Heptanuclear hydroxo-bridged copper cluster of the dicubane-like type: structural and magnetic characterisations of [Cu$_7$(OH)$_6$Cl$_2$(pn)$_6$(H$_2$O)$_2$](C(CN)$_3$)$_4$Cl$_2$ (pn = 1,3-diaminopropane)†

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A new polynuclear copper(II) complex [Cu$_7$(OH)$_6$Cl$_2$-(pn)$_6$(H$_2$O)$_2$](C(CN)$_3$)$_4$Cl$_2$ with hydroxo-bridging ligands has been prepared; the centrosymmetric cluster cation can be described as two Cu$_4$O$_3$Cl distorted cubane units sharing one copper cation.

Various multinuclear copper(II) complexes have been reported in the last decade with a great number of simple and sophisticated bridging ligands;[1–5] however, some nuclearities remain comparatively scarce. In the case of tetranuclear complexes with Cu$_4$O$_4$ cubane-like clusters some examples have been thoroughly described,[2] but to date little is known about clusters involving more than four metal centres.[3,4] Concerning the heptanuclear copper(II) clusters, as far as we are aware, only one example of the dicubane-like type has been described.[5] Here we report the structure and preliminary magnetic studies of a novel vertex sharing dicubane-like heptanuclear copper(II) cluster [Cu$_7$(OH)$_6$Cl$_2$(pn)$_6$(H$_2$O)$_2$]-(tcm)$_4$Cl$_2$ (**1**) [pn = 1,3-diaminopropane; tcm$^-$ = C(CN)$_3^-$ = tricyanomethanide] with chloro- and hydroxo-bridging ligands.

1.00 mL (12 mmol) of 1,3-diaminopropane (pn) was slowly added to a warm aqueous solution of CuCl$_2$·2H$_2$O (12 mmol) and then an aqueous solution of sodium hydroxide (12 mmol) was added. To the resulting clear solution were immediately and consecutively added concentrated aqueous solutions of CuCl$_2$·2H$_2$O (2 mmol) and potassium tricyanomethanide (8 mmol). Slow evaporation gave prismatic blue crystals of [Cu$_7$(OH)$_6$Cl$_2$(pn)$_6$(H$_2$O)$_2$](tcm)$_4$Cl$_2$ (yield 1.28 g, 42%) suitable for crystallography.‡ The structure of **1** is unique and consists of a centrosymmetric hydroxo-bridged heptanuclear copper(II) cation (Fig. 1) which can be described as two Cu$_4$O$_3$Cl distorted cubanes which share one copper cation (Cu1) (Fig. 1 and 2). The four crystallographically independent Cu(II) centres differ markedly in their co-ordination geometry.

† Electronic supplementary information (ESI) available: detailed synthesis and X-ray crystallography of **1**. See http://www.rsc.org/suppdata/cc/b1/b105231b/

The central atom (Cu1) presents a strongly elongated octahedral coordination which involves a CuO$_4$ equatorial plane with essentially equivalent Cu–O bonds [see Fig. 2(a)] and two semi-coordinated Cl anions in axial positions (Cu···Cl = 3.029(2) Å). The Cu2 and Cu3 cations have distorted square pyramidal CuO$_2$N$_2$Cl environments. In both cases, the basal planes are occupied by two hydroxo bridging ligands (O1 and O3 for Cu2; O2 and O3 for Cu3) and two nitrogen atoms of the chelating pn ligand (Cu–O range 1.977–2.016 Å and Cu–N range 1.975–2.021 Å). Both pyramids share a strongly elongated axial position filled by the bridging Cl1 atom (Cu2–Cl1 = 2.654(2) Å and Cu3–Cl1 = 2.679(2) Å) (Fig. 1). The co-ordination
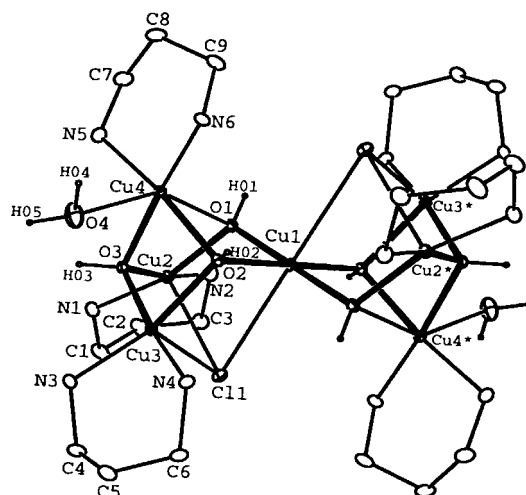

Fig. 1 ORTEP of the heptanuclear cation in **1** showing atomic labelling scheme (30% probability ellipsoids). Shortest Cu···Cu distances (Å) and selected bond angles (°): Cu1–Cu2 3.3796(5), Cu1–Cu3 3.3719(5), Cu1–Cu4 3.1873(5), Cu2–Cu3 3.2829(8), Cu3–Cu4 3.1607(8), Cu3–Cu4 2.9610(8); O1–Cu1–O2 83.9(1), O1–Cu1–O3 84.5(1), O2–Cu3–O3 80.1(1), O1–Cu4–O2 72.0(1), O1–Cu4–O3 73.7(1), O2–Cu4–O3 79.5(1). Code of equivalent positions: (*) ½ − x, ½ − y, 1 − z.
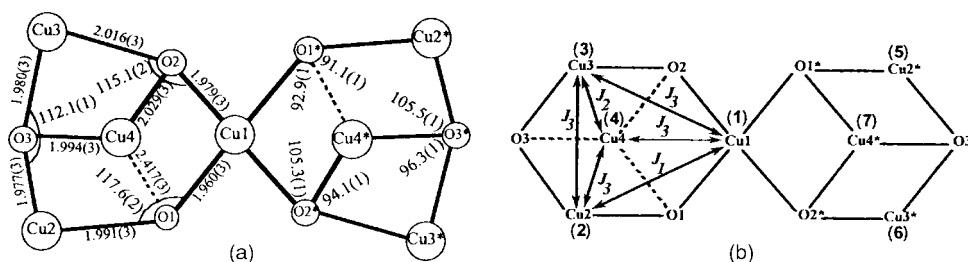

Fig. 2 (a) Schematic projection of the copper cluster including pertinent bond lengths and bond angles; (b) schematic representation of the magnetic coupling model in **1**. Code of equivalent positions: (*) ½ − x, ½ − y, 1 − z.
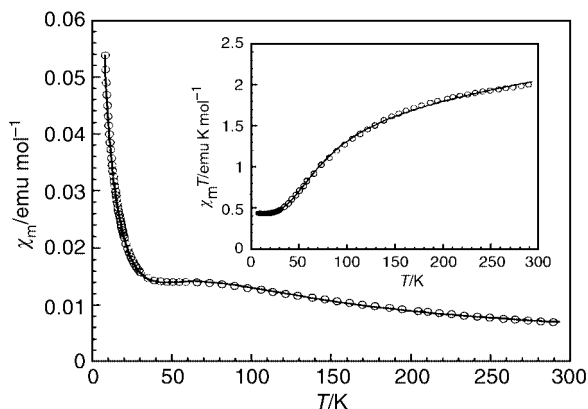
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Fig. 3 Plots of molar susceptibility χ_m *vs. T* (the inset shows the $\chi_m T$ product *vs. T*) for **1** measured in a field of 1 T. The solid line was calculated using the magnetic coupling model (see text).

polyhedron of the Cu4 cation can be described as a $Cu(N_2O_2)(O_2)$ pseudo-octahedron generated by a CuN_2O_2 plane arising from two nitrogen atoms of the chelating pn ligand and the two μ_3-hydroxo ligands (O2 and O3), and two axial positions filled by the O1 hydroxo ligand and a water molecule (O4) ($Cu\cdots O4 = 2.524(4)$ Å). Note that the O1 hydroxo ligand may be viewed as a μ_2-bridging group since it involves two short and one long Cu–O distances as clearly shown on Fig. 2(a). Further examination of the structure shows that the tcm units, which usually act as μ_2- or μ_3-bridging ligands, are here uncoordinated; however, there are significant hydrogen bonds formed between their nitrogen atoms and the hydroxo-bridging ligands [N7(tcm)$\cdots$O2 = 2.826(6) Å, O1–H$\cdots$N7 = 167.3(3)° and N8(tcm)$\cdots$O1 = 2.961(6) Å, O1–H$\cdots$N7 = 160.6(2)°]. Such intermolecular hydrogen bonds may contribute to the stabilisation of the cluster conformation.

Magnetic susceptibility data for **1** were collected in the temperature range 2–300 K, the χ_m and $\chi_m T$ product *vs. T* plots are depicted in Fig. 3. From room temperature down to 25 K the $\chi_m T$ product decreases continuously and then reaches a plateau close to 0.43 emu K mol^{-1}, which corresponds to an $S = 1/2$ ground state. This behaviour is indicative of an overall antiferromagnetic coupling between the Cu(II) centres; this is in agreement with the strongly reduced magnetic moment at room temperature ($\chi_m T = 2.01$ emu K mol^{-1}). Taking into account the cluster topology and connectivity (Fig. 2), it is possible to distinguish up to six different exchange pathways. However, in order to avoid an overparameterization and in view of the Cu–O–Cu angles and connectivity of the OH bridges (μ_2-OH or μ_3-OH), these six exchange pathways have been grouped into three averaged different exchange parameters. The magnetic data have been analysed with the following spin Hamiltonian:

$$\hat{H} = -2J_1(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_5) - 2J_2(\hat{S}_3\hat{S}_4 + \hat{S}_6\hat{S}_7)$$
$$-2J_3(\hat{S}_1\hat{S}_3 + \hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_3 + \hat{S}_2\hat{S}_4 + \hat{S}_1\hat{S}_6 + \hat{S}_1\hat{S}_7 + \hat{S}_5\hat{S}_6 + \hat{S}_5\hat{S}_7)$$

Calculations have been performed with the magnetism package MAGPACK.[6] The best fit obtained from a least-squares analysis of the $\chi_m T$ is $J_1 = -188.4$ cm^{-1}, $J_2 = -52.6$ cm^{-1}, $J_3 = -10.8$ cm^{-1} and $g = 2.15$ ($R = \Sigma [((\chi_m T)_{obs}^2 - (\chi_m T)_{calc}^2)/(\chi_m T)_{obs}^2] = 7.8 \times 10^{-3}$). Attempts to fit it with only one or two averaged exchange parameters failed. As expected from the structural parameters depicted in Fig. 2(a) (Cu–O distances and Cu–O–Cu angles), the results show the presence of two weak antiferromagnetic interactions (J_2 and J_3) associated to the interactions by μ_3-OH as have been observed in previous cubane-type systems[2,3] and a strong one (J_1) corresponding to the exchange interaction between the two Cu connected by O1 that has a main component of μ_2-OH and a large Cu–O–Cu angle (117.6°).

Notes and references

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