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Magnetic and magnetocaloric properties of an unusual family of carbonate-panelled \([\text{Ln}_{6}^{\text{III}}\text{Zn}_{2}^{\text{II}}]\) cages

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

The reaction of the pro-ligand \(\text{H}_2\text{L}\), which combines the complementary phenolic oxime and diethanolamine moieties within the same organic framework, with \(\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}\) and \(\text{Ln(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O}\) in a basic methanolic solution generates a family of isostructural heterometallic coordination compounds of general formula \([\text{Ln}_{6}(\text{CO}_3)_5\text{(OH)}(\text{H}_2\text{L})_4(\text{H}_2\text{L})_2(\text{H}_2\text{L})_2]\text{NO}_3 \cdot x\text{MeOH}\) \([\text{Ln} = \text{Gd}, x = 30 (1), \text{Ln} = \text{Dy}, x = 32 (2), \text{Ln} = \text{Sm}, x = 31 (3), \text{Ln} = \text{Eu}, x = 29 (4), \text{Ln} = \text{Tb}, x = 30 (5)]\). The octametallic skeleton of the cage describes a heavily distorted \([\text{Gd}_{11}^{\text{III}}]\) octahedron capped on two faces by \(\text{Zn}_{12}^{\text{II}}\) ions. The metal core is stabilised by a series of \(\mu_7\)- and \(\mu_5\)-\(\text{CO}_3\)\(^{2-}\) ions, originating from the serendipitous fixation of atmospheric \(\text{CO}_2\). The magnetic properties of all family members were examined via SQUID magnetometry, with the \(2mT\) product and VTVB data of the Gd analogue (1) being independently fitted by numerical diagonalisation to afford the same best-fit parameter \(J_{\text{Gd-Gd}} = -0.004 \text{ cm}^{-1}\). The MCE of complex 1 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\(^{\text{III}}\) 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.\(^{15}\) 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 centers 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\(^{\text{III}}\) 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\(^{\text{III}}\) centres.\(^{13-18}\) We continue this trend by reporting the syntheses, structures, magnetic and magnetocaloric properties of a rather unusual set of complexes of general formula \([\text{Ln}_{6}(\text{CO}_3)_5\text{(OH)}(\text{H}_2\text{L})_4(\text{H}_2\text{L})_2(\text{H}_2\text{L})_2]\text{NO}_3 \cdot x\text{MeOH}\) \([\text{Ln} = \text{Gd}, x = 30 (1), \text{Ln} = \text{Dy}, x = 32 (2), \text{Ln} = \text{Sm}, x = 31 (3), \text{Ln} = \text{Eu}, x = 29 (4), \text{Ln} = \text{Tb}, x = 30 (5)]\) built with the ligand \((Z)-1-(3-(\text{bis}(2\text{-hydroxyethyl})\text{amino})\text{methyl}-2\text{-hydroxy-5-methylphenyl})\text{ethan-1-one oxime}), [\text{H}_2\text{L}],\) 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.\textsuperscript{19}

\section*{Experimental}

\subsection*{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-methylphenylethan-1-one oxime \([\text{H}_2\text{L}]\) was synthesised as described in the literature.\textsuperscript{19}

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-crystallised solvent. Dc susceptibility data were obtained with \(H_{dc} = 1000\) Oe in the temperature range 1.8–280 K and magnetisation data at \(H_{dc} \leq 50\) kOe at selected low temperatures. All data were corrected for diamagnetic contributions from the sample, hexadecane and the capsule by means of Pascals constants. Specific heat measurements were carried out at temperatures down to 0.3 K by using a Quantum Design 9T-PPMS, equipped with a \(^{3}\)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.

\subsection*{Syntheses}

General synthetic procedure for complexes 1-3: \([\text{Ln(NO}_3]_{2}\cdot x\text{H}_2\text{O}\) \((0.25\) mmol), \(\text{Zn(NO}_3]_{2}\cdot 6\text{H}_2\text{O}\) \((75\) mg, 0.25 mmol), \(\text{H}_2\text{L}\) \((140\) mg, 0.5 mmol), \(\text{BuONa}\) \((100\) mg, 1 mmol) and \(\text{Et}_3\text{N}\) \((300\) 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 (100 mg) \(\text{BuONa}\), whilst no \(\text{BuONa}\) was added to the reaction mixture to make 5. Elemental analyses, calculated \((\text{found})\): 1: C 36.18 (36.24), H 4.27 (4.61), N 6.14 (6.19); 2: C 35.85 (34.97), H 4.24 (4.52), N 6.09 (5.81); 3: C 36.62 (35.40), H 4.31 (4.38), N 6.20 (5.73); 4: C 36.07 (34.91), H 4.26 (4.42), N 6.13 (5.95).

\subsection*{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.

\section*{Results and Discussion}

Compounds 1-5 are isostructural, and so for the sake of brevity we limit discussion to complex 1, \([\text{Gd}^{III},\text{Zn}^{II}_{2}(\text{CO}_3)_3](\text{OH})\) \((\text{H}_2\text{L})_2(\text{H}_2\text{L})(\text{H}_2\text{L})\text{NO}_3\cdot 30\text{MeOH}\) (Figure 1). The metallic skeleton of the cage describes a highly distorted \([\text{Gd}^{III}]_{4}\) octahedron with the two \(\text{Zn}^{II}\) ions each capping a triangular face. The core of the molecule is stabilised by the presence of five \(\text{CO}_3^{2-}\) ions, originating from the serendipitous fixation of atmospheric \(\text{CO}_2\). These exhibit several different bonding modes \([\mu_5-\text{Gd}_6, \mu_7-\text{Gd}_2\text{Zn}, \mu_7-\text{Gd}_6, \mu_7-\text{Gd}_6, \mu_7-\text{Gd}_2\text{Zn}]\) as shown in Figure 1B. There is a single \(\mu\)-OH ion which \(\mu\)-bridges between \(\text{Gd}4\) and \(\text{Gd}6\) (\(\text{Gd}-\text{O}-\text{Gd}, 112°\)) and four \(\text{H}_2\text{L}^2-\), two \(\text{H}_2\text{L}^2-\) and one \(\text{H}_2\text{L}\) ligands that adorn the outer periphery of the molecule. These

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{A) The structure of the cation of complex 1. B) The metal core highlighting the role of the bridging carbonate ions. C) The metal skeleton of the cage emphasising the highly distorted Gd octahedron and two face-capping Zn ions. Colour code: Gd = purple, Zn = gold, O = red, N = blue, C = grey. H atoms, the nitrate counter ion and solvent molecules of crystallisation are omitted for clarity.}
\end{figure}
Gd octahedron, or between a Gd vertex and a Zn cap. One ligand (H$_2$L) 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 [GdO$_8$N$_2$] and square antiprismatic; the latter being the only Ln ion that is not chelated by the diethanolamine moieties. The Zn ions are both five coordinate [ZnO$_5$] and in distorted trigonal bipyramidal geometries.

There are several close intermolecular contacts. The diethanolamine O-atoms coordinated to Zn2 are H-bonding to the equivalent group on their nearest neighbour (O...O, 2.46 Å; Zn...Zn, 4.14 Å), and at the opposite end of the molecule the Ph rings of the organic ligands are involved in π...π stacking interactions (C...C, 3.58 Å). The result is the formation of a serpentine-like H-bonded chain of cationic cages (Figure S3). Closest contacts between these chains are through the Me-groups on the Ph rings of the organic ligand and between the same moiety and the -CH$_3$ arms of the diethanolamine unit (Me...CH$_3$/CH$_3$, ~4 Å). This produces a 2D sheets of cations of metal cluster compounds containing carbonate anions.

![Figure 2](Image 65x223 to 297x388)

**Figure 2.** The different bonding modes of the H$_3$L$^+$, H$_4$L$^-$ and H$_6$L$^-$ ligands highlighting the diverse levels of protonation.

The d.c molar magnetic susceptibility, $\chi_M$, 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 $\chi_M T$ products, where $\chi = M / B$, and $M$ is the magnetisation of the sample. At room temperature, the $\chi_M T$ product of 1 - 5 have values of 47.2, 84.1, 0.3, 8.9 and 71.3 cm$^3$K mol$^{-1}$, respectively. These are in good agreement with the sum of Curie constants for a [Gd$^{III}$] unit (47.3 cm$^3$K mol$^{-1}$, $g_{\text{Gd}} = 2.0$) for 1, a [Dy$^{III}$] unit (85.0 cm$^3$K mol$^{-1}$, $g_{\text{Dy}} = 4/3$) for 2, a [Sm$^{III}$] unit (0.5 cm$^3$K mol$^{-1}$, $g_{\text{Sm}} = 2/7$) for 3, and a [Tb$^{III}$] unit (70.9 cm$^3$K mol$^{-1}$, $g_{\text{Tb}} = 3/2$) for 5. In the case of 4, although the $F_2g$ ground state of Eu$^{III}$ possesses no magnetic moment and thus, the [Eu$^{III}$] unit should be diamagnetic at low temperatures, a finite magnetic moment is observed at room temperature, due to the low-lying $F_1$ first excited state that is partly populated at room temperature. Upon cooling, the $\chi_M T$ product of 1 remains essentially constant down to approximately 20 K, wherefrom it begins to decrease upon further cooling to reach 42.3 cm$^3$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 $\chi_M T$ product of 2 and 5 decreases continuously upon cooling, reaching 64.3 and 53.5 cm$^3$K mol$^{-1}$, respectively, at 2 K. This behaviour can be ascribed to the large magnetic anisotropy of Dy$^{III}$ and Tb$^{III}$ and potentially to the presence of weak intramolecular magnetic exchange interactions. The $\chi_M T$ product of 3, remains essentially constant in the investigated temperature range, at the low, but finite, value of 0.3 cm$^3$K mol$^{-1}$, a consequence of the low Landé $g$-factor of the ground $^4H_{15/2}$ term, indicating a splitting between the ground and first excited Kramers doublets of the $^4H_{15/2}$ term larger than the thermal energy at 280 K. Finally, the $\chi_M T$ product of 4 decreases continuously upon cooling and reaches virtually zero at 2 K, reflecting the thermal depopulation of the $F'_1$ first excited state upon cooling, likely indicating mixing of the $F'_2g$ 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 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 $\mu_B$ ($\mu_B$ is the Bohr magneton), thus, 7.0 $\mu_B$ per Gd$^{III}$ and in good agreement with the expected (7.0 $\mu_B$ for $g_{\text{Gd}} = 2.0$). 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 $\mu_B B / kT$ (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 $\mu_B$, respectively, thus 5.3 and 4.9 $\mu_B$ per Dy$^{III}$ and Tb$^{III}$, respectively. These values are significantly lower than the expected magnetic moment of isolated Dy$^{III}$ (10.0 $\mu_B$).
and TbIII (9.0 \( \mu_B \)) centres, for which the \( m_J = -15/2 \) projection of the \(^{4}H_{15/2}\) ground term or the \( m_J = -6 \) projection of the \(^{7}F_6\) 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 \(^{4}H_{15/2}\) ground term, in agreement with the analysis of the temperature dependence of the \( \chi_B T \) 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 \(^{7}F_6\) ground state with excited states possessing a magnetic moment, consistent with the analysis of the temperature dependence of the \( \chi_B T \) product.

Field parameters per LnIII ion, precludes any quantitative interpretation of the magnetic properties of these complexes. However, in the case of 1, given that the orbital angular moment for GdIII 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)

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

where the summation indexes \( i, j \) run through the constitutive GdIII 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: \( J_{12}, J_{13}, J_{15}, J_{16}, J_{23}, J_{24}, J_{25}, J_{26}, J_{34}, J_{35}, J_{36} \) (Figure 3, top, inset) and set them all equal to \( J_{Gd-Gd} = 2.0 \). Thus our model contains only one free parameter, namely, \( J_{Gd-Gd} \). The \( \chi_B T \) product and VTVB data of 1 were independently fitted to spin-Hamiltonian (1) by numerical diagonalization and by use of the Levenberg-Marquardt algorithm. Both fits result in the same best-fit parameter: \( J_{Gd-Gd} = -0.004 \) 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, \( B = 0, 1, 3 \) and 7 T (Figure 4). At the higher temperatures, the specific heat is dominated by nonmagnetic contribution arising from thermal vibrations of the lattice, which can be modelled by the Debye-Einstein model (dotted line).\(^{3}\) The phonon specific heat simplifies to a Schottky curve depending on inverse temperatures (solid line).\(^{3}\) The phonon specific heat simplifies to a Schottky curve depending on inverse temperatures (solid line).

The hexanuclear nature of complexes 2 - 5, combined with the low symmetry of the local coordination sphere of the LnIII centres and the ensuing large number (twenty-seven) of associated ligand

\[\text{Figure 3. (Top) Temperature dependence of the } \chi_B T \text{ product of polycrystalline samples of 1 - 5 with } B = 0.1 \text{ T. The inset shows the magnetic exchange pathways in the GdIII unit. The low-temperature field-dependence of the magnetization of 1.}\]

The hexanuclear nature of complexes 2 - 5, combined with the low symmetry of the local coordination sphere of the LnIII centres and the ensuing large number (twenty-seven) of associated ligand
based on highly distorted bicapped octahedra can be constructed
to produce dodecametallic wheels and truncated tetrahedra.
Magnetic exchange between the Gd
ions in the octahedron is shown to be vanishingly small by independent fits of both
the maximum entropy value per mole expected from six Gd
spins, 23.7 J kg⁻¹ K⁻¹,

Achieved.

Figure 4. (Top) Specific heat vs. T for the labelled applied magnetic fields. Solid and dotted lines are, respectively, the Schottky and lattice contributions, calculated as explained in the text. Dashed line is the Schottky contribution, as obtained for an effective Bₐₐ = 0.25 T. (Bottom) Temperature dependence of the magnetic entropy change for the indicated magnetic field changes. Data are obtained from specific heat (empty markers) and magnetization (full markers) experiments.

Conclusions
A highly unusual family of Ln₆Zn₂ cages whose structures are based on highly distorted bicapped octahedra can be constructed from the simple one-pot self-assembly reaction between the two metal salts and the ligand H₆L in basic methanolic solutions. The ligand has been previously used in Mn coordination chemistry to produce dodecametallic wheels and truncated tetrahedra. Magnetic exchange between the Gd³⁺ ions in the octahedron is shown to be vanishingly small by independent fits of both susceptibility and magnetisation data. The MCE of complex 1 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 Gd³⁺ spins, 23.7 J kg⁻¹ K⁻¹.

Acknowledgements
S.P. thanks the Danish Ministry of Science, Innovation and Higher Education for a Sapere Aude Fellowship (10-081659), M.E. acknowledges financial support from MINECO through grant MAT2012-38318-C03-01. EKB thanks the EPSRC.

Notes and references

