Binuclear Antiferromagnetically-coupled Hydroxo-bridged Copper(II) Complexes with Positive Reduction Potentials and involving Sequential Two Electron Transfer at the Same Potential

Sanat K. Mandal,[a] **Laurence K. Thompson,**[a] **and Alfred W. Hanson**[b]

[a] *Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7*
[b] *Atlantic Research Laboratory, National Research Council of Canada, Halifax, Nova Scotia, Canada B3H 3Z1*

Binuclear hydroxo-bridged copper(II) complexes of some tetradentate phthalazine and pyridazine ligands represent the first examples of binuclear copper(II) complexes exhibiting sequential two electron reduction at positive potentials (0.40 to 0.45 V *vs.* standard calomel electrode), comparable to those observed for Type III copper protein centres.

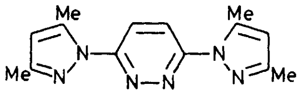
The current widespread interest in the design and synthesis of binuclear copper(II) complexes as mimics for the active sites of Type III copper proteins[1] and hemocyanin[1] has led to reports of many binuclear copper systems involving oxygen bridge groups which exhibit strong antiferromagnetic exchange,[2] a characteristic feature of the binuclear protein centres.[3,4] Electrochemical studies have shown that, almost without exception, negative reduction potentials (*vs.* standard calomel electrode, s.c.e.) prevail for binuclear copper(II) complexes in which the dominant bridging structural feature is just an oxygen atom,[5,6] even though in many cases strong antiferromagnetic exchange is observed.[7] In a recent report the antiferromagnetically-coupled complex $[Cu_2(bpnp)(\mu\text{-}Cl)(\mu\text{-}OH)Cl_2]$ [bpnp = 2,7-bis(2-pyridyl)-1,8-naphthyridine], involving a binuclear copper(II) centre with a naphthyridine, a chlorine, and a hydroxo bridge, was shown to exhibit two one-electron quasi-reversible cyclic voltammetry (c.v.) waves ($E_{\frac{1}{2}}$ = 0.36, 0.16 V *vs.* Ag/AgCl) at positive potentials in aqueous solution.[8] We report here two examples of hydroxo-bridged binuclear copper(II) complexes of the tetradentate pyridazine and phthalazine ligands (**L1**) and (**L2**) which exhibit both antiferromagnetic exchange between the copper centres and sequential two electron reduction at the same positive potential.

$$\underset{(\mathbf{1})}{[Cu_2(\mathbf{L1})(OH)Cl_2][CuCl_3(H_2O)]\cdot H_2O}$$

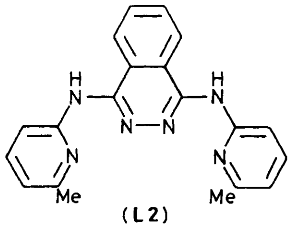
$$\underset{(\mathbf{2})}{[Cu_2(\mathbf{L2})(OH)Cl_3]\cdot 3H_2O}$$

The ligands (**L1**) and (**L2**) and the complexes (**1**) and (**2**) were prepared by published procedures.[9,10] The structures of both (**1**) and (**2**) have been determined and a structural representation of the binuclear cation in (**1**) is shown in Figure 1 (full structural details of this system, including the unusual tetrahedrally distorted anion $[CuCl_3(H_2O)]^-$, are reported elsewhere[10]). The binuclear centre in this complex is characterized by a large copper–copper separation [3.384(2) Å] and a large oxygen bridge angle [126.0(5)°] with both copper centres being essentially square planar.

Crystal data for (**2**): $C_{20}H_{25}O_4N_6Cl_3Cu_2$, green, M = 646.9, monoclinic $C2/c$ (No. 15), a = 21.139(6), b = 12.797(1), c = 20.312(7) Å, β = 111.37(2)°, (Mo-K_α, $\lambda\alpha_1$ = 0.7093 Å, T = 24 °C), U = 5116.9 Å^3, Z = 8, D_c = 1.68 g cm^{-3}, D_m = 1.69 g cm^{-3}. The 4532 independent reflections with $2\theta < 50°$ were measured on a four-circle diffractometer, with graphite-monochromatized Mo-K_α radiation, and the 2632 absorption-corrected reflections observed above background (3σ) were used in the analysis. During refinement it became apparent (because of improbably high thermal motion of the chlorine atoms and the oxygen bridge) that Cl(3) (Figure 2) must be



(**L1**)



(**L2**)

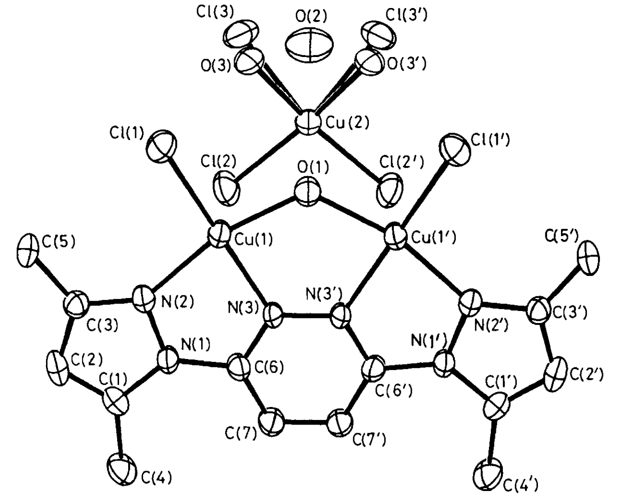


Figure 1. The structure of $[Cu_2(\mathbf{L1})(OH)Cl_2][CuCl_3(H_2O)] \cdot H_2O$ (**1**).

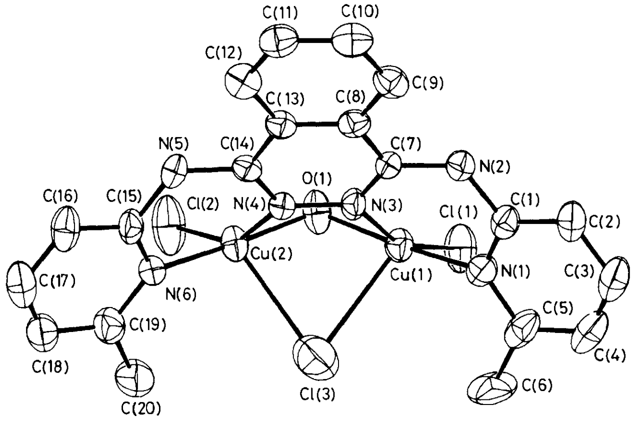


Figure 2. The structure of $[Cu_2(\mathbf{L2})(OH)Cl_3] \cdot 3H_2O$ (**2**): bond lengths: Cu(1)–O(1) 1.893(7), Cu(2)–O(1) 1.886(7), Cu(1)–Cl(3) 2.686(5), Cu(2)–Cl(3) 2.678(6), Cu(1)–N(3) 2.021(8), Cu(2)–N(4) 2.003(8) Å.

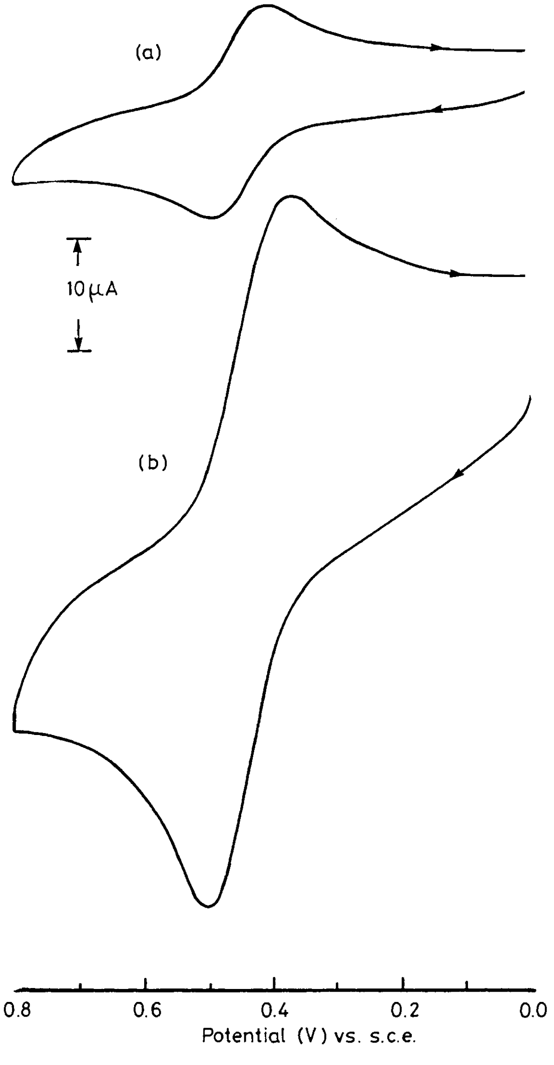


Figure 3. (b) C.v. ($100\ mV\ s^{-1}$) for (**2**) in DMF, 0.1 M Et_4NClO_4 at a glassy carbon electrode; (a) ferrocene/ferrocinium couple.

present only at a proportion (estimated at 78%) of molecular sites. We speculate that an alternative, probably four-co-ordinate species, resembling (**2**) but with Cl(3) absent, replaces (**2**) at the remaining molecular sites [with Cl(3) present as an ion]. The hydrogen atoms (other than methyl) were included in the final structure factor calculations and the final *R* index (for observed reflections) was 0.058.† The structure of (**2**) is illustrated in Figure 2, and consists of a binuclear copper centre with two five-co-ordinate (distorted square pyramidal) copper(II) ions separated by 3.137(2) Å and with a Cu–O–Cu bridge angle of 112.2(4)°. These are bound to four nitrogen atoms N(1), N(3), N(4), and N(6) of the tetradentate ligand, and bridged by a chlorine atom Cl(3) at the shared apex and an oxygen atom O(1) at a shared basal corner (this bridge group has been shown chemically and spectroscopically to be a hydroxide[9]).

Variable temperature (6—300 K) magnetic studies indicate moderately strong antiferromagnetic exchange between the copper(II) centres in (**2**) with $g = 2.11$ and $-2J = 432\ cm^{-1}$, while for (**1**) variable temperature magnetic data (80—200 K) have been interpreted in terms of an essentially diamagnetic cation with an isolated, non-magnetically interacting, paramagnetic anion.[10,11]

C.v. for (**1**) in dried, distilled dimethylformamide, DMF, (1×10^{-3} M; 0.1 M Et_4NClO_4, glassy carbon working electrode, platinum counter electrode *vs.* s.c.e. ferrocene/ferrocinium couple $E_{\frac{1}{2}} = 0.41$ V) gives a single redox wave ($E_{\frac{1}{2}} = 0.42$ V) with a peak separation which varies with scan rate indicating a quasi-reversible redox process ($\Delta E_p = 160$ mV at 200 mV s^{-1}). An additional reduction wave is observed below −0.3 V associated with the mononuclear anion. The current heights of the two reduction waves correspond to reduction processes involving two and one electrons respectively. Compound (**2**) displays similar c.v. (Figure 3), under the same experimental conditions, at a positive potential ($E_{\frac{1}{2}} = 0.44$ V) with a peak

---

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

separation (ΔE_p = 140 mV at 200 mV s^{-1}) which varies slightly with scan rate, indicating a more reversible redox process. Controlled potential electrolysis (platinum electrode at −0.05 V *vs.* s.c.e.) in DMF indicates two electron reduction of the binuclear copper(II) species to copper(I), in both cases, at a high single positive potential.

Compounds (**1**) and (**2**) represent the first examples of antiferromagnetically-coupled, oxygen (hydroxo) bridged, binuclear copper(II) complexes involving nitrogen donors which exhibit sequential two electron transfer at the same, high, positive potential. This behaviour can be rationalized in terms of two equivalent copper(II) centres in the complex in solution, and a very small conproportionation constant. These features make systems of this sort attractive models for the Type III copper protein centres, where in particular, one step, two electron reversible reduction is observed at positive potentials.[1]

We thank the Natural Sciences and Engineering Research Counil of Canada for financial support for this study.

Received, 3rd July 1985; Com. 947

References

1 'Metal Ions in Biological Systems,' ed. H. Sigel, Marcel Dekker, New York, 1981; 'Copper Proteins,' ed. T. G. Spiro, John Wiley, New York, 1981.
2 L. K. Thompson, F. W. Hartstock, P. Robichaud, and A. W. Hanson, *Can. J. Chem.*, 1984, **62**, 2755 and references therein.
3 D. M. Dooley, R. A. Scott, J. Ellinghaus, E. I. Solomon, and H. B. Gray, *Proc. Natl. Acad. Sci. USA*, 1978, **75**, 3019.
4 E. I. Solomon, D. M. Dooley, R. H. Wang, H. B. Gray, M. Cerdonio, F. Mogno, and G. L. Romani, *J. Am. Chem. Soc.*, 1976, **98**, 1029.
5 R. L. Lintvedt and L. Stecher Kramer, *Inorg. Chem.*, 1983, **22**, 796.
6 S. K. Mandal and K. Nag, *Inorg. Chem.*, 1983, **22**, 2567.
7 D. E. Fenton, R. R. Schroeder, and R. L. Lintvedt, *J. Am. Chem. Soc.*, 1978, **100**, 1931.
8 W. R. Tikkanen, C. Kruger, K. D. Bomben, W. J. Jolly, W. C. Kaska, and P. C. Ford, *Inorg. Chem.*, 1984, **23**, 3633.
9 D. V. Bautista, J. C. Dewan, and L. K. Thompson, *Can. J. Chem.*, 1982, **60**, 2583.
10 L. K. Thompson, T. C. Woon, D. B. Murphy, E. J. Gabe, Y. Le Page, and F. L. Lee, *Inorg. Chem.*, in the press.
11 A. W. Hanson and L. K. Thompson, unpublished results.