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High-Nuclearity 3d−4f Clusters as Enhanced Magnetic Coolers and Molecular Magnets

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Supporting Information

ABSTRACT: Four 52-metal-ion 3d−4f cluster complexes featuring a common core of $Ln_{42}M_{10}$ (Ln = Gd^{3+}, Dy^{3+}; M = $Co^{2+/3+}$, Ni^{2+}) were obtained through self-assembly of the metal ions templated by mixed anions (ClO_4^- and CO_3^{2-}). Magnetic studies revealed that the $Gd_{42}Co_{10}$ and $Gd_{42}Ni_{10}$ clusters exhibit the largest magnetocaloric effect (MCE) among any known 3d−4f complexes. Replacement of Gd^{3+} ions with anisotropic Dy^{3+} ions caused significant changes in the magnetic behavior of the clusters; both $Dy_{42}Co_{10}$ and $Dy_{42}Ni_{10}$ displayed slow relaxation of the magnetization.

The exploratory synthesis and property investigation of molecule-based magnetic materials are of great current interest, largely stimulated by their envisioned technological applications.[1] Most notable in this vein is the research on polynuclear metal complexes, many of which display fascinating molecular structures and, more importantly, interesting magnetic properties due to the unique exchange interactions between the metal ions.[2] For example, many homo- and heterometallic complexes have been shown to display single-molecule or single-chain magnetism.[2a,3,4] Large values of the magnetocaloric effect (MCE), a property critical to the potential application of such materials in achieving magnetic refrigeration at ultralow temperatures, have also been observed in a number of molecular clusters.[5−7]

Recent studies have suggested that high-nuclearity 3d metal ion−Gd^{3+} cluster complexes with small ligands are most promising for achieving a large MCE.[7−9] On the one hand, the assembly of such clusters is frequently templated by anionic species. With the use of small organic ligands, the resulting large metal/ligand mass ratio ensures a high magnetic density.[10,11] On the other hand, the isotropic Gd^{3+} ion affords multiple low-lying excited spin states, while the large number of metal ions offers the possibility of a ground state with a large spin. All of these factors are conducive to achieving a large MCE. Our recently reported $Gd_{36}Ni_{12}$ cluster complex with acetate and templated by Cl^- and NO_3^-, which exhibits one of the largest entropy changes (a key parameter in evaluating the MCE), clearly validates such a molecular design.[11]

The present work was aimed at (1) investigating the influence of the metal ions on the magnetic properties of the polynuclear complex and (2) exploring the use of anions of different geometry or charge in the hope of creating even larger clusters. Toward the first goal, combinations of Gd^{3+} or anisotropic Dy^{3+} with Co^{2+} or Ni^{2+} were studied. The different ground states resulting from the various metal ions were expected to lead to different magnetic behaviors, including MCEs. For the second goal, lanthanide perchlorates were used rather than nitrates as in our previous work.

Compounds **1**−**4**, formulated as $[Ln_{42}Co^{II}_9Co^{III}(\mu_3\text{-}OH)_{68}(CO_3)_{12}(CH_3COO)_{30}(H_2O)_{70}]\cdot(ClO_4)_{25}\cdot(CH_3CH_2OH)_n\cdot 70H_2O$ [Ln = Gd (**1**, $Gd_{42}Co_{10}$), Dy (**2**, $Dy_{42}Co_{10}$)] and $[Ln_{42}Ni^{II}_{10}(\mu_3\text{-}OH)_{68}(CO_3)_{12}(CH_3COO)_{30}(H_2O)_{70}]\cdot(ClO_4)_{24}\cdot 80H_2O$ [Ln = Gd (**3**, $Gd_{42}Ni_{10}$), Dy (**4**, $Dy_{42}Ni_{10}$)], were obtained from the reaction of $Ln(ClO_4)_3$ and $M(CH_3COO)_2$ in a 20 mL mixture of ethanol and water [see the Supporting Information (SI)]. They were found to be isostructural, as revealed by single-crystal X-ray diffraction studies. It should be noted that there are 25 ClO_4^- counterions in $Ln_{42}Co_{10}$ (**1** and **2**) versus 24 ClO_4^- ions in $Ln_{42}Ni_{10}$ (**3** and **4**) because of the presence of one Co^{3+} in the former (see below). Elemental analysis results were consistent with the crystallographic findings.

As a representative, the structure of **1** is discussed to illustrate the structural features common to the four compounds. The bowl-like cationic cluster core of $[Gd_{42}Co_{10}(\mu_3\text{-}OH)_{68}(CO_3)_{12}]^{55+}$ (Figure 1a) can be viewed as being constructed from three different types of cluster units (I, II, and III). Type I, formulated as $[Gd_8(\mu_3\text{-}OH)_9]^{15+}$, is made up of one $[Gd_5(\mu_3\text{-}OH)_5]^{10+}$ square pyramid and one cubane-like $[Gd_4(\mu_3\text{-}OH)_4]^{8+}$ unit that share one Gd^{3+} vertex (Figure 1b). Type II, formulated as $[Gd_6Co_2(\mu_3\text{-}OH)_{12}]^{10+}$, can be viewed as two distorted cubane-like $[Gd_3Co(\mu_3\text{-}OH)_4]^{7+}$ units and one cuboidal $[Gd_3(\mu_3\text{-}OH)_4]^{5+}$ unit joined together through sharing of three Gd^{3+} vertices (Figure 1c); the cuboidal $[Gd_3(\mu_3\text{-}OH)_4]^{5+}$ unit can be readily derived from a $[Gd_3Co(\mu_3\text{-}OH)_4]^{7+}$ unit by removing its Co^{2+} vertex. Type III, formulated as $[Co^{III}Co^{II}_3(\mu_3\text{-}OH)(CO_3)_3]^{2+}$, is a distorted tetrahedron featuring a μ_3-OH-capped trimetallic basal plane with each of its three metal ions (Co^{2+}) connected to the fourth one (Co^{3+}) through a bridging CO_3^{2-} that is also chelating toward the basal metal atom (Figure 1d). The CO_3^{2-} is thought to be formed through the absorption of atmospheric CO_2 by the reaction mixture, as also observed by others.[12,13]

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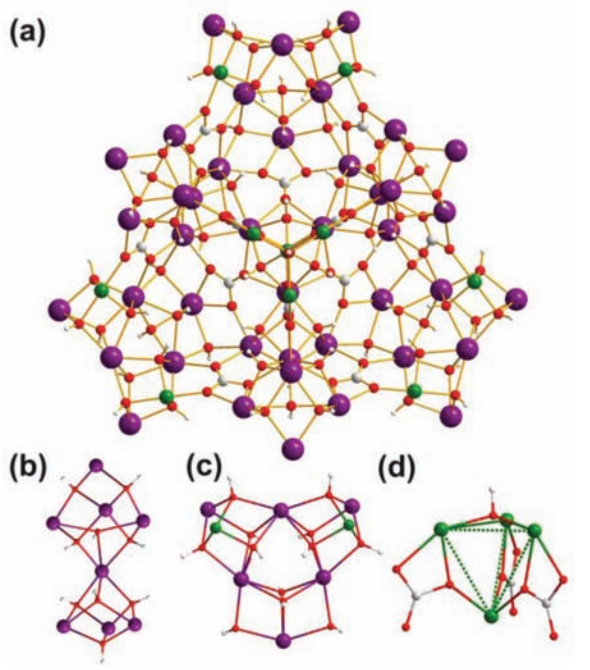

Figure 1. Ball-and-stick views of the structures of (a) the $[Gd_{42}Co^{II}_9Co^{III}(\mu_3\text{-}OH)_{68}(CO_3)_{12}]^{55+}$ cationic cluster and (b−d) the type I ($[Gd_8(\mu_3\text{-}OH)_9]^{15+}$), type II ($[Gd_6Co_2(\mu_3\text{-}OH)_{12}]^{10+}$), and type III ($[Co^{III}Co^{II}_3(\mu_3\text{-}OH)(CO_3)_3]^{2+}$) cluster units, respectively.

Three type-I and three type-II clusters are joined together alternately through nine CO_3^{2-} anions and one μ_3-OH, forming the bowl-like $[Gd_{42}Co^{II}_6(\mu_3\text{-}OH)_{64}(CO_3)_9]^{56+}$ core (Figure 2a). One type-III unit is situated in the center of the bowl, making connections through three CO_3^{2-} anions to units of the other two types of clusters (Figure 2b). As such, the bowl-like cavity is separated into three cup-shaped regions. Presumably acting as templates, three ClO_4^- anions are located in these cup-shaped regions, each being hydrogen-bonded to its surroundings. The bowl-like core is further coordinated by 30 acetato and 70 aqua ligands.

Each of the Co ions displays a distorted octahedral coordination geometry. Analysis of the Co−O bond distances, charge balancing, and bond valence sum calculations collectively indicate that Co1 is trivalent while the others (Co2−Co6) are divalent (see the SI).[14] We note that the present $Gd_{42}Co^{II}_9Co^{III}$ core has the highest nuclearity among all known Co−Ln clusters and is also a rare example of a mixed-valent Co^{II}−Co^{III}−Ln aggregate.[15] The Gd···Co and Gd···Gd separations are 3.321(2)−3.451(2) Å and 3.5839(10)−4.0346(11) Å, respectively, which are comparable to the corresponding values found in previously reported Gd−Co clusters.[7b,16]

The temperature dependence of the magnetic susceptibilities of **1**−**4** was measured between 300 and 2 K with an applied direct-current (dc) magnetic field of 1000 Oe (Figure 3). The observed and calculated $\chi_M T$ values at room temperature, together with the relevant parameters for calculations (S, L, J, and g_J), are summarized in Table 1. For **1** and **2**, the observed $\chi_M T$ values at 300 K are larger than the calculated spin-only values, which is attribute to the significant orbital contributions of the distorted octahedral high-spin Co^{2+} ions.[7b,17] For **3** and **4**, the observed $\chi_M T$ values at 300 K are close to the corresponding calculated spin-only values.

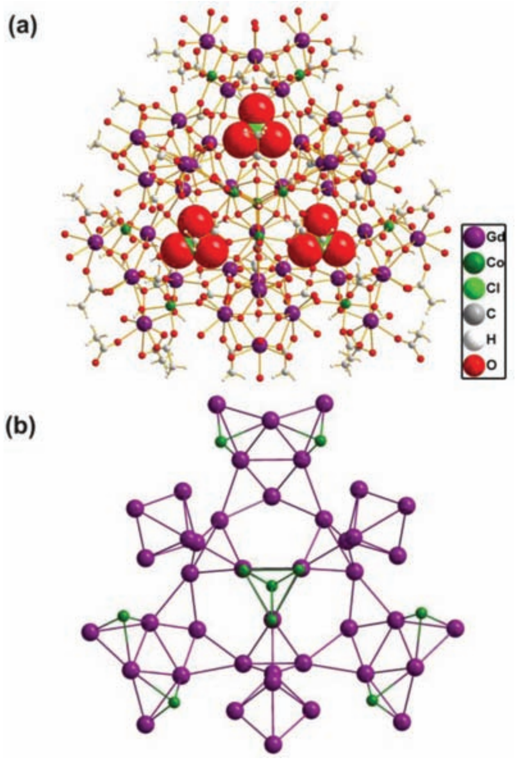

Figure 2. (a) Ball-and-stick view of the cationic $Gd_{42}Co_{10}$ cluster in **1**. (b) Arrangement of the 52 metal ions in the core.

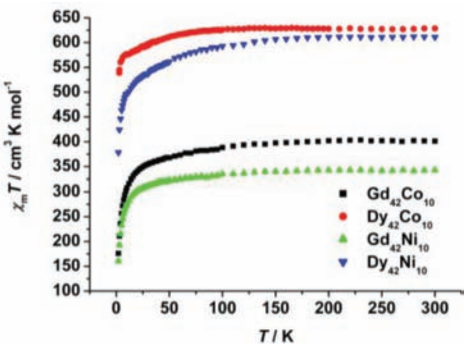

Figure 3. Plots of the temperature dependence of $\chi_M T$ for **1**−**4** under a 1000 Oe dc field between 2 and 300 K.

Table 1. Magnetic Data at 300 K for 1−4[a]

	1	2	3	4
$S(Ln^{3+})$	$^7/_2$	$^5/_2$	$^7/_2$	$^5/_2$
$S(M^{2+})$	$^3/_2$	$^3/_2$	1	1
$L(Ln^{3+})$	0	5	0	5
$J(Ln^{3+})$	$^7/_2$	$^{15}/_2$	$^7/_2$	$^{15}/_2$
$g_J(Ln^{3+})$	2	$^4/_3$	2	$^4/_3$
$g_J(M^{2+})$	2	2	2	2
$\chi_M T$ (calcd)[b]	347.85	612.02	340.96	605.14
$\chi_M T$ (obs)[b]	402.26	628.63	342.62	611.10

[a] S, L, and J are the quantum numbers for total spin angular momentum, total orbital angular momentum, and total angular momentum, respectively, of the ground multiplet. g_J is the Landé factor. [b] Values of $\chi_M T$ are given in cm³ mol⁻¹ K.

As the samples were cooled, the $\chi_M T$ values remained essentially constant down to 100 K, after which they decreased gradually as T decreased to 30 K and then abruptly as T decreased to 2 K, possibly as a result of a combination of the antiferromagnetic interactions and the zero-field splitting of the ground states.[18] The data in the range 50−300 K were fitted to the Curie−Weiss law, yielding $C = 408.16$ cm^3 K mol^{-1} and $\theta = -4.27$ K for **1**, $C = 632.91$ cm^3 K mol^{-1} and $\theta = -1.32$ K for **2**, $C = 346.02$ cm^3 K mol^{-1} and $\theta = -3.13$ K for **3**, and $C = 621.12$ cm^3 K mol^{-1} and $\theta = -3.73$ K for **4**.

Measurements of the field (H) dependence of the magnetizations (M) of **1**−**4** at low temperature (2−10 K) were also performed (Figures S3 and S4 in the SI). The magnetization values at 2 K and 7 T for **1** and **3** reached 341.81 and 298.35 $N\mu_B$, respectively, without saturation, suggesting the presence of low-lying excited states.[7c,9] For **2** and **4** under the same conditions, the maximum magnetization values were 234.79 and 251.73 $N\mu_B$, respectively, also lower than the expected saturation values. This lack of saturation of M versus H suggests the presence of a significant anisotropy and low-lying excited states,[15] consistent with the observed non-superposition of the M versus H/T curves at different magnetic fields (Figure S5).

The large magnetization values of **1** and **3** are helpful for enhanced MCEs. The magnetic entropy change ΔS_m can be obtained from the Maxwell relation as follows: $\Delta S_m(T)_{\Delta H} = \int[\partial M(T,H)/\partial T]_H \, dH$.[5,6] As shown in Figure 4, the value of $-\Delta S_m$ for **1** is 41.26 J kg^{-1} K^{-1} at 2 K for $\Delta H = 7$ T. This is smaller than the value of 51.86 J kg^{-1} K^{-1} calculated for the spins of 42 uncorrelated Gd^{3+} ($S_{Gd} = {}^7/_2$) and nine Co^{2+} ($S_{Co} = {}^3/_2$) ions using the equation $-\Delta S_m = nR \ln(2S + 1) = 42R \ln(8) + 9R \ln(4) = 99.8R$, but it is much larger than any other known $-\Delta S_m$ value calculated by the same method and is comparable to the highest value calculated by Evangelisti and co-workers using heat capacity data.[10] The large MCE observed may be attributable to the large metal/ligand mass ratio. For **3**, $-\Delta S_m$ value of 38.2 J kg^{-1} K^{-1} at 2 K and $\Delta H = 7$ T is also smaller than the corresponding calculated value of 49.10 J kg^{-1} K^{-1} expected for 42 uncorrelated Gd^{3+} and 10 Ni^{2+} ions ($S_{Ni} = 1$). That the entropy changes of **1** and **3** are both smaller than the respective theoretical values suggests the presence of intracluster antiferromagnetic interactions and crystal-field effects.[11] The larger $-\Delta S_m$ value for **1** than for **3** can be rationalized in terms of the larger ground-state spin of Co^{2+} in **1** relative to Ni^{2+} in **3**.

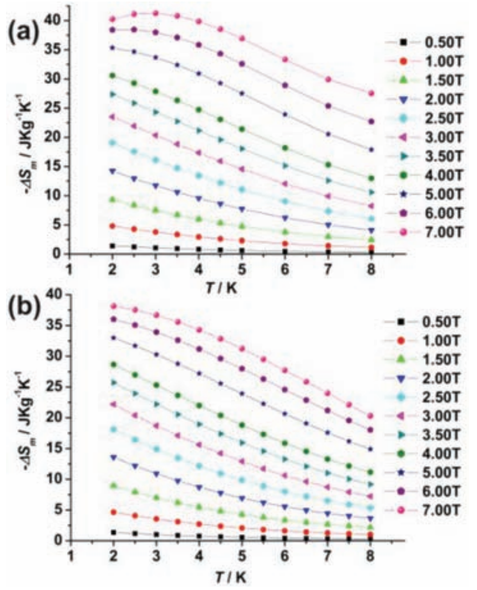

Figure 4. Values of $-\Delta S_m$ calculated using the magnetization data for (a) **1** and (b) **3** at various fields (0.5−7 T) and temperatures (2−8 K).

Heat capacity measurements were also performed to investigate the MCEs of **1** and **3**. Figure 5a,b shows the temperature dependence of the heat capacities of **1** and **3** over the 2.0−25 K temperature range at applied fields (B_0) of 0, 1, 3, 5, and 7 T. The corresponding magnetic entropy changes ΔS_m (Figure 5c,d) were then obtained from the heat capacity data using the equation $\Delta S_m(T, B) = \int[C(T', B) - C(T', 0)]/T' \, dT'$.[19−21] The values of ΔS_m at 2 K were calculated from the magnetization data, as we could obtain heat capacity data down to only ~2 K because of the limitations of our instrument. As shown in Figure 5c,d, the $-\Delta S_m$ values determined using the heat capacity data are in perfect agreement with those obtained from the magnetization data, demonstrating that the use of our approximate $-\Delta S_m$ at 2 K did not alter our evaluation of ΔS_m for **1** and **3**. The ΔT could not be obtained because of the lack of heat capacity data below 2 K. The refrigerant capacities (RCs) of **1** and **3** were found using the equation $\mathrm{RC} = \Delta S_m(T_h - T_c)$.[19−21] Taking T_h and T_c as the temperatures of the half-maxima of the peak in the $\Delta S_m(T)$ function gave RC values of ca. 280 and 210 J/kg for **1** and **3**, respectively, for $\Delta B = 7$ T and T_c taken as approximately 1 K. These RC values are significantly higher than those reported for molecule-based magnetic materials in the temperature range below 20 K.[19a]

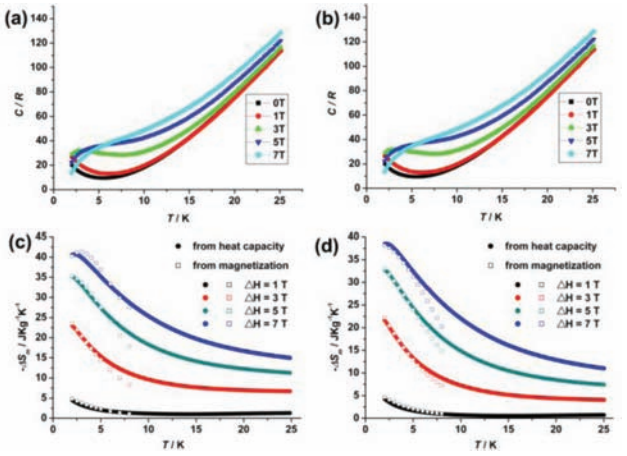

Figure 5. (top) Temperature dependence of the heat capacities of (a) **1** and (b) **3** (normalized to the gas constant R) collected at $B_0 = 0$, 1, 3, 5, and 7 T. (bottom) Temperature dependence of ΔS_m for (c) **1** and (d) **3** as obtained from the heat capacity data and the magnetization data for the indicated field changes.

In view of the significant anisotropy inherent to Dy^{3+},[22,23] alternating-current (ac) magnetic susceptibility measurements were performed to probe the dynamics of magnetization for **2** and **4**. Such measurements were carried out over the temperature range 2.0−10 K with a zero dc field and a 3.0 Oe ac field at various frequencies from 1 to 1500 Hz. Both **2** and **4** displayed frequency-dependent out-of-phase signals, indicating slow relaxation of the magnetization (Figure S6). However, maxima of the out-of-phase susceptibility signals were not observed because of fast quantum tunneling of the magnetization. As a result, the energy barrier could not be obtained from fitting the Arrhenius expression.[24,25] However, if it is assumed that there is only one characteristic relaxation process, the energy barrier and τ_0 values can be obtained from fits of the ac susceptibility data by adopting the Debye model and using the equation $\ln(\chi''/\chi') = \ln(\omega\tau_0) + E_a/k_BT$, which has been applied in the literature for cluster compounds.[25] This gave $\tau_0 = 9.78 \times 10^{-7}$ s and $E_a = 3.67$ K for **2** (Figure S7a) and $\tau_0 = 1.27 \times 10^{-6}$ s and $E_a = 3.43$ K for **4** (Figure S7b).

In summary, four 52-metal-ion 3d−4f cluster complexes with acetate ligands were synthesized. The two Gd^{3+}-containing clusters, $Gd_{42}Co_{10}$ and $Gd_{42}Ni_{10}$, exhibit impressively large MCEs, which is significant for their potential application in developing magnetic cooling technology in the ultralow temperature range. Their Dy^{3+}-containing cognates $Dy_{42}Co_{10}$ and $Dy_{42}Ni_{10}$, on the other hand, display slow relaxation of the magnetization, largely because of the anisotropy of Dy^{3+}. Our results clearly establish the validity of the anion-templated synthesis using small organic ligands in producing giant clusters that are not only structurally aesthetic but also magnetically stimulating.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and characterization details and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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