Communication

A Fan-Shaped Polynuclear GdCu Amino Acid Cluster: A "Hollow" and Ferromagnetic [Gd(□-OH)] Octahedral Core Encapsulated by Six [Cu] Glycinato Blade Fragments

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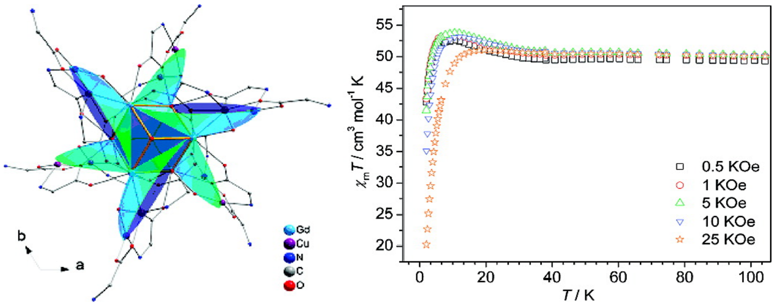

J|A|C|S COMMUNICATIONS

A Fan-Shaped Polynuclear Gd_6Cu_{12} Amino Acid Cluster: A "Hollow" and Ferromagnetic $[Gd_6(\mu_3\text{-}OH)_8]$ Octahedral Core Encapsulated by Six $[Cu_2]$ Glycinato Blade Fragments

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The cluster chemistry of high-nuclearity transition metals has been well-established over the past decades,[1] while that of lanthanides (Ln) is much less advanced[2,3] although the Ln clusters have their importance in biological applications[4] as well as in electronic,[5] optical,[3b,6] magnetic,[7] and catalytic materials.[8] Compared with the well-understood and deeply developed mechanisms responsible, respectively, for magnetic interactions of 3d−3d[9] and of 3d−4f ions,[10] the situation between lanthanides remains unclear due to the complexity with highly contracted 4f orbitals and the scarcity of experimental data. Except for a one-dimensional Gd^{3+} chain[11] and a few binuclear Gd^{3+} carboxylates reported with molecular ferromagnetism,[12] all homometal Ln_n oxo clusters ($n \geq 3$) exhibit magnetic noninteraction or antiferromagnetism.[2,13] Nevertheless, synthesis of ferromagnetic polynuclear Ln_n clusters is still a desired avenue to new high ground state spin materials,[14] since 4f elements have the potential to yield a large number of unpaired electrons and can introduce large magnetic anisotropy.

Sparked by the structural diversity and interesting properties found and proposed for 3d−4f clusters, interest in their rational syntheses has been increasing rapidly.[15,16] In this context, we concentrate our efforts on the 3d−4f clusters containing the Ln_n oxo cluster cores, because they not only can exhibit special properties similar to other 3d−4f clusters arising from the close proximity of dissimilar metal ions, but also can enrich the cluster chemistry of lanthanides with fascinating structures and inherit interesting physical properties from the Ln_n oxo cluster cores. Herein, by a stepwise growth process,[17] a high-nuclearity cluster $[Gd(H_2O)_8][Gd_6Cu_{12}(OH)_{14}(Gly)_{15}(HGly)_3(H_2O)_6]\cdot 16ClO_4\cdot 14H_2O$ (**1**) (HGly = glycine) containing a "hollow" and unprecedentedly ferromagnetic $[Gd_6]$ octahedral core was obtained.

Single-crystal X-ray analysis of **1** reveals a highly symmetrical molecule which features a crystallographically imposed $\bar{3}$ symmetry. Compound **1** is composed of a discrete octadecanuclear cation $[Gd_6Cu_{12}(OH)_{14}(Gly)_{15}(HGly)_3(H_2O)_6]^{13+} \equiv [Gd_6Cu_{12}]$, an octa-aqua Gd^{3+} ion, several perchlorates, and lattice water (Figure 1). There is one crystallographically independent Gd and two Cu atoms as well as three Gly ligands in the octadecanuclear cation (Figure 1a). The Cu1 and Cu2 ions adopt four-coordinated NO_3 square-planar and five-coordinated NO_4 square-pyramidal geometry, respectively, while the Gd1 ion adopts a nine-coordinated O_9 monocapped square antiprismatic geometry. The two Cu atoms are linked to form a binuclear copper−Gly fragment $[Cu_2(Gly)_3(OH)(H_2O)] \equiv [Cu_2]$ by one μ_3-O(3)H ligand as well as one Gly in a *syn−syn* binding mode. Six symmetry-related Gd1 atoms are connected by two μ_3-O(1)H and six μ_3-O(2)H groups to form a homometal octahedral cluster $[Gd_6(OH)_8] \equiv [Gd_6]$ (Figure 1b). The $[Gd_6]$ core is encapsulated by six symmetry-related $[Cu_2]$ fragments via the μ_3-O(3)H and another two Glys, leading the unique axial-fan-shaped cation $[Gd_6Cu_{12}]$ (Figure 1c). Each $[Cu_2]$ fragment as the blade of the fan is fastened by three Gd nails onto the fan axial−octahedral core. The two Glys in the blade employ a new mode to chelate a Cu^{2+} ion and further to coordinate two Ln^{3+} ions via their two O atoms. The octa-aqua Gd^{3+} ion in the periphery is disorder, similar to that observed in *p*-sulfonatocalix[4]arene systems.[18]

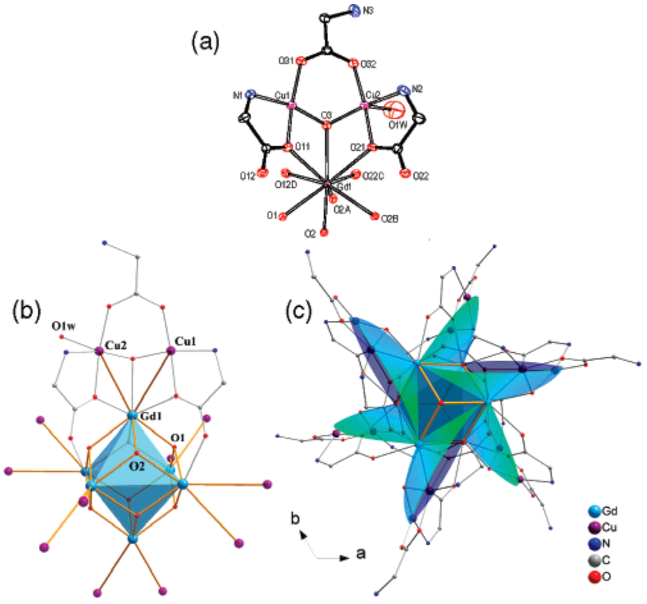

Figure 1. (a) ORTEP view of **1** at 30% probability level shows the coordination geometries of Gd^{3+} and Cu^{2+} atoms. Hydrogen atoms, perchlorates, octa-aqua Gd^{3+} ion, and lattice water molecules are omitted for clarity. The symmetry codes for A, B, C, and D are $1 - y$, $1 + x - y$, z; $2/3 + x - y$, $1/3 + x$, $1/3 - z$; $1/3 + y$, $1/3 - x + y$, $1/3 - z$ and $-x + y$, $1 - x$, z, respectively. (b) Six $[Cu_2]$ blades encapsulate an octahedral $[Gd_6]$ core to form a $[Gd_6Cu_{12}]$ cluster cation with an axial-fan shape viewed along the *c*-axis (c). Only one of the vertices of the $[Gd_6Cu_{12}]$ cluster is shown in (b). The bridging angle of Cu1−O3−Cu2 is 105.91°. The torsion angles of Gd1−O3−O11−Cu1 and Gd1−O3−O21−Cu2 are 173.06 and 173.27°, respectively.

Interestingly, compound **1** features the largest and hollow $[Gd_6]$ cluster without the support and "contracted" effect of a centered μ_6-oxo ligand. Except for the reported $[Tb_6]$ unit in the $[Tb_{14}]$ cluster[3] and an octa-coordinated hexanuclear Ce(IV) cluster,[19] all previously known octahedral $[Ln_6]$ clusters in molecular compounds have a μ_6-oxo ligand in the center of the octahedron, which is believed to play a key role in stabilizing the $[Ln_6]$ unit.[20] The absence of the μ_6-oxo ligand in the $[Gd_6]$ core of **1** leads to the larger Gd−μ_3-OH and Gd−Gd distances (ranges from 2.389 to 2.416 and 3.955 to 3.959 Å) and the Gd−μ_3-O−Gd angles (110.17−111.60°), in comparison with the corresponding distances (2.345−2.408 and 3.5612−3.6204 Å) and angles (97.81−99.62°) in the reported $[Gd_6]$ cluster perchlorate.[20c] Actually, to the best of

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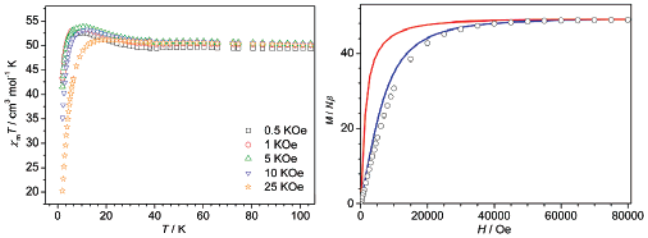

Figure 2. (left) Plot of experimental $\chi_m T$ versus T for **1** at H_{dc} of 0.5, 1, 5, 10, and 25 kOe. (right) Field dependence of the magnetization of **1** at 2 K (○) compared with the Brillouin function for seven uncoupled Gd^{3+} ions (blue line) and the Brillouin function for an $S = 42/2$ state plus an $S = 7/2$ state (red line).

our knowledge, the mean Gd$-\mu_3$-O$-$Gd angle of 110.92° in **1** is the largest one among the polynuclear [Gd_n] oxo clusters.

Temperature-dependent magnetic susceptibilities of **1** are measured from ground crystalline samples in the temperature ranges of 2−300 K under various applied fields and are shown in Figure 2 in the forms of $\chi_m T$ versus T per a molecule, where χ_m is the molar magnetic susceptibility as calculated with correcting for the diamagnetic contribution of the compound. At room temperature (300 K) and the field of 500 Oe, its $\chi_m T$ value is 48.8 cm^3 mol^{-1} K, compared with the expected values 59.6 cm^3 mol^{-1} K for free and noninteracting 12 Cu^{2+} ions and 7 Gd^{3+} ions. The difference may be a result from the strong antiferromagnetic contribution within the six [Cu_2] blades of the compound. Upon cooling, **1** shows a continuous slight increase in $\chi_m T$ and a subsequently much sharper increase below ca. 40 K with a maximum value 52.5 cm^3 mol^{-1} K at 10 K, suggesting **1** with an overall ferromagnetism, as confirmed by a positive Weiss constant (+0.8 K). Then the $\chi_m T$ drops rapidly to 42.8 cm^3 mol^{-1} K at 2 K, which is mainly attributed to the weak intermolecular antiferromagnetic coupling and the zero field splitting.[21] The similar situation is also observed at the fields of 1 and 5 kOe. The maximum value of $\chi_m T$ at 10 K slightly increases with the increasing field, and that of 53.8 cm^3 mol^{-1} K at 5 kOe is still smaller than the spin-only value, indicating the existence of the antiferromagnetic interaction or spin frustration. However, by further increasing the field (10 and 25 kOe), the data display significant field dependence, reaching a maximum that shifts to higher temperature. This behavior indicates the presence of a high-spin ground state.[22] The decrease of the maximum value at high fields and low temperatures may be attributed to the depopulation of the highest-energy Zeeman levels[22] and to the magnetic decoupling between Gd ions.[12a,23]

From two empirical formulas suggested by the pioneers, the interaction for Cu−Cu coupling (J') with the Cu−O−Cu angle (ϕ) of 105.91° may be of antiferromagnetic nature with a magnitude about 623.5 cm^{-1},[24] while that between Cu−Gd ions (J) with the dihedral angles (c) of 6.8° may be ferromagnetic with a magnitude about 8.0 cm^{-1}.[25] So the frustration will be occurred within the $GdCu_2$ trigon (Figure 1a). Indeed, the magnetization curve without a compromise gives a large saturated value of 48.9 $N\beta$, close to an expected value 49 $N\beta$ for seven Gd^{3+} ions (Figure 2). In the high-field regime (≥25 kOe), single-ion behavior of Gd^{3+} is observed. This suggests that, at the high field, the two unpaired electrons on each of the six [Cu_2] blades will be forced to be paired so that the spin frustration effect within the $GdCu_2$ trigon will be minimized. It is worth mentioning that, at 25 kOe, the weak ferromagnetism for **1** is still remained with a Weiss constant of +0.5 K (Figure S4). In the low-field regime, the magnetization values lie below the calculated curve for the isolated Gd^{3+} systems, indicating **1** as a ferrimagnet with strong spin frustration.

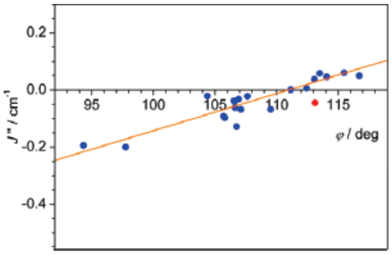

Figure 3. The dependence of the exchange parameters J'' for Gd^{3+} compounds with a Gd_2O_2 unit on the Gd−O−Gd bridging angle (φ). The red dot represents the exception with $J'' < 0$ and $\varphi > 110.9°$.[26]

The magnetic properties for **1** are dominated by three types of interactions of Cu−Cu, Cu−Gd, and Gd−Gd coupling. It is well-known that the interaction sequence 4f−4f < 4f−3d < 3d−3d is important as far as the mechanism of the interaction phenomenon is concerned.[10f,21] To interpret the magnetic phenomena of **1** and evaluate the magnetic interaction within the [Gd_6] core, we have collected the exchange and structural parameters of the complexes containing the GdO_2Gd unit (Table S1 and Figure 3), yielding the exchange parameters J'' between Gd ions

$$J'' = 0.0123\varphi - 1.364 \text{ cm}^{-1} \tag{1}$$

where φ is the mean Gd−O−Gd bridging angle. It can be concluded from eq 1 that $\varphi > 110.9°$ is a prerequisite for a GdO_2Gd complex being ferromagnetic. Although there is an exception with $J'' < 0$ and $\varphi > 110.9°$,[26] eq 1 reproduces well that φ values for all ferromagnetic Gd_2O_2 compounds are larger than 110.9°.[11,12] Additionally, two Gd_2 complexes bridged by a single oxo atom with the respective angles φ of 123.82 and 140.11° also exhibit the ferromagnetic behavior.[27] Among the polynuclear Gd clusters, the hollow [Gd_6] core in compound **1** has the largest mean Gd$-\mu_3$-O−Gd bridging angle (φ), which is slightly larger than the critical value above, suggesting a very weak ferromagnetic interaction with a magnitude about 0.00035 cm^{-1}. The strengths of the Cu−Cu and Gd−Cu coupling are, respectively, up to 10^6 and 10^4 times larger than the strength of the Gd−Gd coupling, so that the latter can be ignored. The magnetic structure of compound **1** can be described as six spin-frustrated $GdCu_2$ triangles plus one isolated Gd^{3+} ion. The simulation of the data set in the form of χ_m/6 (per $GdCu_2$ unit) versus T under 500 Oe field was carried out by employing the spin Hamiltonian for symmetrical ABA compounds[9] as given in eq 2:

$$H = -J(\boldsymbol{S}_{Gd}\cdot\boldsymbol{S}_{Cu1} + \boldsymbol{S}_{Gd}\cdot\boldsymbol{S}_{Cu2}) - J'\boldsymbol{S}_{Cu1}\cdot\boldsymbol{S}_{Cu2} \tag{2}$$

The best simulation was found with $g = 2.00$, $J = 9.6$ cm^{-1}, and $J' = -857.3$ cm^{-1} (Figure S5).

At 25 kOe field, if one considers that the saturation of ferromagnetic impurities[14] and the takeout of spin frustration within the $GdCu_2$ trigons, the magnetic structure for **1** can be seen as a Gd_6 octahedron. With the help of the program OW0Lb, the energy spectrum with the total dimensions of 18152 and the largest dimension of 1896 was obtained (Figure S6). The expression of χ_m resulting from the spectra was used to fit the magnetic data with the results $g_{Gd} = 2.051$ and $J'' = 0.0016$ cm^{-1} (Figure S7). The three fitting exchange constants are in agreement with their values estimated from the empirical formula. The magnetic properties for **1** are mainly predominated by the antiferromagnetic interaction of Cu−Cu coupling and the ferromagnetic interactions of Gd−Gd and of Gd−Cu coupling. The positive J'' values from the empirical estimation and data fitting confirm the very weak ferromagnetism for the [Gd_6] core, so the weak ferromagnetism for **1** still remains even at the field of 25 kOe. The [Gd_6] core in

1 is the first example of high-nuclearity Ln_n ($n \geq 3$) cluster exhibiting the molecular ferromagnetism, although the ferromagnetism was also observed in the intermetallic Gd compounds recently.[14]

Herein, we report an axial-fan-like and high-nuclearity 3d−4f cluster containing a hollow $[Gd_6]$ octahedral core. Without the support and contracted effect of a μ_6-oxo ligand, the $[Gd_6]$ core in **1** features the largest mean Gd−μ_3-OH−Gd bridging angle among the Gd_n ($n \geq 3$) oxo clusters, which brings unique molecular ferromagnetism into it. At the low field, **1** is a frustrated ferrimagnet, while it exhibits the single-ion behavior of Gd^{3+} ions at the high field. Further work on the cluster with other lanthanides, such as Tb^{3+} and Dy^{3+} ions, is underway to search for new single molecular magnets.

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Supporting Information Available: X-ray crystallographic data in CIF format, detailed synthesis process, and some supplementary figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) **Caution:** Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of materials should be prepared, and these should be handled with caution. The complexes described in this report have, so far, been found to be safe when used in small quantities.

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