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Molecular Magnets

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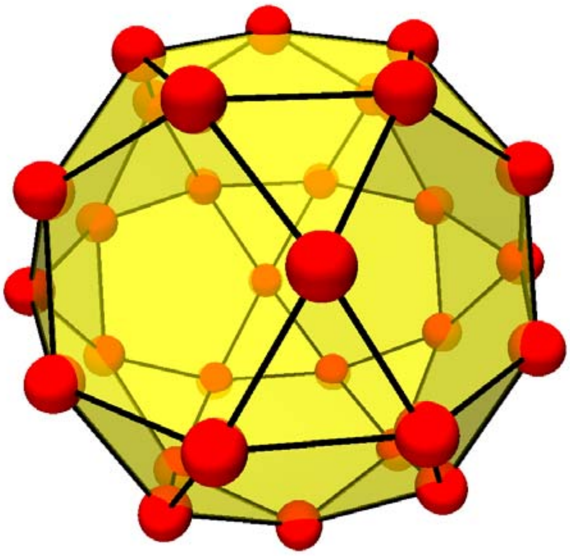

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3d–4f Clusters with large spin ground states and SMM behaviour†‡

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Three new Cu–Ln cage complexes bridged by phosphonates and acetates are reported; one—a $Cu_{24}Dy_8$ cage—is a new single molecule magnet (SMM).

There is a great deal of interest in the preparation of molecular assemblies containing metal ions and phosphonate ligands.[1–4] Earlier studies from our group have shown that phosphonates can be used to make cages containing iron, manganese, cobalt, nickel and vanadium.[1a–c,2] With tritylphosphonic acid (TPA) we have reported tetranuclear clusters of manganese, cobalt and copper where the copper cluster showed interesting EPR properties.[3] In contrast to the transition metal phosphonates, molecular assemblies containing mixed 3d–4f or purely 4f metal ions are rare.[4] In this communication we report the synthesis, structure and magnetic properties of multinuclear Cu^{II}–Ln^{III} clusters (Ln = Gd, Dy, Y) using TPA as ligand. There are previous reports of 3d–4f clusters that behave as single molecule magnets (SMM),[5] to our knowledge, these are the first examples of 3d–4f clusters with phosphonate ligands.

Reaction of $Ln(NO_3)_3.xH_2O$ (Ln = Dy, Gd, Y) and $Cu(OAc)_2.H_2O$ with TPA in 1 : 2 : 1 ratio in the presence of base leads to the formation of 3d–4f heterometallic clusters, $[H_3O][Cu_{24}Dy_8(Ph_3C–PO_3)_6(Ph_3C–PO_3H)_6(MeCO_2)_{12}(MeCO_2H)_6(OH)_{42}(NO_3)(OH_2)_6]$ (**1**), $[(Me_4N)_2K_2][Cu_{24}Gd_8(Ph_3C–PO_3)_6(Ph_3C–PO_3H)_6(MeCO_2)_{12}(MeCO_2H)_{12}(OH)_{42}(NO_3)][(OH)_3]$ (**2**) and $[Me_4N]_3[Cu_{16}Y_{12}(Ph_3C–PO_3)_{12}(MeCO_2)_{22}(OH)_{24}(NO_3)_2(OH_2)_6][OH]$ (**3**) respectively as evidenced by single crystal X-ray studies.†

The solid state structures of **1** and **2** are very similar in the arrangement of the metal atoms but the binding modes of ligands (carboxylates and phosphonates) differ slightly. The structure of **1** consists of eight Dy^{III} centers at the vertices of a cube with twelve coppers inside and twelve coppers outside the cube (Fig. 1a).† The twelve inner coppers are arranged in the form of a cuboctahedron which are connected by one NO_3^- and twenty four OH^- bridges (Fig. 1b). Each Dy^{III} caps a triangular face of the copper cuboctahedron; hence forming a $DyCu_3$ tetrahedron with each Cu^{II} atom being part of two such tetrahedra. Further each square face of the Dy^{III} cube is capped externally by a copper dimer; hence twelve copper (six dimers) surround the Dy^{III} cube. Six of the eight Dy^{III} centres are eight-coordinate and two are nine-coordinate. The Cu^{II} atoms of the cuboctahedron have approximately tetragonally elongated octahedral geometry with short bonds to four hydroxides (1.903(5) to 2.028(5) Å), and additional long contacts to one to the oxygen atoms of a disordered NO_3^- present in the centre of the cluster (2.242(5) to 2.655(4) Å) and to an oxygen of a hydroxyl group bound to the lanthanide centres (2.372(4) to 2.802(6) Å). The Cu^{II} sites within the dimers are bridged by a hydroxyl bridge and a phosphonate bridge; they also have square planar coordination geometries. The six Cu^{II} dimers are connected to the $Cu_{12}Dy_8$ core through a carboxylate and two phosphonate bridge (Fig. 1a).

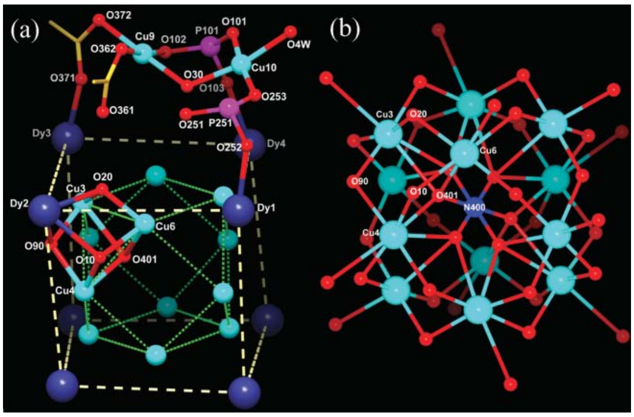

Fig. 1 (a) View of the Dy_8 cube encapsulating a Cu_{12} cuboctahedron and one of the six outer Cu_2 dimers present outside the six face of the Dy_8 cube in **1**. (b) View showing the Cu_{12} cuboctahedron.

The metal core is surrounded by an organic sheath of ligands consisting of twelve phosphonates and eighteen acetate groups. Of the twelve phosphonates present, six are dianionic while the other six being monoanionic. Phosphonate binding modes in the cluster **1** can be described in terms of Harris notation[6] as [3.111] and [2.110] (Fig. S1 and S3†). Of the eighteen acetate units, twelve are anionic and the other six are neutral acids. For charge balance one of the oxygen atoms present outside the cluster core as solvent is considered as a hydroxonium ion.

The solid state structure of **2** is very similar to **1** including bonding parameters, with a Cu_{12} cuboctahedron inside the Gd_8 cube and six Cu^{II} dimer units present outside the six face of the Gd_8 cube (Fig. S2 and S1†). However in the asymmetric unit of **2**, a six coordinate K^+ ion in present[7] which is bound to phosphonate oxygen belonging to three different monoanionic phosphonate

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† Electronic supplementary information (ESI) available: Experimental details, X-ray data and additional figures. CCDC reference numbers 655327–655329. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b927114g

‡ Dedicated to Prof. David Rankin, with gratitude for advice and encouragement.

ligands while the other three bonds come through the interaction of the π-cloud of three neighbouring phenyl groups of three different TPA ligands. The K–O and K–π(phenyl) distances vary from 2.754(7) to 2.777(6) Å and 3.160(3) to 3.285(3) Å respectively. Phosphonate binding modes in the cluster **2** can be described in terms of Harris notation[6] as [3.111] and [3.210] (Fig. S2 and S3†). The copper centers of the external dimers have a different coordination sphere, with water ligands in **1** replaced by acetic acid in **2**. A tetramethyl ammonium ion is also found in the asymmetric unit. For charge balance three oxygen atoms present outside the cluster core as solvent must be hydroxyls.

We attempted to replace the paramagnetic lanthanides in **1** and **2** by a diamagnetic metal and thus study the magnetic properties of the Cu_{12} cuboctahedral core; such a core has been reported previously in Cu–Ln cages.[8] The reaction was carried out in similar conditions to **1** and **2** except that $Y(NO_3)_3{\cdot}6H_2O$ was used in place of the paramagnetic lanthanides. Compound **3** was isolated from this reaction.†

The asymmetric unit of **3** consists of a heterometallic core comprising of eight Cu^{II} and six Y^{III} atoms connected together by OH^- and NO_3^- bridges (Fig. 2). All the Cu^{II} atoms have a square planar geometry with the Cu–O distances varying from 1.910(7) to 2.142(8) Å. Further, four of these Cu^{II} atoms (Cu1, Cu5, Cu7 and Cu8) have two long contacts to OH^- groups (2.337(9) to 2.750(8) Å); three other Cu^{II} atoms (Cu2, Cu3 and Cu6) have one long contact to NO_3^- and acetate units (2.337(8) to 2.394(8) Å). One yttrium (Y4) is seven coordinate while the others are eight coordinate, with square *anti*-prism coordination geometries (Y–O distance vary from 2.227(7) to 2.534(7) Å). The asymmetric unit contains twelve OH^- groups of which ten are μ_3- and two μ_2 bridging. A NO_3^- group is also present in the asymmetric unit which binds three Y^{III} and three Cu^{II} centers.

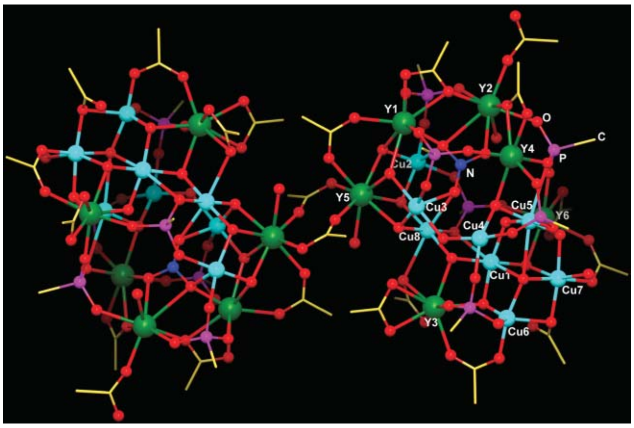

Fig. 2 View showing the molecular structure of **3**. All the protons and phenyl groups on phosphonates are removed for clarity.

The metal-hydroxo core in the asymmetric unit of **3** is surrounded by six dianionic phosphonates and eleven acetate ligands. Four phosphonates exhibit the [3.111] binding mode and two exhibit the [4.211] mode (Fig. 2 and S3†).[6] Of the four phosphonates showing [3.111] binding mode, two phosphonates bind to two Cu^{II} atoms and a Y^{III} while the other two bind to two Y^{III} and a Cu^{II} center. Of the two phosphonates showing the [4.211] binding mode,[6] one coordinates to three Cu^{II} and one Y^{III} while the other binds to three Y^{III} and a Cu^{II}. Two Me_4N^+ ions are found in the asymmetric unit, one refines well with full occupancy and the other with 50% occupancy. For charge balance a single atom fragment present in the lattice is considered to be a hydroxyl ion. Analytical data for **3** show a low value for C content which we do not understand at present.

Direct current (dc) magnetic susceptibility (χ_M) data for compounds **1–3** were collected in the 2–300 K range in magnetic fields ranging from 0.5 to 5 kG (Fig. 3). The room temperature $\chi_M T$ value for **1** is 121.5 cm^3 K mol^{-1} (1 kG field), close to the expected value (122 cm^3 K mol^{-1}) for twenty four Cu^{II} ($S = \frac{1}{2}$; $g = 2$) and eight Dy^{III} ($S = 5/2$; $J = 15/2$; $g = 4/3$) non-interacting ions. χ_MT decreases with T to 100 cm^3 K mol^{-1} at 12 K, after which it increases to 101 cm^3 K mol^{-1} at 6 K before dropping sharply to 95.3 cm^3 K mol^{-1} at 2 K. For **2**, the room temperature $\chi_M T$ value of 83.1 cm^3 K mol^{-1}, above the calculated spin only value, and decreases to 77.0 cm^3 K mol^{-1} at 30 K, before increasing to a value of approximately 80.6 cm^3 K mol^{-1} at 5 K or 85.7 cm^3 K mol^{-1} at 2 K.

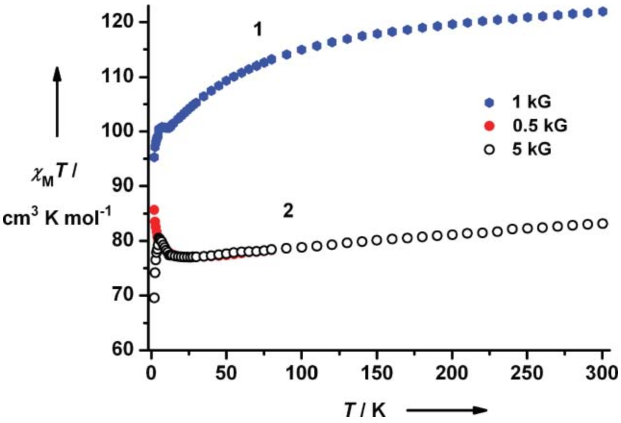

Fig. 3 Temperature-dependence of the $\chi_M T$ value for polycrystalline samples of **1** and **2** at fields of 1, 0.5 and 5 kG.

The high-temperature behavior is due to antiferromagnetic exchange interactions within the outer Cu^{II} dimeric entities; for **1** crystal field effects are also important as it contains Dy^{III}. The data measured below 12 K suggest large spin ground-states. For **1**, the sharp decrease at the lowest temperatures is assigned to zero-field splitting and/or weak intermolecular interactions. For **2**, in small fields there is no fall at low temperature. In both cases assigning a spin ground state is problematic.

Variable field (0–70 kG) isothermal magnetization experiments were carried out (Fig. 4). For **1**, the magnetization does not saturate even to 70 kG, this is consistent with the anisotropy of the Dy^{III} ion. For **2**, the magnetization curve saturates at about 68 μ_B, consistent with a spin state value of $S_T = 34$. The curve does not follow the Brillouin function for such a large spin, but is close to the function calculated if the twelve Cu and eight Gd of the core were non-interacting (Fig. S4†). We attempted to use χ'_mT plots, as described by Manoli *et al.*,[9]–to calculate the ground state (Fig. S5†) but here χ'_mT is increasing rapidly at 1.8 K, unlike previous work where it is either constant or changing slowly. Extrapolating to 0 K gives an intercept of 88 cm^3 K mol^{-1}, consistent with a smaller spin state.

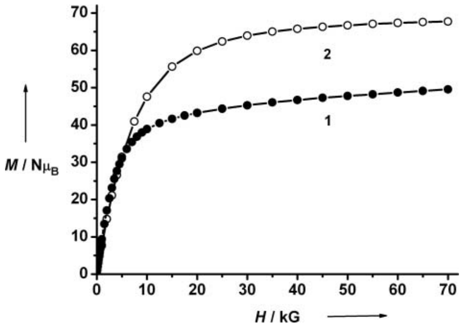

Fig. 4 Magnetization *vs.* field data for **1** and **2** recorded at 2 K.

An S_T value of 34 can be rationalized by considering all interactions within the central $[Cu^{II}_{12}Gd^{III}_8]$ core bridged by hydroxides as being ferromagnetic[10] and the exchange between the six external Cu-dimers to be strongly *anti*-ferromagnetic. However, even if the spin ground state is $S = 34$, it is not isolated and many other spin states remain populated even at 1.8 K. Such a molecule may be useful for magnetic cooling where low anisotropy and high degeneracy would be ideal.[11]

We investigated whether **1** and **2** are SMMs. Zero-field ac susceptibility measurements between 1.8 and 10 K were carried out at frequencies of 1, 10, 100, 450 and 997 Hz. The results for **2** show that it is not an SMM–presumably because Gd^{III} is much less anisotropic than Dy^{III}. However for **1** both the 'in phase' (χ') and 'out-of-phase' (χ'') signals were frequency dependent (Fig. S6†), suggesting slow relaxation of the magnetization. To probe the possible SMM behaviour further, single-crystal measurements were performed using a micro-SQUID technique.[12] The observed magnetization hysteresis loops show increasing coercivity with decreasing temperature (Fig. 5) and analysis of the sweep-rate dependence is only consistent with **1** being an SMM.[13] As expected for large SMMs, the loops do not show steps due to quantum tunneling of the magnetization since they are more susceptible to various step-broadening effects.[14] Decay of remnant magnetization (Fig. S7†) was monitored over 0.04–1 K temperature range, and the resulting relaxation time (τ) data were used to derive an effective energy barrier for the reorientation of the magnetization of $U_{eff} \approx 4.6$ K and $\tau_0 = 2.1 \times 10^{-8}$ s. Compound **1** is therefore a new SMM, albeit it one with a very small energy barrier.

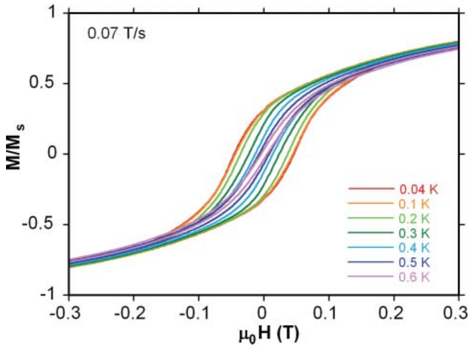

Fig. 5 Hysteresis loops for **1** measured at 0.04 to 0.6 K.

The magnetic behavior of compound **3** is less interesting. $\chi_M T$ is 6.6 cm³ K mol⁻¹ at 300 K (5 kG field), a value which is close to that expected (6 cm³ K mol⁻¹; $g = 2$) for sixteen non-interacting Cu^{II} ions with $S = \frac{1}{2}$ (Fig. S8†). With decreasing temperature $\chi_M T$ decreases to reach a plateau of *ca* 4.0 cm³ K mol⁻¹ near 20 K and decreases rapidly below 5 K.

Future work is in progress to search for new 3d–4f phosphonate cages of different combination of metal ions with new topologies and interesting magnetic properties.

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