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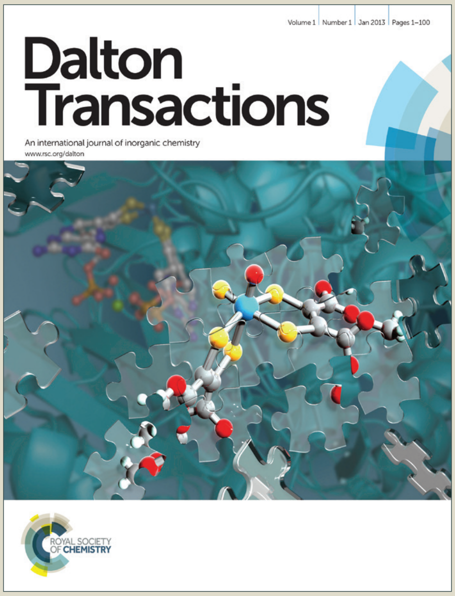

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ARTICLE TYPE

Modulating the magnetic properties by structural modification in a family of Co-Ln (Ln= Gd, Dy) molecular aggregates[#]

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Two types of heterometallic aggregates of general formula, $[(Co^{II})_3(Co^{III})_2Ln_3(\mu_3\text{-}OH)_5(O_2C^tBu)_{12}(L)_2]\cdot 2H_2O$ (Ln = Gd^{III} (**1**), Dy^{III} (**2**)) and $[(Co^{III})_3Ln_3(\mu_3\text{-}OH)_4(O_2C^tBu)_6(L)_3](NO_3)_2\cdot 2CH_3CN\cdot 2H_2O$ (Ln = Gd^{III} (**3**), Dy^{III} (**4**)) were successfully isolated in reactions with $[Co_2(\mu\text{-}OH_2)(O_2C^tBu)_4]\cdot(HO_2C^tBu)_4$, $Ln(NO_3)_3$ and *n*-N-butyldiethanolamine (H_2L) under ambient conditions by a change in the stoichiometry of the reactants from 1:1:1 to 1:1:2 in order. Bond Valence Sum (BVS) calculations and bond lengths indicate the presence of mixed valent Co (Co^{II}, Co^{III}) centres in compounds **1** and **2** and only Co^{III} centres in **3** and **4** as required for the charge balances and supported by the magnetic measurements. Isostructural crab shaped complexes **1** and **2** feature distorted cubane cores that edge share to each other whereas the metallic core of **3** or **4** displays hemicubane like arrangement of metal centres and oxygen atoms. Overall structural symmetry was found to enhance on moving from former to the latter series of complexes. Magnetic studies reveal significant magnetic entropy changes for complexes **1** and **3** ($-\Delta S_m$ = 21.57 and 19.39 $JKg^{-1}K^{-1}$) and single molecular magnetic behaviours for **2** and **4**.

Introduction

Polynuclear 3d-4f cages have emerged as one of the most active area of research in the field of coordination and magneto chemistry for the development of single-molecule magnets (SMMs) with aesthetically pleasing structures.[1-3] Considerably, their unique magnetic properties make the SMMs potentially applicable in information storage.[4] Another promising application exhibited by such systems is magnetic refrigeration which is based on magnetocaloric effect that in turn relies on the entropy change of a material in a magnetic field.[5] Magnetic refrigerants have been proposed to replace the expensive and rare helium-3 in some ultra low temperature cooling applications. The approach of integration of 4f ions (e.g; Dy^{III}, Tb^{III} etc) with 3d metals in nanoscale cages (3d-4f approach) has been used to incorporate large ground state and high anisotropy for obtaining SMMs. Whereas, for magnetic refrigeration, isothermal entropy change can be maximized by incorporation of Gd^{III} ions into the molecule as it provides the largest entropy per single ion.[1-3, 6-11] Therefore, 3d-Ln cages comprised of highly anisotropic Ln^{III} ions (such as Dy^{III}, Tb^{III}) are possibly ideal candidates for SMM behaviour[1-3,12] and those with highly isotropic Gd^{III} ions are suitable as cryogenic magnetic refrigeration material.[7,13]

Alkoxy ligands have widely been employed in the synthesis of 3d/3d-4f cages of variable nuclearity and interesting magnetic properties.[14] In this work, we have employed *n*-N-butyl-diethanolamine for the construction of 3d-4f cages because of its ability to form polynuclear cages with short intermetallic distance for better magnetic interactions. Further, compounds incorporating this ligand to give 3d-4f cages are still rare.[15] It therefore seemed logical to investigate the use of this ligand in the pursuit for new examples of magnetic refrigerants and SMMs. In this regard, we have reacted it with a preformed precursor, $[Co_2(\mu\text{-}OH_2)(O_2C^tBu)_4]\cdot(HO_2C^tBu)$ (**Co_2** from here onwards) and lanthanide salts and successfully isolated four complexes with two different classes in terms of structural features. Herein, we report the synthesis, structural and magnetic characterisation of these two types of heterometallic cages having general formula, $[(Co^{II})_3(Co^{III})_2Ln_3(\mu_3\text{-}OH)_5(O_2C^tBu)_{12}(L)_2]\cdot 2H_2O$ (Ln = Gd^{III} (**1**), Dy^{III} (**2**)) and $[(Co^{III})_3Ln_3(\mu_3\text{-}OH)_4(O_2C^tBu)_6(L)_3](NO_3)_2\cdot 2CH_3CN\cdot 2H_2O$ (Ln = Gd^{III} (**3**), Dy^{III} (**4**)) The two different series of heterometallic cages resulted by a change in the stoichiometry of reactants from 1:1:1 to 1:1:2 respectively. Bond Valence Sum (BVS) calculations[16a] and magnetic measurements authenticate the presence of mixed valent Co (Co^{II}, Co^{III}) centres in complexes **1** and **2** as required for the charge balance. The BVS method is used in coordination chemistry to estimate the oxidation state of atoms. Structural investigation reveals that isostructural complexes **1** and **2** are crab shaped and featuring distorted cubane cores that edge share to each other whereas the metallic core of **3** or **4** displays hemicubane like arrangement of metal centres and oxygen atoms. Magnetic studies reveal significant magnetic entropy changes for complexes **1** and **3** and single molecular magnetic behaviors for **2** and **4** respectively.

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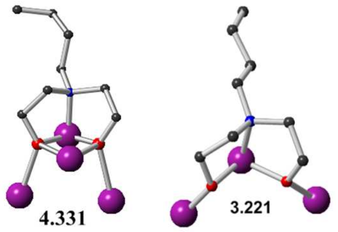
Table 1. Crystallographic Data and Structure Refinement Parameters for Complexes **1-4.**

	1	**2**	**3**	**4**
Formula	$C_{76}H_{151}Co_5Gd_3N_2O_{35}$	$C_{76}H_{151}Co_5Dy_3N_2O_{35}$	$C_{58}H_{125}Co_3Gd_3N_7O_{33}$	$C_{58}H_{125}Co_3Dy_3N_7O_{33}$
Formula weight	2419.30	2476.03	2097.18	2112.93
T (K)	110(2)	110(2)	110(2)	110(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Space group	*C*2/c	*C*2/c	*P*21/c	*P*6(1)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Hexagonal
a/Å	14.2172(9)	14.1684(7)	14.900(3)	16.173(5)
b/Å	27.711(2)	27.6583(16)	31.505(5)	16.173(5)
c/Å	25.4221(17)	25.4178(13)	19.332(3)	54.305(2)
α/deg	90.00	90.00	90.00	90.00
β/deg	96.105(19)	96.0392(15)	103.363(4)	90.00
γ/deg	90.00	90.00	90.00	120.00
V/Å^3	9958.8(12)	9905.3(9)	8829(3)	12301(5)
Z	4	4	4	6
D_{calcd} (g cm^{-3})	1.608	1.627	1.505	1.674
μ (mm^{-1})	2.855	3.125	2.845	3.371
F(000)	4876	4900	4004	6209.6
θ_{min}, θ_{max} (deg)	2.17, 25	2.18, 25	2.16, 28.57	2.08, 29.60
Reflection collected	8778	8721	22155	22131
unique reflections	8181	7648	18557	20764
R_1, wR_2 ($I \geq 2\sigma(I)$)	0.0622, 0.2075	0.0587, 0.1500	0.0949, 0.2273	0.0522, 0.1060
Goodness of fit (GOOF) on F^2	1.056	1.103	1.123	1.064

Results and Discussion

The reaction of $\mathbf{Co_2}$ and Ln $(NO_3)_3 . 6H_2O$ (Ln = Gd^{III}, Dy^{III}) with H_2L in 1:1:1 molar ratio under ambient conditions afforded the isostructural complexes **1** and **2**.



Scheme 1. Bridging modes of H_2L (Harris notation) ligand in complexes **1-4**.

A change in the ratio of reactants from 1:1:1 to 1:1:2 in order resulted in two more isostructural complexes **3** and **4**. Similar synthesis at other molar ratios of the reactants led to either type of the above complexes. TGA shows a weight loss of around 3% for complexes **1** and **2** up to 170°C that can be assigned to two non coordinated water molecules. Similarly a weight loss of around 8% in complexes **3** and **4** up to 170°C corresponds to two non coordinated acetonitrile molecules and five water molecules of which three are coordinated and two uncoordinated (Fig. S1)

Structural Description of 1 and 2

Single crystal X-ray analysis shows that complexes **1** and **2** crystallise in *C*2/c space group. Both the complexes (Fig's 1a and S2) were found to be isostructural heterometallic octanuclear crab shaped cages comprising of a total of five cobalt centres and three Dy^{III} ions. BVS calculations and bond lengths indicate that out of the five cobalt centres, three are in +2 oxidation state (Co1, Co1A and Co3) and the remaining two (Co2, Co2A) are in +3 oxidation state. The metal centres of this octanuclear core are principally linked by five μ_3-hydroxo groups (Fig. 1b). Periphery of each cage is enclosed by two doubly deprotonated amine-based tritopic diol ligands, H_2L where hydrophobic aliphatic parts of the ligands are pointed outwards. The ligands coordinate via the N atom to the cobalt ions and then bridge them to the Ln^{III} ions via their two μ_2-alkoxo groups. Both the dianionic H_2L ligands are bridging the metal centres in a rare 4.321 mode (Harris notation).[16b] The digits on the left and right side of the decimal indicate the total no of metal centres coordinated to one ligand and to each donor atom of the ligand respectively. The core is also wrapped by a hydrophobic sheath of twelve pivalate ligands bridging in 2.11 mode, thus completing the coordination sphere of each ion. This finally results in the cobalt ions being six-coordinated with an octahedral geometry except one of the Co^{II} centre (Co3) featuring tetrahedral geometry. The average Co^{III}-O and Co^{III}-N bond distances are 1.91(2) and 1.99(1) Å respectively whereas the average Co^{II}-O bond distance is 2.08 (3) Å. These values are in good agreement with those reported for the low spin Co^{III} and high spin Co^{II} ions. [12,17] The Ln^{III} ions are all eight-coordinated with a distorted square antiprismatic geometry and average Ln−O bond lengths of 2.40(1) and 2.38 (3) for 2a and 2b respectively. The average Co-O-Co, Co-O-Ln and Ln-O-Ln bond angles are 101.5 $(2)^0$, 100.2 $(2)^0$ and 114.6 $(3)^0$ respectively.

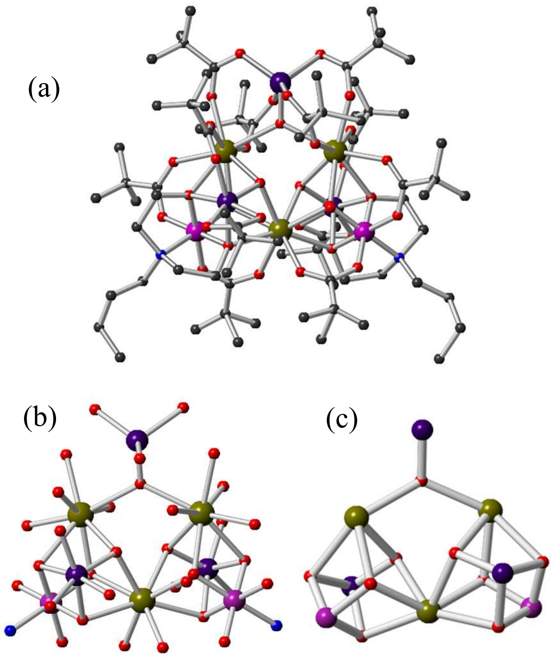


Fig. 1 (a) Ball & stick model showing molecular structure of **1** in the crystal. Hydrogen atoms are omitted for clarity. (b) Core structure of **1** (c) Distorted cubic core view, colour code: purple, Co^{III}; blue violet, Co^{II}; olive, Gd; red, O; blue, N; gray, C.

Careful investigation of the core shows that it is made of two distorted cubanes that edge share to each other (Fig. 1c). These cubanes are formed from the μ_3-hydroxo bridges and μ_3-O atoms of the doubly deprotonated tripodal H_2L ligand. These distorted cubanes are further interlinked via a μ_3-hydroxo group that also bridges cobalt centre (Co3) to the two Ln^{III} sites (Fig. 1c).

Structural Description of 3 and 4

Single-crystal X-ray diffraction measurements show that complexes **3** and **4** crystallize in the monoclinic and hexagonal space groups, *C*2/c and *P*6(1) respectively. Both the complexes (Fig's 2a and S3) are isostructural heterometallic hexanuclear cages consisting of three Co^{III} and three Ln^{III} ions. The metal-oxo core for each cage displays a hemicubane like arrangement of the metal ions and oxygen atoms. The metal centres of this hexanuclear core are primarily linked by four μ_3-hydroxo groups. Peripheral ligation is provided by two doubly deprotonated amine-based tritopic diol ligands (H_2L) that coordinate via the N atom to the Co^{III} ions and then bridge the Co^{III} centres to the Ln^{III} ions via its two μ_2-alkoxo groups. The core is further surrounded by six pivalate groups bridging in 2.11 mode and three water molecules, one each coordinating to the Ln^{III} ions, thus completing the coordination sphere for each ion. This finally results in the Co^{III} ions being six-coordinated with an octahedral geometry having average Co-O and Co-N bond distances of 1.91 (1) and 1.98(2) Å respectively. All the Ln^{III} ions are eight-coordinated having a distorted square antiprismatic geometry (as in **1** and **2**) and average Ln−O bond lengths of 2.38 (9) Å and 2.34 (1) Å for **3** and **4** respectively. The average Co-O-Ln and Ln-O-Ln bond angles are 100.5 $(3)^0$ and 110.3 $(3)^0$ respectively.

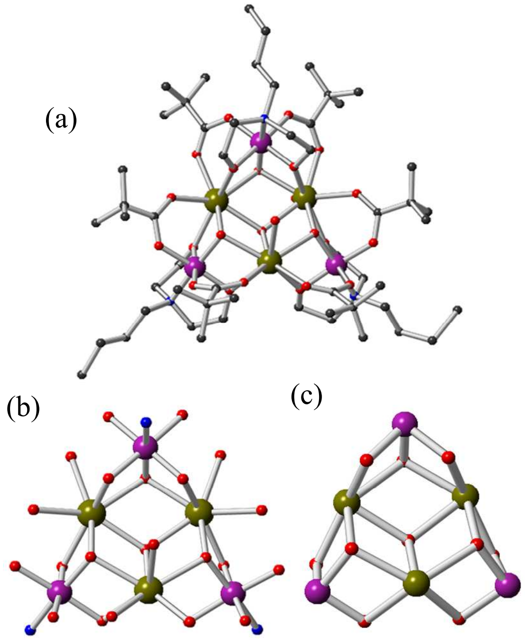


Fig. 2 (a) Ball & stick model showing molecular structure of **3** in the crystal. Hydrogen atoms are omitted for clarity (b) Core structure of **3** (c) Hemicubane like core structure of **3**, Colour code: same as in Fig. 1.

Careful analysis of the two structural types (**1, 2** and **3, 4**) reveals some interesting inference. We can conclude that the presence of one additional chelating H_2L ligand in the latter series (**3, 4**) prevents the formation of cubane cores (as in **1, 2**) and instead leads to hemicubane like cores. The chelating nature of H_2L ligand seems to restrict the number of pivalate groups (from 12 in earlier series to 6 in the latter series) that complete the cubane cores in the earlier type of complexes (**1, 2**) by coordinating to more cobalt centres. Number of μ_3-hydroxo groups is also decreased from five to four from former to latter series respectively. One μ_3-hydroxo group is found bridging the three Ln^{III} centres in latter series (**3, 4**) and is not present in the former series (**1, 2**). This enhances the symmetry of the overall structure for the latter. Another difference is that each of the Ln^{III} centres in the latter series is coordinated to one water molecule to complete the coordination sphere.

Magnetic Properties

The variable-temperature DC magnetic susceptibility data of complexes **1-4** were collected in the temperature range 1.8 – 300 K under a field of 0.1 T and are shown in the form of $\chi_M T$ (χ_M is molar magnetic susceptibility). The DC magnetic studies (Fig. 3) for complexes **1-4** show room temperature χ_MT values of 30.24, 54.16, 23.50 and 42.39 $cm^3\ mol^{-1}$ K respectively, that are in good agreement with the expected values of 29.24 (**1**, 3 uncoupled Gd^{III}, g = 1.99 and 3 Co^{II} ions, g = 2), 48.71 (**2**, 3 uncoupled Dy^{III}, g = 4/3 and 3 Co^{II} ions, g = 2), 23.62 (**3**, 3 uncoupled Gd^{III} ions, g = 1.99) and 43.09 $cm^3\ mol^{-1}$ K (**4**, 3 uncoupled Dy^{III} ions, g = 4/3) considering the orbital contribution of octahedral Co^{II} ions with $^4T_{1g}$ ground term (for **1** and **2**).[17,18]

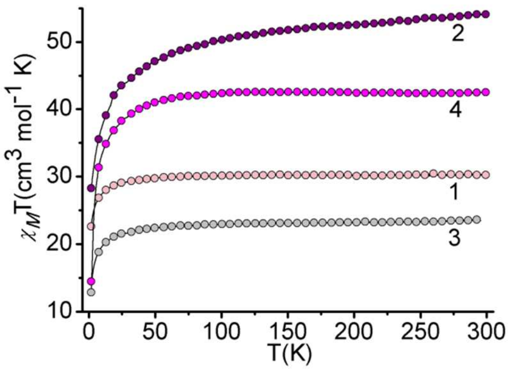


Fig. 3 Temperature dependence of χ_MT measured at 0.1 T for complexes **1-4**.

As the temperature is lowered, for the complexes **1** and **3**, the $\chi_M T$ products remain almost constant down to 25 K where a sharp decrease is observed, reaching to a value of 22.6 and 12.84 $cm^3\ mol^{-1}$ K at 1.8 K for **1** and **3** respectively. The constant $\chi_M T$ value of **1** down to 25 K suggests the quenching of the orbital contribution for Co^{II} ions probably due to a lower symmetry around the Co^{II} centres that can remove the degeneracy of the ground state whereas the same behaviour for **3** can be attributed to the presence of isotropic Gd^{III} ions. For the complexes **2** and **4**, upon lowering the temperature, the $\chi_M T$ values decrease very gradually (300 – 50 K) before a sharp decrease occurring below 50 K , reaching the values of 28.24 and 14.45 $cm^3\ mol^{-1}$ K at 1.8 K for **2** and **4** respectively. 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. Magnetization measurements at low temperature (Fig's S4 and S5) show saturation values of 26.66 $N\mu_B$ and 20.88 $N\mu_B$ at 7 T for complexes **1** and **3** respectively. These are close to the theoretical values of 30 $N\mu_B$ and 21 $N\mu_B$ respectively. However, the M/$N\mu_B$ versus H/T plots of complexes **1** and **3** (Fig's S6 and S7) show that all isotherm magnetization curves do not collapse on the same master curve, indicating significant anisotropic nature of the cobalt ions. The magnetic entropy changes (-ΔS_m) for **1** and **3** were calculated at various fields and temperatures from magnetization data using the Maxwell equation:

$$\Delta S_m(T)_{\Delta H} = \int[\partial M(T,H)/\partial T]_H dH \ldots(1)\ (H = \text{magnetic field}).^{19}$$

The resulting values gradually increase with lowering the temperature from 9 K to 2 K (Fig. 4). The highest values of -ΔS_m = 21.57 (**1**) and 19.39 J $Kg^{-1}\ K^{-1}$ (**3**) were obtained at 3 K (**1**), 4 K (**3**) and ΔH = 7 T respectively. These values are comparable with the other reported Co-Gd cages in the literature.[20] The slightly larger MCE value in former complex can be attributed to the presence of three paramagnetic Co^{II} ions as the number of Gd^{III} ions is same in both the complexes. The maximum entropy value per mol corresponds to n = 3 Co^{II} spins S = 3/2 and 3 Gd^{III} spins S = 7/2, and is calculated as: $\sum nR\ln(2S+1)$ = 10.4 and 6.2 R, which correspond to 35.8 and 26.2 J $kg^{-1}\ K^{-1}$ for **1** and **3** respectively. The differences between the theoretical and observed values can be attributed to the anisotropic nature of Co^{II} ions and/or presence of antiferromagnetic interactions between the paramagnetic metal centres. Corresponding volumetric entropy changes are 34.5 and 28.6 mJ $cm^{-3}\ K^{-1}$ for **1** and **3** respectively.

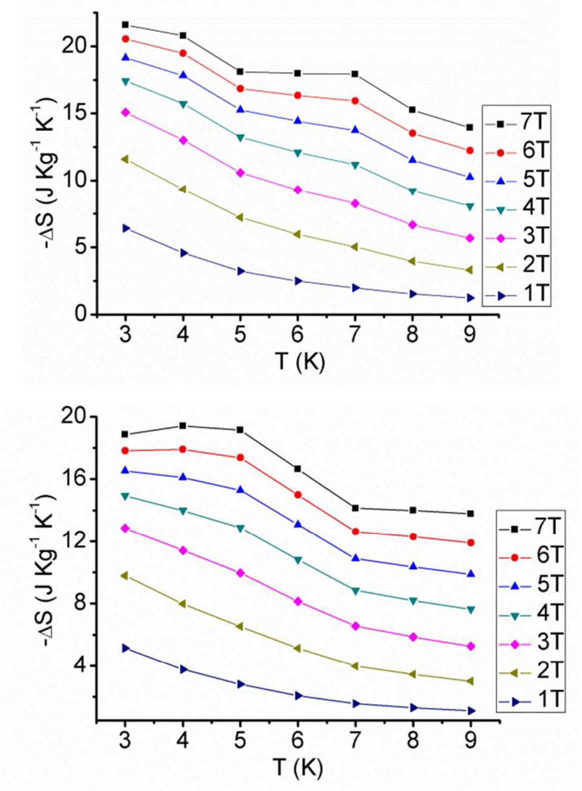


Fig. 4 Temperature dependencies (3 to 10 K) of magnetic entropy change (-ΔS_m) for complexes **1** (top) and **3** (bottom) as obtained from magnetization data.

The M/Nμ_B vs H plots for **2** and **4** (Fig’s S8 and S9) show sharp increase with increasing field at low temperature and fields followed by linear increase at higher fields without any saturation even at the highest experimental field of 7 T. M/Nμ_B versus H/*T* plots of complexes **2** and **4** (Fig’s S10 and S11) show that all isotherm magnetization curves do not collapse on the same master curve, indicating significant anisotropic nature of the Co^{II} and Dy^{III} ions.

AC measurements for **2** and **4** were performed at the temperature of 1.8-10 K in the frequency range of 1-800 Hz at 3.5 Oe ac field and zero dc field to examine the SMM behaviours. The in-phase susceptibility (χ') for **2** does not display any temperature or frequency dependency (Fig’s 5 (top) and S12). However, the out-of-phase susceptibility shows both temperature and frequency dependent ac signals below 10 K (Fig’s 5 (bottom) and S13), indicating the slow relaxation of magnetisation characteristic of SMMs. Both in-phase (χ') and out-of-phase (χ'') ac susceptibility measurements for **4** in a zero DC applied field showed temperature and frequency dependent ac signals below 5 K (Fig’s S14-S116). However, no full peaks were observed for both complexes (**2** and **4**) under zero DC field, which can be attributed mainly to quantum tunnelling of the magnetisation (QTM), often occurring in lanthanide SMMs.[21]

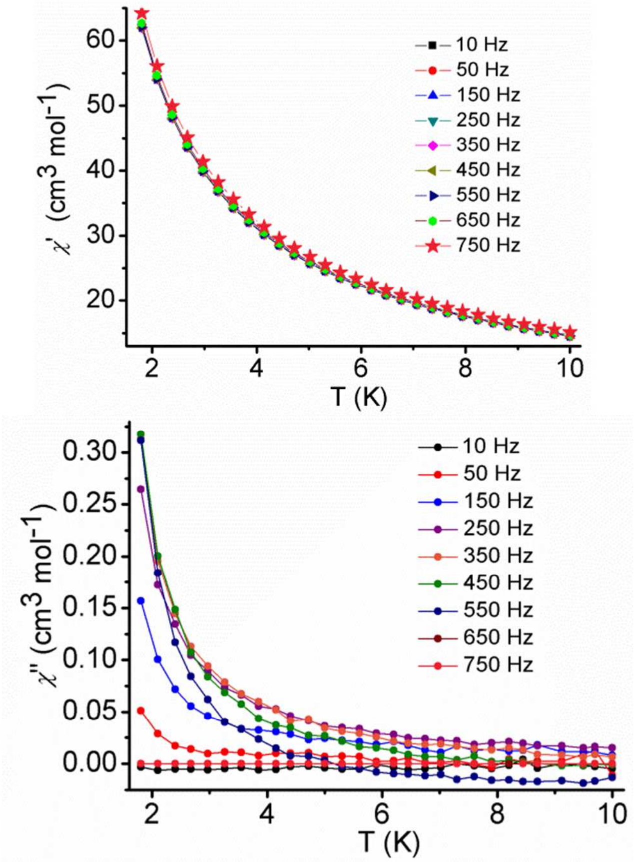


Fig. 5. Temperature dependence of the in-phase (χ', top) and out-of-phase (χ'', bottom) ac susceptibility for complex **2** under zero dc field.

In order to minimise the quantum tunnelling we re-measured the data in presence of an optimum static DC field of 2000 Oe. Peak maxima were observed for **4** under this field below 5 K in the out-of-phase (χ'') vs T plot (Fig. 6 (bottom)) confirming SMM behaviour. Such behaviour is often referred to as field induced SMM behaviour.[12] Frequency dependent in-phase (χ') and out-of-phase (χ'') susceptibility plots also confirmed this behaviour (Fig. 7). However, no change was observed in the ac signals of **2** even in the presence of static dc field of 4000 Oe. Thus, it can be said that small energy barrier and not QTM is responsible for the absence of a maxima in **2**.

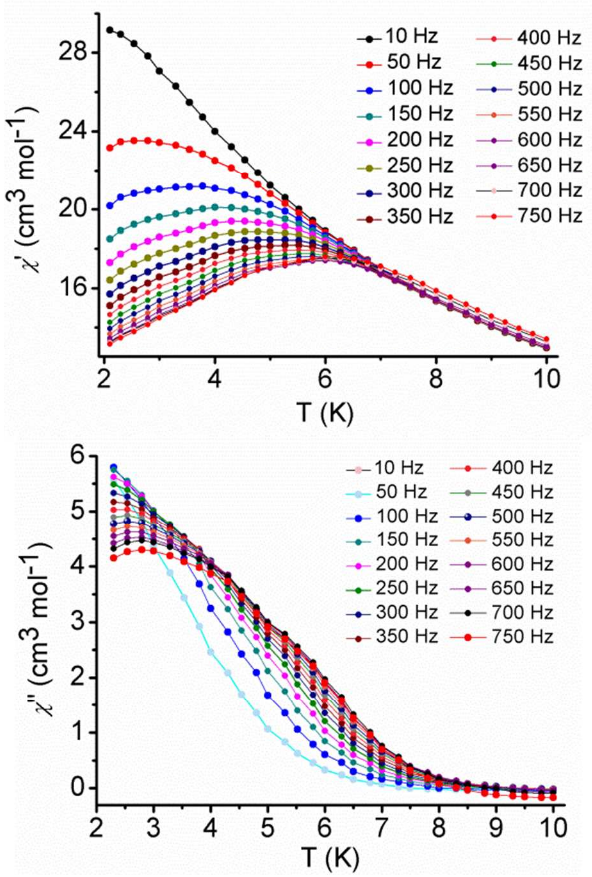


Fig. 6 Temperature dependence of the in-phase (χ', top) out-of-phase (χ'', bottom) ac susceptibility for complex **4** under 2000 Oe dc field.

In order to derive the effective energy barrier value (U_{eff}) and relaxation time (τ_0) from the out-of-phase ac susceptibility data fitting to the Arrhenius equation (eqn. 2)[22] is generally done but this requires the presence of maxima in χ'' vs *T* plot:

$\ln(1/\tau) = \ln(1/\tau_0) - U_{eff}/kT$ .... (2)

where, k is the Boltzmann constant and $1/\tau_0$ is the pre-exponential factor. However, like some reported Dy-based complexes, the out-of-phase signals do not give the peaks of **2** in the measured temperature range.[12] Thus, the energy barrier of the system cannot be obtained by Arrhenius formula fitting. Hence to roughly estimate the energy barrier and relaxation time, another method [23], assuming single relaxation process of the Debye model and equation (eqn. 3) was used:

$\ln(\chi''/\chi') = \ln(\omega\tau_0) + U_{eff}/kT$ ......(3)

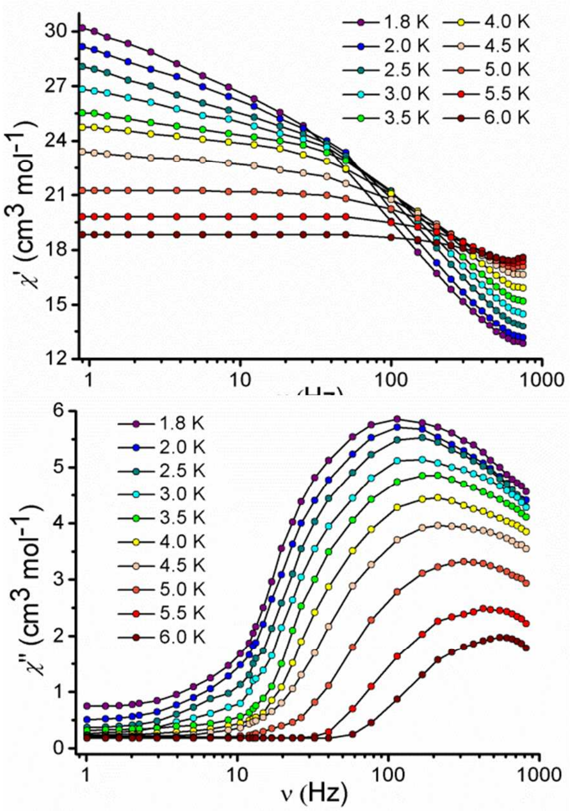


Fig. 7 Frequency dependency of the in-phase, χ' (top) and out of phase, χ'' (bottom) ac susceptibility for complex **4** under 2000 Oe dc field.

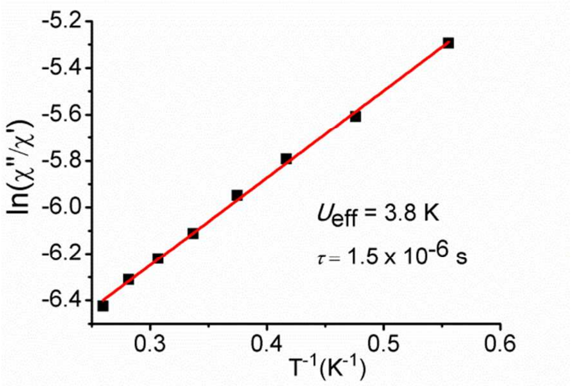


Fig. 8 Natural logarithm of the ratio of χ"over χ' *vs.*1/*T* plot for complex **2**. The red line is the best fit of the Debye equation.

The best fitting results give the energy barrier $U_{eff} \approx 3.8$ K and the relaxation time $\tau_0 \approx 1.5\times10^{-6}$ s for complex **2** (Fig. 8). For complex **4**, the magnetic relaxation time (τ_0) from frequency dependencies of the ac susceptibility (Fig. 9) has been estimated between 1.8-10 K, affording U_{eff} = 17.4 K and $\tau_0 = 2.5\times10^{-6}$ s based on equation 2. Thus, for both the Dy complexes the relaxation time values are consistent with the expected value of $10^{-6} - 10^{-11}$ for a SMM.[12] The plot of χ'' vs χ' known as the Cole-Cole or Argand plot is shown in the inset of fig. 9 as an evidence of the relaxation process occurring in the complex **4**.

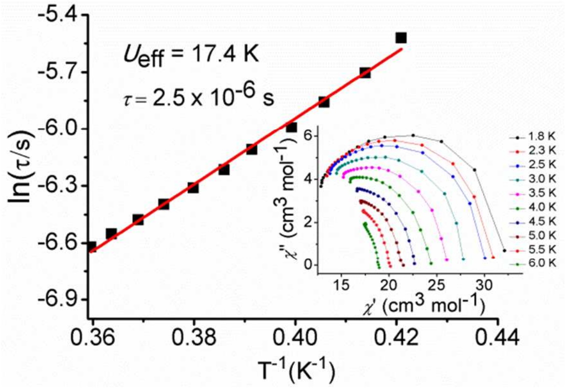


Fig. 9 ln (1/τ) *vs.* 1/*T* plot for complex **4**. The red line is the best fit of the Arrhenius relationship.

Conclusion

Employing heterometallic synthetic strategy, we successfully isolated two series of heterometallic aggregates incorporating highly isotropic (Gd^{III}) as well as highly anisotropic (Dy^{III}) lanthanide ions. The Gd analogues display significant magnetocaloric effect and the Dy containing complexes show single molecular magnet (SMM) behaviour. This synthetic approach represents a promising route towards the design of new heterometallic cages and novel magnetic materials. It also signifies the inherent properties of Ln ions (such as Gd^{III}, Dy^{III}) in combination with 3d metals that makes them potential candidates for magnetic refrigeration and SMM behaviour.

Experimental Section

X-ray Crystallography

Data collection of the compounds were performed at 110 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[24] and the absorption correction program SADABS[25] 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)[26] with atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The structures of complexes **1-3** contain solvent accessible voids, hence SQUEEZE[27] module of the program suite PLATON[28] was used to generate a fresh reflection file. For compounds **1** and **2**, the cobalt centre (Co3) was found to be disordered over two sites and hence was modelled splitting its occupancy into two parts. Because of several disorders, some atoms remain as ADP. To suppress it, we have used few EADP commands to restrain the thermal ellipsoid and to share between two bonded atoms. Besides command DFIX has been used to fix some C-C bond distances of the disordered t-Butyl group of pivalate ligands and N-C bond of ethanolamine group. X-ray crystallographic data in CIF format is available in CCDC numbers 991802 – 991805. The crystallographic data are also summarized in Table 1.

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. The measured values were corrected for the experimentally measured contribution of the sample holder, while the derived susceptibilities were corrected for the diamagnetism of the samples, estimated from Pascal's tables.[29] 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 and data for thermogravimetric analysis (TGA) was collected on a PerkinElmer TGA 4000..

Synthesis

$[Co_5Gd_3(\mu_3\text{-}OH)_5(O_2C^tBu)_{12}(L)_2]\cdot 2H_2O$ (1)

$[Co_2(\mu\text{-}OH_2)(O_2C^tBu)_4]\cdot(HO_2C^tBu)_4$, **$Co_2$** (100mg, 0.1mmol) was dissolved in CH_3CN (8mL) and n-N-butyldiethanolamine, H_2L (24mg, 0.15mmol) was added to the solution while stirring followed by the addition of $Gd(NO_3)_3.6H_2O$ (45mg, 0.1mmol) and final mixture was further stirred for ~12 hrs at room temperature. The solution was filtered and the filtrate was kept at 4^0C for slow evaporation. Within 3-4 days purple block shaped single crystals suitable for X-ray analysis were formed. The crystals were collected by filtration, washed with cold CH_3CN and dried in air. Yield, 47% based on **Co_2.** Elemental analysis: Calcd.(found) for $C_{76}H_{151}Co_5Gd_3N_2O_{35}$: C, 37.73(37.74); H, 6.29(5.84); N, 1.16(1.29). Selected IR data (KBr pellet): 3424.6 (b), 2962.6 (s), 1584.7 (b), 1484.3 (s), 1406.6 (m), 1374.3(w), 1227.6 (s), 1107.5 (w), 897.5 (w), 594.5 (b) cm^{-1}.

$[Co_5Dy_3(\mu_3\text{-}OH)_5(O_2C^tBu)_{12}(L)_2]\cdot 2H_2O$ (2)

The same procedure as that of **1** was used for the synthesis of this compound except that $Dy(NO_3)_3.6H_2O$ (45mg, 0.1mmol) was added after the addition of H_2L. Yield, 47% based on **Co_2.** Elemental analysis: Calcd.(found) for $C_{76}H_{151}Co_5Dy_3N_2O_{35}$: C, 37.48(37.57); H, 6.25(5.78); N, 1.15(1.09). Selected IR data (KBr pellet): 3416.4 (b), 2960.4 (m), 1562.3 (w), 1483.7 (s), 1408.8 (s), 1373 (m), 1227.5 (s), 1102.4 (w), 924.9 (m), 538 (b) cm^{-1}.

$[Co_3Gd_3(\mu_3\text{-}OH)_4 (O_2C^tBu)_6 (L)_3] (NO_3)_2\cdot 2CH_3CN\cdot 2H_2O$ (3)

This compound was synthesised in a manner similar to **1** except H_2L was scaled to double (48mg, 0.3mmol). Yield, 47% based on **Co_2.** Elemental analysis: Calcd.(found) for $C_{58}H_{125}Co_3Gd_3N_7O_{33}$: C, 33.22(32.93); H, 6.01(5.41); N, 4.68(3.39). Selected IR data (KBr pellet): 3453.5 (b), 2963.1 (s), 2073.6 (b), 1560.7 (m), 1484.7 (s), 1418.3 (m), 1375.3 (w), 1227.6 (s), 1065.4 (4), 901.9 (w), 592.1 (b) cm^{-1}.

$[Co_3Dy_3(\mu_3\text{-}OH)_4 (O_2C^tBu)_6 (L)_3](NO_3)_2\cdot 2CH_3CN\cdot 2H_2O$ (4)

The same procedure as that of **1** was used for the synthesis of this compound except that $Dy(NO_3)_3.6H_2O$ (45mg, 0.1mmol) was added and H_2L was scaled to double (48mg, 0.3mmol).. Yield, 47% based on **Co_2.** Elemental analysis: Calcd.(found) for $C_{58}H_{125}Co_3Dy_3N_7O_{33}$: C, 32.97(32.88); H, 5.96(5.39); N, 4.64(3.31). Selected IR data (KBr pellet): 3438.7 (b), 2961.7 (s), 2075.2 (b), 1560.3 (w), 1484 (s), 1410.5 (m), 1227.9 (s), 1103.5 (m), 923.9 (w), 558.7 (b) cm^{-1}.

Dedication

[#]Dedicated to Professor Francesc Lloret on the occasion of his 60th birthday

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Notes

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† Electronic supplementary information (ESI) available: Figures illustrating the molecular structure of **2** and **4**, BVS table,magnetic plots, are provided. See DOI: 10.1039/b000000x.

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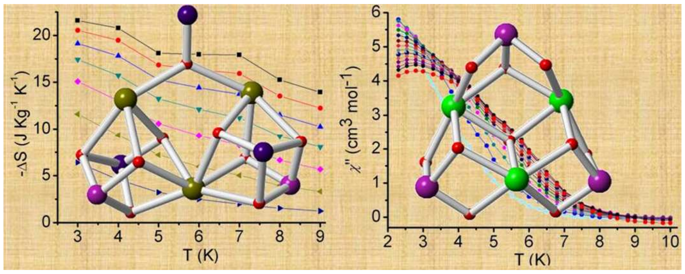

Two types of 3d-4f cages are reported where the Gd analogues show significant magnetic refrigeration and the Dy containing compounds display SMM behaviours.