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Heterometallic Clusters

A Four-Shell, Nesting Doll-like 3d–4f Cluster Containing 108 Metal Ions**

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High-nuclearity metal complexes are a unique class of molecules.[1–6] Often in the nanoscopic size regime, they display fascinating structural diversity and possess properties that are potentially useful for developing novel catalysts,[1] materials for adsorption and storage,[2] molecular electronics,[3] optics,[4] and magnetism.[5,6]

Particular interest in this field has been directed towards heterometallic complexes that feature both d- and f-block elements, and the distinct coordination behaviors of different metal ions have been observed in a large number of stunningly beautiful complexes.[7–17] The unique arrangement of the multiple metal centers within the complex framework, coupled with their inherently disparate electronic structures, often leads to attractive properties, of which novel magnetic phenomena such as single-molecule[14,15] and single-chain magnetism[16,17] are arguably the most notable.

Our own efforts along this line of research have resulted in a number of giant 3d–4f clusters containing up to 50 metal ions.[18,19] These clusters display both stunningly beautiful structures and magnetic behaviors ranging from ferromagnetic to antiferromagnetic couplings. Herein we report the synthesis, structure, and magnetic studies of a giant heterometallic cluster containing 108 metal ions. This compound, formulated as $[Gd_{54}Ni_{54}(ida)_{48}(OH)_{144}(CO_3)_6(H_2O)_{25}](NO_3)_{18}\cdot 140\,H_2O$ (**1**; ida = iminodiacetate) based on crystallographic analysis,[20] was obtained under hydrothermal conditions from a mixture of $Ni(NO_3)_2\cdot 6\,H_2O$, $Gd(NO_3)_3\cdot 6\,H_2O$, and iminodiacetic acid in deionized water and its composition was verified by satisfactory microanalysis.

The four-shell, nesting doll-like structure of the cationic cluster is shown in Figure 1 a. Moving outward, the innermost shell (shell 1) contains six Ni^{II} and two Gd^{III} ions and is followed by shell 2 with 20 Gd^{III} ions, shell 3 with 32 Gd^{III} ions, and the outermost shell (shell 4) with 48 Ni^{II} ions (Figure 1 b). The geometry of the shells approximates that of a cube. Inter-shell connections are provided primarily by triply bridging hydroxo groups, which afford a highly compact, brucite-like core structure. Similar structural motifs have been observed in both transition metal[21] and lanthanide clusters.[22] The appearance of the multi-shell structure is comparable to those of multi-shell Pd/Pt clusters,[23,24] nanocapsules of polyoxometalates,[25] and fullerene-like structures built from interpenetrating reciprocal polyhedra.[26,27]

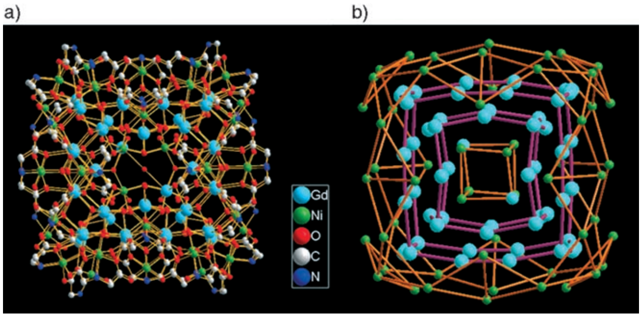

Figure 1. a) A ball-and-stick view of the cationic cluster of **1**; b) a four-shell presentation of **1** showing only the metal frameworks.

Six Ni^{II} and two Gd^{III} ions occupy the vertices of the cube in shell 1 (Figure 2 a). The Gd^{III} ions, which are disposed diagonally, are bridged by an aqua ligand. Triply bridging OH groups, each of which bridges two neighboring metal ions (Gd or Ni) within the cube and a Gd^{III} ion at the edge center of shell 2, form the 12 cube sides (Figure 2 b). The coordination sphere of each of the eight metal ions is completed by three additional μ_3-OH groups. All Ni^{II} ions are therefore hexa-

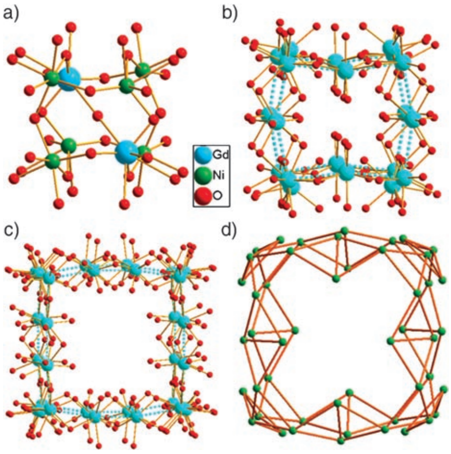

Figure 2. Ball-and-stick view of individual shell structures: Gd_2Ni_6 (shell 1, a), Gd_{20} (shell 2, b), Gd_{32} (shell 3, c), Ni_{48} (shell 4, d).

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coordinate and form distorted octahedra, whereas the Gd^{III} ions are heptacoordinate. Complexes with heptacoordinate Gd^{III} ions, though less common, have been reported.[28] Each of the metal ions in shell 1 is situated near one corner of shell 2 formed by a vertex Gd^{III} ion and its three edge neighbors; a μ_3-OH group connects the shell 1 metal ion, the shell 2 vertex Gd^{III} ion, and one of the three edge Gd^{III} ions. The distances between neighboring metal ions (Ni···Ni: 3.542–5.357 Å (av 5.039 Å); Ni···Gd: 3.183–3.683 Å (av 3.522 Å); Gd···Gd: 3.101–4.016 Å (av 3.687 Å)) are all comparable to those reported for similar compounds.[29–31]

Shell 2, which encapsulates shell 1, contains 20 Gd^{III} ions. Its roughly cubic framework is distinctly different from those of the recently reported Ln$_{20}$ (Ln = La, Pr, Nd) clusters.[18,19] The disposition of the 20 metal ions, with eight of them being at the vertices and the rest in the middle of the cube edges, can be seen in Figure 2 b. A pair of μ_3-OH groups, one of which is coordinated to a shell 1 metal ion and the other to shell 3, connects each edge Gd^{III} ion to each of its two vertex neighbors (Figure 2 c). This latter cross-shell linking results in the presence of two Gd^{III} ions on each edge of the encasing shell 3; there should be $2\times 12 = 24$ edge Gd^{III} ions. Two additional ligands complete the coordination sphere of the heptacoordinate edge Gd^{III} ion, one of which is a μ_3-OH group that bridges two additional Gd^{III} ions in shell 3, while the other is an O atom from a carbonate ion generated in situ by the decomposition of ida.[18,19] This carbonato ligand crosses one of the six faces of the cube by bridging the two opposite edge Gd^{III} ions on that particular face. Six such bridging CO_3^{2-} ions contribute a total of 12 O atoms to the coordination spheres of the edge Gd^{III} ions. Each vertex Gd^{III} ion is bound to three additional μ_3-OH groups and is thus nonacoordinate. These μ_3-OH groups are connected to four Gd^{III} ions in shell 3, one vertex Gd^{III} ion, and three of its immediate edge neighbors: each of them bridges the vertex Gd^{III} ion, the corresponding vertex Gd^{III} ion in shell 3, and its immediate edge neighbor in exactly the same way as between shells 1 and 2.

There are 32 Gd^{III} ions in shell 3, with two Gd^{III} ions on each edge. There are three μ_3-OH groups between each pair of edge Gd^{III} ions, one of which bridges an edge Gd^{III} ion in shell 2 with the other two coordinating to two separate Ni^{II} ions from shell 4, the outermost shell (Figure 2 d). In other words, $2\times 12 = 24$ Ni^{II} ions in shell 4 are associated with the edge Gd^{III} ions. Furthermore, there are two μ_3-OH groups between each vertex Gd^{III} ion and each of its three immediate edge neighbors, one of which is used to connect to a vertex Gd^{III} ion of shell 2 and the other to connect to a Ni^{II} ion in shell 4. This results in the presence of 8 (vertices) $\times 3 = 24$ Ni^{II} ions. The coordination sphere of Gd^{III} is completed by ida ligands, via three carboxylato O atoms, each from a different ida ligand. Shell 3 is therefore intimately connected to the outermost shell of Ni^{II} ions and all Gd^{III} ions in shell 3 are nonacoordinate.

Shell 4, which contains 48 Ni^{II} ions, can be viewed as a truncated cube with each of its vertex being a triangle of Ni^{II} ions (Figure 3). Each cube edge is occupied by two Ni^{II} ions whose connection runs perpendicular to the edge itself. Although all Ni^{II} ions are situated in a distorted octahedral environment, three different types of Ni^{II} coordination are observed. The first type involves the Ni^{II} ions within the vertex-occupying triangle; each Ni^{II} ion features one primary ida ligand that contributes its N atom and two O atoms (one from each of its carboxylate groups) arranged in a facial fashion for coordination. These O atoms also coordinate two separate Gd^{III} ions in shell 3, while the two remaining carboxylato O atoms of the same ida ligand bridge two neighboring Ni^{II} ions, one within the same triangle and the other at the edge position. The carboxylate groups participate in these bridging interactions exclusively in an *anti–syn* fashion. There are two secondary ida ligands, each of which contributes one carboxylato O atom to fill two of the three remaining coordination sites. Thus, each of the Ni^{II} ions in the vertex triangle is connected to four neighbors. A μ_3-OH group *trans* to the N atom of the primary ida ligand completes the coordination sphere of the Ni^{II} ion and bridges two Gd^{III} ions from shell 3.

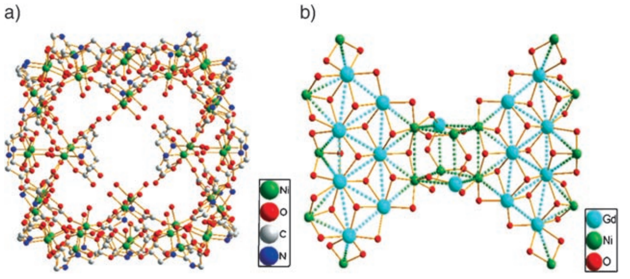

Figure 3. A ball-and-stick view of the outmost framework of $\{Ni(ida)\}_{48}$ (a) and the brucite-like cluster core structure (b).

The other two types of coordination involve the edge Ni^{II} ions. One of these types is very similar to that of the vertex Ni^{II} ion except that two carboxylato O atoms of the primary ida ligand remain uncoordinated. As such, only two Ni^{II} neighbors are associated with this particular edge Ni^{II} ion, which is linked in an *anti–syn* fashion by the secondary ida ligands. The third type of Ni^{II} coordination involves only primary ida ligands, which coordinate exactly the same as to the vertex Ni^{II} ions. Two aqua ligands take the place of the secondary ida ligands in the previous two cases. As a result, there are a total of $12\times 2 = 24$ aqua ligands in the molecule. Each of these type-3 Ni^{II} ions also has two Ni^{II} neighbors, which are connected by the two remaining carboxylato O atoms of the primary ida ligand rather than by two secondary ida ligands.

The magnetic susceptibilities of **1** measured in an applied field of 1000 Oe over the temperature range 2–300 K are shown in Figure 4 in the form of plots of $\chi_M T$ versus T. The $\chi_M T$ value of 463.0 cm^3 K mol^{-1} at 300 K is slightly smaller than the value of 479.49 cm^3 K mol^{-1} calculated for 54 uncorrelated Ni^{II} ions (53.97 cm^3 K mol^{-1} for $S = 1$, $g = 2.00$) and 54 uncorrelated Gd^{III} ions ($S = 7/2$, $g = 2$; 425.52 cm^3 K mol^{-1} using the Landé formula).[7] $\chi_M T$ decreases gradually upon lowering the temperature and reaches a value of 402.7 cm^3 K mol^{-1} at 2 K, thereby indicating the presence of antiferromagnetic interactions. The data over the temperature range 20–300 K fit well the Curie–Weiss equation with $C = 462.29$ cm^3 K mol^{-1} and $\Theta = -2.56$ K, which is consistent

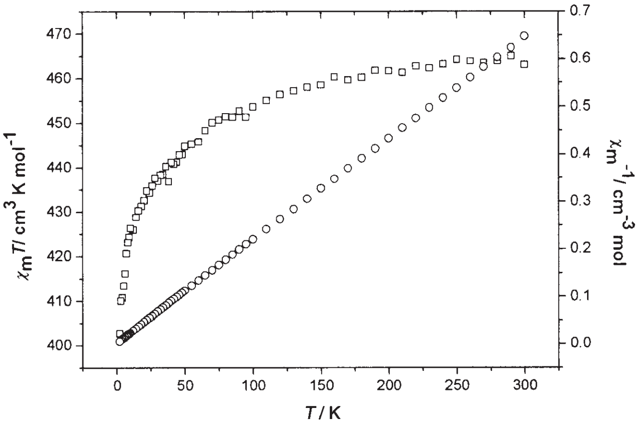

Figure 4. Plots of $\chi_M T$ (□) and χ_M^{-1} (○) for complex **1** over the temperature range 2–300 K.

with an overall antiferromagnetic coupling. This behavior can be ascribed to the exchange interactions between the metal ions (Ni···Ni, Ni···Gd, and Gd···Gd) via the bridging ligands.

It is difficult to quantify the individual contributions of the transition metal and the lanthanide ions due to the sophisticated framework structure. However, two recently reported heptanuclear complexes with a common $GdNi_6$ core that display similar key structural features to that of **1** are enlightening,[30,31] especially the predominantly ferromagnetic character of the magnetic coupling in both cases. Comparative studies with the isostructural $LaNi_6$ complex clearly suggest antiferromagnetic Ni···Ni superexchange.[30] On the basis of these results, it may be reasonable to assume that the ligand-mediated Ni···Ni antiferromagnetic interactions and, to a lesser degree, the Gd···Gd interactions, dominate the magnetic behavior of this cluster complex. Zero-field splitting of the Ni^{II} ground state may also contribute to the decrease of the $\chi_M T$ product upon lowering of the temperature. The field-dependence of the magnetization at 2 K appears to be saturated at 7 T to 465 Nβ (see the Supporting Information), which is smaller than the value expected if all spins were ferromagnetically aligned (486 Nβ).

In summary, a structurally fascinating heterometallic cluster containing 54 Ni^{II} and 54 Gd^{III} ions has been reported. The metal ions are arranged into an unprecedented four-shell, nesting doll-like structure, with triply bridging hydroxo groups providing extensive inter-shell connections to generate a compact, brucite-like giant cluster. Overall antiferromagnetic interactions are observed. We are presently attempting to synthesize analogs containing various combinations of 3d and 4f elements with an eye on systematic and comparative studies of the magnetic exchange in these sophisticated clusters.

Experimental Section

NaOH (1.00 M in H_2O) was added to a mixture of $Ni(NO_3)_2\cdot 6H_2O$ (0.727 g, 2.50 mmol), $Gd(NO_3)_3\cdot 6H_2O$ (0.451 g, 1.00 mmol), and iminodiacetic acid (0.266 g, 2.00 mmol) in deionized water (10.0 mL) to the point of incipient but permanent precipitation. The resulting mixture was transferred to a Parr Teflon-lined stainless-steel vessel (25 mL), heated to 180 °C over a period of 200 min, and maintained at this temperature for 6000 min. The mixture was then cooled to 100 °C over a period of 1000 min, kept at this temperature for 2000 min, and finally cooled to room temperature over a period of 2000 min. Block-shaped blue crystals were obtained in 50.0 % yield. C,H,N analysis (%) calcd for $C_{192}H_{634}Gd_{54}N_{66}Ni_{54}O_{533}$ (24130, based on 100 cocrystallized water molecules using a thoroughly dried sample): C 9.86, H 2.65, N 3.83; found: C 9.99, H 2.74, N 3.86. UV/Vis: λ = 390, 640 nm (see the Supporting Information).

Magnetic measurements were carried out with a Quantum Design SQUID MPMS magnetometer working in the 2–300 K range at a magnetic field of 1000 G. Diamagnetic corrections were made with Pascal's constants.

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