteanu, T. Kajiwar, K.-Y. Choi, H. Nojiri, A. Nakamoto, N. Kojima, F. Cimpoesu, Y. Fujimura, S. Takaishi, and M. A. Yamashita, *J. Am. Chem. Soc.* 128, 9008 (2006).
- [78] F. Pointillart, K. Bernot, R. Sessoli, and D. Gatteschi, *Chem. Eur. J.* 13 (5), 1602 (2007).
- [79] G. Abbas, Y. Lan, V. Mereacre, W. Wernsdorfer, R. Clerac, G. Buth, M. T. Sougrati, F. Grandjean, G. J. Long, C. E. Anson, and A. K. Powell, *Inorg. Chem.* 48, 9345 (2009).
- [80] V. Mereacre, D. Prodius, C. Turta, S. Shova, G. Filoti, J. Bartolome, R. Clerac, C. E. Anson, and A. K. Powell, *Polyhed.* 28 (14), 3017 (2009).
- [81] M. N. Akhtar, V. Mereacre, G. Novitchi, J.-P. Tuchagues, C. E. Anson, and A. K. Powell, *Chem. Eur. J.* 15 (30), 7278 (2009).
- [82] D. Schray, G. Abbas, Y. Lan, V. Mereacre, Al. Sundt, J. Dreiser, O. Waldmann, G. E. Kostakis, C. E. Anson, and A. K. Powell, *Angew. Chem. Int. Ed.* 49, 5185 (2010).
- [83] S. Nayak, O. Roubeau, S. J. Teat, C. M. Beavers, P. Gamez, and J. Reedijk, *Inorg. Chem.* 49 (1), 216 (2010).
- [84] Y.-F. Zeng, G.-Ch. Xu, X. Hu, Zh. Chen, X.-H. Bu, S. Gao, and E. C. Sanudo, *Inorg. Chem.* 49 (1), 9734 (2010).
- [85] G.-F. Xu, P. Gamez, J. Tang, R. Clérac, Y.-N. Guo and Y. Guo, *Inorg. Chem.* 51 (10), 5693 (2012).
- [86] G. Abbas, Y. Lan, V. Mereacre, G. Buth, M. T. Sougrati, F. Grandjean, G. J. Long, C. E. Anson, and A. K. Powell, *Inorg. Chem.* 52, 11767 (2013).
- [87] S. Chen, V. Mereacre, D. Prodius, G. E. Kostakis, and A. K. Powell, *Inorg. Chem.* 54 (7), 3218 (2015).
- [88] S. Schmidt, D. Prodius, V. Mereacre, G. E. Kostakis, and A. K. Powell, *Chem. Commun.* 49, 1696 (2013).
- [89] Pr. Bag, J. Goura, V. Mereacre, Gh. Novitchi, A. K. Powell, and V. Chandrasekhar, *Dalt. Trans.* 43, 16366 (2014).
- [90] G. Peng, V. Mereacre, G. E. Kostakis, J. A. Wolny, V. Schnemann, and A. K. Powell, *Chem. Eur. J.* 20, 12381 (2014).
- [91] S.-D. Han, S.-J. Liu, Q.-L. Wang, X.-H. Miao, T.-L. Hu, and X.-H. Bu, *Cryst. Growth Des.* 15 (5), 2253 (2015).
- [92] H. Li, W. Shi, Zh. Niu, J.-M. Zhou, G. Xiong, L.-L. Lia, and P. Cheng, *Dalt. Trans.* 44, 468 (2015).
- [93] Y. Zhang, Zh. Guo, Sh. Xie, H.-L. Li, W.-H. Zhu, L. Liu, X.-Q. He, W.-X. Dong, J.-C. Ren, L.-Z. Liu, and A. K. Powell, *Inorg. Chem.* 54 (21), 10316 (2015).
- [94] C. D. Polyzou, A. Baniodeh, N. Magnani, V. Mereacre, N. Zill, C. E. Anson, S. P. Perlepes, and A. K. Powell, *Royal Soc. Chem. Adv.* 5, 10763 (2015).
- [95] S. Chen, V. Mereacre, C. E. Anson, and A. K. Powell, *Dalt. Trans.* 45, 98 (2016).
- [96] O. Botezat, J. van Leusen, V. Ch. Kravtsov, P. Kögerler, and S. G. Baca, *Inorg. Chem.* 56(4), 1814 (2017).

- [97] F. N. Allen, *Acta Crystallogr. Sec. B*, 58, 380 (2002).
- [98] R. E. P. Winpenny, *J. Am. Chem. Soc., Dalt. Trans.* 1 (2002).
- [99] R. F. Weinland, *A Herz. Ber. Deut. Chem. Gesell.* 45 (2), 2662 (1912).
- [100] S. Wocadlo, W. Massa, and J.-V. Folgado, *Inorg. Chim. Acta*, 207, 199 (1993).
- [101] D. N. Prodius, C. I. Turta, V. M. Mereacre, S. G. Shova, Iu. A. Simonov, J. Lipkowski, and A. Caneschi, *Polyhed.* 25, 2175 (2006).
- [102] J. F. Duncan, C. R. Kanekarand, and K. F. Mok, *J. Am. Chem. Soc.* 480 (1969).
- [103] N. V. Gerbeleu, A. S. Batsanov, G. A. Timko, Y. T. Struchkov, K. M. Indrichan, and G. A. Popovich, *Dokl. Akad. Nauk SSSR* 293, 361 (1987).
- [104] T. Nakomoto, M. Hanaya, M. Katada, K. Endo, S. Kitagawa, and H. Sano, *Inorg. Chem.* 36 (20), 4347 (1997).