

A Mini-Review on Emerging Trend of Co(II)/Ln(III) Complexes as Single-Molecule Magnets



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1 Introduction

The field of SMM which was first pioneered by the discovery of a dodecanuclear $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{CO}_2)_{12}(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}\cdot 2\text{CH}_3\text{COOH}$ [1] (**1**) complex has sparked a worldwide research interest based on their multifarious application in the field of storage device [2], quantum computing [3], spintronic devices [4] and magnetic refrigeration [5], and others. The success (or not) of an SMM depends on two main parameters which are effective energy barrier U_{eff} and blocking temperature T_{B} [6]. The value of T_{B} is governed by the height of the anisotropy barrier which is regulated by ground-state spin S and negative anisotropy D . Later on theoretical studies have shown that large S and strong D cannot be simultaneously observed within one molecule [7]. This led to the blossoming of Ln-based SMM with the pioneering work of double-decker phthalocyanine (Pc) complexes $[\text{LnPc}_2]^-$ ($\text{Ln}^{\text{III}} = \text{Tb}, \text{Dy}$) [8], where Ln ions provide large magnetic anisotropy to the system. Using Ln ions remarkable energy barrier as high as 1837 K [9] and blocking temperature of 80 K [10] are reported. However, one major drawback of these Ln^{III} -based complexes is a decrease in blocking temperature because of quantum tunneling of magnetization (QTM) [11]. The main challenge for the researcher is to overcome QTM which can be reduced by the introduction of exchange interaction in complex, thereby increasing the exchange coupling interaction (J) which enhances the degree of covalency of the metal–ligand bond [12]. For that reason, 3d-4f heterometallic

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architecture induces strong interaction between metal ions where magnetic exchange between the metal center occurs via super exchange mechanism through diamagnetic ligand which reduces the QTM and enhances U_{eff} and T_B . In that respect ligand designing plays an important role. An axial ligand field is required for the ions that possess largest angular momentum belongs from oblate states like Tb^{III} , Dy^{III} , and on the other hand, equatorial field is required for prolate states like Er^{III} and Yb^{III} [13]. So, to overcome the QTM several methods are applied; one of them includes synthesizes of heterometallic complexes. The first heterometallic metal complex SMM synthesized was a Cu_2Tb_2 complex whose structure is shown in Fig. 1 [14]. Later on, a variety of 3d metal ions were used owing to their individual characteristics. For example, Murray and group have reported a heterometallic $\text{Cr}_2^{\text{III}}\text{Ln}_2^{\text{III}}$ complex where strong magnetic interaction between Cr^{III} and Ln^{III} metal ions, QTM was significantly quenched, thereby enhancing the blocking temperature T_B [15]. Another aspect of heterometallic complexes is that by using several 3d metal ions one can elevate the crystal field present in lanthanide ions and thus can increase the energy barrier [16]. One of the main categories is cobalt lanthanide-based SMM. For Co^{II} ion, the magnetic anisotropy does not depend on first-order orbital angular momentum, however, based on second-order orbital angular momentum [17, 18]. This mixing of ground state to excited state is regulated by the geometry of the system. Further, the D value of the cobalt ion can also be tuned by utilizing certain multidentate ligands to link Co^{II} ions with other Ln^{III} ions. This becomes the main focus of this chapter where recent examples of $\text{Co}(\text{II})/\text{Ln}(\text{III})$ are used to depict the importance of ligand design and coordination geometry on the magnetic properties. The later sections will deal with very recent examples based on their nuclearity.

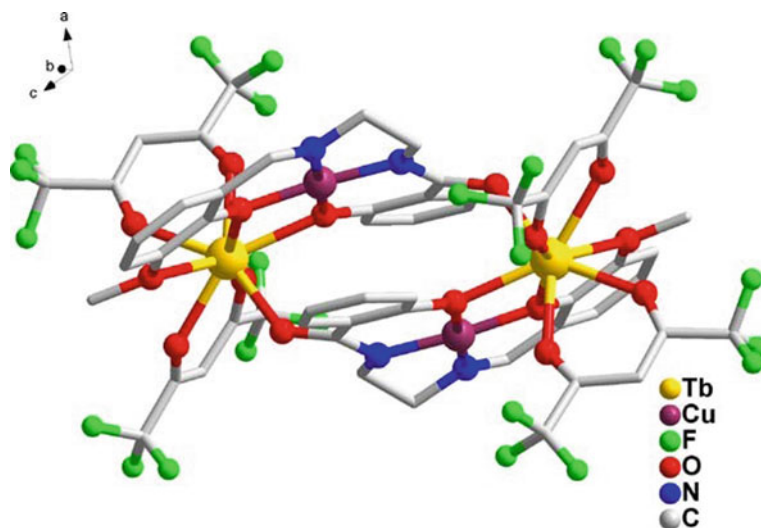


Fig. 1 Ball and stick diagram of Cu_2Tb_2 complex

2 Co/Ln Coordination Clusters with Various Nuclearity

2.1 Dinuclear Complexes

Ray and group have utilized a simple ligand LH = 3-methoxy-N-(2(methylsulfanyl)phenyl)salicylaldimine) to synthesize a new dinuclear Co^{II}/Ln^{III} complexes [Ln^{III}Co^{II}L₂(NO₃)₃].H₂O {Ln^{III} = La(**2**), Gd(**3**), Tb(**4**), Dy(**5**), Ho(**6**)} whose detailed experimental and theoretical properties are studied [19]. The ligand used is chosen due to its coordination pockets which consists of coordination pockets favoring the binding of both Co^{II} and Ln^{III} ions simultaneously. Also, the binding of lanthanide metal ion provides a distortion to the geometry of Co^{II} ion which is further favored due to the presence of -SM e group at axial position which due to its large size creates a large deviation in bond parameters. Thus, this feature makes this Co^{II}-Ln^{III} family the first example of a dinuclear heterometallic complex having a distorted octahedral Co^{II} metal that exists in between *fac* and *mer* geometric isomers. These complexes are formed by the action of the ligand with LiOH in acetonitrile; to which CoCl₂.6H₂O was added and stirred for three hours which was filtered to give red colored crystals. The neutral complex comprises of two ligand L⁻ bridging metal centers with two phenoxido bridges. Magnetic analysis reveals ferromagnetic interaction in compounds **3-6** between the Co-Ln ions. Theoretical calculations show **2** and **3** as weak SIM (single ion magnet) and SMM, respectively, solely based on anisotropy of Co^{II} ion. Kou and group [20] have synthesized a Co^{II}/Ln^{III} [Co(H_{0.5}L)Dy(DBM)₂(H₂O)](ClO₄)_{0.5}.3H₂O (**7**) chiral complex where the enantiomer of **7** is obtained in the same pot. The complex **7** consists of a cationic structure [Co(H_{0.5}L)Dy(DBM)₂(H₂O)]^{0.5+} with one ligand, Co^{II} ion, Dy^{III} ion along with two DBM⁻ molecules. The experimental $\chi_{\text{M}}T$ value of **7** is similar to that of the theoretical value for one Dy^{III} ion. Ac magnetic susceptibility measurement under 2000 Oe shows an energy barrier of 53.1 K and $\tau_0 = 2.0 \times 10^{-8}$ s. Further, the experimental energy barrier matches well with the theoretical value and depicts that QTM between two ground states was suppressed in fitting temperature range and the relaxation mechanism in **7** is governed by Orbach and Raman process (Fig. 2). Chandrasekhar and group [21] have used a ferrocene-based ligand to synthesize four complexes [Co(μ -L)(μ -CCl₃COO)Y(NO₃)₂].2CHCl₃.CH₃CN.2H₂O (**8**), [Co(μ -L)(μ -CH₃COO)Y(NO₃)₂].CH₃CN (**9**), [Co(μ -L)(μ -PhCOO)Y(NO₃)₂].3CH₃CN.2H₂O (**10**), and [Co(μ -L)(μ -tBuCOO)Y(NO₃)₂].CHCl₃.2H₂O (**11**); all have them having Co^{II}Y^{III} core. The complex was synthesized by the addition of ligand LH₂ in CHCl₃/MeOH to Co(ClO₄)₂ and Y(NO₃)₃ along with base triethylamine. For complex **9**, Co(OAc)₂ is used instead of Co(ClO₄)₂ and the solution is refluxed for three hours. The experimental $\chi_{\text{M}}T$ value of all complexes is comparable with that of theoretical ones. Ac magnetic susceptibility measurement for all complexes was studied at 1200 Oe. The data from Arrhenius plot reveals energy barrier and τ_0 of 8.4(6) K and $3.2(4) \times 10^{-6}$ s for **8**; U_{eff} of 11.0(4) K and $\tau_0 = 2.5(2) \times 10^{-6}$ s for **9**; U_{eff} of

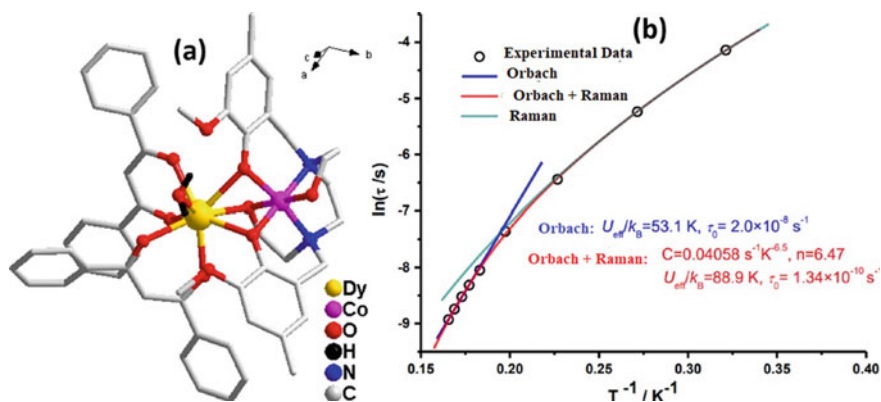


Fig. 2 a Ball and stick diagram of **7**. b Temperature dependence of relaxation time for **7**

13.7(8) K and $\tau_0 = 2.6(4) \times 10^{-6}$ s for **10** and U_{eff} of 18.7(6) K and $\tau_0 = 7.4(9) \times 10^{-7}$ s for **11**. The Debye model reveals a single relaxation process for **8–10**.

2.2 Trinuclear Complexes

The first $\text{Co}^{\text{II}}/\text{Ln}^{\text{III}}$ SMM $[\text{L}_2\text{Co}_2\text{Gd}][\text{NO}_3] \cdot 2\text{CHCl}_3$ (**12**) was synthesized by Chandrasekhar and group using a phosphorus-based tris hydrazone ligand where all metal ions Co–Gd–Co are arranged in a linear manner [22]. The structure involves two ligands holding together three metal ions along with one mole of nitrate ion. Ac magnetic susceptibility measurement shows an energy barrier of 27.2 K and $\tau_0 = 1.7 \times 10^{-7}$ s confirming the SMM behavior of the complex (Fig. 3).

Nguyen and group have synthesized a stable trinuclear complex $[\text{LnCo}_2(\text{L})_2(\mu_{1,3}\text{OOCCH}_3)_2\text{X}]$ where $\text{Ln}^{\text{III}} = \text{La}$ (**13**), Ce(**14**), Nd(**15**), Sm(**16**),

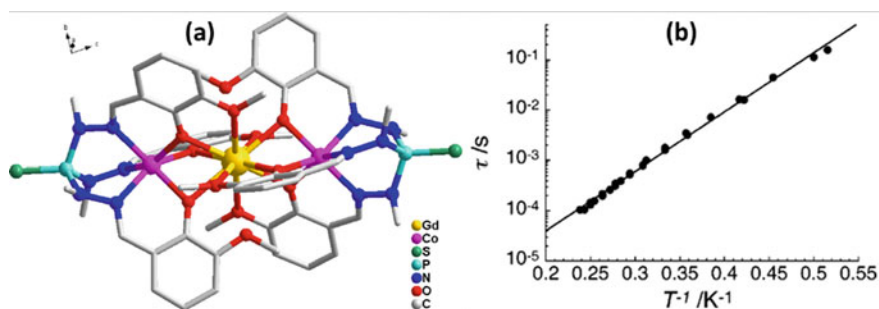


Fig. 3 a Ball and stick diagram of **12**. b τ versus T^{-1} plot at $H_{\text{dc}} = 0$

Gd(**17**), Dy(**18**), Er(**19**), and Yb(**20**) and $X = \kappa_2\text{-CH}_3\text{COO}^-$ or Cl^- using one-pot reaction of 2,6-dipicolinoylbis(N, Ndiethylthiourea) with cobalt acetate and lanthanide chloride in methanol along with base trimethylamine [23]. The structure consists of two ligands with two moles of cobalt ion and one lanthanide ion along with two acetate ions acting as bridging mode between Co^{II} and Ln^{III} ion. Further, coordination around Ln^{III} ion is provided by acetate ion for **13**, **17**, while rest of complex is coordinated by chloride ion. Magnetic studies reveal weak antiferromagnetic interaction with $J_{\text{Co-Co}} = -0.49 \text{ cm}^{-1}$. Further, CoDyCo analogue shows antiferromagnetic interaction while rest of the CoLnCo analogues shows ferromagnetic interaction. Papatrifiantafyllopoulou and group have employed di-2-pyridyl ketone, $(\text{py})_2\text{CO}$ to prepare four $\text{Co}^{\text{II}}/\text{Ln}^{\text{III}}$ clusters $[\text{Co}_2\text{Ln}\{(\text{py})_2\text{C}(\text{OEt})(\text{O})\}_4(\text{NO}_3)(\text{H}_2\text{O})]_2[\text{M}(\text{NO}_3)_5](\text{ClO}_4)_2$ ($\text{Ln}^{\text{III}} = \text{Gd}$ (**21**), Dy (**22**), Tb (**23**), Y (**24**)) [24]. The cationic part of the complex consists of two Co^{II} ion, one Gd^{III} ion along with four ligands $(\text{py})_2\text{C}(\text{OEt})(\text{O})^-$. Weak ferromagnetic interaction of $J_{\text{Co-Co}} = +1.3$ and $+0.40 \text{ cm}^{-1}$ is observed for **21** and **24**, respectively. Ac magnetic susceptibility measurement reveals a weak out-of-phase signal which might depict complex **22** being a weak SMM.

2.3 Tetranuclear Complexes

Ray and group have reported two families of $\text{Co}^{\text{II/III}}\text{-Ln}^{\text{III}}$ [$\text{Ln}^{\text{III}}_2\text{Co}^{\text{III}}_2\text{L}_2(\text{N-BuDEA})_2(\text{O}_2\text{CCMe}_3)_4(\text{H}_2\text{O})_2$] ($\text{Ln} = \text{Gd}$ (**25**), Tb (**26**), Dy (**27**)) and pentanuclear $\text{Ln}^{\text{III}}_2\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2\text{L}_2(\text{N-BuDEA})_2(\text{O}_2\text{CCMe}_3)_6(\text{MeOH})_2$ ($\text{Ln} = \text{Dy}$ (**28**), Ho (**29**)) using ligands H_2L (o-vanillin oxime) and N-BuDEAH₂ (N-butyldiethanolamine) (Fig. 4a) [25]. The tetranuclear series is formed by the reaction of $\text{Co}_2(\mu\text{-OH}_2)(\text{O}_2\text{CCMe}_3)_4(\text{HO}_2\text{CCMe}_3)_4$ and $\text{Ln}(\text{NO}_3)_3$ with N-BuDEAH₂ followed by addition of ligand and base in ratio 0.5:1:1:1:4 in MeOH/DCM. The tetranuclear complex consists of $\{\text{Ln}^{\text{III}}_2\text{Co}^{\text{III}}_2\}$ core with two ligands and two N-BuDEA²⁻

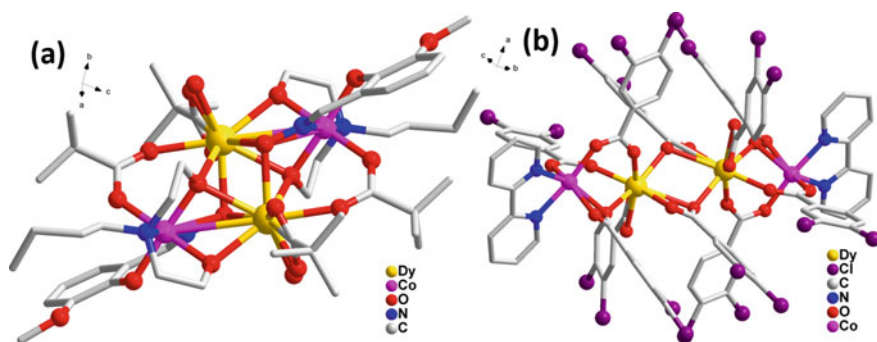


Fig. 4 Ball and stick diagram of **a 27** and **b 35** where H atoms apart from in water molecules are omitted

anions. With the J value of -0.09 cm^{-1} , the presence of weak antiferromagnetic exchange interaction between Gd^{III} centers is reported. No maxima peaks are reported for **27** in Ac magnetic susceptibility measurement. Dong and group have synthesized a linear $[\text{Ln}_2\text{Co}_2(3,4\text{-DCB})_{10}(2,2'\text{-bpy})_2]$ ($\text{Ln}^{\text{III}} = \text{Nd}$ (**30**), Sm (**31**), Eu (**32**), Gd (**33**), Tb (**34**), Dy (**35**), and Er (**36**)) complex using 3,4-dichlorobenzoic acid (3,4-HDCB), 2,2'-bipyridine (2,2'-bpy) as ligands (Fig. 4b) [26]. The structural analysis reveals complexes having linear arrangement $\text{Co}^{\text{II}}\text{-Ln}^{\text{III}}\text{-Ln}^{\text{III}}\text{-Co}^{\text{II}}$ formed with two Co^{II} and Dy^{III} ions each, two 2,2'-bpy co-ligands and ten 3,4-DCB anions. Ac magnetic susceptibility measurements at zero dc field of **35** reveal frequency-dependent out-of-phase signal; however, no maxima peak is observed. Li and group have reported tetranuclear complexes $[\text{Ln}_2\text{Co}_2(\text{hfac})_{10}(\text{NITPhPybis})_2]$ [$\text{Ln}^{\text{III}} = \text{Gd}$ (**37**), Tb (**38**), Dy (**39**), and Ho (**40**); formed using nitronyl nitroxide biradical ligands having pyridine groups which grasps Co^{II} and Ln^{III} ions together [27]. A centrosymmetric cyclic structure is formed using Co^{II} and Ln^{III} depicting a rare octaspin motif. Ac magnetic susceptibility measurement reveals **38** and **39** displaying slow relaxation of the magnetization behavior.

2.4 Higher Nuclearity Complexes

In this section, complexes having nuclearity higher than four are described. Only recent representative examples are discussed.

The pentanuclear complexes **28** and **29** described in the previous section consist of $\{\text{Ln}^{\text{III}}_2 \text{Co}^{\text{III}}_2 \text{Co}^{\text{II}}\}$ core with two L^{2-} and two N-BuDEA^{2-} anions [25]. The Co-Ln exchange interaction is ferromagnetic for **28** while it is antiferromagnetic for **29**. Magnetic analysis depicts out-of-phase susceptibility in **28**. Zhao and group have synthesized a hexanuclear $\text{Co}^{\text{III}}_4\text{Ln}^{\text{III}}_2$ clusters $[\text{Co}_4\text{Ln}_2(\mu_3\text{-O})_2(\mu\text{-N}_3)_2(\text{OH})_2(\text{H}_2\text{O})_2(\text{HL})_4]\cdot(\text{CH}_3\text{CO}_2)_2\cdot 20\text{H}_2\text{O}$ [$\text{Ln}^{\text{III}} = \text{Dy}$ (**41**), Gd (**42**), Tb (**43**), Eu (**44**) and Ho (**45**)] using 2-[Bis(pyridin-2-ylmethyl)amino]-2-(hydroxymethyl)propane-1,3-diol ligand [28]. The structural arrangement consists of four Co^{III} ions, two Dy^{III} ions, four HL^{2-} , two N^{3-} ligands, two $\mu_3\text{-O}^{2-}$, two water molecules and two acetate ions forming a lucanidae like arrangement. Ac magnetic susceptibility measurements reveal an energy barrier of 73.51 K and $\tau_0 = 1.68 \times 10^{-8}$ s. Liang and group have recently explored the effect of solvent by synthesizing two decanuclear clusters $[\text{Dy}_2\text{Co}_8(\mu_3\text{OCH}_3)_2(\text{L})_4(\text{HL})_2(\text{OAc})_2(\text{NO}_3)_2(\text{CH}_3\text{CN})_2]\cdot\text{CH}_3\text{CN}\cdot\text{H}_2\text{O}$ (**46**) and $[\text{Dy}_4\text{Co}_6(\text{L})_4(\text{HL})_2(\text{OAc})_6(\text{OCH}_2\text{CH}_2\text{OH})_2(\text{HOCH}_2\text{CH}_2\text{OH})(\text{H}_2\text{O})]\cdot 9\text{CH}_3\text{CN}$ (**47**) [29]. The only difference in the reaction process was the change of reaction solvent from methanol and acetonitrile in **46** to acetonitrile and ethylene glycol in **47**. The structure of **46** is formed by two Dy^{III} , eight Co^{II} ions, four L^{3-} , two HL^{2-} , two acetate ions, two $(\text{CH}_3\text{O})^-$ and CH_3CN ligand. While for **47**, it contains four Dy^{III} , six Co^{II} ions, three L^{3-} , three HL^{2-} , six acetate ions, three coordinated $(\text{HOCH}_2\text{CH}_2\text{O})^-$ ion along with one coordinated water molecule. Ac magnetic susceptibility measurements reveal an energy barrier of 14.89 K and $\tau_0 = 1.68 \times$

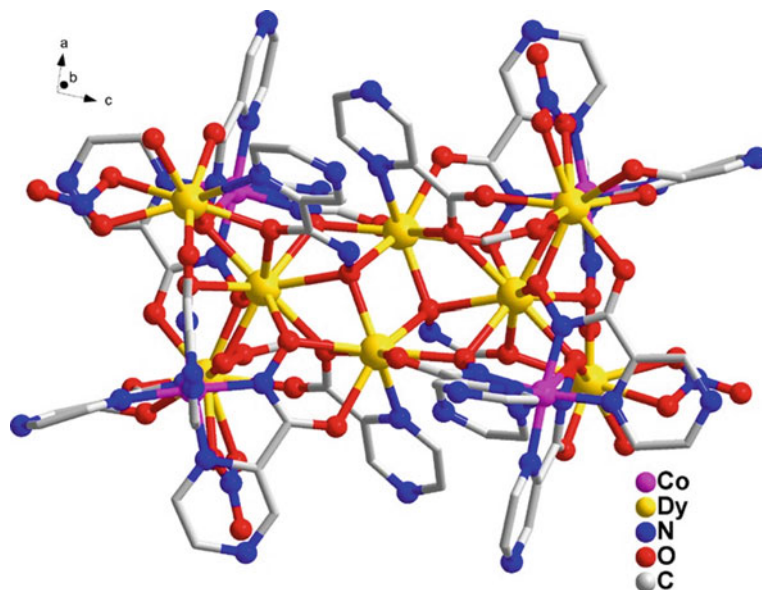


Fig. 5 Ball and stick diagram of **48**

10^{-7} s for **46** and energy barrier of 5.49 K and $\tau_0 = 2.88 \times 10^{-5}$ s for **47** at zero dc field. Dou and group have synthesized a series of butterfly shaped metallacrowns (MCs) $[\text{Dy}(\text{pyzic})\{\text{Dy}_3\text{Co}_2(\text{pyzha})_6(*\text{pyzha})(\text{NO}_3)_2(\text{H}_2\text{O})(\text{MeOH})_2\}]_2$ ($\text{Ln}^{\text{III}} = \text{Dy}$ (**48**), Ho (**49**) and Tm (**50**)) using pyrazinehydroxamic acid and pyrazinic acid ligands (Fig. 5) [30]. At zero dc field, U_{eff} is 1.46 K and $\tau_0 = 2.4 \times 10^{-5}$ s for **48** (Table 1).

3 Summary

The heterometallic complexes of Co/Ln represent an interesting class of molecular magnets with fascinating structures and magnetic properties. Co^{II} provides a large spin-orbit coupling which when combined with highly anisotropic Ln^{III} ion can lead to the formation of SMMs with better properties. The role of ligand and the coordination geometry surrounding the metal ions plays a vital part in modulating the magnetic properties. While considerable progress is made in this field, proper designing of complexes can certainly lead to the development of SMM with superior properties. Apart from this, a chemist also requires a strong theoretical understanding of the complexes which seems to be lacking. Backed by this knowledge, synthetic chemists can strategically plan designs to enhance the SMM behavior of Co/Ln complexes.

Table 1 Magnetic parameter of $\text{Co}^{\text{II}}/\text{Ln}^{\text{III}}$ complexes

Molecular formula	U_{eff}	τ_0	References
$[\text{Co}_2\text{Dy}_2(\text{L})_2(\text{CH}_3\text{COO})_4(\text{OH})_2(\text{H}_2\text{O})_2] \cdot (\text{ClO}_4)_2 \cdot \text{H}_2\text{L} = \text{N}1, \text{N}3\text{-bis}(3\text{-methoxysalicylidene})\text{diethylenetriamine}$	33.8 K	$3.73 \times 10^{-6} \text{ s}$	[31]
$[\text{Co}_2\text{Dy}(\text{HL})_4][\text{NO}_3 \cdot 2\text{CH}_3\text{CN}]$ $\text{H}_3\text{L} = 3\text{-}[(2\text{-Hydroxy-3-methoxy-benzylidene})\text{-amino}]\text{-propane-1,2-diol}$	40 K	$1.8 \times 10^{-6} \text{ s}$	[32]
$[\text{CoDy}(\text{mepao})_3(\text{NO}_3)_3]$ mepaoH = methyl 2-pyridyl ketone oxime	16 K	$2.5 \times 10^{-8} \text{ s}$	[33]
$[\text{CoDy}(\text{HL})(\text{OAc})_3(\text{H}_2\text{O})_3] \cdot (\text{OAc})(\text{H}_2\text{O})_3$ 2-hydroxy-1,3-diaminopropane + o-vanillin	113 K	$7.0 \times 10^{-9} \text{ s}$	[34]
$[\text{Ln}_4\text{Co}_2(\mu_3\text{-OH})_2(\text{NO}_3)_4(\text{CH}_3\text{COO})_4\text{L}_4(\text{DMF})_2] \cdot 2\text{C}_2\text{H}_5\text{OH}$ $\text{H}_2\text{L} = 2\text{-}((2\text{-hydroxymethyl})\text{phenylimino})\text{methyl phenol} (\text{H}_2\text{L})$	41.9 K	$1.21 \times 10^{-7} \text{ s}$	[35]
$[\text{Co}_4\text{Dy}_3\text{L}_4(\mu_4\text{-O})_2(\mu_1,3\text{-OAc})_4(\text{H}_2\text{O})_2(\text{NO}_3)_2] \cdot \text{NO}_3 \cdot 3\text{CH}_3\text{OH} \cdot 1.5\text{H}_2\text{O} \cdot \text{H}_2\text{L} = 3\text{-methoxysalicylaldehyde and 2-amino-2methyl-1-propanol}$	73.954 K 34.963 K	$9.40 \times 10^{-7} \text{ s}$ $6.91 \times 10^{-7} \text{ s}$	[36]
$[\text{Co}_4\text{Ln}(\text{L})_4(\text{OAc})_2(\text{S}_4)](\text{NO}_3)(\text{H}_2\text{O})$ $\text{HL}_2 = 6\text{-formyl-2-(hydroxymethyl)-4methylphenol}$	Slow magnetic relaxation	–	[37]
$[\text{Co}_2\text{Dy}_2(\text{L})_4(\text{NO}_3)_2(\text{THF})_2] \cdot 4\text{THF}$ $\text{L} = \text{o-vanillin and 2-aminophenol}$	15.827 K 118.12 K	$7.7 \times 10^{-4} \text{ s}$ $6.2 \times 10^{-7} \text{ s}$	[38]

References

1. Sessoli R, Gatteschi D, Caneschi A, Novak MA (1993) Magnetic bistability in a metal-ion cluster. *Nature* 365:141–143
2. Zhang P, Guo Y-N, Tang J (2013) Recent advances in dysprosium-based single molecule magnets: structural overview and synthetic strategies. *Coord Chem Rev* 257:1728–1763
3. Bogani L, Wernsdorfer W (2010) Molecular spintronics using single-molecule magnets. *Nat Mater* 7:194–201
4. Lehmann J, Gaita-Arino A, Coronado E, Loss DJ (2009) Quantum computing with molecular spin systems. *J Mater Chem* 19:1672–1677
5. Zheng Y-Z, Evangelisti M, Winpenny REP (2011) Co–Gd phosphonate complexes as magnetic refrigerants. *Chem Sci* 2:99–102
6. Harriman KL, Brosmer JL, Ungur L, Diaconescu PL, Murugesu M (2017) Pursuit of record-breaking energy barriers: a study of magnetic axiality in diamide ligated Dy^{III} single molecule magnets. *J Am Chem Soc* 139:1420–1423
7. Ruiz E, Cirera J, Cano J, Alvarez S, Loose C, Kortus J (2008) Can large magnetic anisotropy and high spin really coexist? *Chem Comm* 1:52–54
8. Ishikawa N, Sugita M, Ishikawa T, Koshihara S-Y, Kaizu Y (2003) Lanthanide doubledecker complexes functioning as magnets at the single-molecular level. *J Am Chem Soc* 125:8694–8695
9. Guo FS, Day BM, Chen YC, Tong ML, Mansikkamäki A, Layfield R (2017) A dysprosium metallocene single-molecule magnet functioning at the axial limit. *Angew Chem Int Ed* 129:11603–11607
10. Guo F-S, Day BM, Chen Y-C, Tong M-L, Mansikkamäki A, Layfield R (2018) Magnetic hysteresis up to 80 kelvin in a dysprosium metallocene single-molecule magnet. *Science* 362:1400–1403
11. Liu J-L, Chen Y-C, Tong M-L (2018) Symmetry strategies for high performance lanthanide-based single-molecule magnets. *Chem Soc Rev* 47:2431–2453
12. Ding YS, Yu KX, Reta D, Ortu F, Winpenny REP, Zheng YZ, Chilton NF (2018) Field- and temperature-dependent quantum tunneling of the magnetization in a large barrier single-molecule magnet. *Nat Commun* 9:3134
13. Lin PH, Yang BY, Tsai MH, Chen PC, Huang KF, Lin HH, Lai CH (2019) Manipulating exchange bias by spin-orbit torque. *Nat Mater* 18:335–341
14. Osa S, Kido T, Matsumoto N, Re N, Pochaba A, Mrozinski J (2004) A tetranuclear 3d–4f single-molecule magnet: [Cu^{II}LTb^{III}(hfac)₂]₂. *J Am Chem Soc* 126:420–421
15. Langley SK, Wielechowski DP, Vieru V, Chilton NF, Moubaraki B, Abrahams BF, Chibotaru LF, Murray KS (2013) A Cr^{III}₂Dy^{III}₂ single-molecule magnet: enhancing the blocking temperature through 3d magnetic exchange. *Angew Chem Int Ed* 52:12014–12019
16. Shao D, Wang XY (2020) Development of single-molecule magnets. *Chin J Chem* 38:1005–1018
17. Tripathi S, Dey A, Shanmugam M, Narayanan RS, Chandrasekhar V (2018) Cobalt (II) complexes as single-ion magnets. In: *Organometallic magnets*. Springer, pp 35–75
18. Dey A, Tripathi S, Shanmugam M, Narayanan RS, Chandrasekhar V (2018) Cobalt (II)/(III)–Lanthanide (III) complexes as molecular magnets. In: *Organometallic magnets*. Springer, pp 77–100
19. Basak D, Leusen JV, Gupta T, Kögerler P, Bertolasi V, Ray D (2020) Unusually distorted pseudo-octahedral coordination environment around Co^{II} from thioether Schiff base ligands in dinuclear [CoLn] (Ln = La, Gd, Tb, Dy, Ho) complexes: synthesis, structure, and understanding of magnetic behavior. *Inorg Chem* 59:2387–2405
20. Liu M-J, Yuan J, Wang B-L, Wu S-T, Zhang Y-Q, Liu C-M, Kou H-Z (2018) Spontaneous resolution of chiral Co(II)Dy(III) single-molecule magnet based on an achiral flexible ligand. *Cryst Growth Des* 18:7611–7617

21. Acharya J, Swain A, Chakraborty A, Kumar V, Kumar P, Gonzalez JF, Cador O, Pointillart F, Rajaraman G, Chandrasekhar V (2019) Slow magnetic relaxation in dinuclear $\text{Co}^{\text{II}}\text{Y}^{\text{III}}$ complexes. *InorgChem* 58:10725–10735
22. Chandrasekhar V, Pandian BM, Azhakar R, Vittal JJ, Clérac R (2007) Linear trinuclear mixed-metal $\text{Co}^{\text{II}}\text{—Gd}^{\text{III}}\text{—Co}^{\text{II}}$ single-molecule magnet: $[\text{L}_2\text{Co}_2\text{Gd}][\text{NO}_3]_2\cdot 2\text{CHCl}_3$ ($\text{LH}_3 = (\text{S})\text{P}[\text{N}(\text{Me})\text{NCH—C}_6\text{H}_3\text{—2-OH-3-OMe}]_3$). *Inorg Chem* 46:5140–5142
23. Jesudas JJ, Pham CT, Hagenbach A, Abram U, Nguyen H (2019) Trinuclear $\text{Co}^{\text{II}}\text{Ln}^{\text{III}}\text{Co}^{\text{II}}$ complexes ($\text{Ln} = \text{La}, \text{Ce}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Dy}, \text{Er}, \text{and Yb}$) with 2,6-dipicolinoylbis (N,N-diethylthiourea): synthesis, structures, and magnetism. *Inorg Chem* 59:386–395
24. Efthymiou CG, Ní Fhuaráin Á, Mayans J, Tasiopoulos A, Perlepes SP, Papatriantafyllopoulou C (2019) A novel family of triangular $\text{Co}^{\text{II}}_2\text{Ln}^{\text{III}}$ and $\text{Co}^{\text{II}}_2\text{Y}^{\text{III}}$ clusters by the employment of di-2-pyridyl ketone. *Magnetochemistry* 5:35
25. Basak D, Smythe L, Herchel R, Murrie M, Nemeč I, Ray D (2021) From tetranuclear to pentanuclear $[\text{Co—Ln}]$ ($\text{Ln} = \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}$) complexes across the lanthanide series: effect of varying sequence of ligand addition. *Dalton Trans* 50:11861–11877
26. Zhang J-W, Liu W-H, Wang C-R, Liu B-Q, Dong Y-P (2020) A series of linear $\text{Co}^{\text{II}}_2\text{Ln}^{\text{III}}_2$ clusters derived from 3,4-dichlorobenzoate and 2,2'-bipyridine: syntheses, structures, and properties. *Inorganica Chim Acta* 502:119343
27. Li H, Sun J, Yang M, Sun Z, Tang J, Ma Y, Li L (2018) Functionalized nitronyl nitroxide biradicals for the construction of 3d–4f heterometallic compounds. *Inorg Chem* 57:9757–9765
28. Li Q, Peng Y, Qian J, Yan T, Du L, Zhao Q (2019) A family of planar hexanuclear $\text{Co}^{\text{III}}_4\text{Ln}^{\text{III}}_2$ clusters with lucanidae-like arrangement and single-molecule magnet behavior. *Dalton Trans* 48:12880–12887
29. Yu S, Wang H-L, Chen Z, Zou H-H, Hu H, Zhu Z-H, Liu D, Liang Y, Liang F-P (2021) Two decanuclear $\text{Dy}^{\text{III}}_x\text{Co}^{\text{II}}_{10-x}$ ($x = 2, 4$) nanoclusters: structure assembly mechanism, and magnetic properties. *Inorg Chem* 60:4904–4914
30. Zhang H-G, Du Y-C, Yang H, Zhuang M-Y, Li D-C, Dou J-M (2019) A new family of Co_4Ln_8 metallacrowns with a butterfly-shaped structure. *Inorg Chem Frontiers* 6(7):1904–1908
31. Zhao L, Wu J, Xue S, Tang J (2012) A linear 3d–4f tetranuclear $\text{Co}^{\text{III}}_2\text{Dy}^{\text{III}}_2$ single-molecule magnet: synthesis, structure, and magnetic properties. *Chem Asian J* 7:2419–2423
32. Modak R, Sikdar Y, Gómez-García CJ, Benmansour S, Chatterjee S, Goswami S (2021) Slow magnetic relaxation in a Co_2Dy trimer and a Co_2Dy_2 tetramer. *Chem Asian J* 16:666–677
33. Polyzoou C, Koumoussi ES, Lada ZG, Raptopoulou C, Psycharis V, Rouzières M, Tsipis AC, Mathoniere C, Clerac R, Perlepes SP (2017) “Switching on” the single-molecule magnet properties within a series of dinuclear cobalt (III)–dysprosium (III) 2-pyridyloximate complexes. *Dalton Trans* 46:14812–14125
34. Dolai M, Ali M, Titiš J, Boča R (2015) Cu (II)–Dy (III) and Co (III)–Dy (III) based single-molecule magnets with multiple slow magnetic relaxation processes in the Cu (II)–Dy (III) complex. *Dalton Trans* 44:13242–13249
35. Zhang H, Liu R, Zhang J, Li Y, Liu W (2016) Chair-like $[\text{Ln}^{\text{III}}_4\text{Co}^{\text{III}}_2]$ ($\text{Ln} = \text{Dy}, \text{Eu}, \text{Gd}, \text{Tb}$) clusters including a $[\text{Dy}^{\text{III}}_4\text{Co}^{\text{III}}_2]$ single-molecule magnet. *CrystEngComm* 18:8246–8252
36. Roy S, Hari N, Mohanta S (2019) Synthesis, crystal structures, magnetic properties, and fluorescence of two heptanuclear $\text{Co}^{\text{III}}_4\text{Ln}^{\text{III}}_3$ compounds ($\text{Ln} = \text{Gd}^{\text{III}}, \text{Dy}^{\text{III}}$): multiple relaxation dynamics in the Dy^{III} analogue. *Eur J Inorg Chem* 2019:3411–3423
37. Chandrasekhar V, Das S, Dey A, Hossain S, Lloret F, Pardo E (2013) Synthesis, structure, and magnetic properties of a family of heterometallic pentanuclear $[\text{Co}_4\text{Ln}]$ ($\text{Ln} = \text{Gd}^{\text{III}}, \text{Dy}^{\text{III}}, \text{Tb}^{\text{III}}, \text{and Ho}^{\text{III}}$) assemblies. *Eur J Inorg Chem* 2013:4506–4514
38. Mondal KC, Sundt A, Lan Y, Kostakis GE, Waldmann O, Ungur L, Chibotaru LF, Anson CE, Powell AK (2012) Coexistence of distinct single-ion and exchange-based mechanisms for blocking of magnetization in a $\text{Co}^{\text{II}}_2\text{Dy}^{\text{III}}_2$ single-molecule magnet. *Angew Chem Int Ed* 51:7550–7554