Preparation, structure and preliminary magnetic studies of an octanuclear alkoxo-bridged copper(II) cluster of the acetato-bridged dicubane type

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A novel double-cubane copper complex $[Cu_8L_8(O_2CMe)_4][ClO_4]_4$ is prepared, and structurally and magnetically characterised (L = the monoanion of the hydrated, *gem*-diol form of di-2-pyridyl ketone).

The arrangement of four metal ions and four triply bridging ligands at alternating vertices of a cube is a well precedented unit in inorganic chemistry.[1] Restricting further discussion to alkoxo-bridged copper(II) cubanes, the $[Cu_4(\mu_3\text{-}OR)_4]^{4+}$ core has been structurally characterised in several complexes.[2] Their magnetic properties have been described by considering exchange interactions between all four metals,[3,4] although much controversy exists concerning the relative order of the various multiplets.[5]

In searching for tetranuclear copper(II) clusters, we report herein the remarkable dicubane complex $[Cu_8L_8(O_2CMe)_4](ClO_4)_4 \cdot 9H_2O$ **1**. Solid di-2-pyridyl ketone (1.09 mmol) and $NaClO_4 \cdot H_2O$ (0.57 mmol) were added to a warm solution of $[Cu_2(O_2CMe)_4(H_2O)_2]$ (0.55 mmol) in H_2O (30 ml). Following overnight storage at room temp., pure green crystals of **1** were obtained in 30% yield.

X-Ray analysis† reveals that the unit cell contains two well separated $[Cu_8L_8(O_2CMe)_4]^{4+}$ cations, each lying on an inversion centre and each comprising a distorted double cubane (Figs. 1 and 3). The asymmetric unit contains two structurally similar, independent cubanes [Cu(1)–Cu(4), Cu(5)–Cu(8)], each belonging to a different cation, four ClO_4^- ions and nine water molecules. The two centrosymmetrically related cubanes in the tetracation are doubly bridged by two *syn,anti* acetate groups *via* the two Cu(3) atoms. One oxygen atom [O(2), O(12), O(22), O(32)] of each ligand L remains protonated and unbound to the metals. The resulting monoanion functions as an $\eta^1 : \eta^3 : \eta^1 : \mu_3$ ligand. This ligation mode is unprecedented in the coordination chemistry of hydrated di-2-pyridyl ketone.[6] Finally, a terminal monodentate acetate is ligated to Cu(2). The Cu(1) and Cu(4) centres have similar axially elongated, distorted octahedral coordination geometries with CuO_3N_3 chromophores. For Cu(3), a less irregular NO_5 six-coordination is preserved. The Cu(2) atom displays a distorted square-pyramidal geometry in which and alkoxide oxygen, O(1), occupies the apical position. Complex **1** joins a very small family of discrete copper(II) aggregates with nuclearity of eight.[7] Moreover, since the tetrameric cubane-type molecules are usually classified into two groups[2]—according to their structural properties—each cubane moiety of **1** belongs to type I.

Variable-temperature, solid-state, magnetic susceptibility studies have been performed on a powdered sample of **1** in the 4.2–300 K range (Fig. 2) using a SQUID magnetometer. The product $\chi_M T$, where χ_M is the molar magnetic susceptibility per cubane moiety (tetramer), continuously decreased as the temperature was lowered (2.05 cm^3 K mol^{-1} at 300 K and 1.1 cm^3 K mol^{-1} at *ca.* 50 K) indicating the presence of an antiferromagnetic exchange interaction between the Cu^{II} ions, and remained steady between 50 and 8 K with a slight decrease only below 8 K. The $\chi_M T$ value in the 50–8 K plateau corresponds to a triplet state of a copper(II) tetramer. These experimental susceptibility data preclude strong exchange between the cubanes of the octamer as was expected from the long Cu(3)–O(112′) distance [2.723(1) Å]. Hence, even though structurally **1** is referred to as a dicubane, its magnetic behaviour should be considered as that of a simple cubane with a molecular-field correction to account for the intercubane magnetic interactions. Fitting of the experimental χ_M data to the analytical expressions obtained by using eqns. (5) and (6) of ref. 3 failed, revealing strong correlation between the J and θ

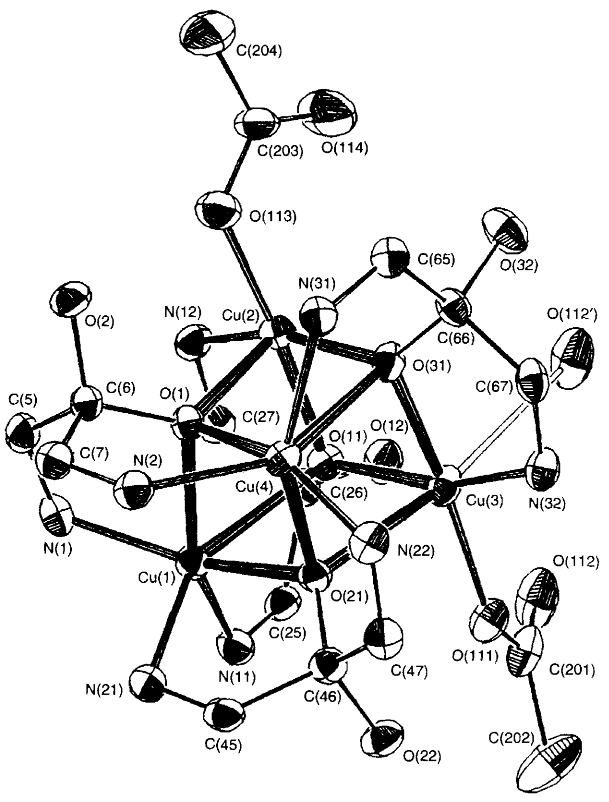

Fig. 1 ORTEP representation of one of the 'half' cations, *i.e.* one cubane segment, of complex **1**. To avoid congestion, most aromatic carbon atoms of L are omitted. Note that only the oxygen atom [O(112′)] of the second intercubane acetate is shown. Selected distances (Å): Cu(1)···Cu(2) 3.305(2), Cu(1)···Cu(4) 3.005(2), Cu(2)···Cu(3) 3.039(2), Cu(3)···Cu(4) 3.375(2), Cu(1)–O(1) 2.062(7), Cu(1)–O(11) 2.573(6), Cu(1)–O(21) 1.975(7), Cu(2)–O(1) 2.355(6), Cu(2)–O(113) 1.922(8), Cu(3)–O(111) 1.936(8), Cu(3)–O(112′) 2.723(1), Cu(4)–O(21) 2.032(6), Cu(4)–N(22) 2.016(9).

values. This indicates stronger interactions in the four 'dimers' than those observed[3] in $[Cu_4(NCO)_4(OCH_2CH_2NMe_2)_4]$ **2**, which is also a type I tetrameric cubane complex. Hence, the experimental data were fitted to the analytical expression obtained by using the spin-Hamiltonian corresponding to C_2 symmetry[4] [$J_2 = J_{Cu(2)Cu(3)}$, $J_4 = J_{Cu(1)Cu(4)}$, $J_1 = J_{Cu(1)Cu(2)} = J_{Cu(3)Cu(4)}$, $J_3 = J_{Cu(1)Cu(3)} = J_{Cu(2)Cu(4)}$ (Fig. 3)]. The final expression of the calculated susceptibility, χ, is given in eqn. (1), where χ'_M stands for the χ_M also involving a

$$\chi = (1 - x)\chi'_M + \frac{xNg^2\beta^2}{4kT} + N\alpha \qquad (1)$$

molecular-field correction, χ_{MFC}, to account for the intercubane interaction, J; x is the mole fraction of a monomeric impurity, while the interaction Hamiltonian is $H = -2\sum_{i<j} J_{ij}S_iS_j$. The temperature-independent paramagnetism, $N\alpha$, was fixed at 60×10^{-6} cm^3 mol^{-1}. The best fit‡ of the exchange parameters (according to the numbering scheme shown in Fig. 3) and the Lande g factor was obtained from $J_1 = 6(1)$, $J_2 = -144(5)$, $J_3 = -14(2)$, $J_4 = 3(1)$, $J = -0.5(1)$ cm^{-1} and $g = 2.29(1)$ {$R = \Sigma_n[(\chi T)_{exptl} - (\chi T)_{calc}]^2 = 2.9 \times 10^{-4}$, with $x = 0.007$}; g was treated as an adjustable parameter.[8]

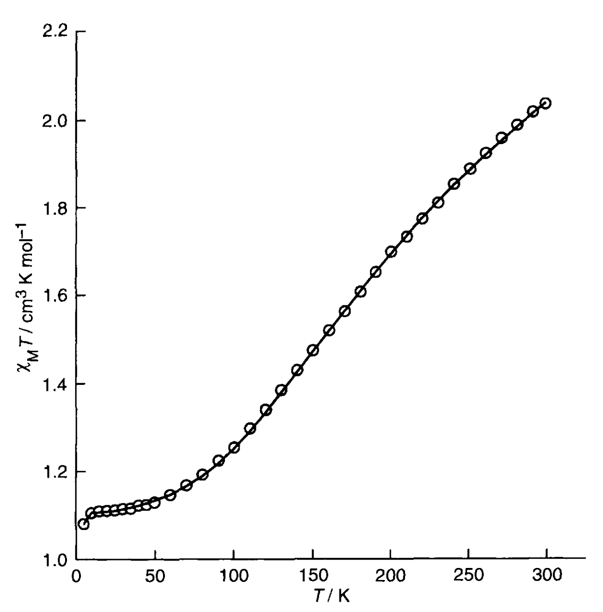

Fig. 2 Plot of $\chi_M T$ per cubane *vs.* T for a polycrystalline sample of complex **1**. The solid line results from a least-squares fit of the data to the appropriate theoretical expression; see text for fitting parameters.

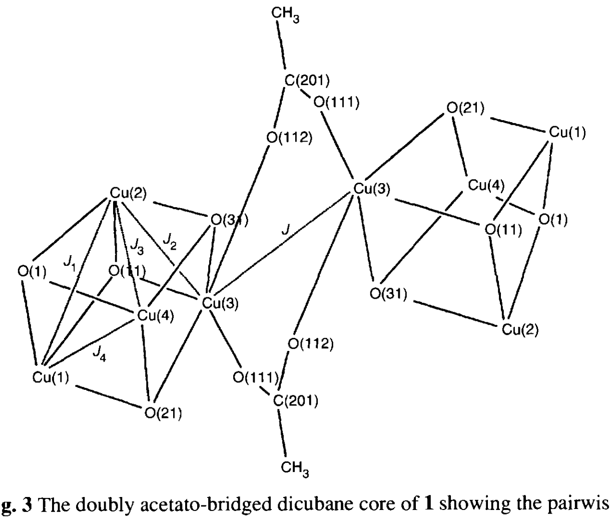

Fig. 3 The doubly acetato-bridged dicubane core of **1** showing the pairwise magnetic exchange interactions in one of the cubane moieties of complex **1**; to avoid congestion, the Cu(1)···Cu(3) [J_3] and Cu(3)···Cu(4) [J_1] exchange parameters are omitted

Ferro- and antiferro-magnetic interactions within the same molecule are a principal feature of tetranuclear oxygen-bridged copper(II) complexes of the cubane type.[9] Moreover, the relative magnitudes of all J parameters in **1** are in agreement with the magnetostructural correlations established for the di-μ-alkoxo-bridged copper(II) dimers,[3,10] whereas the *syn,anti* configuration of the acetato groups and the long Cu(3)–O(112) distances account well for the very weak antiferromagnetic intercubane interactions calculated. Note that the ground state of the cubane, based upon the order of the energy levels obtained from the analysis of the temperature dependence of the magnetic susceptibility, is a triplet, which is in agreement with the low-temperature EPR spectra of **1** (to be presented in the full paper). However, an overall antiferromagnetic interaction results, depending on the relative magnitudes of the antiferro- and ferro-magnetic interactions, related to structural features. Finally, **1** constitutes an example of a compound that allows an adequate characterization of its low-lying levels.[5]

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Footnotes

† *Crystal data* for **1**: $C_{96}H_{102}Cl_4Cu_8N_{16}O_{49}$, $M = 2914.06$, triclinic, space group $P\bar{1}$, $a = 18.396(1)$, $b = 16.720(1)$, $c = 19.171(1)$ Å, $\alpha = 96.10(1)$, $\beta = 87.68(1)$, $\gamma = 99.14(1)°$, $U = 5786.9(7)$ Å^3, $F(000) = 2964$, $Z = 2$, $D_c = 1.672$ g cm^{-3}, $\lambda = 0.7107$ Å, $T = 25$ °C, $2\theta_{max} = 50.1°$, $wR2$ (on F^2), $R1$ (on F) = 0.3286, 0.1217 for 16164 unique reflections with $I > 2\sigma(I)$. The structure was solved by direct methods using SHELXS-86 (G. M. Sheldrick, University of Gottingen, 1986) and refined by full-matrix least-squares techniques using SHELXL-93 (G. M. Sheldrick, University of Gottingen, 1993). Most non-hydrogen atoms were refined anisotropically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/60.

‡ Initially we considered all four parameters within each cubane entity and the best fit was made for a high negative intracubane parameter value, a much lower negative one, two positive and a very low negative J value. Retaining this fit, with J_1 and J_3 as variables and $J_2 = J_4 = 0$, then with these J_1 and J_3 values J_2 and J_4 were fitted. This procedure was continued until self-consistent values for all parameters were found.

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