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Three Different Co-ordination Geometries in the Pentacopper(II) Unit of $[Cu_5(OH)_2(H_2O)(O_2CMe)_6(Him)_4][ClO_4]_2$ (Him = imidazole)

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The reaction of imidazole (Him) with $[Cu_2(\mu\text{-}O_2CMe)_4(H_2O)_2]$ in water–$NaClO_4$ led to the formation of a polynuclear copper(II) complex, $[Cu_5(OH)_2(H_2O)(O_2CMe)_6(Him)_4][ClO_4]_2$ **1**, in which the pentanuclear units, showing four, five and six co-ordination geometries for the copper(II) centres and Cu···Cu distances of 3.043(1), 3.178(1) and 3.578(1) Å, were linked by aqua bridges to give an intra-chain inter-unit Cu···Cu separation of 4.507(1) Å.

Dimeric copper(II) carboxylates are known[1-3] to form diaxial adducts, $Cu_2(O_2CR)_4L_2$ (R = alkyl or aryl, L = axial ligand) with N- and O-donor ligands. Here we describe an unprecedented conversion of the tetraacetato core of $[Cu_2(O_2CMe)_4(H_2O)_2]$ by imidazole (Him). The reaction of tetraacetatodicopper(II) dihydrate (200 mg, 0.5 mmol) with imidazole (34 mg, 0.5 mmol) in water (5 cm^3) followed by addition of $NaClO_4$ (281 mg, 1 mmol), leads to the formation of an unique polynuclear copper(II) complex which is characterized as $[Cu_5(OH)_2(H_2O)(O_2CMe)_6(Him)_4][ClO_4]_2$ **1** from elemental analysis† and X-ray crystallographic‡,[4] studies. The discovery of complex **1** is a significant development in the virtually unknown[1,5] chemistry of the pentanuclear copper(II) complexes.

An ORTEP[6] view of the pentanuclear unit in **1** is shown in Fig. 1. In the centrosymmetric complex, the co-ordination geometries of the Cu(1), Cu(2) and Cu(3) centres are square-pyramidal, tetragonally elongated octahedral and square-planar, respectively. The Cu(1)···Cu(2), Cu(1)···Cu(3) and Cu(2)···Cu(3) distances are 3.178(1), 3.578(1) and 3.043(1) Å, respectively. While the Cu(1) and Cu(3) centres are bonded to two $\sigma:\sigma:\mu$-O_2CMe ligands, the Cu(2) atom is bonded to four such ligands and two μ_3-OH ligands. In the Cu_3O moiety, the O(7) atom is displaced 0.579(4) Å from the plane consisting of Cu(1), Cu(2) and Cu(3) atoms. The imidazole co-ordinates as a terminal ligand to the Cu(1) and Cu(3) atoms. The Cu(2)–O(6) distance is considerably longer than the Cu(2)–O(3) and Cu(2)–O(7) distances. The three Cu–O–Cu angles of 129.8(2), 105.1(1) and 99.2(1)° are indicative of the presence of three significantly different Cu^{II}–Cu^{II} interactions in the pentanuclear unit.

The pentanuclear units are linked symmetrically by μ-aqua ligands[7] forming a one-dimensional chain.[8,9] The inter-unit Cu(1)···Cu(1″) separation is 4.507(1) Å. The chains are found to be weakly interacting through hydrogen-bonding networks involving the O(8) and N(2) atoms of the chain and the oxygen atoms of the perchlorate anion, O(8)···O(11) 2.976(5) and N(2)···O(13) 2.938(3) Å. Complex **1** exhibits an axial ESR spectrum giving a g value of 2.05 in the polycrystalline state at 25 °C. The infrared data† are consistent with the X-ray structure of **1**. Preliminary susceptibility measurements† at 304.5 K on complex **1** show an average μ_{eff} value of 1.54 per copper(II) centre in the pentanuclear unit. Further studies aimed towards understanding the magnetic exchange and redox behaviour of the pentanuclear core are in progress.

† Yield 25% (Found: C, 24.1; H, 3.2; N, 9.8. $C_{24}H_{38}Cl_2Cu_5N_8O_{23}$ requires C, 24.1; H, 3.2; N, 9.4%). IR (Nujol): 3514 (OH), 3334 (NH), 3148 (Me), 1575 (OCO) and 1068 cm^{-1} (ClO_4). Magnetic susceptibility data at 304.5 K: $\chi_g = 3.64 \times 10^{-6}$ cm^3 g^{-1}, $\chi_M^{corr}(Cu) = 0.967 \times 10^{-3}$ cm^3 mol^{-1}, $\mu_{eff}(Cu) = 1.54$ (George Associates model 300 lewis-coil-force magnetometer).

‡ *Crystal data:* $C_{24}H_{38}Cl_2Cu_5N_8O_{23}$, M(polymer unit) = 1195.2, monoclinic, space group $C2/c$, $a = 26.889(4)$, $b = 11.077(3)$, $c = 18.936(2)$ Å, $\beta = 134.07(1)°$, $U = 4052(2)$ Å^3, $Z = 4$, $D_c = 1.96$ g cm^{-3}, $T = 290$ K, $4 \leqslant 2\theta \leqslant 50°$, $\mu = 29.6$ cm^{-1}, $R = 0.0362$, $R' = 0.0471$ {weighting scheme applied: $w = 1/[\sigma^2|F_o| + 0.001\,688\,|F_o|^2]$} for 3092 reflections with $I \geqslant 2.5\sigma(I)$. Intensity data collected on an Enraf-Nonius CAD4 diffractometer (Mo-Kα radiation, $\lambda = 0.7107$ Å) using a blue crystal of dimensions 0.2 × 0.3 × 0.2 mm. Data corrected for Lorentz, polarization and absorption effects. The structure was solved and refined using the SHELX 76 program,[4a] Fourier syntheses and full-matrix least squares.

Atomic coordinates, thermal parameters and bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

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4 (*a*) G. M. Sheldrick, SHELX 76, Program for Crystal Structure

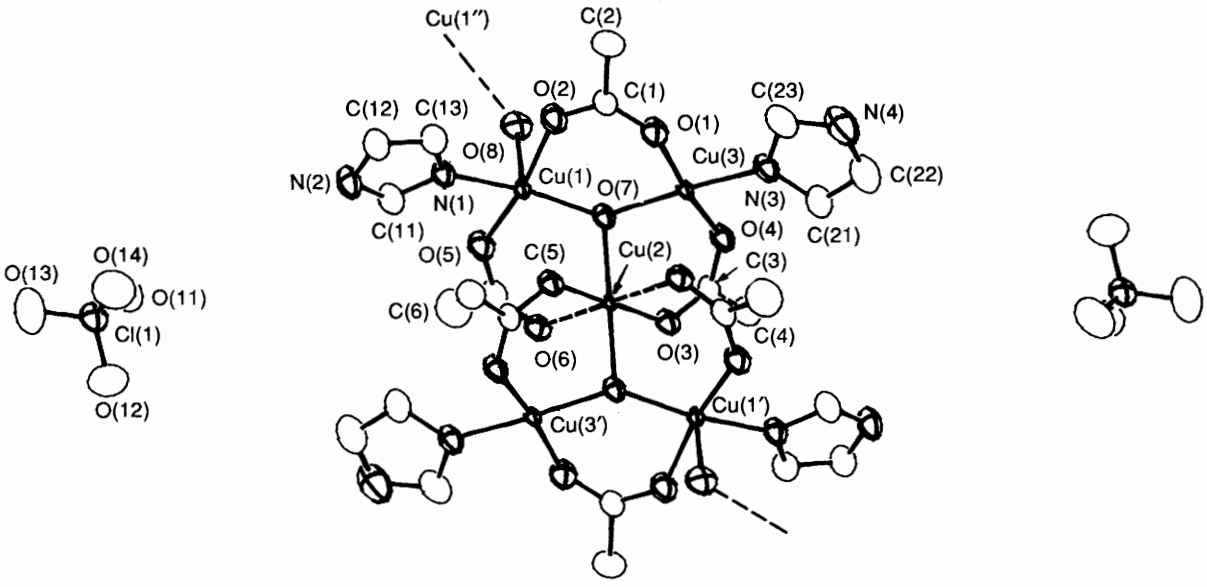

Fig. 1 A view of the pentanuclear unit of the one-dimensional chain in complex **1**. Selected distances and angles are Cu(1)···Cu(1″) 4.507(1), Cu(1)···Cu(2) 3.178(1), Cu(1)···Cu(3) 3.578(1), Cu(2)···Cu(3) 3.043(1), Cu(1)–O(2) 1.955(4), Cu(1)–N(1) 1.984(3), Cu(1)–O(7) 1.980(2), Cu(1)–O(8) 2.425(2), Cu(1)–O(5) 1.965(5), Cu(2)–O(3) 1.977(4), Cu(2)–O(6) 2.268(6), Cu(2)–O(7) 2.023(2), Cu(3)–O(1) 1.922(4), Cu(3)–O(4) 1.959(4), Cu(3)–O(7) 1.971(4) and Cu(3)–N(3) 1.972(6) Å; Cu(1)–O(7)–Cu(3) 129.8(2), Cu(1)–O(7)–Cu(2) 105.1(1), Cu(2)–O(7)–Cu(3) 99.2(1), Cu(1)–O(8)–Cu(1″) 136.7(1), O(2)–Cu(1)–O(8) 86.7(1), O(5)–Cu(1)–O(8) 82.7(1), O(5)–Cu(1)–N(1) 88.3(2), O(8)–Cu(1)–N(1) 103.4(2), O(7)–Cu(1)–O(8) 89.5(1), O(2)–Cu(1)–O(5) 167.5(2), O(5)–Cu(1)–O(7) 92.7(1), O(7)–Cu(1)–N(1) 167.2(2), O(2)–Cu(1)–N(1) 87.9(2), O(2)–Cu(1)–O(7) 93.7(1), O(3)–Cu(2)–O(7) 88.3(1), O(6)–Cu(2)–O(7) 89.9(1), O(3)–Cu(2)–O(6) 84.4(2), O(1)–Cu(3)–O(4) 170.7(1), O(1)–Cu(3)–O(7) 94.6(1), O(1)–Cu(3)–N(3) 86.7(2), O(4)–Cu(3)–N(3) 89.2(2), O(4)–Cu(3)–O(7) 90.0(1) and O(7)–Cu(3)–N(3) 177.0(2)°

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