



# Synthesis, Crystal Structures and Magnetic Properties of New Hexanuclear Mn<sup>III</sup><sub>2</sub>Ln<sup>III</sup><sub>4</sub> Complexes: SMM Behavior of the Terbium(III) Analogue

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This investigation reports the syntheses, crystal structures and magnetic properties of a series of isomorphous hexanuclear  $Mn_{2}^{III}Ln_{4}^{III}$  compounds of compositions  $[Mn_{2}^{III}Ln_{4}^{III}L_{2}^{1}L_{2}^{2}(\mu_{3}-\mu_{3})]$  $OH_{4}(\mu_{1,3}-Pivalate)_{6}(NO_{3})_{2}] \cdot 2CH_{3}CN$  (Ln = Tb (1), Dy (2), Ho (3), Er (4)), where  $H_{2}L^{1}$  is the Schiff base ligand that is obtained by [1+1] condensation of 3-methoxysalicylaldehyde (HL<sup>2</sup>) with 2-amino-2-methyl-1-propanol. While the O(phenoxo)N(imine)O(alkoxo) pocket of the ligand  $[L^1]^{2-}$  binds a Mn<sup>III</sup> ion, the other pocket, O(methoxy)O(phenoxo), remains noncoordinated. In contrast, each of the O(methoxy)O(phenoxo) and O(phenoxo)O(aldehyde)) sites of  $[L^2]^-$  is occupied by a  $Ln^{III}$  ion. Additionally, there are four  $\mu_3$ -hydroxo, six  $\mu_{1,3}$ -pivalate and two chelating nitrate ligands, stabilizing the hexanuclear cores. Magnetic susceptibility (2-300 K) and magnetization (M) data reveal significant anisotropy in 1-4. Detailed ac susceptibility measurements have revealed single molecule magnet (SMM) behavior in the Tb<sup>III</sup> analogue with  $U_{\rm eff} = 11.12 \text{ cm}^{-1}$  and  $\tau_0 = 1.04 \times 10^{-7} \text{ s}$ under 1000 Oe dc field and  $U_{\rm eff} = 10.42 \text{ cm}^{-1}$  and  $\tau_0 = 1.62 \times 10^{-7} \text{ s under 3500 Oe dc field}$ while the other three analogues do not show slow relaxation of magnetization.

# Introduction

Single molecule magnets (SMMs) are molecules possessing one or more paramagnetic centers that exhibit slow relaxation.<sup>[1-5]</sup> The origin of slow relaxation of magnetization in SMMs is the existence of an energy barrier  $(U_{eff})$  that opposes the reversal of the magnetization after the removal of the magnetic field. They may also exhibit a hysteresis loop below a blocking temperature,  $T_{\rm B}$ .<sup>[4,5]</sup> In contrast to the conventional magnets where magnetism arises from the bulk, the magnetic memory of SMMs arises solely from the molecule itself and therefore SMMs have potential application in advanced technological devices related to high-density data storage,<sup>[2a,6]</sup> quantum computing<sup>[7]</sup> and spintronics.<sup>[8]</sup> The larger the  $U_{\rm eff}$  and  $T_{\rm B}$  values of an SMM, the greater the feasibility of its application in devices. The best reported  $U_{\rm eff}$  and  $T_{\rm B}$  values for a SMM are 1223 cm<sup>-1</sup> and 60 K, respectively, and the concerned system is a mononuclear dysprosium(III) molecule, dysprosocenium, which has been published very recently.<sup>[4a,b]</sup> Much efforts in this field are directed toward the enhancement of  $U_{\rm eff}$  and  $T_{\rm B}$  values with the aim of pushing the applications of this class of materials. This requires synthesis of new molecules that show slow magnetic relaxation and particularly metal complexes assembled from ligands that have not been utilized in the area of SMMs. The later aspect is one focus of our investigation.

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Gatteschi and co-workers have reported the first observation of SMM behaviour in a molecular system, a dodecanuclear  $Mn_{8}^{II}Mn_{4}^{IV}$  cluster ( $Mn_{12}$ ), in early 1990s.<sup>[1]</sup> The inherent single-ion zero-field splitting of the Jahn-Teller Mn<sup>III</sup> ion was assumed to be the key responsible factor for the overall uniaxial anisotropy (negative D value) and magnetic bistability of the compound, and thus sufficient energy barrier is observed. Despite extensive research on exchange-coupled 3d SMMs containing anisotropic Mn<sup>III</sup>, Co<sup>II</sup> or other 3d ions, no much improvement in SMM properties was observed; the blocking temperature  $(T_{\rm B})$  of any 3d-SMM is below 5  $K^{[9-11]}$  and the best  $U_{eff}$  value obtained is only 63 cm<sup>-1.[10e]</sup> The second milestone in the area of SMMs was laid by Ishikawa et al. who reported the first lanthanide based SMM, [NBu<sub>4</sub>][Tb(phthalocyanine)<sub>2</sub>], with  $U_{eff} = 230 \text{ cm}^{-1}$ .<sup>[12]</sup> Since then, numerous 4f<sup>[2e,3-5,13-21]</sup> and 3d-4f<sup>[22-27]</sup> systems of different nuclearity and dimensionality have been reported with the orientation to improve the key parameter values of the SMMs and also to understand the underlying fundamental aspects. Theoretical models have been proposed and *ab initio* calculations have been performed to rationalize the magnetic phenomena of the lanthanide based systems.<sup>[4c,5b,c,13a-c,15a,17,18a,c,21c,23a,b,25a-c,26a]</sup> It has been understood that high magnetic moment and inherent anisotropy associated with most lanthanides (particularly heavier ones) as a result of strong spin-orbit coupling make these metal ions alluring members to explore the area of SMMs.

Here we describe the results of our investigation focused on hexametallic systems that comprise both anisotropic Mn<sup>III</sup> ions and anisotropic Ln<sup>III</sup> ions. It is worth mentioning that the [1+1] condensation products of 3-methoxysalicylaldehyde and an aminoalcohol<sup>[18a,28,29]</sup> or an aminophenol<sup>[27a,30]</sup> have previously been used to isolate 4f and 3d-4f compounds, with a number of them being shown to be SMMs; in fact, it is not overwhelming to say that this family of ligands have occupied a dominating position in 3d-4f and 4f molecular magnetic systems. The interesting aspect of such ligands is that there are two types of pockets, O(phenoxo)O(alkoxido)N(imine) (Pocket I; as in Scheme 1) that can bind with a 3d metal ion more potentially, and O(phenoxo)O(methoxy) (Pocket II; as in Scheme 1) that preferentially coordinates a 4f metal ion. It is also well known that different types of compounds with different types of properties may be obtained through slight modification of the ligands. It is worth noting that although several aminoalcohols and aminophenols have been utilized to derive 4f or 3d-4f compounds from 3-methoxysalicylaldehyde–aminoalcohol/aminophenol ligands, 2-amino-2-methyl-1-propanol has not been so far utilized in this area.

We have prepared a series of  $Mn_{2}^{III}Ln_{4}^{III}$  compounds of composition  $[Mn_{2}^{III}Ln_{4}^{III}L_{2}L_{2}^{2}(\mu_{3}-OH)_{4}(\mu_{1,3}-Pivalate)_{6}(NO_{3})_{2}]\cdot 2CH_{3}CN$  (Ln = Tb (1), Dy (2), Ho (3), Er

(4)), where  $H_2L^1$  is the Schiff base ligand (Scheme 1) obtained from [1+1] condensation of 3methoxysalicylaldehyde with 2-amino-2-methyl-1-propanol and  $HL^2$  is 3methoxysalicylaldehyde. Herein, we report the syntheses, crystal structures and dc and ac magnetic properties of 1–4.



Scheme 1. Chemical structures of the ligands.

#### **Result and Discussion**

#### Syntheses

 $H_2L^1$  solution. A solution of 2-amino-2-methyl-1-propanol (0.09 g, 1 mmol) in 5 mL methanol was added dropwise to a 10 mL methanol solution of 3-methoxy salicylaldehyde (0.15 g, 1 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 'H<sub>2</sub>L<sup>1</sup> solution' was considered to contain 1 mmol of the ligand H<sub>2</sub>L<sup>1</sup> and was utilized for subsequent reactions without further purification.

#### Description of the crystal structures of 1-4.

All four compounds of general composition  $[Mn^{III}_{2}Ln^{III}_{4}L^{1}_{2}L^{2}_{2}(\mu_{3}-OH)_{4}(\mu_{1,3}-Pivalate)_{6}(NO_{3})_{2}]\cdot 2CH_{3}CN$  (1, Ln = Tb; 2, Ln = Dy; 3, Ln = Ho; 4, Ln = Er) crystallize in the same crystal system, monoclinic, and same space group,  $P2_{1}/n$ , with closely similar values of unit cell parameters (Table 1), revealing that these four 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 the four compounds are shown in Figures 1 (1), S1 (2), S2 (3) and 2 (4). The structures show that these four compounds are isostructural as well; a simplified and general schematic presentation of their structures is shown in Scheme 2.

1	<u> </u>	3	4
$C_{74}H_{108}N_6O_{34}Mn_2Tb_4$	$C_{74}H_{108}N_6O_{34}Mn_2Dy_4$	$C_{74}H_{108}N_6O_{34}Mn_2Ho_4$	$C_{74}H_{108}N_6O_{34}Mn_2Er_4$
2371.22	2385.54	2395.26	2404.58
Monoclinic	Monoclinic	Monoclinic	Monoclinic
$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
13.0489(4)	13.0539(7)	12.9833(7)	+12.9864(16)
20.7132(7)	20.7041(12)	20.6228(11)	20.648(2)
17.3890(6)	17.3673(10)	17.2875(9)	17.278(2)
90	90	90	90
91.7740(10)	91.817(2)	91.883(2)	91.976(2)
90	90	90	90
4697.7(3)	4691.5(5)	4626.3(4)	4630.1(9)
2	2	2	2
296(2)	296(2)	296(2)	296(2)
3.058 - 73.396	3.062 - 55.60	3.076 - 55.99	3.074 - 51.80
3.311	3.486	3.726	3.930
1.676	1.689	1.719	1.725
2352	2360	2368	2376
Multi-scan	Multi-scan	Multi-scan	Multi-scan
$-21 \le h \le 21$	$-16 \le h \le 16$	$-16 \le h \le 16$	$0.5 \le h \le 15$
$-34 \le k \le 33$	$-27 \le k \le 27$	$-27 \le k \le 27$	$-25 \le k \le 23$
$-29 \le l \le 29$	$-22 \le l \le 21$	$-22 \le l \le 20$	$21 \le l \le 20$
83444	59112	60066	33613
22901 (0.0399)	10871 (0.0682)	10938 (0.0541)	8818 (0.0689)
			ö
0.0384, 0.0808	0.0374, 0.0769	0.0379, 0.0911	0.0427, 0.0853
0.0758, 0.1001	0.0784, 0.0928	0.0634, 0.1048	0 0780, 0.0989
1.027	1.004	1.022	1.002
	1 $C_{74}H_{108}N_6O_{34}Mn_2Tb_4$ 2371.22         Monoclinic $P2_1/n$ 13.0489(4)         20.7132(7)         17.3890(6)         90         91.7740(10)         90         4697.7(3)         2         296(2)         3.058 - 73.396         3.311         1.676         2352         Multi-scan $-21 \le h \le 21$ $-34 \le k \le 33$ $-29 \le l \le 29$ 83444         22901 (0.0399)         0.0384, 0.0808         0.0758, 0.1001         1.027	12 $C_{74}H_{108}N_6O_{34}Mn_2Tb_4$ $C_{74}H_{108}N_6O_{34}Mn_2Dy_4$ 2371.222385.54MonoclinicMonoclinic $P2_1/n$ $P2_1/n$ 13.0489(4)13.0539(7)20.7132(7)20.7041(12)17.3890(6)17.3673(10)909091.7740(10)91.817(2)90904697.7(3)4691.5(5)22296(2)296(2)3.058 - 73.3963.062 - 55.603.3113.4861.6761.68923522360Multi-scanMulti-scan $-21 \le h \le 21$ $-16 \le h \le 16$ $-34 \le k \le 33$ $-27 \le k \le 27$ $-29 \le l \le 29$ $-22 \le l \le 21$ 834445911222901 (0.0399)10871 (0.0682)0.0384, 0.08080.0374, 0.07690.0758, 0.10010.0784, 0.09281.0271.004	$L_{74}H_{108}N_6O_{34}Mn_2Tb_4$ $C_{74}H_{108}N_6O_{34}Mn_2Dy_4$ $C_{74}H_{108}N_6O_{34}Mn_2Ho_4$ 2371.222385.542395.26MonoclinicMonoclinicMonoclinic $P_{21}/n$ $P_{21}/n$ $P_{21}/n$ 13.0489(4)13.0539(7)12.9833(7)20.7132(7)20.7041(12)20.6228(11)17.3890(6)17.3673(10)17.2875(9)90909091.7740(10)91.817(2)91.883(2)90909091.7740(10)91.817(2)296(2)296(2)296(2)296(2)3.058 - 73.3963.062 - 55.603.076 - 55.993.3113.4863.7261.6761.6891.719235223602368Multi-scanMulti-scanMulti-scan $-21 \le h \le 21$ $-16 \le h \le 16$ $-16 \le h \le 16$ $-34 \le k \le 33$ $-27 \le k \le 27$ $-22 \le l \le 20$ $83444$ 591126006622901 (0.0399)10871 (0.0682)10938 (0.0541)0.0384, 0.08080.0374, 0.07690.0379, 0.09110.0758, 0.10010.0784, 0.09280.0634, 0.10481.0271.0041.022

# Table 1. Crystallographic data for 1–4.

<sup>[a]</sup>  $R_1 = [\Sigma ||F_0| - |F_c|| / \Sigma |F_0|].$  <sup>[b]</sup> w $R_2 = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w F_0^4]^{1/2}$ 



**Figure 1.** Crystal structure of  $[Mn^{III}_{2}Tb^{III}_{4}L^{1}_{2}L^{2}_{2}(\mu_{3}-OH)_{4}(\mu_{1,3}-Pivalate)_{6}(NO_{3})_{2}]\cdot 2CH_{3}CN$ (1). Hydrogen atoms, except those of the hydroxide ligands, and acetonitrile molecules of crystallization have been omitted for clarity. Symmetry code: D = -x, 2-y, 2-z.



**Figure 2.** Crystal structure of  $[Mn^{III}_{2}Er^{III}_{4}L^{1}_{2}L^{2}_{2}(\mu_{3}-OH)_{4}(\mu_{1,3}-Pivalate)_{6}(NO_{3})_{2}]\cdot 2CH_{3}CN$  (4). Hydrogen atoms, except those of the hydroxide ligands, and acetonitrile molecules of crystallization have been omitted for clarity. Symmetry code: D = -x, 2-y, -z.



Scheme 2. Simplified illustration of the hexanuclear core in 1–4.

It may be simpler to describe the structures by fragment analyses. Each structure consists of the following species: (i) Two Mn<sup>III</sup>; (ii) Four Ln<sup>III</sup>; (iii) Two deprotonated O(methoxy)O(phenoxo)N(imine)O(alkoxo) Schiff base ligands,  $[L^1]^{2-}$ , where both phenoxo  $H_2L^1$ and alkoxo moieties of are deprotonated; (iv) Two deprotonated O(methoxy)O(phenoxo)O(aldehyde) ligands,  $[L^2]^-$ , where the phenoxo moiety of  $HL^2$  (3methoxysalicylaldehyde) is deprotonated; (v) Four  $\mu_3$ -hydroxo ligands; (vi) Six  $\mu_{1,3}$ -pivalate ligands; (viii) Two chelating nitrate ligands. Of the two pockets of each of the two  $[L^1]^{2-}$ , the O(phenoxo)N(imine)O(alkoxo) pocket is occupied by a Mn<sup>III</sup> ion (Mn1 in O1N1O2/Mn1D in O1DN1DO2D), while the O(methoxy)O(phenoxo) pocket (O3O1/O3DO1D) remains noncoordinated. In this way, the coordination of two  $[L^1]^{2-}$  with two Mn<sup>III</sup> produces two mononuclear Mn<sup>III</sup> fragments. On the other hand, each of the two sites (O(methoxy)O(phenoxo) and O(phenoxo)O(aldehyde)) of each of the two  $[L^2]^-$  ligand fragments is occupied by a  $Ln^{III}$  ion (Ln1 and Ln2D in one  $[L^2]^-$  and Ln1D and Ln2 in the second  $[L^2]^-$ ). Clearly, the two  $Ln^{III}$  centers in one  $[L^2]^-$  ligand are phenoxo bridged. This way, the coordination of two  $[L^2]^-$  with four  $Ln^{III}$  produces two phenoxo-bridged dinuclear Ln<sup>III</sup><sub>2</sub> fragments. The two mononuclear Mn<sup>III</sup> and two dinuclear Ln<sup>III</sup><sub>2</sub> fragments are assembled by the two alkoxo oxygen atoms (O2/O2D) of two  $[L^1]^{2-}$  units and two aldehyde oxygen atoms (O5/O5D) of two  $[L^2]^-$  units to generate a macrocycle; each alkoxo oxygen atom (O2/O2D) coordinates to a Ln<sup>III</sup> ion (Dy1/Dy1D) in addition to a Mn<sup>III</sup> ion (Mn1/Mn1D) and each aldehyde oxygen atom (O5/O5D) coordinates to a Mn<sup>III</sup> ion (Mn1/Mn1D) in addition to a Ln<sup>III</sup> ion (Ln2/Ln2D). One can follow the so-said macrocycle in

Scheme 2 as the following shortest route (a part of blue coloured lines/curves): Mn1– O2(alkoxo)–Ln1–O4(phenoxo)–Ln2D–O5D(aldehyde)–Mn1D–O2D(alkoxo)–Ln1D–

O4D(phenoxo)–Ln2–O5(aldehyde)–Mn1. The already mentioned four  $\mu_3$ -hydroxo ligands in the structures of **1–4** are of two types: (i) The hydroxo oxygen atom (O7/O7D) of each of the two first type hydroxo ligands that bridges one Mn<sup>III</sup> (Mn1/Mn1D) and two Ln<sup>III</sup> (Ln1 and Ln2/Ln1D and Ln2D) ions; (ii) The hydroxo oxygen atom (O8/O8D) of each of the two second type hydroxo ligands that bridges three Ln<sup>III</sup> ions (Ln1, Ln2 and Ln2D/Ln1D, Ln2 and Ln2D). The already mentioned six  $\mu_{1,3}$ -pivalate ligands are of three types: (i) Two type 1 – two oxygen atoms (O9 and O10/O9D and O10D) of this type bridge a 3d and a 4f metal ions (Mn1 and Ln1/Mn1D and Ln1D), which are also bridged by an alkoxo oxygen atom (O2/O2D); (ii) Two type 2 – two oxygen atoms (O11 and O112/O11D and O11D) of this type bridge two phenoxo-bridged 4f metal ions (Ln1 and Ln2D/Ln1D and Ln2) in the said dilanthanide(III) fragments; (iii) Two type 3 – two oxygen atoms (O13 and O14/O13D and O14D) of this type bridge two 4f metal ions (Ln1 and Ln2/Ln1D and Ln2D), which are symmetrically nonequivalent and evidently belong to two different said dilanthanide(III) fragments. Finally, each of the two nitrates in **1–4** coordinates to a Ln<sup>III</sup> center, Ln2/Ln2D, in  $\eta^2$ - mode through two of its oxygen atoms (O15 and O16/O15D and O16D).

The Mn<sup>III</sup> center (Mn1) in 1-4 is six-coordinated by one imine nitrogen atom (N1) and one phenoxo (O1), one  $\mu$ -alkoxo (O2), one  $\mu$ -aldehyde (O5), one  $\mu_3$ -hydroxo (O7) and one  $\mu_{1,3}$ -pivalate (O10) oxygen atoms. As compared in Table 2, the values of corresponding bond lengths and angles involving Mn<sup>III</sup> center in all the four compounds are very close in all but the Mn<sup>III</sup>–O(aldehyde) bond distance; the maximum difference between the maximum and minimum values of Mn<sup>III</sup>–O(aldehyde) bond distances is 0.05 Å, while the ranges of differences between the maximum and minimum values of other Mn<sup>III</sup>–O/N bond distances and O/N-Mn<sup>III</sup>-O/N bond angles are, respectively, 0.004-0.012 Å and 0.15-0.97°. The Mn<sup>III</sup>–O/N bond distances follow a general trend, Mn<sup>III</sup>–O(aldehyde) (e. g., 2.642 Å in 1) >  $Mn^{III}-O(\mu_{1,3}-pivalate (e. g., 2.132 Å in 1) > Mn^{III}-N(imine) (e. g., 1.979 Å in 1) > Mn^{III}-O(\mu_{1,3}-pivalate (e. g., 2.132 Å in 1) > Mn^{III}-O(\mu_{1,3}-pivalate (e. g., 2.132 Å in 1) > Mn^{III}-N(imine) (e. g., 1.979 Å in 1) > Mn^{III}-O(\mu_{1,3}-pivalate (e. g., 2.132 Å in 1) > Mn^{III}-N(imine) (e. g., 1.979 Å in 1) > Mn^{III}-O(\mu_{1,3}-pivalate (e. g., 2.132 Å in 1) > Mn^{III}-N(imine) (e. g., 1.979 Å in 1) > Mn^{III}-O(\mu_{1,3}-pivalate (e. g., 2.132 Å in 1) > Mn^{III}-N(imine) (e. g., 1.979 Å in 1) > Mn^{III}-O(\mu_{1,3}-pivalate (e. g., 2.132 Å in 1) > Mn^{III}-N(imine) (e. g., 1.979 Å in 1) > Mn^{III}-O(\mu_{1,3}-pivalate (e. g., 1.979 Å in 1) > Mn^{III}-O(\mu_{1,3}-pival$ hydroxo) (e. g., 1.937 Å in 1) > Mn<sup>III</sup>–O( $\mu$ -phenoxo) (e. g., 1.863 Å in 1)  $\approx$  Mn<sup>III</sup>–O( $\mu$ alkoxo) (e. g., 1.873 Å in 1). The values of Mn<sup>III</sup>–N/O bond distances involving imine, phenoxo, hydroxo and alkoxo moieties clearly indicate that oxidation state of this metal ion is +3, which is also supported by BVS calculations<sup>[31]</sup> (range of BVS values in 1-4: 3.05–3.10, Table S1). The Mn<sup>III</sup>O<sub>5</sub>N coordination geometry is distorted octahedral as evident from the ranges of the transoid angles (e. g., 162.54-172.21° in 1) and cisoid angles (e. g., 72.83-102.03° in 1).

Coordination	Bond Lengths (Å)	1	2	3	4
environment of Mn(III)					
	Mn1–N1	1.979(3)	1.976(4)	1.975(4)	1.971(6)
	Mn1–O1	1.863(2)	1.869(4)	1.864(4)	1.866(5)
	Mn1–O2/O2D	1.873(2)	1.877(3)	1.866(4)	1.873(5)
	Mn1-O5/O5D	2.6421	2.6280	2.6071	2.5905
	Mn1–O7	1.937(2)	1.939(3)	1.934(4)	1.936(5)
	Mn1-O10	2.132(2)	2.133(4)	2.121(4)	2.123(5)
05/05D	Bond Angles (°)				
	O1-Mn1-O2/O2D	172.21(11)	172.33(17)	172.20(17)	172.5(2)
02/02D	O5/O5D-Mn1-O10	164.482	164.203	163.815	163.67
02/020	O7-Mn1-N1	162.54(10)	162.38(17)	162.48(17)	162.5(2)
Min1	O1-Mn1-N1	91.47(11)	91.31(17)	91.26(17)	91.4(2)
07	O1-Mn1-O5/O5D	87.004	87.246	86.962	87.437
	O1-Mn1-O7	98.27(10)	98.67(16)	98.96(16)	99.1(2)
	O1-Mn1-O10	94.32(10)	94.33(16)	94.28(17)	94.1(2)
010	O2/O2D -Mn1-N1	82.59(10)	82.65(16)	82.61(17)	82.5(2)
	O2/O2D -Mn1- O5/O5D	88.326	88.427	88.640	88.608
	O2/O2D-Mn1-O7	86.27(9)	86.04(15)	85.84(15)	85.7(2)
	O2/O2D-Mn1-O10	91.85(10)	91.57(15)	91.75(16)	91.5(2)
	O5/O5D-Mn1-N1	93.377	93.522	93.87	94.352
	O5/O5D-Mn1-O7	72.829	72.621	72.635	72.407
	O7-Mn1-O10	91.69(10)	91.62(15)	91.25(16)	91.3(2)
	O10-Mn1-N1	102.03(11)	102.12(17)	102.21(17)	101.9(2)
				0	
	Transoid angle ranges	162.54(10)-	162.38(17)-	162.48(17)-	162.5(2)-
		172.21(11)	172.33(17)	172.20(17)	172.5(2)
	Cisoid angle ranges	72.829-102.03	72.621-102.12	72.635-102.21	72.407-101.9
		(11)	(17)	(17)	(2)

Table 2. The values of bond lengths (Å) and angles (°) around the $Mn^{III}$ centers in 1-
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The coordination number of the two types of Ln<sup>III</sup> centers in 1–4 is different. The Ln1 center is eight-coordinated by one  $\mu$ -alkoxo (O2), one  $\mu$ -phenoxo (O4), two  $\mu_3$ -hydroxo (O7) and O8), one methoxy (O6) and three  $\mu_{1,3}$ -pivalate (O9, O11 and O13) oxygen atoms. On the other hand, the Ln2 center is nine-coordinated by one µ-phenoxo (O4D), one µ-aldehyde (O5), three  $\mu_3$ -hydroxo (O7, O8 and O8D), two  $\mu_{1,3}$ -pivalate (O12D and O14) and two  $\eta^2$ nitrate (O15 and O16) oxygen atoms. The selected bond distances and angles around the lanthanide(III) centers, Ln1 and Ln2, are listed in Tables 3 and 4, respectively. As can be seen from these Tables, the Ln–O bond distances gradually decrease from 1 (Ln = Tb) to 4(Ln = Er) for both crystallographically different metal ions (Ln1 and Ln2) and for each of the eight (for Ln1)/nine (for Ln2) bonds; such an order is expected due to lanthanide contraction. The ranges of the Ln–O bond distances in the Tb<sup>III</sup> and Er<sup>III</sup> analogues are, respectively, 2.304-2.529 Å and 2.267-2.493 Å for the Ln1 center and 2.309-2.511 Å and 2.269-2.534 Å for the Ln2 center. The corresponding bond angles involving Ln1 center in all the four compounds are not very different (the range of differences is 0.19-1.78°), as are those involving Ln2 center (the range of differences is 0.06–2.76°); the ranges of the O-Ln-O bond angles in the Tb<sup>III</sup> and Er<sup>III</sup> analogues are, respectively, 63.86–147.88° and 65.00–147.17° for the Ln1 center and 50.08–143.26° and 50.0–144.38° for the Ln2 center. SHAPE<sup>[32]</sup> analyses (Tables S2 and S3) reveal that biaugmented trigonal prism (BTPR-8) and spherical capped square antiprism (CSAPR-9) are the 'most ideal' geometries of the Ln1 and Ln2 centers, respectively. The general illustrations of the BTPR-8 and CSAPR-9 geometries of Ln1 and Ln2 centers, respectively, are shown in Figure 3. In the BTPR-8 case, two trigonal planes are defined by O2, O9 and O11 atoms and O4/O4D, O8 and O13 atoms, while O6 and O7/O7D are the augmented atoms; the dihedral angle between the two trigonal planes is 9.82°. In the CSAPR-9 geometry, the two square planes are defined by O4/O4D, O5, O8D/O8 and O8/O8D atoms and O7/O7D, O14, O12/O12D and O16 atoms, while O15 is the capping atom; the dihedral angle between the two least-squares square planes is 23.23°.

One C–H hydrogen atom (C11–H11A / C11–H11C) of a methyl group of the imino-alkoxo moiety of one of the two  $[L^1]^{2-}$  ligands of a hexanuclear moiety interacts with an oxygen atom (O17E) of a nitrate ligand of a neighbouring hexanuclear unit. Due to this single type of C–H····O hydrogen bond, one hexanuclear unit is interlinked with four other symmetry related hexanuclear units to form a two-dimensional topology in all the compounds **1–4** (Figures S3–S6 and Table S4).



**Figure 3.** General illustration of the co-ordination environment showing biaugmented trigonal prism (BTPR-8) geometry of each Ln1 center (a) and spherical capped square antiprism (CSAPR-9) geometry of each Ln2 center (b) in **1–4**.

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Table 5 The values	or bond lengths ( A	and nond angles is	around the LnL	centers in 1–4
	or bond tenguns (Tr	und bond unglob	) urbund the Lin	

Coordination environment of Ln1	Bond Lengths (Å)	1	2	3	4
	Ln1–O2	2.402(2)	2.391(3)	2.369(3)	2.359(4)
	Ln1-O4/O4D	2.400(2)	2.383(3)	2.366(3)	2.359(4)
	Ln1–O6	2.529(2)	2.518(4)	2.498(4)	2.493(5)
09	Ln1-07/07D	2.486(2)	2.475(4)	2.449(4)	2.444(5)
<b>7</b> 011	Ln1–O8	2.3040(19)	2.290(3)	2.272(3)	2.267(5)
02	Ln1-O9	2.315(2)	2.308(4)	2.286(4)	2.274(5)
	Ln1-O11	2.341(2)	2.328(4)	2.306(4)	2.293(5)
Ln1 O6	Ln1-O13	2.368(3)	2.346(4)	2.330(4)	2.330(5)
	Bond Angles (°)				
07/07D	O2-Ln1-O4/O4D	136.80(7)	136.95(11)	137.02(12)	137.31(15)
	O2-Ln1-O6	136.28(8)	136.05(12)	135.95(13)	135.50(16)
O8 O4/O4D	O2-Ln1-O7/O7D	64.40(7)	64.67(11)	64.94(12)	65.28(16)
	O2-Ln1-O8	73.95(7)	74.28(12)	74.51(12)	74.49(16)
	O2-Ln1-O9	75.34(8)	75.44(13)	75.71(13)	75.77(17)
	O2-Ln1-O11	73.79(8)	73.81(12)	74.04(13)	74.19(17)
	O2-Ln1-O13	137.37(8)	137.50(13)	137.30(13)	137.49(17)

O4/O4D-Ln1-O6	63.86(7)	64.35(11)	64.64(12)	65.00(15)
O4/O4D-Ln1-O7/O7D	122.02(7)	121.45(11)	121.22(12)	120.73(15)
O4/O4D-Ln1-O8	70.39(7)	70.17(11)	70.01(12)	70.19(15)
O4/O4D-Ln1-O9	144.39(8)	144.22(12)	143.90(13)	143.59(16)
O4/O4D-Ln1-O11	80.95(8)	81.36(12)	81.38(13)	81.56(17)
O4/O4D-Ln1-O13	78.72(8)	78.21(13)	78.15(13)	77.47(17)
O6-Ln1-O7/O7D	147.88(8)	147.64(13)	147.23(13)	147.17(17)
O6-Ln1-O8	132.51(7)	132.81(12)	133.01(12)	133.39(16)
O6-Ln1-O9	81.96(8)	81.35(12)	80.75(13)	80.18(17)
O6-Ln1-O11	73.90(9)	73.85(14)	73.68(14)	73.33(18)
O6-Ln1-O13	73.58(10)	73.66(14)	73.90(14)	74.25(18)
O7/O7D-Ln1-O8	70.03(7)	69.76(12)	69.80(12)	69.65(16)
O7/O7D-Ln1-O9	81.92(8)	82.41(13)	82.69(13)	83.17(17)
O7/O7D-Ln1-O11	136.35(8)	136.62(13)	137.16(13)	137.58(18)
O7/O7D-Ln1-O13	76.90(8)	76.69(13)	76.14(13)	75.88(17)
O8-Ln1-O9	145.04(8)	145.40(13)	145.85(13)	145.99(17)
O8-Ln1-O11	87.39(8)	87.93(13)	88.35(13)	88.41(17)
O8-Ln1-O13	109.85(8)	109.13(13)	108.60(13)	108.23(18)
O9-Ln1-O11	99.70(9)	99.35(14)	99.19(14)	99.03(18)
O9-Ln1-O13	82.48(9)	82.84(14)	82.86(14)	83.38(18)
O11-Ln1-O13	146.75(9)	146.68(14)	146.70(14)	146.54(18)
Angle ranges	63.86(7)-	64.35(11)-	64.64(12)-	65.00(15)-
	147.88(8)	146.68(14)	146.70(14)	147.17(17)

Table 4. The values of bond lengths (Å) and bond angles (°) around the Ln2 centers in 1–4.

Coordination	Bond Lengths (Å)	1	2	3	4
environment of Ln2					
	Ln2-O4/O4D	2.358(2)	2.347(3)	2.324(3)	2.320(4)
	Ln2–O5	2.511(2)	2.505(4)	2.488(4)	2.481(5)
	Ln2-07/07D	2.484(2)	2.467(3)	2.447(3)	2.434(5)
	Ln2-O8/O8D	2.3777(19)	2.387(3)	2.367(3)	2.342(5)
	Ln2-O8D/O8	2.394(2)	2.367(3)	2.347(3)	2.363(5)
	Ln2-O12/O12D	2.344(2)	2.334(4)	2.311(4)	2.303(5)
	Ln2-O14	2.309(2)	2.295(4)	2.279(4)	2.269(5)
	Ln2-O15	2.539(3)	2.538(4)	2.520(4)	2.534(6)
	Ln2-O16	2.500(3)	2.494(4)	2.478(4)	2.464(6)
	Bond Angles (°)				
	O4/O4D-Ln2-O5	70.94(7)	71.18(12)	71.38(12)	71.59(16)
	O4/O4D-Ln2-O7/O7D	137.92(7)	138.01(11)	138.25(12)	138.24(17)
015	O4/O4D-Ln2-O8/O8D	69.89(7)	69.50(11)	69.47(11)	69.59(15)
	O4/O4D-Ln2-O8D/O8	92.09(7)	92.14(12)	92.21(12)	91.99(16)
014	O4/O4D-Ln2-O12/O12D	80.27(9)	79.90(13)	79.84(13)	79.90(17)
012/0120	O4/O4D-Ln2-O14	142.91(8)	142.39(12)	142.18(12)	141.98(16)
Ln2	O4/O4D-Ln2-O15	127.33(9)	127.36(14)	127.44(14)	127.43(18)
108D/08	O4/O4D-Ln2-O16	79.96(9)	79.86(14)	80.21(15)	80.52(19)
O8/O8D	O5-Ln2-O7/O7D	67.56(7)	67.47(12)	67.55(12)	67.35(16)
	O5-Ln2-O8/O8D	121.01(7)	120.90(12)	121.17(12)	121.66(16)
04/04D	O5-Ln2-O8D/O8	71.60(7)	71.60(12)	71.79(12)	71.53(16)
	O5-Ln2-O12/O12D	136.15(9)	135.97(14)	135.61(14)	135.33(17)
	O5-Ln2-O14	137.74(9)	138.57(13)	139.32(13)	139.88(17)
	O5-Ln2-O15	100.08(9)	100.06(14)	100.01(14)	99.74(19)
	O5-Ln2-O16	68.82(9)	68.40(14)	68.20(15)	68.02(19)
	O7/O7D-Ln2-O8/O8D	128.10(7)	128.05(12)	127.93(12)	127.99(17)
	O7/O7D-Ln2-O8D/O8	68.68(7)	68.39(11)	68.35(11)	68.31(17)
	07/07D-Ln2-012/012D	136.92(8)	137.32(13)	137.08(13)	136.88(18)
	O7/O7D-Ln2-O14	72.87(8)	73.55(12)	73.91(13)	74.44(17)
	O7/O7D-Ln2-O15	67.99(8)	68.27(13)	68.32(13)	68.32(18)
	O7/O7D-Ln2-O16	91.36(9)	91.47(13)	91.29(14)	90.97(19)
	O8/O8D-Ln2-O8D/O8	67.67(8)	67.73(14)	67.77(14)	68.17(19)
	O8/O8D-Ln2-O12/O12D	76.02(8)	76.00(13)	76.32(13)	76.55(17)

O8/O8D-Ln2-O14	73.80(8)	73.89(12)	73.93(12)	73.80(16)
O8/O8D-Ln2-O15	138.81(9)	138.93(14)	138.70(14)	138.48(19)
O8/O8D-Ln2-O16	140.52(9)	139.68(14)	139.63(14)	141.02(19)
O8D/O8-Ln2-O12/O12D	143.26(8)	143.31(13)	143.69(13)	144.38(17)
O8D/O8-Ln2-O14	80.87(9)	81.66(14)	82.52(13)	83.63(18)
O8D/O8-Ln2-O15	135.60(8)	135.59(13)	135.58(13)	135.64(17)
O8D/O8-Ln2-O16	140.08(9)	140.44(14)	140.75(14)	139.18(19)
O12/O12D-Ln2-O14	84.00(10)	83.32(15)	82.64(15)	82.05(19)
O12/O12D-Ln2-O15	71.92(9)	72.00(14)	71.62(14)	71.30(18)
O12/O12D-Ln2-O16	74.23(10)	74.47(15)	74.24(16)	74.0(2)
O14-Ln2-O15	77.74(10)	77.41(15)	76.73(15)	76.3(2)
O14-Ln2-O16	127.28(10)	127.18(15)	126.32(15)	125.6(2)
O15-Ln2-O16	50.08(10)	50.38(15)	50.25(16)	50.0(2)
Angle ranges	50.08(10)	50.38(15)	50.25(16)	50.0(2)
	-143.26(8)	-143.31(1	-143.69(1	-144.38(1
		3)	3)	7)

Previously, two series of  $Mn_{2}^{III}Ln_{4}^{III}$  compounds were reported. The general composition (excluding solvent of crystallization) of one series is  $[Mn^{III}_{2}Ln^{III}_{4}(\mu_{4}-O)_{2}(2$ pyridinemethoxido)<sub>4</sub>(picolinate)<sub>2</sub>(pivalate)<sub>6</sub>( $\mu$ -azide)<sub>2</sub>] (Ln = Sm, Eu, Gd, Tb, Dy, Ho)<sup>[33]</sup>. The general composition (excluding solvent of crystallization) of the second series is  $[Mn^{III}_{2}Ln^{III}_{4}L_{2}(\mu_{4}-O)_{2}(azide)_{2}(methoxido)_{2}(methanol)_{4}(NO_{3})_{2}]$  (Ln = Y, Gd, Tb, Dy)<sup>[34]</sup>. So, in terms of the ligands and bridges, the three series are drastically different, i. e., the present series represent a new type of hexanuclear Mn<sup>III</sup><sub>2</sub>Ln<sup>III</sup><sub>4</sub> compounds. Interestingly, the bridging pattern observed in this series of compounds resembles to that of Mn<sup>II</sup><sub>2</sub>Ln<sup>III</sup><sub>4</sub> compounds derived from an aminohydrazide ligand.<sup>[35]</sup> As already discussed, an aldehyde oxygen atom bridges one Mn<sup>III</sup> and one Ln<sup>III</sup> ions in 1–4. The bridging ability of aldehyde oxygen atom is generally weak and therefore metal complexes having  $\mu$ -O(aldehyde) moiety (ies) are rare.<sup>[36]</sup> In all of those very few examples, the aldehyde oxygen atom bridges one type of metal ions (e. g. either of Na<sup>I [36a,b,c]</sup>, Mg<sup>II[36d]</sup>, Zn<sup>II[36e]</sup>, Hg<sup>II[36f]</sup>, Cu<sup>II[36g]</sup>, Ni<sup>II[36e,h]</sup>, Co<sup>II[36i]</sup>, Zr<sup>IV[36j]</sup>, Tb<sup>III[36k]</sup> and Ho<sup>III[36l]</sup>). Hence, bridging of an aldehyde oxygen atom to two different ions (a 3d metal ion Mn<sup>III</sup> and a 4f metal ion Tb<sup>III</sup>-Er<sup>III</sup>) in 1-4 is a new type of observation in coordination chemistry.

#### **Magnetic Properties**

Variable-temperature (2–300 K) magnetic susceptibilities of powdered samples of 1–4 were measured at an applied dc field of 0.1 T. The cryomagnetic behavior of the four  $Mn_{2}^{III}Ln_{4}^{III}$  compounds 1 (Ln = Tb), 2 (Ln = Dy), 3 (Ln = Ho) and 4 (Ln = Er) are shown in Figure 4 in terms of  $\chi_M T$  versus *T* plots and the  $\chi_M T$  values at the highest and lowest temperatures of measurements along with theoretical values are listed in Table 5. The  $\chi_M T$  values at 300 K for

**1–4** are, respectively, 53.19, 61.80, 61.40 and 50.41 cm<sup>3</sup> K mol<sup>-1</sup>. The theoretical values (53.27, 62.68, 62.25 and 51.90 cm<sup>3</sup> K mol<sup>-1</sup>, respectively) for a system with non interacting two high spin Mn<sup>III</sup> (S = 2) and four Ln<sup>III</sup> ions are very close to the observed for all the four compounds. The cryomagnetic features in **1–4** are similar. On lowering the temperature,  $\chi_M T$  values remain practically constant between 300 and 150 K, after which it decreases slowly to a lower temperature (*ca.* 12 K, 30 K, 50 K and 40 K for, respectively, for Tb<sup>III</sup>, Dy<sup>III</sup>, Ho<sup>III</sup> and Er<sup>III</sup> analogues) and then more rapidly down to 2 K, reaching the values of 11.88, 28.76, 22.18 and 22.14 cm<sup>3</sup> K mol<sup>-1</sup>, respectively. The decrease in  $\chi_M T$  values on lowering the temperature in **1–4** may take place due to three factors, namely, depopulation of the upper Stark levels of Ln<sup>III</sup> ions, single-ion zero-field effect of Mn<sup>III</sup> or weak/very weak antiferromagnetic Mn<sup>III</sup>....Ln<sup>III</sup>/Ln<sup>III</sup>....Ln<sup>III</sup> exchange interactions or two or more of these.



**Figure 4.** Temperature dependence of the dc magnetic susceptibility for 1–4 having composition  $[Mn^{III}_{2}Ln^{III}_{4}L^{1}_{2}L^{2}_{2}(\mu_{3}-OH)_{4}(\mu_{1,3}-Pivalate)_{6}(NO_{3})_{2}]\cdot 2CH_{3}CN$  (Ln = Tb (1), Dy (2), Ho (3), Er (4)).

	1,	2,	3,	4,
	$Mn_{2}^{III}Tb_{4}^{III}$	$Mn_{2}^{III}Dy_{4}^{III}$	$Mn_{2}^{III}Ho_{4}^{III}$	$Mn_{2}^{III}Er_{4}^{III}$
Ground state of Ln	$^{7}F_{6}$	${}^{6}\mathrm{H}_{15/2}$	${}^{5}I_{8}$	${}^{4}I_{15/2}$
Expected $\chi T$ at 300 K,	53.27	62.68	62.25	51.90
$cm^3 K mol^{-1}$				
Observed $\chi T$ at 300 K,	53.19	61.80	61.40	50.41
$cm^3 K mol^{-1}$				

Table 5. Summary of static magnetic properties of 1–4.

Observed $\chi$ T at 2 K,	11.88	28.76	22.18	22.14
$cm^3 K mol^{-1}$				
Magnetization at 7 T,	25.22	29.28	30.41	26.37
2K, Nβ				
Saturation	44.00	47.90	48.00	44.00
Magnetization, N $\beta^a$				

<sup>*a*</sup>Formula used for  $(Mn_{2}^{III}Ln_{4}^{III})$  metallic core to calculate saturation magnetization, Saturation Magnetization  $(M_s) = 4g_{Ln}J + 2g_{Mn}S_{Mn}$ .

The magnetization (M) data up to 7 T at 2 and 4 K for 1–4 have been collected, which are shown in Figures S7–S10. The magnetization curves of all four compounds do not reach saturation even at 7 T. The magnetization values at 2 K and 7 T are in fact significantly smaller than the theoretical saturation values (Table 5). Moreover, as shown in Figures 5, 6, S11 and S12, the M versus H/T plots of each of the four compounds do not pass through a master curve and extent of divergence is appreciable. All these indicate significant anisotropy or low lying excited states in these systems. As all the four compounds 1–4 have significant anisotropy, they may behave as single molecule magnets and exploration of that aspect is discussed below.



**Figure 5.** Magnetizations versus field/temperature plots for  $[Mn_{2}^{III}Tb_{4}^{II}L_{2}^{1}L_{2}^{2}(\mu_{3}-OH)_{4}(\mu_{1,3}-Pivalate)_{6}(NO_{3})_{2}]\cdot 2CH_{3}CN$  (1), collected at 2 K and 4 K (Solid lines are guide for eyes only).



**Figure 6.** Magnetizations versus field/temperature plots for  $[Mn^{III}_2Dy^{III}_4L^1_2L^2_2(\mu_3-OH)_4(\mu_{1,3}-Pivalate)_6(NO_3)_2]\cdot 2CH_3CN$  (2), collected at 2 K and 4 K (Solid lines are guide for eyes only).

Variable-temperature (1.8–20 K) ac susceptibilities of the  $Ho^{III}$  (3) and  $Er^{III}$  (4) analogues at three frequencies, 1, 10 and 956 Hz and under both zero dc field and applied dc field of 0.1 T are shown in Figures S13 and S14. The out-of-phase susceptibilities under both zero-field and 0.1 T dc field of these two compounds are practically non-detectable, revealing that these two compounds do not show slow relaxation of magnetization. Variabletemperature (1.8–20 K) ac susceptibilities of the Dy<sup>III</sup> (2) analogue at three frequencies, 1, 10 and 956 Hz and under zero dc field are shown in Figure S15 which reveals that out-of-phase susceptibilities of 2 (Dy<sup>III</sup>) under zero field are detectable but no maxima are observed above 1.8 K (which is the detection limit of the magnetometer used). For better understanding of the possible SMM behavior of 2 (Dy<sup>III</sup>), the following measurements have been carried out: (i) Temperature-dependent (1.8–3.6 K)  $\chi_{M}$ ' and  $\chi_{M}$ " at frequencies ranging from 1 to 1399 Hz under both 1000 Oe (Figure S16) and 3500 Oe (Figure S17) applied dc fields; (ii) Frequencydependent (10–1399 Hz)  $\chi_{M}$  and  $\chi_{M}$  under several dc fields (0–4500 Oe) at 1.8 K (Figure S18). As is obvious from these data in these three figures, compound 2 is not an SMM. As expected, no loop is observed in hysteresis data at 1.8 K between +6.5 T and -6.5 T field of 2 (Figure S15), 3 (Figure S13) and 4 (Figure S14).

Variable-temperature (1.8–20 K) ac susceptibilities of the Tb<sup>III</sup> (1) analogue at three frequencies, 1, 10 and 956 Hz and under zero dc field are shown in Figure S19. Although no maxima appear in the  $\chi_{M}$ " versus *T* plots, the  $\chi_{M}$ " values are detectable well and a frequency-dependent splitting takes place below around 4 K. Therefore, the following measurements

have been carried out for understanding the possible SMM properties of 1 (Tb<sup>III</sup>): (i) Temperature-dependent (1.8–3.6 K)  $\chi_{M}$ ' and  $\chi_{M}$ " at frequencies ranging from 1 to 1399 Hz under both 1000 Oe (Figure S20) and 3500 Oe (Figure 7) applied dc fields; (ii) Frequencydependent (1–1399 Hz)  $\chi_{M}$ ' and  $\chi_{M}$ " under several dc fields (0–4500 Oe) at 1.8 K (Figure 8); (iii) Frequency-dependent (1–1399 Hz)  $\chi_{\rm M}$ ' and  $\chi_{\rm M}$ " at fixed temperatures between 1.8 and 2.4 K under both 1000 Oe (Figure S21) and 3500 Oe (Figure 9) applied dc fields. Clear splitting of both  $\chi_{M}$ ' and  $\chi_{M}$ " in all these five figures (Figures 7, 8, 9, S20 and S21) along with either indication (Figures 7 and S20) or clear appearance (Figures 8, 9 and S21) of maxima in the  $\chi_{M}$ " plots confirm that the Tb<sup>III</sup> system is an SMM. The Cole-Cole plots corresponding to Figures 8 (fixed temperature of 1.8 K), S21 (fixed field of 1000 Oe) and 9 (fixed field of 3500 Oe) are shown in Figures S22, S23 and 10, which could be simulated<sup>[37]</sup> with the generalized Debye model<sup>[38]</sup> giving the values of relaxation time ( $\tau$ ) and relaxation distribution parameter ( $\alpha$ ), as listed in Tables S5, S6 and S7, respectively. The ranges of the  $\alpha$ values are almost similar (0.23-0.31 (Table S5), 0.23-0.26 (Table S6) and 0.23-0.27 (Table S7)) corresponding to the three Cole-Cole plots. Notably, the Cole-Cole plots could not be fitted with modified Debye model,<sup>[39]</sup> revealing that single relaxation takes place in 1; slightly larger value (> 0.1) of  $\alpha$  arises most probably due to intermolecular interactions (hydrogen bonds in **1** have already been discussed).<sup>[22c,40]</sup> The relaxation times ( $\tau$ ) at different temperatures corresponding to the frequency-dependent and temperature-dependent out-ofphase data at 1000 Oe (Figures S21 and S23 and Table S6) and at 3500 Oe (Figures 9 and 10 and Table S7) could be fitted well (as in Figures 11 and 12) with the Arrhenius equation (ln  $\tau$ = ln  $\tau_0$  +  $U_{\rm eff}/k_{\rm B}$ T), giving  $U_{\rm eff}$  values of 11.12 cm<sup>-1</sup> and 10.42 cm<sup>-1</sup> and  $\tau_0$  values of 1.04 ×  $10^{-7}$  s and  $1.62 \times 10^{-7}$  s, respectively. As **1** is a weak SMM, no loop is observed in Hysteresis data at 1.8 K between +6.5 T and -6.5 T field of 2 (Figure S19).



**Figure 7.** Temperature dependence of the in-phase  $(\chi_M')$  and out-of-phase  $(\chi_M'')$  ac magnetic susceptibility for  $[Mn^{III}_{2}Tb^{III}_{4}L^{1}_{2}L^{2}_{2}(\mu_{3}\text{-}OH)_{4}(\mu_{1,3}\text{-}Pivalate)_{6}(NO_{3})_{2}]\cdot 2CH_{3}CN$  (1) collected at 1.55 G ac field oscillating at frequencies between 1 and 1399 Hz, and under 3500 Oe dc field.



**Figure 8.** Frequency dependence of the in-phase ac molar susceptibility  $(\chi_M')$  components (a) and out-of-phase ac molar susceptibility  $(\chi_M'')$  components (b) for  $[Mn^{III}_2Tb^{III}_4L^2_2L^2_2(\mu_3-OH)_4(\mu_{1,3}-Pivalate)_6(NO_3)_2]\cdot 2CH_3CN$  (1) at 1.8 K under different dc fields. Solid lines are guide for eyes only.



**Figure 9.** Frequency dependence of the in-phase ac molar susceptibility  $(\chi_M')$  components (a) and out-of-phase ac molar susceptibility  $(\chi_M'')$  components (b) for  $[Mn^{III}_{2}Tb^{III}_{4}L^{1}_{2}L^{2}_{2}(\mu_{3}-OH)_{4}(\mu_{1,3}-Pivalate)_{6}(NO_{3})_{2}]\cdot 2CH_{3}CN$  (1) under 3500 Oe dc field. Solid lines are guide for eyes only.



**Figure 10.** Cole-Cole plots for the frequency-dependent ac data (in Figure 9) at the indicated temperatures under 3500 Oe dc field for  $[Mn_{2}^{III}Tb_{2}^{III}L_{2}^{1}L_{2}^{2}(\mu_{3}-OH)_{4}(\mu_{1,3}-Pivalate)_{6}(NO_{3})_{2}]\cdot 2CH_{3}CN$  (1). The solid lines are the best fits to the experimental data obtained with the generalized Debye model.



**Figure 11.** Plot of  $\ln(\tau)$  versus reciprocal temperature corresponding to the frequencydependent ac data (in Figures S21 and S23 and Table S6) at several temperatures under 1000 Oe dc field for  $[Mn^{III}_{2}Tb^{III}_{4}L^{1}_{2}L^{2}_{2}(\mu_{3}\text{-}OH)_{4}(\mu_{1,3}\text{-}Pivalate)_{6}(NO_{3})_{2}]\cdot 2CH_{3}CN$  (1). The red solid line represents the linear fitting in the temperature range 1.80K–2.15K.



**Figure 12.** Plot of  $\ln(\tau)$  versus reciprocal temperature corresponding to the frequencydependent ac data (in Figures 9 and 10 and Table S7) at several temperatures under 3500 Oe dc field for  $[Mn^{III}_{2}Tb^{III}_{4}L^{1}_{2}L^{2}_{2}(\mu_{3}\text{-OH})_{4}(\mu_{1,3}\text{-Pivalate})_{6}(NO_{3})_{2}]\cdot 2CH_{3}CN$  (1). The red solid line represents the linear fitting in the temperature range 1.80–2.20 K.

A MAGELLAN<sup>[41]</sup> analysis (Figure 13) of the  $Mn^{III}_{2}Dy^{III}_{4}$  compound 2 reveals the following: (i) The local anisotropic axes of the lanthanide centers are much deviated from colinearity; (ii) The local anisotropic axis of any of the two lanthanide centers and the Jahn Teller axis of the manganese(III) ion are far from being collinear. This actually reduces the overall anisotropy of the molecule. As a result, compound 2 and other compounds herein exhibit either no slow relaxation of magnetization or weak SMM property.



**Figure 13.** The direction of the local anisotropy axes (green dotted lines) of  $Dy^{III}$  ions and Jahn-Teller axes (black solid lines) of  $Mn^{III}$  ions in  $[Mn^{III}_2Dy^{III}_4L^1_2L^2_2(\mu_3-OH)_4(\mu_{1,3}-Pivalate)_6(NO_3)_2]\cdot 2CH_3CN$  (2).

It is relevant to compare the present series of compounds with those of the two previously reported  $Mn^{III}_{2}Ln^{III}_{4}$  series. Of the six compounds of the  $[Mn^{III}_{2}Ln^{III}_{4}(\mu_{4}-O)_{2}(2-pyridinemethoxido)_{4}(picolinate)_{2}(pivalate)_{6}(\mu-azide)_{2}]$  (Ln = Sm, Eu, Gd, Tb, Dy, Ho) series, only Tb<sup>III</sup> analogue exhibit slow relaxation of magnetization under zero-field.<sup>[33]</sup> Of the four compounds of the  $[Mn^{III}_{2}Ln^{III}_{4}L_{2}(\mu_{4}-O)_{2}(azide)_{2}(methoxido)_{2}(methanol)_{4}(NO_{3})_{2}]$  (Ln = Y, Gd, Tb, Dy) series, the Tb<sup>III</sup> and Dy<sup>III</sup> analogues are SMMs under a applied dc field of 0.1 T.<sup>[34]</sup>

#### Conclusions

Although a number of aminoalcohol/aminophenol was previously utilized to derive either 4f or 3d-4f compounds from 3-methoxysalicylaldehyde–aminoalcohol/aminophenol Schiff base ligands, this investigation introduces 2-amino-2-methyl-1-propanol in this area and our aim of getting new types of compounds has been fulfilled as the present series of four isomorphous/isostructural, hexanuclear 3d-4f  $Mn^{III}_{2}Ln^{III}_{4}$  compounds (Ln = Tb, Dy, Ho, Er) represent a new type of structure having these two types of metal ions. The bridging ability of aldehyde oxygen atom is seldom observed. In those rare examples, aldehyde oxygen atom bridges one type of metal ion. In contrast, interestingly, aldehyde oxygen atom acts as a bridging ligand to two different types of metal ions (Mn<sup>III</sup> and Ln<sup>III</sup>) in the present series of

compounds. The  $Mn_{2}^{III}Ln_{4}^{III}$  compounds in this investigation are also rare examples of hexanuclear systems having two manganese(III) and four lanthanide(III) ions. Hopefully, 3d-4f compounds with other 3d metal ions with  $H_{2}L^{1}$  will stabilize new types of structures and so this area may be further explored.

Detailed dc and ac magnetic studies reveal the following: (i) All compounds are significantly anisotropic; (ii) The Tb<sup>III</sup> analogue is an SMM while the Dy<sup>III</sup>, Ho<sup>III</sup> and Er<sup>III</sup> analogues do not show slow relaxation of magnetization even under an applied dc field of 0.1/0.35 T. Some compounds (Dy<sup>III</sup>, Ho<sup>III</sup> and Er<sup>III</sup> analogues) here do not show slow relaxation of magnetization and only one (Tb<sup>III</sup> analogue;  $U_{eff} = ca. 11 \text{ cm}^{-1}$ ) is a weak SMM, which are probably related to both the relative orientations of the anisotropic axes of lanthanides and Jahn-Teller axes of manganese(III) as well as to intermolecular hydrogen bonding interactions in these molecules.<sup>[22c]</sup>

# **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<sup>-1</sup> on a Bruker-Optics Alpha–T spectrophotometer with samples as KBr disks. The magnetic measurements were carried out with a SQUID magnetometer (MPMS, Quantum Design).

#### Syntheses of 1–4:

 $[Mn^{III}_{2}Ln^{III}_{4}(L^{1})_{2}(L^{2})_{2}(\mu_{3}-OH)_{4}(\mu_{1,3}-Pivalate)_{6}(NO_{3})_{2}]$ ·2CH<sub>3</sub>CN (1, Ln = Tb; 2, Ln = Dy; 3, Ln = Ho; 4, Ln = Er). All the four complexes were prepared by employing a general synthetic protocol, as follows: 5 mL 'H<sub>2</sub>L<sup>1</sup> solution' consisting of 0.2 mmol H<sub>2</sub>L<sup>1</sup> was taken and diluted to 15 mL with acetonitrile. To it, triethylamine (0.056 mL, 0.4 mmol) and 2 mL methanol solution of corresponding Ln(NO\_{3})\_{3}·5H\_{2}O (0.2 mmol) were successively added and stirred for 20 min. To the yellow coloured clear solution, a solution of MnCl<sub>2</sub>·4H<sub>2</sub>O (0.04 g, 0.2 mmol) in 2 mL methanol was added. Finally, a solution of pivalic acid (0.04 g, 0.4 mmol) and triethylamine (0.056 g, 0.4 mmol) in 3 mL methanol was added and stirred for further 5 h. The resulting brown coloured reaction mixture was filtered to remove any suspended

particles and the filtrate was kept at ambient temperature for slow evaporation. After a few days, dark brown crystalline compound was obtained, which was collected by filtration, washed with cold methanol and dried in vacuum. Recrystallization from acetonitrilediethylether mixture (diffusion technique) produced dark brown crystalline compound containing diffraction quality single crystals.

Data for **1**. Yield: 0.067 g, 57% (based on lanthanide).  $C_{74}H_{108}N_6O_{34}Mn_2Tb_4$  (2371.22): calcd. C 37.48, H 4.59, N 3.54; found: C 37.15, H 4.44, N 3.40. FT-IR (KBr): 1628 [vs, v(C=N)], 1384, 1313 [s, m,  $v(NO_3^{-})$ ], 1564, 1470 [(asym, s), (sym, m),  $v(COO^{-})$ ] cm<sup>-1</sup>.

Data for **2**. Yield: 0.073 g, 62% (based on lanthanide).  $C_{74}H_{108}N_6O_{34}Mn_2Dy_4$  (2385.54): calcd. C 37.26, H 4.56, N 3.52; found: C 37.05, H 4.34, N 3.45. FT-IR (KBr): 1627 [vs, v(C=N)], 1376, 1311 [s, m,  $v(NO_3^-)$ ], 1565, 1469 [(asym, s), (sym, m),  $v(COO^-)$ ] cm<sup>-1</sup>.

Data for **3**. Yield: 0.076 g, 64% (based on lanthanide).  $C_{74}H_{108}N_6O_{34}Mn_2Ho_4$  (2395.26): calcd. C 37.11, H 4.54, N 3.51; found: C 36.85, H 4.48, N 3.36. FT-IR (KBr): 1627 [vs, v(C=N)], 1384, 1314 [s, m,  $v(NO_3^{-})$ ], 1567, 1470 [(asym, s), (sym, m),  $v(COO^{-})$ ] cm<sup>-1</sup>.

Data for **4**. Yieid: 0.072 g, 60% (based on lanthanide).  $C_{74}H_{108}N_6O_{34}Mn_2Er_4$  (2404.58): calcd. C 36.96, H 4.52, N 3.49; found: C 36.62, H 4.36, N 3.30. FT-IR (KBr): 1627 [vs, v(C=N)], 1384, 1311 [s, m,  $v(NO_3^{-})$ ], 1567, 1469 [(asym, s), (sym, m),  $v(COO^{-})$ ] cm<sup>-1</sup>.

#### Crystal structure determination of 1–4.

The crystallographic data for **1–4** are summarized in Table 1. X-ray diffraction data were collected on a Bruker-APEX II SMART CCD diffractometer at 296 K using graphitemonochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The packages SAINT<sup>[42a]</sup> and SADABS<sup>[42b]</sup> 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<sup>[42c]</sup> and SHELXL-2014/7<sup>[42d]</sup> packages.

During the refinement of the structures, two/three pivalate carbon atoms in 1/2/3/4 were found disordered over two sites. The disordered carbon atoms are as follows: C25 of one pivalate and C33 of another pivalate in 1; C24 of one pivalate and C33 of another

pivalate in **2**; C24 and C25 of one pivalate and C33 of another pivalate in **3**; C24, C25 of one pivalate and C33 of another pivalate in **4**. 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 C25 and 0.65 and 0.35 for C33 in **1**; 0.70 and 0.30 for C24 and 0.55 and 0.45 for C33 in **2**; 0.80 and 0.20 for C24, 0.50 and 0.50 for C25 and 0.60 and 0.40 for C33 in **3**; 0.50 and 0.50 for C24, 0.55 and 0.45 for C25 and 0.45 for C33 in **4**.

Each structure contains two acetonitrile (CH<sub>3</sub>CN) molecules as solvent of crystallisation and those molecules have been properly assigned for each complex. All the hydrogen atoms of 1–4 were inserted in geometrically calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically, while all the hydrogen atoms were refined isotropically. The final refinement converged at the R<sub>1</sub>/wR<sub>2</sub> (I>2 $\sigma$ (I)) values of 0.0384/0.0808, 0.0374/0.0769, 0.0379/0.0911 and 0.0427/0.0853 for 1–4, respectively.

CCDC 1841040–1841043 for **1–4**, respectively, contains 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–S23 and Tables S1–S7.

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Keywords: SMM / Hexanuclear / Magnetic properties / Lanthanide(III) / Manganese(III)

# References

- [1] a) R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* **1993**, *365*, 141.
- [2] a) D. Gatteschi, R. Sessoli, J. Villain, *Molecular Nanomagnets* (Oxford Univ. Press, 2006); b) R. E. Winpenny, *Struct. Bonding* 2006, 122, 1; c) T. C. Stamatatos, G. Christou, *Inorg. Chem.* 2009, 48, 3308; d) M. Murrie, *Chem. Soc. Rev.* 2010, 39, 1986; e) R. Sessoli, A. K. Powell, *Coord. Chem. Rev.* 2009, 253, 2328; f) I. G. Rau, S. Baumann, S. Rusponi, F. Donati, S. Stepanow, L. Gragnaniello, J. Dreiser, C. Piamonteze, F. Nolting, S. Gangopadhyay, O. R. Albertini, R. M. Macfarlane, C. P. Lutz, B. A. Jones, P. Gambardella, A. J. Heinrich, H. Brune, *Science* 2014, 344, 988; g) S. Mandal, S. Mondal, C. Rajnák, J. Titiš, R. Boča, S. Mohanta, *Dalton Trans.* 2017, 46, 13135; h) L. Rigamonti, N. Bridonneau, G. Poneti, L. Tesi, L. Sorace, D. Pinkowicz, J. Jover, E. Ruiz, R. Sessoli, A. A. Cornia, *Chem. Eur. J.* DOI: 10.1002/chem.201801026.
- [3] a) J. D. Rinehart, J. R. Long, *Chem. Sci.* 2011, 2, 2078; b) L. Sorace, C. Benelli, D. Gatteschi, *Chem. Soc. Rev.* 2011, 40, 3092.
- [4] a) C. A. P. Goodwin, F. Ortu, D. Reta, N. F. Chilton, D. P. Mills, *Nature* 2017, 548, 439; b) F. S. Guo, B.-M. Day, Y.-C. Chen, M.-L. Tong, A. Mansikkamaki, R. A. Layfield, *Angew. Chem. Int. Ed.* 2017, 56, 11445; *Angew. Chem.* 2017, 129, 11603; 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, M.-L. Tong, J. Am. Chem. Soc. 2016, 138, 2829.
- [5] a) J. D. Rinehart, M. Fang, W. J. Evans, J. R. Long, J. Am. Chem. Soc. 2011, 133, 14236; b) J. J. L. Roy, L. Ungur, I. Korobkov, L. F. Chibotaru, 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, M.-L. Tong, J. Am. Chem. Soc. 2016, 138, 5441.
- [6] a) D. Gatteschi, *Adv. Mater.* 1994, *6*, 635; b) 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, H. Brune, *Science* 2016, *352*, 318.
- [7] a) M. N. Leuenberger, D. Loss, *Nature* 2001, *410*, 789; b) M. Shiddiq, D. Komijani,
   Y. Duan, A. Gaita-Ariño, E. Coronado, S. Hill, *Nature* 2016, *531*, 348.
- [8] a) L. Bogani, W. Wernsdorfer, *Nat. Mater.* **2008**, *7*, 179; b) Molecular spintronics and quantum computing., *J. Mater. Chem.* **2009**, *19*, 1670.
- [9] a) C. Benelli, D. Gatteschi (Eds.), Introduction to Molecular Magnetism: From Transition Metals to Lanthanides, *John Wiley & Sons* 2015; b) W. Linert, M. Verdaguer (Eds), Molecular Magnets Recent Highlights, *Springer Science & Business Media* 2012; c) R. E. P. Winpenny, G. Aromí, Single-Molecule Magnets and Related Phenomena, *Springer* 2006; d) D. Gatteschi, *Adv. Mater.* 1994, *6*, 635; e) L. Bogani, W. Wernsdorfer, *Nat. Mater.* 2008, *7*, 179; f) Y.-Z. Zheng, G.-J. Zhou, Z. Zheng, R. E. P. Winpenny, *Chem. Soc. Rev.* 2014, *43*, 1462.

- 28
- [10] a) S. M. J. Aubin, M. W. Wemple, D. M. Adams, H.-L. Tsai, G. Christou, 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, D. N. Hendrickson, J. Am. Chem. Soc. 1998, 120, 839; c) H. Andres, F. Basler, H.-U. Güdel, G. Aromí, G. Christou, H. Büttner, B. Rufflé, J. Am. Chem. Soc. 2000, 122, 12469; d) T. C. Stamatatos, G. Christou, Inorg. Chem. 2009, 48, 3308; e) S. Mukherjee, K. A. Abboud, W. Wernsdorfer, G. Christou, Inorg. Chem. 2013, 52, 873; f) P. Cucos, L. Sorace, C. Maxim, S. Shova, D. Patroi, A. Caneschi, M. Andruh, Inorg. Chem. 2017, 56, 11668.
- [11] a) G. Aromí, E. K. Brechin, *Struct. Bonding* 2006, *122*, 1; b) M. Murrie, *Chem. Soc. Rev.* 2010, *39*, 1986.
- [12] N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara, Y. Kaizu, J. Am. Chem. Soc. 2003, 125, 8694.
- [13] a) J. Long, F. Habib, P.-H. Lin, I. Korobkov, G. Enright, L. Ungur, W. Wernsdorfer, L. F. Chibotaru, M. Murugesu, J. Am. Chem. Soc. 2011, 133, 5319; b) F. Habib, G. Brunet, V. Vieru, I. Korobkov, L. F. Chibotaru, M. Murugesu, J. Am. Chem. Soc. 2013, 135, 13242; c) S. Xue, Y.-N. Guo, L. Ungur, J. Tang, L. F. Chibotaru, Chem. Eur. J. 2015, 21, 14099.
- [14] a) D. N. Woodruff, R. E. P. Winpenny, R. A. Layfield, *Chem. Rev.* 2013, *113*, 5110;
  b) R. J. Holmberg, M. Murugesu, *J. Mater. Chem. C* 2015, *3*, 11986; c) Y.-S. Meng, S.-D. Jiang, B.-W. Wang, S. Gao, *Acc. Chem. Res.* 2016, *49*, 2381; d) S. T. Liddle, J. V. Slageren, *Chem. Soc. Rev.* 2015, *44*, 6655; e) K. Liu, X. Zhang, X. Meng, W. Shi, P. Chengab, A. K. Powell, *Chem. Soc. Rev.* 2016, *45*, 2423; f) Y.-N. Guo, G.-F. Xu, Y. Guo, J. Tang, *Dalton Trans.* 2011, *40*, 9953.
- [15] a) S. K. Gupta, T. Rajeshkumar, G. Rajaraman, 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, E. Colacio, *Chem. Commun.* 2012, 48, 7916; c) A. J. Brown, D. Pinkowicz, M. R. Saber, K. R. Dunbar, *Angew. Chem. Int. Ed.* 2015, 54, 5864; *Angew. Chem.* 2015, 127, 5962; d) M. Ren, D. Pinkowicz, M. Yoon, K. Kim, L.-M. Zheng, B. K. Breedlove, M. Yamashita, *Inorg. Chem.* 2013, 52, 8342.
- [16] a) Y. Peng, V. Mereacre, A. Baniodeh, Y. Lan, M. Schlageter, G. E. Kostakis, A. K. Powell, *Inorg. Chem.* 2016, 55, 68; b) P. Comba, M. Großhauser, R. Klingeler, C. Koo, Y. Lan, D. Müller, J. Park, A. Powell, M. J. Riley, H. Wadepohl, *Inorg. Chem.* 2015, 54, 11247; c) E. C. Mazarakioti, J. Regier, L. Cunha-Silva, W. Wernsdorfer, M. Pilkington, J. Tang, T. C. Stamatatos, *Inorg. Chem.* 2017, 56, 3568; d) Y.-L. Wang, C.-B. Han, Y.-Q. Zhang, Q.-Y. Liu, C.-M. Liu, S.-G. Yin, *Inorg. Chem.* 2016, 55, 5578; e) J. D. Rinehart, M. Fang, W. J. Evans, J. R. Long, *Nature Chem.* 2011, *3*, 538; f) A. Gorczyński, M. Kubicki, D. Pinkowicz, R. Pełka, V. Patroniak, R. Podgajny, *Dalton Trans.* 2015, 44, 16833; g) M. Fang, H. Zhao, A. V. Prosvirin, D. Pinkowicz, B. Zhao, P. Cheng, W. Wernsdorfer, E. K. Brechin, K. R. Dunbar, *Dalton Trans.* 2013, 42, 14693; h) A. Gorczyński, D. Marcinkowski, M. Kubicki, M. Löffler, M. Korabik, M. Karbowiak, P. Wiśniewski, C. Rudowicz, V. Patroniak, *Inorg. Chem. Front.* 2018, 5, 605.

- [17] L. F. Chibotaru, L. Ungur, 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, M. Shanmugam, *Chem. Eur. J.* 2015, *21*, 15639; b) H.-L. Gao, S.-X. Huang, X.-P. Zhou, Z. Liu, J.-Z. Cui, *Dalton Trans.* 2018, *47*, 3503; c) S. Biswas, S. Das, T. Gupta, S. K. Singh, M. Pissas, G. Rajaraman, V. Chandrasekhar, *Chem. Eur. J.* 2016, *22*, 18532.
- [19] a) R.-P. Li, Q.-Y. Liu, Y.-L. Wang, C.-M. Liu, S.-J. Liu, *Inorg. Chem. Front.* 2017, 4, 1149; b) I. J. Hewitt, J. Tang, N. T. Madhu, C. E. Anson, Y. Lan, J. Luzon, M. Etienne, R. Sessoli, A. K. Powell, *Angew. Chem. Int. Ed.* 2010, 49, 6352.
- [20] a) S. Biswas, H. S. Jena, A. Adhikary, S. Konar, *Inorg. Chem.* 2014, *53*, 3926; b) A. K. Mondal, H. S. Jena, A. Malviya, S. Konar, *Inorg. Chem.* 2016, *55*, 5237; c) S. Biswas, A. K. Mondal, S. Konar, *Inorg. Chem.* 2016, *55*, 2085; d) D. Peng, L. Yin, P. Hu, B. Li, Z.-W. Ouyang, G.-L. Zhuang, Z. Wang, *Inorg. Chem.* 2018, *57*, 2577.
- [21] a) H. Zhang, S.-Y. Lin, S. Xue, C. Wanga, J. Tang, *Dalton Trans.* 2014, 43, 6262; b)
  B. Joarder, A. K. Chaudhari, G. Rogezb, 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, S. Gao, *J. Mater. Chem. C* 2017, 5, 9488.
- [22] a) H.-R. Wen, P.-P. Dong, S.-J. Liu, J.-S. Liao, F.-Y. Liana, C.-M. Liu, *Dalton Trans.* 2017, 46, 1153; b) J. Goura, A. Chakraborty, J. P. S. Walsh, F. Tuna, V. Chandrasekhar, *Cryst. Growth Des.* 2015, 15, 3157; c) M. A. Palacios, S. Titos-Padilla, J. Ruiz, J. M. Herrera, S. J. A. Pope, E. K. Brechin, E. Colacio, *Inorg. Chem.* 2014, 53, 1465.
- [23] a) M. M. Hänninen, A. J. Mota, R. Sillanpää, S. Dey, G. Velmurugan, G. Rajaraman, E. Colacio, *Inorg. Chem.* 2018, 57, 3683; b) K. R. Vignesh, S. K. Langley, B. Moubaraki, K. S. Murray, G. Rajaraman, *Chem. Eur. J.* 2015, 21, 16364.
- [24] D. Schray, G. Abbas, Y. Lan, V. Mereacre, A. Sundt, J. Dreiser, O. Waldmann, G. E. Kostakis, C. E. Anson, A. K. Powell, *Angew. Chem.* 2010, 122, 5312.
- [25] a) K. R. Vignesh, A. Soncini, S. K. Langley, W. Wernsdorfer, K. S. Murray, G. Rajaraman, *Nat. Commun.* 2017, *8*, 1023; b) K. R. Vignesh, S. K. Langley, A. Swain, B. Moubaraki, M. Damjanović, W. Wernsdorfer, G. Rajaraman, K. S. Murray, *Angew. Chem. Int. Ed.* 2018, *57*, 779; *Angew. Chem.* 2018, *130*, 787; c) P. Comba, L. J. Daumann, R. Klingeler, C. Koo, M. J. Riley, A. E. Roberts, H. Wadepohl, Johannes Werner, *Chem. Eur. J.* 2018, *24*, 5319.

M.-G. Alexandru, B. Jurca, C. Mathonière, R. Clérac, M. Andruh, *Dalton Trans*. **2012**, *41*, 13578.

- [27] a) N. Ahmed, C. Das, S. Vaidya, S. K. Langley, K. S. Murray, 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, S. Mohanta, *Eur. J. Inorg. Chem.* DOI: 10.1002/ejic.201800359.
- [28] a) H. Ke, G.-F. Xu, L. Zhao, J. Tang, X.-Y. Zhang, H.-J. Zhang, Chem. Eur. J. 2009, 15, 10335; b) A. Dey, S. Das, S. Kundu, V. Chandrasekhar, CrystEngComm, 2014, 16, 1304; c) H. Ke, L. Zhao, G.-F. Xu, Y.-N. Guo, J. Tang, X.-Y. Zhang, H.-J. Zhang, Dalton Trans. 2009, 10609; d) P.-P. Yang, X.-L. Wang, L.-C. Li, D.-Z. Liao, Dalton Trans. 2011, 40, 4155; e) H. Ke, L. Zhao, Y. Guoa, J. Tang, Dalton Trans. 2012, 41, 2314; f) H. Ke, L. Zhao, Y. Guo, J. Tang, *Dalton Trans.* 2012, 41, 9760; g) S. Shen, S. Xue, S.-Y. Lin, L. Zhao, J. Tang, *Dalton Trans.* 2013, 42, 10413; h) H.-H. Zou, R. Wang, Z.-L. Chen, D.-C. Liu, F.-P. Liang, Dalton Trans. 2014, 43, 2581; i) H.-H. Zou, L.-B. Sheng, F.-P. Liang, Z.-L. Chena, Y.-O. Zhang, Dalton Trans. 2015, 44, 18544; j) Y.-M. Li, W.-W. Kuang, L.-L. Zhu, Y. Xu, 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, A. K. Powell, Inorg. Chem. 2007, 46, 7229; 1) T. Kajiwara, M. Nakano, S. Takaishi, M. Yamashita, Inorg. Chem. 2008, 47, 8604; m) A. K. Jami, V. Baskar, E. C. Sañudo, Inorg. Chem. 2013, 52, 2432; n) I. A. Kühne, G. E. Kostakis, C. E. Anson, A. K. Powell, Inorg. Chem. 2016, 55, 4072; o) Y.-Z. Zheng, Y. Lan, C. E. Anson, A. K. Powell, Inorg. Chem. 2008, 47, 10813.
- [29] a) C.-B. Tian, D.-Q. Yuan, Y.-H. Han, Z.-H. Li, P. Lin, S.-W. Du, *Inorg. Chem. Front.* 2014, 1, 695; b) Z.-Y. Liu, H.-H. Zou, R. Wang, M.-S. Chen, F.-P. Liang, *RSc. Adv.* 2018, 8, 767.
- [30] a) Y. Peng, V. Mereacre, C. E. Anson, A. K. Powell, *Dalton Trans.* 2017, 46, 5337; b)
  K. C. Mondal, G. E. Kostakis, Y. Lan, W. Wernsdorfer, C. E. Anson, A. K. Powell, *Inorg. Chem.* 2011, 50, 11604; c) H. Ke, L. Zhao, Y. Guo, J. Tang, *Inorg. Chem.* 2012, 51, 2699.
- [31] a) H. H. Thorp, *Inorg. Chem.* **1992**, *31*, 1585; b) W. Liu, H. H. Thorp, *Inorg. Chem.* **1993**, *32*, 4102.
- [32] a) J. Cirera, E. Ruiz, S. Alvarez, *Chem. Eur. J.* 2006, *12*, 3162; b) M. Pinsk, D. Avnir, *Inorg. Chem.* 1998, *37*, 5575.
- [33] J. Feuersenger, D. Prodius, V. Mereacre, R. Clérac, C. E. Anson, A. K. Powell, *Inorganic Chemistry Communications* **2011**, *14*, 1851
- [34] Q.-W. Xie, A.-L. Cui, J. Taob, H.-Z. Kou, *Dalton Trans.* 2012, 41, 10589.
- [35] A. Chakraborty, P. Bag, J. Goura, A. K. Bar, J.–P. Sutter, V. Chandrasekhar, *Cryst. Growth Des.* **2015**, *15*, 848.

- [36] a) L. W. Haynes, V. B. Pett, J. Org. Chem. 2007, 72, 839; b) S.-N. Li, Q.-G. Zhai, M.-C. Hu, Y.-C. Jiang, Z. Anorg. Allg. Chem. 2010, 636, 1142; c) M. Lalia-Kantouri, C. D. Papadopoulos, A. G. Hatzidimitriou, S. Skoulika, Struct. Chem. 2009, 20, 177; d) Y. Gao, Z. Dai, J. Zhang, X. Ma, N. Tang, J. Wu, *Inorg. Chem.* **2014**, *53*, 716; e) M. Fondo, N. Ocampo, A. M. Garcia-Deibe, J. Sanmartin, Inorg. Chem. 2009, 48, 4971; f) L. E. Garcia-Megias, E. Colacio-Rodriguez, A. Garcia-Rodriguez, J. M. Salas-Peregrin, M. Simard, A. L. Beauchamp, Inorg. Chim. Acta 1989, 156, 149; g) L. La-Sheng, L. Hung-Key, C. Xiao-Ming, J. Liang-Nian, H. Rong-Bin, Z. Lan-Sun, Private Communication 2004; h) A. B. Burdukov, K. S. Bekker, G. A. Stepanov, A. L. Bogatyrev, N. V. Pervukhina, A. S. Bogomyakov, V. A. Reznikov, Zh. Strukt. Khim. (Russ.) (J. Struct. Chem.) 2010, 51, 951; i) J. Laugier, V. Ovcharenko, P. Rey, Inorg. Chim. Acta 1995, 236, 49; j) U. Blaschke, F. Menges, G. Erker, R. Frohlich, Eur. J. Inorg. Chem. 1999, 621; k) X. Yang, R. A. Jones, M .J. Wiester, Dalton Trans. 2004, 1787; 1) Y.-N. Chi, P.-P. Shen, F.-Y. Cui, Z.-G. Lin, S.-L. Chen, C.-W. Hu, Inorg. Chem. 2014, 53, 5020.
- [37] Y.-N. Guo, G.-F. Xu, Y. Guo and J. Tang, *Dalton Trans.*, **2011**, *40*, 9953;.
- [38] D. Gatteschi, R. Sessoli, J. Villain, *Molecular Nanomagnets*, OUP, Oxford, **2006**, 69.
- [39] M. Grahl, J. Kotzler, I. Sessler, J. Magn. Magn. Mater. 1990, 90-1, 187.
- [40] M. Yadav, A. Mondal, V. Mereacre, S. K. Jana, A. K. Powell, P. W. Roesky, *Inorg. Chem.* 2015, 54, 7846.
- [41] N. F. Chilton, D. Colliso. n, E. J. L. McInnes, R. E. P. Winpenny, A. Soncini, *Nat. Commun.* 2013, 4, 2551.
- [42] 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.

# Illustrated Synopsis For

Synthesis, Crystal Structures and Magnetic Properties of New Hexanuclear Mn<sup>III</sup><sub>2</sub>Ln<sup>III</sup><sub>4</sub> Complexes: SMM Behavior of the Terbium(III) Analogue

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**Key Topic: Magnetic Properties** 

A Schiff base ligand (1:1 condensation product of 3-methoxysalicylaldehyde and 2-amino-2-methyl-1-propanol), which was not utilized so far to isolate 3d-4f compounds, has been employed here to prepare four  $Mn_{2}^{III}Ln_{4}^{III}$  compounds (Ln = Tb, Dy, Ho, Er) having some new types of structural features. Detailed dc and ac magnetic studies reveal that only the Tb<sup>III</sup> analogue is an SMM ( $U_{eff} \approx 11 \text{ cm}^{-1}$ ).

