Inorganic Chemistry
Communication
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A Dodecanuclear Dysprosium Wheel Assembled by Six Vertex-Sharing Dy_3 Triangles Exhibiting Slow Magnetic Relaxation

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Supporting Information

ABSTRACT: Reactions of lanthanide(III) (Ln^{III}) perchlorate (Ln = Dy and Ho) and a polydentate Schiff base resulted in the unprecedented assembly of novel Ln_{12} wheels containing six vertex-sharing Ln_3 triangles. The Dy_{12} derivative represents the largest lanthanide wheel based on the peculiar Dy_3 triangles showing slow magnetic relaxation.

Slow magnetic relaxation is an important property of molecular complexes that can bring technological breakthroughs to information storage and optical applications.[1,2] Because of the large intrinsic magnetic anisotropies of lanthanide (Ln) ions, Dy^{III}-based complexes have shown significant slow magnetic relaxation and obtained increased attention in the area of molecular magnets.[3−5] The magnetic anisotropy of an exchange-coupled system depends not only on the individual anisotropies of the metal ions but also on the relative orientation of the local axes.[6] In this respect, the design of a new dysprosium cluster with new topology might provide a unique opportunity to probe the relaxation dynamics of lanthanide aggregates, thus enriching the structure correlation to the magnetic properties of the dysprosium family.

The design of metallic wheels has caught great attention because of their aesthetically pleasing structures and unusual magnetic properties. Several wheel-shaped single-molecule magnets (SMMs) have been reported, mainly composed of transition-metal (TM) ions, such as Mn_{12}, Co_8, Fe_9, and Ni_{12}, and so on.[7] However, there are very few reported wheels of lanthanide ions.[8] A structurally unique wheel with high nuclearity could be synthesized through the careful selection of a suitable multidentate ligand. The Schiff bases obtained from the *o*-vanillin moiety have proven to be particularly suitable for the synthesis of 4f complexes with interesting magnetic properties. The assembly of the N_1,N_3-bis(3-methoxysalicylidene)diethylenetriamine ligand (H_2L; Scheme S1 in the Supporting Information, SI) with lanthanide salts in the presence of CO_3^{2-} ligands derived from atmospheric CO_2 produces novel dodecanuclear lanthanide wheels, $[Ln_{12}(L)_6(OH)_4O_2(CO_3)_6][Ln_{12}(L)_6(OH)_4O_4(CO_3)_6]\cdot(ClO_4)_4\cdot xH_2O$, where Ln = Dy (**1**), Ho (**2**) (see the SI), composed of six vertex-sharing Ln_3 triangle units in a staggered double-crown fashion. Recently, a peculiar triangular Dy^{III} cluster has attracted much interest because of its unusual slow relaxation brought about by the toroidal arrangement of local magnetization vectors.[9,10] The title wheel complexes are not only ones of very few lanthanide wheel complexes but also the largest lanthanide wheels consisting of peculiar triangular units, providing a valuable opportunity to probe the magnetization dynamics of such unique systems.

The reaction of $Ln(ClO_4)_3\cdot 6H_2O$ (Ln = Dy, Ho) with H_2L in a mixture of methanol and acetonitrile (1:2 ratio) in the presence of NEt_3 gave a pale-yellow solution from which yellow crystals of **1** and **2** were formed after 7 days. Single-crystal X-ray diffraction studies revealed that **1** and **2** were isomorphous (Table S1 in the SI); hence, only the details of **1** were given in the ensuing discussion. The structure consists of two crystallographically unique but structurally similar Dy_{12} units in the unit cell (denoted as a and b), as depicted in Figure 1.

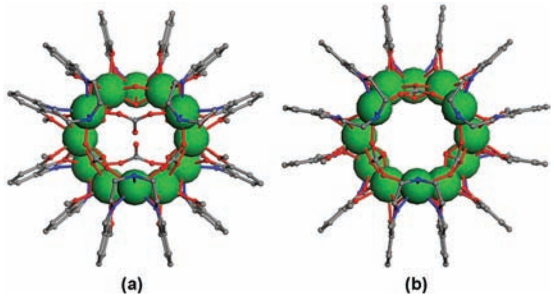

Figure 1. Ball-and-stick views of two crystallographically unique Dy_{12} units in the unit cell (a and b). Hydrogen atoms and solvent molecules are omitted for clarity.

Because of the structure similarity of these two Dy_{12} units, only a is described in detail. The cluster core is formed by 12 Dy^{III} ions, of which four are eight-coordinated with a distorted square-antiprismatic (SAP) geometry and grouped into two different types: Dy1 and Dy2 with O_8 coordination and Dy3 and Dy4 with N_3O_5 coordination. Each of the square planes of Dy1 with similar coordination configurations is constructed by one methoxy oxygen (O1), one deprotonated phenolic oxygen (O2) of the same ligand, one bridging μ_3-OH ligand, and one carbonate oxygen atom. The square plane of Dy2 is similar to that of Dy1, except that one carbonate oxygen atom is replaced by a μ_2-oxygen atom. The SAP geometries of Dy3 and Dy4 are the same, but each has two different square planes: one plane is composed of two imine nitrogen atoms and two phenolic oxygen atoms of the same ligand; the other plane is formed by

Received: March 19, 2012
Published: May 23, 2012

an imine nitrogen atom, one bridging μ_3-OH ligand, and two carbonate oxygen atoms (Figure S1 in the SI).

H_2L is wrapping around three dysprosium ions in such a way that the inner donors N_3O_2 of H_2L, namely, three nitrogen atoms and two phenoxido bridging oxygen atoms, coordinate one dysprosium ion, while the outer donors O_4 of H_2L, namely, two phenoxido bridging oxygen atoms and two methoxy oxygen atoms, coordinate with two other dysprosium ions (Figure 2a). The ligand displays two distinct coordination pockets for lanthanide ions. Both pockets accommodate heavy lanthanide ions such as Dy^{III} and Ho^{III}.[11] The formation of a dodecanuclear cluster is most likely due to the presence of NEt_3, which promotes deprotonation of H_2L. The deprotnated H_2L subsequently provides phenoxido bridging groups. The methoxy oxygen atom of the Schiff base chelates the Dy^{III} ion, which may play a crucial role in forming this large cluster. Moreover, to complete the coordination sphere of lanthanide ions, carbonate anions are coordinated to the ions. Both chelating and bridging capacities of the ligand, in combination with the carbonates, consolidate this Dy_{12} cluster. Space-filling views of a and b are depicted in Figure S2 in the SI.

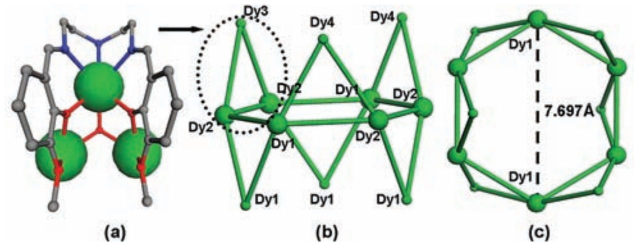

Figure 2. (a) Dy_3 triangle core showing coordination of the H_2L ligand. (b) Dy_{12} cluster core with six fused Dy_3 triangles reminiscent of a staggered double crown. (c) Dy_{12} cluster core with a six-membered ring of a diameter of 7.697 Å (Dy1⋯Dy1) viewed along the *a* axis.

For clarity, the large Dy_{12} cluster core can be regarded as an assembly of six vertex-sharing Dy_3 triangle motifs, as shown in Figure 2. Three Dy^{III} ions are linked by one μ_3-OH group to give a trinuclear core of $[Dy_3(\mu_3\text{-OH})]$, which is further stabilized by the voluble H_2L ligands, forming a Dy_3 subunit (Figure 2a). Six vertex-sharing Dy_3 subunits are further linked by six anionic carbonates as bridging ligands to form a Dy_{12} wheel with an approximately equilateral hexagonal six-membered ring of a diameter of 7.697 Å (Dy1⋯Dy1; Figure 2c). This novel Dy_{12} cluster is remarkably different from the reported $\{Dy_{12}(OH)_{16}\}^{20+}$ cluster core in terms of linkage modes.[6a] The adjacent capped Dy^{III} ions of the Dy_3 triangles are alternately positioned above and below the plane of the six-membered ring around the wheel. The Dy_{12} cluster core with six fused Dy_3 triangles assembled by three dysprosium ions through the wrapped ligand H_2L is reminiscent of a staggered double crown (Figure 2b).

The bridging carbonates have two coordination configurations in cluster a: four of the six carbonates are in the 4.1111 binding mode with each coordinating to four Dy ions, the other two are in the 2.11 binding mode with each coordinating to two dysprosium ions, leaving a terminal oxygen atom protruding into the six-membered ring (Figure S3a in the SI), while the six carbonates in cluster b are all in the 4.1111 binding mode with each coordinating to four Dy^{III} ions (Figure S3b in the SI).[12] Most likely, the presence of the carbonate anions can be ascribed to CO_2 fixation from the atmosphere, and the slow absorption of atmospheric CO_2 is consistent with the lengthy crystallization time required for the crystal growth from the solution. The IR stretching bands characteristic of coordinated carbonate are observed at 1528 and 1382 cm^{-1} (Figure S4 in the SI).[13] It has been previously shown that lanthanide hydroxido complexes and cages are able to modify their structures by incorporating CO_3^{2-} anions from atmospheric CO_2, thus constructing further aggregation and growth.[14]

Direct-current (dc) magnetic susceptibility studies of polycrystalline samples **1** and **2** were carried out in an applied magnetic field of 1000 Oe in the temperature range 2−300 K. The plots of $\chi_M T$ versus T for compounds **1** (Dy_{12}) and **2** (Ho_{12}) are shown in Figure 3. Both curves show similar thermal evolution at the high-temperature region. The $\chi_M T$ values are 147.02 and 143.98 cm^3 K mol^{-1} for **1** and **2** at room temperature (300 K), lower than the expected values of 170.04 and 169 cm^3 K mol^{-1} for 12 noninteracting Dy^{3+} ions ($^6H_{15/2}$; $g = {}^4/_3$) and Ho^{3+} ions ($^5I_8$; $g = {}^5/_4$), respectively.[15] For **1** and **2**, the $\chi_M T$ product gradually decreases until 100 K and then further decreases to reach a minima of 83.43 and 62.46 cm^3 K mol^{-1} at 2 K, respectively. The abrupt decrease of $\chi_M T$ at low temperature could be due to the antiferromagnetic interaction between Ln^{III} ions and the field saturation effect.

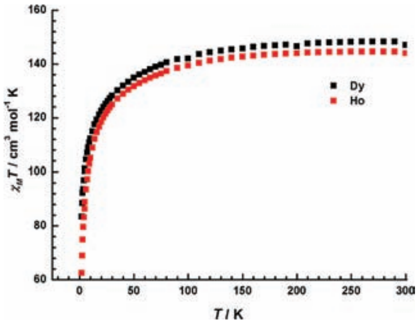

Figure 3. Plots of $\chi_M T$ vs T for **1** (Dy_{12}) and **2** (Ho_{12}) in a dc field of 1000 Oe (2−300 K).

The M versus H/T data at different fields show a rapid increase of the magnetization at low fields, reaching values of 59.59 and 59.53 μ_B at 1.9 K and 7 T for **1** and **2**, respectively (Figures S5 and S6 in the SI). The nonsuperimposed curves confirm the presence of anisotropy and/or low-lying excited states, which is expected for compounds containing anisotropic ions. The significant deviation from the expected magnetization saturation values (120 μ_B for 12 Dy^{III} or Ho^{III} ions) indicates a strong contribution from the ligand field. Given the interesting magnetic behavior of the Dy_3 triangle, the dynamics of the magnetization were investigated from the alternating-current (ac) susceptibility measurements. The results of the ac magnetic susceptibility measurements operating in a 3.0 Oe ac field oscillating at the indicated frequencies (3−1200 Hz) and with a zero dc field for **1** are depicted in Figures 4 and S7 in the SI as plots of χ'' versus T and χ' versus T. Frequency-dependent out-of-phase signals were observed, indicating the onset of slow magnetization relaxation. Although such ac signals were observed above 1.9 K, no hysteresis was detected in the M versus H data obtained using a traditional SQUID magnetometer, which may be caused by the presence of a relatively fast zero-field relaxation.[16] However, the potential SMM behavior of **1** has to be confirmed by further magnetic measurements such as magnetization versus dc field scans on

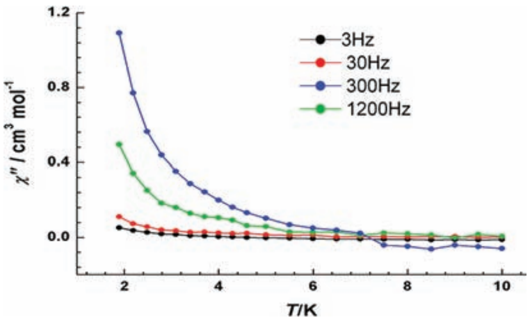

Figure 4. Temperature dependence of the out-of-phase ac susceptibility for **1** under a zero dc field.

single crystals using a micro-SQUID. The dynamics of the magnetization for **2** were also investigated using ac susceptibility measurements. However, no out-of-phase ac signal is detected for **2** under zero dc field (Figure S8 in the SI).

In summary, we have demonstrated the formation of two novel Ln_{12} wheel complexes with six vertex-sharing Ln_3 triangles arranged in a staggered double-crown fashion by incorporating the polydentate Schiff base ligand H_2L and CO_3^{2-} groups derived from the atmospheric CO_2. The Dy_{12} compound represents the largest lanthanide cluster based on the peculiar Dy_3 triangles, therefore opening a promising route toward the design of novel magnetic materials. Controlling the formation and understanding the properties of these unique structures may provide valuable information on the future manufacture of nanodevices based on magnetic properties related to well-defined molecular units.

■ ASSOCIATED CONTENT

S Supporting Information

X-ray crystallographic data in CIF format, detailed experimental procedures, and additional structural and magnetic data for complexes **1** and **2**. 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.

■ ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (Grants 91022009 and 20921002) for financial support. Prof. Yangguang Li and Dr. Peng Chen are gratefully acknowledged for structural refinements.

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