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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

New strategy to construct single-ion magnets: a unique Dy@Zn₆ cluster exhibiting slow magnetic relaxation†

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Two unique heptanuclear clusters Ln@Zn₆ (Ln = Dy (1), Er (2)) were structurally and magnetically characterized. Each Dy³⁺/Er³⁺ locates in the nona-coordinate D_{3h} coordination environment, and is capsulated in diamagnetic Zn₆ cage. Compound 1 exhibits single-ion magnetism behavior, and it is the first example to construct SIMs through embedding one magnetic anisotropic metal ion into a diamagnetic cage.

The investigations on single-ion magnets (SIMs) enthrall more and more eyes owing to their fascinating chemical/physical properties and potential applications in high-density information storage, quantum computing, and molecular spintronics^[1]. The metal ions with unquenched orbital angular momentum, such as high spin Fe²⁺^[2] and Co^{2+/3+}, lanthanide^[1] and actinide ion^[4], usually are used to act as the spin centers of SIMs. Among these, the SIMs containing lanthanide ions are predominant due to their large *J* value from coupling quantum number *L* and *S* and easy uniaxial magnetic anisotropy.^[1] In constructing SIMs, two key factors need to be considered: 1) only one anisotropy spin carrier was involved in the discrete molecular structure; 2) adjacent spin carriers are well separated with enough long distance to effectively weaken the magnetic couplings among them. To avoid metal ions aggregating into multinuclear clusters, the metal ions in reported lanthanide-based SIMs are usually protected by special organic molecules (such as phthalocyanine (Pc)^[5,6], β-diketone^[7] and COT systems^[8]) and the large inorganic anions polyoxometalates (for example [ErW₁₀O₃₆]⁹⁻^[9] and [LnP₅W₃₀O₁₁₀]¹²⁻ (Ln=Dy, Ho)^[10]). Recently, the compounds Ln^{III}Zn^{II}₃ (Ln=Dy^[11a], Er^[11b]) as SIMs were reported, and displayed planar tetranuclear motifs, in which the Ln ions stay in the centroid of triangle [Zn₃] unit. Inspired by this, we may expect that embedding single metal ion into a cage consisted of diamagnetic ions and organic ligands would be one of effective methods of fabricating SIMs. Nevertheless, to our knowledge, the explorations associated with this idea have never been reported hitherto.

On the other hand, when single anisotropy lanthanide ion is placed in a suitable crystal field, the (2*J*+1) degenerate ground state splits into ±*M_J* sublevels, which generate a uniaxial magnetic anisotropy and an energy barrier for magnetic relaxation. Therefore, the crystal field symmetry becomes a crucial role in controlling the uniaxial anisotropy and various magnetic parameters of SIMs.^[1] For the lanthanide-based SIMs, most of metal centers possess the antiprismatic D_{4d} symmetry, such as [Pc₂Ln]^[5] and their derivatives^[6], [ErW₁₀O₃₆]⁹⁻^[9] and β-diketone systems^[7]. The

other symmetries have also been observed, for example, D_{2h} in Er:CaWO₄^[12], C₅ in [LnP₅W₃₀O₁₁₀]¹²⁻^[10], C_∞ in (Cp*)Er(COT)^[8], D_{3d} in six coordinated Yb^{III}-based molecule^[13] and D_{3h} in actinide compounds of U(Ph₂BPz₂)₃ and UTP₃^[4a]. Comparably, the lanthanide-based SIMs with D_{3h} symmetry were rather rare with the only one exception of compound NdTp₃.^[4a]

In this contribution, two unique heptanuclear clusters, [LnZn₆(μ₃-OH)(Gly)₆(μ₂-NO₃)₃](OH)(NO₃)₂·8H₂O (Gly = glycine, Ln = Dy(1), Er(2)), were synthesized and structurally characterized. The Ln^{III} locates in the nona-coordinate D_{3h} coordination environment and is capsulated in a Zn₆ cage, which consists of six diamagnetic Zn^{II} ions and ligands. Magnetic investigations reveal that 1 possesses a SIM behavior.

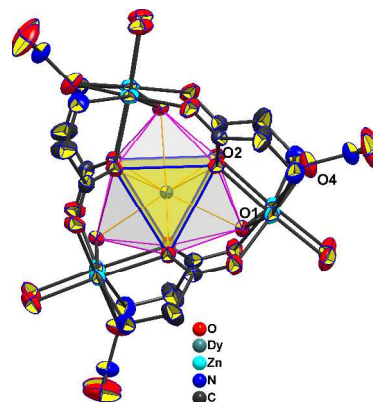


Fig. 1 The molecular structure of 1 with ellipsoid probability of 50%.

The single crystals of compounds 1 and 2 were obtained by evaporating water/acetonitrile/methanol (2.5:10) solutions of Zn(NO₃)₂·6H₂O, Ln(NO₃)₃·6H₂O (Ln=Dy(1), Er(2)), glycine, isobutyric lithium and LiOH with molar ratio of 5:1:5:5:5. X-ray single crystal diffraction revealed that compounds 1 and 2 are isomorphism and crystallize in the space group P6₃/m, hexagonal system (See TableS1 in ESI). Compound 1 as representative is described in detailed. The molecular structure comprises of one heptanuclear cation [DyZn₆(μ₃-OH)(Gly)₆(μ₂-NO₃)₃]³⁺, one OH⁻, two NO₃⁻ and eight lattice water molecules (Fig. 1). The heptanuclear cation can be described as a perfect trigonal prism constructed by six Zn²⁺ cations as the apexes and Dy³⁺ as the center (Fig. S1). Dy³⁺ locates in the center of D_{3h} symmetric nona-coordinate tricapped trigonal prism, which is completed by six carboxyl oxygen atoms as apexes from glycine and three oxygen atoms

as caps from μ_3 -OH groups (Fig. S2). The average Dy-O bond length is 2.443 Å, which falls into the reported normal range.^[7] The Zn^{2+} is six coordinated, exhibiting an elongated octahedron completed by [O5N] set, which consists of one nitrogen atom of glycine, and five oxygen atoms from two glycine, one coordinated water molecule, one NO_3^- and one μ_3 -OH group, respectively. The Zn-N and Zn-O bond lengths are about 2 Å with the exception of Zn-O4 (2.425(3) Å) (see TableS2 in ESI). The carboxyl oxygen atom (O2) of glycine and μ_3 -OH groups (O1) as linkers bridge the Dy^{3+} and Zn^{2+} ions. The ligand glycine with the μ_3 - η^1 , η^1 , η^1 -coordination mode between Dy^{3+} and Zn^{2+} ions cover the periphery of the heptanuclear metal-based cage. Six Zn^{2+} are connected by μ_3 -OH groups and the oxygen atoms (O4) of nitrate groups, forming the upper and bottom faces of the trigonal prism with the separation of about 3.463 Å. The nitrate groups in the lattice and the heptanuclear clusters arrange into lines in the form of ABBA along *c* axis, as depicted in Fig.S3 in ESI. The adjacent Dy^{3+} in Zn_6 cage is well separated by two nitrate groups with the distance of 15.240Å, and among adjacent lines, the nearest distance between Dy^{3+} ions is 11.327Å, indicative of that the magnetic couplings between Dy^{3+} ions can be very weak, and even neglectful (Fig. S4).

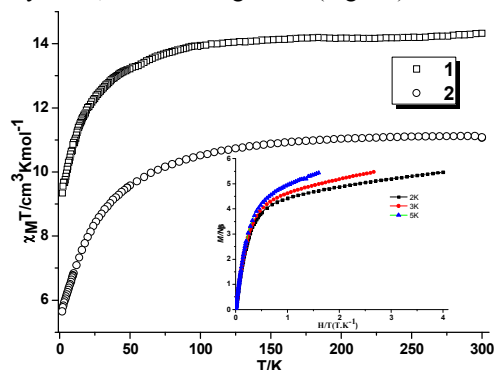


Fig. 2 The $\chi_m T$ vs T curves for **1** and **2**. Inset: Field dependence of the magnetization drawn as M vs H/T plots for **1** under the temperature of 2, 3 and 5 K.

The phase purities of crystalline aggregations of **1** and **2** were determined by Powder X-ray diffraction (Fig. S5 in ESI). The temperature-dependent magnetic susceptibilities of **1** and **2** were carried out from 2 to 300 K under 1000 Oe using crystalline aggregations (Fig. 2). At room temperature, $\chi_m T$ value is 14.13 $cm^3 K mol^{-1}$ for **1** and 11.07 $cm^3 K mol^{-1}$ for **2**, which is very closed to the theoretical value of 14.17 $cm^3 K mol^{-1}$ and 11.07 $cm^3 K mol^{-1}$ calculated based on one Dy^{3+} ($^6H_{15/2}$, $g = 4/3$) and one Er^{3+} ($^4I_{15/2}$, $g = 6/5$), respectively. $\chi_m T$ values decrease slowly from 300 to 100 K, and then decline fleetly to the minimum value of 9.34 $cm^3 K mol^{-1}$ for **1** and 5.64 $cm^3 K mol^{-1}$ for **2** at 2 K. The magnetic behaviors of **1** and **2** may be ascribed to thermal depopulation of Dy^{III}/Er^{III} excited Stark sublevels and/or very weak antiferromagnetic interactions between Dy^{3+}/Er^{3+} ions. The M vs H/T plots of **1** (Fig. 2 (inset)) and **2** (Fig. S6) at different temperatures show nonsuperposition, and the magnetization maximum value at 2 K is far lower than the theoretical value for **1** and **2**. The magnetic phenomenon mentioned above suggests the existence of significant magnetic anisotropy and/or low lying excited states in **1** and **2**.^[7b,11b]

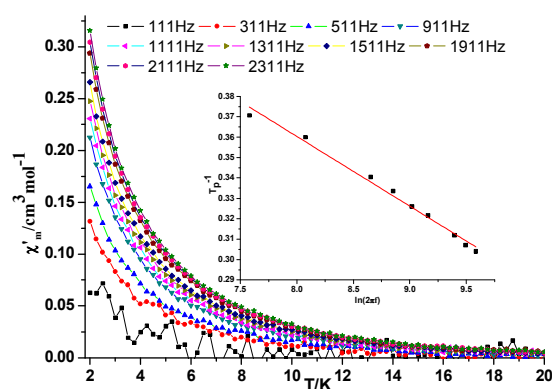


Fig. 3 Temperature dependence of the out-of-phase (χ'') ac susceptibility components at different frequencies for **1** under zero dc field and an oscillation of 3 Oe. Inset: Relaxation time τ of the magnetization for **1** versus inverse temperature at different frequencies under 5000 Oe dc field.

Temperature dependencies of the alternating-current (ac) magnetic susceptibilities for **1** and **2** were measured to probe the dynamics of the magnetization at zero direct-current (dc) field with an oscillation of 3 Oe between 111 - 2311Hz, and plots of χ'' and χ' vs T of **1** and **2** were given in Fig.3, Fig. S7 and S11, respectively. Although the frequency dependences of the ac-susceptibility were observed under a zero-dc field, the out of phase signals is very weak compared with those of in phase. Unfortunately, the peak-values are not obtained above 2 K, which mainly caused by fast quantum tunneling of magnetization (QTM). Actually, QTM can be suppressed by appending a given static magnetic field. To obtain the optimized dc filed, the frequency and temperature dependency ac susceptibilities for **1** were measured under several dc fields. The results suggest that 5000 Oe dc filed can efficiently suppress QTM and was used to measure ac susceptibility. The peaks are observed in the plots of χ'' and χ' vs T (Fig. S13 in ESI). In order to obtain the relaxation energy barrier and relaxation time, the peak temperature T_p may be gained by the Lorentzian peak function fitting from the plots of χ'' vs T , and the plot of $1/T_p$ vs $\ln(2\pi\nu)$ based on the Arrhenius law $1/T_p = -k_B/\Delta E [\ln(2\pi\nu) + \ln(\tau_0)]$ obeys a linear correlation (Fig. 3, inset), where ν is the frequency. The best fitting yields the energy barrier $\Delta E/k_B = 37.04$ K and pre-exponential factor $\tau_0 = 4.21 \times 10^{-10}$ s. Among Dy-based SIMs, this energy barrier is slightly smaller than the reported values of 40.16 K in $[DyPc_2]^{[5a]}$, 39.1 K in $[KDy(Pc)(L)CH_3OH]^{[6c]}$, 40.05 K in $[CaDy_2(Pc)_2(L)_2(CH_3OH)_2]^{[6c]}$ (L=N, N'-bis(3-methyloxysalicylidene)benzene-1, 2-diamine) and 41 K in $Dy\{Pc(a-OC_5H_{11})_4\}(TCIPP)^{[6c]}$ (TCIPP = meso-tetrakis-(4-chlorophenyl)porphyrinate) and higher than 22.4 K and 35 K in $DyZn_2^{[14]}$, 20.7 K in sandwich-type tetrakis(phthalocyaninato) dysprosium-cadmium ($DyCdDy$)^[7b]. τ_0 agrees with expected value of $10^{-6}-10^{-12}$ s for a SMM.^[3-15] ϕ parameter was obtained from the equation $\phi = (\Delta T_p/T_p)/\Delta(\log \nu)$ falls into the range ($0.1 < \phi < 0.3$) expected for paramagnetic materials, excluding the possibility of spin glass behavior.^[15] The frequency dependence of ac susceptibilities at different temperatures also was carried out to further explore the relaxation dynamics (Fig. S10). The Cole-Cole plots were shown in the Fig. S11, and the alpha values were obtained by fitting these data based on the Debye

model, which are listed in the Table S2. The alpha values range from 0.29 to 0.38 in the temperature 2-4.5 K. The relatively large alpha values and the asymmetric Cole-Cole plots at low temperature can indicate a wide distribution of relaxation time and the occurrence of multiple relaxations.^[16] All these magnetic parameters suggest that complex **1** possesses SMM behavior. For **2**, frequency dependence of the ac-susceptibility was not observed under a zero-dc field (Fig.S12).

In summary, a unique mononuclear dysprosium ion encapsulated inside the cage consisted of six diamagnetic Zn²⁺ ions and glycine was structurally and magnetically characterized, and exhibits a slow magnetic relaxation behavior. To our knowledge, it is the first example to construct SIMs through embedding one magnetic anisotropic metal ion into a diamagnetic cage-like motif, and this new synthetic strategy was expected to open wider space in the SIMs field. Indeed, in order to obtain more SIMs, more diamagnetic metal ions including Cd²⁺, Cu⁺, Ag⁺, Hg⁺ and the others can be used to synthesize the diamagnetic cage internally located one magnetic anisotropic metal ion, which can largely enrich and deepen the investigation on the SIMs.

This work was supported by the 973 Program (2012CB821702 and 2011CB935902), NSFC (91122004, 21271137, 81202421).

Notes and References

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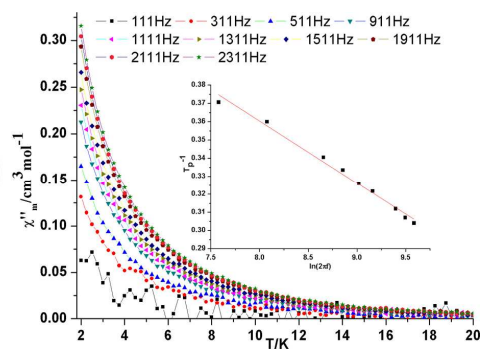
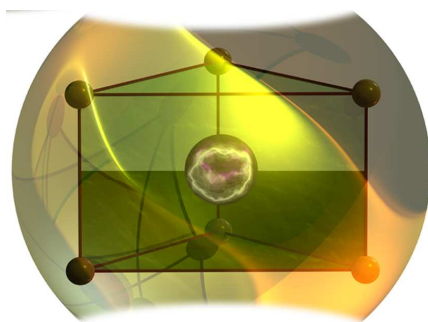
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[†]Electronic Supplementary Information (ESI) available: Synthesis, structural characterizations, and other magnetic data. CCDC: 948391 (1), 949715 (2). ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0xx00000x.

[‡] Gang Xiong and Xiang-Yang Qin contributed equally to this work.

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A unique mononuclear dysprosium ion capsulated inside a diamagnetic Zn_6 cage exhibits a single-ion magnet behavior.