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Giant Heterometallic Cu$_{17}$Mn$_{28}$ Cluster with T_d Symmetry and High-Spin Ground State

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Since the 1990s, manganese clusters with large spin ground states have received increasing attention mainly due to their single-molecule magnet behavior.[1,2] A number of high nuclearity homometallic manganese complexes from Mn$_{16}$ to Mn$_{84}$ have been explored to date.[3-11] However, the rational synthesis of high nuclear heterometallic manganese clusters remains a challenge. Triethanolamine (teaH$_3$) is a potentially versatile ligand, and several polynuclear complexes have been recently reported.[12] Enlightened by the facile reactions of zerovalent copper with Co^{II}/Zn^{II}/Cd^{II}/Pd^{II} salts and aminoalcohols,[13] we tried to extend such reactions into a new synthetic route to heterometallic manganese clusters. We report herein the synthesis, structure, and magnetic properties of a giant heterometallic Cu^I$_4$Cu^{II}$_{13}$Mn^{II}$_4$Mn^{III}$_{12}$Mn^{IV}$_{12}$ cluster, [Cu$_{17}$Mn$_{28}$O$_{40}$-(tea)$_{12}$(HCO$_2$)$_6$(H$_2$O)$_4$]·36H$_2$O (**1**). To our knowledge, **1** is the largest manganese teaH$_3$ cluster and unprecedented with five metal oxidation states.

The reaction of copper powder, Mn(OAc)$_2$·4H$_2$O, and teaH$_3$ in a 1:2:1 ratio in *N,N'*-dimethylformamide (DMF) (30 mL) at 85 °C gave a dark green solution from which dark block crystals of **1** were slowly deposited after several months. The in situ generated formate ligand arises from hydrolysis of DMF which has been previously documented.[14]

The crystal structure of **1**[15] contains a giant [Cu$_{17}$Mn$_{28}$O$_{40}$]$^{42+}$ core of T_d symmetry with 4 Cu^I ions, 13 Cu^{II} ions, 4 Mn^{II} ions, 12 Mn^{III} ions, 12 Mn^{IV} ions, 28 μ_4-O^{2-}, and 12 μ_3-O^{2-} ions. Each μ_4-O^{2-} ion joins three Mn ions and one Cu ion (2Mn^{III} + Mn^{II} + Cu^{II} or 2Mn^{IV} + Mn^{III} + Cu^I or 3Mn^{IV} + Cu^{II}), while each μ_3-O^{2-} ion joins one Mn^{IV} ion and two Mn^{III} ions. There are five metal oxidation states of Mn^{2+}, Mn^{3+}, Mn^{4+}, Cu$^+$, and Cu^{2+} in **1**, which were established by consideration of bond lengths, bond valence sum (BVS) calculations,[16] charge considerations, and the observation of Jahn−Teller (JT) distortions for the Mn^{III} centers. The [Cu$_{17}$Mn$_{28}$O$_{40}$]$^{42+}$ core is surrounded by 12 tea^{3-} groups, 6 HCO$_2$$^-$ groups, and 4 aqua ligands into a neutral cluster (Figure 1).

Each Cu^I ion is coordinated in a tetrahedral geometry by three μ_4-O^{2-} ions and one aqua ligand. The Cu^{II} ions have two different coordination environments: the central Cu1 ion is coordinated in a perfect tetrahedral environment by 4 μ_4-O^{2-} ions (Cu−O = 1.975-(11) Å), while each of the outer 12 symmetry-related Cu3 ions is coordinated in a distorted trigonal bipyramidal environment by three alkoxo O atoms in the plane (O−Cu3−O = 102.9(3)−127.58(17)°) and one amino N atom and one μ_4-O^{2-} ion at the axial positions (N1−Cu3−O4 = 172.6(3)°). Each tea^{3-} ligand acts in a μ_4:η^1:η^2:η^2:η^2 mode to cap an outer Cu^{II} atom and bridge one Mn^{II} and two

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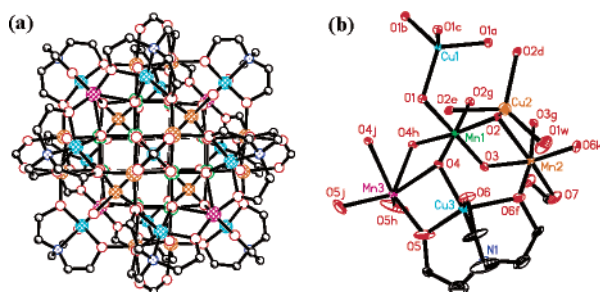
Figure 1. Molecular structure (a) and coordination environments (b) of **1**. H atoms and lattice water molecules have been omitted for clarity. Symmetry: (*a*) −*y*, *x*, −*z*; (*b*) *y*, −*x*, −*z*; (*c*) −*x*, −*y*, *z*; (*d*) −*y*, −*x*, *z*; (*e*) −*z*, −*x*, *y*; (*f*) *x*, *z*, *y*; (*g*) −*x*, *y*, −*z*; (*h*) *y*, *z*, *x*; (*i*) *z*, *x*, *y*; (*j*) *y*, *x*, *z*; (*k*) −*y*, *z*, −*x*.
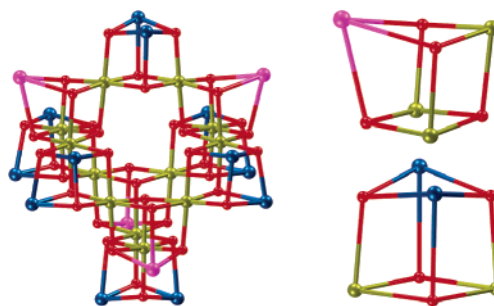
Figure 2. The adamantane-like Mn$_{28}$ cluster containing six [Mn^{IV}$_2$Mn^{III}$_2$O$_4$] and four [Mn^{IV}$_3$Mn^{II}O$_4$] cubanes via sharing all Mn^{IV} atoms. Atom color code: Mn^{IV}, dark yellow; Mn^{III}, navy blue; Mn^{II}, magenta; O, red.
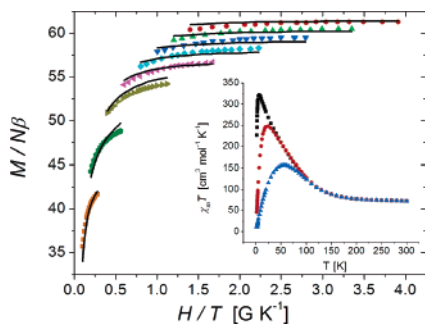
Mn^{III} ions. There are three oxidation states for the manganese ions, which is uncommon for the manganese clusters.[8,10,17] All Mn centers are six-coordinate (Figure S1), through interactions with five μ_4-O^{2-} ions and one μ_3-O^{2-} ion for Mn1 in an essentially octahedral geometry (average Mn1−O = 1.904 Å), one μ_4-O^{2-} ion, two μ_3-O^{2-} ions, two formate O atoms, and one alkoxide O atom for Mn2 in a tetragonally elongated octahedral geometry (Mn2−O2 and Mn2−O7 = 2.221(6) and 2.143(8) Å constituting the JT axis), and three μ_4-O^{2-} ions and three alkoxide O atoms for Mn3 forming a distorted trigonal prism (average Mn3−O = 2.190 Å), respectively.

The most striking structural feature is that all the 28 Mn ions are bridged by the 28 μ_4-O^{2-} and 12 μ_3-O^{2-} ions into 6 Mn^{III}$_2$-Mn^{IV}$_2$O$_4$ cubanes (Mn−O−Mn = 93.6(2)−102.5(2)°) and 4 Mn^{II}-Mn^{IV}$_3$O$_4$ cubanes (Mn^{II}−O−Mn^{IV}, Mn^{IV}−O−Mn^{IV} = 97.5(3)−99.9(3)°), which are further joined to be a cubane-based manganese cage via sharing all the 12 Mn^{IV} ions (Figure 2). Such a structure is unprecedented in the known high nuclearity Mn clusters. Finally, the connectivity of the [Cu$_{17}$Mn$_{28}$O$_{40}$]$^{42+}$ core can be precisely
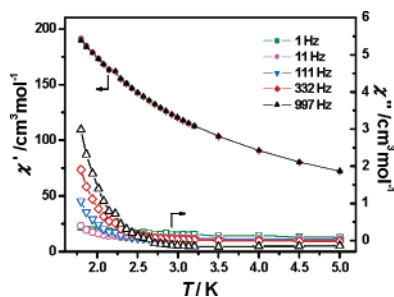
Figure 3. Plot of reduced magnetization ($M/N\beta$) versus H/T for **1** in the temperature range of 1.8−4.0 K (5 kG (orange), 10 kG (dark green), 20 kG (brown), 30 kG (dark red), 40 kG (teal), 50 kG (dark blue), 60 kG (green), 70 kG (red)). Solid lines represent best theoretical fit. Inset illustrates $\chi_m T$ versus T plot for complex **1** from 1.8 to 300 K (1 kG (black), 10 kG (red), 50 kG (blue)).

Figure 4. AC magnetic measurements for **1** at H_{ac} = 5 G and H_{dc} = 0.

described by noting that the central Cu1 ion connects four Mn^{II}-$Mn^{III}{}_3O_4$ cubanes into a tetrahedral array. Six $Mn^{II}{}_2Mn^{IV}{}_2O_4$ cubanes are located on the midlines of the six edges of the tetrahedron and connect the four $Mn^{II}Mn^{IV}{}_3O_4$ cubanes via the 12 Mn^{IV} corners into an adamantane-like cage. Each of the four [Cu^I-(H_2O)] groups (on 3-fold axes) connects three $Mn^{II}{}_2Mn^{IV}{}_2O_4$ cubanes, and the outer 12 Cu^{II} ions connect the Mn_{28} cluster via the remaining μ_4-O^{2-} sites.

DC magnetic susceptibility data were collected in fields ranging from 70 to 1 kG in the temperature range of 1.8−300 K (Figure 3). The reduced magnetization (M) versus H/T data cannot be fit to one state experiencing axial zero-field splitting $D\hat{S}_z^2$ (in fact, T_d symmetry does not allow this). The χT versus T data (inset Figure 3) taken at fields of less than 1 kG show a maximum of ∼325 cm^3 mol^{-1} K. This suggests a $S = {}^{51}/_2$ ground state in small fields, which is reasonable given that the $Mn^{III}\cdots Mn^{III}$, $Mn^{IV}\cdots Mn^{IV}$, and $Mn^{III}\cdots Mn^{IV}$ interactions within the cubane units are expected to be ferromagnetically coupled, while the $Mn^{II}\cdots Mn^{IV}$, $Cu^{II}\cdots Mn^{III}$, and $Cu^{II}\cdots Mn^{IV}$ interactions are antiferromagnetic which would give $S = 12S_{Mn(IV)} + 12S_{Mn(III)} - 4S_{Mn(II)} - 13S_{Cu(II)} = {}^{51}/_2$. The non-superimposability of isofields in the reduced magnetization versus H/T plot usually indicates the presence of axial zero-field interactions. However, we have fit all the data (solid lines in Figure 3) assuming that there is a $S = {}^{63}/_2$ excited state lying 5 K above the $S = {}^{51}/_2$ ground state. The fit is quite good, and it is important to emphasize that the model has no zero-field splitting for either of the states. This is consistent with the T_d symmetry that precludes the $D\hat{S}_z^2$ term in the spin Hamiltonian. High-frequency EPR studies have been initiated to verify the two spin state model.

AC magnetic susceptibility data for **1** (Figure 4) do show a frequency-dependent out-of-phase signal; however, only the onset of the signal is seen. Lower temperature AC data or micro-SQUID data are needed to establish whether this interesting complex **1** functions as a single-molecule magnet.

In summary, we have established an approach to generate a giant heterometallic mixed-valent $Cu^I/Cu^{II}/Mn^{II}/Mn^{III}/Mn^{IV}$ cluster which contains an unprecedented adamantane-like Mn_{28} core connected wholly by Mn_4O_4 cubane units and exhibits unusual magnetic properties.

Supporting Information Available: Synthesis details, additional plots, and an X-ray crystallographic file in CIF format for the structural determination of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Crystal data for **1**: $C_{78}H_{230}Cu_{17}Mn_{28}N_{12}O_{128}$, 6003.24 g mol^{-1}, cubic $I\bar{4}3m$, a = 20.3441(9) Å, V = 8420.1(6) Å^3, Z = 2, ρ = 2.368 g cm^{-3}, T = 123 K, μ = 4.229 mm^{-1}, $F(000)$ = 5998, $2\theta_{max}$ = 56.0°, S = 1.086. The structure was solved by direct methods and refined on F^2 to $R_1(wR_2)$ 0.0456 (0.1177) using 1758 reflections with $I > 2\sigma(I)$.
(16) (a) Bond valence sum calculations for Mn^{II}, Mn^{III}, and Mn^{IV} ions gave oxidation state values of 2.193, 3.350, and 4.413, respectively, and Cu^I and Cu^{II} ions gave oxidation state values of 1.284 and 1.797−1.951, respectively. (b) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, *32*, 4102−4105.
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