Inorganic Chemistry

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Trigonal Bipyramidal Dy_5 Cluster Exhibiting Slow Magnetic Relaxation

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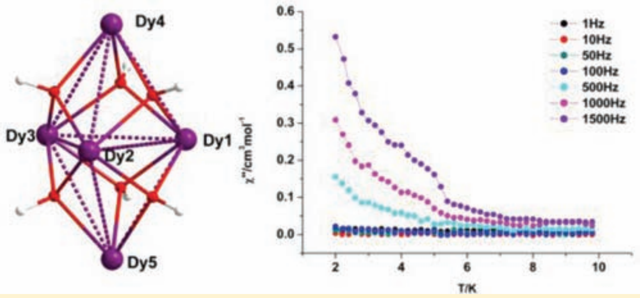
Supporting Information

ABSTRACT: A pentanuclear dysprosium cluster, $[Dy_5(\mu_3\text{–}OH)_6(Acc)_6(H_2O)_{10}]\cdot Cl_9\cdot 24H_2O$ (**1**), has been synthesized through the reaction of 1-amino-cyclohexanel-carboxylic acid (Acc) and $DyCl_3\cdot 5H_2O$. Crystal structural analysis reveals that the metal core of cluster **1** shows an unprecedented trigonal bipyramidal (TBP) geometry. Magnetic studies indicate that the Dy_5 cluster exhibits slow magnetic relaxation.



INTRODUCTION

Polynuclear lanthanide clusters have received much interest in the last two decades, because of their appealing structures and their interesting magnetic property.[1,2] Recently, chemists found that high spin lanthanide ions, especially the Dy^{3+} ion, are good candidates for constructing new SMMs, due to their large intrinsic magnetic anisotropy.[1,2] However, pure lanthanide-based SMMs are extremely rare not only because of the synthetic challenges, but also because of the difficulty in promoting magnetic interactions in these system.[3−8] Recent investigations on the cluster-based molecular magnetism indicate that the topology of the metal ions plays an important role in the magnetic properties, especially when dealing with strongly anisotropic metal ions such as Co(II) and Dy(III),[9] where the influence of the single ion anisotropies appears to have a considerable influence. Thus, synthesis of lanthanide clusters with different topologies is of fundamental importance for the understanding of the relationship between structures and properties of lanthanide-based SMMs.[6f]

Polynuclear lanthanide hydroxide clusters are an interesting class of metal clusters, because they can be rationally synthesized via a ligand-controlled hydrolytic approach.[7,8] On the basis of this approach, a large number of the isolated polynuclear lanthanide hydroxide complexes have been synthesized, such as Ln_3, Ln_4, Ln_5, Ln_6, Ln_7, Ln_8, Ln_9, Ln_{10}, Ln_{12}, Ln_{14}, Ln_{15}, Ln_{26}, and Ln_{60}.[4−8] Despite the distinctly different structures, an investigation of their structures indicates that these clusters are invariably formed with certain cluster motifs, such as triangular $Ln_3(\mu_3\text{-}OH)$ or $Ln_3(\mu_3\text{-}OH)_2$, planar $Ln_4(\mu_3\text{-}OH)_2$, tetrahedral (cubane-like) $Ln_4(\mu_3\text{-}OH)_4$, square pyramidal $Ln_5(\mu_3\text{-}OH)_4(\mu_4\text{-}O)$, and octahedral $Ln_6(\mu_3\text{-}OH)_8(\mu_6\text{-}O)$ (Figure 1). Accordingly, it is possible to construct different lanthanide hydroxide clusters under different reaction conditions, even with the same organic ligand adopted.

During the investigation of the preparation of lanthanide hydroxide clusters, we used 1-amino-cyclohexanel-carboxylic acid (Acc) as an ancillary ligand, and have reported a series of dinuclear, linear trinuclear and cubane-like tetranuclear lanthanide clusters.[10] As a continuation of our work in this field, we report here a pentanuclear dysprosium cluster, formulated as $[Dy_5(\mu_3\text{-}OH)_6(Acc)_6(H_2O)_{10}]\cdot Cl_9\cdot 24H_2O$ (**1**) (Acc =1-amino-cyclohexanel-carboxylic acid). Crystal structural analysis shows that five Dy^{3+} ions are arranged in an unprecedented trigonal bipyramidal (TBP) geometry. To the best of our knowledge, this is the first example of a TBP lanthanide hydroxide cluster,[11] although this core geometry has been obtained previously with transition metals.[9a,12] Alternating current susceptibility measurements reveal that the Dy_5 cluster exhibits slow relaxation of magnetization.

EXPERIMENTAL SECTION

Materials and Methods. All reagents were of commercial origin and were used as received. The C, H, and N microanalyses were carried out with a CE instruments EA 1110 elemental analyzer. The infrared spectrum was recorded on a Nicolet AVATAR FT-IR330 spectrophotometer with pressed KBr pellets. TGA curve was prepared on a SDT Q600 thermal analyzer. Magnetic susceptibility was measured by a Quantum Design MPMS superconducting quantum interference device (SQUID).

Synthesis and Characterization of $[Dy_5(\mu_3\text{-}OH)_6(Acc)_6(H_2O)_{10}]\cdot Cl_9\cdot 24H_2O$ (1). A 1.076 g portion of $DyCl_3\cdot 5H_2O$ (3.0 mmol) and 0.072 g of 1-aminocyclohexanecaboxylic acid (Acc, 0.5 mmol) were dissolved in 8.0 mL of demineralized water. This solution was stirred at about 80 °C while a freshly prepared NaOH solution (aq 1.0 M) was added dropwise to the point of incipient but permanent precipitation. The mixture was maintained at reflux for another 2 h, and then was filtered while hot. Evaporation of the filtrate under

Received: October 4, 2011
Published: February 6, 2012

dx.doi.org/10.1021/ic202147h | *Inorg. Chem.* 2012, 51, 2186−2190

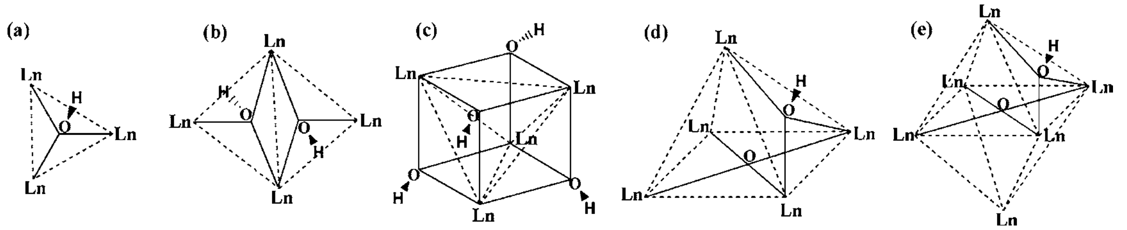


Figure 1. Familiar motifs of lanthanide hydroxy clusters: (a) triangular $Ln_3(\mu_3\text{-OH})$ or $Ln_3(\mu_3\text{-OH})_2$; (b) planar tetranuclear $Ln_4(\mu_3\text{-OH})_2$; (c) tetrahedral (cubane-like) $Ln_4(\mu_3\text{-OH})_4$; (d) square pyramidal $Ln_5(\mu_3\text{-OH})_4(\mu_4\text{-O})$; (e) octahedral $Ln_6(\mu_3\text{-OH})_8(\mu_6\text{-O})$. Several μ_3-OH species were left out for clarity. Dashed lines denote the Ln···Ln distances, solid lines denote the Ln-O bonds.

Table 1. Selected Bonds and Angles for 1

Dy(1)−O(2)	2.275(4)	Dy(2)−O(5W)	2.381(5)	Dy(4)−O(13)	2.311(4)
Dy(1)−O(11)	2.313(4)	Dy(2)−O(17)	2.414(4)	Dy(4)−O(15)	2.332(4)
Dy(1)−O(11)	2.313(4)	Dy(2)−O(13)	2.429(4)	Dy(4)−O(5)	2.363(4)
Dy(1)−O(16)	2.349(5)	Dy(3)−O(4W)	2.417(4)	Dy(4)−O(14)	2.363(4)
Dy(1)−O(15)	2.368(4)	Dy(3)−O(3W)	2.462(4)	Dy(4)−O(3)	2.399(5)
Dy(1)−O(17)	2.386(4)	Dy(3)−O(16)	2.408(4)	Dy(4)−O(1)	2.427(5)
Dy(1)−O(13)	2.401(4)	Dy(3)−O(15)	2.386(4)	Dy(4)−O(7W)	2.436(4)
Dy(1)−O(2W)	2.424(5)	Dy(3)−O(7)	2.286(4)	Dy(4)−O(8W)	2.445(5)
Dy(1)−O(1W)	2.482(4)	Dy(3)−O(4)	2.300(4)	Dy(5)−O(9)	2.316(4)
Dy(2)−O(10)	2.361(4)	Dy(3)−O(14)	2.349(4)	Dy(5)−O(17)	2.323(4)
Dy(2)−O(18)	2.353(4)	Dy(3)−O(18)	2.368(4)	Dy(5)−O(16)	2.333(4)
Dy(2)−O(6)	2.330(4)	Dy(5)−O(9W)	2.525(5)	Dy(5)−O(18)	2.364(4)
Dy(2)−O(14)	2.343(4)	Dy(5)−O(8)	2.371(5)	Dy(5)−O(12)	2.369(5)
Dy(2)−O(6W)	2.446(5)	Dy(5)−O(10W)	2.434(4)	Dy(2)−Dy(3)	3.7100(5)
Dy(2)−Dy(5)	3.8261(5)	Dy(2)−Dy(4)	3.8223(4)	Dy(1)−Dy(2)	3.8316(5)
Dy(1)−Dy(4)	3.8054(4)	Dy(3)−Dy(4)	3.8476(5)	Dy(1)−Dy(3)	3.7371(5)
Dy(1)−Dy(5)	3.7508(5)	Dy(3)−Dy(5)	3.8721(4)		
Dy(4)−O(13)−Dy(1)	107.71(17)	Dy(5)−O(16)−Dy(1)	106.48(18)		
Dy(4)−O(13)−Dy(2)	107.45(19)	Dy(5)−O(16)−Dy(3)	109.50(16)		
Dy(1)−O(13)−Dy(2)	104.97(16)	Dy(1)−O(16)−Dy(3)	103.56(14)		
Dy(2)−O(14)−Dy(3)	104.50(15)	Dy(5)−O(17)−Dy(1)	105.59(17)		
Dy(2)−O(14)−Dy(4)	108.62(19)	Dy(5)−O(17)−Dy(2)	107.74(18)		
Dy(3)−O(14)−Dy(4)	109.46(17)	Dy(1)−O(17)−Dy(2)	105.91(14)		
Dy(4)−O(15)−Dy(1)	108.13(19)	Dy(2)−O(18)−Dy(5)	108.43(19)		
Dy(4)−O(15)−Dy(3)	109.28(17)	Dy(2)−O(18)−Dy(3)	103.60(15)		
Dy(1)−O(15)−Dy(3)	103.67(14)	Dy(5)−O(18)−Dy(3)	109.83(16)		

ambient conditions within three months afforded 0.22 g of block-shaped colorless crystals (yield: 54.5%, based on Acc). Elemental analysis (%) calcd for $C_{42}H_{152}Cl_9Dy_5N_6O_{52}$ (%, fw = 2435.01): C, 18.65; H, 5.66; N, 3.11. Found: C, 18.36; H, 5.53; N, 2.98. IR (KBr, cm^{-1}): 3440 (vs), 2920 (w), 1629(s), 1500 (w), 1420 (w), 1384 (vs),610 (w).

Single-Crystal X-ray Structure Determination. A suitable single crystal with dimensions of 0.15 × 0.10 × 0.06 mm^3 for compound **1** was selected for single-crystal X-ray diffraction analysis. Data collection was performed at 123 K on an Oxford Gemini S Ultra CCD area detector with monochromatic Mo Kα radiation (λ = 0.710 73 Å) for **1**. Absorption corrections were applied by using the multiscan program CrysAlis Red. The structure was solved by direct methods, and non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL-97 program.[13] The hydrogen atoms of the organic ligand were generated geometrically (C—H, 0.96 Å). Crystal data for **1** follow: $C_{42}H_{122}Cl_9Dy_5N_6O_{37}$, M_r = 2435.01, triclinic, space group $P\bar{1}$, with a = 14.6560(4) Å, b = 16.6661(6) Å, c = 17.7302(6) Å, α = 79.293(3)°, β = 87.162(2)°, γ = 88.395(2)°, V = 4249.4(2) $Å^3$, Z = 2, μ = 4.706 mm^{-1}, D_c = 1.903 g cm^{-3}. R_{int} = 0.0702, 16 659 reflections collected, and S = 1.003, 11 014 reflections are observed ($I > 2\sigma(I)$), R1 = 0.0381 ($I > 2\sigma(I)$), wR2 = 0.0651 (all data). Owing to severe disorder, 15 guest water molecules per formula unit are not indicated through crystal structural analysis. This value is calculated on the basis of the element analysis and TGA analysis. CCDC contains the supplementary crystallographic data for this paper with a deposition number of CCDC 826888 for **1**. The crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. The selected bonds and angles for **1** are summarized in Table 1.

■ RESULTS AND DISCUSSION

Synthesis of Compound 1. Amino acid ligands have been studied most extensively to construct polynuclear lanthanide clusters. However, the formation of lanthanide-based clusters is not only related to the particular ancillary ligand, but also related to the reaction conditions. Recently, our studies in search for polynuclear lanthanide clusters have shown that the anions play an important role in the formation of the lanthanide clusters.[10] The dinuclear Dy_2 and tetranuclear Dy_4 clusters were obtained through the reaction of the Acc ligand with $DyCl_3$ and $Dy(ClO_4)_3$ in the ratio of 1:2, respectively. Here, the reaction of the Acc ligand reaction with $DyCl_3$ in the ratio 1:6 generates the present Dy_5 cluster, suggesting that the higher ratio of lanthanide/ligand favors the formation of higher nuclearity lanthanide clusters.

Description of Crystal Structure of Compound 1. Single-crystal X-ray diffraction reveals that compound **1** consists of a pentanuclear $[Dy_5(\mu_3\text{-}OH)_6(Acc)_6(H_2O)_{10}]^{9+}$ cations, 9 uncoordinated Cl^- anions and 24 guest water molecules. As shown in Figure 2, five dysprosium ions and six bridging μ_3–OH groups form a TBP $[Dy_5(\mu_3\text{-}OH)_6]^{9+}$ core, which is encapsulated by six Acc ligands through bridging carboxylate groups. The pentanuclear $[Dy_5(\mu_3\text{-}OH)_6(Acc)_6(H_2O)_{10}]^{9+}$ cluster exhibits a sandwich-like structure.

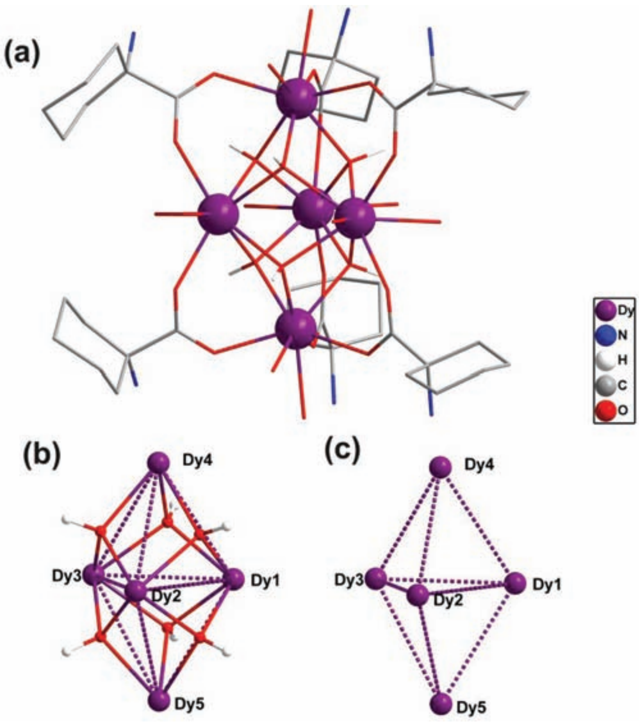


Figure 2. (a) $[Dy_5(\mu_3\text{-}OH)_6(Acc)_6(H_2O)_{10}]^{9+}$ cluster. (b) $[Dy_5(\mu_3\text{-}OH)_6]^{9+}$ units. (c) Trigonal bipyramidal geometry of five Dy^{3+} ions.

The TBP $[Dy_5(\mu_3\text{-}OH)_6(Acc)_6(H_2O)_{10}]^{9+}$ cluster contains five different Dy^{3+} centers, in which Dy1, Dy2, and Dy3 ions reside in the equatorial plane and Dy4 and Dy5 occupy the apical positions. Each Dy^{3+} is eight-coordinated with contributions from eight oxygen atoms. The coordination geometry of Dy1, Dy2, and Dy3 may be described as square-antiprism. One square of the antiprism is formed by four O atoms from four μ_3-OH groups, and another square is formed by two aqua ligands and two oxygen atoms from two Acc ligands in unidentate mode. Dy4 and Dy5 are each coordinated by two aqua ligands, three μ_3-OH groups, and three oxygen atoms from three Acc ligands, organized into a dicapped trigonal prism. Five Dy^{3+} ions display a TBP geometry (Figure 2c), with Dy···Dy separations in the range 3.7100(5)–3.8721(4) Å. The bond lengths of Dy–O range from 2.274(4) to 2.524(5) Å, comparable to those in the reported Dy complex.[4−7,10] It is noted that the Acc ligands exist in the zwitterionic form which is similar to those in the previous reported (Table S1).[10]

The geometric parameter $\tau = (\beta - \alpha)/60$ was defined by Addison et al. to describe the five-coordination structures as an index of the degree of trigonality, within the structural continuum between trigonal bipyramidal and rectangular pyramidal, for which α and β are the two largest angles.[14] Here we introduced the parameter τ to describe the topology of the lanthanide ions for compound **1**. In compound **1**, $\tau = 0.89$ ($\alpha = 177.26°$ and $\beta = 123.96°$), indicating that the topology of the metal ions in coordination cluster is trigonal bipyramidal geometry.

Magnetic Properties. The temperature dependence of direct-current (dc) magnetic susceptibility of **1** was carried out in an applied magnetic field of 1000 Oe in the temperature range 300–2 K. As shown in Figure 3, the observed $\chi_M T$ value of **1** is 64.62 $cm^3\ mol^{-1}$ K at 300 K, close to the expected value of 70.85 cm^3 K mol^{-1} for five uncoupled Dy^{III} ions ($S = {}^5/_2$, $L = 5$, ${}^6H_{15/2}$, $g = {}^4/_3$). The $\chi_M T$ gradually decreases until 50 K and then quickly decreases and reaches a minimum of 36.70 $cm^3\ mol^{-1}$ K at 2 K, which is probably ascribed to a combination of the antiferromagnetic interaction between the Dy^{3+} ions and the thermal depopulation of excited Stark sublevels.[15] The data in the range 30–300 K can be fitted to the Curie–Weiss law, yielding $C = 65.87\ cm^3\ mol^{-1}$ K and $\theta = -4.01$ K for **1**.

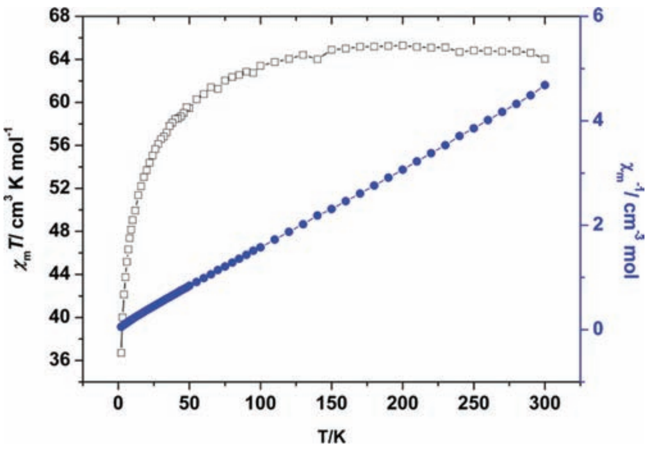


Figure 3. Plots of temperature dependence of $\chi_M T$ vs T and χ_M^{-1} vs T.

The field dependence of magnetization of **1** is shown in Figure 4. The magnetization at 2 K increases rapidly below 1.6 T, and then slowly and linearly increases and is even unsaturated at 7 T. The maximum value for M is 26.92 μ_B at 7 T, which is consistent with the expected value of $5 \times 5.23\ \mu_B$ for five isolated Dy^{3+} ions suggesting the presence of considerable ligand–field effects.[3,4a,16] Indeed, the values are lower than

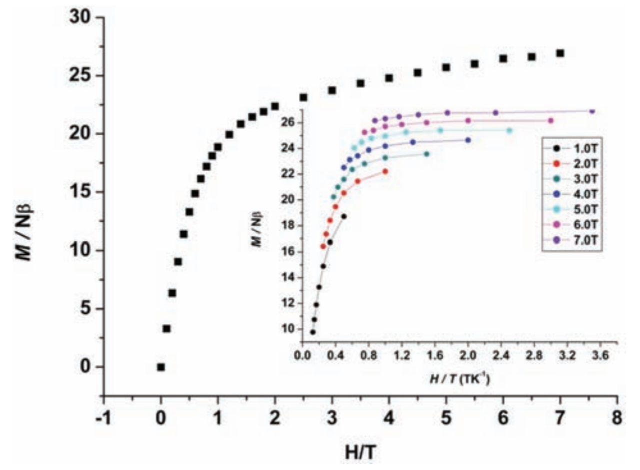


Figure 4. M vs H/T plots measured in different fields below 7 T.

the expected saturation value of 50 μ_B (10 μ_B for each Dy^{3+} ion). The lack of saturation on the M versus H data and the nonsuperposition M vs H/T plots (Figure 4) suggest the presence of a significant anisotropy and/or low-lying excited states.[3]

The temperature dependence of ac magnetic susceptibility under H_{dc} = 0 Oe and H_{ac} = 3 Oe was characterized at the indicated frequencies (1−1500 Hz). As shown in Figure 5a, the Dy_5 cluster displaying a frequency dependent out-of-phase signal was observed below 10 K, indicating the onset of slow magnetization relaxation. However, owing to the absence of frequency-dependent peaks in out-of-phase susceptibility signals, the energy barrier and characteristic relation time of the system cannot be obtained by fitting the peak temperatures to an Arrhenius-type expression. Alternatively, assuming that there is only one characteristic relaxation process, the energy barrier and τ_0 values can be obtained from fitting the frequency-dependent ac susceptibility data by using the Debye model based on the relationship $\ln(\chi''/\chi') = \ln(\omega\tau_0) + E_a/K_BT$, which has been applied in reported clusters.[17,18] As shown in Figure 5b, the extracted E_a = 1.91 K and $\tau_0 = 1.01 \times 10^{-6}$ s, which are consistent with the expected numbers ($\tau_0 = 10^{-6}$–10^{-11} s) for SMMs.[17]

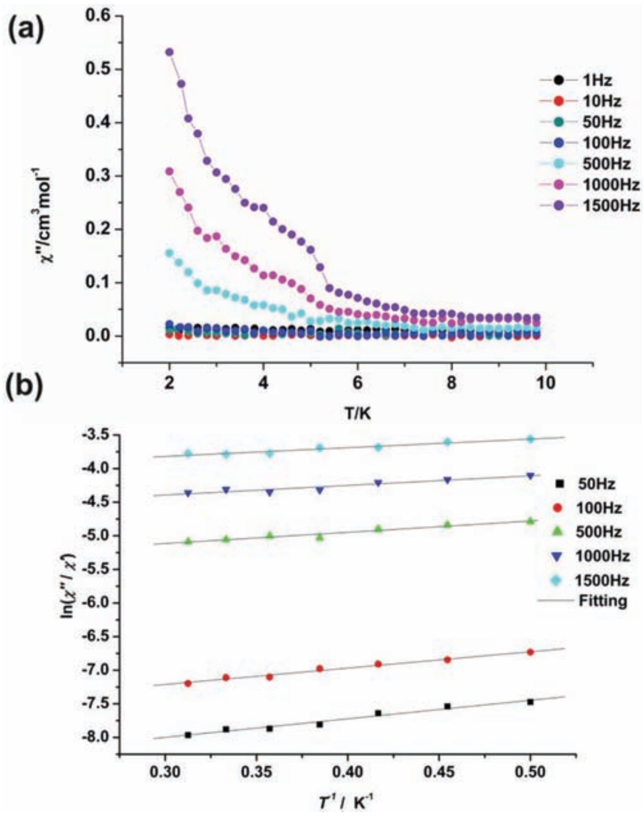


Figure 5. (a) Temperature dependence of the out-of-phase ac susceptibilities at the indicated frequencies for **1**. (b) Plots of natural logarithm of χ''/χ' vs $1/T$ for **1**. The solid line represents the fitting results over the range 2.0−3.2 K.

■ CONCLUSION

In summary, an unprecedented trigonal bipyramidal Dy_5 cluster has been isolated through the reaction of 1-amino-cyclohexanelcarboxylic acid (Acc) and $DyCl_3 \cdot 5H_2O$. Magnetic studies reveal the Dy_5 exhibits slow magnetic relaxation behavior. The present work not only affords the first example of lanthanide hydroxide cluster with TBP topology, but also provides a unique opportunity to probe the slow relaxation mechanism in lanthanide-based SMMs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Thermogravimetric analysis and detailed structural and magnetic data for compound **1**. 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 NNSFC (Grants 20901064, 20825103, 21021061, and 90922031), the 973 project (Grant 2012CB821704) from the Ministry of Science and Technology of China, and the Fundamental Research Funds for the Central Universities (2010121016) for financial support.

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