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

Waqas Sethi,*a Sergio Sanz,‡b Kasper S. Pedersen,* Mikkel A. Sørensen,* Gary S. Nichol,† Giulia Lorusso,† Marco Evangelisti,*ac Euan K. Brechin*ab and Stergios Piligkos*ab

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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 \(\text{Zn(NO}_3)_2\cdot6\text{H}_2\text{O}\) and \(\text{Ln(NO}_3)_3\cdot6\text{H}_2\text{O}\) in a basic methanolic solution generates a family of isostructural heterometallic coordination compounds of general formula \([\text{Ln}_{\text{X}}\text{Zn}_{\text{Y}}(\text{CO}_3)_3(\text{OH})(\text{H}_2\text{L})_2(\text{H}_2\text{L})_3\text{NO}_3] x\text{MeOH}\) [\(\text{Ln} = \text{Gd, } x = 30\) (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 \([\text{Gd}^{\text{III}}]_8\) octahedron capped on two faces by \(\text{Zn}^{\text{II}}\) ions. The metal core is stabilised by a series of \(\mu_3\)- and \(\mu_5\)-\(\text{CO}_3^{2-}\) ions, originating from the serendipitous fixation of atmospheric CO\(_2\). The magnetic properties of all family members were examined via SQUID magnetometry, with the \(\chi M^T\) product and VTVB data of the Gd analogue (1) being independently fitted by numerical diagonalisation to afford the same best-fit parameter \(J_{\text{Gd-Gd}} = -0.004\) 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. In academia these have been much exploited for the construction of Single-Molecule Magnets (SMMs) and Molecular Coolers. 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. 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.

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. 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.

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. We continue this trend by reporting the syntheses, structures, magnetic and magnetocaloric properties of a rather unusual set of complexes of general formula \([\text{Ln}_{\text{X}}\text{Zn}_{\text{Y}}(\text{CO}_3)_3(\text{OH})(\text{H}_2\text{L})_2(\text{H}_2\text{L})_3\text{NO}_3] \times \text{MeOH}\) [\(\text{Ln} = \text{Gd, } x = 30\) (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-((bis(2-hydroxyethyl)amino)methyl)-2-hydroxy-5-methylphenyl)ethan-1-one oxime), [\(\text{H}_2\text{L}\)], shown in Scheme 1.

![Scheme 1](image_url)
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). \((Z)-1-(3-((bis(2-hydroxyethyl)amino)methyl)-2-hydroxy-5-methylphenyl)ethan-1-one\) oxime \([H_2L]\) was synthesised as described in the literature.\textsuperscript{19} Magnetical 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 \((\text{MPt} = 18 ^\circ\text{C})\) in order to suppress loss of co-crystallised solvent. Crystalline material was covered immediately with hexadecane.

\subsection*{Syntheses}

General synthetic procedure for complexes \(1-3\): \(\text{Ln(NO}_3\text{)}_3 \cdot x\text{H}_2\text{O (0.25 mmol), Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O (75 mg, 0.25 mmol), H}_2\text{L (140 mg, 0.5 mmol), BuONa (100 mg, 1 mmol) and 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 \((100\text{mg})\) \(\text{BuONa, whilst no 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 6.14 (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 4.33 (4.28), N 6.22 (5.92). 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).}

\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 \(1\). \([\text{Gd}^{III}\text{Zn}^{II}(\text{CO}_3)_3\text{OH}]\)

\([\text{H}_2\text{L}]_2(\text{H}_2\text{L})_2(\text{H}_2\text{L})\text{NO}_3\cdot 30\text{MeOH}\) (Figure 1). The metal core of the cage describes a highly distorted \([\text{Gd}^{III}]\) 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 \([\mu_2-\text{Gd}_2\text{Zn}, \mu_2-\text{Gd}_2\text{Zn}, \mu_2-\text{Gd}_2\text{Zn}, \mu_2-\text{Gd}_2\text{Zn}]\) as shown in Figure 1B. There is a single \(\text{OH}\) ion which \(\mu\)-bridges between \(\text{Gd}_4\) and \(\text{Gd}_6\) \((\text{Gd}(\text{O-Gd}, 112^\circ)\) and four \(\text{H}_2\text{L}^{2-}\) and one \(\text{H}_2\text{L}\) ligands that adorn the outer periphery of the molecule. These ligands exhibit four different coordination modes as shown in Figure 2: the majority bond in a \(\mu\)-fashion along the edges of the

\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 \(\text{Gd}\) octahedron and two face-capping \(\text{Zn}\) ions. Colour code: \(\text{Gd} = \text{purple, Zn} = \text{gold, O} = \text{red, N} = \text{blue, C} = \text{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 (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 {GdO₈} 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 [ZnO⁵N] 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 -CH₂ arms of the diethanolamine unit (Me…CH₂/CH₂, ~4 Å). This produces a 2D sheets of cations of I forming an overall layered structure in the crystal (Figure S3). The presence of the carbonate ligands is intriguing, and one that is becoming ever more prevalent with the increasing number of Ln-based cages being reported. Of the ~130 entries in the CSD of metal cluster compounds containing carbonate anions approximately ~25% are 4f complexes and ~5% are heterometallic 3d-4f complexes. While the majority have been formed serendipitously, this observation has led some researchers to deliberately employ Na₂CO₃, NaHCO₃ and CO₂ as reaction ingredients. The CSD search also highlights the extraordinary coordinative flexibility of the CO₃²⁻ 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.

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 χM/T products, where χ = M / B, and M is the magnetisation of the sample. At room temperature, the χM/T product of I - 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, g₀d = 2.0) for I, a [DyIII₆] unit (85.0 cm³ K mol⁻¹, g₀d = 4/3) for 2, a [SmIII₆] unit (0.5 cm³ K mol⁻¹, g₀m = 2/7) for 3, and a [TbIII₆] unit (70.9 cm³ K mol⁻¹, g₀b = 3/2) for 5. In the case of 4, although the F₆ 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 χM/T product of I 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 GdIII is negligible, this behaviour is consistent with the presence of weak intramolecular antiferromagnetic exchange interactions. The χM/T 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 TbIII and potentially to the presence of weak intramolecular magnetic exchange interactions. The χM/T 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 ⁴H₁₅/₁₂ term, indicating a splitting between the ground and first excited Kramers doublets of the ⁴H₁₅/₁₂ term larger than the thermal energy at 280 K. Finally, the χM/T 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 F₆ 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 I and 2 to 8 K and 0 to 5 T for the remaining complexes. The VTVB magnetisation data of I are shown in Figure 3. At the highest investigated field (5 T) and the lowest investigated temperature (2 K), the magnetisation of I 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 g₀d = 2.0). This observation is consistent with the presence of very weak exchange interactions operating in I. Furthermore, when the VTVB data of I are plotted against the reduced quantity μB/B / kT (Figure S4), no nesting of the VTVB data is observed. This observation indicates that the energy spectrum of I 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 TbIII, respectively. These values are significantly lower than the expected magnetic moment of isolated DyIII (10.0 μB)
and Tb III (9.0 $\mu_B$) centres, for which the $m_J = -15/2$ projection of the $^1H_{15/2}$ ground term or the $m_J = -6$ projection of the $^7F_{6}$ 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 $^1H_{15/2}$ 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 $^7T_{0}$ 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 LnIII centres and the ensuing large number (twenty-seven) of associated ligand 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 Gd 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)

$$\hat{H} = \mu_B B \sum_i g_i S_i \cdot \sum_{j \neq i} J_{ij} S_j$$  \hspace{1cm} (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: $J_{12}, J_{13}, J_{15}, J_{16}, J_{23}, J_{24}, J_{26}, J_{34}, J_{45}, J_{56}$ (Figure 3, top, inset) and set them all equal to $J_{Gd-Gd}$. Furthermore we fix $g_{Gd} = 2.0$. Thus our model contains only one free parameter, namely, $J_{Gd-Gd}$. 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. Both fits result in the same best-fit parameter: $J_{Gd-Gd} = -0.004 \text{ cm}^{-1}$. 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). The phonon specific heat simplifies to a Schottky curve as the sum of the Schottky curves arising from the field-split levels of GdIII independent spins (solid lines).

The overall nice agreement with the experimental data, suggesting that applied fields of $B \geq 1$ 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 $B_{eff} = 0.25$ T, as the result of the magnetic interactions involved. By making use of the specific heat data, we calculate the entropy ($S$) 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, $\Delta S_m = EM/\theta dB$. 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 ($\Delta B = 7$ T), the magnetic entropy change, $-\Delta S_m$ reaches 22.6 J kg$^{-1}$ K$^{-1}$ at $T = 1.7$ 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 GdIII spins ($S_{Gd} = 7/2$), calculated as $6Rln(2 S_{Gd} + 1) = 103.7$ J mol$^{-1}$ K$^{-1}$, that is, 23.7 J kg$^{-1}$ K$^{-1}$. Thus, in 1, nearly the full magnetocaloric potential of GdIII is
produced dodecametallic wheels and truncated tetrahedra. Shown to be vanishingly small by independent fits of both the maximum entropy value per mole expected from six Gd 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, 23.7 J kg\(^{-1}\) K\(^{-1}\).

**Conclusions**

A highly unusual family of LaA\(_n\)Zn\(_{2n}\) 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 H\(_2\)L 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 Gd\(^{III}\) 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 Gd\(^{III}\) spins, 23.7 J kg\(^{-1}\) K\(^{-1}\).

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**Notes and references**


