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ARTICLE TYPE

Magnetic refrigeration and slow magnetic relaxation in tetranuclear lanthanide cages (Ln = Gd, Dy) with *in situ* ligand transformation.

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Three new Ln^{3+} coordination compounds having formulae, $[Gd_4(\mu_3\text{-}OH)_2(L)_2L_1L_2(HOCH_3)_2]\cdot 11H_2O$ **(1)**, $[Dy_4(\mu_3\text{-}OH)_2(L)_2L_1L_2(H_2O)_2]\cdot 11H_2O$ (**2**) and $[Dy_4(\mu_4\text{-}O)(OMe)(HOMe)_2(CH_3COO)_3(L_3)_2]\cdot 2H_2O$ **(3)** have been synthesized in one pot synthesis from O-vanillin, diaminomaleonitrile (DAMN), $LnCl_3\cdot 6H_2O$ (Ln = Gd^{3+}, Dy^{3+}) and sodium acetate for **3,** {H_2L = 2,3-bis((E)-(2-hydroxy-3-methoxy benzylidene) amino)maleonitrile, HL_1 =(2-amino-3-((E)-(2-hydroxy-3-methoxy benzylidene)amino)maleonitrile), H_3L_2 = ((1E,3Z,8Z,10E)-1,6,11-tris(2-hydroxy-3-methoxyphenyl)-2,5,7,10-tetraazaundeca-1,3,8,10-tetraene-3,4, 8,9-tetracarbonitrile) and H_2L_3 = 2-((cyano(2-hydroxy-3-methoxyphenyl)methyl)amino)-3-((E)-(2-hydroxy-3-methoxybenzylidene)amino)maleonitrile}. Single-crystal X-ray diffraction studies reveal that compounds **1** and **2** are quasi-isostructural exhibiting tetranuclear hemicubane like cores. For **3** the metal centers are arranged in a tetrahedral arrangement. Complexes **1-3** were formed with the ligands (L_1-L_3) which resulted *in situ* during synthesis. Magnetic study reveals that compound **1** shows significant magnetocaloric effect (ΔS_m = -27.2 J kg^{-1} K^{-1}) at 3 K and 7 T. Magnetic properties of **2** and **3** are considerably different. Indeed, no out-of-phase alternating current (ac) signal is noticed for **2,** whereas **3** shows slow relaxation of magnetization. These differences are most likely due to the different Dy-O-Dy angles observed for the respective cores.

Introduction

Lanthanide based molecular magnetic materials are a current area of research in chemistry as well as in physics because of some of their envisaged applications including magnetic refrigeration[1], ultra high-density data storage[2], as well as quantum computation.[3] Choosing 4f ions for the purpose has certain advantages due to their large spins and abundance of two distinct metal ions one of which shows isotropic (Gd^{III}) and the other anisotropic (Dy^{III}) magnetic behaviour. But at the same time, synthetic challenges involve the difficulty in promoting magnetic interactions via super-exchange with the "contracted" 4f orbitals. Recently, significant magnetic refrigerant materials with Gd^{III} as a constituent element have been documented in the literature showing large magneto caloric effect (MCE).[4-7] On the other hand, the intrinsic magnetic anisotropy and the increased number of unpaired *f*-electrons may be responsible for the high energy barrier for reversal of magnetization in dysprosium and thereby exhibit SMM behaviour.[8-12] Although significant number of polymetallic cages has already been documented in the literature[13-16] and some of them featuring cubane cores and displaying SMM behaviour,[17,18] yet the logical approaches for the inclusion of large numbers of metal ions in a small, single molecular entity with interesting functional properties[19] is a synthetic challenge.

Three lanthanide coordination complexes were prepared in separate one pot reactions and having molecular formulae, $[Gd_4(\mu_3\text{-}OH)_2(L)_2L_1L_2(HOCH_3)_2]\cdot 11H_2O$ (**1**), $[Dy_4(\mu_3\text{-}O)_2(L)_2 L_1 L_2(H_2O)_2]\cdot 11H_2O$ (**2**) and $[Dy_4(\mu_4\text{-}O)(OMe)(HOMe)_2(CH_3COO)_3(L_3)_2]\cdot 2H_2O$ **(3),** {H_2L = 2,3-bis ((E)-(2-hydroxy-3-methoxy benzylidene)amino)maleonitrile, HL_1 = (2-amino-3-((E)-(2-hydroxy-3-methoxybenzylidene)amino) maleonitrile) and H_3L_2 = ((1E,3Z, 8Z, 10E)-1,6,11-tris(2-hydroxy-3-methoxy phenyl)-2,5,7,10-tetra-azaundeca 1,3,8,10-tetraene-3,4,8,9-tetracarbonitrile), H_2L_3 = 2-((cyano(2-hydroxy-3-methoxy phenyl)methyl) amino)-3-((E)-(2-hydroxy-3-methoxybenzylidene)amino)maleonitrile}. X-ray crystallography unveils that the quasi-isostructural complexes **1**, **2** are composed of two hemicubanes sharing both vertices and edges, whereas complex **3** contains two distorted hemicubane cores and metal centers placed in an approximate tetrahedral shape. All the complexes (**1-3)** were formed with the ligands (L_1-L_3) which resulted *in situ* during synthesis. Magnetic studies reveal significant magnetic entropy changes for complex **1.** Magnetic properties of **2** and **3** are considerably different as a result of inclusion of acetate bridges and absence of ligand transformation in latter. Indeed, no out-of-phase alternating current (ac) signal is noticed for **2** whereas **3** shows slow relaxation of magnetization. These significant disparities are most likely due to the different Dy-O-Dy angles observed in the respective cores.

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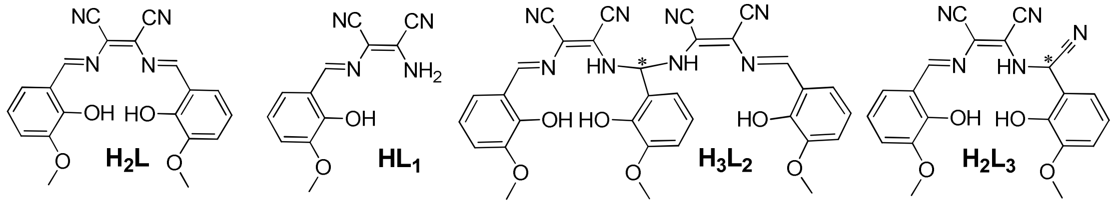
Scheme 1: Schematic Drawing of the Desired Ligand (H_2L) and Transformed Moieties



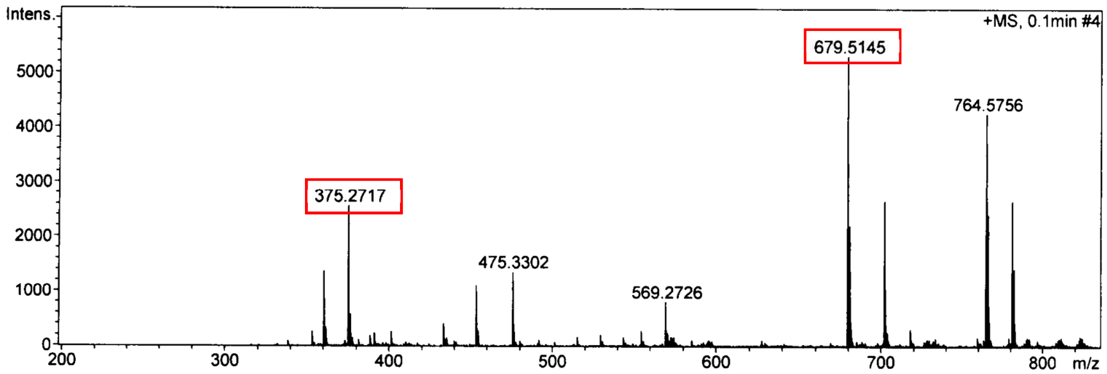


Fig. 1 ESI-MS Spectra of complex **1**. The highlighted peaks match in order with L^{2-} and $(L_2)^{4-}$ + 2 CH_3OH.

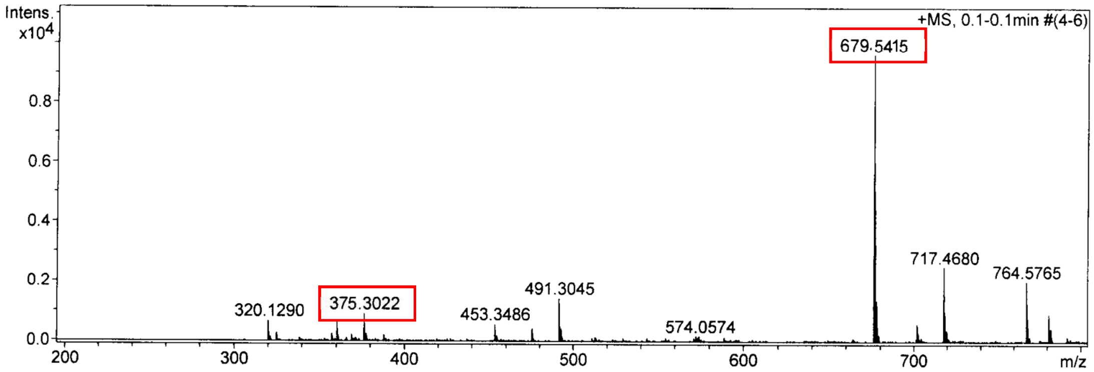


Fig. 2 ESI-MS Spectra of complex **2**. The highlighted peaks match in order with L^{2-} and $(L_2)^{4-}$ + 2 CH_3OH.

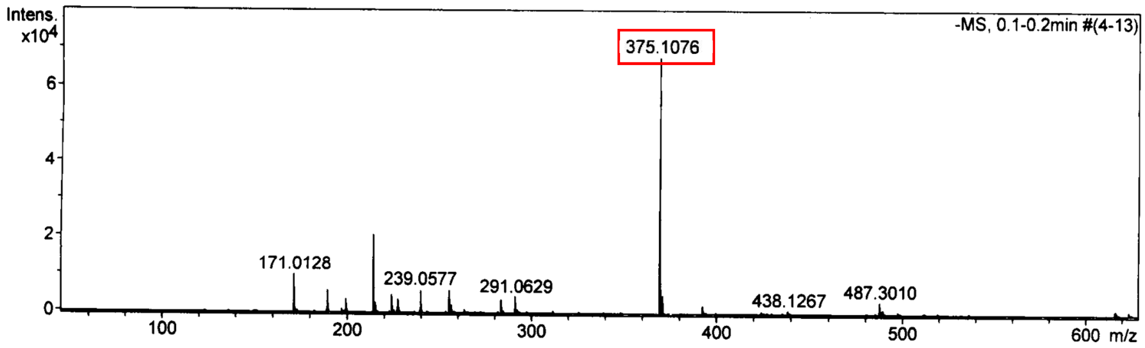


Fig. 3 ESI-MS Spectra of complex **3**. The highlighted peaks match with H_2L.

Table 1. Crystal Data and Structure Refinement for Complexes **1-3**

	1	**2**	**3**
Formula	$C_{86}Gd_4H_{90}N_{20}O_{31}$	$C_{84}Dy_4H_{86}N_{20}O_{31}$	$C_{51}Dy_4H_{51}N_{10}O_{20}$
Formula weight	2528.77	2521.70	1774.01
T (K)	296(2)	296(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Space group	*P*21/n	*P*21/c	*P*-1
Crystal system	Monoclinic	Monoclinic	Triclinic
a/Å	14.799(2)	14.645(3)	13.605(3)
b/Å	21.032(3)	21.095(4)	20.387(5)
c/Å	32.997(5)	35.775(8)	21.600(5)
α/deg	90.00	90.00	75.167(6)
β/deg	92.249(10)	112.012(15)	88.823(6)
γ/deg	90.00	90.00	88.595(6)
V/Å^3	10262(3)	10247(4)	5789(2)
Z	4	4	4
D_{calcd} (g cm^{-3})	1.506	1.502	1.993
μ (mm^{-1})	2.622	2.953	5.182
F(000)	4544	4504	3320
θ_{min}, θ_{max} (deg)	2.38, 25.45	5.36, 25.89	2.43, 25.00
Reflection collected	18994	19886	20408
unique reflections	14843	15099	17834
R$_1$, wR$_2$ ($I \geq 2\sigma(I)$)	0.0741, 0.1960	0.0760, 0.2041	0.0709, 0.1923
Goodness of fit (GOF) on F^2	1.023	1.193	1.061

Results and Discussion:

Synthetic aspects.

Reaction of O-vanillin, diaminimaleonitrile (DAMN) and $Ln^{III}Cl_3$ (Ln= Gd^{III}, Dy^{III}) in 2:1:2 ratio in refluxing MeOH for 3h in presence of NEt_3 as a base resulted in quasi-isostructural tetranuclear cages (**1** and **2**) featuring hemicubane cores with *in situ* ligand transformation. Although, our intention was to prepare the ligand H_2L but additionally we found both the ligands L_1 and L_2 in the crystal structures as well as in the mass spectra of **1** and **2**. Based on these observations, it can be assumed that HL_1 formed initially along with the desired ligand, H_2L. This was followed by the nucleophilic attack of the amine group of HL_1 on one of the imine carbon of H_2L, generating H_3L_2 (Scheme S1). Addition of potassium acetate in the reaction mixture of **2** prevented the above ligand transformation leading to another tetranuclear cage (**3**) with acetate bridges. However, to our surprise, we found from the crystal structure of **3** that cyanide addition took place on one of the imine carbon leading to the generation of a chiral centre (Scheme 1, H_2L_3). This type of cyanide addition on imines is documented in the literature using different catalysts.[20] ESI-MS studies of complexes **1-3** are given in Fig's 1-3. The peaks corresponding to the ligand (H_2L) and transformed ligand (H_3L_2) can be seen clearly from the ESI MS spectra of both complexes, **1** and **2** (Fig's 1 and 2). However, no peak corresponding to the ligand formed after cyanide addition (H_2L_3) was found in the ESI MS spectra of complex **3**. We have also isolated the ligand before the addition of Ln salt, the ESI MS spectra of which shows two prominent peaks corresponding to H_2L and HL_1 (Fig. S1, ESI). These observations show that the transformed ligands (H_3L_2 and H_2L_3) form after the addition of Ln salt only. Our efforts to isolate all the ligands separately and rationalise the complex formation were not conclusive. Thermo-gravimetric analysis plots for compounds **1-3** are given in Fig. S2, ESI. The weight loss of around 10 % (for **1** and **2**) up to 150° C corresponds to approximately eleven water molecules of crystallization and two coordinated methanol or water molecules respectively. Similarly, weight loss of around 4.4 % (for **3**) corresponds to approximately two water molecules of crystallization and three coordinated methanol molecules.

Structural Description

X-ray crystallography shows that compounds **1** and **2** crystallize in *P21/n* and *P21/c* space groups respectively. Perspective views of the structures are represented in Fig's 4 and S3. Details of the structure solution and refinement are summarized in Table 1, and selected bond distances and angles are listed in Table S1. Both the molecules exhibit discrete tetranuclear Ln^{3+} (Ln = Gd, Dy) hemicubane cores. The metal centers of the tetranuclear core are linked by two μ_3-hydroxido groups and four phenoxido oxygen atoms from the ligands resulting in the hemi-cubic arrangement of the metal ions and oxygen atoms (Fig. 5). Both the compounds consist of one nona-coordinated (Ln4, O7N2) and three eight-coordinated (Ln1, Ln2, Ln3, O6N2) metallic centers respectively. The former displays a trigonal prismatic and latter square antiprismatic geometry respectively (Fig. S4). The core is encapsulated by two ligands (L), a one side condensation moiety (L_1) and one in situ transformed ligand (L_2). Ln-O-Ln bond angles are in the range of $95.8(4)^{o}$-$109.8(8)^{o}$ for both complexes. The μ_3-hydroxo groups do not bridge symmetrically to the three metal centers in both complexes (2.28(2)-2.51(2) Å). Similar is the case with the μ_2-phenoxido groups of the ligands (2.26(2)-2.52(2) Å. The Ln-O_{PhO}, Ln-O_{OH}, Ln-O_{H2O} and Ln-$N_{C=N}$ bond distances fall in the reported range (Table S1, ESI).[21-23]

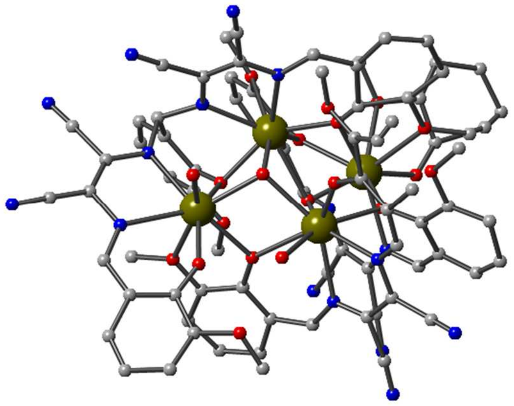


Fig. 4 Ball & stick model showing molecular structure of **1** in the crystal. Colour code: olive, gadolinium; blue, nitrogen; red, oxygen; gray, carbon; Hydrogen atoms are omitted for clarity.

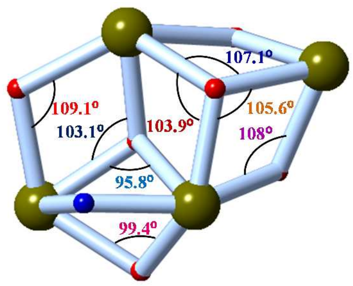


Fig. 5 Core structure of **1** showing hemicubane like arrangement of metal and oxygen atoms with characteristic Ln-O-Ln angles. Colour code: same as in Fig. 1.

The equilibrium N-O separation for both complexes **1** and **2** (e.g; N10-O14 = 2.79(7) Å for complex **2**) is around 0.3 Å shorter than the sum of the van der Waals radii and hence results in weak intermolecular interactions between the N atom of the CN group and the methoxy O atom (Fig. S5). Two O-vanillin rings of the ligands result in intermolecular π-π interaction (centriod-centriod distance = 3.71(5) Å) and provide extra stability to the structure (Fig. S6) in solid state.

Compound **3** crystallizes in *P-1* space group. This is also a tetranuclear cage comprised of four Dy^{3+} ions interconnected with two L^{3-}, one μ_4-oxo group and three acetate co-ligands (Fig. 6). Out of the four Dy centers, two of them are eight coordinated (Dy3, Dy4, O8) featuring square antiprismatic geometry and the other two are seven coordinated (Dy2, Dy8, O5N2) having pentagonal bipyramidal geometry (Fig. S7). The metal centers of this tetranuclear core are connected by a μ_4-oxo group and four μ_2-phenoxido groups from the two ligands generating a distorted hemicubane like core of metal and oxygen atoms (Fig. 7), where the metal centers are arranged roughly in a tetrahedral shape. The remaining coordination positions of the metal centers are fulfilled by the acetate anions and methanol molecules, also balancing the overall charge of the complex. Intra-cage Dy-Dy separations in this resulting array of Dy and oxygen atoms is in the range of 3.59(5)-3.99(7) Å. Dy-O and Dy-N bond distances are in the range of 2.19(7)-2.72(7)Å and 2.31(3)-2.62(5)Å respectively. Dy-O-Dy bond angles are in the range of $84.0(2)^{o}$-$130.3(3)^{o}$. The μ_4-oxo group does not bridge symmetrically to the four Dy centers (2.19(7)-2.35(7) Å. Similar is the case with the μ_2-phenoxido groups of the ligands (2.27(4)-2.40(2) Å).

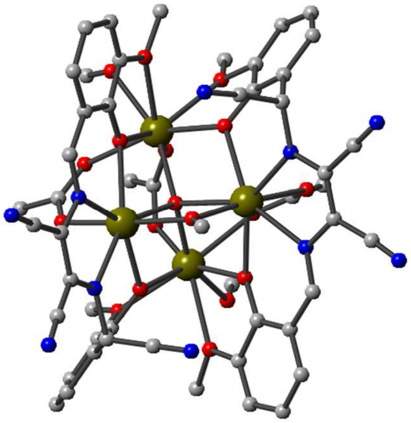


Fig. 6 Ball & stick model showing molecular structure of **3** in the crystal. Colour code: olive, Dysprosium; blue, nitrogen; red, oxygen; gray, carbon; Hydrogen atoms are omitted for clarity.

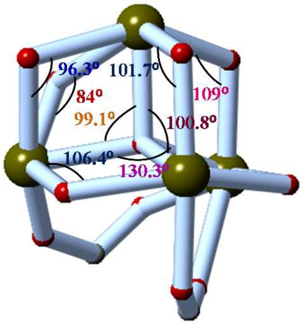


Fig. 7 Core structure of **3** showing tetrahedra like arrangement of metal atoms. Colour code: same as in Fig. 1.

Magnetic properties

The variable-temperature DC magnetic susceptibility data of complexes **1-3** were collected in the temperature range 1.8 – 300 K under an applied field of 0.1 T and the results are shown in the form of $\chi_M T$ (χ_M is molar magnetic susceptibility) vs T (Fig.8). The room temperature $\chi_M T$ value for **1** is 31.10 cm^3 K mol^{-1} which is consistent with the spin only value of 31.20 cm^3 K mol^{-1} (g = 2) for four isolated Gd^{III} centers (Fig. 8). As the temperature is lowered from 300 K, $\chi_M T$ value remains almost constant up to ~ 54 K (30.30 cm^3 K mol^{-1}) below which it decreases gradually to reach the value of 17.93 cm^3 K mol^{-1} at 1.8 K. The gradual decline at lower temperatures may be attributed to the presence of intramolecular antiferromagnetic interactions.[24-26] Experimental χ_MT *vs.* T plot was fitted using the Hamiltonian (1) based on the model given in inset Fig. 8. The data was fitted nicely with g = 2.0 and J = -0.10 cm^{-1}. Low J values suggest weak antiferromagnetic exchange between the adjacent Gd^{3+} centres.

$$H_{Gd4} = -J(S_1S_2+S_3S_4+S_1S_3+S_2S_4+S_1S_4) - g\mu_B H.\sum_{i=1}^{4} Si \quad .... (1)$$

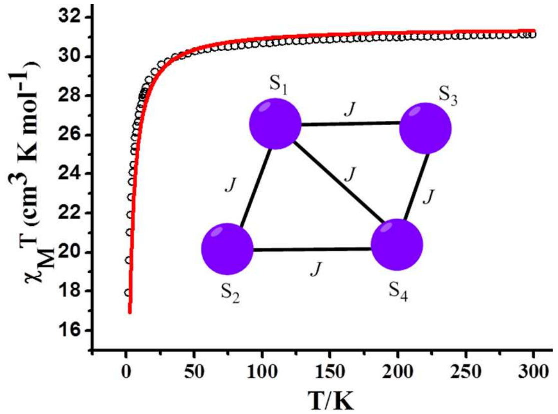


Fig. 8 Temperature dependence of $\chi_M T$ vs T for **1**, measured at 0.1 T. Red sold line is the best fit obtained.

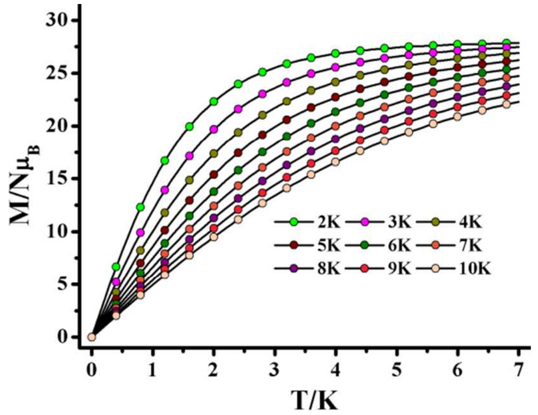


Fig. 9 Field-dependencies of isothermal normalized magnetizations for complex **1**, collected for temperatures ranging from 2 to 10 K.

Magnetization measurements at low temperature (Fig. 9) show saturation value of 27.8 $N\mu_B$ at 7 T for complex **1**. The value is in well agreement with the theoretical value of 28 $N\mu_B$ (for four isolated Gd^{III}, g = 2). The magnetic entropy change (ΔS_m) for **1** was calculated at various fields and temperatures from magnetization data using the Maxwell equation $\Delta S_m(T)_{\Delta H} = \int[\partial M(T,H)/\partial T]_H dH$.[27] The resulting value is gradually increased with lowering the temperature from 9 K to 2 K (Fig. 10). The highest value of ΔS_m = -27.2 J kg^{-1} K^{-1} was obtained at 3 K and 7 T. Corresponding volumetric entropy change is 41.5 mJ cm^{-3} K^{-1}. This value is comparable with the other discrete complexes based on highly isotropic Gd^{III} ions (Table S2).[7b-7f] The maximum entropy value per mole corresponds to n = 4 Gd^{III} spins s=7/2, and is calculated as nRln(2s+1)= 8.2R, which corresponds to 29.7 J kg^{-1} K^{-1}. The differences between the theoretical and observed values can be attributed to the presence of antiferromagnetic interactions between the paramagnetic metal centers.

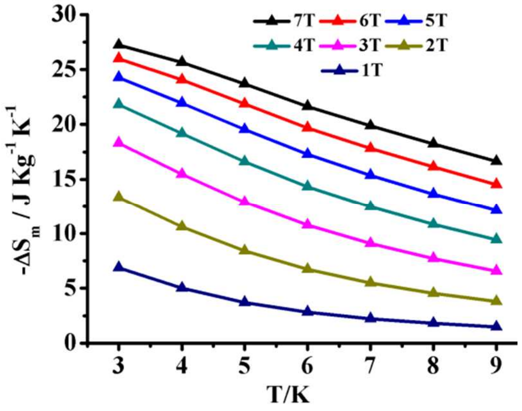


Fig. 10 Temperature dependencies (3 to 10 K) of magnetic entropy change (-ΔSm) for complex 1 as obtained from magnetization data.

The room temperature $\chi_M T$ values for complexes **2** and **3** are 54.1 cm^3 mol^{-1} K and 55.6 cm^3 mol^{-1} K respectively which are close to the calculated spin-orbit values 56.7 cm^3 mol^{-1} K for four isolated Dy^{III} ($^6H_{15/2}$, S = 5/2, L = 5, g = 4/3) (Fig. 11). The $\chi_M T$ values decrease gradually from room temperature and finally drop down to 38.3 cm^3 mol^{-1} K for **2** and 28.2 cm^3 mol^{-1} K for **3** at 1.8 K. This decrease can be attributed to the depopulation of the Stark (m_J) sublevels of the ground J multiplet, with the possibility of weak antiferromagnetic exchange and dipolar interactions also contributing to the behaviour.

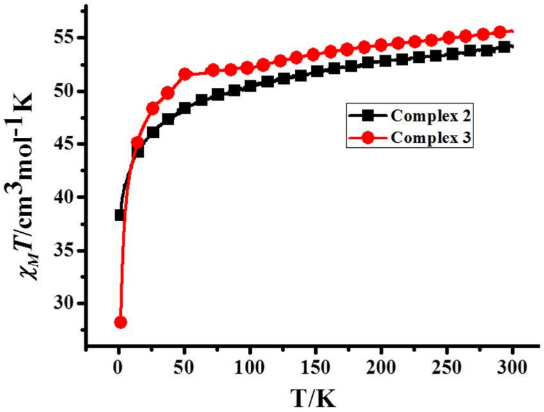


Fig. 11 Temperature dependence of χMT vs T plot for **2** and **3** measured at 0.1 T.

Magnetization value in M/Nμ_B *vs* H plots for both **2** and **3** do not reach saturation even at the highest experimental field of 7 T but are tending towards saturation (Fig's S8, S9). The M/Nμ_B values increase sharply with increasing field at low temperature and fields, followed by a linear increase at higher fields reaching the values of 19.58 and 20.78 Nμ_B for **2** and **3** respectively. These values are much lower than the theoretical values for four non interacting Dy^{III} ions (g_J x J = 4/3 x 15/2 = 10 μ_B per Dy^{III}) suggesting the presence of anisotropy and significant crystal field effects from the Dy^{III} ions eliminating the 16-fold degeneracy of the $^6H_{15/2}$ ground state. M/Nμ_B versus H/T plots of complexes **2** and **3** (Fig's S10, S11) show that all isotherm magnetization curves do not collapse on the same master curve, indicating significant anisotropic nature of the Dy^{III} ion, however magnetization isotherms for **3** are more separated as compared to **2.**

AC measurements for **2** and **3** were performed at the temperature of 1.8-10 K in the frequency range of 1-800 Hz at zero dc field to examine the SMM behaviours. In phase components of ac susceptibility (χ') are found to be frequency independent for both complexes **2** and **3** (Fig's S12, S13). Complex **2** does not show any frequency or temperature dependency of out of phase component χ'' (Fig. S13) whereas complex **3** shows temperature (Fig. 12) as well as frequency dependency (Fig. S14) of out of phase component (χ'') of ac susceptibilities below 5 K indicating the slow relaxation of magnetisation characteristic of SMMs.

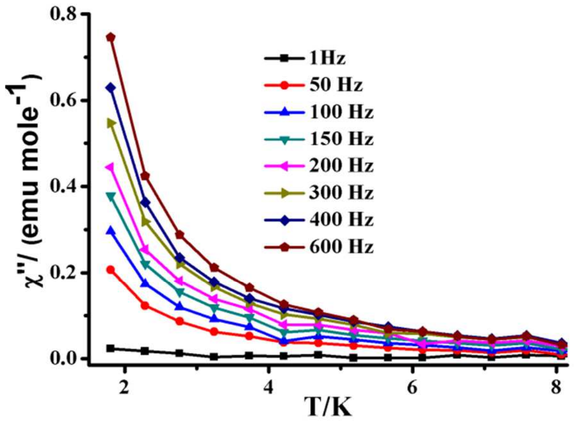


Fig. 12 Temperature dependence of the out of phase (χ'') ac susceptibility for complex **3** under zero dc field.

However, no full peaks were observed under zero DC field, which can be attributed mainly to quantum tunnelling of the magnetisation (QTM), often occurring in lanthanide SMMs. In order to minimise the quantum tunnelling we re-measured the data in presence of an optimum static dc field of 1800 Oe but no change was observed in the ac signals of **3** (Fig. S15). Although the expected maxima could not be observed due to blocking but to roughly estimate the energy barrier (U_{eff}) and relaxation time (τ_0), another method[28] was used, assuming single relaxation process of the Debye model and equation:

$$\ln(\chi''/\chi') = \ln(\omega\tau_0) + U_{eff}/kT \text{ ....(1)}$$

The best fitting results give the energy barrier $U_{eff} \approx 3.8$ K and the relaxation time $\tau_0 \approx 6.4\times10^{-6}$ s (Fig. 13) which is consistent with the expected value of $10^{-6} – 10^{-11}$ for a SMM.[8-12]

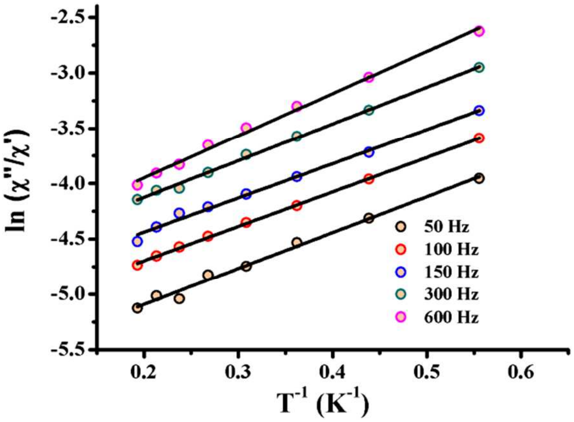


Fig. 13 Natural logarithm of the ratio of χ''over χ' vs.1/T for complex **3**. Red lines represent best fit obtained of equation (1).

Magneto-structural Correlation

Both the dysprosium analogues (**2** & **3**) contain four Dy^{III} centres however their magnetic properties are significantly different. The distinct behaviour can be attributed to the nature and symmetry of the crystal field which determines the magnetic anisotropy.[8-12] The absence of slow relaxation of magnetisation for **2** may result from the fact that the magnetic anisotropy axes in core **2** are not parallel.[29] These differences in turn can result from the structural differences between the respective cores.[11c-e, 12b, 18c] The complex **2** contains hemicubane like core where two μ_3-hydroxo groups bridge four dysprosium centers. Additionally, adjacent Dy^{III} centers are bridged by phenoxido oxygen atoms of the ligand. The resulting core is defined by Dy-O-Dy bond angles in the range of (95.8(7)°- 109.1(8)° (Fig. 5). In compound **3** the Dy^{III} centers show tetrahedral like arrangement where one μ_4-oxo group connects four metal centers. In addition to this two acetate bridges and four phenoxido oxygen atoms are also present. This gives Dy-O-Dy bond angles in the range of (84.0(2)°- 130.3(3)°) (Fig. 7). The main differences between the two cores are thus in the Dy-O-Dy bond angles. The geometry and coordinating atoms around the Dy^{III} centers are also different for **2** and **3**. Complex **2** consists of one nona-coordinated (Dy3, O7N2) and three eight-coordinated (Dy1, Dy2, Dy4, O6N2) Dy^{III} centers respectively. The former displays a trigonal prismatic and latter square antiprismatic geometry respectively (Fig. S3). On the other hand, out of the four Dy^{III} centers in complex **3** two are eight coordinated (Dy2, Dy3, O8) featuring square antiprismatic geometry and the other two are seven coordinated (Dy1, Dy4, O5N2) having pentagonal bipyramidal geometry (Fig. S6). This would result in different magnetic interactions between the metal centers induced by the hydroxide and acetate bridges. It is well-known for dysprosium[11c-e, 12b, 18c] and other metal ions linked by μ-OH$^-$ ligands that the M-O-M angles have a great influence on the magnetic exchange coupling.[30] More specifically, the local tensor of anisotropy on each Dy site and their relative orientations caused by the change of Dy-O-Dy angle could be a crucial feature to induce or not a SMM behavior in these complexes. Because of the challenges in describing the crystal field of Dy^{III}, it is difficult to make any further comment at this stage.

Conclusion

Three new tetranuclear Ln^{III} coordination compounds are reported. Two of them are quasi-isostructural and feature hemicubane cores whereas third one comprises of core with metal centers in approximately tetrahedral arrangement. The Gd analogue shows significant cryogenic magnetic refrigeration and one of the Dy containing compounds undergoes slow magnetic relaxation. The results are good addition to the relatively rare class of magnetic molecules based on purely lanthanides.

Experimental Section

X-ray Crystallography

Data collection of the compounds **1** and **2** were performed at 296 K and that of compound **3** at 100 K on a Bruker Smart Apex 2 CCD diffractometer with Mo-Kα(λ) 0.71073 Å) radiation using a cold nitrogen stream (Oxford). Data reduction and cell refinements were performed with the SAINT program[31] and the absorption correction program SADABS[32] was employed to correct the data for absorption effects. Crystal structures were solved by direct methods and refined with full-matrix least-squares (SHELXTL-97)[33] with atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. Crystals of compounds **1-3** were notably poorly diffracting and after several attempts, we were unable to grow better quality crystals. The lower angle reflection data consequences a poor data to parameter ratio and in anisotropic refinement few atoms became anisotropic displacement parameters (ADPs). The thermal parameters of all the carbon atoms were restrained to approximately the same values using the XShell "rigid bond displacement" (DELU), "isotropic displacement" (ISOR) command. The structures of all complexes contain solvent accessible voids, hence SQUEEZE[34] module of the program suite PLATON[35] was used to generate a fresh reflection file. X-ray crystallographic data in CIF format is available in CCDC numbers 964479 – 964481.

Materials and Methods

All the reagents were used as received from Sigma Aldrich without any further purification. Magnetic susceptibility and magnetization measurements were carried out on a Quantum Design SQUID-VSM magnetometer. Direct current magnetic measurements were performed with an applied field of 1000 G in the 1.8 K-300 K temperature range. AC magnetic susceptibilities were performed in 3.5 G field oscillating at 1-800 Hz in the 1.8-10 K range. Infrared Spectra were recorded in the solid state (KBr pellets) on a Perkin Elmer FTIR spectrometer in the range of 400-4000 cm^{-1}. Elemental analyses were performed on an Elementar vario Microcube elemental analyzer.

Synthesis

$[Gd_4(\mu_3\text{-}OH)_2(L)_2L_1L_2(OCH_3)_2]\cdot 11H_2O$ (1)

O-vanillin (61mg, 0.4mmol) and DAMN (22mg, 0.2mmol) were taken in MeOH (15 mL) and refluxed for 2h and the reaction mixture was cooled to room temperature. This was followed by the addition of $GdCl_3\cdot 6H_2O$ (150mg, 0.4 mmol) and stirred for few minutes, followed by the addition of triethylamine (20 mg, 0.2 mmol). This solution was refluxed for additional 30 minutes. The reaction mixture was cooled to room temperature and filtered. The filtrate was kept unperturbed to allow the slow evaporation of the solvent. Brown single crystals, suitable for X-ray diffraction analysis, were obtained from solution within 4 days. The crystals were collected by filtration, washed with cold methanol and dried in air, yield: 76 mg (32 %, based on Gd). Elemental analysis: Calcd.(found) for $C_{86}Gd_4H_{90}N_{20}O_{31}$: C, 40.84(40.67); H, 3.58(3.39); N, 11.07(11.21). Selected IR data (KBr pellet): 3179.4 (b), 1672.6 (s), 1592.6 (w), 1567.4 (m), 1534.8 (s), 1437.6 (w), 1305.8 (m), 1236.5 (m), 1154.7 (s), 999.5 (m), 746.3 (m) cm^{-1}.

$[Dy_4(\mu_3\text{-}OH)_2(L)_2\ L_1L_2\ (H_2O)_2]\cdot 11H_2O$ (2)

This compound was synthesised following a similar procedure as for **1** but $DyCl_3\cdot 6H_2O$ (152mg, 0.4mmol) was used here instead of $GdCl_3\cdot 6H_2O$. Brown single crystals, suitable for X-ray diffraction were collected by filtration after 4 days, yield 69 mg (30.4%, based on Dy). Elemental analysis: Calcd.(found) for $C_{84}Dy_4H_{86}N_{20}O_{31}$: C, 40.0(40.39); H, 3.43(3.26); N, 11.10 (10.96). IR (KBr, cm^{-1}); 3432 (b), 3179 (b), 2963 (s), 2871 (s), 2374 (m), 2171 (w), 1623 (b), 1547 (m), 1485 (vs), 1458 (m), 1429 (s), 1379 (m), 1363 (m), 1270 (s), 1231 (vs), 1205 (m), 1098 (m), 1029 (s), 990 (vs), 898 (vs), 830 (s), 809 (m), 788 (s), 755 (s), 670 (w), 628 (s).

$[Dy_4(\mu_4\text{-}O)(OMe)(HOMe)_2(CH_3COO)_3(L_3)_2]\cdot 2H_2O$ (3)

This compound was synthesised following a similar procedure as for **2** but potassium acetate (40mg, 0.4mmol) was also added after the addition of $DyCl_3\cdot 6H_2O$. Red single crystals suitable for X-ray diffraction were collected by filtration after 4 days, yield 57 mg (34.8%, based on the ligand). Elemental analysis: Calcd.(found) for Elemental analysis: Calcd.(found) for $C_{51}Dy_4H_{51}N_{10}O_{20}$: C, 34.52(34.81); H, 2.89(3.09); N, 7.89(7.96). IR (KBr, cm^{-1}); 3423 (b), 3180 (b), 2958 (s), 2870 (m), 2369 (m), 1670 (s), 1602 (s), 1508 (m), 1483 (vs), 1458 (m), 1419 (s), 1373 (s), 1360 (m), 1270 (m), 1229 (vs), 1122 (s), 1090 (vs), 1028 (s), 991 (vs), 879 (b), 834 (m), 785 (s), 750 (s), 611 (vs), 588 (s), 530 (s).

Supporting Information

Figures illustrating the molecular structure of **2**, coordination environments of the Ln^{III} ions in **1- 3**; Magnetic plots, selected bond distance and bond angle table. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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† Figures illustrating the ESI MS spectra of ligand, molecular structure of **2**, coordination environments of the Ln^{3+} ions in **1-3**; Magnetic plots, selected bond distance and bond angle tables are provided in the ESI.

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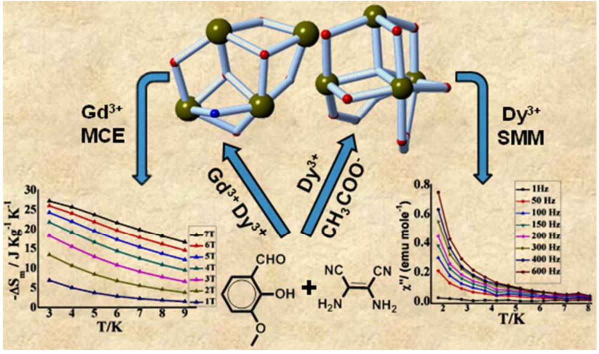

Three tetranuclear Lanthanide cages featuring either hemicubane (**1** and **2**) or distorted hemicubane (**3**) like cores are reported. Magnetic studies reveal significant magnetic entropy changes for complex **1** and slow relaxation of magnetisation for **3.**