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Short communication

A tetranuclear holmium compound exhibiting single molecule magnet behavior

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ABSTRACT

The synthesis, structure, and magnetic properties of a new tetranuclear holmium cluster $[Ho^{III}_4(\mu_3\text{-}OH)_2(L)_4(piv)_2(DMF)_2]\cdot 2DMF$ (**1**) is reported, where the Schiff base H_2L ligand is 2-hydroxy-3-methoxy-phenylsalicylaldimine and piv is pivalate. The cluster has a planar "butterfly" Ho_4 core, which is bridged by two μ_3-hydroxide and six phenoxide oxygen atoms. Magnetically, compound **1** displays field-induced slow relaxation of magnetization. Fitting the dynamic magnetic data to the Arrhenius law gives energy barrier $\Delta E/k_B = 21.49$ K and $\tau_0 = 6.97 \times 10^{-7}$ s.

In the past two decades or so, single-molecule magnets (SMMs), the individual molecules that behave as magnets below a certain blocking temperature (T_B), have attracted increasing interest due to their potential applications in high-density information storage, quantum computing, and molecular spintronics [1–3]. The origin of SMM behavior is the existence of an appreciable thermal barrier U for spin-reversal called magnetic anisotropy barrier which depends on the total spin number of a ground state (S) and the zero-field splitting parameter of a molecule (D) [4]. Many attempts have been directed to increase S and D. Some progress has been achieved in this regard, however, a breakthrough essentially needs to be made from a practical point of view.

Recently, particular emphasis has been placed on the design of new SMMs applying 4*f* metal ions, by virtue of their significant magnetic anisotropy arising from the large, unquenched orbital angular momentum which increases the D value for the compound resulting in higher energy barriers [5]. In particular, the Dy^{III} ion has been proved to be one of the excellent lanthanide ions to generate slow relaxation of magnetization when incorporated into molecular aggregates with structures of n nuclearity ($n = 1$–5) [6–14]. An encouraging output in such system is a square-pyramidal $[Dy_5O(O^iPr)_{13}]$ molecular nanomagnet which was observed with slow relaxation at temperature as high as 40 K with a very high thermal barrier of 530 K [6].

Compared with Dy^{III} families of various nuclearities, examples of Ho^{III} SMMs are still scarce to date and only three cases with mono- and pentanuclear entities have been structurally and magnetically characterized so far; they include the monometallic $[Ho(W_5O_{18})_2]^{9-}$ [15] and $(Bu_4N)[Ho(Pc)_2]$ [16], and a *iso*-propoxide bridged holmium square-based pyramid $[Ho_5O(O^iPr)_{13}]$ [17]. The development of polymetallic Ho^{III} systems is desirable to advance the understanding of magnetization relaxation with respect to local symmetry and magnetic coupling.

Remarkably, the alteration of bridging ligands turns out to be a key factor in constructing lanthanide-based SMMs. The Schiff base ligand, 2-hydroxy-3-methoxy-phenylsalicylaldimine (H_2L), which possesses two different pocket sites: Pocket-I, ONO-donating; Pocket-II, OO-donating (Scheme 1), has been successfully employed in the synthesis of polynuclear 4*f* [18], or 3*d*-4*f* [19–22] clusters before. In this context, we report the preparation, structural description, and magnetic properties of a planar "butterfly" tetranuclear cluster $[Ho^{III}_4(\mu_3\text{-}OH)_2(L)_4(piv)_2(DMF)_2]\cdot 2DMF$ (**1**). Interestingly, the $[Ho^{III}_4(\mu_3\text{-}OH)_2(O_{phenol})_6]$ core in **1** has the same connectivity as for that in the reported $[Ho^{III}_4(\mu_3\text{-}OH)_2(L)_4(HL)_2]$ (**2**) cluster [18], however, compound **1** shows slow relaxation of magnetization and no out-of-phase alternating current signal is noticed for **2**. Notably, compound **1** is the first example of a tetranuclear Ho^{III}_4 system that exhibits field-induced SMM behavior.

Compound **1** was synthesized according to the literature [23]. Single crystal X-ray diffraction analyses [24] show that compound **1** crystallizes in the monoclinic space group $P2_1/c$. Selected bond lengths and angles for compound **1** are given in Table 1. The core structure of **1** has a precisely coplanar tetranuclear arrangement of Ho^{III} ions with crystallographic inversion symmetry (Fig. 1). This motif is often referred to as a butterfly motif in terms of the positions of the metal centers with Ho1 and Ho1′ defining the wing-tips and Ho2 and Ho2′ the hinge (or body). The two oxygen atoms (O1 and O1′) of the μ_3-OH ligands are located on opposite sides of the Ho_4 plane and are displaced out of that plane by 0.9627 Å. The hydroxo group forms a fairly symmetrical triple bridge, with the Ho–O1 distances 2.371(3), 2.326(3), and 2.344(3) Å

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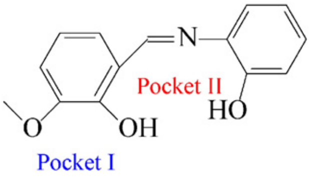


Scheme 1. The structure of 2-hydroxy-3-methoxy-phenylsalicylaldimine ligand (H_2L).

Table 1
Selected bond lengths (Å) and bond angles (deg) for compound **1**.

Ho(1)–O(1)	2.371(3)	Ho(1)–N(2)	2.437(3)
Ho(1)–O(2)	2.348(3)	Ho(1)–O(5)	2.324(3)
Ho(1)–O(6)	2.192(3)	Ho(1)–O(8)^{a}	2.366(3)
Ho(1)–O(9)	2.348(3)	Ho(1)–O(10)	2.596(3)
Ho(2)–O(1)	2.326(3)	Ho(2)–O(1)^{a}	2.344(3)
Ho(2)–O(3)	2.378(3)	Ho(2)–O(4)	2.375(3)
Ho(2)–N(3)	2.500(3)	Ho(2)–O(5)^{a}	2.311(3)
Ho(2)–O(8)	2.376(3)	Ho(2)–O(9)	2.313(3)
Ho(2)^{a}–O(5)	2.311(3)	Ho(1)^{a}–O(8)	2.366(3)
Ho(2)^{a}–O(1)	2.344(3)	Ho(1)–Ho(2)	3.8402(8)
Ho(2)–Ho(2)^{a}	3.4480(8)	Ho(2)–Ho(1)^{a}	3.4480(8)
Ho(1)–Ho(2)^{a}	3.7918(14)	O1…Ho_4(plane)	0.9627
Ho(1)–O(1)–Ho(2)	109.69(11)	Ho(2)^{a}–O(1)–Ho(1)	93.99(10)
Ho(2)^{a}–O(1)–Ho(2)	108.59(11)	Ho(1)^{a}–O(8)–Ho(2)	93.29(9)
Ho(1)–O(5)–Ho(2)^{a}	96.13(10)	Ho(2)–O(9)–Ho(1)	110.96(11)
O(9)–Ho(2)–O(1)^{a}	96.51(9)	O(1)–Ho(2)–N(3)	130.48(10)
O(6)–Ho(1)–O(5)	118.83(10)	O(1)–Ho(1)–O(10)	115.50(9)
O(9)–Ho(1)–O(2)	101.10(10)	O(8)^{a}–Ho(1)–N(2)	113.66(10)
O(5)^{a}–Ho(2)–O(4)	109.09(10)	O(8)–Ho(2)–O(3)	124.34(10)

Symmetry transformations used to generate equivalent atoms: a: $-x+1, -y+1, -z+1$.

and the Ho–O1–Ho angles 93.99(10), 108.59(11) and 109.69(11)°, respectively. Such a tetranuclear structure is often viewed in terms of two edge-sharing triangles, which in this case are close to scalene triangles, because the distances for Ho1…Ho2, Ho2…Ho2′, and Ho1…Ho2′ equal to 3.8402(8), 3.7918(14), and 3.4480(8) Å, respectively. The shortest edge, Ho1…Ho2′, is that which involves three oxygen bridges rather than just two.

There are two different bridging modes of the four deprotonated L^{2-} ligands ($\eta^0:\eta^1:\eta^1:\eta^2:\mu_2$ and $\eta^1:\eta^2:\eta^1:\eta^2:\mu_3$ Scheme 2). All ligands act in a chelating and bridging mode: the first ligand with Ho1–Ho2′ and the second with Ho1–Ho2–Ho1′. The coordination sphere is completed by a DMF molecule for Ho1 and a chelating piv$^-$ ligand for Ho2. Therefore, each eight-coordinate Ho^{III} ion possesses a distorted square-antiprismatic (SAP) geometry with a NO_7 coordination environment. The Ho-Dy-O bond lengths are in the range of 2.192(3)–2.596(3) Å and the Ho–N bond lengths are 2.437(3) and 2.500(3) Å. The two square bases of the square antiprism for Ho1 consist of N2, O5, O6, and O8′ and O1, O2, O9, and O10, respectively, whereas for Ho2, the two square bases are defined by the atoms N3, O1, O1′, and O9 and O3, O4, O5′, and O8, respectively. (Fig. 2).

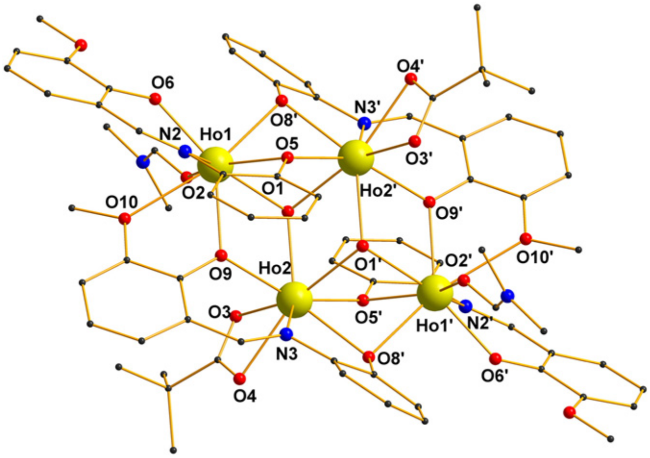
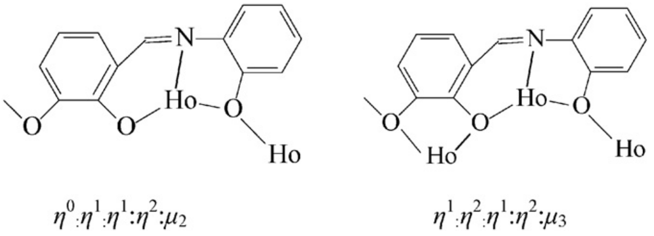


Fig. 1. Molecular structure of the neutral $[Ho^{III}_4(\mu_3\text{-}OH)_2(L)_4(piv)_2(DMF)_2]$ in compound **1** (hydrogen atoms and solvent molecules have been omitted for clarity).



Scheme 2. The coordination modes of the two dianionic ligands in **1**.

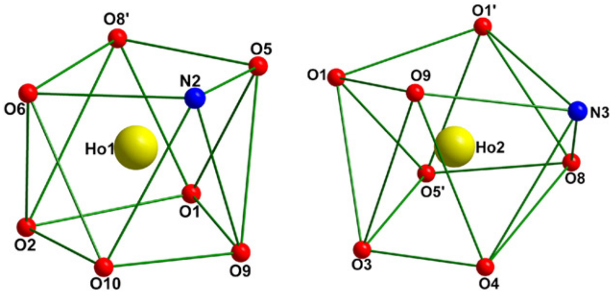


Fig. 2. Coordination polyhedra of distorted square-antiprismatic (SAP) geometry for Ho^{3+} ion in **1**.

In 2013, Powell et al. reported a tetranuclear Ho_4 compound derived from the Schiff base H_2L ligand, formulated as $[Ho^{III}_4(\mu_3\text{-}OH)_2(L)_4(HL)_2]$ (**2**). Compound **1** has similar connectivity with **2**, the only difference being the replacement of the two HL^- ligands in **2** by two piv$^-$ and two DMF ligands in **1**. The two HL^- ligands in **2** adopt a $\eta^1:\eta^1:\eta^0:\eta^1:\mu_2$ coordination mode and act in a chelating group ($\eta^1:\eta^1:\mu_1$) like the piv$^-$ ions in **1** and a terminal group like the DMF molecules in **1**. The above-mentioned small differences will be seen to have significant effects on the magnetic behavior of the two Ho_4 compounds.

The temperature dependence of the direct-current (dc) magnetic susceptibilities (χ_m) of compound **1** has been measured on polycrystalline samples in the temperature range of 2–300 K at 0.1 T (1000 Oe) dc magnetic field. The result is shown as χ_mT vs T plots in Fig. 3. For **1**, the χ_mT value at room temperature is 56.56 cm^3 K mol^{-1}, which is in line with the expected value of 56.32 cm^3 K mol^{-1} for four uncoupled Ho^{III} ions ($^5I_8$, $S = 2$, $L = 6$, $J = 8$, $g_J = 5/4$, and $C = 14.08$ cm^3 K mol^{-1}). Upon cooling, the χ_mT value slowly decreases to 14 K with the value of 51.36 cm^3 K mol^{-1}, and then increases to 52.65 cm^3 K mol^{-1} at

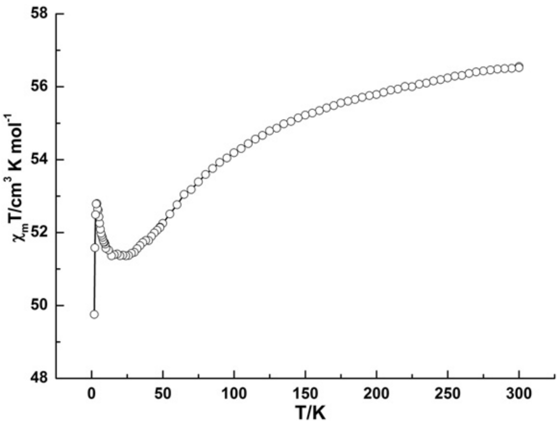


Fig. 3. The plots of χ_mT versus T under 1 kOe for compound **1**.