

Crystal structure and ferromagnetic behaviour of a novel tetranuclear copper(II) complex with an open cubane-like Cu_4O_4 framework

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The novel tetranuclear copper(II) complex $[\text{Cu}_4(\text{hpda})_4][\text{ClO}_4]_4 \cdot \text{H}_2\text{O}$ (Hhpda = *N*-(2-hydroxyethyl)-1,3-propanediamine) with an open cubane-like Cu_4O_4 framework has been obtained and characterized by X-ray crystallography and magnetic measurements, exhibiting strongly ferromagnetic exchange interaction.

Over the years multinuclear copper(II) complexes have been receiving much attention, much of which stems from magneto-structural correlations in copper(II) complexes. The flexibility of the coordination sphere around Cu(II), in combination with steric and crystal packing forces, leads to its tremendous structural diversity. Small changes in structure can have far reaching effects on the magnetic properties of these systems.¹ Another reason for interest in multinuclear copper(II) complexes is the growing awareness of the involvement of cluster compounds at the active sites of biomolecules. Up to now several kinds of tetranuclear copper(II) complexes have been studied, most of which show antiferromagnetic coupling.² We have been studying some copper(II) complexes which catalyze the hydrolysis of phage DNA or peptides.³ Recently, during our study of the hydrolytic cleavage of peptides promoted by the copper(II) [*N*-(2-hydroxyethyl)-1,3-propanediamine] complex, a novel tetranuclear copper(II) complex with an open cubane-like Cu_4O_4 framework has been isolated and characterized by X-ray crystallography and magnetic measurements, which shows strongly ferromagnetic interactions *via* single-oxygen bridged copper(II) ions. We present here the crystal structure and magnetic behaviour of this compound.

The copper(II)-hpda complex was isolated as its perchlorate salt $\{[\text{Cu}_4(\text{hpda})_4][\text{ClO}_4]_4 \cdot \text{H}_2\text{O} \mathbf{1}\}$ in 60% yield from the reaction solution (H_2O -MeOH) of copper(II) perchlorate hexahydrate (2 mmol) and *N*-(2-hydroxyethyl)-1,3-propanediamine (Hhpda) (2 mmol) at pH 8. Blue crystals were grown by slow evaporation of an ethanol-water solution of this compound. The crystal structure of $[\text{Cu}_4(\text{hpda})_4][\text{ClO}_4]_4 \cdot \text{H}_2\text{O} \mathbf{1}$ (Fig. 1)[†] exhibits an open cubane-like Cu_4O_4 core structure arrangement of four copper(II) ions and four bridging oxygens from deprotonated *N*-(2-hydroxyethyl)-1,3-propanediamine and the four Cu(II) ions form a tetrahedral configuration. This structure is different from all other cubane-like Cu_4O_4 core structures in which two neighbouring Cu(II) atoms are dibridged with oxygen atoms or acetates.² Each hpda acts as a tridentate ligand to one copper atom leading to a five-membered ring and a six-membered ring. Each Cu(II) atom is found in a slightly distorted square-planar N_2O_2 coordination environment. The dihedral angle between the two square planes of Cu(II) atoms bridged with single oxygen is nearly perpendicular (95.08° for Cu1 and Cu2, 96.57° for Cu1 and Cu3, and 82.58° for Cu3 and Cu4), respectively, while the other kind of dihedral angles between two square planes of copper(II) atoms without an oxygen bridge are 37.91° for Cu1 and Cu4 and 38.19° for Cu2 and Cu3, respectively. The bridged Cu...Cu separation is in the range from 3.15(1) (Cu1...Cu2) to 3.22(1) Å (Cu1...Cu3), while

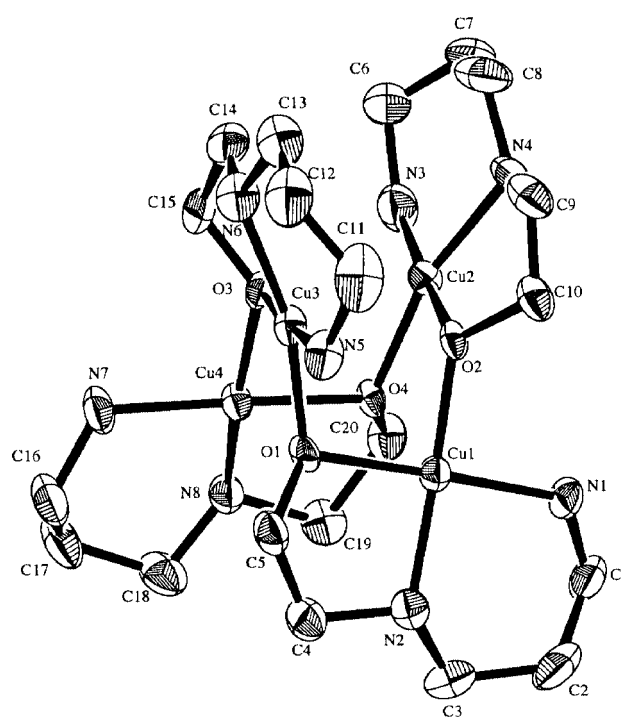


Fig. 1 An ORTEP⁴ representation of the cation in $[\text{Cu}_4(\text{hpda})_4][\text{ClO}_4]_4 \cdot \text{H}_2\text{O} \mathbf{1}$ with 30% probability ellipsoids. H atoms have been omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): Cu(1)–O(1) 1.957(8), Cu(1)–O(2) 1.957(8), Cu(1)–N(1) 1.99(1), Cu(1)–N(2) 2.00(1), Cu(2)–O(2) 1.935(9), Cu(2)–O(4) 1.994(8), Cu(2)–N(3) 1.96(1), Cu(2)–N(4) 2.04(1), Cu(3)–O(1) 1.979(8), Cu(3)–O(3) 1.923(9), Cu(3)–N(5) 1.97(1), Cu(3)–N(6) 2.02(1), Cu(4)–O(3) 1.966(8), Cu(4)–O(4) 1.960(8), Cu(4)–N(7) 1.98(1), Cu(4)–N(8) 2.00(1), Cu(1)···Cu(2) 3.15(1), Cu(1)···Cu(3) 3.22(1), Cu(1)···Cu(4) 3.41(1), Cu(2)···Cu(3) 3.38(1), Cu(2)···Cu(4) 3.22(1), Cu(3)···Cu(4) 3.19(1), Cu(1)–O(2)–Cu(2) $108.0(4)$, Cu(1)–O(1)–Cu(3) $110.1(4)$, Cu(3)–O(3)–Cu(4) $110.0(4)$, Cu(2)–O(4)–Cu(4) $108.9(4)$.

the unbridged Cu...Cu separation is 3.41(1) (Cu1...Cu4) or 3.38(1) Å (Cu2...Cu3), respectively.

The magnetic properties of the complex have been investigated down to 5 K (Fig. 2).[‡] The magnetic exchange interaction for this tetranuclear complex can be described as in Fig. 3 with J ($J = J_{12} = J_{13} = J_{34} = J_{24}$) for bridged Cu(II) atoms and J' ($J' = J_{14} = J_{23}$) for unbridged Cu(II) atoms. The magnetic susceptibility data for the complex was least-squares fitted to the Heisenberg–van Vleck equation^{2f} and the fitting parameters were found to be $J = 44.9 \text{ cm}^{-1}$, $J' = -16.3 \text{ cm}^{-1}$, $g = 2.06$, $\rho = 5.1 \times 10^{-4}$ (for the molar fraction of mononuclear Cu(II) ions) and N_A (temperature independent magnetic susceptibility) taken as $240 \times 10^{-6} \text{ emu mol}^{-1}$. The solid lines in Fig. 2 represent a least-squares fit to the theoretical equation, which can be seen to be good ($R = \Sigma(\chi_{\text{calc}} - \chi_{\text{obs}})^2 / \Sigma(\chi_{\text{obs}})^2 = 0.043$).

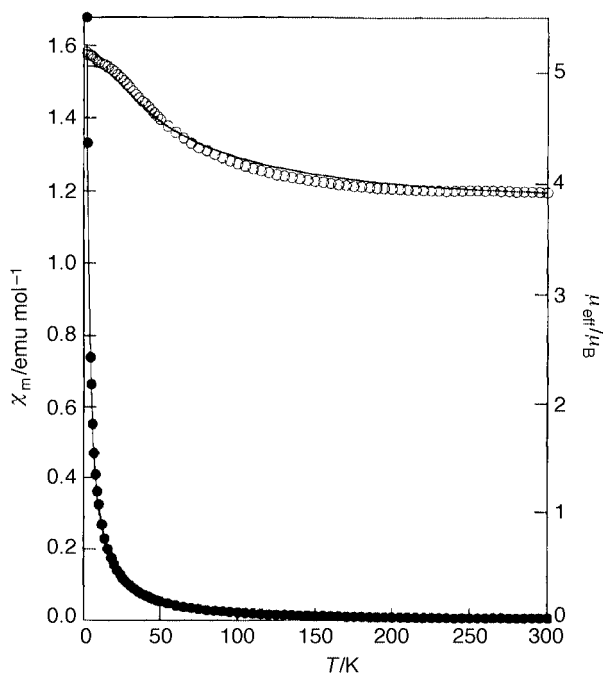
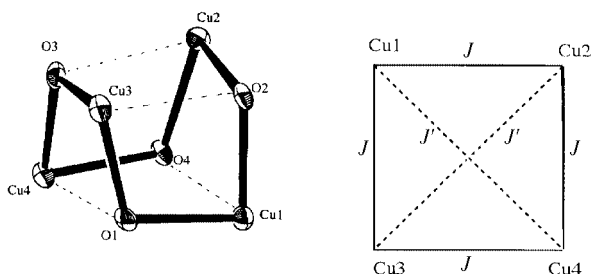


Fig. 2 Plots of molar susceptibility ($\chi_m/\text{emu mol}^{-1}$) and effective magnetic moment (μ_{eff}/μ_B) versus temperature of a powdered sample of $[\text{Cu}_4(\text{hpda})_4][\text{ClO}_4]_4 \cdot \text{H}_2\text{O}$. The solid lines represent the best fit of the data.



$J = J_{12} = J_{13} = J_{34} = J_{24}$, between single-oxygen-bridged Cu(II) atoms

$J' = J_{14} = J_{23}$, between unbridged Cu(II) atoms.

Fig. 3 Schematic representation of the magnetic coupling model in $[\text{Cu}_4(\text{hpda})_4][\text{ClO}_4]_4 \cdot \text{H}_2\text{O}$.

The results show the presence of both strongly ferromagnetic (between bridged Cu(II) atoms) and weakly antiferromagnetic (between unbridged Cu(II) atoms) interactions, which are different from those of other dioxygen-bridged tetranuclear copper(II) complexes with antiferromagnetic spin coupling.^{2c,d} The magnetic behaviour of this compound is similar to that of another tetranuclear Cu(II) complex^{2e} in which each copper atom is strictly five-co-ordinate and the magnetic exchange interaction is relatively weak. The ferromagnetic intratetramer interaction could be attributed to the orthogonality of the magnetic orbitals of square-planar copper(II) atoms ($d_{x^2-y^2}$ orbitals) and bridging oxygen atom (p orbitals). Effects for the magnetic exchange mechanism study of this complex by performing a quantum calculation to find the relationship between energy gaps of two singly occupied orbitals of Cu(II) atoms and some structural factors is underway.

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Notes and references

† Crystal data for $\text{C}_{20}\text{H}_{54}\text{N}_8\text{O}_{21}\text{Cl}_4\text{Cu}_4$, $M = 1138.68$, monoclinic, space group $P2_1/n$, $a = 19.458(5)$, $b = 11.518(3)$, $c = 19.846(4)$ Å, $\beta = 109.15(1)^\circ$, $U = 4201(1)$ Å³, $\lambda = 0.71069$ Å, $Z = 4$, $D_c = 1.800$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 2.335$ mm⁻¹, $T = 296.2$ K. 12453 Reflections measured, 6935 unique ($R_{\text{int}} = 0.075$), 3092 observed ($I > 2.00\sigma(I)$). Crystal structure solution was by direct methods with (SIR92)⁵ and was expanded using Fourier techniques with DIRDIF94.⁶ Full-matrix least-squares refinement was carried out on F with most non-hydrogen atoms anisotropic, while several oxygen atoms of disordered perchlorates were refined isotropically. Hydrogen atoms were included but not refined. Final R and R_w values on observed data are 0.068 and 0.071. CCDC reference number 186/1528. See <http://www.rsc.org/suppdata/dt/1999/2415/> for crystallographic files in .cif format.

‡ Magnetic susceptibility measurements were measured on a Quantum Design MPMS-5S SQUID susceptometer with a powdered sample of the copper tetramer. Measurements were made in the temperature region 5–300 K and at external field strengths of 0.5 T. Fig. 2 shows the plots of molar susceptibility ($\chi_m/\text{emu mol}^{-1}$) and effective magnetic moment (μ_{eff}/μ_B) versus temperature. The magnetic data were analysed using the Heisenberg Hamiltonian and the magnetic susceptibility can then be expressed as:^{2h}

$$\chi_m = \frac{2Ng^2\beta^2}{kT} \cdot \frac{A}{B} (1 - \rho) + \frac{Ng^2\beta^2}{kT} \rho + N_a$$

$$A = 2\exp(2J'/kT) + \exp[4J' - 2J/kT] + 5\exp[4J' + 2J/kT]$$

$$B = 1 + 6\exp(2J'/kT) + \exp[(4J' - 4J)/kT] + 3\exp[(4J' - 2J)/kT] + 5\exp[(4J' + 2J)/kT]$$

where ρ is the (molar) fraction of mononuclear copper(II) ions and the other symbols have their usual meanings.

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