

A Linear Trinuclear Macrocylic Copper(II) Complex

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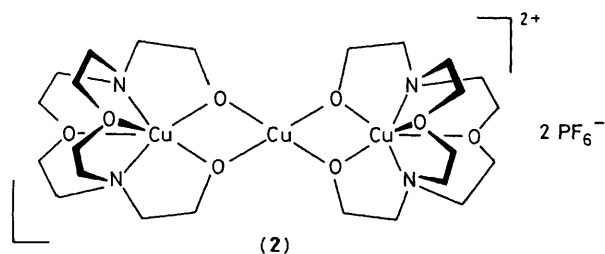
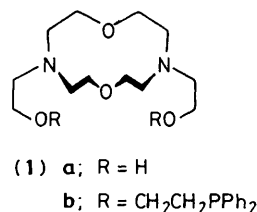
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Reaction of the functionalised macrocycle (**1a**) with copper (II) ions in solution leads to the assembly of a trinuclear bis(macrocylic) complex which has been studied by X-ray crystallography and cyclic voltammetry; the complex contains a linear trinuclear array of copper atoms in which the central copper is in a square-planar environment.

A series of heterodinucleating macrocyclic ligands has recently been described, *e.g.* (**1b**), in which the side-arm ether oxygens were bound to a 'hard' cation, held by the macrocycle, thereby regulating the ligand structure and facilitating complexation of a second dissimilar metal.¹ In order to confirm and define the nature of this regulating interaction, the reaction of the model compound 4,10-bis(2-hydroxyethyl)-1,7-dioxo-4,10-diazacyclodecane (**1a**)² with copper ions in solution was examined.

Reaction of (**1a**) with a 1 molar excess of copper(II) perchlorate in aqueous ethanol led to slow formation of a green crystalline solid (**2**) (λ_{\max} , 273 nm, ϵ 9.7×10^3 dm³ mol⁻¹ cm⁻¹; 720, 120) whose positive ion fast atom bombardment mass spectrum in a glycerol matrix³ gave peaks centred at m/z 811 and 711 corresponding to [(**1a**)₂·Cu₃ClO₄]⁺ and [(**1a**)₂·Cu₃]⁺. Crystals of the complex (**2**), as the hexafluorophosphate salt, having composition [(**1a**)₂·Cu₃][PF₆]₂ were grown from PrOH-H₂O. The structure of the complex cation is shown in Figure 1. The two hydroxy oxygen atoms of (**1a**)



† Crystal Data: C₂₄H₄₈Cu₃F₁₂N₄O₈P₂; M_r = 1001.2; monoclinic, a = 7.112(2), b = 18.507(5), c = 14.106(4) Å, β = 101.44(3)°; U = 1819(2) Å³, Z = 2, D_c = 1.83 g cm⁻³, $F(000)$ = 1018, $\mu(\text{Mo-K}\alpha)$ = 19.4 cm⁻¹. Space group determined uniquely from the systematic absences as $P2_1/c$. The structure was determined by the heavy atom method. Isotropic followed by anisotropic refinement of the non-hydrogen atoms with the hydrogens in geometrically idealised positions converged with R = 0.047 and R_w = 0.058 for 1491 observed reflections measured on a CAD 4 diffractometer. Calculations were made with the SDP system of programs⁸ on a PDP-11/73 computer. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

have lost their protons during complex formation. The central copper atom lies on an inversion centre and has square-planar geometry. The Cu(2) atom is six-co-ordinated with Cu(2), O(1), O(2), N(1), and N(2) essentially coplanar and O(3) and O(4) above and below this plane.

The complex has a magnetic moment at 295 K of 1.1 μ_B (per copper atom) suggesting that there are strong antiferromagnetic interactions operating within each Cu₂O₂ ring, and that the spin doublet ($S = \frac{1}{2}$) state is the ground state at room temperature.^{4,5} The powder e.s.r. spectrum is of the axial type with g_{\parallel} = 2.23 and g_{\perp} = 2.04, and a normal A_{\parallel} hyperfine splitting was observed (0.015 cm⁻¹).

The electrochemical behaviour of (**2**) has been studied in H₂O (μ = 0.1 M, NBu₄ClO₄) on a glassy carbon electrode by cyclic voltammetry. Two quasi-reversible peaks were observed at +0.23 and -0.04 V (relative to the standard calomel electrode), as indicated by $i_a/i_c \approx 1$ and by the observation that the peak separation ΔE remains constant for scan rates between 10 and 100 mV s⁻¹. Coulometric reductions indicate that 2 Faradays per mole of complex are exchanged at +0.23 V and that the redox process at -0.04 V is a one-electron one. Similar two-electron reduction waves have been observed at +0.28 V for dinuclear copper(II) cryptates which possess two [12]-N₂O₂ or [12]-N₂S₂ macrocyclic rings.^{6,7} Complex (**2**) may therefore be regarded as a [2 + 1] three-electron receptor.

In conclusion, the X-ray structure of the complex has confirmed that both side-arm oxygen atoms may bind to copper, lending support to the premise that in heterodinuclear complexes of (**1b**), co-ordination of a hard cation regulates the ligand structure.¹ The trinuclear complex is antiferromagnetic and may be regarded as a trielectronic receptor complex; further studies of its magnetic and redox behaviour are under investigation.

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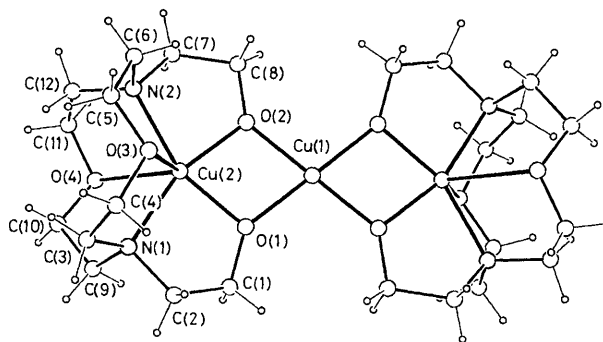


Figure 1. A view of the tri-copper complex cation showing the crystallographic numbering scheme. Main dimensions are: Cu(1)-O(1) 1.918(4), Cu(1)-O(2) 1.902(5), Cu(2)-O(1) 1.918(4), Cu(2)-O(2) 1.904(5), Cu(2)-O(3) 2.444(4), Cu(2)-O(4) 2.681(5), Cu(2)-N(1) 2.086(5), Cu(2)-N(2) 2.101(5) Å; O(1)-Cu(1)-O(2) 77.6(2), O(1)-Cu(2)-O(2) 77.6(2), O(3)-Cu(2)-O(4) 118.8(2), N(1)-Cu(2)-N(2) 116.8(2)°.

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