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Magnetic and magnetocaloric properties of an unusual family of carbonate-panelled [Ln$^\text{III}$$_6$Zn$^\text{II}$$_2$] cages

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The reaction of the pro-ligand H$_2$L, which combines the complementary phenolic oxime and diethanolamine moieties within the same organic framework, with Zn(NO$_3$)$_2$·6H$_2$O and Ln(NO$_3$)$_2$·6H$_2$O in a basic methanolic solution generates a family of isostructural heterometallic coordination compounds of general formula [Ln$_6$Zn$_2$(CO$_3$)$_3$(OH)$_2$(H$_2$L)$_3$(H$_2$L)$_3$]NO$_3$·xMeOH [Ln = Gd, x = 30 (1), Ln = Dy, x = 32 (2), Ln = Sm, x = 31 (3), Ln = Eu, x = 29 (4), Ln = Tb, x = 30 (5)]. The octametallic skeleton of the cage describes a heavily distorted [Gd$_{2}$] octahedron capped on two faces by Zn$^{II}$ ions. The metal core is stabilised by a series of µ$_3$- and µ$_2$-CO$_3$$^2$ ions, originating from the serendipitous fixation of atmospheric CO$_2$. The magnetic properties of all family members were examined via SQUID magnetometry, with the $X_{2/1}T$ product and VTVB data of the Gd analogue (I) being independently fitted by numerical diagonalisation to afford the same best-fit parameter $J_{\text{Gd-Gd}}$ = -0.004 cm$^{-1}$. The MCE of complex I was elucidated from specific heat data, with the magnetic entropy change reaching a value of 22.6 J kg$^{-1}$ K$^{-1}$ at $T$ = 1.7 K, close to the maximum entropy value per mole expected from six Gd$^{III}$ spins ($S_{\text{Gd}} = 7/2$), 23.7 J kg$^{-1}$ K$^{-1}$.

Introduction

The large value of their total angular momentum, their often strong magnetic anisotropy and the inherently weak magnetic exchange mediated via their contracted f-orbitals engender Ln-based molecular cages with some fascinating and potentially useful low temperature physics.$^{1,5}$ In academia these have been much exploited for the construction of Single-Molecule Magnets (SMMs)$^6$ and Molecular Coolers.$^7$ The prospect of employing molecular cages in low temperature cooling applications is based upon the compounds magneto-caloric effect (MCE), as derived from the change in magnetic entropy upon application of a magnetic field.$^{8}$ The design of such molecular materials therefore requires the control and optimisation of quantum properties at the molecular level (spin ground state, magnetic anisotropy, the presence of low-lying excited spin states), which in turn requires the synthetic chemist to follow a particular recipe that includes high spin, anisotropic metal ions and lightweight organic bridging ligands.$^9$

When a magnetic field is applied to a polynuclear molecular magnetic material in which the magnetic exchange interaction between constitutive metal centres and the local magnetic anisotropies are small, the magnetic moments of the constitutive paramagnetic centres become polarised by the magnetic field. When this magnetisation process is performed at constant temperature, the total magnetic entropy of the material is reduced.

In a subsequent adiabatic demagnetisation process, the temperature of the material decreases, thereby cooling the material.$^{10}$ This is a particularly attractive, and potentially technologically important phenomenon, since recent studies have shown that the MCE of some molecular clusters can be much larger than that found in the best intermetallic and lanthanide alloys, and magnetic nanoparticles employed commercially.$^{11-12}$ The obvious metal ion of choice is Gd$^{III}$ since it possesses an isotropic $S = 7/2$, and its clusters will exhibit weak magnetic exchange courtesy of the contracted f-orbitals, resulting in the presence of field-accessible, low-lying excited states. Indeed the vast majority of clusters reported recently to display an enhanced MCE have contained multiple Gd$^{III}$ centres.$^{13-15}$ We continue this trend by reporting the syntheses, structures, magnetic and magnetocaloric properties of a rather unusual set of complexes of general formula [Ln$_6$Zn$_2$(CO$_3$)$_3$(OH)$_2$(H$_2$L)$_3$(H$_2$L)$_3$]NO$_3$·xMeOH [Ln = Gd, x = 30 (1), Ln = Dy, x = 32 (2), Ln = Sm, x = 31 (3), Ln = Eu, x = 29 (4), Ln = Tb, x = 30 (5)] built with the ligand (Z)-1-(3-((bis(2-hydroxyethyl)amino)methyl)-2-hydroxy-5-methylphenyl)ethan-1-one oxime), [H$_2$L], shown in Scheme 1.
We have previously shown that this ligand is highly effective in forming transition metal cages with aesthetically pleasing structures and fascinating magnetic properties, and we now extend its coordination chemistry to the 4f elements.  

5 Experimental  

Materials and physical measurements  

All manipulations were performed under aerobic conditions, using materials as received (reagent grade). (Z)-1-(3-((bis(2-hydroxyethyl)amino)methyl)-2-hydroxy-5-methylphenyl)ethan-1-one oxime) [H4L] was synthesised as described in the literature. Magnetisation data were acquired on a MPMS-XL SQUID magnetometer equipped with a 5 T dc magnet. Freshly isolated crystalline material was covered immediately with hexadecane (MPT = 18 °C) in order to suppress loss of co-crystallized solvent. Dc susceptibility data were obtained with He cryostat. The experiments were performed on thin pressed pellets (ca. 1 mg) of a polycrystalline sample, thermalised by ca. 0.2 mg of Apiezon N grease, whose contribution was subtracted using a phenomenological expression.  

Syntheses  

General synthetic procedure for complexes 1-3: Ln(NO3)3·xH2O (0.25 mmol), Zn(NO3)2·6H2O (75 mg, 0.25 mmol), H4L (140 mg, 0.5 mmol), BuONa (100 mg, 1 mmol) and Et3N (300 µL, 2.15 mmol) were stirred in 25 ml MeOH for 2 hours. The solution was then filtered and allowed to stand. X-ray quality crystals formed via slow evaporation of the mother liquor over a period of 5 days in ~30-40 % yield. Complex 4 was made in the same manner, but using 0.5 mmol (100mg) t-BuONa, whilst no t-BuONa was added to the reaction mixture to make 5. Elemental analyses, calculated (found): 1: C 36.18 (36.24), H 4.27 (4.61), N 6.09 (5.81). 2: C 35.85 (34.97), H 4.24 (4.52), N 6.22 (5.92). 3: C 36.62 (35.40), H 4.31 (4.38), N 6.19 (5.95). 4: C 36.52 (35.36), H 4.31 (4.38), N 6.20 (5.73). 5: C 36.07 (34.91), H 4.26 (4.42), N 6.13 (5.95).  

X-ray crystallography  

Diffraction data were collected on a Bruker Smart Apex CCD diffractometer equipped with an Oxford Cryosystems LT device, using Mo radiation. Data collection parameters and structure solution and refinement details are listed in Table S1. Full details can be found in the CIF files provided in the supporting information and CCDC 1055091-1055095.  

Results and Discussion  

Compounds 1-5 are isostructural, and so for the sake of brevity we limit discussion to complex 1. [GdIII(ZnII(CO3)3(OH)3(H4L)3](H4L)2(H2L)2(NO3)30MeOH (Figure 1). The metallic skeleton of the cage describes a highly distorted [GdIII] octahedron with the two ZnII ions each capping a triangular face. The core of the molecule is stabilised by the presence of five CO32- ions, originating from the serendipitous fixation of atmospheric CO2. These exhibit several different bonding modes [µ1-GdII, µ2-GdII-Zn, µ2-GdII, µ1-GdII, µ1-GdII-Zn] as shown in Figure 1B. There is a single ‘OH ion which µ-bridges between Gd4 and Gd6 (Gd-O-Gd, 112°) and four H2L2-, two H4L- and one H2L ligands that adorn the outer periphery of the molecule. These molecules of crystallisation are omitted for clarity.
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bipyramidal geometries. HMbonding to the alkoxide OMatom on a neighbouring ligand with its oximic OM and NMatoms remaining nonMcoordinating, and

There are several close intermolecular contacts. Th e coordinative flexibility of the CO moiety and the MCH interactions (C…C, 3.58 Å). The result is the forma tion of a rings of the organic ligands are involved in π…π st acking on the Ph rings of the organic ligand and between t he same Zn…Zn, 4.14 Å), and at the opposite end of the mole cule the Ph equivalent group on their nearest neighbour (O…O, 2.46 Å; Gd octahedron, or between a Gd vertex and a Zn cap. One ligand (H2L) chelates Gd5 through its phenolic and alkoxide O-atoms, with its oximic O- and N-atoms remaining non-coordinating, and H-bonding to the alkoxide O-atom on a neighbouring ligand (O…O, ~2.6 Å). Indeed all of the organic ligands are involved in extensive intramolecular H-bonding interactions with their neighbouring ligands and to the MeOH molecules of crystallisation (Figure S2–3). All of the Gd ions are nine coordinate [GdO8N] and in capped square antiprismatic geometries, with the exception of Gd6 which is eight coordinate {GdO8N} and in distorted trigonal bipyramidal geometries.

There are several close intermolecular contacts. The diethanolamine O-atoms coordinated to Zn2 are HMbonding to the diethanolamine unit approximately ~25% are 4f complexes and ~5% are heterometallic 3d-4f complexes.20 While the majority have been formed serendipitously, this observation has led some researchers to deliberately employ Na2CO3, NaHCO3 and CO2 as reaction ingredients.21 The CSD search also highlights the extraordinary coordinate flexibility of the CO2− ion demonstrating bridging modes ranging from bidentate to nonadentate - with the majority (65%) being tridentate and forming M3 triangles, a topology of inherent interest to the magnetochemist.22

Magnetic properties

The d.c molar magnetic susceptibility, χM, of polycrystalline samples of complexes 1 - 5 were measured in an applied magnetic field, B, of 0.1 T, over the 2-280 K temperature, T, range. The experimental results are shown in Figure 3 in the form of χMT products, where χ = M / B, and M is the magnetisation of the sample. At room temperature, the χMT product of 1 - 5 have values of 47.2, 84.1, 0.3, 8.9 and 71.3 cm3 K mol−1, respectively. These are in good agreement with the sum of Curie constants for a [GdIII6] unit (47.3 cm3 K mol−1, gGd = 2.0) for 1, a [DyIII4] unit (85.0 cm3 K mol−1, gDy = 4/3) for 2, a [SmIII6] unit (0.5 cm3 K mol−1, gSm = 2/7) for 3, and a [TbIII6] unit (70.9 cm3 K mol−1, gTb = 3/2) for 5. In the case of 4, although the F2g ground state of EuIII possesses no magnetic moment and thus, the [EuIII6] unit should be diamagnetic at low temperatures, a finite magnetic moment is observed at room temperature, due to the low-lying F1 first excited state that is partly populated at room temperature. Upon cooling, the χMT product of 1 remains essentially constant down to approximately 20 K, wherefrom it begins to decrease upon further cooling to reach 42.3 cm3 K mol−1 at 2 K. Given that the anisotropy of Gd III is negligible, this behaviour is consistent with the presence of weak intramolecular antiferromagnetic exchange interactions. The χMT product of 2 and 5 decreases continuously upon cooling, reaching 64.3 and 53.5 cm3 K mol−1, respectively, at 2 K. This behaviour can be ascribed to the large magnetic anisotropy of DyIII and Tb III and potentially to the presence of weak intramolecular magnetic exchange interactions. The χMT product of 3, remains essentially constant in the investigated temperature range, at the low, but finite, value of 0.3 cm3 K mol−1, a consequence of the low Landé g-factor of the ground 4H1/2 term, indicating a splitting between the ground and first excited Kramers doublets of the 4H1/2 term larger than the thermal energy at 280 K. Finally, the χMT product of 4 decreases continuously upon cooling and reaches virtually zero at 2 K, reflecting the thermal depopulation of the F1 first excited state upon cooling, likely indicating mixing of the F2g ground state with excited states possessing a magnetic moment. To better define the low-temperature magnetic properties of complexes 1 - 5, low temperature variable-temperature-and- variable-field (VTVB) magnetisation data were measured in the temperature and magnetic field ranges 2 to 12 K and 0 to 5 T for 1 and 2 to 8 K and 0 to 5 T for the remaining complexes. The VTVB magnetisation data of 1 are shown in Figure 3. At the highest investigated field (5 T) and the lowest investigated temperature (2 K), the magnetisation of 1 is of 42.1 μB (μB is the Bohr magneton), thus, 7.0 μB per GdIII and in good agreement with the expected (7.0 μB, for gGd = 2.0). This observation is consistent with the presence of very weak exchange interactions operating in 1. Furthermore, when the VTVB data of 1 are plotted against the reduced quantity μB/ kT (Figure S4), no nesting of the VTVB data is observed. This observation indicates that the energy spectrum of 1 does not present significant splitting with respect to the temperature of measurement at zero magnetic field.

The VTVB magnetisation data of 2 to 5 are shown in Figures S5 - S8, respectively. At the highest investigated field (5 T) and the lowest investigated temperature (2 K), the magnetisation of 2 and 5 is 32.0 and 29.4 μB, respectively, thus 5.3 and 4.9 μB per DyIII and Tb III, respectively. These values are significantly lower than the expected magnetic moment of isolated DyIII (10.0 μB)
and Tb\textsuperscript{III} (9.0 \( \mu_B \)) centres, for which the \( m_J = -15/2 \) projection of the \( ^{1}\text{H}_3/2 \) ground term or the \( m_J = -6 \) projection of the \( ^{7}\text{T}_6 \) ground term, respectively, is the lowest energy state. Furthermore, the VTVB data of 2 (Figure S5) and 5 (Figure S8) present nesting when plotted against \( \mu_B B/kT \). These observations indicate that the energy spectrum of 2 and 5 presents significant splittings with respect to the temperature of measurement, at zero magnetic field.

The VTVB magnetisation data of 3 (Figure S6) present no nesting when plotted against the reduced quantity \( \mu_B B / kT \) and are also linear with magnetic field. This behaviour is consistent with the presence of a thermally isolated Kramers doublet as the ground state of the \( ^{1}\text{H}_3/2 \) ground term, in agreement with the analysis of the temperature dependence of the \( \chi_M T \) product. Finally, the VTVB magnetisation data of 4 (Figure S7) responds in a linear fashion with magnetic field and constant temperature, and are temperature independent at a constant field. This behaviour indicates a field-induced mixing of the \( ^{7}\text{T}_6 \) ground state with excited states possessing a magnetic moment, consistent with the analysis of the temperature dependence of the \( \chi_M T \) product.

The hexanuclear nature of complexes 2 - 5, combined with the low symmetry of the local coordination sphere of the Ln\textsuperscript{III} centres and the ensuing large number (twenty-seven) of associated ligand field parameters per Ln\textsuperscript{III} ion, precludes any quantitative interpretation of the magnetic properties of these complexes. However, in the case of 1, given that the orbital angular momentum for Gd\textsuperscript{III} is quenched, a quantitative analysis is possible through the use of a spin-Hamiltonian parameterisation. Thus, we employed the general form of the isotropic spin-Hamiltonian (1)

\[
\hat{H} = \mu_B B \sum_i g_S \hat{S}_i - 2 \sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j \quad (1)
\]

where the summation indexes \( i, j \) run through the constitutive Gd\textsuperscript{III} centres, \( \hat{S} \) is a spin operator and \( J \) is the isotropic exchange interaction parameter. In our spin-Hamiltonian model we include the following isotropic exchange parameters: \( J_{12}, J_{13}, J_{14}, J_{15}, J_{23}, J_{24}, J_{25}, J_{26}, J_{34}, J_{35}, J_{36} \) (Figure 3, top, inset) and set them all equal to \( J_{\text{Gd-Gd}} = 2.0 \). Thus our model contains only one free parameter, namely, \( J_{\text{Gd-Gd}} \). The \( \chi_M T \) product and VTVB data of 1 were independently fitted to spin-Hamiltonian (1) by numerical diagonalization and by use of the Levenberg-Marquardt algorithm.\textsuperscript{23} Both fits result in the same best-fit parameter: \( J_{\text{Gd-Gd}} = -0.004 \text{ cm}^{-1} \). The best-fit curves are shown as solid lines in Figure 3.

Next, we report the specific heat (\( C \)) data collected for a polycrystalline sample of 1, in the temperature range 0.3 to 30 K and in applied magnetic fields, \( B, \) of 0, 1, 3 and 7 T (Figure 4). At the higher temperatures, the specific heat is dominated by a nonmagnetic contribution arising from thermal vibrations of the lattice, which can be modelled by the Debye-Einstein model (dotted line).\textsuperscript{5} The phonon specific heat simplifies to a \( C/R = a T^3 \) dependence at the lowest temperatures, where \( R \) is the gas constant and \( a = 1.1 \times 10^{-2} \text{ K}^{-3} \). For \( B \geq 1 \text{ T} \), we model the field-dependent specific heat as the sum of the Schottky curves arising from the field-split levels of Gd\textsuperscript{III} independent spins (solid lines).

Note the overall nice agreement with the experimental data, suggesting that applied fields of \( B \geq 1 \text{ T} \) are nearly sufficient for fully decoupling the spin centres. The zero-applied-field specific heat can be described by the Schottky curve depicted in Figure 4 as a dashed line. This curve is calculated by assuming that every spin centre is experiencing an effective field \( B_{\text{eff}} = 0.25 \text{ T} \), as the result of the magnetic interactions involved. By making use of the specific heat data, we calculate the entropy (5) according to the expression \( S/R = 1/CdT \), which we plot in Figure S10 as a function of temperature and for the corresponding applied field values. The final step in the evaluation of the MCE of 1 consists in obtaining the magnetic entropy change \( -\Delta S_m(T) \), for selected applied field changes \( \Delta B \). The result is shown in Figure 4. This calculation is straightforwardly obtained from the \( S(T) \) curves in Figure S10 and also from the magnetisation data in Figure 3 by employing the Maxwell relation, \( \Delta S_m = \mu M/\alpha_{\text{Curie}} \Delta B \). As can be seen in Figure 4, the nice agreement between the results obtained via both methods is validation of the approaches employed. For the largest applied field change (\( \Delta B = 7 \text{ T} \)), the magnetic entropy change, \( -\Delta S_m \) reaches 22.6 J kg\(^{-1}\) K\(^{-1}\) at \( T = 1.7 \text{ K} \). Because of the very weak strength of the magnetic exchange interactions, this value of \( -\Delta S_m \) is close to the maximum entropy value per mole involved, corresponding to six Gd\textsuperscript{III} spins (\( S_{\text{Gd}} = 7/2 \)), calculated as \( 6\ln(2) S_{\text{Gd}} + 1 = 103.7 \text{ J mol}^{-1}\text{ K}^{-1} \), that is, 23.7 J kg\(^{-1}\) K\(^{-1}\). Thus, in 1, nearly the full magnetocaloric potential of Gd\textsuperscript{III} is...
produce dodecametallic wheels and truncated tetrahedra.

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Notes and references

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