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Citation for published version:

Digital Object Identifier (DOI):
10.1002/anie.201208781

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Publisher's PDF, also known as Version of record

Published In:
Angewandte Chemie International Edition

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Directed Synthesis of $\{\text{Mn}_{18}\text{Cu}_6\}$ Heterometallic Complexes**

Victoria A. Milway, Floriana Tuna, Andrew R. Farrell, Laura E. Sharp, Simon Parsons, and Mark Murrie*

Dedicated to Professor David Collison on the occasion of his 60th birthday

The development of new synthetic strategies to assemble high-nuclearity transition metal complexes is a key target in modern coordination chemistry. One of the driving forces for this is their fascinating magnetic properties for example, single-molecule magnets or magnetic refrigerants and molecules with large spin ground states or large anisotropy barriers. The use of two, or more, different metal ions to assemble these clusters is an attractive synthetic target and controlling the bottom-up assembly of large heterometallic molecules is a considerable challenge. However, the potential rewards are significant, as there is a real possibility of control/design over the individual magnetic parameters that contribute to the overall molecular properties. Furthermore, new functionality can be added, such as the combination of magnetic and optical properties, or the production of catalysts or catalyst precursors with high activity and/or selectivity.

Previously, polydentate ligands with specific binding sites/donor atoms linear linkers such as cyanide or rigid structure-directing ligands have been used to prepare heterometal complexes. Herein, we describe a new step-by-step approach to synthesize large 3d–3d heterometallic oxo-bridged clusters. Firstly, we use a preformed CuII complex, which contains multiple, latent hydroxy binding sites, to target the trapping and encapsulation of an inner metal-oxo core. Secondly, the choice of CuIII as the central ion increases the flexibility further, due to its range of typical coordination environments from 4+ to 6+. We report two compounds that contain a striking “core-shell” $\{\text{Mn}_{18}\text{Cu}_6\}$ complex as either a hexa- or dication, where the CuII precursors encapsulate a hexacapped cuboctahedral manganese oxide $[\text{Mn}_{18}\text{II}\text{Mn}_{18}\text{III}O_{14}]$ nanocluster.

The CuIII center is enclosed using the bis-tris propane ligand $[2,2’-(\text{propane-1,3-diylidimino})\text{bis}(2-(\text{hydroxymethyl})-\text{propane-1,3-diol})](\text{H}_2\text{L}, \text{Scheme 1})$ forming the precursor complex $[\text{Cu(H}_2\text{L})\text{Cl}]\text{Cl}\cdot1.25\text{H}_2\text{O} (1:1.25\text{H}_2\text{O})$ (see Supporting Information, Figure S1) in almost quantitative yield (see Experimental). This is then redissolved and utilized in a second reaction to generate the heterometallic complexes: addition of base to a solution of I, followed by addition of MnCl$_2$·4H$_2$O leads to the formation of $[\text{Mn}_9\text{Cu}_6\text{O}_{16}\text{(H}_2\text{L})_6\text{Cl}_3\text{H}_2\text{O} \cdot \text{H}_2\text{O}]$ using NMe$_4$OH/EtOH or $[\text{Mn}_9\text{Cu}_6\text{O}_{16}\text{(H}_2\text{L})_6\text{Cl}_3\text{H}_2\text{O} \cdot \text{H}_2\text{O}]$ using NEt$_3$/MeOH. Both compounds can be prepared reproducibly, albeit in low yields, which is not uncommon in the area of high-nuclearity complexes. We have been unable to obtain these complexes using a range of one-pot reactions and preformation of the CuIII complex appears to be essential.

The structure of the cationic cluster in 2 is based upon a $[\text{Mn}_{11}\text{II}\text{Mn}_{11}\text{III}O_{14}\text{Cu}^\text{II}]$ core, encapsulated by six $[\text{Cu(H}_2\text{L})]^+$ groups. Oxidation states have been confirmed by bond-valence sum (BVS) calculations and by consideration of charge balance/coordination environments. The twelve MnIII and fourteen O$^-$ anions, form a hollow cube (ca. 3.8 Å O–O edge (Figure 1a)). The MnIII cations describe a cuboctahedron, capped on each square face by a MnII center, which resides off-center, above one of the smaller constituent $[\text{Mn}_{11}\text{II}\text{Mn}_{11}\text{III}]$ triangular faces (Figure 1c). The CuII ions describe a further octahedron, twisted with respect to the $[\text{Mn}_{11}\text{III}]$ octahedron, giving a remarkable level of self-assembly: polyhedral shells of expanding size describing archimedean $[\text{Mn}_{11}\text{III}] < \text{platonic}[\text{Mn}_{11}\text{II}] < \text{platonic}[\text{Cu}_{12}^\text{II}]$ solids (Figure 2).

The outer (final) coordination site of each MnII center is occupied by either a terminal water $[\text{Mn}(1), \text{Mn}(3)$ and symmetry equivalent (s.c.) or chloride ligand $[\text{Mn}(2)$ and s.c.) (Figure 1b). Each $\text{H}_2\text{L}^+$ ligand displays the same bonding

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and each Cu II center is bridged to a Mn II and two Mn III centers via two m₃ ligand alkoxide arms (Figures 1c and 3). The Cu II centers are best described as distorted [4+1] coordinate, with the apical bond (ca. 2.6 Å) to either a core oxide anion {for Cu(1), Cu(3)} or an (outer) water ligand {for Cu(2)}. Hence, four [CuN₂O₂O₂O₆] pyramids point towards the core and two point away (Figure 4) and the coordinative flexibility of the Cu II center (i.e. the direction of the Cu II axial bonds) modulates the shape of the [Mn₉Cu₆] complex. For Cu(1) and Cu(3) there is an additional (outer) weak interaction with a lattice chloride anion {2.9808(1), 2.959(3) Å} and for Cu(2) an additional (inner) weak interaction with a cube corner oxide anion {O(6), 2.986(3) Å} (Figure 1c).

Figure 1. POV-Ray depictions of a) the [Mn₁₂O₁₄] core of 2, b) expansion to include the Mn II octahedron encapsulating the core, c) the overall heterometallic core of 2. Mn III, purple; Mn II, pink; Cu II, bronze; Cl, green; O, red (oxide = capped stick, alkoxide = ball and stick); N, blue (C and H atoms omitted for clarity).

Figure 2. Expanding polyhedral shells {Mn III}₁₂ < {Mn II}₆ < {Cu II}₆ in 2 (colors as previously described).

Figure 3. H₂L⁴⁻ ligand binding mode in 2; the apical bond of Cu2 is pointing outwards from the core, to a H₂O ligand. Colors are as previously described, plus C, gray (H atoms not shown).

Figure 4. Differing coordination environments of the Cu II cations; yellow pyramids indicate Cu II centers where the apical bond points away from the core, green pyramids have the apical Cu II bond pointing to the core. Red cube represents the core Mn II oxide cube. Cu1a = Cu1[1.5–x, 0.5–y, 1–z].

Compound 3 contains a similar [Mn₉Cu₆] complex, as a dication, where the core structure is largely the same as for compound 2 (Figure S2 and Tables S5 and S6). However, in this case, each Mn II center is equivalent and has a terminal chloride ligand (cf. either Cl⁻ or H₂O in 2) (Figure 5). If we describe each Cu II center as [4+1] as in 2, then each apical ligand (ca. 2.6 Å) bonds to a core oxide anion (cf. two of these were to an [outer] water ligand in 2, that is, pointing away.
Further high-nuclearity Mn/Cu complexes include: [MnIII<sub>8</sub>CuIV<sub>4</sub>] and [MnIII<sub>6</sub>CuII<sub>4</sub>]<sup>[11]</sup> or [MnIII<sub>4</sub>CuII<sub>6</sub>] and [MnIII<sub>6</sub>MnIV<sub>4</sub>CuII<sub>6</sub>]<sup>[10]</sup> However, none of these one-pot reactions result in either similar metal ion topologies or oxidation levels to those found in 2 and 3. Interestingly, the [MnIII<sub>12</sub>] core structure of the [Mn<sub>10</sub>Cu<sub>4</sub>] complexes is related to the smaller Mn-oxo clusters, [MnIV<sub>3</sub>MnIII<sub>3</sub>MnII<sub>3</sub>O<sub>4</sub>(OEt)<sub>2</sub>](O<sub>2</sub>CPh)<sub>3</sub>]<sup>[17]</sup> and [MnIII<sub>12</sub>(μ<sub>6</sub>-O)(μ<sub>4</sub>-Cl)(μ<sub>6</sub>-BuPO<sub>3</sub>)<sub>3</sub>]<sup>[18]</sup> where the central position is occupied by a MnIV or a MnIII cation, respectively (cf. empty in 2 and 3). Hence, our approach may provide a more general route to trap and build upon stable metal-oxo core architectures: here trapping a [MnIII<sub>12</sub>] core and adding [MnIII<sub>4</sub>] and [CuII<sub>4</sub>] shells.

Structurally closest to 2 and 3 is perhaps the polyoxometalate anion [Ti<sub>2</sub>IIINbV<sub>11</sub>O<sub>40</sub>]<sup>[15]</sup>–, which also has an empty central cavity, in which TiIV and NbV take the place of MnIII and MnII, respectively.<sup>[19]</sup> Comparisons can also be drawn with Pd<sub>d</sub> clusters: [Pd<sub>13</sub>(CO)<sub>20</sub>(PEt)<sub>10</sub>] consists of a centered cuboctahedral [Pd<sub>1</sub>] core, with square faces capped by Pd atoms in the sites occupied by the six MnII in [MnIII<sub>10</sub>CuII<sub>4</sub>].<sup>[20]</sup> The resulting [Pd<sub>13</sub>] giant octahedron is capped on four of its eight faces by additional Pd atoms, in positions close to those occupied by CuII in 2 and 3.

The core of 2 is observed by ESI-MS (Figure S5, Table S7). All labile aquo ligands are lost and ion-pairs are observed for [[CuII<sub>4</sub>MnIII<sub>8</sub>MnII<sub>1</sub>(H<sub>2</sub>L)<sub>12</sub>O<sub>14</sub>Cl<sub>2</sub>]<sup>[11]</sup> (m/z 1146.7) and [[CuII<sub>4</sub>MnIII<sub>8</sub>MnII<sub>1</sub>(H<sub>2</sub>L)<sub>12</sub>O<sub>14</sub>Cl<sub>2</sub>]<sup>[11]</sup> (m/z 1737.5) and some fragmentation of the parent ion is observed, [CuII(H<sub>2</sub>L)<sub>14</sub>]<sup>[14]</sup> (m/z 344.1). The solution stability provides further potential for using these reaction systems to probe heterometallic cluster assembly.

The bridging in 2 is complex and each metal cation is bridged to between three and eight others, via single oxygen bridges. Bridging angles range from 88.28–107.83°. The overall picture is similar for 3, except that the higher symmetry of the molecule results in a minimum of four bridging connections to neighboring metal ions. The majority of the bridging angles are large, and as a result, we would expect antiferromagnetic coupling to dominate; which proves to be the case (Figure S6). Magnetization vs. field data (Figure S7) suggests a large number of excited states with similar energies, and a poorly defined ground state. AC measurements do not show any evidence of frequency dependence: this is unsurprising as the Jahn–Teller axes of the MnIII centers are nearly perpendicular, leaving little net magnetic anisotropy.

Using our step-by-step approach, starting with a preformed CuII complex, we can trap and encapsulate manganese oxide nanoclusters. Reactions changing the anion (Cl⁻), precursor (CuII) and core metal ion (Mn) are all underway, in order to assemble new heterometallic clusters and to explore the self-assembly of high-nuclearity complexes.

**Experimental Section**

All reagents and solvents were obtained from commercial suppliers and used without further purification.

Synthesis of 1: H<sub>2</sub>L (5.70 g, 20.2 mmol) and CuCl<sub>2</sub>·2H<sub>2</sub>O (5.28 g, 31.0 mmol) were combined in ethanol (120 mL) and heated to 60°C.
A dark green solution formed, followed by precipitation of a pale blue solid (15 mins). The mixture was heated for 5 h. After cooling, the blue precipitate \([\text{Cu(H}_6\text{L})\text{Cl}]\) \(1.25\text{H}_2\text{O}\) (1.25 \(\text{H}_2\text{O}\)) was collected from the solution after removal of the single crystals. IR: \(\nu = 3140, 3018, 2934, 1470, 1428, 1307, 1263, 1114, 1077, 1064, 1011, 761\) \(\text{cm}^{-1}\). Elemental analysis (\(\text{C}_5\text{H}_6\text{N}_3\text{O}_5\text{CuCl}_{0.5}\) \(\text{H}_2\text{O}\) \(\%\)) found: C \(30.01\), H \(6.50\), N \(4.47\); calc: C \(30.07\), H \(6.54\), N \(4.38\).

Single crystals suitable for X-ray study were obtained from recrystallization from ethanol yielding \(1.5\text{EtOH}\) (see Supporting Information).

Synthesis of \(2\): \(1.25\text{H}_2\text{O}\) (109 mg, 0.263 mmol) was dissolved in hot ethanol (60 ml at \(60^\circ\text{C}\)). \(\text{NaCl}\) \(5\text{H}_2\text{O}\) (166 mg, 0.842 mmol) was added, and immediately dissolved, resulting in a clear royal blue solution which was heated for 30 min. \(\text{MnCl}_2\cdot4\text{H}_2\text{O}\) (110 mg, 0.557 mmol) was added, and immediately dissolved, resulting in a clear royal blue solution which was heated for 3 h, and filtered. Black crystals of \([\text{Mn}_{18}\text{Cu}_6\text{O}_{14}\text{(H}_2\text{L})_6\text{Cl}_6]\) \(\text{Cl}_2\cdot\text{H}_2\text{O}\) formed in the filtrate over 1 month (ca. 6 mg, 4\% (see Supporting Information). IR: \(\nu = 3351, 3262, 3212, 2921, 2664, 1634, 1455, 1426, 1393, 1260, 1154, 1100, 1079, 1027, 923, 791, 761\) \(\text{cm}^{-1}\). Elemental analysis (\(\text{C}_{36}\text{H}_{70}\text{N}_{18}\text{O}_{42}\text{Cu}_{21}\text{Mn}_{42}\)) \(\%\)), found: C \(21.81\), H \(4.08\), N \(4.60\); calc: C \(21.72\), H \(3.97\), N \(4.61\). MS (ESI+ \(m/z\)): \(341.1, 1146.7, 1737.5\) (see Table S7).

Synthesis of \(3\): \(1.25\text{H}_2\text{O}\) (108 mg, 0.259 mmol) was dissolved in methanol (30 mL). \(\text{NEt}_3\) (0.07 mL, 0.502 mmol) was added, and immediately dissolved, resulting in a clear royal blue solution which was stirred at ambient temperature for 30 min. \(\text{MnCl}_2\cdot4\text{H}_2\text{O}\) (110 mg, 0.557 mmol) was added, resulting in an immediate color change to black-gray, followed by formation of a precipitate. The mixture was heated for 4 h, and the precipitate (108 mg) was removed by filtration and washed with ethanol. Yield 8.63 g, 96%.

IR: \(\nu = 3361, 3234, 3215, 2947, 2688, 1622, 1458, 1429, 1390, 1262, 1156, 1101, 1084, 1061, 1026, 940, 932, 793, 720\) \(\text{cm}^{-1}\). Elemental analysis (\(\text{C}_{36}\text{H}_{70}\text{N}_{18}\text{O}_{42}\text{Cu}_{21}\text{Mn}_{42}\)) \(\%\)), found: C \(22.39\), H \(4.59\), N \(4.62\); calc: C \(22.38\), H \(4.59\), N \(4.62\). Total yield: 21 mg, 18%.

CCDC 907989 (1), 907990 (2), and 907991 (3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: November 1, 2012
Revised: December 11, 2012
Published online: January 10, 2013

Keywords: copper · heterometallic complexes · magnetic properties · manganese · polynuclear clusters
