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Heterometallic Complexes

Directed Synthesis of \{Mn_{18}Cu_6\} Heterometallic Complexes**

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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.[1] One of the driving forces for this is their fascinating magnetic properties for example, single-molecule magnets[2] or magnetic refrigerants[3] and molecules with large spin ground states[4] or large anisotropy barriers.[5] 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.[6,7] However, the potential rewards are significant, as there is a real possibility of controlling the individual magnetic parameters that contribute to the overall molecular properties.[8] Furthermore, new functionality can be added, such as the combination of magnetic and optical properties,[9] or the production of catalysts or catalyst precursors with high activity and/or selectivity.[10]

Previously, polydentate ligands with specific binding sites/donor atoms[11] linear linkers such as cyanide[12] or rigid structure-directing ligands[13] have been used to prepare heterometallic complexes. Herein, we describe a new step-by-step approach to synthesize large 3d–3d heterometallic oxo-bridged clusters. Firstly, we use a preformed Cu\textsuperscript{II} complex, which contains multiple, latent hydroxy binding sites, to target the trapping and encapsulation of an inner metal-oxo core. Secondly, the choice of Cu\textsuperscript{II} as the central ion increases the flexibility further, due to its range of typical coordination environments from [4] to [4+2]. We report two compounds that contain a striking “core-shell” \{Mn_{18}Cu_{6}\} complex as either a hexa- or dication, where the Cu\textsuperscript{II} precursors encapsulate a hexacapped cuboctahedral manganese oxide \{Mn_{18}^{III}\cdotMn_{18}^{II}\cdotO_{14}\} nanocluster.

The Cu\textsuperscript{II} center is enclosed using the bis-tris propane ligand \{2,2’-(propane-1,3-diylidino)bis[(2-hydroxymethyl)propane-1,3-diol]\} (H\textsubscript{2}L, Scheme 1) forming the precursor complex \{Cu(H\textsubscript{2}L)Cl\}Cl·1.25H\textsubscript{2}O (1·1.25H\textsubscript{2}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 \textbf{I}, followed by addition of MnCl\textsubscript{2}·4H\textsubscript{2}O leads to the formation of \{Mn\textsubscript{12}Cu\textsubscript{6}O\textsubscript{14}·(H\textsubscript{2}L)\textsubscript{6}Cl\textsubscript{2}·(H\textsubscript{2}O)\textsubscript{6}\}·H\textsubscript{2}O·6CH\textsubscript{3}OH (2) using NMe\textsubscript{4}OH/EtOH or \{Mn\textsubscript{12}Cu\textsubscript{6}O\textsubscript{14}·(H\textsubscript{2}L)\textsubscript{6}Cl\textsubscript{2}·10H\textsubscript{2}O·6CH\textsubscript{3}OH\} (3) using NEt\textsubscript{3}/MeOH. Both compounds can be prepared reproducibly, albeit in low yields, which is not uncommon in the area of high-nuclearity complexes.[14] We have been unable to obtain these complexes using a range of one-pot reactions and preformation of the Cu\textsuperscript{II} complex appears to be essential.

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

The outer (final) coordination site of each Mn\textsuperscript{II} center is occupied by either a terminal water \{Mn(1), Mn(3) and symmetry equivalent (s.e.) or chloride ligand \{Mn(2) and s.e.\} (Figure 1b). Each H\textsubscript{2}L\textsuperscript{+} ligand displays the same bonding
mode $\eta^1 \eta^1 \eta^1 \eta^1 \eta^1 \eta^4$ (Figure 3) and each Cu$^{II}$ center is bridged to a Mn$^{II}$ and two Mn$^{III}$ centers via two $\mu_3$ 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 $[\text{Cu}N_2O_2(OH)_3]$ 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 [Mn$_6$Cu$_4$] 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).

Compound 3 contains a similar [Mn$_6$Cu$_4$] 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 H$_2$O in 2) (Figure 5). If we describe each Cu$^{II}$ center as [$4\!+\!1$] 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: \([\text{Mn}^{II}\text{Cu}^{II}]_8\) and \([\text{Mn}^{IV}\text{Cu}^{II}]_4\) or \([\text{Mn}^{III}\text{Cu}^{II}]_8\) and \([\text{Mn}^{III}\text{Mn}^{IV}\text{Cu}^{II}]_8\). 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 \([\text{Mn}^{III}]_8\) core structure of the \([\text{Mn}^{II}\text{Cu}^{II}]_8\) complexes is related to the smaller Mn-oxo clusters, \([\text{Mn}^{IV}\text{Mn}^{III}\text{Mn}^{IV}\text{O}([\text{OEt})_2(\text{O}_{2}\text{CPH})_2)]^{17}\) and \([\text{Mn}^{III}\text{Mn}^{II}([\text{m}-\text{O}([\text{Bu-PO}))_3])^{18}\) where the central position is occupied by a \(\text{Mn}^{IV}\) or a \(\text{Mn}^{II}\) 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 \([\text{Mn}^{III}]_8\) core and adding \([\text{Mn}^{IV}]_4\) and \([\text{Cu}^{II}]_8\) shells.

Structurally closest to 2 and 3 is perhaps the polyoxometalate anion \([\text{Ti}^{IV}\text{Nb}^{IV}]_{12}^{\text{O}44}\text{Cl}^{10}\), which also has an empty central cavity, in which \(\text{Ti}^{IV}\) and \(\text{Nb}^{IV}\) take the place of \(\text{Mn}^{III}\) and \(\text{Mn}^{II}\), respectively. Comparisons can also be drawn with \(\text{Pd}^0\) clusters: \([\text{Pd}_{23}(\text{CO})_{20}(\text{PEt})_{10}]\) consists of a centered cuboctahedral \([\text{Pd}_{19}]\) core, with square faces capped by \(\text{Pd}\) atoms in the sites occupied by the six \(\text{Mn}^{III}\) in \([\text{Mn}^{II}\text{Cu}^{II}]_8\). The resulting \([\text{Pd}_{19}]\) giant octahedron is capped on four of its eight faces by additional \(\text{Pd}\) atoms, in positions close to those occupied by \(\text{Cu}^{II}\) 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 \([\{\text{Cu}^{II}\text{Mn}^{III}\text{Mn}^{III}\text{H}([\text{L}]_8\text{O}_6\text{Cl}_4\text{Cl}^{2-}\}^{11}\text{m}/\text{z} 1146.7\} \) and \([\{\text{Cu}^{II}\text{Mn}^{III}\text{Mn}^{III}\text{H}([\text{L}]_8\text{O}_6\text{Cl}_4\text{Cl}^{2-}\}^{11}\text{m}/\text{z} 1737.5\) and some fragmentation of the parent ion is observed, \([\text{Cu}^{II}\text{L}^{4-}]^{11}\text{m}/\text{z} 344.1\). 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).

Using our step-by-step approach, starting with a pre-formed \(\text{Cu}^{II}\) complex, we can trap and encapsulate manganese oxide nanoclusters. Reactions changing the anion (Cl\(^{-}\)), precursor (Cu\(^{II}\)) 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: \(\text{H}[\text{L}]/(5.70\text{g}, 20.2\text{mmol})\) and \(\text{CuCl}_2\cdot2\text{H}_2\text{O}/(5.28\text{g}, 31.0\text{mmol})\) 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 [Cu(H 6L)Cl]Cl·1.25H 2O was collected by filtration and washed with ethanol. Yield 6.3 g, 96%. IR: v ≈3310, 3232, 2947, 1430, 1084, 1064, 1011, 761 cm⁻¹. Elemental analysis (C 66H 144N 12O 56Cu 6Mn 18Cl 8, found: C 30.01, H 6.50, N 6.38; calcd: C 30.07, H 6.54, N 6.38. Single crystals suitable for X-ray study were obtained by recrystallization from ethanol yielding 1.05EtOH (see Supporting Information).

Syntesis of 2: 1.125H 2O (109 mg, 0.263 mmol) was dissolved in hot ethanol (60 mL at 60°C). NMe 3·H 2O·5H 2O (166 mg, 0.242 mmol) was added, and immediately dissolved, resulting in a clear royal blue solution which was heated for 30 min. MnCl 2·4H 2O (110 mg, 0.557 mmol) was added, resulting in an immediate color change to blue-black. The solution was heated for 3 h, and filtered. Black crystals of [Mn 18Cu 6O 14(H 2L)6Cl 2(H 2O)6]Cl 6·H 2O formed in the filtrate over 1 month (ca. 4 mg, 3%) (see Supporting Information).

Black crystals of [Cu(H 6L)Cl]Cl·1.25H 2O (109 mg, 0.263 mmol) was dissolved in methanol (30 mL). NEt 3 (0.07 mL, 0.502 mmol) was added, and immediately dissolved, resulting in an immediate color change to blue-black. The solution was heated for 4 h, and the precipitate (108 mg) was removed by filtration.

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