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Chloride templated formation of {Dy$_{12}$(OH)$_{16}$}$^{20+}$ cluster core incorporating 1,10-phenanthroline-2,9-dicarboxylate†

Yan-Li Miao,[ab] Jun-Liang Liu,[a] Ji-Dong Leng,[a] Zhuo-Jia Lin[a] and Ming-Liang Tong*[ac]

Two unique dysprosium(III) coordination compounds with similar dodecanuclear clusters composed of four vertex-sharing cubane-like units, [2Cl⁻ ⊂ {Dy$_{12}$(OH)$_{16}$(phenda)$_8$(H$_2$O)$_8$}]$^{2+}$, were reported. Magnetic studies reveal that both compounds exhibit slow magnetic relaxation.

Since the dodecanuclear manganese clusters were discovered as the first example and archetype of single-molecule magnet (SMM), numerous polynuclear homo- and heterometallic clusters have been obtained.[1,2] Due to the large inherent magnetic anisotropy of the lanthanide ions, heavy lanthanide metal systems, in particular dysprosium(III) based complexes, have attracted increasing interest in the area of molecular magnets.[3–6] Although research on mixed 3d/4d–4f SMM systems has been rapidly developed in recent years,[3] pure lanthanide-based SMMs are still extremely rare owing to the difficulty in promoting magnetic interactions *via* the overlap between the bridging ligand orbitals and the 4f orbitals of the lanthanide ions in these systems as a result of the efficient shielding of the unpaired electrons in the 4f orbitals.[7–9] Therefore, the synthesis of homo-metallic molecular magnetic materials based on lanthanide coordination complexes is currently a great challenge in the area of inorganic and physical chemistry.

A number of discrete and polymeric metal clusters in a cubic geometry displaying SMM behaviour, including many dysprosium compounds,[16] have been reported.[10–16] To achieve effective SMM property, ligand design is one of the key factors in pure lanthanide-based coordination compound systems. Recently we speculated that the ligands with multichelating sites, for example 1,10-phenanthroline-2,9-dicarboxylic acid (H$_2$phenda, Scheme S1†),[17] may be favorable for the formation of lanthanide cluster compounds with

interesting magnetic properties.[6b] Polynuclear lanthanide clusters can be easily assembled by H$_2$phenda *via* the phenanthroline ring and one or both of the carboxylic groups. On the basis of these interesting results, we prepared two new Dy cluster compounds, that is, [2Cl⁻ ⊂ {Dy$_{12}$(OH)$_{16}$(phenda)$_8$(H$_2$O)$_8$}$^{4+}$](X)$_2$·S (X/S = [Dy(phenda)$_2$]⁻/16DMSO·10MeOH·45H$_2$O for (**1**) and X/S = OH⁻/15MeOH·40H$_2$O for (**2**), and report their structures‡ and magnetic properties.

Solvothermal reactions of Dy(OAc)$_3$·4H$_2$O, H$_2$phenda and DyCl$_3$·6H$_2$O in mole ratio of 2 : 1 : 0 or 2 : 1 : 0.5 in MeOH/DMSO (12 mL) sealed in a HCl-acidified 23 mL Teflon lined stainless steel autoclave at 120 °C for 6 days resulted in compounds **1** and **2** (see ESI†), which were characterized by single crystal X-ray analysis, IR spectra, powder X-ray diffraction (PXRD) and elemental analysis (Figs. S2, S3†). The structural similarity in **1** and **2** comes from the analogous coordination behaviours for the metal ions and the ligands. The [Dy$_{12}$(OH)$_{16}$(phenda)$_8$(H$_2$O)$_8$]$^{4+}$ cores in **1** and **2** are almost the same yet the counterion is [Dy(phenda)$_2$]⁻ in **1** and OH⁻ in **2**.

The asymmetric unit of **1** contains three unique dysprosium(III) ions, one and a half phenda^{2-} ligands, two OH⁻ groups, one quarter of uncoordinated chloride, one terminal water molecule and disordered H$_2$O, MeOH and DMSO solvent molecules (Fig. 1a). The Dy1, Dy2 and Dy3 atoms have distinctly different coordination environments. The Dy1 atom is nine-coordinated in a distorted tri-capped trigonal prismatic geometry, which is surrounded with two
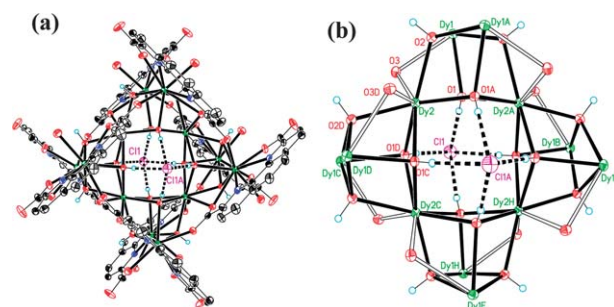
[a] MOE Key Laboratory of Bioinorganic and Synthetic Chemistry/State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou, 510275, P. R. China. E-mail: tongml@mail.sysu.edu.cn

[b] College of Science, Guangdong Ocean University, Zhanjiang, 524088, P. R. China

[c] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, 350002, P. R. China

Fig. 1 ORTEP views of 2Cl⁻ ⊂ [Dy$_{12}$(OH)$_{16}$(phenda)$_8$(H$_2$O)$_8$]$^{4+}$ unit (a) with thermal ellipsoids at 30% probability (H atoms of the phenda ligands are omitted for clarity) and the {Dy$_{12}$(μ$_3$-OH)$_{16}$(μ$_2$-O$_{phenda}$)$_8$Cl$_2$} core (b) in **1**. Symmetry codes: a) x, −y + 1/2, −z + 1/2; b) y, −x + 1/2, z; c) −y + 1/2, x, z; d) y, x, −z + 1/2; e) y−1/2, −x, −z; f) −x−1/2, −y + 1/2, z; g) −y, x + 1/2, −z; h) −x + 1/2, −y + 1/2, z.

phenda^{2-} ligands *via* the O,N,N,O-tetradentate and *syn*-carboxylate binding, three μ_3-OH$^-$ groups and one aqua molecule (Fig. S4a†). Dy2 is coordinated by two oxygen atoms from two phenda^{2-} ligands and six μ_3-OH$^-$ groups in a distorted square antiprismatic geometry (Fig. S4b†). The two dysprosium ions Dy1 and Dy2, two μ_3-OH$^-$ and one terminal aqua molecule consist of the [Dy$_{12}$(OH)$_{16}$-(phenda)$_8$(H$_2$O)$_8$]$^{4+}$ core. Dy3 is connected by two phenda^{2-} ligands in the O,N,N,O-tetradentate mode (Fig. S4c†) and forms a discrete counterion. The carboxylate groups from the phenda^{2-} ligand on the dodecanuclear cluster link three metal atoms in the *anti* and μ_3-η^1:η^2 binding manner while those on the discrete Dy3 segment connect one Dy both in the *anti* fashion. Dy2 is at a site with twofold imposed symmetry while Dy3 is at a site with fourfold imposed symmetry. The intermolecular Dy$\cdots$Dy distances are 16.9 Å in **1** and 9.8 Å in **2**, respectively.

The large {Dy$_{12}$} cluster can be regarded as the fusion of four vertex-sharing cubane-like [Dy$_4$(μ_3-OH)$_4$]$^{8+}$ units. Each cubane-like unit is capped by the η^2-oxygen (O3) atoms from eight phenda^{2-} ligands forming a [Dy$_{12}$(OH)$_{16}$(phenda)$_8$(H$_2$O)$_8$]$^{4+}$ core (Fig. 1b). The Cl$^-$ ion acts as a template in the assembly of the dodecanuclear cluster and forms four hydrogen-bonds with the μ_3-OH$^-$ (Fig. 1b). Neighbouring {Dy$_{12}$} cluster are packed *via* off-set π–π interaction of the aromatic rings on phenda^{2-} at a distance of 3.577(8) Å (Fig. S6†). A 3D supramolecular architecture is formed with 1D square channels in the dimensions of 7.0 × 7.0 Å along the *c*-axis, and 3.2 × 3.2 Å along the *a*-axis or *b*-axis, respectively (Fig. 2a and S7a†). The cationic core in the structure of **1** is closely related to the reported compound[18] [Dy$_{12}$(μ_3-OH)$_{16}$I$_2$(μ_3-Tyr)$_8$(H$_2$O)$_{20}$]$^{10+}$ except that the μ_4-Cl$^-$ takes the place of μ_4-I$^-$ in **1**. However, they have quite different crystal packing structures and different O–H$\cdots$X$^-$ hydrogen bonding parameters. Especially, the distances between the iodide ion and the hydrogen atoms of the μ_3-OH groups are almost the same as the corresponding sum of the van der Waals radii, leading to a very compact core structure.

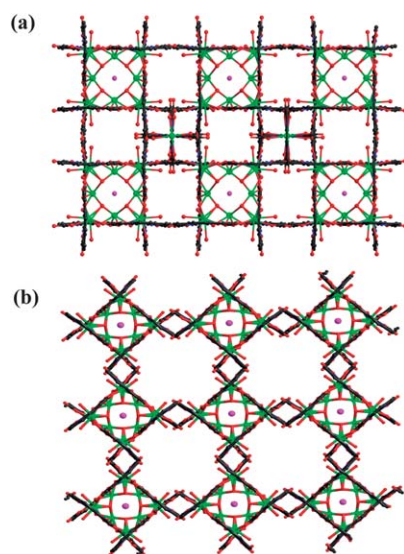The cluster structure of complex **2** is almost the same as **1**. However, their 3D supramolecular architectures are quite different due to the different counterions. For **2**, the 3D supramolecular architecture has three types of channels extended along the three crystal axes, *i.e.* the square channels in the dimensions of 8.4 × 8.4 Å along the *c*-axis (Fig. 2b) and circular channels in the size of 6.0 × 6.0 Å along the *a*-axis and *b*-axis, respectively (Fig. S7b†). The anionic [Dy(phenda)$_2$]$^-$ units or hydroxyl groups, chlorides and highly disordered guest molecules are occupied within the channels. The void volume of the channels excluding the counterions and guest molecules calculated by PLATON is 37.7% for **1** and 49.2% for **2**, respectively.

Thermogravimetric analysis (TGA) showed that **1** and **2** have similar thermal stability (Fig. S9†). For compound **1**, the first weight loss of 13.6% (calcd. 13.5%) occurred below 95 °C, corresponding to the loss of lattice aqua and MeOH molecules. Eight coordinated water molecules and sixteen guest DMSO were released gradually from 95 to 280 °C (weight loss observed 15.0%, calcd. 16.2%). The compound began to decompose at above 300 °C. No plateau was observed, indicating a relatively low thermal stability of the guest-free frameworks for **1** and **2**.

The temperature dependence of magnetic susceptibilities for **1–2** were examined in the temperature range of 2–300 K at a direct current field of 500 Oe (Fig. 3a and 4a). The $\chi_M T$ values are 195.6 and 157.8 cm^3 K mol^{-1} for **1** and **2** at room temperature, slightly smaller than the expected values of 197 and 169 cm^3 K mol^{-1} for fourteen and twelve isolating noninteracting Dy^{3+} ions ($S = {}^5/_2$, $L = 5$, $g = {}^4/_3$)[3], respectively. As the temperature decreased from room temperature to *ca.* 8 K, the $\chi_m T$ values decrease gradually and finally reach minimum values of 169.8 and 142.9 cm^3 K mol^{-1} at 8 K. After that,

Fig. 2 The 3D supramolecular networks of **1** (a) and **2** (b) viewed along the *c*-axis. The H atoms and guest molecules are omitted for clarity.

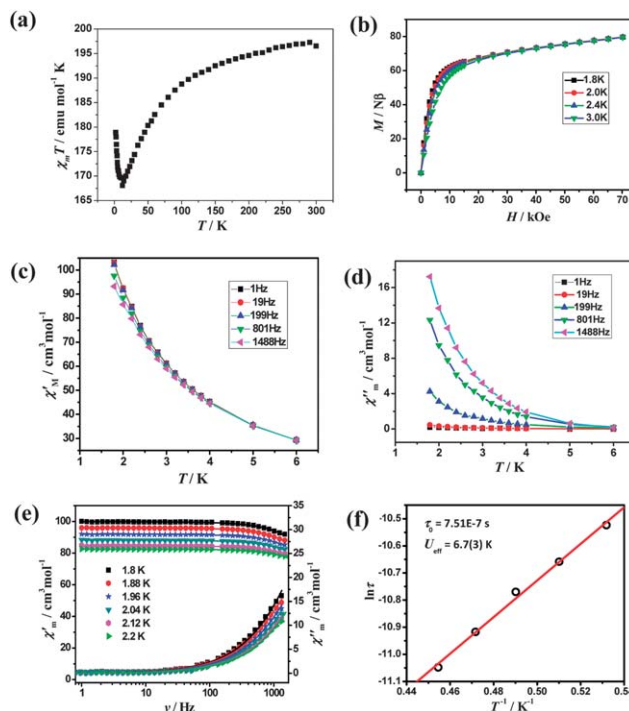**Fig. 3** Temperature dependence of $\chi_M T$ plot of **1** at 500 Oe (a). Magnetization (*M*) *versus* field (*H*) at applied fields of 0–70 kOe in the temperature range 1.8–3 K (b). The zero dc field of $\chi'(T)$ (c) and $\chi''(T)$ (d) plots of **1** at indicated frequencies. The isothermal $\chi'(\nu)$ and $\chi''(\nu)$ plots of **1** at indicated temperatures (e). Magnetization relaxation time (τ) *versus* T^{-1} plot for **1** (f). The solid lines correspond to the Arrhenius law.
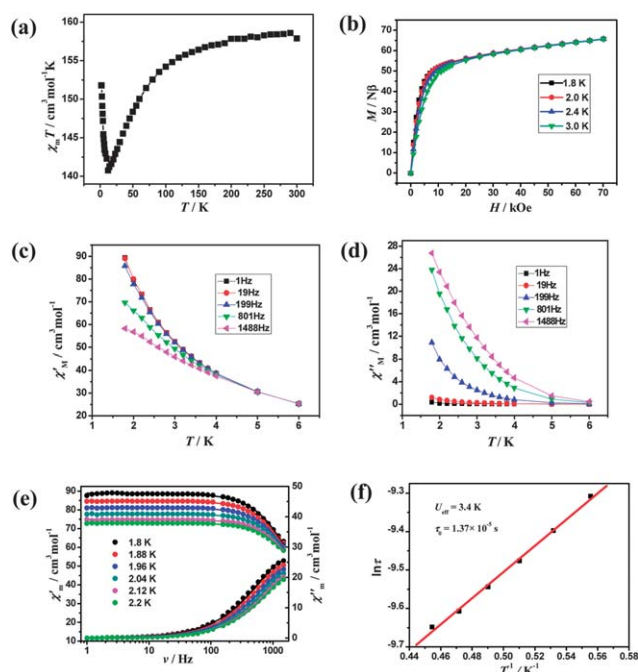
Fig. 4 Temperature dependence of $\chi_M T$ plots of **2** at 500 Oe (a). Magnetization (M) *versus* field (H) at applied fields of 0–70 kOe in the temperature range 1.8–3 K (b). The zero dc field of $\chi'(T)$ (c) and $\chi''(T)$ (d) plots of **2** at indicated frequencies. The isothermal $\chi'(\nu)$ and $\chi''(\nu)$ plots of **2** at indicated temperatures (e). Magnetization relaxation time (τ) *versus* T^{-1} plot for **2** (f). The solid lines correspond to the Arrhenius law.

the $\chi_m T$ values increase rapidly to 178.9 and 151.79 cm³ K mol⁻¹ at 2 K, respectively, suggesting the intra-Dy₁₂ dominant ferromagnetic interactions in **1** and **2** at low temperature.[19]

The field-dependence of the magnetization of **1** and **2** show a sharp increase in the magnetization at low magnetic fields (Fig. 3b and 4b). For complex **1**, the *M vs. H* plot below 3 K rises abruptly at low fields. At higher fields, *M* increases gradually and the maximum up to 7 T is 79.64 μ$_B$, which is in good agreement with the expected value (14 × 5.23 μ$_B$) for fourteen isolated Dy³⁺ ions. The lack of saturation for the *M vs. H* data at 2.0 K suggests the presence of a significant anisotropy and/or low-lying excited states in these systems. For **2**, the *M* value is 65.64 μ$_B$ at 7 T.

The temperature dependencies of ac magnetic susceptibility under H_{dc} = 0 Oe and H_{ac} = 5 Oe were characterized as well (Fig. 3d and 4d). The frequency-dependent increase in the in-phase signal and a concomitant appearance of an out-of-phase signal were observed; this indicates the onset of slow magnetization (*M*) relaxation. Although it possesses high symmetry, the anisotropy axis is still uncompensated, yielding a small magnetic anisotropy.[20] To further investigate this behaviour, isothermal frequency-dependent ac susceptibility data were collected to evaluate the effective energy barriers for **1** and **2** (Fig. 3e–f and 4e–f). However, the energy barrier cannot be derived by fitting the peak temperatures to an Arrhenius-type expression due to the absence of maxima of χ'' above 1.8 K. Alternatively, similar to the recently reported case,[21] the τ values obtained from fitting the frequency-dependent ac susceptibility data (Fig. 3e and 4e) can be used to a generalized Debye model to fit the Arrhenius law [$\tau = \tau_0 \exp(U_{eff}/k_B T)$], giving $\tau_0 = 7.51 \times 10^{-7}$ s, U_{eff} = 6.7(3) K for **1** and $\tau_0 = 1.37 \times 10^{-5}$ s, U_{eff} = 3.4(3) K for **2**,

respectively. Cole–Cole diagrams for **1** and **2** (χ'' *vs.* χ' plots) as shown in Fig. S10 and S11† were performed using the Debye Functions.[22] **1** and **2** also illustrate the possible presence of only one relaxation process as they exhibit a quasi-semicircle shape that can be fitted to the generalized Debye model with $\alpha < 0.10$ (**1**) and $\alpha < 0.15$ (**2**). To the best of our knowledge, **1** and **2** are among the largest lanthanide SMMs based on cubane-like [Dy₄(μ₃-OH)₄] units. The similar slow relaxation behaviours observed in **1** and **2** probably result from their structural similarity.

In summary, we have synthesized two novel dysprosium(III) complexes composed of the fusion of four cubane units templated by two Cl⁻ guests. Neighbouring {Dy₁₂} cores are packed by off-set π–π interactions to generate a 3D supramolecular architecture with 3D channels. Both complexes exhibit slow magnetic relaxation behaviour. The extension of this study to other polynuclear metal series is currently in progress.

Acknowledgements

Notes and references

‡ Crystal and structure refinement parameters for **1**: C₂₁₀H₃₃₀Cl₂Dy₁₄-N₂₄O₁₄₃S₁₆, $\lambda = 0.71073$ Å, Mr = 8337.84, tetragonal, $P4/nnc$ a = 20.0609 (3), b = 20.0609(3), c = 37.6855(12) Å, V = 15166.1(6) ų, Z = 2, T = 150 (2) K, ρ_c = 1.826 g cm⁻³, μ(Mo-Kα) = 3.629 mm⁻¹, 41657 reflections collected, 8407 independent reflections. R_1 = 0.0399 [$I > 2\sigma(I)$], wR_2 = 0.1060 (squeeze). For **2**: C₁₂₇H₂₂₂Cl₂Dy₁₂N₁₆O₁₁₃, tetragonal, $P4/nnc$, a = 21.7073(5), b = 21.7073(5), c = 22.5476(7) Å, V = 10624.6(5) ų. Z = 2, T = 150(2) K, ρ_c = 1.814 g cm⁻³, μ(Mo-Kα) = 4.287 mm⁻¹, 35705 reflections collected, 5707 independent reflections. R_1 = 0.0337 [$I > 2\sigma(I)$], wR_2 = 0.0806 (squeeze). CCDC-809181 (**1**) and 809182 (**2**).

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