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Beauty, Symmetry, and Magnetocaloric Effect—Four-Shell Keplerates with 104 Lanthanide Atoms

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Supporting Information

ABSTRACT: The hydrolysis of $Ln(ClO_4)_3$ in the presence of acetate leads to the assembly of the three largest known lanthanide-exclusive cluster complexes, $[Nd_{104}(ClO_4)_6(CH_3COO)_{60}(\mu_3\text{-}OH)_{168}(\mu_4\text{-}O)_{30}(H_2O)_{112}]\cdot(ClO_4)_{18}\cdot(CH_3CH_2OH)_8\cdot xH_2O$ (**1**, $x \approx 158$) and $[Ln_{104}(ClO_4)_6(CH_3COO)_{56}(\mu_3\text{-}OH)_{168}(\mu_4\text{-}O)_{30}(H_2O)_{112}]\cdot(ClO_4)_{22}\cdot(CH_3CH_2OH)_2\cdot xH_2O$ (**2**, Ln = Nd; **3**, Ln = Gd; $x \approx 140$). The structure of the common 104-lanthanide core, abbreviated as $Ln_8@Ln_{48}@Ln_{24}@Ln_{24}$, features a four-shell arrangement of the metal atoms contained in an innermost cube (a Platonic solid) and, moving outward, three Archimedean solids: a truncated cuboctahedron, a truncated octahedron, and a rhombicuboctahedron. The magnetic entropy change of $\Delta S_m = 46.9$ J kg^{-1} K^{-1} at 2 K for $\Delta H = 7$ T in the case of the Gd_{104} cluster is the largest among previously known lanthanide-exclusive cluster compounds.

Nature has never ceased to amaze us with its complexity and beauty, which are frequently associated with the symmetry of the object. Such structural aesthetics is shared by certain human-made molecules whose syntheses are either directly inspired by natural beauty or mere synthetic serendipity. A particularly enlightening example is the seminal discovery of buckminsterfullerene (C_{60}).[1] Its exquisite symmetry and overall structural beauty have inspired the search for molecules of comparable symmetry but distinctly different chemical composition and properties.[2−4]

However, high-symmetry molecules are not limited to fullerene-like species. Chemical entities possessing the same symmetries as those of convex uniform polyhedra, namely, Platonic and Archimedean solids, are undeniably attractive.[5−9] Even more sophisticated are molecular or supramolecular architectures in which component Platonic and Archimedean polyhedral units are integrated in such a way that one polyhedron is inside the other, like Russian dolls.[10,11] Such structures are herein referred as "keplerates", a term introduced by Müller and coworkers for the description of metal-oxo nanocapsules with icosahedral symmetry.[12]

A few years ago, in search of molecules with novel magnetic properties, we obtained a heterometallic complex with a double-shell core, denoted as $La_{20}@Ni_{30}$, featuring a dodecahedron (a Platonic solid) of La(III) ions encaged by an icosidodecahedron (an Archimedean solid) of Ni(II) ions.[13] More recently, we obtained three 60-metal lanthanide hydroxide clusters.[14] Though not exactly of a keplerate structure, the cluster core displays a fascinating double-shell structure with a truncated octahedron (an Archimedean solid) of 24 lanthanide atoms encapsulating a doubly truncated octahedron of 36 lanthanide atoms. In both cases, the polyhedral cluster cores are "passivated" by organic ligands. These magnetically interesting clusters are of potential interest to the development of magnetic cooling, a technology that is highly desirable and being actively pursued because of the anticipated compactness, energy efficiency, and environmental benignness.[15−20] Furthermore, magnetic cooling is of particular interest in achieving ultralow temperatures, as there is no need to use increasingly rare and expensive helium-3 as a coolant.

Key to the potential magnetic cooling application of a substance is its large magnetocaloric effect (MCE), a magnetothermodynamic phenomenon in which a reversible change in temperature of a suitable material is caused by its exposure to a changing magnetic field.[21−23] Chemical and structural analyses of compounds with large MCEs have revealed a number of shared features, one of which is a high magnetic density due to the large metal/ligand mass ratio, especially when small ligands are used.[24−26]

Recognizing that the surface of a spherical architecture like C_{60} is minimized compared with other geometric shapes, we submit that the metal/ligand mass ratio of a molecule, which translates into its magnetic density, should be maximized if a metal cluster core is contained in a sphere (vs other architectures) surfaced by small organic ligands. Herein we report three such spherical cluster complexes, $[Nd_{104}(ClO_4)_6(CH_3COO)_{60}(\mu_3\text{-}OH)_{168}(\mu_4\text{-}O)_{30}(H_2O)_{112}]\cdot(ClO_4)_{18}\cdot(CH_3CH_2OH)_8\cdot xH_2O$ (**1**, $x \approx 158$) and $[Ln_{104}(ClO_4)_6(CH_3COO)_{56}(\mu_3\text{-}OH)_{168}(\mu_4\text{-}O)_{30}(H_2O)_{112}]\cdot(ClO_4)_{22}\cdot(CH_3CH_2OH)2\cdot xH_2O$ (**2**, Ln = Nd; **3**, Ln = Gd; $x \approx 140$), that are self-assembled upon hydrolysis of a

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mixture containing $\mathrm{Ln(ClO_4)_3}$ (Ln = Nd, Gd), $\mathrm{Co(CH_3COO)_2{\cdot}4H_2O}$, and *N*-acetyl-D-glucosamine, a reaction originally aiming at the production of high-nuclearity heterometallic cluster complexes. Beyond the pleasing molecular structures shared by these cluster complexes, the 104-Gd cluster **3** was shown to possess a large MCE.

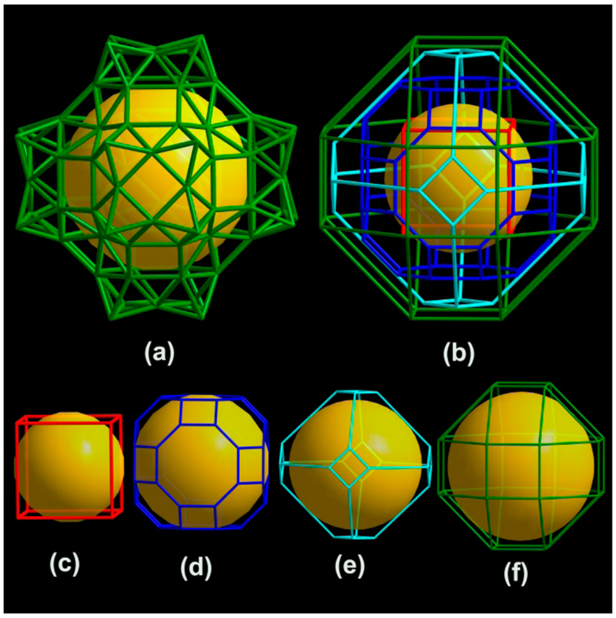

Figure 1. (a) Arrangement of the 104 metal ions in the cluster core of **1**. (b) Nested four-shell arrangement of the 104 metal ions. (c) The eight-Nd (4.4.4) shell with a diameter of 0.86 nm for the inscribed sphere. (d) The 48-Nd (4.6.8) shell with a diameter of 1.52 nm for the inscribed sphere. (e) The 24-Nd (4.6.6) shell with a diameter of 1.47 nm for the inscribed sphere. (f) The 24-Nd (3.4.4.4) shell with a diameter of 2.06 nm for the inscribed sphere.

The crystal structure of compound **1** is detailed to illustrate the salient features shared by the three isostructural compounds. Figure 1 shows a common cluster core with its 104 lanthanide atoms organized into four distinct shells. From the innermost outward, the core, denoted as $\mathrm{Nd_8@Nd_{48}@Nd_{24}@Nd_{24}}$, features a cube of eight Nd atoms (a Platonic solid), a truncated cuboctahedron of 48 Nd atoms (an Archimedean solid), a truncated octahedron of 24 Nd atoms (an idealized Archimedean solid), and a rhombicuboctahedron of 24 Nd atoms (an idealized Archimedean solid), with each of the vertices occupied by a Nd atom. Interestingly, extensive bridging interactions through acetate ligand and hydroxo groups exist within and between shells. We note that all of the polyhedra in this keplerate belong to the cubic system, each possessing an octahedral symmetry. A truncated octahedral arrangement of lanthanide atoms was previously observed in our recent report of 60-metal lanthanide hydroxide cluster complexes, in which each vertex of the polyhedron is occupied by a cubelike $[\mathrm{Ln_4}(\mu_3\text{-OH})_4]^{8+}$ unit rather than by a single lanthanide ion as in the present case.[14]

Including the metal-bridging oxo (O) and hydroxo (OH) groups, the cationic cluster core of $[\mathrm{Nd_{104}}(\mu_3\text{-OH})_{168}(\mu_4\text{-O})_{30}]^{84+}$ displays a giant cagelike structure (Figure 2a). It can be conveniently viewed as constructed by using 24 square-pyramidal $[\mathrm{Nd_5}(\mu_4\text{-O})(\mu_3\text{-OH})_4]^{9+}$ units (Figure 2b) and eight $[\mathrm{Nd}(\mu_3\text{-OH})_6]^{3-}$ units (Figure 2d). Four square-pyramidal building blocks centered around a μ_4-O^{2-} group are joined together by sharing of corners to produce an unprecedented 16-metal wheel, $[\mathrm{Nd_{16}}(\mu_4\text{-O})_5(\mu_3\text{-OH})_{20}]^{18+}$ (Figure 2c). Six such wheel-like assemblies are further linked by the eight $[\mathrm{Nd}(\mu_3\text{-OH})_6]^{3-}$ units to generate the cagelike structure, whose nanoscopic interior houses 8 aqua ligands, 8 guest $\mathrm{H_2O}$ molecules, 6 $\mathrm{ClO_4}^-$, and 12 acetate ligands with inwards orientations. We note that acetate is a time-honored supporting ligand for the assembly of high-nuclearity cluster complexes.[27−29] The formal assembly of the cluster core is shown in Figure 3. The cationic cluster core is enveloped by 60 acetate anions with outwards orientations and 104 terminal aqua ligands, leading to the nanoscopic and highly symmetric molecule whose structural beauty is comparable to that of the celebrated buckminsterfullerene and nanocapsules of polyoxometalates.[4]

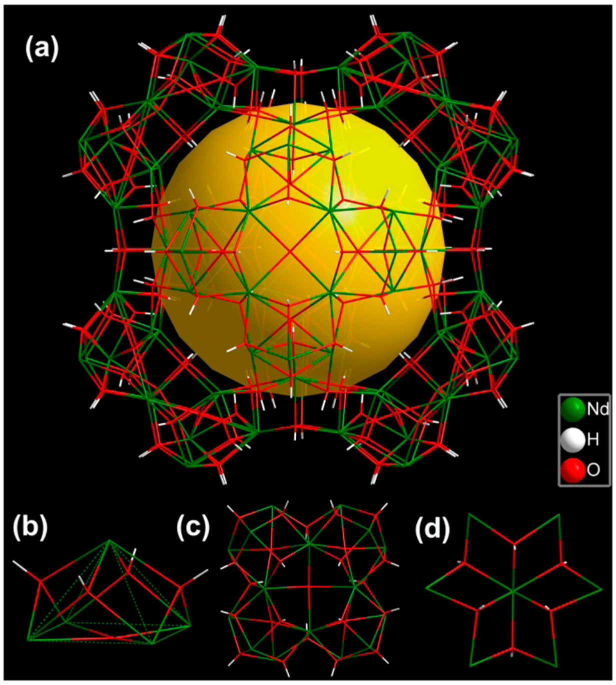

Figure 2. (a) Plot of the cationic cluster core of $[\mathrm{Nd_{104}}(\mu_3\text{-OH})_{168}(\mu_4\text{-O})_{30}]^{84+}$ in compound **1**. (b) Plot of the square-pyramidal $[\mathrm{Nd_5}(\mu_4\text{-O})(\mu_3\text{-OH})_4]^{9+}$ unit. (c) Plot of a caplike $[\mathrm{Nd_{16}}(\mu_4\text{-O})_5(\mu_3\text{-OH})_{20}]^{18+}$ structure featuring four corner-sharing square-pyramidal $[\mathrm{Nd_5}(\mu_4\text{-O})(\mu_3\text{-OH})_4]^{9+}$ units centered around a μ_4-O group. (d) Plot of the $[\mathrm{Nd}(\mu_3\text{-OH})_6]^{3-}$ unit that bridges three adjacent $[\mathrm{Nd_{16}}(\mu_4\text{-O})_5(\mu_3\text{-OH})_{20}]^{18+}$ units.

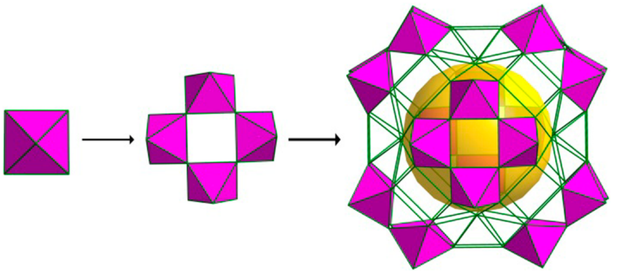

Figure 3. Formal assembly of the $\mathrm{Ln_{104}}$ cage. Purple polygons represent the square-pyramidal $[\mathrm{Nd_5}(\mu_4\text{-O})(\mu_3\text{-OH})_4]^{9+}$ units.

The temperature dependence of the magnetic susceptibility of **3** was measured over the temperature range from 300 to 2.0 K with an applied magnetic field of 1000 Oe (Figure S4 in the Supporting Information). The measured $\chi_\mathrm{M}T$ value of 804.26 $\mathrm{cm^3\ mol^{-1}\ K}$ at 300 K agrees well with the value of 819.52 $\mathrm{cm^3}$

mol^{-1} K expected for 104 uncoupled Gd(III) ions ($S = {}^{7}/_{2}, g = 2$). This value remains essentially constant upon lowering of the temperature to about 120 K. From 120 to 2 K, the $\chi_M T$ value decreases gradually to 735.22 cm^3 mol^{-1} K at 40 K and then to 278.48 cm^3 mol^{-1} K at 2 K. These changes may be ascribed to the dominant antiferromagnetic interactions between the Gd(III) ions.[30] The data over the range of 2−300 K can be fitted to the Curie−Weiss law, yielding C = 813.00 cm^3 K mol^{-1} and θ = −4.11 K. Magnetization measurements on **3** at low temperatures were also performed (Figure 4a); at 2 K, the saturation value of 708.43 NμB was obtained.

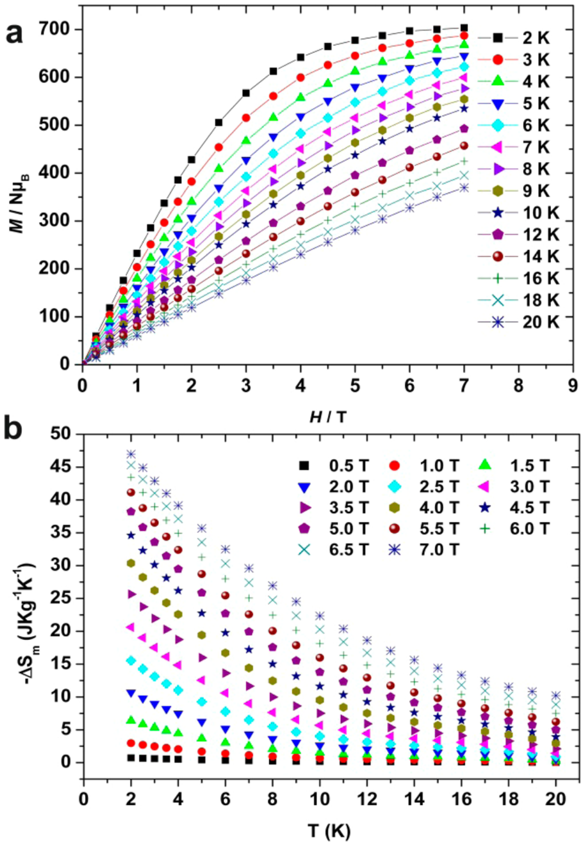

Figure 4. (a) Field-dependent experimental magnetization plots for **3** at the indicated temperatures. (b) Calculated changes of magnetic entropy for **3** at various fields and temperatures.

Magnetization data can be used to estimate the magnetic entropy change ΔS_m by making use of the Maxwell relation, $\Delta S_m(T)\Delta H = \int [\partial M(T,H)/\partial T]H\, dH$.[15−20] At 2 K and ΔH = 7 T, the calculated $-\Delta S_m$ value of 46.9 J kg^{-1} K^{-1} is the largest among previously known lanthanide-exclusive cluster compounds.[19] Probably responsible are the presence of low-lying excited spin states and the high magnetic density of the high-nuclearity Gd cluster, both of which favor a large MCE.

To further investigate the magnetothermal effect of **3**, the temperature-dependent heat capacities (C) at different fields were measured. Figure 5a shows the temperature dependence of C/R for selected applied magnetic fields (B_0 = 0, 1, 3, 5, and 7 T). At lower temperatures, the experimentally obtained C values are dominated by the magnetic contribution of the applied field, whereas nonmagnetic contributions due to thermal vibrations of the lattice are dominant at higher temperatures. Such effects were fitted using a modified Debye model. Specifically, the data were analyzed using a first term representing the high-temperature component of the magnetic specific heat and a second term reflecting the lattice contribution. Fitting between 3.2 and 11 K (Figure 5a) yielded a = 2.83923 J K mol^{-1}, b = 0.00101 J K^{-c-1} mol^{-1}, and c = 2.49. The deviation of c from the value used in the standard Debye model (c = 3) may be an indication of the presence of vibrational modes present in Platonic and Archimedean solids.

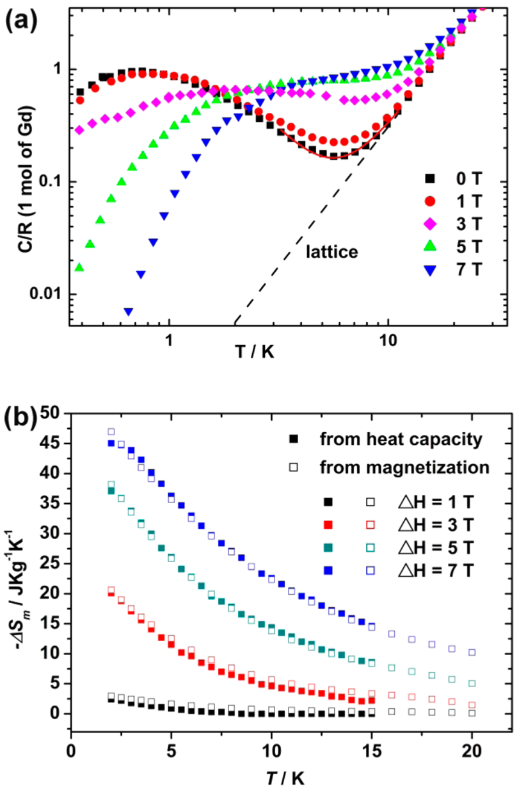

Figure 5. (a) Temperature dependence of the heat capacity C normalized to the gas constant R for **3** at various fields. The solid red line represents the results of the fit, and the dashed black line is the estimated lattice contribution. (b) Temperature-dependence of the magnetic entropy change derived from heat capacity C and magnetization data at various fields.

The magnetic entropy S of compound **3** was then obtained from the heat capacity data by numerical integration using $S_m = \int C_m/T\, dT$, where the magnetic heat capacity C_m was obtained by subtracting the lattice contribution from C. As shown in Figure S5, the zero-field S_m increases rapidly to 54.4 J kg^{-1} K^{-1} at 2.6 K and then more slowly to saturation at 9 K, reaching the anticipated value of 59.1 J kg^{-1} K^{-1} based on $S_m = nR\ln(2S+1) = 104R\ln(8) = 216.3R$ (assuming $S_{Gd} = {}^{7}/_{2}$).

The temperature dependence of $-\Delta S_m$ can be calculated from the temperature dependence of the entropy, and the results are presented in Figure 5b. A value of 46.6 J kg^{-1} K^{-1} at 2 K for an applied magnetic field change of 7 T was obtained, in excellent agreement with that derived from the magnetization data (46.9 J kg^{-1} K^{-1} at 2 K). The volumetric magnetic entropy change (in units of mJ cm^{-3} K^{-1}) is very important for assessing the applications of refrigerant materials. For the present Gd$_{104}$ cluster, the 104 metal ions are contained in a sphere, affording a density of 2.945 g cm^{-3}, which is significantly higher than those of previously reported molecular-based refrigerant materials. Thus, the Gd$_{104}$ cluster shows a very large volumetric magnetic entropy change of 137.2 mJ cm^{-3} K^{-1} for the applied field change

ΔH = 7 T. This is the largest value reported for lanthanide-exclusive cluster compounds.

In summary, three nanoscopic lanthanide-exclusive keplerate clusters have been synthesized. The beautiful 104-metal core structure shared by the isostructural compounds feature a four-shell arrangement of the metal atoms with an innermost cube (a Platonic solid) and, moving outward, three successively circumscribing Archimedean solids: a truncated cuboctahedron, a truncated octahedron, and a rhombicuboctahedron. One of these compounds, the Gd_{104} cluster complex, possesses one of the largest changes in entropy with changing field known for lanthanide-exclusive cluster molecular materials and is of interest for its application in magnetic cooling. The present results validate our strategy for making cluster-based molecular magnetocaloric materials. We are presently attempting the preparation of other magnetic clusters with large MCEs by controlling the reaction conditions, including the use of other metal ions, small organic ligands, and templating anions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and characterization details and CIF files for **1**−**3**. 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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