

# Dodecanuclear 3d/4f-Metal Clusters with a ‘Star of David’ Topology: Single-Molecule Magnetism and Magnetocaloric Properties

Dimitris I. Alexandropoulos,<sup>a</sup> Luis Cunha-Silva,<sup>c</sup> Giulia Lorusso,<sup>d</sup> Marco Evangelisti,<sup>d</sup> Jinkui Tang<sup>\*b</sup> and Theocharis C. Stamatatos<sup>\*a</sup>

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A family of interwoven molecular inorganic knots, shaped like the ‘Star of David’, was prepared by the employment of naphthalene-2,3-diol in 3d/4f-metal cluster chemistry; the isoskeletal dodecanuclear compounds exhibit slow relaxation of the magnetization and magnetocaloric properties, depending on the metal ion.

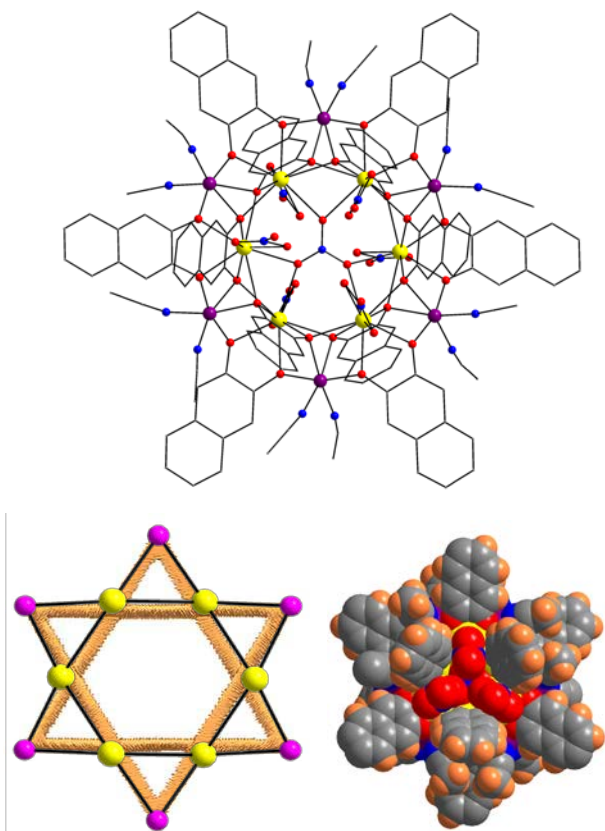
The last three decades or so molecular chemistry has received a tremendous attention due to the potential applications of molecular nanoscale materials in both applied and fundamental areas of research. In addition to their interesting physicochemical properties, molecular organic and inorganic chemistry has supplied literature with aesthetically beautiful and complex structures such as highly-symmetric rotaxanes<sup>1</sup> and catenanes,<sup>2</sup> molecular nanocars and machines,<sup>3</sup> and polynuclear coordination cluster compounds.<sup>4</sup> Undoubtedly, it is really fascinating for everyone to come across molecular structures reminiscent to the complicated Archimedean and Platonic solids,<sup>5a</sup> “molecular Meccanos”,<sup>5b</sup> or even to daily life geometric shapes, such as triangles, wheels, stars, etc. In addition to the synthetic challenges and aesthetic appeal associated with such architectures, current efforts are also driven by the desire to produce multifunctional systems.

From an inorganic chemistry viewpoint, the choice of metal(s) and organic chelate(s) is of significant importance because they do not only dictate the structures and topologies but also the resulting properties and applications. In the field of molecular magnetism, polynuclear heterometallic 3d/4f-metal cluster complexes are excellent candidates for single-molecule magnetism<sup>6</sup> and/or magnetic refrigeration<sup>7</sup> properties when the paramagnetic metal ions are highly anisotropic (i.e., Dy<sup>III</sup>) or high-spin and isotropic (i.e., Gd<sup>III</sup>), respectively. Although there are numerous 3d/4f-metal cluster compounds reported to date,<sup>8</sup> there is still a thirst for the synthesis of new, structurally notable complexes and for building-up families of high-nuclearity, isoskeletal transition metal-lanthanide clusters, where the 3d-metal ion will be deliberately replaced in the polymetallic motif without breaking the core structure but instead altering the physical (magnetic, optical, etc.) properties. Families of previously reported isoskeletal 3d/4f-metal complexes with a variety of different 3d-metals are restricted to few oligonuclear compounds (i.e., dimers,<sup>9</sup> trimers,<sup>10</sup> and tetramers<sup>11</sup>) with known structural motifs such as triangles and butterflies.

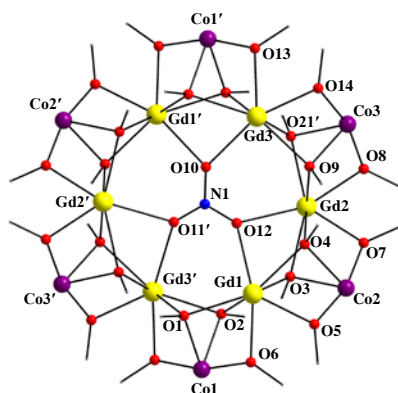
In this work, we report the first family of isoskeletal, high-nuclearity [ $\{3d\}_6\{4f\}_6$ ] clusters with a unique ‘Star of David’ topology resulting from the use of naphthalene-2,3-diol (ndH<sub>2</sub>) as chelating/bridging ligand.<sup>12a</sup> The described compounds exhibit a variety of different magnetic behaviors, from slow relaxation of the magnetization to magnetic refrigeration, depending on the degree of magnetic anisotropy involved,<sup>8a</sup> as determined by the transition metal and lanthanide ion used. The reaction of equimolar amounts of M(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Ln(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (M = Co<sup>II</sup>, Ni<sup>II</sup>, Zn<sup>II</sup>; Ln = Gd<sup>III</sup>, Dy<sup>III</sup>) with two equivalents of each ndH<sub>2</sub> and NEt<sub>3</sub> in MeCN/Et<sub>2</sub>O gave the dodecanuclear compounds [M<sub>6</sub>Ln<sub>6</sub>(NO<sub>3</sub>)<sub>6</sub>(nd)<sub>12</sub>(H<sub>2</sub>O)<sub>x</sub>(MeCN)<sub>y</sub>] (x = 2 and y = 12 for **1**-Co<sub>6</sub>Gd<sub>6</sub>, **2**-Co<sub>6</sub>Dy<sub>6</sub> and **3**-Ni<sub>6</sub>Gd<sub>6</sub>; x = 10 and y = 4 for **4**-Ni<sub>6</sub>Dy<sub>6</sub> and **6**-Zn<sub>6</sub>Dy<sub>6</sub>; x = 6 and y = 8 for **5**-Zn<sub>6</sub>Gd<sub>6</sub>.) in very good yields (>65%).<sup>†</sup> The chemical and structural identities of the reported compounds were confirmed by single-crystal X-ray crystallography (complete data sets for **1**, **3**, **4**, **5**, **6**, and adequate unit cell indexing for **2**), elemental analyses (C, H, N), powder XRD analyses, and IR spectral comparison.<sup>†</sup>

All complexes **1-6** possess similar structures (Fig. 1, top) reminiscent to a ‘Star of David’ topology (Fig. 1, bottom left), which is unprecedented in metal cluster chemistry.<sup>12b</sup> The structures differ only in the divalent 3d-metal ion and the number of terminally bound H<sub>2</sub>O and MeCN molecules. Representative complex **1** (Fig. 1, top) consists of an internal non-planar ring of six Gd<sup>III</sup> ions, templated around a η<sup>2</sup>:η<sup>2</sup>:η<sup>2</sup>:μ<sub>6</sub>-NO<sub>3</sub><sup>-</sup> ion<sup>13</sup> locked at the center of the structure. The Gd<sub>6</sub> unit is further linked to a planar ring of six external Co<sup>II</sup> ions through the μ<sub>3</sub>-OR arms of six η<sup>3</sup>:η<sup>3</sup>:μ<sub>5</sub> nd<sup>2-</sup> ligands. Additional bridging between the Co<sup>II</sup> and Gd<sup>III</sup> ions is provided by 12 μ-OR groups from six η<sup>2</sup>:η<sup>2</sup>:μ<sub>3</sub> nd<sup>2-</sup> ligands (Scheme S1). The complete [Co<sub>6</sub>Gd<sub>6</sub>(μ<sub>6</sub>-NO<sub>3</sub>)(μ<sub>3</sub>-OR)<sub>12</sub>(μ-OR)<sub>12</sub>]<sup>5+</sup> core (Fig. 2) has a rare D<sub>3d</sub> symmetry which is crystallographically imposed. The remaining NO<sub>3</sub><sup>-</sup> groups are acting as bidentate chelating ligands to the 4f-metal ions; all Co<sup>II</sup> atoms are six-coordinate with distorted octahedral geometries and all the Gd<sup>III</sup> atoms are nine-coordinate with spherical capped square antiprismatic geometries (program SHAPE;<sup>14</sup> CS<sub>HM</sub> values = 1.37, 1.45, 2.05, see Fig. S1). The ‘Star of David’ is a six-pointed metal star, made of two equilateral Co<sub>3</sub> triangles (Co-Co-Co = 60°) that cross at six places, the six Gd<sup>III</sup> atoms. The space-filling representation

(Fig. 1, bottom right) shows that **1** has a beautiful spherical structure with distances across the three corners of  $\sim 25$  Å, as defined by the longest C...C distance of the externally bound  $\text{nd}^{2-}$  ligands. Finally, the reported compounds join the family of  $\{\text{M}_6\text{Ln}_6\}$  clusters with a Wells-Dawson<sup>15</sup> and octahedron-in-octahedron<sup>16</sup> topologies.



**Fig. 1** Complete structure of **1** (top), the Co<sub>6</sub>Gd<sub>6</sub> 'Star of David' topology (enumerated as 2,4M12-1)<sup>17</sup>, with the black lines indicating the metal...metal vectors (bottom, left), and a space-filling representation of **1** (bottom, right). H atoms are either omitted for clarity or shown in orange. Color scheme: Co<sup>II</sup> purple, Gd<sup>III</sup> yellow, O red, N blue, C dark gray.



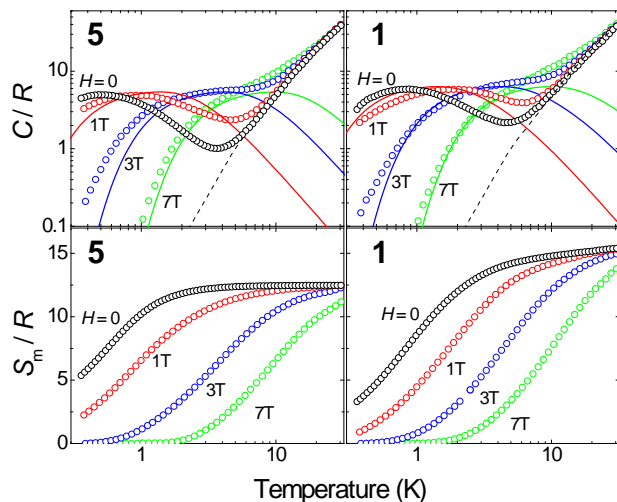
**Fig. 2** Partially-labeled core of **1**. Color scheme as in Fig. 1. Symmetry operation for the primed atoms: 1-x, -y+1, -z+1.

Solid-state direct-current (dc) magnetic susceptibility ( $\chi_M$ ) data on dried and analytically-pure samples of **1-6** were collected in the 2.0-300 K range in an applied field of 0.1 T, and are plotted as  $\chi_M T$  vs  $T$  in Fig. S2. The experimental  $\chi_M T$

values at 300 K for all complexes are in excellent agreement with the theoretical ones expected for 6 HS ( $S = 3/2$ ,  $g = 2$ ) Co<sup>II</sup> and 6 Gd<sup>III</sup> or 6 Dy<sup>III</sup> ( $58.50$  or  $96.27$   $\text{cm}^3\text{Kmol}^{-1}$ ), 6 Ni<sup>II</sup> ( $S = 1$ ,  $g = 2.2$ ) and 6 Gd<sup>III</sup> or 6 Dy<sup>III</sup> ( $54.51$  or  $92.28$   $\text{cm}^3\text{Kmol}^{-1}$ ), and 6 Gd<sup>III</sup> ( $^8S_{7/2}$ ,  $S = 7/2$ ,  $L = 0$ ,  $g = 2$ ) or 6 Dy<sup>III</sup> ( $^6H_{15/2}$ ,  $S = 5/2$ ,  $L = 5$ ,  $g = 4/3$ ) ( $47.25$  or  $85.02$   $\text{cm}^3\text{Kmol}^{-1}$ ) non-interacting ions. In the  $\sim 70$ -300 K regime, the magnetic response of **1-6** is essentially identical for all complexes, with the  $\chi_M T$  products remaining almost constant suggesting very weak to negligible magnetic exchange interactions between the metal centers. At temperatures below  $\sim 60$  K, the  $\chi_M T$  product of Zn<sub>6</sub>Gd<sub>6</sub> (magnetically a homo-lanthanide Gd<sub>6</sub> compound) steadily decreases, indicative of weak antiferromagnetic exchange interactions between the 6 Gd<sup>III</sup> centers propagated by the alkoxido arms of  $\text{nd}^{2-}$  and likely the O atoms of the  $\mu_6$ -bridging NO<sub>3</sub><sup>-</sup> group. The  $\chi_M T$  products for the corresponding Co<sub>6</sub>Gd<sub>6</sub> (**1**) and Ni<sub>6</sub>Gd<sub>6</sub> (**3**) clusters are similar in decreasing with decreasing  $T$  down to 10 K, albeit **1** shows a  $\chi_M T$  rise in the 10-3.5 K in contrast to the  $\chi_M T$  of **3** which keeps decreasing. As corroborated by the specific heat experiments discussed below, the magnetic behavior of **1** can be described by the sum of two contributions: an outer ferromagnetic Co<sub>6</sub> 'shell', which is responsible for the  $\chi_M T$  rise, and an antiferromagnetic inner Gd<sub>6</sub> core. Since the occupied orbitals of Gd<sup>III</sup> are quite centered, we can reasonably approximate these two contributions as magnetically independent. For all the M<sub>6</sub>Dy<sub>6</sub> analogues, the low temperature ( $< 60$  K) magnetic behavior is very similar, with the  $\chi_M T$  products rapidly decreasing down to 2 K indicating the presence of predominant antiferromagnetic exchange interactions between the metal centers and/or depopulation of the excited  $M_J$  states. Magnetization ( $M$ ) vs field ( $H$ ) studies for the M<sub>6</sub>Gd<sub>6</sub> analogues from 2 to 10 K show a continuous increase of  $M$  as  $H$  increases and a trend for saturation at the maximum possible  $S$  values (Fig. S3). In contrast, for the M<sub>6</sub>Dy<sub>6</sub> members the magnetization shows a steady increase with increasing  $H$  but does not saturate, indicative of the presence of magnetic anisotropy and/or population of low-lying excited states (Fig. S4).

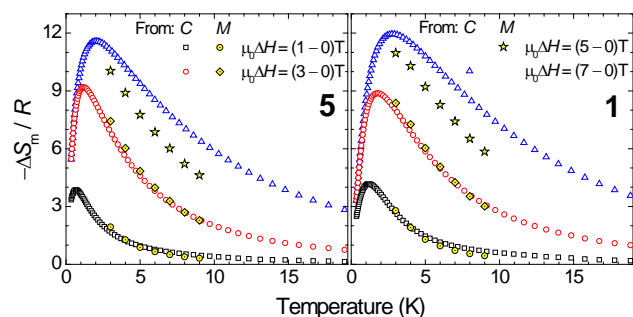
Given the interest in 3d/Gd-metal clusters as low-temperature magnetic coolers,<sup>7,15</sup> we decided to investigate the magnetocaloric properties of the Gd-containing complexes **1** and **5**. In the top panels of Fig. 3, we report the specific heat, normalized to the gas constant  $R$ , for Zn<sub>6</sub>Gd<sub>6</sub> (**5**) and Co<sub>6</sub>Gd<sub>6</sub> (**1**), respectively. Since the two compounds are isostructural, we obtain the same lattice contribution,  $C_{\text{latt}}$ , which can be described by the Debye model (dashed lines), with a Debye temperature  $\Theta_D = 29.6$  K. From the magnetic contribution,  $C_m$ , obtained by subtracting  $C_{\text{latt}}$  to the total heat capacity, we estimated the  $T$ -dependence of the magnetic entropy,  $S_m(T) = \int C_m(T)/T dT$  for both compounds (bottom panels of Fig. 3). For **5**, we compare the experimental data with the contributions (solid lines in Fig. 3) that result by summing together the Schottky curves arising from the field-split levels of 6 Gd<sup>III</sup> independent spins. It can be seen that the Gd<sup>III</sup> spins are weakly correlated, since the applied field gradually promotes a large decoupling, yielding thus a good agreement. Besides, the weak interactions permit  $S_m(T)$  to

reach the maximum entropy value per mole involved, i.e.,  $6R\ln(2S_{\text{Gd}}+1) \cong 12.5R$ . For **1**, assuming the ferromagnetic interactions between the 6 peripheral  $\text{Co}^{\text{II}}$  ions to be strong enough to yield a well-defined  $S = 9$  state, one would expect  $S_{\text{m}}$  to be well described by the sum of Schottky contributions (solid lines of Fig. 3) for 6 independent  $\text{Gd}^{\text{III}}$  spins and a  $S = 9$  net spin, as indeed observed. Ordering of these  $S = 9$  spins within each  $\text{Co}_6\text{Gd}_6$  molecule yields an entropy change  $R\ln(2S+1) \cong 2.9R$ . Therefore,  $S_{\text{m}}(T)$  is seen to gradually tend to  $(12.5 + 2.9)R = 15.4R$  (Fig. 3).



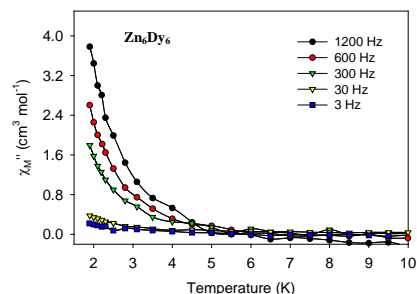
**Fig. 3** (top) Temperature-dependence of the specific heat, normalized to the gas constant  $R$ , for  $\text{Zn}_6\text{Gd}_6$  (left) and  $\text{Co}_6\text{Gd}_6$  (right) at the indicated fields. Solid thick lines are the sums of the calculated Schottky contributions (see text); dashed line is the fitted lattice contribution. (bottom) Temperature-dependence of the magnetic entropy, normalized to the gas constant  $R$ , as obtained from the specific heat data.

Figure 4 shows the magnetic entropy changes,  $\Delta S_{\text{m}}$ , for  $\text{Zn}_6\text{Gd}_6$  (**5**) and  $\text{Co}_6\text{Gd}_6$  (**1**), as derived from specific heat (C, Fig. 3) and magnetization ( $M$ , Fig. S3) data, following known data analysis procedures.<sup>18</sup> The nice agreement between the so-differently obtained sets of data proves the validity of our results. For **5**, the experimental  $-\Delta S_{\text{m}}$  approaches the maximum entropy value per mole ( $12.5R = 25.1 \text{ J kg}^{-1} \text{ K}^{-1}$ ), reaching  $11.6R$ , equivalent to  $22.8 \text{ J kg}^{-1} \text{ K}^{-1}$ , for the  $\mu_0\Delta H = 7 \text{ T}$  maximum field change, at  $T = 2.0 \text{ K}$ . For **1**, the additional  $\text{Co}^{\text{II}}$  magnetic centers, thus the relatively larger magnetic density, promote an overall larger magnetocaloric effect with  $-\Delta S_{\text{m}}$  reaching  $12.0R = 23.7 \text{ J kg}^{-1} \text{ K}^{-1}$  for  $\mu_0\Delta H = 7 \text{ T}$ , at  $T = 2.7 \text{ K}$ . Note that the stronger interactions in **1**, combined with the magnetic anisotropy of the  $\text{Co}^{\text{II}}$  ions, shift the  $-\Delta S_{\text{m}}$  maxima towards somewhat higher temperatures than in **5**.<sup>18,19</sup> The observed magnetocaloric effect for  $\text{Zn}_6\text{Gd}_6$  and  $\text{Co}_6\text{Gd}_6$  has a similar strength with that already reported for other molecular cluster complexes based on  $\text{Zn}(\text{II})/\text{Gd}(\text{III})$  and  $\text{Co}(\text{II})/\text{Gd}(\text{III})$ .<sup>18</sup>



**Fig. 4** Magnetic entropy changes, normalized to the gas constant  $R$ , for  $\text{Zn}_6\text{Gd}_6$  (left) and  $\text{Co}_6\text{Gd}_6$  (right), as obtained from specific heat (C) and magnetization ( $M$ ) experiments for the indicated applied field changes.

Alternating-current (ac) magnetic susceptibility studies have also been carried out in order to investigate the magnetization dynamics of **1-6** in the absence of an external dc magnetic field. Only the compounds with the most prominent magnetic anisotropies, that are the  $\text{Ni}_6\text{Dy}_6$  (Fig. S5) and  $\text{Zn}_6\text{Dy}_6$  (Fig. 5) analogues, showed frequency-dependent out-of-phase  $\chi''_{\text{M}}$  tails at temperatures below  $\sim 3$  and  $\sim 5 \text{ K}$ , respectively. This behavior, which mainly originates from single-ion anisotropy effects of the individual  $\text{Dy}^{\text{III}}$  Kramers ions,<sup>6</sup> is a signature of slow relaxation of the magnetization that is frequently observed in high-nuclearity single-molecule magnets.<sup>4,6,8</sup>



**Fig. 5** Frequency-dependent out-of-phase ( $\chi''_{\text{M}}$ ) ac susceptibility signals for  $\text{Zn}_6\text{Dy}_6$  in a 3 G oscillating field.

In conclusion, we have shown that the self-assembly reaction of various divalent transition metals and lanthanides with the bulky naphthalene-2,3-diol ligand has led to the first dodecanuclear 3d/4f-metal clusters with a beautiful ‘Star of David’ topology. The molecular skeleton resembles a hexagram which is flexible enough to accommodate many different  $\text{M}^{\text{II}}$  and  $\text{Ln}^{\text{III}}$  ions, thus leading to compounds with a variety of physical behaviors, from magnetic refrigeration to slow relaxation of the magnetization. Finally, the reported compounds are distinctly different than the  $\text{Mn}_4\text{Ln}$  clusters of Coucouvanis et. al.,<sup>20</sup> obtained from the use of catechol chelate which is structurally similar to  $\text{ndH}_2$ . Work in progress includes the extension of this family of clusters to all possible  $\text{M}^{\text{II}}_6\text{Ln}_6$  members, their photophysical characterization, and *ab initio* calculations for the  $\text{Zn}_6\text{Dy}_6$  in a quest for important magnetic phenomena such as the toroidal magnetic moment.

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## Notes and references

<sup>a</sup> Department of Chemistry, Brock University, St. Catharines, Ontario, L2S3A1, Canada. Tel: (+1)-905-688-5550 Ext. 3400; E-mail: [stamatatos@brocku.ca](mailto:stamatatos@brocku.ca)

<sup>b</sup> State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China.

<sup>c</sup> REQUIMTE / LAQV & Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal.

<sup>d</sup> Instituto de Ciencia de Materiales de Aragón (ICMA) and Departamento de Física de la Materia Condensada, CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain.

† Electronic Supplementary Information (ESI) available: Full synthetic and crystallographic discussion, structural figures, various plots and magnetic data. See DOI: 10.1039/b000000x/

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