

Synthesis, Crystal Structures, Magnetic and Fluorescence Properties of Two Heptanuclear Co^{III}₄Ln^{III}₃ Compounds (Ln= Gd^{III}, Dy^{III}): Multiple Relaxation Dynamics in Dy^{III} Analogue

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This report describes the synthesis, crystal structures, magnetic and spectroscopic properties of two heptanuclear $Co_{4}^{III}Ln_{3}^{III}$ systems of composition $[Co_{4}^{III}Gd_{3}^{III}L_{4}(\mu_{4}-O)_{2}(\mu_{4}-O)$ $OMe_{2}(\mu_{1,3}-OAc)_{4}(H_{2}O)_{2}(NO_{3})_{2}] \cdot NO_{3} \cdot 2CH_{3}OH \cdot 2H_{2}O$ (1) and $[Co^{III}_{4}Dy^{III}_{3}L_{4}(\mu_{4}-O)_{2$ $OMe_{2}(\mu_{1,3}-OAc_{4}(H_{2}O_{2}(NO_{3})_{2}]\cdot NO_{3}\cdot 3CH_{3}OH\cdot 1.5H_{2}O$ (2), where H₂L is [1+1] condensation product of 3-methoxysalicylaldehyde and 2-amino-2-methyl-1-propanol. The heptametallic cores in 1 and 2 may be taken as consisted of two symmetry related trinuclear Co^{III}Ln^{III}Co^{III} moieties and a central lanthanide center in such a way that each of the three metal ions of each of the two trinuclear moieties are bridged with the central lanthanide through bridging oxo/alkoxo/acetate ligands. DC magnetic measurements of 1 and 2 reveal very weak Gd^{III} ... Gd^{III} antiferromagnetic interaction ($J = -0.01 \text{ cm}^{-1}$) in 1 and significant anisotropy in 2. Variable-temperature and variable-frequency ac susceptibility measurements of 2 reveal that it is a zero-field SMM with multiple relaxation dynamics. Above 5 K, two well resolved relaxation channels are observed; $U_{\rm eff}$ and τ_0 are 51.4 cm⁻¹ and 9.40 × 10⁻⁷ s for the slow relaxation channel and 24.3 cm⁻¹ and 6.91×10^{-7} s for the fast relaxation channel. The characteristic Dy^{III} based transitions, ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$, ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{6}H_{11/2}$, can be well assigned in the fluorescence spectrum of 2 at solid state. All in all, compound 2 is a bifunctional molecular material.

Introduction

It was observed in the early 1990s that a dodecanuclear $Mn^{III}_8Mn^{IV}_4$ cluster (Mn_{12}), the first reported^[1] single molecule magnet (SMM), exhibits slow relaxation of magnetization after the removal of the applied magnetic field. Magnetic bistability and sufficient energy barrier (U_{eff}) for magnetization reversal in this molecule take place due to overall uniaxial anisotropy (negative *D* value), which, in turn, arises because of inherent single-ion zero-field splitting of Mn^{III} . In contrast to the bulk magnets where magnetism is a bulk phenomenon, the magnetic memory of SMMs originate solely from the molecule itself, and, therefore such magnetic systems have potential applications in advanced technological areas such as molecular spintronics,^[2] ultrahigh density magnetic information storage,^[3] quantum computing,^[4] magneto-chiral dichroism^[5] and magneto-electric effects,^[6] etc. Notably, blocking temperature (T_B) below which the magnetic hysteresis takes place and U_{eff} are the

two parameters to govern the efficiency of an SMM; the larger the values of these two parameters the better is the SMM.

As the anisotropy is the key factor for magnetization reversal, lanthanides are much more promising^[7–9] than 3d metal ions for getting better SMMs because most of the lanthanides have large unquenched orbital angular momentum, which gives rise to large anisotropy. However, although lanthanide containing alloys (e. g., SmCo₅ and Nd₂Fe₁₄B) are known^[7b,c,10] since long ago to produce strong bulk magnets, magnetism of lanthanides in molecular level was invented only before 15 years when, in 2003, Ishikawa and coworkers reported^[11] slow magnetic relaxation of a mononuclear Tb^{III} compound, tetrabutylammonium bis(phthalocyanine)terbiumate(III). The U_{eff} of this system is 230 cm⁻¹,^[11] significantly larger than any SMM of non-lanthanide metal ions reported so far.^[12–14] Since then, main focus of molecule based magnetic materials was shifted to lanthanide containing systems and, in the last fifteen years, numerous mono/di/oligonuclear SMMs having only 4f metal ions^[7–9, 15–20] or both 3d and 4f metal ions^[21–26] as the paramagnetic centers, have been reported.

Apparently, a diamagnetic metal ion should have no role in the SMM behavior of a heteronuclear system containing a lanthanide and a diamagnetic metal ion, such as Zn^{II} , Mg^{II} , Ba^{II} , K^{I} , Co^{III} , etc.^[27c,f] However, interestingly, it has been observed and theoretically explained that M–Ln^{III} compounds (M = a diamagnetic metal ion), particularly M–Dy^{III} compounds are better SMMs than the analogous 3d-4f or 4f compounds.^[27] Therefore, combination of an anisotropic lanthanide and a diamagnetic metal ion has been proposed as an approach to get more efficient SMMs. Therefore, isolation and studies of Co^{III}Dy^{III} systems deserve attention, which is the major focus of this investigation.

Luminescence of lanthanides is generally characterized with narrow line-like emissions, long excited-state lifetimes and high quantum yields and some of Ln(III) ions exhibit characteristic emission from visible to near-IR region.^[28] As f-f transitions are Laporte-forbidden, Ln(III) ions need to be sensitized indirectly via the intervention of an organic ligand that efficiently transfers the energy to the Ln(III) ion, the so called "antenna effect".^[29] Luminescent lanthanide complexes are promising candidates for their potential application in biological systems, optoelectronic devices and as biological sensors.^[28a,30] Dy^{III} based luminescent complexes deserve special attention as they can behave as a SIM/SMM too due to the intrinsically anisotropic nature of Dy^{III} center. Hence, combination of dual properties, magnetic and optical on a single Dy^{III} based entity leads to the development of multifunctional molecular material and this has become a burgeoning interest of researchers in very recent times. Moreover, there are few numbers of luminescent magnets (i.e;

combining both magnetic and luminescent properties on a single molecule). Those systems are either purely Dy^{III} based^[31a–e] or Zn^{II}Dy^{III} based^[31f] while Co^{III}Dy^{III} based luminescent magnets are significantly scarce.^[31g,h] Obviously, this area needs much exploration.

The family of Schiff base ligands which are obtained on [1+1] condensation of 3methoxysalicylaldehyde or 3-ethoxysalicylaldehyde and an aminoalcohol or aminophenol, can stabilize 3d-4f systems,^[26c, 32, 33] owing to the presence of two types of compartments (as in Scheme 1); O(alcohol/phenol)N(imine)O(phenol) and O(ether)O(phenol), where the former is more potential to occupy a 3d metal ion while the latter is more potential to bind a lanthanide. Some Co^{III}Ln^{III} compounds derived from such ligands are also known.^[32i,33a] However, condensation product (H₂L; Scheme 1) of 3-methoxysalicylaldehyde and 2-amino-2-methyl-1-propanol was not previously utilized to prepare a Co^{III}Ln^{III} compound. As slight change in the ligand periphery may result in the generation of drastically different type of structure as well, we reacted H₂L with cobalt(II) acetate tetrahydrate and hydrated Ln(NO₃)₃ (Ln = Gd and Dy) and isolated two compounds of composition $[Co^{III}_4Gd^{III}_3L_4(\mu_4-O)_2(\mu OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdotNO_3\cdot 2CH_3OH\cdot 2H_2O$ (1) and $[Co^{III}_4Dy^{III}_3L_4(\mu_4-O)_2(\mu OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdotNO_3\cdot 3CH_3OH\cdot 1.5H_2O$ (2), which represent a new type of structure indeed. Herein, we report the syntheses, crystal structures and dc and ac magnetic properties of 1 and 2.



Scheme 1. Chemical structure of the ligand.

Results and discussion

Syntheses

 H_2L solution. A solution of 2-amino-2-methyl-1-propanol (0.045 g, 0.5 mmol) in 5 mL methanol was added dropwise to a 10 mL methanol solution of 3-methoxy salicylaldehyde (0.075 g, 0.5 mmol) under warming condition. The reaction mixture was refluxed for 2 h.

After cooling, the volume of the solution was diluted to 25 mL in a volumetric flask. The resulting orange coloured 'H₂L solution' was considered to contain 0.5 mmol of the ligand H₂L and was utilized for subsequent reactions without further purification.

Description of the crystal structures of 1 and 2.

Compounds $[Co^{III}_4Gd^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3\cdot 2CH_3OH\cdot 2H_2O$ (1) and $[Co^{III}_4Dy^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3\cdot 3CH_3OH\cdot 1.5H_2O$ (2) crystallize in the same crystal system, monoclinic, and same space group, *C2/c*, with closely similar values of unit cell parameters (Table 1), revealing that these two compounds are isomorphous. One half of each structure is symmetry related to the another half due to the presence of inversion center. The crystal structures of 1 and 2 are shown, respectively, in Figure 1 and Figure 2. The structures show that both compounds are heptanuclear $Co^{III}_4Ln^{III}_3$ systems (Ln = Gd or Dy) having similar core structure; the compositions are different only in terms of solvents of crystallization, 2CH₃OH and 2H₂O in 1 while 3CH₃OH and 1.5H₂O in 2. A simplified and general schematic presentation of the heptametallic cores is shown in Scheme 2.

	1	2			
Empirical formula	$C_{58}H_{78}N_7O_{35}Co_4Gd_3$	$C_{58}H_{78}N_7O_{35}Co_4Dy_3$			
Formula weight	2140.74	2156.49			
Crystal system	Monoclinic	Monoclinic			
Space group	C2/c	<i>C2/c</i>			
<i>a</i> [Å]	17.505(6)	17.531(6)			
b[Å]	19.784(7)	20.038(7)			
c[Å]	24.106(8)	24.325(8)			
<i>α</i> [°]	90	90			
eta[°]	103.413(4)	102.979(4)			
χ[°]	90	90			
V[Å ³]	8121(5)	8326(5)			
Ζ	4	4			
T[K]	296(2)	296(2)			
<i>2θ</i> [°]	3.156-51.798	3.132-51.000			
μ [mm ⁻¹]	3.297	3.518			
$\rho_{\rm calcd}[{\rm g \ cm}^{-3}]$	1.751	1.720			
F(000)	4220	4244			
Absorption-correction	Multi-scan	Multi-scan			
Index ranges	$-20 \le h \le 21$	$-21 \le h \le 21$			
	$-23 \le k \le 24$	$-23 \le k \le 23$			
	$-29 \le l \le 29$	$-29 \le l \le 29$			
Reflections collected	29203	28955			
Independent reflections	7767 (0.0616)	7610 (0.0688)			
$(R_{\rm int})$					
$R_1^{a}, wR_2^{b} [I > 2\sigma(I)]$	0.0605, 0.1595	0.0546, 0.1404			
R_1^a , w R_2^b [for all F_0^2]	0.0910, 0.1723	0.0892, 0.1544			
Goodness-of-fit on F^2 , S	1.090	1.003			
${}^{a}R_{1} = [\sum F_{o} - F_{c} / \sum F_{o}]. {}^{b}wR_{2} = [\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum wF_{o}^{4}]^{1/2}$					

 Table 1. Crystallographic data for 1 and 2.



Figure 1. Crystal structure of $[Co^{III}_4Gd^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]$ · NO₃·2CH₃OH·2H₂O (1). All the Hydrogen atoms and counter nitrate ion have been omitted for clarity. Symmetry code: D = 1–x, y, 1.5–z.



Figure 2. Crystal structure of $[Co^{III}_4Dy^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]$ · NO₃· 3CH₃OH·1.5H₂O (**2**). All the Hydrogen atoms and counter nitrate ion have been omitted for clarity. Symmetry code: D = 1–x, y, 1.5–z.

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Scheme 2. Simplified illustration of the heptanuclear $[Co^{III}_4Ln^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]^+NO_3^-$ part in **1** and **2**. All solvent of crystallization molecules have been omitted for clarity. Ln^{III} = Gd^{III} for **1** and Ln^{III} = Dy^{III} for **2**, respectively.

The heptametallic core in **1** and **2** consists of the following species: (i) Four Co^{III}; (ii) Three Ln^{III}; (iii) Four deprotonated O(methoxy)O(phenoxo)N(imine)O(alkoxo) Schiff base ligands, $[L]^{2-}$, where both phenoxo and alkoxo moieties of H₂L are deprotonated; (iv) Two μ_4 -oxo ligands; (v) Two μ -methoxide ligands (vi) Four $\mu_{1,3}$ -acetate ligands; (vii) Two chelating nitrate ligands; (viii) Two water ligands. Bond Valence Sum (BVS) calculations on oxygen atoms^[34a,b] in **1** and **2** (Table S1) confirm their appropriate protonation level on alkoxo, oxo, methoxide and water oxygen atoms.

It may be simpler to describe the structures by fragment analyses. The heptametallic cores in **1** and **2** may be taken as consisted of two symmetry related trinuclear Co^{III}Ln^{III}Co^{III} moieties (Co1Ln1Co2 and Co1DLn1DCo2D) and a central lanthanide center (Ln2) in such a way that each of the three metal ions of each of the two trinuclear moieties are bridged with

the central lanthanide through bridging oxo/alkoxo/acetate ligands. Each symmetry related trinuclear core contains two $[L]^{2-}$. The O(phenoxo)N(imine)O(alkoxo) compartment of each of the two $[L]^{2-}$ is occupied by a Co^{III} ion (Co1 in O1N1O2 site and Co2 in O4N2O5 $[L]^{2-}$ compartment) and the two are placed so that а O(phenoxo)O(methoxy)O(methoxy)O(phenoxo) site (O1O3O6O4) is generated by their (i. O(phenoxo)O(methoxy) compartments). second compartments e. The O(phenoxo)O(methoxy)O(methoxy)O(phenoxo) site thus generated is occupied by a Ln^{III} ion (Ln1) to result in the formation of the trinuclear core, which contains a number of other bridging/chelating/monodentate ligands to stabilize it and those are as follows: (i) One μ methoxide ligand (containing O12) which bridges Co1 and Co2; (ii) A μ_4 -oxo ligand (containing O11) which bridges Co1, Ln1 and Co2 in the trinuclear core as well as the central lanthanide ion, Ln2; (iii) A $\mu_{1,3}$ -acetate ligand which bridges Co1 and Ln1 (through O7 and O8); (iv) A $\mu_{1,3}$ -acetate ligand which bridges Co2 of the trinuclear core and the central lanthanide ion, Ln2 (through O9 and O10); (iv) A bidentate nitrate ligand which chelates Ln1 through O13 and O14; (v) A water ligand (containing O16) which coordinates Ln1. It has already been mentioned that the central lanthanide (Ln2) is bridged with Co2 by a $\mu_{1,3}$ -acetate ligand and all the three metal ions (Co1, Ln1 and Co2) of a trinuclear core by a μ_4 -oxo ligand. There are two more linkings between a trinuclear core and the central lanthanide and those are the two alkoxo oxygen atoms (O2 and O5) which bridge the central lanthanide with Co1 and Co2, respectively, of a trinuclear core. Thus, the central lanthanide is bridged with each of the two trinuclear cores by one μ_4 -oxo, two μ -alkoxo and one $\mu_{1,3}$ -acetate ligands. The disposition of two symmetry related trinuclear Co^{III}Ln^{III}Co^{III} core with the central lanthanide ion leads to the generation of 'sand clock' like (Figure 3) topology in 1 and 2.



Figure 3. 'Sand Clock' like topology of the $\text{Co}_{4}^{\text{III}}\text{Ln}_{3}^{\text{III}}$ core in (1) (Ln= Gd) and (2) (Ln= Dy); color code: Navy blue for Ln^{III}, olive green for Co^{III} and red for oxygen.

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It is relevant to summarize the nature of bridging ligands between two metal ions in different bridged pairs: (i) Between Co1 and Co2 – one μ_4 -oxo and one μ_4 -methoxide; (ii) Between Co1 and Ln1 – one μ -phenoxo, one μ_4 -oxo and one μ_1_3 -acetate; (iii) Between Co2 and Ln1 – one μ -phenoxo and one μ_4 -oxo; (iv) Between Co1 and Ln2 – one μ_4 -oxo and one μ -alkoxo; (iv) Between Co2 and Ln2 – one μ_4 -oxo, one μ -alkoxo and one μ_1_3 -acetate; : (v) Between Ln1 and Ln2 – one μ_4 -oxo. Both Co^{III} centers (Co1 and Co2) are hexacoordinated, Ln1 center is 9-coordinated and Ln2 center is 8-coordinated. The bond distances involving the metal ions and the metal-O-metal bridge angles in 1 and 2 are listed in Table 2, 3, 4 and 5. The coordination environment of Co1 and Co2 are similarly and slightly distorted octahedral. The six Co–O/N bond distances for both Co^{III} centers lie within a narrow range of ca. 1.86–1.92 Å, whereas that involving $\mu_{1,3}$ -acetate/ μ -methoxide moiety is the longest and that involving μ -alkoxo is the shortest. This also indicates +3 oxidation state of this metal ion and also supported by BVS calculations (Table S2).^[34c,d] The overall (for Co1 and Co2) ranges of the *cisoid* and *transoid* angles in 1 and 2 are 82.3–95.2° and 174.9–178.0°. All these indicate slight distortion from octahedral geometry, which is further supported by SHAPE analyses^[35] (Table S3).

Coordination environment	Bond Lengths	1	2
of Co1 and geometry	(Å)		
	Co1-N1	1.899(8)	1.885(7)
	Co1-O1	1.890(6)	1.903(6)
	Co1-O2	1.861(5)	1.864(5)
	Co1–O7	1.921(6)	1.927(6)
	Co1-O11	1.900(5)	1.901(6)
	Co1-O12	1.921(6)	1.918(6)
07		Bond Angles (°)	
	N1-Co1-O11	175.1(3)	175.5(3)
	O7-Co1-O12	176.5(2)	176.3(3)
01	O1-Co1-O2	176.9(3)	177.4(3)
011	O1-Co1-N1	95.2(3)	94.9(3)
	O1-Co1-O7	90.0(3)	89.9(3)
N1 02	O1-Co1-O11	88.6(3)	88.5(3)
	O1-Co1-O12	92.2(2)	92.3(2)
and the second sec	O2-Co1-N1	86.2(3)	86.6(3)
	O2-Co1-O7	87.3(3)	88.1(3)
Octabedron	O2-Co1-O11	90.1(2)	90.2(2)
Octunicui on	O2-Co1-O12	90.4(2)	89.7(2)
	O7-Co1-N1	88.1(3)	88.3(3)

Table 2.	The values	of bond	lengths ((Å)	and angles	(°)) around	the	Co1	center in	1 and	2.
I abic 2.	The values	or bond	ionguis ((1)	and angles		/ urounu	une	001	contor in	I unu A	

O7-Co1-O11	94.9(3)	94.6(2)
O11-Co1-O12	82.3(2)	82.5(2)
O12-Co1-N1	94.4(3)	94.4(3)
Tr	ansoid angle rai	nge
	175.1(3) -	175.5(3) -
	176.9(3)	177.4(3)
(<i>Cisoid</i> angle rang	ge
	82.3(2) -	82.5(2) -
	95.2(3)	94.9(3)

Table 3. The values of bond lengths (Å) and angles (°) around the Co2 center in 1 and 2.

Coordination environment	Bond Lengths	1	2	
of Co2 and geometry	(Å)			
	Co2-N2	1.896(7)	1.889(7)	
	Co2-O4	1.895(5)	1.890(5)	
	Co2-O5	1.863(5)	1.857(5)	
	Co2-O9	1.918(6)	1.920(6)	
	Co2-O11	1.904(5)	1.914(5)	
	Co2-O12	1.892(6)	1.902(6)	
	Bond Angles (°)			
	O9-Co2-O12	174.9(3)	175.0(3)	
Q 9	N2-Co2-O11	176.5(3)	177.0(3)	
	O4-Co2-O5	178.0(3)	177.4(3)	
N2 05	O4-Co2-N2	95.1(3)	95.2(3)	
NZ	O4-Co2-O9	86.1(3)	85.6(3)	
Co2	O4-Co2-O11	87.9(2)	87.4(2)	
04	O4-Co2-O12	91.7(3)	92.4(3)	
	O5-Co2-N2	86.1(3)	86.1(3)	
	O5-Co2-O9	92.4(3)	92.2(2)	
	O5-Co2-O11	90.9(2)	91.4(2)	
012	O5-Co2-O12	89.6(3)	89.7(2)	
Octaneuron	O9-Co2-N2	89.7(3)	88.9(3)	
	O9-Co2-O11	92.3(2)	92.8(2)	
	O11-Co2-O12	83.0(2)	82.6(2)	
	O12-Co2-N2	95.0(3)	95.8(3)	
	,	Transoid angle range		
		174.9(3) -	175.0(3) -	
		178.0(3)	177.4(3)	
		Cisoid angle range		
		83.0(2) -	82.6(2) -	
		95.1(3)	95.8(3)	

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Ln1 and geometry	Ln1–O1 Ln1–O3 Ln1–O4 Ln1–O6 Ln1–O8 Ln1–O11 Ln1–O13 Ln1–O14 Ln1–O16	$\begin{array}{c} 2.331(7) \\ 2.614(8) \\ 2.318(6) \\ 2.757(6) \\ 2.347(7) \\ 2.298(5) \\ 2.516(8) \\ 2.446(8) \\ 2.446(8) \end{array}$	2.309(7) 2.611(7) 2.303(5) 2.771(6) 2.320(7) 2.272(5) 2.498(7)			
	Ln1–O1 Ln1–O3 Ln1–O4 Ln1–O6 Ln1–O8 Ln1–O11 Ln1–O13 Ln1–O14 Ln1–O16	2.331(7) 2.614(8) 2.318(6) 2.757(6) 2.347(7) 2.298(5) 2.516(8) 2.44	2.309(7) 2.611(7) 2.303(5) 2.771(6) 2.320(7) 2.272(5) 2.498(7)			
	Ln1–O3 Ln1–O4 Ln1–O6 Ln1–O8 Ln1–O11 Ln1–O13 Ln1–O14 Ln1–O16	2.614(8) $2.318(6)$ $2.757(6)$ $2.347(7)$ $2.298(5)$ $2.516(8)$ $2.446(8)$	2.611(7) 2.303(5) 2.771(6) 2.320(7) 2.272(5) 2.498(7)			
	Ln1–O4 Ln1–O6 Ln1–O8 Ln1–O11 Ln1–O13 Ln1–O14 Ln1–O16	2.318(6) 2.757(6) 2.347(7) 2.298(5) 2.516(8) 2.44	2.303(5) 2.771(6) 2.320(7) 2.272(5) 2.498(7)			
	Ln1–O6 Ln1–O8 Ln1–O11 Ln1–O13 Ln1–O14 Ln1–O16	2.757(6) 2.347(7) 2.298(5) 2.516(8) 2.446(8)	2.771(6) 2.320(7) 2.272(5) 2.498(7)			
	Ln1–O8 Ln1–O11 Ln1–O13 Ln1–O14 Ln1–O16	2.347(7) 2.298(5) 2.516(8) 2.446(8)	2.320(7) 2.272(5) 2.498(7)			
	Ln1–O11 Ln1–O13 Ln1–O14 Ln1–O16	2.298(5) 2.516(8) 2.446(8)	2.272(5) 2.498(7)			
	Ln1–O13 Ln1–O14 Ln1–O16	2.516(8) 2.446(8)	2.498(7)			
	Ln1–O14 Ln1–O16	2.446(8)				
	Ln1-O16		2.451(7)			
		2.400(7)	2.352(7)			
	Bond Angles (°)					
	O1-Ln1-O3	62.5(2)	63.0(2)			
	O1-Ln1-O4	73.9(2)	75.0(2)			
	01-Ln1-06	89.8(2)	87.4(2)			
	O1-Ln1-O8	72.6(2)	73.9(2)			
	O1-Ln1-O11	69.76(19)	70.8(2)			
014	O1-Ln1-O13	149.1(2)	148.5(2)			
013	O1-Ln1-O14	140.2(2)	137.8(2)			
	O1-Ln1-O16	133.7(2)	135.5(2)			
	O3-Ln1-O4	107.7(2)	110.2(2)			
	O3-Ln1-O6	65.7(2)	65.3(2)			
16	O3-Ln1-O8	72.4(3)	71.8(2)			
	O3-Ln1-O11	130.2(2)	131.1(2)			
	O3–Ln1–O13 118.0(2)		116.1(2)			
	O3-Ln1-O14	77.8(3)	74.9(3)			
08	O3-Ln1-O16	130.5(3)	129.4(2)			
011	O4-Ln1-O6	59.34(19)	59.58(19)			
	O4-Ln1-O8	141.5(2)	143.1(2)			
pherical tricapped	O4-Ln1-O11	69.67(18)	70.12(18)			
rigonal prism	O4-Ln1-O13	77.2(2)	76.5(2)			
-Borran brushi	O4-Ln1-O14	120.2(2)	119.4(2)			
	O4-Ln1-O16	121.6(2)	119.9(2)			
	O6-Ln1-O8	138.0(2)	137.1(2)			
	O6-Ln1-O11	128.63(19)	128.89(19)			
	O6-Ln1-O13	65.9(2)	66.4(2)			
	O6-Ln1-O14	71.6(2)	71.4(2)			
	O6-Ln1-O16	136.4(2)	137.0(2)			
	08-Ln1-011	81.3(2)	81.3(2)			
	08-Ln1-013	138.2(3)	137.5(3)			
	08 - Ln1 - 014	97.8(3)	97.0(3)			
	08 - Ln1 - 016	72.2(3)	72.6(3)			
	011-Ln1-013	109.9(2)	111.4(2)			
	011 - Ln1 - 014	148.6(2)	1500(2)			
	011 - Ln1 - 016	75 9(2)	75 9(2)			
	013 - In1 - 010	51.9(2)	515(2)			
	013 - Lin - 014 013 - Lin - 016	720(2)	71.9(2)			
	013-LII-010 014-1 n1 016	72.0(2) 74.0(2)	71.0(2)			
	014-LIII-010	(4.0(3)	15.0(2)			
		51 6(2)	51 5(2)			
		1/0(3) =	1500(2) -			

Table 4. The values of bond lengths (Å) and bond angles (°) around the Ln1 center in 1 and2.

ble	5. ′	Гh

Coordination	Bond Lengths (Å)	1	2
environment of Ln2 and geometry			
	Ln2–O2	2.350(5)	2.344(5)
	Ln2–O5	2.300(5)	2.290(5)
	Ln2-O10	2.409(6)	2.404(5)
	Ln2-011	2.431(5)	2.425(5)
	В	Sond Angles (°)	
	O2-Ln2-O2D	101.8(3)	101.8(3)
	O2-Ln2-O5	78.9(2)	79.5(2)
	O2-Ln2-O5D	75.94(18)	75.68(18)
010	O2-Ln2-O10	138.96(18)	139.61(18)
05	O2-Ln2-O10D	103.2(2)	102.5(2)
	O2-Ln2-O11	67.67(18)	67.95(18)
0110 Ln2	O2-Ln2-O11D	144.74(18)	145.16(17)
	O5-Ln2-O5D	139.6(3)	140.1(3)
	O5-Ln2-O10	76.3(2)	75.97(19)
O2005D	O5-Ln2-O10D	140.77(19)	140.49(18)
Triangular dodecahedron	O5-Ln2-O11	69.08(18)	69.77(18)
	O5-Ln2-O11D	126.58(18)	125.91(19)
	O10-Ln2-O10D	77.6(3)	78.2(3)
	O10-Ln2-O11	73.10(19)	73.63(19)
	O10-Ln2-O11D	75.59(18)	74.56(18)
	O11-Ln2-O11D	139.5(3)	138.6(3)
		Angle range	
		67.67(18) -	67.95(18) -
		144.74(18)	145.16(17)

e values of bond lengths (Å) and bond angles (°) around the Ln2 center in 1 and Та 2.

The Ln-O bond distances in the 9-coordinated Ln1 environment lie in the ranges 2.298–2.757 Å in 1 (Gd^{III} analogue) and 2.272–2.498 Å in 2 (Dy^{III} analogue), where a clear order of the bond distances involving the following ligand moieties is observed: methoxy>nitrate>water>µ_{1,3}-acetate>µ-phenoxo>µ-oxo. The overall ranges of O-Ln1-O bond angles in 1 and 2 are similar, ca. 51.5-150.0°. The Ln-O bond distances in the 8coordinated Ln2 environment lie in the similar ranges 2.300–2.431 Å in 1 (Gd^{III} analogue) and 2.290–2.425 Å in **2** (Dy^{III} analogue), where a clear order of the bond distances involving the following ligand moieties is observed: $0x_{1,3}$ -acetate>µ-alkoxo. The overall ranges of O–Ln2–O bond angles in **1** and **2** are similar, 67.67–144.74° in **1** and 67.95–145.16° in **2**.

SHAPE^[35] analyses (Table S4 and S5) reveal that spherical tricapped trigonal prism (TCTPR-9) and triangular dodecahedron (TDD-8) are the 'most ideal' geometries of the Ln1 and Ln2 centers, respectively. The general illustrations of the TCTPR-9 and TDD-8 geometries of Ln1 and Ln2 centers, respectively, are shown in Figure 4.



Figure 4. General representation of the co-ordination environment showing a) Octahedral Co1; b) Octahedral Co2; c) Spherical tricapped trigonal prism (D_{3h}) (TCTPR-9) geometry for Ln1 center and d) Triangular dodecahedron (D_{2d}) (TDD-8) geometry of Ln2 center in **1** and **2**.

Magnetic Properties

Variable temperature (2–300 K) dc magnetic susceptibilities of powdered samples of **1** and **2** were measured at an applied dc field of 0.1 T and has been portrayed in Figure 5 and 6, respectively, in terms of $\chi_M T$ versus *T* plots. The $\chi_M T$ values at 300 K for **1** and **2** are, respectively, 23.38 and 39.90 cm³ K mol⁻¹. The observed $\chi_M T$ values are close enough to those (23.63 and 42.51 cm³ K mol⁻¹, respectively) expected for three noninteracting Gd^{III} ions (${}^{8}S_{7/2}$, *L* = 0, *S* = 7/2, *g* = 2) for **1** and three noninteracting Dy^{III} ions (${}^{6}H_{15/2}$, *L* = 5, *S* = 5/2, *g* = 4/3) for **2**. For **1**, on lowering the temperature, the $\chi_M T$ product remains apparently constant down to 10 K followed by rapid drop to a minimum value of 20.90 cm³ K mol⁻¹ at 2 K. This feature could be attributable to weak antiferromagnetic Gd^{III}...Gd^{III} exchange interactions. The dc magnetic susceptibility of complex **2** (Figure 6) features a very gradual decrease of $\chi_M T$ product upon lowering of temperature and finally reaches the minimum value of 32.17 cm³ K mol⁻¹ at 2 K. This is indicative of depopulation of the *M*_J sublevels of Dy^{III} ions or weak Dy^{III}...Dy^{III} antiferromagnetic exchange interactions or both.



Figure 5. Temperature dependence of the dc magnetic susceptibility for $[Co^{III}_4Gd^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3\cdot 2CH_3OH\cdot 2H_2O$ (1) in the temperature region 2–300 K. The pink colored squares are experimental data, while the solid line represents the calculated curve.



Figure 6. Temperature dependence of the dc magnetic susceptibility for $[Co^{III}_4Dy^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3\cdot 3CH_3OH\cdot 1.5H_2O$ (**2**) in the temperature region 2–300 K.

The magnetization (*M*) data up to 5 T and at 2, 4, 6, 8 and 10 K for 1 (Figure 7) and 2 (Figure S1) have been collected. The magnetization curve of 1 displays a steady increase that finally reaches the value of 21.54 $N\mu_{\beta}$ at 2 K and 5 T. This value is close to the saturation magnetisation of 21 $N\mu_{\beta}$ for three noninteracting Gd^{III} ions (⁸S_{7/2}, *g* = 2), indicative of weak nature of the possible exchange interactions. Moreover, *M* versus *H*/*T* plot (Figure S2) of 1 shows that all magnetisation isotherms merge on the same master curve establishing the isotropic nature of Gd^{III} ions. The *M* versus *H* data (Figure S1) of **2** reveals that the magnetisation value (15.33 $N\mu_{\beta}$) even at 2 K and 5 T is significantly smaller than the saturation value (30 $N\mu_{\beta}$) for three noninteracting Dy^{III} ions (⁶H_{15/2}, *g* = 4/3), revealing the existence of appreciable anisotropy which is further strengthened by the non-superimposable nature of the *M* versus *H*/*T* profiles with a master curve (Figure 8).



Figure 7. Magnetizations versus field plots for $[Co^{III}_4Gd^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3\cdot 2CH_3OH\cdot 2H_2O$ (1), collected at the indicated temperatures. The different coloured circles are experimental data, while the solid lines represent the calculated curves.



Figure 8. Magnetizations vs field/temperature plots of the experimental data for $[Co^{III}_{4}Dy^{III}_{3}L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3\cdot 3CH_3OH\cdot 1.5H_2O$ (2), collected at the indicated temperatures.

As Gd1 and Gd2 as well as Gd1D and Gd2 are bridged by diamagnetic atoms and there is no bridging ligand between Gd1 and Gd1D, the magnetic properties of **1** can be modelled by Hamiltonian, $\mathbf{H} = -2\mathbf{J}(S_1 \cdot S_2 + S_2 \cdot S_3)$, where $S_1 = S_2 = S_3 = 7/2$ (Figure 9). With this model Hamiltonian, $\chi_M T$ versus T data and M versus H data were simulated simultaneously to a satisfactory level using *PHI* software^[36] with the following converging parameters: $J = -0.010 \text{ cm}^{-1}$ and $g_{Gd} = 1.99$. This clearly reflects the very weak antiferromagnetic Gd^{III}...Gd^{III} interaction present in **1**.



Figure 9. Simple representation of the core structure of $[Co^{III}_4Gd^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3 \cdot 2CH_3OH \cdot 2H_2O$ (1) showing a) only the metal atoms and b) accounting the magnetic interaction present among Gd^{III} ions. Here, J_1 and J_2 both are equal. Symmetry code: D = 1-x, y, 1.5–z.

The presence of significant magnetic anisotropy may lead to SMM behavior in complex **2**. To explore this aspect, variable-temperature (2–20 K) ac magnetic susceptibility (Figure S3 and 10) at different fixed frequency (1–951 Hz) as well as variable-frequency (1–951 Hz) ac magnetic susceptibility (Figure S4 and 11) at different fixed temperatures (2–20 K) were measured on powdered sample under zero-dc field with 3.5 Oe oscillating field. Both in-phase (χ_M ') and out-of-phase (χ_M '') ac magnetic susceptibility of both types (variable-temperature and variable-frequency) data exhibit significant temperature and frequency dependence under zero-dc field SMM.



Figure 10. Temperature dependence of the out-of-phase ac molar susceptibility (χ_M ") for $[Co^{III}_4Dy^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3\cdot 3CH_3OH\cdot 1.5H_2O$ (**2**) at the indicated frequencies under zero-dc field. Solid lines are guide for eyes only.



Figure 11. Frequency dependence of the out-of-phase ac molar susceptibility (χ_M ") for $[Co^{III}_4Dy^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3\cdot 3CH_3OH\cdot 1.5H_2O$ (**2**) under zero-dc field. Inset shows the magnifying view that displays the clearer presence of two peak maxima in χ_M " versus Frequency plot. The solid lines corresponding to each temperature are visual guide only.

Temperature-dependent out-of-phase (χ_{M} ") signals (Figure 10) reveal the presence of two clear peak maxima which are separated well; one at higher temperature region, *ca.* 14 K, and the other at lower temperature region, *ca.* 7 K. At further lower temperature (below 5 K), χ_{M} " rises rapidly. This complex pattern suggests that multiple relaxation mechanism is operative with quantum-tunneling mechanism prevailing in the low temperature region as one of the relaxation processes.^[37] From the frequency-dependent χ_{M} " data (Figure 11), presence of two peak maxima are more clearly evident; the presence of the higher frequency peak maxima in the data in the lower temperature region, 5–10 K, and the lower frequency peak maxima in the data in the higher temperature region, above 10 K, corroborates the operation of two separate relaxation channels, as observed in some other Dy^{III} based SMMs/SIMs.^[27e,38] Obviousloy, the higher frequency peak is the fast relaxation (FR) channel while lower frequency peak is the slow relaxation (SR) channel.

The Cole-Cole plots (Figure 12) corresponding to the frequency-dependent in-phase (χ_M') (Figure S4) and out-of-phase (χ_M'') (Figure 11) data were constructed in the temperature region 5–11 K. It consists of distorted semicircles, indicative of the presence of two fused semicircles. Thus, from Cole-Cole plots, the presence of two separate relaxation processes is clarified (Figure 12 and S5); left and right semicircles represent the fast relaxation (FR) and slow relaxation (SR) processes, respectively. It is well documented from Figure 12, S5 and S6 that, with increasing temperature from 5 K, a slow collapsing of two relaxation processes

into a single one takes place. These data were nicely fitted by using the sum of two modified Debye functions,^[39] yielding two sets (α_1 and α_2) of relaxation distribution parameters (Table S6); α_1 lies in the range 0.00–0.22 and corresponds to the fast relaxation channel, α_2 lies in the range of 0.00–0.10 and corresponds to the slow relaxation channel. The values of α_2 represent an overall narrow distribution of relaxation time for slow relaxation process. On the other hand, for the fast relaxation process, the values of α_1 take a wider distribution in the low temperature region ($\alpha_1 = 0.17-0.22$ in the temperature range 5–9 K) and switch over to extremely narrower distribution ($\alpha_1 \approx 0$ at T > 9 K) in the higher temperature region, above 9 K. The relaxation times (τ) at different temperatures corresponding to the temperaturedependent out-of-phase data (in Figure 10) could be fitted well (Figure 13) with the Arrhenius equation (ln $\tau = \ln \tau_0 + U_{eff}/k_BT$), giving $U_{eff} = 51.4 \text{ cm}^{-1}$ and $\tau_0 = 9.40 \times 10^{-7} \text{ s for}$ the slow relaxation (SR) channel and $U_{\rm eff} = 24.3 \ {\rm cm}^{-1}$ and $\tau_0 = 6.91 \times 10^{-7} \ {\rm s}$ for the fast relaxation (FR) channel. Linear fitting above 9.2 K (9.2-14.3 K) for the slow relaxation channel and above 5.4 K (5.4-6.5 K) for the fast relaxation channel suggests that both are thermally activated Orbach processes. Appreciable deviation from linearity of the data below 9.2 K and 5.4 K, respectively, reveals a transition from thermally activated to a quantumtunneling mechanism.



Figure 12. Cole-Cole plots for compound $[Co^{III}_4Dy^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3 \cdot 3CH_3OH \cdot 1.5H_2O$ (2) measured at the indicated temperatures under zero-dc field. The black solid lines at each temperature represents the best fits to the experimental data obtained with the sum of two modified Debye functions.

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Figure 13. Plot of $\ln(\tau)$ versus reciprocal temperature (Arrhenius plot) in the temperature region 5.30–14.30 K under zero-dc field for $[Co^{III}_4Dy^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3\cdot 3CH_3OH\cdot 1.5H_2O$ (2). The pink solid line corresponds to the linear fits for both (Fast Relaxation and Slow Relaxation) the thermally activated regime.

To get further insight into the magnetic relaxation dynamics of complex 2, we have collected the ac magnetic susceptibility data under an applied 2000 Oe dc field. Variabletemperature (2-20 K) ac magnetic susceptibility (Figure S7 and 14) at different fixed frequencies (1–951 Hz) and variable-frequency (1–951 Hz) ac magnetic susceptibility (Figure S8 and 15) at different fixed temperatures (2–20 K) were measured on powdered sample under 2000 Oe dc field with 3.5 Oe oscillating field. Temperature-dependent out-of-phase signals (χ_{M} "; Figure 14) display, compared to zero-dc field (Figure 10), further well resolved fast and slow relaxation processes making the fast relaxation process more readily observable with clear presence of fast relaxation peaks (under 2000 Oe dc field) compared to tailing (under zero-dc field). Below 4 K, with increasing frequency, there are upturns in the out-ofphase (χ_M'') signals (Figure 14). This suggests the onset of quantum-tunneling mechanism, a third relaxation process that has been alleviated upon application of 2000 Oe dc field. Frequency-dependent out-of-phase (χ_M ") signals (Figure 15) also exhibit more clear peaks than zero-dc field and as the temperature is lowered the position of peak maxima changes from higher frequency to lower frequency. From this frequency dependent out-of-phase ($\chi_{\rm M}$ ") profile, it is apparent that apart from the observed peaks in the investigated frequency range (1–951 Hz), multiple peaks would be visible if we go beyond either 1 Hz or 951 Hz. But this was the hardware limit.



Figure 14. Temperature dependence of the out-of-phase ac molar susceptibility (χ_M ") for $[Co^{III}_4Dy^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3\cdot 3CH_3OH\cdot 1.5H_2O$ (**2**) at the indicated frequencies under 2000 Oe dc field. Solid lines are guide for eyes only.



Figure 15. Frequency dependence of the out-of-phase ac molar susceptibility (χ_M ") for $[Co^{III}_4Dy^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3\cdot 3CH_3OH\cdot 1.5H_2O$ (**2**) under 2000 Oe dc field. The solid lines corresponding to each temperature are visual guide only.

Cole-Cole plots in the temperature region, 6–9 K (Figure 16), were attempted to fit by using generalized Debye function^[40] but it was unsatisfactory. Hence, we tried to fit the data by employing the sum of two modified Debye functions.^[39] It gives satisfactory fitting and yields α_1 value in the range of 0.20–0.26 while the value of $\alpha_2 \approx 0$. Such a high value of relaxation width ($\alpha_1 = 0.20$ –0.26) for fast relaxation (FR) indicates wider distribution of relaxation time and extremely low value of relaxation width ($\alpha_2 \approx 0$) for slow relaxation (SR) suggests extremely narrower distribution of relaxation time. We have quantified the value of effective energy barrier (U_{eff}) and relaxation time (τ_0) as well by taking the relaxation times (τ) at different temperatures corresponding to the temperature region 10.1–12.8 K for the slow relaxation (SR) gives $U_{eff} = 51.5 \text{ cm}^{-1}$ and $\tau_0 = 4.85 \times 10^{-7}$ s and linear fitting in the temperature region 5.0–7.1 K for the fast relaxation (FR) gives $U_{eff} = 28.4 \text{ cm}^{-1}$ and $\tau_0 = 8.62 \times 10^{-7}$ s. Hence, operation of Orbach processes at thermally activated regime for both slow and fast relaxation processes under zero-dc field is again corroborated by the applied field (2000 Oe) magnetic relaxation dynamics of compound **2**.



Figure 16. Cole-Cole plots for compound $[Co^{III}_4Dy^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3\cdot 3CH_3OH\cdot 1.5H_2O$ (**2**) measured in the temperature region 6K–9K under 2000 Oe dc field. The black solid lines at each temperature represents the best fits to the experimental data obtained with the sum of two modified Debye functions.

A MAGELLAN^[41] analysis (Figure 17) of compound 2 reveals the disposition of local anisotropy axes on the Dy^{III} centers (Dy1, Dy1D and Dy2) are noncolinear, that possibly regulate the relaxation of magnetisation through multiple pathways. In weakly exchange coupled Dy^{III} containing compounds, slow relaxation of magnetisation arises not only due to intrinsic magnetic anisotropy of the Dy^{III} centers but also due to ligand field effects associated with the coordination geometry.^[16a,42] Again, the presence of diamagnetic Co^{III} ions in 2 can potentially influence the magnetic behavior that, in turn, increases the effective energy barrier as observed in previously reported Co^{III}Dy^{III} systems.^[27c] In case of the 9-coordinated Dy1/Dy1D centers having DyO₉ coordination environment, the oxide oxygen atom O11/O11D is closest (2.298 Å) to Dy1/Dy1D while for the 8-coordinated Dy2 center with DyO₈ coordination environment, alkoxo oxygen atom O5 is closest (2.272 Å) to Dy2 among other ligand atoms. Now, the anisotropy axes on Dy1 and Dy1D are closely parallel to Dy1–O11 and Dy1D–O11D bonds, respectively, while the anisotropy axis on Dy2 is not at all parallel to Dy2-O5 bond but the anisotropy axis is closely parallel to Dy2-O2D bond, where O2D is the second closest (2.350 Å) atom to Dy2 among the ligating atoms. Hence, it is difficult to assign the slow relaxation and fast relaxation processes corresponding to the Dy centers.



Figure 17. The direction of the local anisotropy axes (yellow coloured dotted lines) of Dy^{III} ions in $[Co^{III}_4Dy^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3\cdot 3CH_3OH\cdot 1.5H_2O$ (2) showing only the metal atoms with their coordination environment.

Absorption and emission spectra

Diffuse reflectance spectra (Figure S10) of **1** and **2** were recorded at room temperature. Both compounds exhibit three bands at approximately the same positions; 422 nm (sharp), 559 nm (broad) and 710 nm (broad) for **1** and 422 nm (sharp), 547 nm (broad) and 700 nm (broad) for **2**.

Absorption spectra of 5×10^{-6} (M) methanol solutions of **1** and **2** are shown in Figure S10. Four absorptions occur in each case. One among them is a sharp peak while the other three are broad shoulders. The band maxima (λ_{max} in nm) and their corresponding ε (M⁻¹ cm⁻¹) values are as follows: 240 and 111708 (sharp), 269 and 55955 (broad), 324 and 25078 (broad) and 378 and 10011 (broad) for **1**; 241 and 110358 (sharp), 269 and 54506 (broad), 329 and 23292 (broad) and 378 and 10854 (broad) for **2**.

In order to check the emissive property of compound **2**, we performed the steady state fluorescence spectroscopy at room temperature for both solid and solution phases. In solid state, upon excitation in the visible region at 422 nm, the compound exhibits three characteristic bands of Dy^{III} in addition to a ligand based band (Figure 18). The emission maxima of the bands at 506 nm, around 569 nm and 668 nm could be assigned to Dy^{III} based ${}^{4}F_{9/2}\rightarrow{}^{6}H_{15/2}$, ${}^{4}F_{9/2}\rightarrow{}^{6}H_{13/2}$ and ${}^{4}F_{9/2}\rightarrow{}^{6}H_{11/2}$ transitions, respectively. Besides, the emergence of a broad band at around 468 nm could be ascribed to ligand based emission. The split pattern observed in the Dy^{III} based band centerd at around 569 nm (${}^{4}F_{9/2}\rightarrow{}^{6}H_{13/2}$ transition) into two components, one at 562 nm and the other at 576 nm, is attributable to the presence of two crystallographically inequivalent Dy^{III} centers in **2** because the ${}^{4}F_{9/2}\rightarrow{}^{6}H_{13/2}$ transition in Dy^{III} based systems is highly sensitive to Dy^{III} geometry.^[43] Again, the emission band at 506 nm (${}^{4}F_{9/2}\rightarrow{}^{6}H_{15/2}$ transition) is significantly overlapped with the ligand based emission band. In solid state emission spectrum, presence of significant residual ligand based emission reveals that photoinduced energy transfer from the ligand L^{2-} to Dy^{III} is not complete.^[16b] The overall emissive nature in solid state for **2** indicates that L^{2-} is acting as a sensitizer for Dy^{III} .



Figure 18. (a) Solid state fluorescence spectra of $[Co^{III}_4Dy^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3 \cdot 3CH_3OH \cdot 1.5H_2O$ (2) at room temperature; $\lambda_{ex} = 422$ nm. (b) Fluorescence spectra of 5×10^{-6} (M) MeOH solution of $[Co^{III}_4Dy^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3 \cdot 3CH_3OH \cdot 1.5H_2O$ (2) at room temperature; $\lambda_{ex} = 378$ nm.

In contrary to the solid state, the emissive nature of **2** in solution phase is totally diminished with subsequent presence of only ligand based emission band at 431 nm and that is observable under excitation at 378 nm for 5×10^{-6} (M) MeOH solution. The nonemissive nature of **2** in solution phase may be rationalised in terms of the interaction with OH oscillators which favour thermal dissipation of energy that actually inhibits the emission.

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Comparison of the structures and magnetic properties of 1 and 2 with the related systems.

A number of compounds containing both Co^{III} and Dy^{III} have been reported previously (Table S7).^[44] In terms of nuclearity, those systems include $Co^{III}Dy^{III,[27h,43a]} Co^{III}_2Dy^{III,[44b-d]} Co^{III}_2Dy^{III}_2,^{[44e-k]} Co^{III}_4Dy^{III}_2,^{[42a]} Co^{III}Dy^{III}_3,^{[44I]} Co^{III}_3Dy^{III}_3,^{[44m]} and Co^{III}_2Dy^{III}_4,^{[44n-p]} However, no compound of nuclearity <math>Co^{III}_4Dy^{III}_3$ (or $Co^{III}_4Ln^{III}_3$, Ln = Ce-Yb) was reported previously. As already discussed, heptanuclear compounds 1 and 2 consist of two trinuclear $Co^{III}Ln^{III}Co^{III}$ fragments and a central Ln^{III} center. Interestingly, such an assembly of metal ions in 3d-4f family is not known. Few of the known $Co^{III}Dy^{III}$ systems were derived from ligands similar to H₂L.^[32i,33a] In terms of nuclearity, this is only { Co_2Ln_4 }.^[32i,33a] It is worth mentioning that there are few compounds having Co^{III} and Ln^{III} where the metal ions are bridged by μ_4 -oxo moiety.^[45] Among them, there are only three $Co^{IIL}n^{III}$ compounds^[45b] having two μ_4 -oxo moiety but there is no $Co^{III}Ln^{III}$ compound having μ_4 -oxo moiety. Notably, the heptamellic core can be compared with a 'sand clock' like topology (Figure 3), not reported previously in $Co^{II}/^{III}Ln^{III}$ systems. Clearly, the title compounds represent some new aspects from structural point of view.

There are a number of homonuclear compounds $^{\rm [46a-g]}$ of $\rm Dy^{\rm III}$ as well as heteronuclear compounds^[46h] of Dy^{III} and a diamagnetic metal ion of different nuclearity that show double relaxation channels. Some structural and SMM aspects of some of such systems and 2 are compared in Table S8. The reason of two relaxations in most cases is the difference of the surrounding of Dy^{III} centers in terms of ligand atoms, coordination geometry, ligand field, etc. So, in 2, two relaxation channels at higher temperature (T > 5 K) region arise most probably due to the presence of two distinct Dy^{III} centers, *viz*, nine coordinated Dy1/Dy1D centers with TCTPR as the 'most ideal' geometry and eight coordinated Dy2 center with TDD as the 'most ideal' geometry. As listed in Table S7 and S8, the double-relaxation channels in most cases are not well resolved in zero-dc field^[44f,g,k, 46a,c,e,h] and also even under an applied dc field.^[27h, 42a, 44d] Only in very few cases, the two processes are well resolved in zero-dc field.^[44h, 46b] Clearly, compound **2** is among some few examples where the two channels are well resolved in zero-dc field and the $U_{\rm eff}$ values of both channels could be determined. In the Co^{III}Dy^{III} SMMs, the range of $U_{\rm eff}$ values is ca. 23–88 cm⁻¹ and $\tau_0 = 6.0 \times$ 10^{-8} -1.0 × 10⁻⁷ s.^[27h] Thus, 2 with $U_{\rm eff}$ (SR) of 51.4 cm⁻¹ and $\tau_0 = 9.40 \times 10^{-7}$ s is among the good Co^{III}Dy^{III} SMMs.

Although there are several examples in which Dy^{III} containing compounds show fluorescence behavior,^[31a-e] emission properties of the reported heteronuclear clusters^[44] having Co^{III} and Dy^{III} were not reported. Clearly, **2** is the sole example of a Co^{III}Dy^{III} cluster for which emission behavior is studied.

Conclusions

The title compounds $[Co^{III}_4Gd^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3\cdot 2CH_3OH\cdot 2H_2O$ (1) and $[Co^{III}_4Dy^{III}_3L_4(\mu_4-O)_2(\mu-OMe)_2(\mu_{1,3}-OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3\cdot 3CH_3OH\cdot 1.5H_2O$ (2) are the sole examples of $Co^{III}_4Ln^{III}_3$ clusters. The compounds 1 and 2 have two μ_4 -oxo moieties; there are no $Co^{III}Ln^{III}$ cluster having at least one μ_4 -oxo bridge. Some $Co^{III}Ln^{III}$ compounds were reported $^{[32i,33a]}$ previously from ligands which are similar to H_2L but those compounds have nuclearity of the type, only $\{Co_2Ln_4\}$. $^{[32i,33a]}$ Obviously, slight modification in the ligand periphery gives rise to a new type of 3d-4f cluster in the form of 1 and 2.

The variable-temperature and variable-field magnetic data of the Gd^{III} analogue **1** could be simultaneously simulated; it exhibits very weak antiferromagnetic interactions with $J = -0.010 \text{ cm}^{-1}$. The variable-temperature and variable-field dc data of the Dy^{III} analogue **2** reveal that it has significant anisotropy. Variable-temperature and variable-frequency ac data reveal that **2** is a zero-field SMM with multiple relaxation dynamics in the investigated temperature region, 2–20 K. In the temperature region, T > 5 K, two relaxation channels (fast and slow) are well-resolved. Notably, **2** is among only a few examples of Dy^{III} containing SIMs/SMMs which exhibit two well-resolved relaxation channels at zero field. The presence of two different types of Dy^{III} centers (eight coordinated 'TDD' and nine coordinated 'TCTPR') is the reason of the appearance of two channels.

 L^{2-} is a sensitizer for Dy^{III} because the characteristic Dy^{III} based transitions, ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$, ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{6}H_{11/2}$ appear in the fluorescence spectrum of **2** at solid state. Therefore, compound **2** is a bi-functional molecular material, combining SMM and luminescent properties.

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Experimental section

Materials and physical measurements. All the reagents and solvents were purchased from commercial sources and used as received. Elemental (C, H and N) analyses were performed on a Perkin-Elmer 2400 II analyzer. IR spectra were recorded in the region 400–4000 cm⁻¹ on a Bruker-Optics Alpha–T spectrophotometer with samples as KBr disks. UV-Vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Only freshly prepared solutions were used for the spectroscopic study and all experiments have been carried out at room temperature (298 K). Diffuse reflectance spectra of the solid samples were recorded using an integrating sphere set up. A Perkin-Elmer LS-55 spectrofluorimeter was utilized to study emission spectrum of solid sample employing an integrating sphere set up. The molar conductivity ($\Lambda_{\rm M}$) of 1 mM solutions in methanol were measured at 25 °C with a Systronics conductivity bridge. The magnetic measurements were carried out with a SQUID magnetometer (MPMS, Quantum Design). Diamagnetic corrections were taken into account based on Pascal's constants.

Syntheses of 1 and 2:

$$\label{eq:complexes} \begin{split} & [Co^{III}_4Gd^{III}_3L_4(\mu_4\text{-}O)_2(\mu\text{-}OMe)_2(\mu_{1,3}\text{-}OAc)_4(H_2O)_2(NO_3)_2]\text{\cdot}NO_3\text{\cdot}2CH_3OH\text{\cdot}2H_2O \quad (1) \quad \text{and} \\ & [Co^{III}_4Dy^{III}_3L_4(\mu_4\text{-}O)_2(\mu\text{-}OMe)_2(\mu_{1,3}\text{-}OAc)_4(H_2O)_2(NO_3)_2]\text{\cdot}NO_3\text{\cdot}3CH_3OH\text{\cdot}1.5H_2O \quad (2). \end{split}$$

To a 10 mL 'H₂L solution' containing 0.2 mmol H₂L was taken and diluted to 15 mL with acetonitrile. To it, triethylamine (0.056 mL, 0.4 mmol) and 2 mL methanol solution of $Gd(NO_3)_3 \cdot 6H_2O$ (0.067 g, 0.15 mmol) were successively added and stirred for 20 min. To the yellow colored clear solution, a solution of $Co(OAc)_2 \cdot 4H_2O$ (0.050 g, 0.2 mmol) in 2 mL methanol was added and stirred for additional 5 h. The resulting brown colored reaction mixture was filtered to remove any suspended particles and the filtrate was kept at ambient temperature for slow evaporation. After a few days, brown crystalline compound was obtained, which was collected by filtration, washed with cold methanol and dried in vacuum. Recrystallization from MeOH-diethylether mixture (solvent diffusion technique) produced brown crystalline compound containing diffraction quality single crystals.

Data for 1. Yield: 0.064 g (57%). Anal. calcd. For $C_{60}H_{94}N_7O_{39}Co_4Gd_3$ (FW: 2244.92): C, 32.10; H, 4.22; N, 4.37. Found: C, 31.80; H, 4.32; N, 4.53%. Selected FT-IR data (cm⁻¹) on KBr: v(C=N), 1638s; $v_{as}(COO^-)$, 1556vs and $v_s(COO^-)$, 1473m; v(NO₃⁻), 1384vs and 1305s. **Data for 2.** Yield: 0.067 g (59%). Anal. calcd. For $C_{61}H_{97}N_7O_{40}Co_4Dy_3$ (FW: 2291.71): C, 31.97; H, 4.26; N, 4.28. Found: C, 32.26; H, 4.37; N, 4.13%. Selected FT-IR data (cm⁻¹) on KBr: v(C=N), 1638s; $v_{as}(COO^-)$, 1555vs and $v_s(COO^-)$, 1473m; v(NO₃⁻), 1384vs and 1304s.

The molar conductance values at 298 K for **1** and **2** were recorded in methanol solution. The values are 79.5 and 81.7 ohm⁻¹ cm⁻¹ mol⁻¹ for **1** and **2** respectively, indicating the ionic nature in solid state is preserved in methanol solution for both **1** and **2**. The molar conductance values for both **1** and **2** indicate the most probable (1:1) electrolytic nature in solution.^[47]

Crystal structure determination of 1 and 2.

The crystallographic data for **1** and **2** are summarized in Table 1. X-ray diffraction data were collected on a Bruker-APEX II SMART CCD diffractometer at 296 K using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The packages SAINT^[48a] and SADABS^[48b] were used for data processing and absorption correction. The structures were solved by direct and Fourier methods and refined by full-matrix least-squares based on F^2 using SHELXS-97^[48c] and SHELXL-2014/7^[48d] packages.

During the refinement of the structures, C21 and C23 carbon atoms of amine moiety of the doubly deprotonated Schiff base ligand L^{2-} in **1** and **2** were found disordered over two sites. The disorder was fixed/treated allowing each individual atom to refine freely. The final occupancy parameters were set as follows: 0.65 and 0.35 for C21 and 0.50 and 0.50 for C23 in **1**; 0.65 and 0.35 for C21 and 0.65 and 0.35 for C23 in **2**.

Both crystal structures contain solvents of crystallization, all of which were severely disordered. Therefore, squeeze facility of Platon^[48e,f] was utilised to remove disordered solvents. The electron counts per unit cell for the eliminated solvent molecules are 224 (56 per void) and 270 (67 per void) for **1** and **2**, respectively, indicating the presence of two methanol and two water molecules (Z = 4 in **1**) and three methanol and one and half water molecules (Z = 4 in **2**) as solvent of crystallization in the molecular formula. All the hydrogen atoms were inserted in geometrically calculated positions except on O16 oxygen atom of coordinated water ligand that is linked to Ln1 center. All nonhydrogen atoms were refined anisotropically, while all hydrogen atoms were refined isotropically. The final refinement

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converged to the R_1/wR_2 (I>2 σ (I)) values of 0.0605/0.1595, and 0.0546/0.1404 for 1 and 2, respectively.

CCDC 1888578 and 1888579 for **1** and **2**, respectively, contain the supplementary crystallographic data for this paper. These CIF data can also be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information: Figures S1–S10 and Tables S1–S8.

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Keywords: Heptanuclear / Lanthanide(III) / Cobalt(III) / Multiple Relaxation / Luminescent

References

- [1] R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature* **1993**, *365*, 141.
- [2] a) L. Bogani and W. Wernsdorfer, *Nat. Mater.* 2008, 7, 179; b) E. Coronado and A. J. Epsetin, *J. Mater. Chem.* 2009, *19*, 1670.
- [3] a) D. Gatteschi, R. Sessoli and J. Villain, *Molecular Nanomagnets* (Oxford Univ. Press, 2006); b) D. Gatteschi, *Adv. Mater.* 1994, *6*, 635; c) F. Donati, S. Rusponi, S. Stepanow, C. Wäckerlin, A. Singha, L. Persichetti, R. Baltic, K. Diller, F. Patthey, E. Fernandes, J. Dreiser, Z. Šljivančanin, K. Kummer, C. Nistor, P. Gambardella and H. Brune, *Science* 2016, *352*, 318.
- [4] a) M. N. Leuenberger and D. Loss, *Nature* 2001, *410*, 789; b) M. Shiddiq, D. Komijani, Y. Duan, A. Gaita-Ariño, E. Coronado and S. Hill, *Nature* 2016, *531*, 348.

10.1002/ejic.201900383

- [5] R. Sessoli, M.-E. Boulon, A. Caneschi, M. Mannini, L. Poggini, F. Wilhelm and A. Rogalev, *Nature Physics* 2015, 11, 69.
- [6] M. Fittipaldi, A. Cini, G. Annino, A. Vindigni, A. Caneschi and R. Sessoli, *Nature Materials* 2019, 18, 329.
- [7] a) R. Sessoli and A. K. Powell, *Coord. Chem. Rev.* 2009, 253, 2328; b) J. D. Rinehart and J. R. Long, *Chem. Sci.* 2011, 2, 2078; c) L. Sorace, C. Benelli and D. Gatteschi, *Chem. Soc. Rev.* 2011, 40, 3092; d) J.-L. Liu, Y.-C. Chen and M.-L. Tong, *Chem. Soc. Rev.* 2018, 47, 2431; e) M. Feng and M.-L. Tong, *Chem. Eur. J.* 2018, 24, 7574; f) Y.-C. Chen, J.-L. Liu, W. Wernsdorfer, D. Liu, L. F. Chibotaru, X.-M. Chen and M.-L. Tong, *Angew. Chem. Int. Ed.* 2017, 56, 4996.
- [8] a) C. A. P. Goodwin, F. Ortu, D. Reta, N. F. Chilton and D. P. Mills, *Nature* 2017, 548, 439; b) F. S. Guo, B.-M. Day, Y.-C. Chen, M.-L. Tong, A. Mansikkamaki and R. A. Layfield, *Angew. Chem., Int. Ed.* 2017, 56, 11445; c) Y.-C. Chen, J.-L. Liu, L. Ungur, J. Liu, Q.-W. Li, L.-F. Wang, Z.-P. Ni, L. F. Chibotaru, X.-M. Chen and M.-L. Tong, *J. Am. Chem. Soc.* 2016, 138, 2829.
- [9] a) J. D. Rinehart, M. Fang, W. J. Evans and J. R. Long, *J. Am. Chem. Soc.* 2011, *133*, 14236; b) J. J. L. Roy, L. Ungur, I. Korobkov, L. F. Chibotaru and M. Murugesu, *J. Am. Chem. Soc.* 2014, *136*, 8003; c) J. Liu, Y.-C. Chen, J.–L. Liu, V. Vieru, L. Ungur, J.-H. Jia, L. F. Chibotaru, Y. Lan, W. Wernsdorfer, S. Gao, X.-M. Chen and M.-L. Tong, *J. Am. Chem. Soc.* 2016, *138*, 5441.
- [10] a) W. E. Wallace, *Prog. Solid State Chem.* **1985**, *16*, 127; b) R. J. Radwanskia, R. Michalskia, Z. Ropkaa and A. Blaut, *Phys. B: Condens. Matter* **2002**, *319*, 78.
- [11] N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara and Y. Kaizu, J. Am. Chem. Soc. 2003, 125, 8694.
- [12] a) C. Benelli and D. Gatteschi (Eds.), Introduction to Molecular Magnetism: From Transition Metals to Lanthanides, John Wiley & Sons 2015; b) W. Linert and M. Verdaguer (Eds), Molecular Magnets Recent Highlights, Springer Science & Business Media 2012; c) R. E. P. Winpenny and G. Aromí, Single-Molecule Magnets and Related Phenomena, Springer 2006; d) D. Gatteschi, Adv. Mater. 1994, 6, 635; e) L. Bogani and W. Wernsdorfer, Nat. Mater. 2008, 7, 179; f) Y.-Z. Zheng, G.-J. Zhou, Z. Zheng and R. E. P. Winpenny, Chem. Soc. Rev. 2014, 43, 1462.
- [13] a) S. M. J. Aubin, M. W. Wemple, D. M. Adams, H.-L. Tsai, G. Christou and D. N. Hendrickson, J. Am. Chem. Soc. 1996, 118, 7746; b) S. M. J. Aubin, N. R. Dilley, M. W. Wemple, M. B. Maple, G. Christou and D. N. Hendrickson, J. Am. Chem. Soc. 1998, 120, 839; c) H. Andres, F. Basler, H.-U. Güdel, G. Aromí, G. Christou, H. Büttner and B. Rufflé, J. Am. Chem. Soc. 2000, 122, 12469; d) T. C. Stamatatos and

G. Christou, *Inorg. Chem.* **2009**, *48*, 3308; e) S. Mukherjee, K. A. Abboud, W. Wernsdorfer and G. Christou, *Inorg. Chem.* **2013**, *52*, 873; f) P. Cucos, L. Sorace, C. Maxim, S. Shova, D. Patroi, A. Caneschi and M. Andruh, *Inorg. Chem.* **2017**, *56*, 11668.

- [14] a) G. Aromí and E. K. Brechin, *Struct. Bonding* 2006, *122*, 1; b) M. Murrie, *Chem. Soc. Rev.* 2010, *39*, 1986.
- [15] a) D. N. Woodruff, R. E. P. Winpenny and R. A. Layfield, *Chem. Rev.* 2013, *113*, 5110; b) R. J. Holmberg and M. Murugesu, *J. Mater. Chem. C* 2015, *3*, 11986; c) Y.-S. Meng, S.-D. Jiang, B.-W. Wang and S. Gao, *Acc. Chem. Res.* 2016, *49*, 2381; d) S. T. Liddle and J. V. Slageren, *Chem. Soc. Rev.* 2015, *44*, 6655; e) K. Liu, X. Zhang, X. Meng, W. Shi, P. Chengab and A. K. Powell, *Chem. Soc. Rev.* 2016, *45*, 2423; f) Y.-N. Guo, G.-F. Xu, Y. Guo and J. Tang, *Dalton Trans.* 2011, *40*, 9953.
- [16] a) S. K. Gupta, T. Rajeshkumar, G. Rajaraman and R. Murugavel, *Chem. Sci.* 2016, 7, 5181; b) J. Ruiz, A. J. Mota, A. Rodríguez-Diéguez, S. Titos, J. M. Herrera, E. Ruiz, E. Cremades, J. P. Costes and E. Colacio, *Chem. Commun.* 2012, 48, 7916; c) A. J. Brown, D. Pinkowicz, M. R. Saber and K. R. Dunbar, *Angew. Chem. Int. Ed.* 2015, 54, 5864; d) M. Ren, D. Pinkowicz, M. Yoon, K. Kim, L.-M. Zheng, B. K. Breedlove and M. Yamashita, *Inorg. Chem.* 2013, 52, 8342.
- [17] L. F. Chibotaru, L. Ungur and A. Soncini, Angew. Chem. Int. Ed. 2008, 47, 4126.
- [18] a) C. Das, S. Vaidya, T. Gupta, J. M. Frost, M. Righi, E. K. Brechin, M. Affronte, G. Rajaraman and M. Shanmugam, *Chem. Eur. J.* 2015, *21*, 15639; b) H.-L. Gao, S.-X. Huang, X.-P. Zhou, Z. Liu and J.-Z. Cui, *Dalton Trans.* 2018, *47*, 3503; c) S. Biswas, S. Das, T. Gupta, S. K. Singh, M. Pissas, G. Rajaraman and V. Chandrasekhar, *Chem. Eur. J.* 2016, *22*, 18532.
- [19] I. J. Hewitt, J. Tang, N. T. Madhu, C. E. Anson, Y. Lan, J. Luzon, M. Etienne, R. Sessoli and A. K. Powell, *Angew. Chem. Int. Ed.* 2010, 49, 6352.
- [20] a) H. Zhang, S.-Y. Lin, S. Xue, C. Wanga and J. Tang, *Dalton Trans.* 2014, 43, 6262;
 b) B. Joarder, A. K. Chaudhari, G. Rogezb and S. K. Ghosh, *Dalton Trans.* 2012, 41, 7695; c) L. Sun, S. Wei, J. Zhang, W. Wang, S. Chen, Y. Zhang, Q. Wei, G. Xie and S. Gao, *J. Mater. Chem. C* 2017, 5, 9488.
- [21] a) J. Goura, A. Chakraborty, J. P. S. Walsh, F. Tuna and V. Chandrasekhar, *Cryst. Growth Des.* 2015, *15*, 3157; b) S. K. Langley, D. P. Wielechowski, V. Vieru, N. F. Chilton, B. Moubaraki, B. F. Abrahams, L. F. Chibotaru and K. S. Murray, *Angew. Chem. Int. Ed.* 2013, *52*, 12014; c) J.-L. Liu, J.-Y. Wu, Y.-C. Chen, V. Mereacre, A. K. Powell, L. Ungur, L. F. Chibotaru, X.-M. Chen and M.-L. Tong, *Angew. Chem.*

Int. Ed. **2014**, *53*, 12966; d) J.-L. Liu, J.-Y. Wu, G.-Z. Huang, Y.-C. Chen, J.-H. Jia, L. Ungur, L. F. Chibotaru, X.-M. Chen and M.-L. Tong, *Sci. Rep.* **2015**, *5*, 16621.

- [22] a) M. M. Hänninen, A. J. Mota, R. Sillanpää, S. Dey, G. Velmurugan, G. Rajaraman and E. Colacio, *Inorg. Chem.* 2018, 57, 3683; b) K. R. Vignesh, S. K. Langley, B. Moubaraki, K. S. Murray and G. Rajaraman, *Chem. Eur. J.* 2015, 21, 16364.
- [23] D. Schray, G. Abbas, Y. Lan, V. Mereacre, A. Sundt, J. Dreiser, O. Waldmann, G. E. Kostakis, C. E. Anson and A. K. Powell, *Angew. Chem.* 2010, 122, 5312.
- [24] a) K. R. Vignesh, A. Soncini, S. K. Langley, W. Wernsdorfer, K. S. Murray and G. Rajaraman, *Nat. Commun.* 2017, *8*, 1023; b) K. R. Vignesh, S. K. Langley, A. Swain, B. Moubaraki, M. Damjanović, W. Wernsdorfer, G. Rajaraman and K. S. Murray, *Angew. Chem. Int. Ed.* 2018, *57*, 779.
- [25] a) M. J. H. Ojea, V. A. Milway, G. Velmurugan, L. H. Thomas, S. J. Coles, C. Wilson, W. Wernsdorfer, G. Rajaraman and M. Murrie, *Chem. Eur. J.* 2016, 22, 12839; b) D. I. Alexandropoulos, K. M. Poole, L. Cunha-Silva, J. A. Sheikh, W. Wernsdorfer, G. Christou and T. C. Stamatatos, *Chem. Commun.* 2017, 53, 4266; c) E. Lucaccini, M. Briganti, M. Perfetti, L. Vendier, J.-P. Costes, F. Totti, R. Sessoli and L. Sorace, *Chem. Eur. J.* 2016, 22, 5552.
- [26] a) N. Ahmed, C. Das, S. Vaidya, S. K. Langley, K. S. Murray and M. Shanmugam, *Chem. Eur. J.* 2014, 20, 14235; b) A. B. Canaj, D. A. Kalofolias, M. Siczek, T. Lis, R. McNab, G. Lorusso, R. Inglis, M. Evangelisti, C. J. Milios, *Dalton Trans.* 2017, 46, 3449; c) S. Mandal, S. Ghosh, D. Takahashi, G. Christou and S. Mohanta, *Eur. J. Inorg. Chem.* 2018, 2793.
- [27] a) A. Upadhyay, C. Das, S. Vaidya, S. K. Singh, T. Gupta, R. Mondol, S. K. Langley, K. S. Murray, G. Rajaraman and M. Shanmugam, *Chem. Eur. J.* 2017, 23, 4903; b) J. P. Costes, S. Titos-Padilla, I. Oyarzabal, T. Gupta, C. Duhayon, G. Rajaraman and E. Colacio, *Chem. Eur. J.* 2015, 21, 15785; c) K. R. Vignesh, S. K. Langley, K. S. Murray and G. Rajaraman, *Inorg. Chem.* 2017, 56, 2518; d) J. Goura, E, Colacio, J. M. Herrera, E. A. Suturina, I. Kuprov, Y. Lan, W. Wernsdorfer and V. Chandrasekhar, *Chem. Eur. J.* 2017, 23, 16621; e) R. J. Blagg, L. Ungur, F. Tuna, J. Speak, P. Comar, D. Collison, W. Wernsdorfer, E. J. L. McInnes, L. F. Chibotaru and R. E. P. Winpenny, *Nature Chem.* 2013, 5, 673; f) S. Das, K. S. Bejoymohandas, A. Dey, S. Biswas, M. L. P. Reddy, R. Morales, E. Ruiz, S. Titos-Padilla, E. Colacio and V. Chandrasekhar, *Chem. Eur. J.* 2015, 21, 6449; g) A. Amjad, A. M. Madalan, M. Andruh, A. Caneschi and L. Sorace, *Chem. Eur. J.* 2016, 22, 12849; h) S. Hazra, J. Titiš, D. Valigura, R. Boča and S. Mohanta, *Dalton Trans.* 2016, 45, 7510.

- 36
- [28] a) J. C. G. Bünzli, *Chem. Rev.* 2010, *110*, 2729; b) J. C. G. Bünzli, *Coord. Chem. Rev.* 2015, 293–294, 19; c) S. V. Eliseeva and J. C. G. Bünzli, *Chem. Soc. Rev.* 2010, *39*, 189.
- [29] a) J. C. G. Bünzli and C. Piguet, *Chem. Soc. Rev.* 2005, 34, 1048; b) D. Parker, *Chem. Soc. Rev.* 2004, 33, 156; c) Y. Hasegawa, Y. Wada and S. Yanayida, *J. Photochem. Photobiol. C* 2004, 5, 183.
- [30] a) L. D. Carlos, R. A. Ferreira, Z. B. V. De, B. Julián-López and P. Escribano, *Chem. Soc. Rev.* 2011, 40, 536; b) L. Wu, Y. Zhang, M.-Y. Gui, P.-Z. Lu, L.-X. Zhao, S. Tian, Y.-F. Kong and J.-J. Xu, *J. Mater. Chem.* 2012, 22, 6463; c) C. Uetrecht, R. J. Rose, E. V. Duijn, K. Lorenzen and A. J. R. Heck, *Chem. Soc. Rev.* 2010, 39, 1633; d) J. Feng and H. Zhang, *Chem. Soc. Rev.* 2013, 44, 387; e) J. Long, Y. Guari, R. A. S. Ferreira, L. D. Carlos and J. Larionova, *Coord. Chem. Rev.* 2018, 363, 57; f) S. Faulkner, S. J. A. Pope and B. P. Burton-Pye, *Appl. Spectrosc. Rev.* 2005, 40, 1; g) S. Lin, *Chem. Soc. Rev.* 2004, 33, 445.
- [31] a) X.-L. Li, J. Li, C. Zhu, B. Han, Y. Liu, Z. Yin, F. Li and C.-M. Liu, *New J. Chem.* 2018, 42, 16992; b) P.-H. Guo, Y. Meng, Y.-C. Chen, Q.-W. Li, B.-Y. Wang, J.-D. Leng, D.-H. Bao, J.-H. Jia and M.-L. Tong, *J. Mater. Chem. C* 2014, 2, 8858; c) P.-H. Guo, J.-L. Liu, J.-H. Jia, J. Wang, F.-S. Guo, Y.-C. Chen, W.-Q. Lin, J.-D. Leng, D.-H. Bao, X.-D. Zhang, J.-H. Luo and M.-L. Tong, *Chem. Eur. J.* 2013, *19*, 8769; d) F. Pointillart, B. Le. Guennic, O. Cador, O. Maury and L. Ouahab, *Acc. Chem. Res.* 2015, *48*, 2834; e) E. L. Gavey, M. A. Hareri, J. Regier, L. D. Carlos, R. A. S. Ferreira, F. S. Razavi, J. M. Rawson and M. Pilkington, *J. Mater. Chem. C* 2015, *3*, 7738; f) J.-H. Jia, Q.-W. Li, Y.-C. Chen, J.-L. Liu and M.-L. Tong, *Coord. Chem. Rev* 2017, DOI: 10.1016/j.ccr.2017.11.012; g) S. Chorazy, J. Wang and S.-I. Ohkoshi, *Chem. Commun.* 2016, *52*, 10795; h) S. Chorazy, K. Kumar, K. Nakabayashi, B. Sieklucka and S.-I. Ohkoshi, *Inorg. Chem.* 2017, *56*, 5239.
- [32] a) H. Ke, G.-F. Xu, L. Zhao, J. Tang, X.-Y. Zhang and H.-J. Zhang, *Chem. Eur. J.* 2009, *15*, 10335; b) A. Dey, S. Das, S. Kundu and V. Chandrasekhar, *CrystEngComm* 2014, *16*, 1304; c) H. Ke, L. Zhao, G.-F. Xu, Y.-N. Guo, J. Tang, X.-Y. Zhang and H.-J. Zhang, *Dalton Trans.* 2009, 10609; d) P.-P. Yang, X.-L. Wang, L.-C. Li and D.-Z. Liao, *Dalton Trans.* 2011, *40*, 4155; e) H. Ke, L. Zhao, Y. Guo and J. Tang, *Dalton Trans.* 2012, *41*, 2314; f) H. Ke, L. Zhao, Y. Guo and J. Tang, *Dalton Trans.* 2012, *41*, 9760; g) S. Shen, S. Xue, S.-Y. Lin, L. Zhao and J. Tang, *Dalton Trans.* 2013, *42*, 10413; h) H.-H. Zou, R. Wang, Z.-L. Chen, D.-C. Liu and F.-P. Liang, *Dalton Trans.* 2014, *43*, 2581; i) H.-H. Zou, L.-B. Sheng, F.-P. Liang, Z.-L. Chena and Y.-Q. Zhang, *Dalton Trans.* 2015, *44*, 18544; j) Y.-M. Li, W.-W. Kuang, L.-L. Zhu, Y. Xu and P.-P. Yang, *Eur. J. Inorg. Chem.* 2016, 4996; k) G. Wu, I. J. Hewitt, S. Mameri, Y. Lan, R. Cle´rac, C. E. Anson, S. Qiu and A. K. Powell, *Inorg. Chem.* 2008, *47*, 8604; m) A. K. Jami, V. Baskar and E. C. Sañudo, *Inorg. Chem.* 2013, *52*, 2432; n) I. A.

Kühne, G. E. Kostakis, C. E. Anson and A. K. Powell, *Inorg. Chem.* **2016**, *55*, 4072; o) Y.-Z. Zheng, Y. Lan, C. E. Anson and A. K. Powell, *Inorg. Chem.* **2008**, *47*, 10813.

- [33] a) C.-B. Tian, D.-Q. Yuan, Y.-H. Han, Z.-H. Li, P. Lin and S.-W. Du, *Inorg. Chem. Front.* 2014, *1*, 695; b) Z.-Y. Liu, H.-H. Zou, R. Wang, M.-S. Chen and F.-P. Liang, *RSc. Adv.* 2018, 8, 767.
- [34] a) N. E. Brese and M. O'Keeffe, *Acta Cryst.* 1991, *B47*, 192; b) I. D. Brown and D. Altermatt, *Acta Cryst.* 1985, *B41*, 244; c) H. H. Thorp, *Inorg. Chem.* 1992, *31*, 1585; d) W. Liu and H. H. Thorp, *Inorg. Chem.* 1993, *32*, 4102.
- [35] a) J. Cirera, E. Ruiz and S. Alvarez, *Chem. Eur. J.* 2006, *12*, 3162; b) M. Pinsk and D. Avnir, *Inorg. Chem.* 1998, *37*, 5575.
- [36] PHI Software. N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini and K. S. Murray, *J. Comput. Chem.* **2013**, *34*, 1164.
- [37] a) S. D. Jiang, B. W. Wang, H. L. Sun, Z. M. Wang and S. Gao, *J. Am. Chem. Soc.* 2011, *133*, 4730; b) S. D. Jiang, B. W. Wang, G. Su, Z. M. Wang and S. Gao, *Angew. Chem., Int. Ed.* 2010, *49*, 7448; c) P.-H. Lin, W.-B. Sun, M.-F. Yu, G.-M. Li, P.-F. Yan and M. Murugesu, *Chem. Commun.* 2011, *47*, 10993.
- [38] a) Y.-N. Guo, G.-F. Xu, W. Wernsdorfer, L. Ungur, Y. Guo, J. Tang, H.-J. Zhang, L. F. Chibotaru, and A. K. Powell, J. Am. Chem. Soc. 2011, 133, 11948; b) A. Venugopal, F. Tuna, T. R. Spaniol, L. Ungur, L. F. Chibotaru, J. Okuda and R. A. Layfield, Chem. Commun. 2013, 49, 901; c) S.-Y. Lin, Y.-N. Guo, Y. Guo, L. Zhao, P. Zhang, H. Ke and J. Tang, Chem. Commun. 2012, 48, 6924; d) P.-E. Car, M. Perfetti, M. Mannini, A. Favre, A. Caneschi and R. Sessoli, Chem. Commun. 2011, 47, 3751.
- [39] M. Grahl, J. Kotzler and I. Sessler, J. Magn. Magn. Mater. 1990, 90–1, 187.
- [40] D. Gatteschi, R. Sessoli and J. Villain, *Molecular Nanomagnets*, OUP, Oxford, **2006**, 69.
- [41] N. F. Chilton, D. Collison, E. J. L. McInnes, R. E. P. Winpenny, A. Soncini, *Nat. Commun.* 2013, 4, 2551.
- [42] a) A. V. Funes, L. Carrella, E. Rentschler and P. Albores, *Chem. Eur. J.* 2016, 22, 14308; b) S. Mukherjee, J. Lu, G. Velmurugan, S. Singh, G. Rajaraman, J. Tang and S. K. Ghosh, *Inorg. Chem.* 2016, 55, 11283; c) S. K. Langley, N. F. Chilton, I. A. Gass, B. Moubaraki and K. S. Murray, *Dalton Trans.* 2011, 40, 12656.

10.1002/ejic.201900383

- [43] P. Bag, C. K. Rastogi, S. Biswas, S. Sivakumar, V. Mereacre and V. Chandrasekhar, *Dalton Trans.* **2015**, *44*, 4328.
 - [44] a) M. Dolai, M. Ali, J. Titiš and R. Boča, *Dalton Trans.* 2015, 44, 13242; b) C.-M. Liu, D.-Q. Zhang, X. Hao and D.-B. Zhu, Chem. Asian J. 2014, 9, 1847; c) J. Goura, J. Brambleby, P. Goddard and V. Chandrasekhar, *Chem. Eur. J.* 2015, 21, 4926; d) S. Xue, L. Ungur, Y.-N. Guo, J. Tang and L. F. Chibotaru, Inorg. Chem. 2014, 53, 12658; e) S. K. Langley, N. F. Chilton, B. Moubaraki and K. S. Murray, Chem. Commun. 2013, 49, 6965; f) S. K. Langley, C. Le, L. Ungur, B. Moubaraki, B. F. Abrahams, L. F. Chibotaru and K. S. Murray, Inorg. Chem. 2015, 54, 3631; g) S. K. Langley, N. F. Chilton, B. Moubaraki and K. S. Murray, Inorg. Chem. Front. 2015, 2, 867; h) A. V. Funes, L. Carrella, E. Rentschler and P. Alborés, Dalton Trans. 2014, 43, 2361; i) S. K. Langley, N. F. Chilton, B. Moubaraki and K. S. Murray, Inorg. Chem. 2013, 52, 7183; j) L. Zhao, J. Wu, S. Xue and J. Tang, Chem. Asian J. 2012, 7, 2419; k) S. K. Langley, L. Ungur, N. F. Chilton, B. Moubaraki, L. F. Chibotaru and K. S. Murray, Inorg. Chem. 2014, 53, 4303; 1) G.-F. Xu, P. Gamez, J. Tang, R. Clerac, Y.-N. Guo and Y. Guo, Inorg. Chem. 2012, 51, 5693; m) J. A. Sheikh, S. Goswami and S. Konar, Dalton Trans. 2014, 43, 14577; n) S.-Y. Jhan, S.-H. Huang, C.-I Yang and H.-L. Tsai, Polyhedron 2013, 66, 222; o) C.-B. Tian, D.-Q. Yuan, Y.-H. Han, Z.-H. Li, P. Lin and S.-W. Du, Inorg. Chem. Front. 2014, 1, 695; p) J. Feuersenger, D. Prodius, V. Mereacre, R. Clerac, C. E. Anson and A. K. Powell, Polyhedron 2013, 66, 257.
 - [45] a) S. M. Aldoshin, N. A. Sanina, S. E. Solov´eva, I. S. Antipin, A. I. Dmitriev, R. B. Morgunov, D. V. Korchagin, G. V. Shilov, A. N. Utenyshev and K. V. BozhenkoSer, *Russ.Chem.Bull., Int.Ed.* 2014, 63, 1465; b) D. S. Chao, B. Y. Feng, Y. Yang and L. WuPing, *Scientia Sinica Chimica* 2012, 42, 1356; c) W.-B. Yang, H.-Q. Huang, Z.-Y. Li, R.-B. Liu and J.-J. Zhang, *Chin. J. Struct. Chem.* 2012, 31, 971; d) B.-Q. Ma, S. Gao, O. Bai, H.-Ling Sun and G.-X. Xu, *J. C. S., Dalton Trans.* 2000, 1003.
 - [46] a) I. J. Hewitt, Y. Lan, C. E. Anson, J. Luzon, R. Sessoli and A. K. Powell, *Chem. Commun.* 2009, 6765; b) Y.-X. Wang, W. Shi, H. Li, Y. Song, L. Fang, Y. Lan, A. K. Powell, W. Wernsdorfer, L. Ungur, L. F. Chibotaru, M. Shen and P. Cheng, *Chem. Sci.* 2012, *3*, 3366; c) S.-Y. Lin, L. Zhao, Y.-N. Guo, P. Zhang, Y. Guo and J. Tang, *Inorg. Chem.* 2012, *51*, 10522; d) M. M. Hanninen, A. J. Mota, D. Aravena, E. Ruiz, Reijo Sillanpaa, A. Camon, M. Evangelisti and E. Colacio, *Chem. Eur. J.* 2014, *20*, 8410; e) N. F. Chilton, G. B. Deacon, O. Gazukin, P. C. Junk, B. Kersting, S. K. Langley, B. Moubaraki, K. S. Murray, F. Schleife, M. Shome, D. R. Turner and J. A. Walker, *Inorg. Chem.* 2014, *53*, 2528; f) R. Grindell, V. Vieru, T. Pugh, L. F. Chibotaru and R. A. Layfield, *Dalton Trans.* 2016, *45*, 16556; g) I. F. Díaz-Ortega, J. M. Herrera, T. Gupta, G. Rajaraman, H. Nojiri and E. Colacio, *Inorg. Chem.* 2017, *56*, 5594; h) Y. Peng, C. E. Anson and A. K. Powell, *ChemPlusChem* 2018, *83*, 676.
 - [47] W. J. Geary, *Chem. Rev.* **1971**, *7*, 81.

[48] a) Bruker–Nonius 2004, APEX-II, SAINT-Plus and TWINABS. Bruker–Nonius AXS Inc. Madison, Wisconsin, USA; b) G. M. Sheldrick, SAINT (Version 6.02), SADABS (Version 2.03), Bruker AXS Inc. Madison, Wisconsin, 2002; c) G. M. Sheldrick, SHELXS-97, Crystal Structure Solution Program, University of Göttingen, 2008; d) G. M. Sheldrick, SHELXL-2014/7, Crystal Structure Refinement Program, University of Göttingen, 2014; e) A. L. Spek, J. Appl. Crystallogr. 2003, 36, 7; f) A. L. Spek, Acta Crystallogr., Sect. D: Biol. Crystallogr. 2009, 65, 148.

Illustrated Synopsis For

Synthesis, Crystal Structures, Magnetic and Fluorescence Properties of Two Heptanuclear Co^{III}₄Ln^{III}₃ Compounds (Ln= Gd^{III}, Dy^{III}): Multiple Relaxation Dynamics in Dy^{III} Analogue

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Key Topic: Magnetic–Luminescence Bifunctional

This manuscript describes two new types of heptanuclear $\text{Co}^{\text{III}}_{4}\text{Ln}^{\text{III}}_{3}$ (Ln^{III} = Gd^{III} and Dy^{III}) clusters having 'sand-clock' like structure. The Gd^{III} centers in **1** are antiferromagnetically coupled, while the Dy^{III} analogue **2** is a luminescent SMM with two well resolved relaxation channels at zero-field.

