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Family of Mn<sup>III</sup> <sub>4</sub>Ln<sup>III</sup> <sub>2</sub> (Ln<sup>III</sup>= Sm<sup>III</sup>, Gd<sup>III</sup>, Dy<sup>III</sup>) coordination clusters: experimental and theoretical investigations

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# Family of Mn<sup>III</sup><sub>4</sub>Ln<sup>III</sup><sub>2</sub> (Ln<sup>III</sup>= Sm<sup>III</sup>, Gd<sup>III</sup>, Dy<sup>III</sup>) coordination clusters: experimental and theoretical investigations

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#### ABSTRACT

The present work introduces a family of  $Mn^{III}_4Ln^{III}_2$  ( $Ln^{III} = Sm^{III}$ ,  $Gd^{III}$ ,  $Dy^{III}$ ) coordination clusters having a multisite hydroxyl rich ligand, 3-[(2-hydroxy-3-methoxy-benzylidene)-amino]-propane-1,2-diol (H<sub>3</sub>Vapd), namely [ $Mn^{III}_4Sm^{III}_2(Vapd)_4(OAc)_6$ ]·4H<sub>2</sub>O (1), [ $Mn^{III}_4Gd^{III}_2(Vapd)_4(OAc)_6$ ]·4H<sub>2</sub>O (2) and [ $Mn^{III}_4Dy^{III}_2(Vapd)_4(OAc)_6$ ]·4H<sub>2</sub>O (3). The Sm<sup>III</sup> analogue is the first example of a Mn<sub>4</sub>Ln<sub>2</sub> species reported to date. The similarities and differences in terms of structure, topology and magnetic behaviours within the series are investigated extensively. DFT computations were carried out for  $Mn^{III}_4Gd^{III}_2$  to address the experimentally challenging questions regarding the nature of the magnetic interactions in this cluster.

Keywords: Manganese, Lanthanides, Topology, Magnetic properties, Density functional calculations

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#### 1. Introduction

The field of 3d-4f chemistry is broadening due to the remarkable physical and chemical properties associated with this class of materials [1], like magnetism [2-4], luminescence [5,6], gas adsorption [7] and catalysis [8], as well as their intriguing architectures. The 3d transition metal ions exhibit a wide variety of physical and chemical properties by virtue of their diverse 3d electrons. Moreover, the incorporation of Ln<sup>III</sup> ions possesses promising prospects for interesting magnetic phenomena because of their inherent large amounts of anisotropy. Thus, the idea of coupling Ln<sup>III</sup> centers with 3d metal ions opens up a promising avenue for the construction of novel functional materials, boosted by the tremendous development of molecular magnetism [9].

The discovery of the first example of a compound showing single molecule magnet behavior happens to be a (Mn<sup>III</sup>/Mn<sup>IV</sup>) species, [Mn<sub>12</sub>O<sub>12</sub>(OAc)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>] [10]. Thus, Mn<sup>II</sup>/Mn<sup>III</sup>/Mn<sup>IV</sup> centers together with the power of Ln<sup>III</sup> ions, i.e. the Mn/Ln subclass of 3d-4f clusters, continues to reside at the center of attraction as they are projected as components of magnetic spintronic devices based on single molecule magnets [9]. A variety of structural types, compositions and topologies have been identified so far for Mn-Ln clusters, of which high-nuclearity clusters occupy an appreciable volume: Mn<sup>III</sup><sub>2</sub>Ln<sup>III</sup><sub>2</sub> [11a–11e], Mn<sup>IV</sup><sub>2</sub>Ln<sup>III</sup><sub>2</sub> [11f], Mn<sup>III</sup><sub>2</sub>Ln<sup>III</sup><sub>3</sub> [11g],  $Mn^{II}_{3}Ln^{III}$  [11h],  $Mn^{II}_{4}Ln^{II}_{2}$  [9f,11i,j],  $Mn^{II}_{2}Mn^{II}_{2}Ln^{III}_{2}$  [11k,l],  $Mn^{III}_{4}Ln^{III}_{4}$  [11m-110],  $Mn_{2}^{II}Mn_{2}^{III}Ln_{6}^{III}$  [11p],  $Mn_{4}^{IV}Mn_{4}^{III}Ln_{4}^{III}$  [11q],  $Mn_{4}^{IV}Mn_{4}^{III}Ln_{6}^{III}$  [11r],  $Mn_{5}^{III}Ln_{8}^{III}$  [11s],  $Mn^{III}_{6}Ln^{III}_{2}$  [11t,u],  $Mn^{IV}_{2}Mn^{III}_{4}Ln^{III}_{6}$  [11v],  $Mn^{III}_{7}Ln^{IV}_{3}$  [11w],  $Mn^{III}_{9}Ln^{III}_{8}$  [11x],  $Mn^{III}_{10}Ln^{III}_{2}$ [11y],  $Mn^{II}_{2}Mn^{III}_{9}Ln^{III}_{2}$  [11z],  $Mn^{III}_{11}Ln^{III}_{4}$  [11y,12a],  $Mn^{III}_{11}Ln^{IV}_{5}$  [11w],  $Mn^{III}_{11}Ln^{III}_{11}$ [12b],  $Mn^{III}_{12}Ln^{III}_{6}$  [12c],  $Mn^{III}_{12}Mn^{II}_{6}Ln^{III}$  [12d],  $Mn^{IV}_{3}Mn^{III}_{18}Ln^{III}$  [12e]. Interestingly, low-nuclearity aggregates are quite scarce and there are only a few reports of hexanuclear Mn<sub>4</sub>Ln<sub>2</sub> complexes [9f,11i-11]. We envisage that further examples of Mn-Ln compounds would help to improve the experimental and theoretical realization of the complicated magnetic exchange interactions involving transition metals and lanthanide ions.

Here, we report an experimental demonstration of lanthanide contraction within members of an alternately varied series of  $Mn^{III}_{4}Ln^{III}_{2}$  ( $Ln^{III} = Sm^{III}$ ,  $Gd^{III}$ ,  $Dy^{III}$ ) coordination clusters:  $[Mn_{4}Ln_{2}(Vapd)_{4}(OAc)_{6}]\cdot 4H_{2}O$  [ $Ln^{III} = Sm^{III}(1)$ ,  $Gd^{III}(2)$ ,  $Dy^{III}(3)$  and  $H_{3}Vapd = 3$ -[(2-hydroxy-3-methoxy-benzylidene)-amino]-propane-1,2-diol]. The relative consequence of lanthanide contraction has been assessed to clarify the fundamental chemistry of lanthanides. In addition, their magnetic behaviors are investigated in detail. The concerted application of experimental magnetism and theoretical consideration became necessary to define the magnetic behavior of the  $Mn^{III}_{4}Ln^{III}_{2}$  series. We believe that the present investigations are significant because these results can extend the knowledge base regarding prevailing interactions within  $Mn^{III}$ - $Ln^{III}$  cores.

#### 2. Result and Discussion

#### 2.1. Syntheses and general characterization

The course of choosing ligands of the appropriate design has been demonstrated to be an effective strategy for the generation of 3d-4f clusters. In our previous works on the construction of homo and heterometallic 3d and 3d-4f clusters,  $Ni^{II}_4$ ,  $Mn^{III}_2Ni^{II}_2$ ,  $Co^{IIC}O^{III}$ ,  $Co^{II}_2Co^{III}$ ,  $Cu^{II}_4Dy^{III}$ ,  $Cu^{II}_6Dy^{III}_3$  [13a,b,4], we have used the multisite hydroxyl rich ligands 3-[(2-hydroxy-benzylidene)-amino]-propane-1,2-diol (H<sub>3</sub>Sapd), 3-[(2-hydroxy-3-methoxy-benzylidene)-amino]-propane-1,2-diol (H<sub>3</sub>Vapd), 2-[(3-hydroxy2-[(3-hydroxy-propylimino)-methyl]-6-methoxy-phenol (H<sub>2</sub>Vap) and 2-[(3-hydroxy-ethylimino)-methyl]-6-methoxy-phenol (H<sub>2</sub>Vap). Indeed, a couple of groups have also employed these ligands to design promising homo and heterometallic platforms [17c-17g,18,20b]. The ligand H<sub>3</sub>Vapd contains an O<sub>4</sub>N donor set with five potential incorporable sites (one methoxo, one phenoxo, one imino and two alkoxo donor atoms) admitting various coordination pockets with their different bindings modes to the 3d and

4f metal ions (shown in Scheme S1 and Schemes S2-S4 in the Supplementary Information). The versatile ligand H<sub>3</sub>Vapd was prepared by a simple Schiff base condensation reaction using 3-amino-1,2-propanediol and *o*-vanillin under refluxing conditions in ethanol. It is based on a basic phenol-framework and contains two unsymmetrically disposed substituents. Adjacent to the phenol unit, on one side is a 1,2 propanediol amine group and on the other side a methoxy group. The syntheses of the complexes are similar, with the self-assembly of H<sub>3</sub>Vapd, Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O, and Ln(OAc)<sub>3</sub>·*x*H<sub>2</sub>O (in a 2:2:1 stoichiometric ratio) in the presence of triethylamine as a base, in methanol, as in eq 1.

$$4Mn(OAc)_{2} + 2Ln(OAc)_{3} + 4H_{3}Vapd + 8Et_{3}N + O_{2} = [Mn_{4}Ln_{2}(Vapd)_{4}(OAc)_{6}] + 8Et_{3}NH(OAc) + 2H_{2}O$$
(1)

Dark brown block shaped single crystals were obtained by the slow diffusion of diethyl ether into a methanolic solution of the complexes, with yields of 34-37 %, based on the ligand (Scheme 1, see also, Experimental Section). It should be mentioned that NEt<sub>3</sub> not only acts as a proton acceptor, but also provides the basic condition to facilitate the aerial oxidation of the Mn<sup>II</sup> ion to the Mn<sup>III</sup> ion. It is interesting to note that among the previously reported five Mn<sub>4</sub>Ln<sub>2</sub>  $Mn^{III}_{4}Ln^{III}_{2}$ complexes complexes. three [9f,11i,j] used 2,6-bis[((2-(2hydroxyethoxy)ethyl)imino)methyl]-4-methylphenol), salicylhydroxamic acid and 2-(((2hydroxy-3-methoxyphenyl)methylene)amino)-2-(hydroxymethyl)-1,3-propanediol, while the  $Mn_{2}^{II}Mn_{2}^{III}Ln_{2}^{III}$ complexes two [11k,1] N,N,N',N'-tetrakis(2other used hydroxyethyl)ethylenediamine and {1,1,1-tris(hydroxymethyl)ethane, triethanolamine containing pivalic acid} as coordination ligands (Scheme 2). In this work we report the first  $Mn_{4}^{III}Ln_{2}^{III}$ aggregate in which the manganese centers Mn1 and Mn2 (along with their symmetry equivalents) are six and five coordinated respectively.

The experimental powder XRD patterns of the bulk crystalline material of 1-3 are in good agreement with the simulated XRD patterns from the single crystal X-ray diffraction results, confirming the purity of the bulk samples (Fig. S1-S3 in the Supplementary Information). Furthermore, in order to investigate the purity of the bulk crystalline material, energy-dispersive X-ray (EDX) analysis of 1-3 confirmed the homogeneity of our crystals and also showed the presence of both Mn and Ln ions in the complexes, with Mn:Ln ratios of 69.59:30.41 (for 1, where Ln = Sm), 68.16:31.84 (for 2 where Ln = Gd) and 66.03:33.97 (for 3 where Ln = Dy), which corroborated with the results obtained from single crystal X-ray diffraction (shown in the Supplementary Information, Figs. S4-S6). The IR spectra of complexes 1-3 are very similar and display the characteristic bands of the coordinated ligand and the acetato groups (Fig. S7). The broad IR absorption at ~3430 cm<sup>-1</sup> is attributed to the O–H stretching frequency of the H<sub>2</sub>O ligands. A diagnostic sharp absortion at ~1643 cm<sup>-1</sup> is due to the C=N stretching of the Schiff base ligand, which is shifted to ~1619 cm<sup>-1</sup> owing to complexation. In addition, the absorption at ~1225 cm<sup>-1</sup> is assigned to the C–O<sub>phen</sub> bond, which is shifted to ~1250 cm<sup>-1</sup> in the metal complexes, as the ligand coordinates in its deprotonated form. Due to the presence of both

asymmetric  $(\eta^2; \eta^1; \mu_2)$  and symmetric (syn-syn  $\eta^1; \eta^1; \mu_2$ ) acetato bridging, two distinct  $\bar{\nu}(CO)$ stretching frequency absorption bands at ~1560 and ~1438  $\text{cm}^{-1}$  are observed, respectively[15]. ESI-MS spectra of complexes 1-3 were recorded in MeOH medium to explore the principal species present in the solution (see Fig. S8-S10 in the Supplementary Information). All the complexes show a similar kind of behavior by signalling the molecular ion peak at 525.027 and 555.037 a.m.u., which corresponds to  $C_{21}H_{22}N_2O_7Mn_2$ , formulated as  $[Mn_2(Sapd)(Vapd)+H^+]^+$ (where the generation of  $\text{Sapd}^{3-}$  originates from the loss of the –OMe group from  $\text{Vapd}^{3-}$ ), and  $C_{22}H_{24}N_2O_8Mn_2$  for  $[Mn_2(Vapd)_2+H^+]^+$ , respectively. In the case of the  $Mn_4Sm_2$  cluster (1), the 825.718, 882.777 and 903.761 a.m.u. for  $[Mn_4Sm_2(Vapd)_4(OAc)_4]^{2+}$ , peaks at  $[Mn_4Sm_2(Vapd)_4(OAc)_6 + 2H^+]^{2+}$  and  $[Mn_4Sm_2(Vapd)_4(OAc)_6 + 2Na^+]^{2+}$  respectively, prove the molecular integrity in the solution phase. Complex 2 was observed in the ESI-MS peak with the loss of the -OAc group, with peaks appearing at 802.007 and 832.077 a.m.u., which correspond to  $[Mn_4Gd_2(Vapd)_4(OAc)_3+H^-]^{2+}$  and  $[Mn_4Gd_2(Vapd)_4(OAc)_4]^{2+}$  respectively. For complex 3 the 806.032 and 735.974 a.m.u. well corroborate with peaks at the species  $[Mn_4Dy_2(Vapd)_4(OAc)_3+H^-]^{2+}$  and  $[Mn_3Dy_2(Vapd)_3(OAc)_5(H_2O)+H^+]^{2+}$  respectively.

#### 2.2. Crystal structure descriptions

Single-crystal X-ray diffraction measurements revealed that compounds 1-3 crystallize in the triclinic space group  $P\overline{1}$  with Z = 1. The structures consist of heterometallic, hexanuclear Mn<sub>4</sub>Ln<sub>2</sub> [Ln<sup>III</sup> = Sm<sup>III</sup> (1), Gd<sup>III</sup> (2) and Dy<sup>III</sup> (3)] clusters with the general formula [Mn<sup>III</sup><sub>4</sub>Ln<sup>III</sup><sub>2</sub>(Vapd)<sub>4</sub>(OAc)<sub>6</sub>]·4H<sub>2</sub>O and with the asymmetric unit (ASU) containing half of the complex, which lies upon an inversion center (see Figs. 1 and 2). The two different binding modes of the tri-anionic ligand (Vapd<sup>3-</sup>) and the acetato group in the compounds have been shown in Fig. 3. The oxidation states of the manganese ions and the protonation levels on the coordinated oxygen atom of H<sub>3</sub>Vapd in the complexes were assigned by inspection of the metric parameters, charge-balance considerations, Jahn–Teller elongation axes and by bond valence sum analysis (see Tables S1 and S2 in the Supplementary Information) [16a].

Complexes 1 and 2 are isomorphs and therefore only the crystal structures of complex 1, i.e. the  $Mn_4Sm_2$  analogue, and complex 3 will be described here. Selected bond distances and bond angles of all the complexes are summarized in the Supplementary Information, Table S3.

A close scrutiny reveals that the  $[Mn^{III}_{4}Sm^{III}_{2}]^{18+}$  core of **1** can be described as being composed of two parts; (i) a central  $Mn_{2}^{III}Sm_{2}^{III}$  core displaying a planar butterfly type topology (comprising Mn1, Mn1<sup>#</sup>, Sm1 and Sm1<sup>#</sup>). The two Sm<sup>III</sup> ions are found at the "body" sites of the butterfly, whereas the Mn<sup>III</sup> ions occupy the outer "wing" positions. Two  $\mu_{3}$ -alkoxo groups bridge the two Sm<sup>III</sup> ions to each Mn<sup>III</sup> ion and (ii) two isolated Mn<sup>III</sup> ions (Mn2 and Mn2<sup>#</sup>) capping the lanthanides from opposite sides. These are attached to the Sm<sup>III</sup> ions by means of two  $\mu_{2}$ -alkoxo oxygen atoms and are located ~ 2.852 Å above and below the Mn<sup>III</sup><sub>2</sub>Sm<sup>III</sup><sub>2</sub> plane. The overall core of **1** can be perceived as that of a spacecraft (Fig. 4). The central Mn<sup>III</sup><sub>2</sub>Sm<sup>III</sup><sub>2</sub> unit forms the body of the spacecraft and the two capping Mn<sup>III</sup> centers constitute the wings.

The peripheral ligation is provided by two  $\eta^1:\eta^1:\eta^2:\eta^3:\mu_4$  ligands (Vapd<sup>3-</sup>) and two  $\eta^1:\eta^1:\eta^2:\eta^2:\mu_3$  ligands (Vapd<sup>3-</sup>), the two rhombuses enjoy a second contact between the Mn1 and Sm1<sup>#</sup> atoms (Mn1<sup>#</sup> and Sm1) from  $\eta^2:\eta^1:\mu_2$  acetato bridging. This bridging pattern is reflected in the metal-metal distances of each rhombus.

The Mn(1) and Mn(1<sup>#</sup>) ions are in six coordinated  $O_5N_1$  distorted octahedral environments (deviation of 0.808 from the ideal  $O_h$  symmetry, out of the range 0.1-3, CShM value) as pointed out by CShM calculations [16b,c], with the Jahn–Teller axis  $\mu_2$ -O<sub>OAc</sub><sup>...</sup>Mn(1/1<sup>#</sup>)... $\mu$ -O<sub>OAc</sub> expected for d<sup>4</sup> high spin Mn<sup>III</sup> ions (Fig. 5 and Table S4 in the Supplementary Information). Applying the nomenclature developed by Stiefel and Brown, detailed geometrical calculations reveal that the azimuthal expansion in the distorted octahedral geometry occurs with an average azimuthal angle  $\emptyset$  of 65.2°, which is larger than the ideal value ( $\emptyset = 60^{\circ}$ ) [16d], further supporting the J-T distortion characteristic of the d<sup>4</sup> Mn<sup>III</sup> system (see Supplementary Information, Fig. S12 and Table S5). The equatorial positions are occupied by O<sub>3</sub>N donor atoms, contributed by the ligand phenoxo oxygen, imine nitrogen,  $\mu_3$ -alkoxo and  $\mu_2$ -alkoxo atoms. The axial positions are occupied by one  $\eta^2: \eta^1: \mu_2$  and one  $\eta^1: \eta^1: \mu_2$  acetato group. In contrast, the Mn(2) and  $Mn(2^{\#})$  ions are five coordinated, adopting a distorted trigonal bipyramid geometry, (deviation of 1.367 from the ideal  $D_{3h}$  symmetry, out of the range 0.1-3, CShM value) with an O<sub>4</sub>N environment, as depicted by CShM analysis, which is also supported by the Addison parameter ( $\tau$ ) = 0.617 (Fig. 5) [16e]. The equatorial positions are occupied by O<sub>2</sub>N donor atoms from one  $\eta^1:\eta^1:\eta^2:\eta^3:\mu_4$  ligand ( $\mu_2$ -alkoxo), one  $\eta^1:\eta^1:\eta^2:\eta^2:\mu_3$  ligand (imino nitrogen atom) and one  $\eta^{1}$ :  $\eta^{1}$ :  $\mu_{2}$  acetato group. The axial positions are occupied by two oxygen atoms from the same  $\eta^1:\eta^2:\eta^2:\mu_3$  ligand (phenoxo and  $\mu_2$ -alkoxo). The average Mn–O and Mn–N bond distances in the TBP and distorted octahedral coordination environments are 1.935(6), 2.030(6) and 1.987(7), 2.042(7) Å, respectively.

Each Sm<sup>III</sup> ion adopts a nine coordinated coordination polyhedron and can be best described as a distorted spherical capped square antiprism with a minimum deviation of 1.938 (out of the range 0.1-3, CShM value) from the ideal  $C_{4\nu}$  symmetry (Fig. 5) [13b,c]. The analysis of its coordination geometry with SHAPE is shown in the Supporting Information Table S4. The coordination sphere of each Sm<sup>III</sup> ion is formed by two oxygen atoms from one  $\eta^1:\eta^1:\eta^2:\eta^2:\mu_3$ ligand, three oxygen atoms from two  $\eta^1:\eta^1:\eta^2:\eta^3:\mu_4$  ligands, two oxygen atoms from one  $\eta^1:\eta^2:\mu_2$ acetato group and remaining two oxygen atoms from two  $\eta^1:\eta^1:\eta^2:\mu_2$  acetato groups. The Sm–O<sub>alk</sub> and Sm–O<sub>OAc</sub> bond distances are in the ranges 2.363(6)-2.801(5) and 2.414(6)-2.555(6) Å respectively.

The intracluster Sm<sup>III</sup>····Sm<sup>III</sup> and average Sm<sup>III</sup>····Mn<sup>III</sup> distances are 4.485(17) and 3.535(17) Å respectively in the hexanuclear core.

2.3. Differences between the solid state structures of complexes 1/2 with 3

The partially labelled structure of complex 3 is presented in Figure 4. The structure of 3 is to some extent superimposable with that of 1 and 2. The coordination environment of the cores of 1/2 and 3 differ significantly: (i) In 3, the ligand Vapd<sup>3-</sup> binds in the  $\eta^1:\eta^2:\eta^2:\mu_4$  mode instead of the  $\eta^1:\eta^2:\eta^3:\mu_4$  mode (ii) The coordination sites are filled with four alkoxo oxygen atoms  $[Dy-O_{alk} = 2.310(3)-2.466(3) \text{ Å}]$  and four acetato ions  $[Dy-O_{OAc} = 2.352(4)-2.510(4) \text{ Å}]$ . Here, the Dy1 .... O4 (Fig. 4) distance is 2.976 Å, which is borderline to be considered as a Dy-O bond. Again, we have performed CShM calculations based on both eight (no Dy-O bond) and nine (considering Dy-O bond) coordinated Dy<sup>III</sup> ions, but much higher values are observed for the nine coordinated species (Table S4 in the Supplementary Information). Therefore, we have considered the Dy<sup>III</sup> ion as possessing the typical eight-coordinate geometry without the above mentioned Dy....O contact as judged by the reported Dy-O distances and CShM calculations. The CShM results point towards a biaugmented trigonal prism arrangement with a minimum deviation of 1.539 from the ideal  $C_{2\nu}$  symmetry, out of the range 0.1-3, for the Dy<sup>III</sup> center (Fig. 5 and Table S4, in the Supplementary Information) [16b,c]. (iii) In 3, two symmetry related Dy<sup>III</sup> and Mn<sup>III</sup> ions are arranged in a rhombus with two isolated Mn<sup>III</sup> ions capping from opposite directions, but it is marked by the absence of two  $\mu_3$ -alkoxo bridges (Fig. 4), where the intracluster  $Dy^{III...}Dy^{III}$  and average  $Dy^{III...}Mn^{III}$  distances are 4.616(4) and 3.522(8) Å respectively in the hexanuclear core. There is no previous example of such a discrete unit in 3d-4f chemistry.

The molecules of 1, 2 and 3 are well separated within the crystal packing and no intermolecular hydrogen bonds are observed in the crystal packing (Fig. S13 in the Supplementary Information).

#### 2.4. The effect of lanthanide contraction

The hypothesis underlying this work was that, by varying the Ln<sup>III</sup> ions along the most crucial region of the lanthanide series, we might be able to visualize the direct consequence of the lanthanide contraction on the structural outcome. Indeed, a minute balance of lanthanide contraction affects the structural output of 1, 2 and 3. This comparison is better quantitatively described by examination of the metrical data provided in Table 1 which compares the Ln–O and Ln–Mn bond distances. The Ln–O(4) bond distances generally decrease in the order 1 > 2 > 3, in accord with the lanthanide contraction, and as a result the  $Ln1^{\#}-O(4)$  distances vary in the order 1 < 2 < 3. The consequence of the lanthanide contraction is that the smaller Dy<sup>III</sup> ion has significantly shorter Ln1–O4 distance, resulting in a stretched Ln1<sup>#</sup>–O4 separation of 2.976(4) Å. A quick examination of Fig. 6 and Table 1 demonstrates that with decreasing Ln1-O4 bond distance from Sm<sup>III</sup> to Dy<sup>III</sup>, the Ln1<sup>#</sup>–O4 distance difference increases and finally in the dysprosium analogue (3), the O4 atom lies farthest from the  $Dy1^{\#}$  atom and the  $Dy1^{\#}$ -O(4) connectivity is broken, resulting in a rhombus structural motif instead of a butterfly motif. As expected, the  $Ln1-Ln1^{\#}$  distances follow the order 1 < 2 < 3. The Ln1-Mn1, Ln1–Mn1<sup>#</sup> and Ln1–Mn2 distances are also in accord with the lanthanide contraction.

#### 2.5. Topological features of the hexanuclear core

To better appreciate the structural features of 1, 2 and 3, we have adopted the topological approach established by Kostakis and co-workers [17a-17e]. Applying this method, the centrosymmetric hexanuclear [Mn<sup>III</sup><sub>4</sub>Sm<sup>III</sup><sub>2</sub>] and [Mn<sup>III</sup><sub>4</sub>Gd<sup>III</sup><sub>2</sub>] cores can be represented as two fused triangles comprising two Ln<sup>III</sup> and one Mn<sup>III</sup> nodes with two isolated Mn<sup>III</sup> nodes connected to the Ln<sup>III</sup> centers (Fig. 7). Numerically, Mn1 is a 2-connected node, Ln1 is a 4-connected node and Mn2 represents a 1-connected node; thus the cluster is described by the symbol 1,2,4M6-1 [17e]. Following a similar approach, the [Mn<sub>4</sub>Dy<sub>2</sub>] core can be described as a rectangle comprising two Dy<sup>III</sup> and two Mn<sup>III</sup> nodes with two isolated Mn<sup>III</sup> nodes attached to the lanthanides. Here, Mn1 is a 2-connected node, Dy<sup>III</sup> is a 3-connected node and Mn2 is a 1connected node and the cluster is depicted by symbol 1,2,3M6-1. We performed a comparative study of the [Mn<sub>4</sub>Ln<sub>2</sub>] cores reported in the literature. [Mn<sup>III</sup><sub>4</sub>Ln<sup>III</sup><sub>2</sub>( $\mu_3$ -O)<sub>2</sub>(Hbeemp)<sub>2</sub>(OAc)<sub>8</sub>( $\mu_3$ - $OMe_{2}(H_{2}O)_{2}C_{8}H_{17}OH$  (Ln<sup>III</sup> = Gd<sup>III</sup>, Tb<sup>III</sup>, Y<sup>III</sup>) [11i] has a similar topology, but the isolated Mn<sup>III</sup> ion caps both the Ln<sup>III</sup> and Mn<sup>III</sup> ions of the [Mn<sub>2</sub>Ln<sub>2</sub>] rhombus thereby representing a cluster. Pecoraro 2,3,4M6-1 The group reported  $[Mn_4Ln_2]$ cores for  $[Mn^{III}_{4}Ln^{III}_{2}(OAc)(NO_{3})_{2}(shi)_{4}(\mu-O)(\mu-OH)](C_{5}H_{5}N)_{8}(C_{3}H_{7}NO)_{3}H_{2}O (Ln^{III} = Y^{III}, Tb^{III}, Dy^{III}, Dy^{III})$ compounds 1,2,5M6-1 Ho<sup>III</sup>) metallacrown with the as topology [11i].  $[Mn^{III}_{4}Ln^{III}_{2}(H_{2}L)_{2}(HL)_{2}(OAc)_{4}(CH_{3}O)_{2}(CH_{3}OH)_{4}](ClO_{4})_{2} \cdot 6CH_{3}OH (Ln^{III} = La^{III}, Nd^{III}) clusters$ exhibit close topological features [9f]. Here, the Mn<sup>III</sup> nodes are connected, therefore, the symbol becomes 1,3,3M6–1. Scrutinizing the  $[Mn_4Ln_2]$  cores with the  $Mn_2^{II}Mn_2^{III}Ln_2^{III}$  distribution, two different series are found:  $[Mn^{II}_2Mn^{III}_2(O_2CBu^t)_6(edteH_2)_2(NO_3)_2]$  ( $Ln^{III} = Gd^{III}$ ,  $Tb^{III}$ ) [11k] and  $[Mn^{II}_{2}Mn^{III}_{2}Ln^{III}_{2}(Piv)_{8}(thme)_{2}(H_{2}tea)_{2}]$   $(Ln^{III} = Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III})$ [11] with the topological motifs 4,5M6-1 and 2,3,4M6-1 respectively. It is interesting to note here that other than complexes 1 and 2, the 1,2,4M6-1 topological motif can be found in the dodecanuclear compounds reported by Yang et al. [17f]. The 1,2,3M6-1 topological motif is the first example of Mn<sub>4</sub>Ln<sub>2</sub> clusters (Table S6) along with another Co<sub>4</sub>Gd<sub>2</sub> [17g] cluster.

#### 2.6. Comparison with other related complexes

The new compounds **1**, **2** and **3** join a small family of  $Mn_4Ln_2$  complexes reported in the literature. First of all, it should be noted that not all the three lanthanides chosen yielded the same structural types. When Sm<sup>III</sup> and Gd<sup>III</sup> (larger and lighter among the series) were chosen as the starting trivalent cation (**1** and **2**), a  $\mu_3$ -alkoxo bridged cluster was generated, whereas the Dy<sup>III</sup> (**3**) analogue was devoid of any  $\mu_3$ -alkoxo bridging as a direct consequence originating from the minute balancing of the lanthanide contraction effect, as discussed in the earlier section. It is worth noting that the cores of **1** and **2** are very similar to two other  $Mn_4Ln_2$  clusters reported earlier [9f,11i]. In 2008, there was a report on compounds with a  $[Mn^{III}_4Ln^{III}_2]$  core without a systematic variation of the lanthanides (Gd<sup>III</sup>, Tb<sup>III</sup> and Y<sup>III</sup>) [11i], but the compounds were isomorphous. In the hexanuclear core, the butterfly shaped  $Mn^{III}_2Ln^{III}_2$  fragment was supported

by  $\mu_2$ -alkoxo,  $\mu_3$ -methoxo and  $\mu_3$ -oxido groups. The remaining Mn<sup>III</sup> ions were linked to the tetranuclear core by means of two acetato and a phenoxo oxygen atom, thereby capping the Mn–Ln edges of the tetranuclear core (shown in Scheme 2). Here, all the Mn<sup>III</sup> ions were six coordinated and the Ln<sup>III</sup> ions were nine coordinated with an O<sub>8</sub>N environment. Another molecule that features a [Mn<sup>III</sup><sub>4</sub>Ln<sup>III</sup><sub>2</sub>] core is reported by Ke et al. with close structural features [9f]. The structures comprised a central Mn<sup>III</sup><sub>2</sub>Ln<sup>III</sup><sub>2</sub> planar rhombus with two Mn<sup>III</sup> ions located above and below the rhombus (Scheme 2). The structure contains a  $\mu_3$ -methoxo bridge that links the central Mn<sup>III</sup> ions. All the Mn<sup>III</sup> ions were six coordinated and the Ln<sup>III</sup> or service of the service of the service of these compounds are very similar to the cited compounds herein.

Interestingly,  $\mu_3$ -methoxo/ $\mu_3$ -oxo bridging is prevalent in connecting the Mn<sup>III</sup> centers with the Ln<sup>III</sup> ions of the butterfly core in the previous reports; but in our case  $\mu_3$ -alkoxo bridges contribute in linking the ions. The coordination environment around the Mn<sup>III</sup> ions differ from the previously reported complexes in that two Mn<sup>III</sup> ions are hexacoordinated while two others are penta coordinated. In this context it worth mentioning that Pecoraro and co-workers reported a new metallacrown containing two Ln<sup>III</sup> and four Mn<sup>III</sup> ions and a partially systematic series was studied [11j].

Recently two reports on new  $[Mn_4Ln_2]$  cores appeared with the  $[Mn_2^{II}Mn_2^{III}Ln_2^{III}]$  distribution [11k,1]. The molecule  $[Mn_2^{II}Mn_2^{III}Ln_2^{III}(O_2CBu^t)_6(edteH_2)_2(NO_3)_2]$ , made by the Christou group, has a face-fused, double cubane structure comprising four Mn and two Ln atoms bridged by two  $\mu_4$ -oxo and four  $\mu_3$ -alkoxo groups [11k]. In  $[Mn_2^{II}Mn_2^{III}Ln_2^{III}(Piv)_8(thme)_2(H_2tea)_2]$ , four face sharing defective cubanes are held together by alkoxo oxygen atoms with different bridging modes [111].

Our series clearly demonstrates how the identity of the  $Ln^{III}$  ion influences the structural outcome of the  $[Mn_4Ln_2]$  core. The planar butterfly type orientation of the central  $Mn^{III}_2Ln^{III}_2$  core of **1** and **2** contrasts markedly with that observed for **3**. The Ln1–O4 bond length steadily decreases from  $Sm^{III}$  to  $Dy^{III}$ , following the standard lanthanide contraction, indicating that the  $Ln^{III}$  size consistently affects the  $Mn_2Ln_2$  central core. The presence of a smaller  $Dy^{III}$  ion in **3** leads to stretching of the  $Ln1^{#}$ –O4 bond to such an extent that it is broken.

To our knowledge, very few examples of hexanuclear 3d-4f complexes with a similar topology have been reported in recent times. As far our knowledge goes, no example of  $[Mn_4^{III}Ln_2^{III}]$  aggregates including Sm<sup>III</sup> ions has been published to date.

In most of the series encountered in the literature, isostructural series are obtained, but we have chosen alternate lanthanides to compare, thus providing a greater span, and this allowed for the desired structural perturbation, highlighting the immediate effect of lanthanide contraction. The assessment does not include variation of the Mn<sup>III</sup> centers and the ligand system. The uniqueness of the reported series is twofold: (i) the  $\mu_3$ -alkoxo group holds the central core instead of  $\mu_3$ -methoxo/  $\mu_3$ -oxo groups. (ii) a clear demonstration of lanthanide contraction is given. Finally, sufficient numbers of clusters having similar structures are required in order to frame a complete structural correlation, and this work is underway in our laboratory.

#### 2.7. Magnetic studies

The temperature dependence of the magnetic susceptibilities in the temperature range 2.0-300 K under an external magnetic field of 0.5 T for the three complexes are shown in Fig. 8, as plots of  $\chi_M T$  vs. *T* and  $\chi_M$  vs. *T*. The field dependence of the magnetization up to 50000 Oe (5 T) at 2.0 K is shown in Fig. 9, as the plots of  $M_{\text{mol}}/(N_A\mu_B)$  vs. *H*.

For complex 2, the  $\chi_M$ T (where  $\chi_M$  is the molar susceptibility per hexanuclear Mn<sup>III</sup><sub>4</sub>Ln<sup>III</sup><sub>2</sub> unit) values decrease in the low temperature region. This data clearly indicates the presence of effects favouring the formation of ground states possessing either low total spin *S* or low total atomic angular momentum J (J = S + L) of the lanthanide ions [18a]. Such effects may result from spin-orbit coupling or axial splitting of the ground states or/and antiferromagnetic exchange coupling between two Ln<sup>III</sup> ions or Mn<sup>III</sup> and Ln<sup>III</sup> ions. This superexchange interaction should be weak (compared with the crystal field splitting and spin-orbit coupling effects) because the magnetic f orbitals of the lanthanide are better shielded than the d orbitals, leading to a low overlap between the ligand and the f orbitals [18b].

For  $\text{Mn}^{\text{III}}_{4}\text{Gd}^{\text{III}}_{2}$  (2), the  $\chi_M T$  value of 25.80 [cm<sup>3</sup> K mol<sup>-1</sup>] at 300 K is close to the calculated theoretical value of 27.74 [cm<sup>3</sup> K mol<sup>-1</sup>] expected for four  $\text{Mn}^{\text{III}}$  (*S* = 2) and two magnetically isotropic Gd<sup>III</sup> ions possessing the  ${}^{8}S_{7/2}$  ground state (4f, *J* = 7/2, *L* = 0, *S* = 7/2), using the expression [18a].

$$\chi_{M} = 4\chi_{3d} + 2\chi_{4f} \qquad \text{where}$$

$$\chi_{3d} = \left(\frac{\text{Ng}^{2}\beta^{2}}{3\text{kT}}\right)[S(\text{S}+1)] \qquad \text{and}$$

$$\chi_{4f} = \left(\frac{\text{Ng}_{J}^{2}\beta^{2}}{3\text{kT}}\right)[J(\text{J}+1)],$$

$$g_{J} = \frac{3}{2} + [S(\text{S}+1) - L(\text{L}+1)]/2J(\text{J}+1)$$

On lowering the temperature,  $\chi_M T$  decreases very gradually (300-75 K) before a much bigger decrease occurs below 75 K, reaching a value of 2.78 [cm<sup>3</sup> K mol<sup>-1</sup>] at 0.5 T and 2 K. The molar magnetic susceptibility of **2** increases on cooling down to T = 6.0 K, when it passes through a maximum (Fig. 8).

The reciprocal magnetic susceptibilities in the temperature range of 50-300 K (Fig. S14) follow the Curie-Weiss equation  $1/\chi_M = (T - \Theta) / C$  with C = 26.4 [cm<sup>3</sup> K mol<sup>-1</sup>] and  $\Theta = -5.47$  K. The small, negative value of the Weiss constant confirms a very weak antiferromagnetic coupling, which can occur between the Mn<sup>III</sup> and Gd<sup>III</sup> ions or Gd<sup>III</sup> and Gd<sup>III</sup> ions.

Based on the structure, the  $\chi_M T$  value of **2** can be viewed as contributions from a dimer of Gd<sup>III</sup> ions (Gd1 and Gd1<sup>#</sup>) and four isolated Mn<sup>III</sup> ions (Mn1, Mn2, Mn1<sup>#</sup> and Mn2<sup>#</sup>). Therefore,

to analyze the magnetic susceptibility data of **2**, we have employed an expression (see eq M1 in the Supplementary Information; Table S7) which is the sum of a simple isotropic Heisenberg dimer model of Gd [18c] with *J* describing the exchange interaction between the Gd<sup>III</sup>–Gd<sup>III</sup> ions and the second term is a temperature dependent contribution from the Mn<sup>III</sup> ions (eqs M2 and M3 in the Supplementary Information) [18d]. The exchange interaction between the Mn<sup>III</sup> and Gd<sup>III</sup> ions was introduced in terms of molecular field approximation (the Mn<sup>III</sup>–Mn<sup>III</sup> interaction was omitted because of the much longer distance, ~ 6.694 Å, than the Mn<sup>III</sup>–Gd<sup>III</sup> distance of 3.522(9) Å or the Gd<sup>III</sup>–Gd<sup>III</sup> distance of 4.515(4) Å) (eq M4 in the Supplementary Information) [18e]. The best agreement between the experimental and calculated results was obtained with  $J = -0.16 \text{ cm}^{-1}$ ,  $zJ' = -0.09 \text{ cm}^{-1}$ ,  $g_{Mn} = 2.02$ ,  $g_{Gd} = 2.00$  and the agreement factor, defined as

$$R = \left[ (\chi_M T)^{\text{obsd}} - (\chi_M T)^{\text{cald}} \right]^2 / \left[ (\chi_M T)^{\text{obsd}} \right]^2 \text{ is equal to } 2.21 \times 10^{-5}$$

In comparison with literature data, similar weak  $Gd^{III} \cdots Gd^{III}$  antiferromagnetic exchange interactions and g values were found in a series of Schiff–base dinuclear  $Gd^{III}$  complexes, such  $Gd^{III}_2(Salphen)_3(H_2O)$  ( $J = -0.082 \text{ cm}^{-1}$ ) [18b],  $[Gd^{III}_2(LA)(NO_3)_2] \cdot 4H_2O$  ( $J = -0.106 \text{ cm}^{-1}$ ) [18f] or the well–known dinuclear  $Gd^{III}$  carboxylato compounds with J values in the range from 0 to  $-0.15 \text{ cm}^{-1}$  [18b].

The reason for the small interaction between the paramagnetic centers results from the fact that the 4f electrons are influenced very little by the surrounding environment [18h]. Theoretically, the  $Gd^{III}$  ion, with a  $4f^7$  electronic configuration, is very stable in energy and this is responsible for the very difficult transfer of unpaired electrons to the d or s orbitals of the other  $Gd^{III}$  or  $Mn^{III}$  ions.

The field dependence of the magnetization at low temperatures (Fig. 9) shows that the magnetization increases smoothly with an increasing applied direct current (*dc*) field up to 2500 Oe, where a plateau exists, and then a rapid increase was observed without the expected saturation value of 30 B.M. ( $M = 4g_{Mn}S_{Mn} + 2g_{Gd}S_{Gd}$ ) for ( $g_{Mn} = 2.0$ ). This behavior indicates the presence of magnetic anisotropy and/or the lack of well–defined ground states, suggesting the presence of low–lying excited states that might be populated when a field is applied [18i]. The zero-field splitting effect causes a reduction of M to lower than 30, as shown in Fig. 9.

The magnetic behavior of the Mn<sub>4</sub>Sm<sub>2</sub> complex **1** is completely different. As reported in Fig. 8, the value of  $\chi_M T$  at room temperature is 11.94 [cm<sup>3</sup> K mol<sup>-1</sup>], which is in reasonable agreement with the expected value of 12.06 [cm<sup>3</sup> K mol<sup>-1</sup>] for the four Mn<sup>III</sup> ions (S = 2) and two independent Sm<sup>III</sup> ions possessing the <sup>6</sup> $H_{5/2}$  ground state (4f, g = 2/7, S = 5/2, L = 5, J = 5/2), using the expression describe above. On lowering the temperature, the  $\chi_M T$  value increased gradually to reach a maximum of 12.471 cm<sup>3</sup> Kmol<sup>-1</sup> at 8.0 K and then decreased. The increase in the higher temperature range indicates the presence of a ferromagnetic interaction, while the decrease in the lower temperature region is ascribed to a weak intra and/or intermolecular antiferromagnetic interaction.

The reciprocal magnetic susceptibilities in the temperature range 50-300 K follow the Curie-Weiss equation  $1/\chi_M = (T - \Theta) / C$  with C = 11.7 cm<sup>3</sup> K mol<sup>-1</sup> and  $\Theta = + 0.18$  K (Fig. S14). The small, positive value of the Weiss constant confirms a very weak ferromagnetic coupling, which can occur between the Mn<sup>III</sup> and Sm<sup>III</sup> ions or Sm<sup>III</sup> and Sm<sup>III</sup> ions.

The temperature dependence of the magnetic susceptibility of compound **1** can be calculated by eq M5 in the Supplementary Information, as the sum of the independent contribution from four Mn<sup>III</sup> ions (eq M3 in the Supplementary Information) and a dimer of Sm<sup>III</sup> ions. The average exchange interaction was introduced in terms of a molecular field correction (eq M4 in the Supplementary Information).

The magnetic susceptibility of the Sm<sup>III</sup> ion is much more complicated to describe because of its  ${}^{6}H_{5/2}$  ground state, which splits into six states by spin-orbit coupling at room temperature, which are not well separated from the excited ones (about 700 cm<sup>-1</sup> from the ground state to the first excited state), so both the crystal field effect and possible thermal population of the higher energy states should be evaluated [18j]. As far as the existence of strong spin-orbit coupling for the Sm<sup>III</sup> atoms is concerned, the Sm<sup>III</sup> dimer contribution for the magnetic data was analyzed by the Van Vleck expression (eq M6 in the Supplementary Information) [18b].

Least-squares analysis of the magnetic data gives  $zJ' = 0.52 \text{ cm}^{-1}$ ,  $g_{\text{Mn}} = 2.01$ ,  $g_{\text{Sm}} = 2/7$ ,  $\lambda = 198 \text{ cm}^{-1}$  and  $R = 2.76 \times 10^{-3}$ . For the Sm<sup>III</sup> ions,  $\lambda$ -values are usually in the 160-315 cm<sup>-1</sup> range [18b], so our derived  $\lambda$  value is quite acceptable. Absolute zJ' values for Ln<sup>III</sup> complexes are commonly less than 1 cm<sup>-1</sup> [18b,i] and our zJ' estimate is commensurate to this. It might also be noted that, as shown in the literature, the Sm<sup>III</sup> and Sm<sup>III</sup> coupling usually has antiferromagnetic character [e.g. Sm<sup>III</sup><sub>2</sub>(Salphen)<sub>3</sub>(H<sub>2</sub>O) ( $zJ' = -0.97 \text{ cm}^{-1}$ ) [18b] or {[Sm<sup>III</sup><sub>2</sub>(DPPA)<sub>2</sub>( $\mu_2$ -C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O}<sub>n</sub> ( $J = -1.03 \text{ cm}^{-1}$ )] [18j], however a ferromagnetic nature of the Mn<sup>III</sup>····Ln<sup>III</sup> coupling was found in Mn<sup>III</sup><sub>4</sub>Gd<sup>III</sup><sub>2</sub>, Mn<sup>III</sup><sub>4</sub>Dy<sup>III</sup><sub>2</sub> and Mn<sup>III</sup><sub>4</sub>Tb<sup>III</sup><sub>2</sub> complexes [11k].

The magnetization vs magnetic field plot for complex **1** at 2 K is shown in Fig. 9. The expected value of saturation magnetization is 17.4 B.M. ( $M = 4g_{Mn}S_{Mn} + 2g_{Sm}S_{Sm}$ ) for **1** ( $g_{Mn} = 2.0$ ). However, the observed saturation value at 2 K is only 12.5 B.M. This is due to the crystal field effect on the Sm<sup>III</sup> ion that removes degeneration of the  ${}^{6}H_{5/2}$  (Sm<sup>III</sup>) ground state and zero-field splitting at the Mn<sup>III</sup> or Sm<sup>III</sup> centers. The small differences between the value of the magnetization with an increasing magnetic field and decreasing magnetic field can be the result of torqueing effects of the sample.

The temperature dependence of the magnetic susceptibility of the  $Mn_4Dy_2$  derivative **3** is shown in Fig. 8. In the case of  $Ln^{III}$  ions, except for  $Gd^{III}$ , it is very difficult to analyze their magnetic properties because of their orbital contribution. Usually, the 4f<sup>n</sup> configuration of a  $Ln^{III}$ ion is split into  ${}^{2S+1}L_J$  states by inter electronic repulsion and spin-orbit coupling. Further splitting into Stark components is caused by crystal-field perturbation, which depends on the symmetry site of the ion [18k]. Thus, the variable-temperature magnetic properties of a free ion of a rare earth metal generally shows strong deviations from the Curie law and  $\chi_M T$  decreases on cooling because of the depopulation of the Stark levels.

However, as illustrated in Fig. 8, complex 3 obviously shows ferromagnetic coupling between the Dy<sup>III</sup> ions and/or Dy<sup>III</sup>····Mn<sup>III</sup> ions. The  $\chi_M T$  value at room temperature is 38.02 cm<sup>3</sup> K mol<sup>-1</sup>, which is a little bit lower than the value expected for two magnetically isolated Dy<sup>III</sup> ions including the significant contribution of the 4f orbital (4f<sup>9</sup>, J = 15/2, S = 5/2, L = 5,  ${}^{6}H_{15/2}$ ) and four  $Mn^{III}$  ions (S = 2). This can be a result of crystal field effects on the Dy<sup>III</sup> ion, which remove the 16-fold degeneracy of the  ${}^{6}H_{15/2}$  ground state. As the temperature is lowered, the  $\chi_{M}T$  product increases very slowly to reach a maximum value of 40.39 cm<sup>3</sup> K mol<sup>-1</sup> at 5 K, and then decreases abruptly and reaches 13.20 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K, which is comparable with the result reported previously [18j]. The increase in the higher temperature region and the positive value of  $\Theta = 3.18$ K indicate that there are ferromagnetic interactions between the Dy<sup>III</sup>....Dy<sup>III</sup> ions mediated by an oxygen group and/or between  $Dy^{III} \cdots Mn^{III}$  ions. Below 5 K,  $\chi_M T$  decreases with cooling, indicating the presence of possible antiferromagnetic interactions between the tetranuclear molecules. The ligand field effects break the degeneration of the levels of the ground state multiplet of the Dy<sup>III</sup> ion. So, the influence of the ligand field can be seen in the very low temperature region where the theoretical model is unable to reproduce the experimental susceptibility data [18j,1].

The field dependence of the magnetization (in Fig. 9) shows that, upon an increase of the applied external magnetic applied field, the magnetization  $M_{\text{mol}} / (N_A \mu_B)$  decreases to zero, in which the magnetization  $M/(N_A \mu_B)$  in the field decreasing mode is larger than the value in the field increasing mode, due to a strong magnetic anisotropy.

The zero-field-cooling magnetization / field-cooling magnetization curves measured at 25 and 50 Oe coincide and thus confirm the absence of long–range ordering for all complexes. Their course is identical with the temperature evolution of the dc magnetic susceptibility.

Generally, it is expected that Mn/Ln clusters exhibit slow relaxation behaviour because Ln ions have a large magnetic anisotropy. According to the literature data a few examples of hexanuclear 3d-4f complexes with a similar butterfly topology have been reported. Some of them exhibit antiferromagnetic coupling, e.g.  $Ni^{II}_{4}Ln^{III}_{2}$  [Ln<sup>III</sup> = Gd<sup>III</sup>, Dy<sup>III</sup>] [18m], or ferromagnetic splitting with a slow magnetic relaxation of the magnetization,  $Ni^{II}_{4}Ho^{III}_{2}$  [18n], whereas  $Ni^{II}_{4}Ln^{III}_{2}$  [Ln<sup>III</sup> = Tb<sup>III</sup>, Dy<sup>III</sup>] [13f,18n], Fe<sup>III</sup>\_4Dy<sup>III</sup>\_2 [18o] or Co<sup>III</sup>\_2Dy<sup>III</sup>\_4 [13f] complexes with ferromagnetic interactions are found to be SMMs.

However, in our systems, only the  $Mn^{III}_{4}Gd^{III}_{2}$  complex shows a very weak signal in the out of phase component of the alternative current (*ac*) magnetic susceptibility under 1000 Oe *dc*, while the  $Mn^{III}_{4}Sm^{III}_{2}$  and  $Mn^{III}_{4}Dy^{III}_{2}$  complexes do not, as the out–of–phase *ac* magnetic susceptibility remains silent up to 2 K. One of the reasons for this may be the crystal structure differences. On examining complexes **1-3**, it can be seen that the lanthanide ions are situated at the center of the core and manganese ions occupy the peripheral region (Fig. 4), opposite to the examples presented in the literature. As a result, a possible exchange pathway can be realized through a  $Mn^{III}_{-}(\mu-O)_2-Ln^{III}_{-}(\mu-O)_2-Mn^{III}_{-}(\mu-O)_2-Ln^$ 

 $Fe^{III}_{4}Dy^{III}_{2}$  [180] or  $Co^{III}_{2}Dy^{III}_{4}$  [13f] complexes with the same topology. Different coordination environments in compounds 1-3 and reported  $M_4Ln_2$  complexes around the  $Ln^{III}$  ion and/or the different relative orientation of the local axes are probably responsible for the different relaxation dynamics observed.

#### 2.8. EPR Spectroscopic studies

The EPR spectra of both bands do not exhibit intensive wide lines for the measured complexes **1**-**3** (Fig. S8 in the Supplementary Information). Only for **2**, was it possible to determine the value of the g-parameter as 2.00. This value is typical for complexes of gadolinium surrounded by oxygen atoms [19]. The hyperfine structure was not observed. The spectra of **1** and **3** also exhibit lines typical for a Mn<sup>II</sup> sextet due, probably to very small amounts of Mn<sup>II</sup> impurities.

#### 2.9. Theoretical insight

The calculations were focused on the  $Mn^{III}_4Gd^{III}_2$  complex. The two other members of the  $Mn^{III}_4Ln^{III}_2$  series are characterized by strong magnetic anisotropy on the  $Ln^{III}$  sites induced by crystal field splitting of their atomic *J* multiplets and to describe this effect multiconfigurational *ab initio* methods should be used rather than DFT. However, the downside of these methods is that for large systems they turn into a prohibitively expensive task.

To provide a deeper insight into magnetic properties of complex **2**, the isotropic Heisenberg-Dirac-van Vleck Hamiltonian was used:

$$\hat{H}_{\rm HDV} = -2\sum_{i < j} J_{ij} \hat{S}_i \hat{S}_j \tag{2}$$

Where  $\hat{S}$  is the local spin operators for each paramagnetic centre and J is the Heisenberg exchange coupling constant between two paramagnetic centres. On the assumption that there is no coupling between Mn<sup>III</sup> ions, which is justified by the significant Mn<sup>III</sup>–Mn<sup>III</sup> distances in 2, three different exchange pathways can be distinguished (Fig 10) and eq 2 can be rewritten as:

$$\hat{H}_{\rm HDV} = -2J_A \hat{S}_{Gd1} \hat{S}_{Gd1\#} - 2J_B \hat{S}_{Gd1} \hat{S}_{{\rm Mn1}} - 2J_B \hat{S}_{Gd1} \hat{S}_{{\rm Mn1}\#} - 2J_B \hat{S}_{Gd1\#} \hat{S}_{{\rm Mn1}} - 2J_B \hat{S}_{Gd1\#} \hat{S}_{{\rm Mn1}\#} - 2J_C \hat{S}_{Gd1} \hat{S}_{{\rm Mn2}} - 2J_C \hat{S}_{Gd1\#} \hat{S}_{{\rm Mn2}\#}$$
(3)

The  $J_A$ ,  $J_B$  and  $J_C$  values can be computed within the Broken Symmetry (BS) DFT framework. For that purpose, single point calculations for four different spin configurations of complex **2** have to be accomplished. The states used in this study are schematically shown in Fig. 10. They are the high spin configuration  $\{+++\}$  and three BS solutions  $\{-++\}$ ,  $\{+-+\}$  and  $\{++-\}$  with spins flipped on one Gd<sup>III</sup> ion, Mn1 and Mn1<sup>#</sup>, Mn2 and Mn2<sup>#</sup>, respectively.

Application of the Heisenberg-Dirac-van Vleck Hamiltonian from eq 3, to each of these four single determinant wave functions leads to simple expressions of the related energies as shown in eqs 4a-d.

$$E_{\{+++\}} = -24\frac{1}{2}J_A - 56J_B - 28J_C \tag{4a}$$

$$E_{\{-++\}} = +24\frac{1}{2}J_A \tag{4b}$$

$$E_{\{+-+\}} = -24\frac{1}{2}J_A + 56J_B - 28J_C \tag{4c}$$

$$E_{\{++-\}} = -24\frac{1}{2}J_A - 56J_B + 28J_C \tag{4d}$$

From eqs 4a–d, analytical expressions for the  $J_A$ ,  $J_B$  and  $J_C$  values are obtained as eqs 5a–c.

$$J_{A} = \frac{\left(E_{\{+++\}} - E_{\{-++\}}\right) + 56J_{B} + 28J_{C}}{49} \quad (5a)$$

$$J_{B} = -\frac{E_{\{+++\}} - E_{\{+-+\}}}{112} \quad (5b)$$

$$J_{C} = -\frac{E_{\{+++\}} - E_{\{++-\}}}{56} \quad (5c)$$

The results of the DFT calculations are summarized in Table S8. From this data, we can see that all three predicted |J| values are not larger than 1.1 cm<sup>-1</sup>, which is an indication of a fairly weak exchange coupling between the paramagnetic ions. It is important to emphasise that both functionals brought about similar results, but the use of TPSSh tended to give slightly stronger exchange couplings. A good illustration for this is that the  $J_A$  values amounted to -0.60 and -0.82 cm<sup>-1</sup> according to the B3LYP and TPSSh calculations, respectively.

Analysis of experimental magnetic data for complex 2 revealed that the coupling between the two Gd<sup>III</sup> ions should be antiferromagnetic and the DFT results are in line with this conclusion (the  $J_A$  values computed for 2 at the B3LYP and TPSSh theory levels are slightly negative). Moreover, the magnetic picture emerging from the theoretical investigation shows a weak antiferromagnetic interaction between the Gd<sup>III</sup> ion and the neighbouring Mn<sup>III</sup> ions, which agrees well with the experimentally determined negative value of zJ'. It is important to notice that the magnetic interaction between the atoms Gd1 and Mn2 as well as between Gd1<sup>#</sup> and Mn2<sup>#</sup> is slightly stronger than the coupling between Gd1 and Mn1 as well as between Gd1<sup>#</sup> and Mn1<sup>#</sup> ( $|J_C| > |J_B|$ ). The values of  $J_B$  and  $J_C$  predicted at the B3LYP theory level are -0.23 and -0.93 cm<sup>-1</sup>, respectively.

In addition to the exchange couplings listed in the Supporting Information Table S8, in Fig. 11 the spin density isosurfaces in the high spin state  $\{+ + +\}$  are shown. This provides strong evidence that for complex **2** in its high spin state the spin density is not only localised on the Gd and Mn atoms, but also on the oxygen and nitrogen ligand donor atoms. To estimate the scale of this effect, a Löwdin population analysis was carried out and this revealed that in **2** 96.4% (46.9% on two Gd<sup>III</sup> ions and 49.6% on four Mn<sup>III</sup> ions) of the spin population is located on the metal sites. Hence, in the studied complexes the flow of spin density from the paramagnetic cations toward the organic ligands can be considered as limited. As suggested by O. Kahn [18a], the magnetic coupling can be qualitatively explained with the concept of spin delocalization and spin polarization. Both phenomena transfer spin density onto ligands and thus are mirrored in its

isosurface. This was used in magnetochemistry to propose mechanisms governing magnetic coupling in polynuclear clusters of transition metals [24a-f] and in complexes incorporating lanthanides [23s,23t,24g-j]. From the fact that in complex 2 less than 4% of the spin population is transferred onto the ligands it becomes apparent that the spin delocalisation and spin polarization are minor and in consequence the antiferromagnetic interactions observed in complex 2 are weak.

#### 3. Conclusions

In summary, we have investigated a  $Mn^{III}_{4}Ln^{III}_{2}$  ( $Ln^{III} = Sm^{III}$ ,  $Gd^{III}$ ,  $Dy^{III}$ ) series to form a good basis for structural and magnetic rationalization of several experimental observations. Complexes 1-3 are heterometallic but homovalent, with two  $Ln^{III}$  ( $Ln = Sm^{III}$ ,  $Gd^{III}$ ,  $Dy^{III}$ ) and four  $Mn^{III}$  ions. The coordination numbers of both the  $Ln^{III}$  ions are same (nine for 1 and 2, eight for 3). In contrast, two  $Mn^{III}$  ions (Mn1,  $Mn1^{#}$ ) are six coordinate and the remaining two  $Mn^{III}$  centers (Mn2,  $Mn2^{#}$ ) are five coordinate. The central butterfly-like [ $Mn^{III}_{2}Ln^{III}_{2}$ ] core is capped by two  $Mn^{III}$  ions from the lanthanide side, resembling a spacecraft-like overall topology. Synthetic access to the structurally related  $Mn^{III}_{4}Ln^{III}_{2}$  complexes has allowed a direct comparison, showing that replacement of  $Sm^{III}$  (1) and  $Gd^{III}$  (2) with  $Dy^{III}$  (3), leads to significant structural perturbation in 3 as a result of lanthanide contraction. Allowing for the simplification principle regarding topological analysis, the structures of 1 and 2 bear the 1,2,4M6–1 topology whereas, the 1,2,3M6–1 topology is encountered in 3. Further, due to the variations of  $Ln^{III}$  and/or topologies, 1, 2 and 3 present quite different magnetic outcomes. DFT theoretical calculations were done in order to provide additional insight into the magnetic interaction in 2.

#### 4. Experimental Section

#### 4.1 General Information

3-Amino-1,2-propanediol, *o*-vanillin and Ln(OAc)<sub>3</sub>·xH<sub>2</sub>O were procured from Aldrich Chemical Co. Inc. (Germany) and were used as received. Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O and triethylamine (TEA) were purchased from SRL Pvt. Ltd., Mumbai, India. Commercially available solvents were purified according to standard literature. 3-[(2-Hydroxy-3-methoxy-benzylidene)-amino]-propane-1,2diol (H<sub>3</sub>Vapd) was prepared according to literature procedures [20b]. Powder X-ray diffraction (PXRD) patterns were acquired using a PANalytical, XPERT–PRO diffractometer (Netherlands) operated at 40 kV, 30 mA, with graphite monochromatized Cu K $\alpha$  radiation of wavelength 1.5406 Å and a nickel filter. Energy dispersive X-ray (EDX) analysis was done by field emission scanning electron microscopy (FESEM–JEOL JSM 7600F). Elemental analysis for carbon, hydrogen and nitrogen were carried out on a Perkin-Elmer RXI FTIR spectrophotometer with the samples prepared as KBr disks. ESI-MS experiments for **1-3** were carried out using Waters Xevo G2–SQTof instruments in LC-MS grade solvent.

#### 4.2. Synthesis of the hexanuclear complexes 1-3

#### 4.2.2. General procedure for the synthesis of $[Mn^{III}_{4}Ln^{III}_{2}(Vapd)_{4}(OAc)_{6}]\cdot 4H_{2}O(1-3)$

The following general synthetic methodology was applied for the preparation of the heterobimetallic hexanuclear metal complexes under aerobic conditions (shown in Scheme 1). A methanolic solution of  $Et_3N$  (2 equiv.) was added to a methanolic solution of  $H_3Vapd$  (1 equiv.) and the resulting mixture was stirred for 15 min. A methanolic solution of  $Mn(OAc)_2 \cdot 4H_2O$  (1 equiv.) was added dropwise to the ligand solution under continuous stirring conditions and the colour of the mixture changed from yellow to dark brown within a few minutes. After ca. 4 h. stirring, a methanol-water solution (3:1, v/v) of  $Ln(OAc)_3 \cdot xH_2O$  (0.5 equiv.) was added and the stirring was continued vigorously for further ca. 2.5 h. The final reaction mixture was filtered off and the filtrate was evaporated to dryness under reduced pressure. The dark brown solid obtained was left overnight in a vacuumed calcium chloride desiccator. The resulting solid was redissolved in methanol. Crystals suitable for X-ray studies were obtained by slow diffusion of diethyl ether into this methanolic solution over one week. The specific quantities and stoichiometry of the reactants involved in each reaction, the yields of the products and their characterization data are given below.

 $[Mn^{III}_{4}Sm^{III}_{2}(Vapd)_{4}(OAc)_{6}]$ · $4H_{2}O(1)$ . Quantities: H<sub>3</sub>Vapd (0.112 g, 0.5 mmol), Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.122 g, 0.5 mmol), Sm(OAc)<sub>3</sub>·xH<sub>2</sub>O (0.081 g, 0.25 mmol) and Et<sub>3</sub>N (0.138 mL, 1 mmol). Yield: 0.080 g (35% based on ligand). FT-IR data (KBr pellet)  $\upsilon$  cm<sup>-1</sup>: 3435 (br), 1620 (vs), 1557 (vs), 1443 (s),1249 (s), 1049 (m), 742 (m). C<sub>56</sub>H<sub>74</sub>Mn<sub>4</sub>N<sub>4</sub>O<sub>32</sub>Sm<sub>2</sub> (1835.67) calcd: C 36.64, H 4.06, N 3.05; found: C 36.32, H 3.69, N 2.84. ESI–MS m/z, ion in CH<sub>3</sub>OH: 882.777, [Mn<sub>4</sub>Sm<sub>2</sub>(Vapd)<sub>4</sub>(OAc)<sub>6</sub> + 2H<sup>+</sup>]<sup>2+</sup>.

 $[Mn^{III}_{4}Gd^{III}_{2}(Vapd)_{4}(OAc)_{6}]$ · $4H_{2}O(2)$ . Quantities: H<sub>3</sub>Vapd (0.112 g, 0.5 mmol), Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.122 g, 0.5 mmol), Gd(OAc)<sub>3</sub>·xH<sub>2</sub>O (0.083 g, 0.25 mmol) and Et<sub>3</sub>N (0.138 mL, 1 mmol). Yield: 0.085 g (37% based on ligand). FT-IR data (KBr pellet)  $\upsilon$  cm<sup>-1</sup>: 3435 (br), 1618 (vs), 1559 (vs), 1438 (s), 1249 (s), 1049 (m), 743 (m). C<sub>56</sub>H<sub>74</sub>Mn<sub>4</sub>N<sub>4</sub>O<sub>32</sub>Gd<sub>2</sub> (1849.45) calcd: C 36.37, H 4.03, N 3.03; found: C 36.20, H 3.54, N 2.81. ESI–MS m/z, ion in CH<sub>3</sub>OH: 832.077, [Mn<sub>4</sub>Gd<sub>2</sub>(Vapd)<sub>4</sub>(OAc)<sub>4</sub>]<sup>2+</sup>.

 $[Mn^{III}_4Dy^{III}_2(Vapd)_4(OAc)_6]\cdot 4H_2O(3)$ . Quantities: H<sub>3</sub>Vapd (0.112 g, 0.5 mmol), Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.122 g, 0.5 mmol), Dy(OAc)<sub>3</sub>·xH<sub>2</sub>O (0.084 g, 0.25 mmol) and Et<sub>3</sub>N (0.138 ml, 1 mmol). Yield: 0.078 g (34% based on ligand). FT-IR data (KBr pellet) v cm<sup>-1</sup>: 3567 (br), 1619 (vs), 1560 (vs), 1438 (s), 1249 (s), 1055 (m), 742 (m). C<sub>56</sub>H<sub>74</sub>Mn<sub>4</sub>N<sub>4</sub>O<sub>32</sub>Dy<sub>2</sub>(1862.03) calcd: C 36.16, H 4.01, N 3.01; found: C 35.53, H 3.79, N 2.82. ESI–MS *m*/*z*, ion in CH<sub>3</sub>OH: 806.032,  $[Mn_4Dy_2(Vapd)_4(OAc)_3 + H^{-}]^{2+}$ .

4.3. Single crystal X-ray crystallography

Suitable single crystals of 1, 2 and 3 were chosen for X-ray diffraction studies. Crystallographic data and details of the refinement are given in Table 2. The unit cell parameters and the intensity data for the complexes (1, 2 and 3) were collected on a Nonius APEX-II diffractometer with a CCD-area detector at 296 K using graphite-monochromated MoKa radiation ( $\lambda = 0.71073$  Å). The program SMART [21a] was used for collecting frames of data, indexing reflections and determining lattice parameters, SAINT [21a] for integration of the intensity of reflections and scaling, SADABS [21b] for absorption corrections and SHELXTL [21c,d] for space group, structure determination and least-squares refinements on  $F^2$ . All the structures were solved by direct methods and refined by full-matrix least squares calculations using SHELXTL software [21e]. The location of the Ln and Mn atoms were determined and O, N and C atoms were subsequently determined from the difference Fourier maps. All the nonhydrogen atoms were refined with anisotropic displacement parameters. All the hydrogen atoms on carbon frameworks were included in the final stages of the refinement and were refined with a typical riding model. Some hydrogen atoms on the solvent water molecules could not be located; these were included in the molecular formula directly. The crystallographic figures have been generated using Diamond 3.0 software [21f]. CCDC 1451600, 1451601 and 1451602 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/ cif.

#### 4.4. Magnetic measurement (experimental) details

Magnetic measurements in the temperature range 1.8-300 K were performed using a Quantum Design SQUID-based MPMSXL-5-type magnetometer. The SQUID magnetometer was calibrated with a palladium rod sample (Materials Research Corporation, measured purity 99.9985%). The superconducting magnet was generally operated at a field strength ranging from 0 to 5 T. Measurements were made at a magnetic field of 0.5 T. Corrections were based on subtracting the sample-holder signal and contribution  $\chi_D$  estimated from the Pascal constants [22]. Magnetization measurements were conducted at 2 K in a magnetic field from 0 to 5 T.

#### 4.5. EPR spectroscopy (experimental) details

EPR spectra were obtained at room and liquid nitrogen temperatures, using a Bruker Elexsys E500 spectrometer equipped with an NMR teslameter (ER 036TM). X-band spectra were measured using a frequency counter (E 41 FC) and a double rectangular cavity resonator (ER 4105DR) operating in the TD104 mode at a microwave power of 20 mW and a modulation amplitude of 5 G. In the case of low intensity signals, instead of one scan, five scans were accumulated. Q-band spectra (34 GHz) were recorded by the same spectrometer with an ER 5106QTW resonator and Bruker frequency counter using the Li/LiH standard for *g*-factor calibration. The measurements parameters were as follows: microwave power 11mW, modulation amplitude 10 G.

#### 4.6. Computational details

All calculations were carried out with the ORCA 3.0.3 suite of programs [23a]. Due to the size of the studied system, they were based on density functional theory (DFT). Since Gd<sup>III</sup> ions are contained in the studied complex, scalar relativistic effects had to be taken into account in the calculations. This was accomplished with the 0<sup>th</sup> order regular approximation (ZORA) [23b,c]. To facilitate the comparison between theory and experiment, the X-ray structure was used, but only after the positions of all the hydrogen atoms, which were not reliably determined from the X-ray diffraction, were optimised. These optimisations were performed with the GGA functional BP86 [23d,e], taking advantage of the Split-RI-J approximation [23f] employing appropriate auxiliary Coulomb fitting basis sets [23g]. Single point Broken-Symmetry (BS) DFT calculations were performed with the hybrid B3LYP [23h,i,j] and hybrid meta-GGA TPSSh [23k] functionals. In all the calculations, the segmented all-electron relativistically contracted (SARC) basis sets on Gd, ZORA-def2-TZVP on Mn, O and N and ZORA-def2-SVP on C and H atoms were used [23k,1], as well as increased integration grids (Grid5 in the ORCA convention) and tight SCF convergence criteria. The TPSSh and B3LYP functionals were chosen as they were shown to perform well in the studies of exchange coupled systems [23m-r], including complexes with  $[Ni^{II}Gd^{III}]$ ,  $[Ni^{II}Gd^{III}Ni^{II}]$  and  $[Cu^{II}Gd^{III}]$  cores.

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#### Appendix A. Supplementary data

The ligand structure, along with its different coordination pockets and binding modes, simulated and experimental PXRD, EDX spectra, FT–IR, ESI–MS, EPR, crystal data, additional crystallographic diagrams, Stiefel and Brown nomenclature, CShM results, metric parameters, BVS calculations, topology, the magnetic equations used in fitting parameters and the theoretical data of DFT calculations. CCDC 1451600, 1451601 and 1451602. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found in the online version.

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$$\begin{split} & [Mn^{III}{}_4Sm^{III}{}_2(Vapd)_4(CH_3COO)_6]{}^{\cdot}4H_2O~(1,~Ln=Sm) \\ & [Mn^{III}{}_4Gd^{III}{}_2(Vapd)_4(CH_3COO)_6]{}^{\cdot}4H_2O~(2,~Ln=Gd) \end{split}$$

 $[Mn^{III}_{4}Dy^{III}_{2}(Vapd)_{4}(CH_{3}COO)_{6}] \cdot 4H_{2}O (3, Ln = Dy)$ 

Scheme 1. Synthesis of the heterobimetallic hexanuclear complexes 1-3.



Scheme 2. Examples of previously known  $Mn_{4}^{III}Ln_{2}^{III}$  and  $Mn_{2}^{III}Mn_{2}^{III}Ln_{2}^{III}$  oxido clusters.<sup>[9f, 11i-11]</sup>



Fig. 1. Structure of the clusters 1 (above) and 2 (below) with the selected numbering scheme used. Hydrogen atoms and solvent molecules are omitted for clarity. Symmetry transformations used to generate equivalent atoms: ( $^{\#}$ ) 1–x, 1–y, 1–z.



**Fig. 2.** Structure of cluster **3** with selected numbering scheme used. Hydrogen atoms and solvent molecules are omitted for clarity. Symmetry transformations used to generate equivalent atoms: (<sup>#</sup>) 1-x, 1-y, 1-z.



Fig. 3. Binding modes of the tri–anionic ligands (Vapd<sub>3</sub><sup>-</sup>) and coordinated acetateo ions (OAc<sup>-</sup>).



**Fig 4** Representative spacecraft-like  $[Mn^{III}_{4}Ln^{III}_{2}O_{10}]$  core of **1** and **3**. Symmetry transformations used to generate equivalent atoms: (<sup>#</sup>) 1-x, 1-y, 1-z.



**Fig. 5.** Distorted octahedral geometry with azimuthal expansion around (a)  $Mn1/1^{\#}$  in 1-3. Distorted trigonal bipyramid geometry around (b)  $Mn2/2^{\#}$  in 1-3. Distorted spherical capped square antiprism geometry around (c)  $Sm1/1^{\#}$  in 1. Distorted biaugmented trigonal prism geometry around (d)  $Dy1/1^{\#}$  in 3. Symmetry transformations used to generate equivalent atoms: (<sup>#</sup>) 1–x, 1–y, 1–z.



**Fig. 6.** The decrease of the Ln1–O4 bond length ( $\bullet$ ) along with the increase of the Ln1<sup>#</sup>–O4 distance ( $\bullet$ ) against the number of f electrons of the trivalent lanthanide cation.



Fig. 7. Topological motif of the Mn<sub>4</sub>Ln<sub>2</sub> clusters in 1-3.



**Fig. 8.** Thermal dependence of  $(\bullet)$ ,  $(\bullet)$ ,  $(\bullet)$ ,  $(\bullet)$ ,  $\chi_M T$  and  $(\circ)$ ,  $(\circ)$ ,  $(\circ)$ ,  $\chi_M$  for complexes 1, 2 and 3, respectively. The solid lines are the calculated curves.



Fig. 9. Plots of the field dependence of  $M_{mol} / (N_A \mu_B)$  of complexes 1, 2 and 3 at 2 K. The close circle plots are the data for the increasing magnetic field mode and the open circle plots are the data for the decreasing magnetic field mode.



Fig. 10. Schematic view of the magnetic interactions and spin states used in the DFT calculations.



**Fig. 11.** Spin density isosurfaces for the high spin state  $\{+ + +\}$  of **2** (Mn<sub>4</sub>Gd<sub>2</sub>). The Gd atoms are displayed in violet, Mn in green, O in red, N in blue and C in grey; the H atoms are removed. The yellow isosurface indicates  $\alpha$ -type spin density, the blue one,  $\beta$ -type spin density.

Table1. Comparative summary of intermetallic and Ln····O(4) distances of complexes 1-3.

Ionic radius of Ln <sup>III</sup> Complex         (Å)           1         0.96           2         0.94           3         0.91	In Ln1…Mn1 3.383(17) 3.361(9)	ttermetallic dista Ln1Mn1 <sup>#</sup> 3.458(17)	nces (Å) Ln1…Mn2		Ln-O(4) d Ln1-O4	istances (Å
Complex         (Å)           1         0.96           2         0.94           3         0.91	Ln1…Mn1 3.383(17) 3.361(9)	Ln1Mn1 <sup>#</sup>	Ln1Mn2	Ln1…Ln1 <sup>#</sup>	Ln1–O4	Ln1 <sup>#</sup> -0
1     0.96       2     0.94       3     0.91	3.383(17) 3.361(9)	3.458(17)	2.765(10)			
2 0.94 3 0.91	3.361(9)		3./65(18)	4,485(17)	2.551(5)	2.801(5
3 0.91		3.781(9)	3.426(8)	4.515(4)	2.509(3)	2.850(4
	3.336(8)	3.838(8)	3.393(8)	4.616(4)	2.466(3)	2.976(4

	1	2	3
formula	$C_{56}H_{66}Mn_4N_4O_{32}Sm_2$	$C_{56}H_{66}Mn_4N_4O_{32}Gd_2$	$C_{56}H_{66}Mn_4N_4O_{32}Dy_2$
<b>CCDC</b> <sup>a</sup>	1451600	1451601	1451602
molwt	1827.61	1841.39	1851.89
cryst color, habit	dark brown, block	dark brown, block	dark brown, block
temp(K)	296(2)	296(2)	296(2)
λ <sup>b</sup> /Å	0.71073	0.71073	0.71073
crystsyst	Triclinic	Triclinic	Triclinic
space group	PĨ	PĨ	$P\overline{1}$
a/Å	10.614(3)	10.5979(5)	10.6092(4)
b/Å	12.297(4)	12.2734(6)	12.2990(5)
c/Å	14.829(5)	14.8041(7)	14.8504(6)
α/deg	112.354(3)	112.4480(10)	112.6070(10)
β/deg	91.017(4)	91.0620(10)	91.0880(10)
γ/deg	102.399(4)	102.2920(10)	102.1830(10)
V/Å <sup>3</sup>	1737.8(9)	1728.24(14)	1737.75(12)
Z	1	1	1
ρc/g cm <sup>-3</sup>	1.747	1.769	1.770
$\mu/\mathrm{mm}^{-1}$	2.456	2.690	2.917
<b>F(000)</b>	910	914	918
cryst size (mm <sup>3</sup> )	0.28  imes 0.26  imes 0.25	$0.32 \times 0.30 \times 0.29$	$0.33 \times 0.29 \times 0.27$
θ range (deg)	1.49 – 24.6	1.50 - 24.40	1.49 - 25.25
limiting indices	$-12 \le h \le 11$	$-11 \le h \le 12$	$-12 \le h \le 12$
	$-14 \le k \le 14$	$-14 \le k \le 14$	$-14 \le k \le 14$
	$-17 \le l \le 16$	$-17 \le l \le 17$	$-15 \le l \le 17$
no. of rflns collected	11010	18440	20114
no. of indeprflns [R <sub>int</sub> ]	5562 (0.0409)	5694 (0.0295)	6290 (0.0310)
completeness to θ	97.6%, (24.16°)	98.7%, (24.40°)	98.6%, (25.25°)
no. of data/restraints/params	5428/0/447	5621/0/447	6205/0/447
goodness of fit on F <sup>2</sup>	1.045	1.057	1.101
final R indices $(I > 2\theta(I))$			
R1	$0.0468^{\circ}$	0.0317 <sup>c</sup>	0.0323°
wR2	0.1276 <sup>d</sup>	$0.0840^{d}$	$0.0829^{d}$
R indices (all data)			
R1	0.0651 <sup>°</sup>	0.0392 <sup>c</sup>	0.0429 °
wR2	0.1444 <sup>d</sup>	0.0930 <sup>d</sup>	0.0926 <sup>d</sup>
largest diff peak, hole/e Å <sup>-3</sup>	1.556 and -0.882	1.252 and -0.479	1.292 and -0.447

#### Table 2 Crystal data and structure refinement parameters of complexes 1-3.

 $^{a}\underline{www.ccdc.cam.ac.uk/data\_request/\ cif}, ^{b}Graphite\ monochromator,\ ^{c}R_{1} = \Sigma(|F_{o}| - |F_{c}|)/\Sigma|F_{o}|, \ ^{d}wR_{2} = \{\Sigma[w(|F_{o}|^{2} - |F_{c}|^{2})^{2}]/\Sigma[w(|F_{o}|^{2})^{2}]\}^{1/2}$ 



A family of  $Mn_{4}^{III}Ln_{2}^{III}$  ( $Ln_{2}^{III} = Sm_{4}^{III}$ ,  $Gd_{4}^{III}$ ,  $Dy_{4}^{III}$ ) coordination clusters were synthesized utilizing a multisite hydroxyl rich ligand. The structural, topological and magnetic behaviors within the series were investigated extensively. DFT calculations afforded detailed insight into the magnetic exchange interactions between the  $Mn_{4}^{III}$  and  $Gd_{4}^{III}$  centers.

MA

#### **Synopsis**

A family of  $Mn_{4}^{III}Ln_{2}^{III}$  ( $Ln_{4}^{III} = Sm_{4}^{III}$ ,  $Gd_{4}^{III}$ ,  $Dy_{4}^{III}$ ) coordination clusters were synthesized utilizing a multisite hydroxyl rich ligand. The structural, topological and magnetic behaviors di within the series were investigated extensively. DFT calculations afforded detailed insight into the magnetic exchange interactions between the  $Mn^{III}$  and  $Gd^{III}$  centers.