Self-assembly and magnetic properties of a double-propeller octanuclear copper(II) complex with a *meso*-helicate-type metallacryptand core

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An octanuclear copper(II) complex possessing a dimer-of-tetramers structure self-assembles from a binuclear oxamato-copper(II) metallacryptand of the *meso*-helicate type; its magnetic behaviour is consistent with its unique double-propeller molecular topology.

The self-assembly of large, well-defined metal cages is one of the foremost topics in modern coordination chemistry.[1] Apart from their fascinating metallo-supramolecular structures and relevant insights into metal-directed self-assembly processes,[2] these polymetallic species can display unique magnetic properties which result from the assembling topology of the paramagnetic metal ions by the bridging ligands.[3–6]

In the search for rationally designed polynuclear coordination compounds with predetermined spin topologies using oxamate-based ligands, we recently prepared the double-stranded binuclear copper(II) complex **1** from the self-assembly of two Cu^{II} ions and two mpba ligands [mpba = *N,N'*-1,3-phenylenebis(oxamate)].[7] Complex **1** has been further used as a building-block for extended two-dimensional bimetallic networks when coordinating four other metal ions at the free carbonyl oxygen atoms of the bidentate oxamate groups.[8] Here, we examine the related triple-stranded binuclear copper(II) complex **2** that results from the self-assembly of two Cu^{II} ions and three mpba ligands. Similarly to **1**, complex **2** can coordinate six metal ions with partially blocked coordination sites precluding polymerisation, thus yielding discrete high-nuclearity metal cages such as the octanuclear copper(II) complex Na$_2${[Cu$_2$(mpba)$_3$][Cu(pmdien)]$_6$}(ClO$_4$)$_6$·12H$_2$O **3** (pmdien = *N,N,N',N'',N''*-pentamethyldiethylenetriamine).
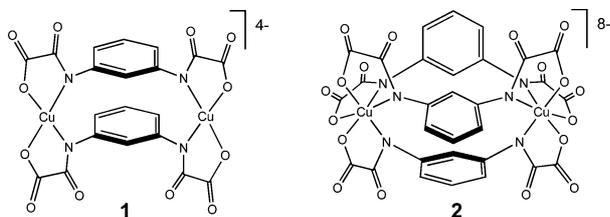
Compound **3** was synthesised in an one-pot reaction from the hexakis-bidentate anionic complex **2** and coordinatively unsaturated [Cu(pmdien)]$^{2+}$ cationic complexes.† This is a strict self-assembly process since these precursors were not isolated; each was formed *in situ* from a mixture of Cu^{2+} and the corresponding ligand in the appropriate stoichiometry. As a matter of fact, all our attempts to isolate **2** have failed, yielding **1** instead.

The structure of **3** consists of octanuclear copper(II) cations with C_{3h} molecular symmetry, {[Cu$_2$(mpba)$_3$][Cu(pmdien)]$_6$}$^{4+}$, together with sodium cations, perchlorate anions, and both coordinated and noncoordinated water molecules.‡ Interestingly, the octacopper cation is bound to two sodium cations through the carboxylate oxygen atoms of the oxamate groups in a *fac* arrangement [Na–O = 2.376(12) Å] (Fig. 1a). These bonding

interactions are likely to stabilise the motif **2** during the metal-directed self-assembly process leading to **3**.

The octacopper cation contains two chiral, oxamato-bridged, propeller-like tetranuclear units that are symmetry-related (Δ and Λ enantiomers) (Fig. 1b). Three *m*-phenylenediamide moieties bridge the central Cu(1) and Cu(1^I) atoms of the tetranuclear units, forming a binuclear metallamacrobicyclic core of the cryptand type (Fig. 1c).[9] Because of the presence of a mirror plane perpendicular to the molecular threefold axis, this achiral metallacryptand is a *meso*-helicate with a strictly zero helicoidal twist angle of the aromatic spacers around the Cu(1)–Cu(1^I) vector.[10] Within the metallacyclic core unit of **3**, the Cu(1) atom has a six-coordinate trigonally distorted octahedral environment [trigonal twist angle of 11.9(7)°]. The rather long metal–ligand bond lengths [Cu–N =
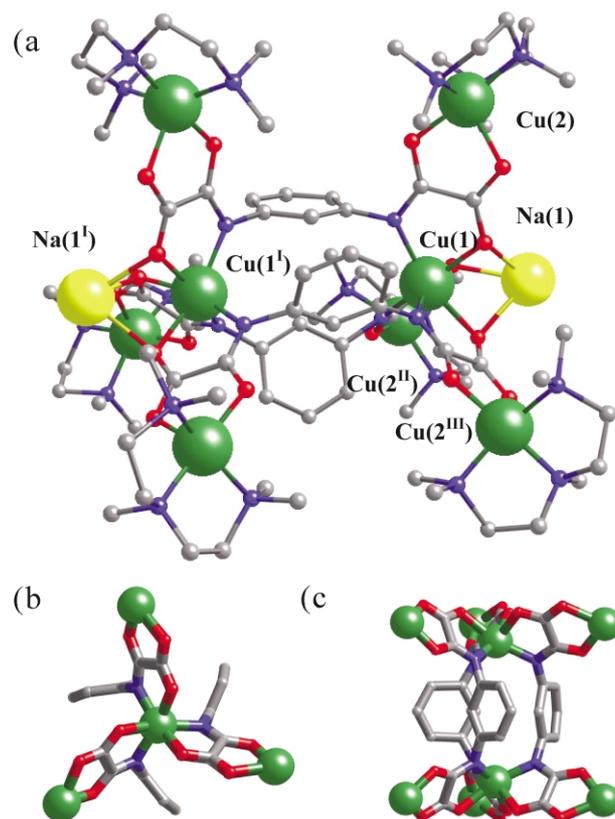

Fig. 1 (a) Perspective view of the cationic octacopper unit of **3** with the numbering scheme for metal atoms. Selected intermetallic distances (Å) with standard deviations in parentheses: Cu(1)–Cu(2) 5.440(13), Cu(1)–Cu(1^I) 6.612(7), Cu(2)–Cu(2^{II}) 9.307(2) (symmetry codes: I = *x*, *y*, 1/2 − *z*; II = −*y*, *x* − *y*, *z*; III = −*x* + *y*, −*x*, *z*). (b) Side and (c) top views of the octacopper skeleton of **3**.

2.079(12) and Cu–O 2.123(9) Å] compared to those of four-coordinate square-planar metal environment in **1** [average values of 1.95 and 1.96 Å, respectively][7] suggest a dynamic Jahn–Teller effect whereby the elongation spreads randomly over the three axes.[11] Moreover, unlike those in metallacyclophane **1**, the aromatic groups in **3** are not stacked parallel but disposed edge-to-face [dihedral angle of 60°] with a weak C–H···π interaction between neighbouring benzene rings [centroid–centroid distance of 5.366(9) Å].

The magnetic properties of **3** are consistent with its dimer-of-tetramers structure.§ Notably, the $\chi_M T$ *versus* T plot, χ_M being the molar magnetic susceptibility per octanuclear unit and T the temperature, presents a minimum at *ca.* 30 K (Fig. 2). This behaviour is characteristic of antiferromagnetically coupled tetra-nuclear complexes having a propeller-type topology whereby the spin topology dictates the non-compensation of the spins in the ground state.[12] Accordingly, the model of two magnetically isolated Cu^{II}_4 molecules with an antiferromagnetic coupling ($J = -57.0$ cm^{-1}) between the Cu(1) and Cu(2) ions through the oxamate bridges fits the experimental data for **3** in the high temperature region (dashed line in Fig. 2). This model predicts a plateau at the lowest temperatures, where only the triplet ground states of the two tetranuclear units ($S_A = S_B = 1$) are thermally populated. However, complex **3** exhibits a different behaviour in the low temperature region, as the $\chi_M T$ product decreases abruptly below 5 K. This is interpreted as the signature of an anti-ferromagnetic coupling ($j = -28.0$ cm^{-1}) between the Cu(1) and Cu(1^I) ions of each tetranuclear unit (solid line in Fig. 2), thus leading to a singlet ground state for **3** ($S = S_A - S_B = 0$). This moderate antiferromagnetic coupling is mediated by the triple *m*-phenylenediamide bridge between the Jahn–Teller distorted octahedral Cu^{II} ions within the core **2**. This situation differs dramatically from that of complex **1** which exhibits a ferromagnetic coupling between its square-planar Cu^{II} ions through the double *m*-phenylenediamide bridge.[7]

In summary, the binuclear metallacryptand of the *meso*-helicate type **2** can be self-assembled in solution from three aromatic bis(oxamate) ligands and two Cu^{II} ions, and then serve as a growing center for high-nuclearity metal cages such as the octanuclear copper(II) complex **3**. We are currently searching for three-dimensional bimetallic network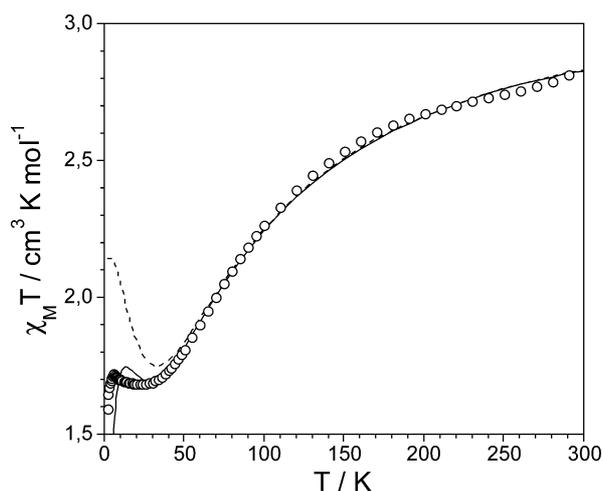s constructed from the binuclear precursor **2** and its analogues with paramagnetic first row transition metal ions other than Cu^{II} in order to elaborate new supramolecular magnetic materials.

Notes and references

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Fig. 2 Temperature dependence of $\chi_M T$ for **3**: (○) experimental data; (- -) best fit for two isolated Cu$_4$ molecules, and (—) best fit for a Cu$_8$ molecule.