

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

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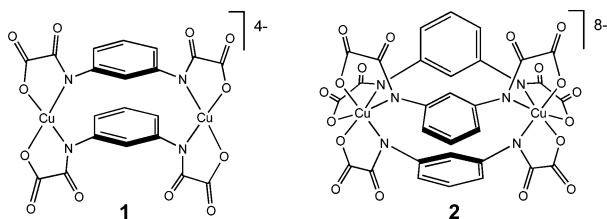
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An octanuclear copper(II) complex possessing a dimer-of-tetramers structure self-assembles from a binuclear oxamato-copper(II) metallacryptand of the *meso*-helicite type; its magnetic behaviour is consistent with its unique double-propeller molecular 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 poly-metallic 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 Na₂{[Cu₂(mpba)₃][Cu(pmdien)]₆}(ClO₄)₆·12H₂O **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 Cu²⁺ 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, {[Cu₂(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, oxamate-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(1¹) 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*-helicite with a strictly zero helicoidal twist angle of the aromatic spacers around the Cu(1)–Cu(1¹) 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 =

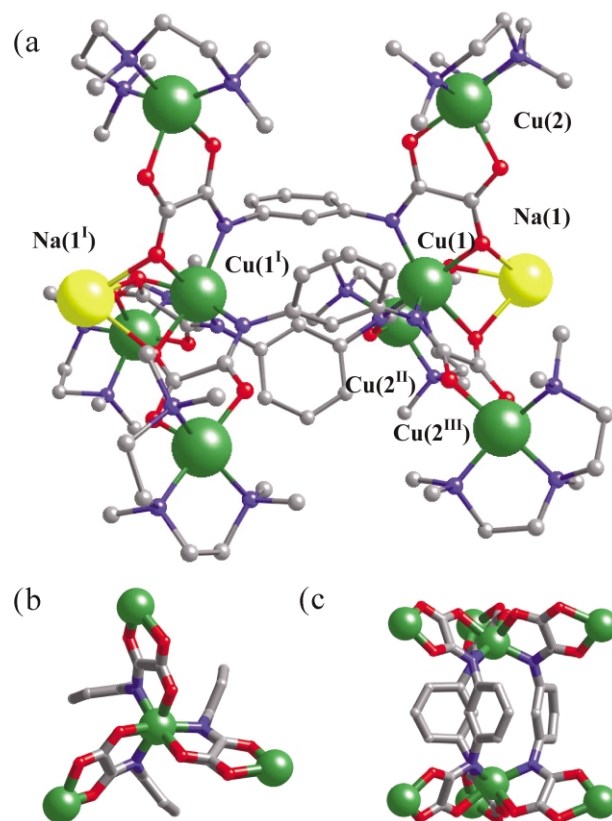


Fig. 1 (a) Perspective view of the cationic octacopper unit of **3** with the numbering scheme for metal atoms. Selected intermetallic distances (Å) with standard deviations in parentheses: Cu(1)–Cu(2) 5.440(13), Cu(1)–Cu(1¹) 6.612(7), Cu(2)–Cu(2^{II}) 9.307(2) (symmetry codes: I = *x*, *y*, 1/2 – *z*; 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 metallacyclopentane **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 tetranuclear 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 antiferromagnetic coupling ($j = -28.0$ cm⁻¹) between the Cu(1) and Cu(1') 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 networks constructed from the binuclear

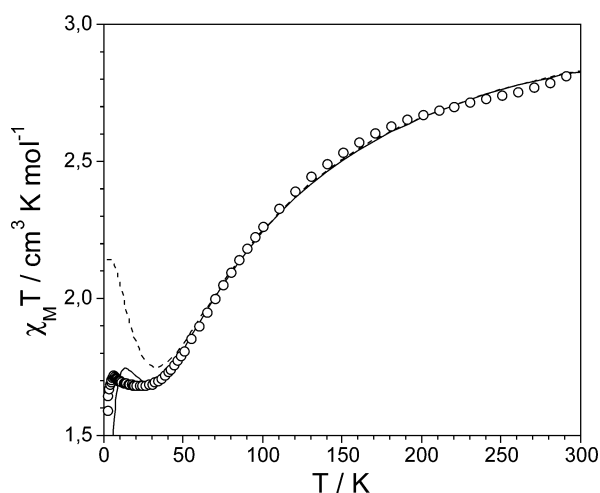


Fig. 2 Temperature dependence of $\chi_M T$ for **3**: (o) experimental data; (---) best fit for two isolated Cu₄ molecules, and (—) best fit for a Cu₈ molecule.

precursor **2** and its analogues with paramagnetic first row transition metal ions other than Cu^{II} in order to elaborate new supramolecular magnetic materials.

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Notes and references

† *Synthesis and selected data*: To a stirred suspension of H₄mpba⁷ (0.38 g, 1.0 mmol) in 5 mL of water was added a solution of NaOH (0.16 g, 4.0 mmol) in 5 mL of water. After complete dissolution, Cu(ClO₄)₂·6H₂O (0.25 g, 0.67 mmol) dissolved in 5 mL of water was added dropwise under stirring. The resulting deep green solution was then added dropwise to a solution of Cu(ClO₄)₂·6H₂O (0.74 g, 2.0 mmol) and pmdien (0.42 mL, 2.0 mmol) in 10 mL of water under stirring. Blue hexagonal prisms of **3** suitable for single crystal X-ray diffraction were obtained after several hours of standing at room temperature. They were filtered on paper and air-dried (60%). $\nu(\text{KBr})/\text{cm}^{-1}$ 3427vs (O–H) from H₂O, 3001w and 2971w (C–H) from mpba, 2930w (C–H) from pmdien, 1623vs and 1603 (sh) (C=O) from mpba, 1144 (sh), 1107 (sh) and 1091vs (Cl–O) from ClO₄.

‡ *Crystal data*: C₈₄H₁₇₄Cl₆Cu₈N₂₄Na₂O₅₄, $M = 3151.47$, hexagonal, $a = 17.4169(11)$, $b = 17.4169(11)$, $c = 31.739(2)$ Å, $U = 8338.1(9)$ Å³, $T = 293(2)$ K, space group $P6c2$, $Z = 2$, $\mu(\text{Mo–K}\alpha) = 1.179$ mm⁻¹, 5026 reflections measured, 2684 assumed as observed with $I > 2\sigma(I)$. Hydrogen atoms were calculated and refined with an overall isotropic thermal parameter (except for the water hydrogen atoms which were not found neither calculated). Refinement on F^2 of 271 variables with anisotropic thermal parameters for all non-hydrogen atoms gave $R = 0.089$ and $wR = 0.1473$ with $S = 1.108$ (observed data). CCDC 227333. See <http://www.rsc.org/suppdata/cc/b3/b316081e/> for crystallographic data in .cif format.

§ Variable-temperature (1.8–300 K) magnetic measurements under a magnetic field of 1.0 T were carried out on powdered samples of **3** with a SQUID magnetometer. Least-squares fitting of the magnetic susceptibility data of **3** were performed by full matrix diagonalisation of the isotropic spin Hamiltonian $H = -J(S_{A1}S_{A2} + S_{A1}S_{A3} + S_{A1}S_{A4} + S_{B1}S_{B2} + S_{B1}S_{B3} + S_{B1}S_{B4}) - jS_{A1}S_{B1} - g\beta(S_{A1} + S_{A2} + S_{A3} + S_{A4} + S_{B1} + S_{B2} + S_{B3} + S_{B4})B$ (with $S_{A1} = S_{A2} = S_{A3} = S_{A4} = S_{B1} = S_{B2} = S_{B3} = S_{B4} = 1/2$) with the VPMAG program.¹³

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