

A Binuclear Antiferromagnetically Coupled Hydroxo-bridged Copper(II) Complex which undergoes Two-electron Oxidation to form a Binuclear Copper(III) Derivative and exhibits an Unusually Intense Visible Absorption

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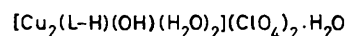
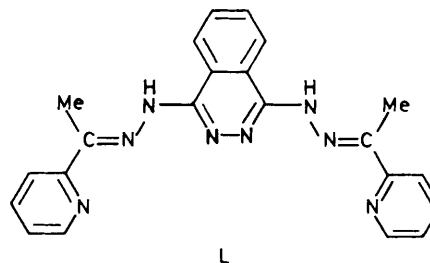
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The binuclear, hydroxo-bridged, five-co-ordinate copper(II) complex of a hexadentate (N₆) phthalazine ligand, the crystal structure of which has been determined, exhibits very strong antiferromagnetic exchange ($-2J = 990 \pm 50 \text{ cm}^{-1}$) and very intense visible absorption (610 nm, $\epsilon 18\,400 \text{ l mol}^{-1} \text{ cm}^{-1}$) and unlike comparable (N₄) diazine complexes undergoes two-electron oxidation at 0.50 V (vs. standard calomel electrode) to produce a stable binuclear copper(III) derivative.

Binuclear antiferromagnetically coupled, hydroxo-bridged copper(II) complexes of a series of tetradentate (N₄) phthalazine and pyridazine ligands have been shown to exhibit two-electron reduction at positive potentials (0.23–0.82 V vs. standard calomel electrode, s.c.e.)^{1–4} comparable with those associated with certain oxidases and oxygenases containing Type III copper centres.^{5,6} Also a linear relationship exists between the Cu–O(H)–Cu bridge angle and the exchange integral for a number of the related phthalazine complexes involving $d_{x^2-y^2}$ copper ion ground states,^{3,7,8} which extrapolates to a value for the exchange integral in oxyhemocyanin, based on the projected Cu–O–Cu bridge angle of 145° determined from EXAFS studies,⁹ which agrees closely with that determined by experiment.^{10,11}

Hexadentate ligands derived by condensation of certain aldehydes (*e.g.* pyridine-2-carbaldehyde, *N*-methylimidazole-2-carbaldehyde) with 1,4-dihydrizinophthalazine generate binuclear hydroxo-bridged copper(II) complexes with magnetic moments (μ_{eff} , room temp.) $\leq 0.30 \mu_{\text{B}}$, indicative of very strong antiferromagnetic exchange.¹² The new ligand, L, was

synthesized by reaction of 2-acetylpyridine (2 equiv.) and 1,4-dihydrizinophthalazine (1 equiv.) in refluxing methanol and obtained as orange crystals (m.p. 185–187 °C; satisfactory analyses for C, H, and N). The complex (1) was



(1)

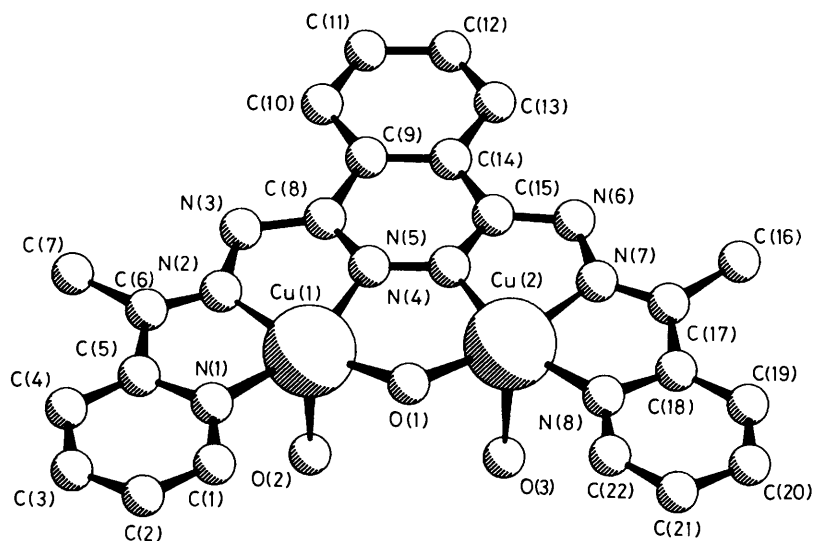


Figure 1. The structure of the cation $[\text{Cu}_2(\text{L} - \text{H})(\text{OH})(\text{H}_2\text{O})_2]^{2+}$ in (1): bond lengths: Cu(1)–O(1) 1.910(6), Cu(2)–O(1) 1.949(6), Cu(1)–Cu(2) 3.295(2), Cu(1)–N(4) 1.991(8), Cu(1)–N(2) 1.964(8), Cu(1)–N(1) 2.025(8), Cu(2)–N(5) 1.910(8), Cu(2)–N(7) 1.989(8), Cu(2)–N(8) 1.946(8), C(15)–N(6) 1.341(13), N(6)–N(7) 1.350(12), N(7)–C(17) 1.264(13), C(8)–N(3) 1.391(13), N(3)–N(2) 1.369(11), N(2)–C(6) 1.282(13) Å).

synthesized by reaction of L and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1:2) in aqueous methanol and obtained as deep red–brown crystals.†

The structure of (1) is illustrated in Figure 1, and consists of an almost planar ligand binding two five-co-ordinate (distorted square pyramidal) copper ions separated by 3.295(2) Å and bridged by a hydroxide with a Cu–O–Cu bridge angle of 117.3(3)°. Two axially bound water molecules complete the square pyramidal co-ordination. The unusual stoichiometry of the complex indicates that the ligand has lost a proton, a feature observed previously with a related ligand.¹² Proton loss has occurred at N(6). A significant hydrogen bonding interaction exists between perchlorate oxygen O(10) and hydrogen H(8) attached to N(3) [N(3)–H(8) 2.11(7), N(3)–O(10) 3.09(1) Å, \angle N(3)–H(8)–O(10) 151(6)°] but no perchlorate oxygen is located close to N(6). The Cu(2)–N(5) separation is significantly shorter than Cu(1)–N(4) suggesting that some electron delocalization into the phthalazine ring has taken place. The bond lengths C(15)–N(6), N(6)–N(7), and N(7)–C(17) are nominally shorter than C(8)–N(3), N(3)–N(2), and N(2)–C(6) suggesting electron delocalization over the framework N(5)–C(15)–N(6)–N(7)–C(17), but with the current refinement these bond lengths are not significantly different (3 σ level).

Variable temperature magnetic studies¹³ (6–300 K) indicate very strong antiferromagnetic exchange between the

† *Crystal data:* $\text{C}_{22}\text{H}_{26}\text{Cl}_2\text{Cu}_2\text{N}_8\text{O}_{12}$, $M = 792.5$, monoclinic, space group $P2_1/n$, $a = 8.011(2)$, $b = 24.100(5)$, $c = 15.675(2)$ Å, $\beta = 100.24(2)^\circ$, (Mo- K_α , $\lambda\alpha_1 = 0.7093$ Å, $T = 22^\circ\text{C}$), $U = 2978.1$ Å³, $Z = 4$, $D_c = 1.74$ g cm⁻³. The 4549 independent reflections with $2\theta < 44^\circ$ were measured on a Nonius CAD4 diffractometer, with graphite monochromatized Mo- K_α radiation, and 2269 reflections [$I_{\text{net}} > 2.5\sigma(I_{\text{net}})$] were used in the analysis. Hydrogen atoms, excluding those associated with the three water molecules, were included in the final structure factor calculations and final residuals of $R_f = 0.077$ and $R_w = 0.039$ were obtained for significant reflections [a hydrogen atom was located on N(3) but not N(6) from a difference map]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

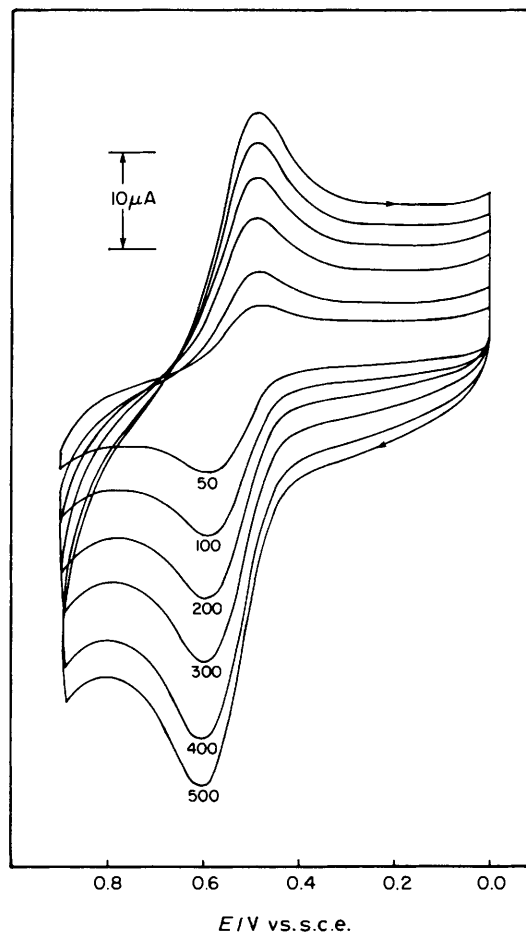


Figure 2. Cyclic voltammograms (scan rates, 50–500 mV s^{-1} , given on the curves) for (1) in DMF, 0.1 M Et_4NClO_4 , at a glassy carbon electrode.

copper(II) centres in (**1**) with $g = 2.11$ and $-2J = 990 \pm 50 \text{ cm}^{-1}$. Cyclic voltammetry for (**1**) in dimethylformamide (DMF) ($1 \times 10^{-3} \text{ M}$; $0.1 \text{ M Et}_4\text{NClO}_4$, glassy carbon working electrode, platinum counter electrode *vs.* s.c.e.) gave a single quasi-reversible redox wave at a positive potential (Figure 2, $E_{1/2} 0.50 \text{ V}$; $\Delta E_p 110 \text{ mV}$ at 200 mV s^{-1}) associated with an oxidation process. Controlled potential electrolysis (platinum electrode) in DMF at $+0.3 \text{ V}$ (*vs.* s.c.e.) gave no electron count and no change in the colour of the deep blue solution occurred. Electrolysis at $+0.65 \text{ V}$ produced a stable orange solution with passage of approximately two equivalents of charge indicating two-electron oxidation of the binuclear copper(II) complex to a binuclear copper(III) species. The single redox wave suggests that in solution both copper(II) centres are in similar environments. The deep blue solution of (**1**) in DMF (1:2 electrolyte; $\Lambda_M 169 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$) is characterized by very intense charge transfer absorptions at 610 and 335 nm ($\epsilon 18400$ and $25400 \text{ l mol}^{-1} \text{ cm}^{-1}$ respectively), while the orange, electrochemically oxidized product has a single, intense absorption in this spectral region at 470 nm ($\epsilon 19400 \text{ l mol}^{-1} \text{ cm}^{-1}$). In the solid state (mull transmittance) (**1**) exhibits two intense absorptions at 500 and 350 nm and an aqueous solution of (**1**) shows emission at 602 nm with 300 nm excitation. Chemical oxidants, *e.g.* iodine, hydrogen peroxide, and benzoyl peroxide, were found to oxidize DMF solutions of (**1**) completely at room temperature to produce an identical species. Redox waves associated with reduction of (**1**) occur at negative potentials ($< -0.7 \text{ V}$).

The synthesis of copper(III) derivatives has been largely restricted to mononuclear species with ligands like biuret and oxamide¹⁴ and peptides,^{15,16} which, in many cases, are quite stable. Examples of polynuclear copper(III) derivatives are rare and are restricted to reports of the single-electron oxidation of a trinuclear species¹⁷ and the electrochemical oxidation of a non-coupled binuclear copper(II) system¹⁸ and a macrocyclic, antiferromagnetically coupled binuclear copper(II) compound by two one-electron steps.¹⁹ The complex $[\text{Cu}_2(\text{L}-\text{H})(\text{OH})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ represents the first example of a hydroxide bridged, strongly spin-coupled binuclear copper(II) complex which is oxidized with ease in a single two-electron step to form a stable binuclear copper(III) species. Two other complexes related to (**1**), $[\text{Cu}_2(\text{L})(\text{OH})](\text{ClO}_4)_3$ and $[\text{Cu}_2(\text{L}-2\text{H})(\text{OH})](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$, involving neutral and dianionic ligands can be synthesized,

depending upon the choice of solvent and the presence of base ($\Lambda_M 232$ and $90.3 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ respectively in DMF). Both these complexes exhibit oxidation waves at positive potentials in DMF.²⁰

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