



# A topologically unique alternating $\{\text{Co}^{\text{III}}\text{Gd}^{\text{III}}\}$ magnetocaloric ring†

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**The adiabatic temperature change of the star-shaped  $\{\text{Co}^{\text{III}}\text{Gd}^{\text{III}}\}$  magnetocaloric ring is enhanced via topological control over the assembly process, by using a pre-formed  $\{\text{Co}^{\text{II}}(\text{H}_6\text{L})\}$  building block that undergoes oxidation to  $\text{Co}^{\text{III}}$ , successfully separating the  $\text{Gd}^{\text{III}}$  ions.**

The magnetocaloric effect (MCE) is described as the reversible adiabatic temperature change ( $\Delta T_{\text{ad}}$ ) and magnetic entropy change ( $\Delta S_{\text{m}}$ ) of a material, following the application or removal of a magnetic field. Promising magnetic refrigerants benefit from the large MCE displayed by certain molecular materials.<sup>1</sup> This is where coordination chemistry and molecular magnetism become powerful tools for optimising design towards the ideal magnetic refrigerant. A large MCE at low temperatures is favoured by a negligible magnetic anisotropy.<sup>1b,2</sup> Hence, several molecule-based refrigerants are complexes of isotropic  $\text{Gd}^{\text{III}}$  ions.<sup>3</sup> Another common trend is to maximise the magnetic : non-magnetic ratio, so as to increase values of the refrigeration power and  $-\Delta S_{\text{m}}$ , when reported per unit mass or unit volume.<sup>3a,4</sup> The inherent drawback of this approach is that spin-spin correlations increase unavoidably, which ultimately limit the lower bound of  $\Delta T_{\text{ad}}$  and the lowest temperature that can be attained in an adiabatic demagnetisation process.<sup>3d</sup> Therefore, a compromise becomes necessary. Some recent studies explore the combined use of 3d/4f ions in search of the enhancement of magnetocaloric properties, such as  $\text{Co}/\text{Gd}$ .<sup>5</sup> As expected,  $\text{Co}^{\text{II}}$  ions influence negatively the MCE, because of the characteristic large magnetic anisotropy, which makes reorientation of the magnetic moment more difficult.<sup>1b</sup> Herein, we explore an attractive

solution to this problem, namely tuning the oxidation state, by changing anisotropic  $\text{Co}^{\text{II}}$  to diamagnetic  $\text{Co}^{\text{III}}$ , concomitantly with an effective dilution of the  $\text{Gd}^{\text{III}}$  ions, in order to favour  $\Delta T_{\text{ad}}$ .

We recently reported large heterometallic  $\{\text{Mn}_{18}\text{Cu}_6\}$  complexes, obtained by following a directed synthesis approach, based on the use of the metallo-organic precursor  $[\text{Cu}(\text{H}_6\text{L})\text{Cl}]\text{Cl}$  ( $\text{H}_6\text{L}$  = bis-tris propane).<sup>6</sup> This prompted us to investigate the reactivity of bis-tris propane with 4f ions in the presence of 3d ions.<sup>7</sup> Similar aminopolyol-type ligands seem to promote the oxidation of different  $\text{Co}^{\text{II}}$  starting materials.<sup>8</sup> Therefore, the exploration of  $\text{Co}^{\text{II}}$  precursors containing  $\text{H}_6\text{L}$  in the design of new magnetic refrigerants becomes highly attractive. Our approach is to use  $\{\text{Co}^{\text{II}}(\text{H}_6\text{L})\}$  precursors that can undergo facile oxidation to diamagnetic  $\text{Co}^{\text{III}}$ , whilst encapsulating the cobalt centres and directing/separating the  $\text{Ln}^{\text{III}}$  ions. Using this strategy, we present the magnetocaloric properties of a new  $\{\text{Co}^{\text{III}}\text{Gd}^{\text{III}}\}$  star-shaped ring, showing that the  $\text{Co}^{\text{III}}$  ions have a significant impact on the adiabatic temperature change in this system, by separating the  $\text{Gd}^{\text{III}}$  ions and weakening the  $\text{Gd}^{\text{III}} \cdots \text{Gd}^{\text{III}}$  interaction. In terms of  $\Delta T_{\text{ad}}$ , this complex is among the best gadolinium-based molecular refrigerants reported so far (*vide infra*).

By combining the metalloligand  $[\text{Co}(\text{H}_6\text{L})(\text{CH}_3\text{COO})_2]$  (1) and  $\text{Gd}(\text{acac})_3 \cdot \text{H}_2\text{O}$  we are able to obtain a new hexametallallic complex  $[\text{Co}^{\text{III}}\text{Gd}^{\text{III}}(\text{H}_2\text{L})_3(\text{acac})_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_2]$  (2) with a unique alternating wheel-like structure (Fig. 1 and Fig. S4, S12, Table S1, ESI†). The pre-formation of the metalloligand (see Fig. S1–S3 and S10, ESI†) seems to be essential for the assembly of 2, as previously seen for the  $\{\text{Mn}_{18}\text{Cu}_6\}$  complexes. During the reaction, under aerobic conditions in the presence of bis-tris propane,  $\text{Co}^{\text{II}}$  is oxidised to  $\text{Co}^{\text{III}}$  and hence, the magnetic properties of 2 are defined exclusively by the paramagnetic  $\text{Gd}^{\text{III}}$  ions. The structure of 2 contains three octahedral  $\text{Co}^{\text{III}}$  ions, each one encapsulated by one tetra-deprotonated  $\text{H}_2\text{L}^{4-}$  ligand through four O and two N atoms. The two remaining ligand arms are uncoordinated. Each  $\{\text{Co}(\text{H}_2\text{L})\}$  unit is linked to two octa-coordinated  $\text{Gd}^{\text{III}}$  ions through four  $\mu$ -O bridging atoms

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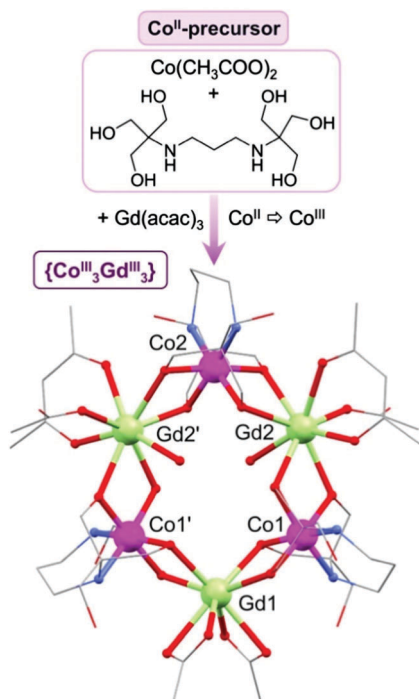


Fig. 1 Synthetic approach and structure of **2**. C, grey; Co, fuchsia; Gd, green; N, blue; O, red; hydrogen atoms and solvent molecules are omitted for clarity.

forming a ring-like structure, in which Co(III) and Gd(III) centres alternately occupy the corners of a six-pointed star.

The oxidation state of each cobalt centre has been confirmed by bond valence sum calculations (BVS).<sup>9</sup> Two different triangular dodecahedral Gd ions can be distinguished based on the co-ligands that complete their coordination sphere: two bidentate acetates for Gd1, or one acac<sup>-</sup>, one monodentate acetate and one water ligand for Gd2 and Gd2' (see Table S2, ESI<sup>†</sup>). The average intramolecular Gd...M distances (M = Co, Gd) are  $d_{\text{Gd} \cdots \text{Co}} = 3.389(1) \text{ \AA}$ , and  $d_{\text{Gd} \cdots \text{Gd}'} = 5.802(9) \text{ \AA}$ . Note that the  $\{\text{Co}_3^{\text{III}}\text{Gd}_3^{\text{III}}\}$  wheel is not perfectly planar (see Fig. S5, ESI<sup>†</sup>), with a dihedral angle between the  $\{\text{Co}_3\}$  and  $\{\text{Gd}_3\}$  planes of  $9^\circ$ . To the best of our knowledge, the structure shown by  $\{\text{Co}_3^{\text{III}}\text{Gd}_3^{\text{III}}\}$  is unprecedented for Co/4f complexes (CSD 5.37, November 2016, where  $3d = \text{Sc} \rightarrow \text{Zn}$ ,  $4f = \text{La} \rightarrow \text{Lu}$ ) and remarkably only larger alternating 3d/4f rings (where  $3d = \text{Mn}$  or  $\text{Fe}$  only), such as  $\{\text{Mn}_4\text{Ln}_4\}$ ,  $\{\text{Mn}_8\text{Ln}_8\}$  or  $\{\text{Fe}_{10}\text{Yb}_{10}\}$  have been reported to date, where the structures are all more puckered than in **2**.<sup>10</sup>

The experimental value of the static magnetic susceptibility temperature product  $\chi_M T$  at 290 K ( $23.37 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ) for **2** is consistent with that expected for three uncoupled Gd(III) centres ( $23.63 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ,  $^8S_{7/2}$ ,  $s = 7/2$ ,  $g = 2$ ).  $\chi_M T$  displays an almost imperceptible decrease between 290 and 26 K and then drops to  $21.33 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 2 K (Fig. 2), consistent with very weak spin ordering promoted either by antiferromagnetic correlations or zero-field splitting (ZFS) of the ground multiplet. Exchange coupling through the diamagnetic Co(III) ions is a potential pathway for very weak Gd...Gd' intramolecular interactions, similar to previous Cu...Cu' coupling through Zn(II) in

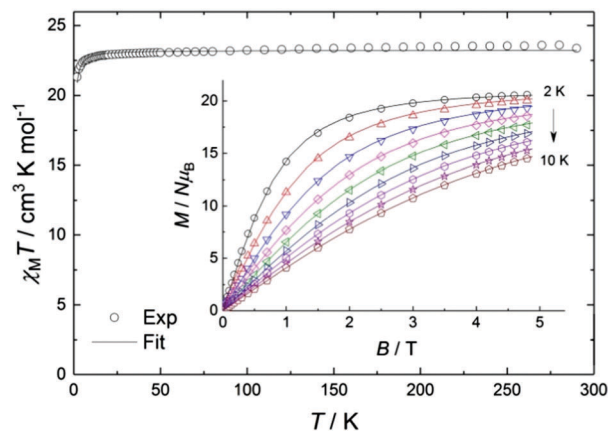


Fig. 2 Temperature dependence of  $\chi_M T$  for **2** in an applied field of 0.1 T (inset shows magnetisation vs. field at 2 to 10 K, step 1 K). The solid lines correspond to the simultaneous fit (see text for details).

heterometallic Cu/Zn bis-tris propane complexes.<sup>11</sup> Within the exchange coupling model, the simultaneous fit of the susceptibility and magnetisation data at  $T = 2$  to 10 K, step 1 K (see spin Hamiltonian below, and magnetic model in Fig. S11, ESI<sup>†</sup>) gives  $\mathcal{J} = -(5.3 \pm 0.5) \times 10^{-3} \text{ cm}^{-1}$ , and  $g = 1.988 \pm 0.002$ .<sup>12</sup>

$$\hat{\mathcal{H}} = -2\mathcal{J}(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_3) + g\mu_B \vec{B} \sum_{i=1}^3 \vec{S}_i \quad (1)$$

In the mean-field approximation, we can interpret  $\mathcal{J}$  as an effective interaction constant resulting from dipole-dipole magnetic interactions, which are well documented for molecular materials.<sup>13</sup> The  $g$  value obtained from the fit is reasonable for Gd(III) ions considering similar complexes.<sup>14</sup> The small deviation from the expected spin-only  $g$  value could be a consequence of a small ZFS, induced by crystal-field effects combined with spin-orbit coupling.<sup>2b,15</sup> Considering the relatively large average Gd...Gd' distance ( $5.802(9) \text{ \AA}$ ), one could argue that exchange coupling is likely to be less effective for spin ordering. All sources, though, are extremely weak and we cannot discriminate between them, on the basis of the experimental data. The DC experiments suggest, therefore, that **2** should display a relatively large MCE, arising from the weakly-interacting Gd(III) ions.<sup>1b,16</sup> The MCE is best evaluated from heat capacity  $c_p$  experiments (Fig. 3, top). As is typical for molecular magnetic materials,<sup>1a</sup> lattice vibrations contribute predominantly to  $c_p$  as a rapid increase above *ca.* 5–10 K. The non-magnetic lattice contribution can be described by the Debye model (dotted line in Fig. 3), which simplifies to a  $c_{\text{lat}}/R = aT^3$  dependence at the lowest temperatures, where  $a = 6.7 \times 10^{-3} \text{ K}^{-3}$  for **2**. At such low temperatures,  $c_p$  is mainly determined by a Schottky-like anomaly, which is strongly dependent on  $B$  and can be well modelled by Hamiltonian (1), using the same parameters obtained from fitting the susceptibility and magnetisation data. For  $B = 0$ , the system becomes sensitive to any perturbation, hence the need to add an effective internal field  $B_{\text{eff}} \approx 0.3 \text{ T}$  to our model, in order to simulate the zero-applied-field  $c_p$ . For  $B \geq 1 \text{ T}$ , such a correction is not necessary. We ascribe  $B_{\text{eff}}$  to the dipole-dipole magnetic interactions,



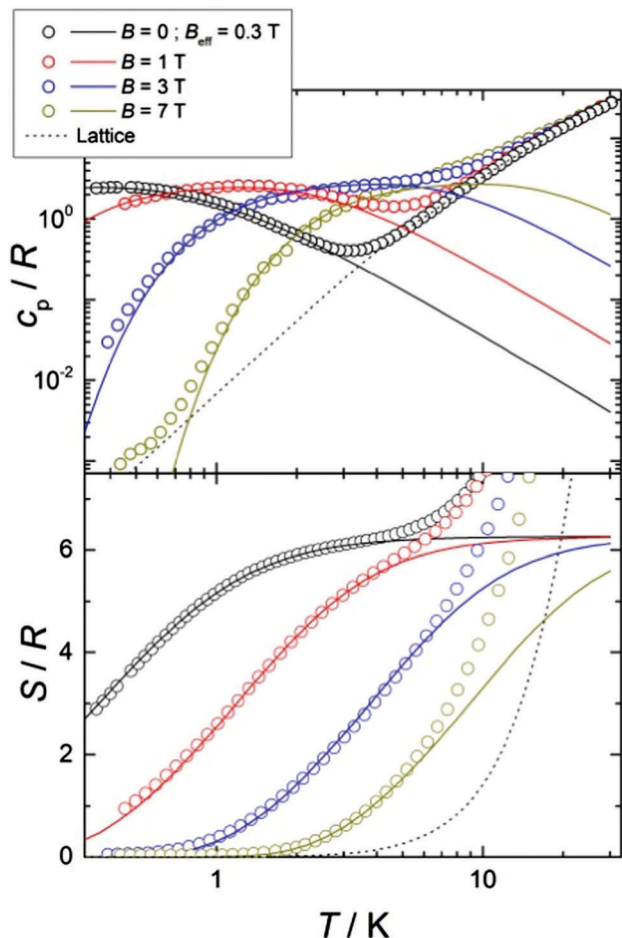


Fig. 3 Top: Temperature dependence of the heat capacity, normalised to the gas constant,  $c_p/R$  for **2** for selected applied fields, as labelled. Bottom: Temperature dependence of the entropy, normalised to the gas constant,  $S/R$  for **2** for selected applied fields, as labelled. The dotted line is the lattice while the solid lines correspond to the magnetic modelling (see text for details).

although to a minor extent, it could also be associated with a small ZFS at the Gd(III) sites. From the experimental heat capacity data, we derive the entropy  $S$  of the system, according to  $S = \int c_p/T dT$ . Similarly, we derive the lattice entropy  $S_{\text{latt}}$  from  $c_{\text{latt}}$  and the magnetic entropy  $S_m$  from  $c_m$ , that is, the magnetic contribution to  $c_p$ , viz., the aforementioned Schottky-like anomaly, calculated on basis of Hamiltonian (1). The bottom panel of Fig. 3 shows the resulting temperature dependence of the experimental entropy  $S$ , which thus corresponds to the sum of  $S_{\text{latt}}$  (dotted line) and  $S_m$  (solid lines), for any applied magnetic field employed. Because of the very weak ZFS and interactions present, temperatures as low as ca. 3–4 K are already sufficient for fully decoupling the Gd(III) spins. Therefore, within the investigated temperature range, the zero-applied-field  $S$  reaches the maximum entropy value per mole involved, which corresponds to three non-interacting Gd(III) spins  $s = 7/2$  and is calculated as  $3 \times R \ln(2s + 1) \approx 6.2R$  (see Fig. 3).

Next, we evaluate  $\Delta S_m$  and  $\Delta T_{\text{ad}}$ , following a change of the applied magnetic field  $\Delta B$ . The temperature dependencies of both  $\Delta S_m$  and  $\Delta T_{\text{ad}}$  can be calculated straightforwardly from

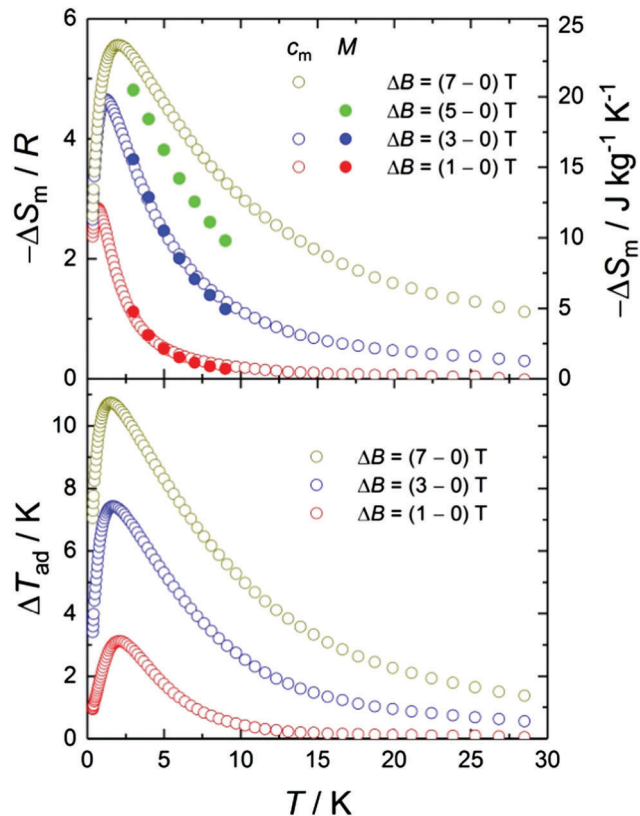


Fig. 4 Temperature dependence of the magnetic entropy change  $\Delta S_m$  (top) and adiabatic temperature change  $\Delta T_{\text{ad}}$  (bottom) for **2** for selected changes of the applied magnetic field  $\Delta B$ , as labelled. Values of  $\Delta S_m$  are reported per unit mole (left) and mass (right), and are obtained from heat capacity (empty dots) and magnetisation (filled dots) data.

the experimental entropy (Fig. 3, bottom panel).<sup>1b</sup> Likewise,  $\Delta S_m$  can also be calculated from the magnetisation data (Fig. 2) by making use of the Maxwell relation  $\Delta S_m = \int [\partial M / \partial T]_B dB$ . Fig. 4 shows the so-obtained dependence of  $\Delta S_m$  and  $\Delta T_{\text{ad}}$  for **2** versus temperature for selected  $\Delta B$  values. Note the nice agreement between the  $\Delta S_m$  results obtained through both methods, thus validating the approaches employed. For the largest applied field change  $\Delta B = (7-0)$  T, i.e., after a full demagnetisation from 7 T, the maximum value of  $-\Delta S_m$  is  $5.6R$  at  $T = 1.9$  K, which corresponds to 90% of the available entropy content and is equivalent to  $23.6 \text{ J kg}^{-1} \text{ K}^{-1}$  per unit mass. Concomitantly, we obtain  $\Delta T_{\text{ad}} = 10.7$  K at  $T = 1.5$  K for the same field change, that is, the temperature decreases down to a final temperature  $T_f = 1.5$  K, on demagnetising adiabatically from  $B = 7$  T and an initial temperature  $T_i = T_f + \Delta T_{\text{ad}} = 12.2$  K. Note that  $\Delta T_{\text{ad}}$  is limited in  $T_f$  by sources of magnetic ordering (spin-spin interactions and magnetic anisotropies) and in  $T_i$  by the lattice entropy, which soon becomes the dominating contribution on increasing the temperature (see Fig. 3).

The precursor  $[\text{Co}(\text{H}_6\text{L})(\text{CH}_3\text{COO})_2]$  (**1**) has successfully directed the molecular assembly in  $[\text{Co}^{\text{III}}\text{Gd}^{\text{III}}(\text{H}_2\text{L})_3(\text{acac})_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_2]$  (**2**), so that the Gd(III) ions are isolated, thus promoting the discussed magnetocaloric properties. Several Co(II)/Gd(III) molecular coolers have been studied so far.<sup>5a,17</sup> The biggest hindrance to a large





MCE in those compounds is the large magnetic anisotropy of the Co(II) ions.<sup>1b,2</sup> In **2** we circumvent this impediment by oxidising Co(II) into Co(III) during the synthesis, thus leaving only the Gd(III) ions to contribute magnetically. In terms of the magnetocaloric properties of **2**, the diamagnetic Co(III) ions still play a role, though passively. On the one hand, they influence negatively on the entropy change per unit mass. The lower the magnetic : non-magnetic ions ratio, the lower are the magnetic heat capacity and entropy per unit mass. The maximum value observed of  $-\Delta S_m = 23.6 \text{ J kg}^{-1} \text{ K}^{-1}$  at  $T = 1.9 \text{ K}$  for **2** is large, though not outstanding. However, the key point is that the Co(III) centres impact positively on the adiabatic temperature change. In **2**, the Co(III) and Gd(III) ions alternate with respect to one another. Therefore, the intermediate presence of the Co(III) ions weakens extremely the magnetic interaction between the Gd(III) ions, so the temperature-dependence of  $\Delta T_{ad}$  has a maximum at a relatively lower temperature than usually found for pure-Gd molecular complexes. Among the few known systems that have a  $\Delta T_{ad}$  maximum below e.g., 2 K for 7 T, complex **2** with  $\Delta T_{ad} = 10.7 \text{ K}$  at  $T = 1.5 \text{ K}$  lags behind only the extraordinary  $\{\text{Gd}_2\text{-ac}\}$  with  $\Delta T_{ad} = 12.6 \text{ K}$  at  $T = 1.4 \text{ K}$ ,<sup>3a</sup> while it outdoes  $\{\text{Zn}_2\text{Gd}_2\}$  with  $\Delta T_{ad} = 9.6 \text{ K}$  at  $T = 1.4 \text{ K}$ ,<sup>18</sup> and  $\{\text{Gd}_7\}$  with  $\Delta T_{ad} = 9.4 \text{ K}$  at  $T = 1.8 \text{ K}$ .<sup>19</sup>

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