

Structure and Magnetic Properties of a Novel Tetranuclear Copper(II) Complex of an Extended Bis-phthalazine Ligand

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The octadentate, tetranucleating ligand *o*-phenylenebis-[6-oxyl-1,4-bis-(2'-pyridylamino)phthalazine] (L) bonds two pairs of well separated, antiferromagnetically coupled copper(II) ions in one molecular entity in the derivative $[\text{Cu}_4(\text{L})(\mu_2\text{-OH})_2(\mu_2\text{-NO}_3)_2(\text{NO}_3)_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ **1**.

There has been significant interest recently in the synthesis and properties of supramolecular complexes of high nuclearity,¹⁻³ and dendritic systems with Ru_{13} ² and Ru_{22} ³ clusters have been reported. However in these systems the clusters were built up by synthetic strategies using metal complexes as ligands and metal complexes as metals, with the result that a large number of ligands is involved in the cluster. A different approach to high nuclearity species involves the two dimensional extension of porphyrazine⁴ or phthalocyanine^{5,6} macrocycles to produce heteropentanuclear systems, involving just one ligand. Template condensation of 2,6-diacetylpyridine with 1,3-diaminopropan-2-ol produces a tetramanganese complex involving one ligand,⁷ while template condensations of isophthalaldehydes with various diaminoalcohols has pro-

duced Cu_4 ^{8,9} and Cu_6 ^{10,11} species with the metals encapsulated by one macrocyclic ligand, within which bridging linkages effectively join all the metal centres. This has led to magnetic properties which, in one case, appear to include all the metals.¹¹ Octadentate (N_8) benzodipyridazine ligands have also been shown to bind four copper(II) centres per ligand in a magnetically cross-coupled entity.^{12,13}

Complexes in which a single polynucleating ligand can bind an ordered array of multiple metal centres, *e.g.* dinuclear centres, are not common, and are firmly based on the chemical and structural features of the ligands themselves. The duplication of such centres, if catalytically active individually, could have a profound effect on the overall catalytic activity of the system. The tetranucleating ligand L (Fig. 1),

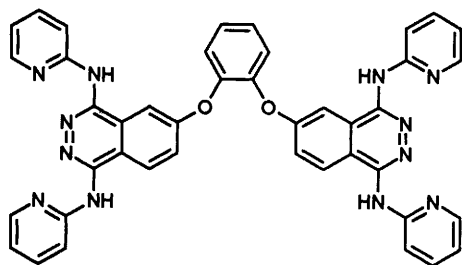


Fig. 1 The ligand L

which has a flexible linkage between remote dinucleating centres, was prepared from benzene-1,2-bis-(4-oxy-1,2-dicyanobenzene) by ring expansion of the intermediate tetrapyrrolyl-bis-isoindoline (L') with 85% hydrazine in CHCl_3 -MeOH (1:2 v/v).^{14,15} The tetranuclear copper(II) complex $[\text{Cu}_4(\text{L})(\mu_2\text{-OH})_2(\mu_2\text{-NO}_3)_2(\text{NO}_3)_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ **1** was obtained by refluxing the ligand L with an excess of $\text{Cu}(\text{NO}_3)_2$ in H_2O for 24 h. Unreacted ligand was removed by filtration and the green filtrate concentrated to a small volume. Green crystals formed on standing after addition of a small amount of EtOH. The product was recrystallized twice from H_2O to afford green crystals suitable for structural determination.[†]

In the unit cell there are two chemically identical, but structurally slightly different, tetranuclear Cu^{II} complexes, and one of these is illustrated in Fig. 2(a). Two pairs of copper(II) ions form two binuclear centres, one on each side of the catechol group, with each pair of Cu^{II} ions bridged by a hydroxide, a bidentate nitrate and a diazine (N_2) group [Fig. 2(b)]. Intradinuclear copper-copper separations fall in the range 3.163(3)–3.188(3) Å with large Cu–OH–Cu bridge angles of 110.4(4)–116.7(5)°. Cross-ligand copper-copper distances are very long [e.g. Cu(4)–Cu(1) 10.475(3) Å]. Each copper has a square-pyramidal geometry with a water molecule or a monodentate nitrate completing a CuN_2O_3 coordination environment at each copper centre. Complex **1** is structurally similar to the antiferromagnetically coupled binuclear Cu^{II} pyridyl-phthalazine complexes $[\text{Cu}_2(\text{PAP4Me})(\mu_2\text{-OH})(\text{H}_2\text{O})_2(\mu_2\text{-NO}_3)(\text{NO}_3)]\text{NO}_3$ and $[\text{Cu}_2(\text{PAP})(\mu_2\text{-OH})\text{Cl}(\mu_2\text{-SO}_4)] \cdot 2\text{H}_2\text{O}$,^{‡16} which involve square-pyramidal copper(II) centres bridged equatorially by diazine (N_2) and hydroxy groups and axially by a bidentate anion. Cu–OH–Cu angles of 115.3 and 115.5° are found in these complexes with $-2J$ values of 501 and 516 cm^{-1} respectively. Monomeric, dinuclear systems of this sort have been shown to exhibit catecholase activity.^{17,18}

Complex **1** is characterized by having a low room-temperature magnetic moment [$\mu_{\text{eff}} = 0.93 \mu_{\text{B}}$ (300 K)], indicating significant antiferromagnetic coupling between the copper(II) centres. Each $d_{x^2-y^2}$ ground-state copper is bridged equatorially by a diazine N_2 , and a hydroxide group, thus providing two non-orthogonal superexchange bridges for spin exchange between the adjacent pairs of Cu^{II} ions. A variable tempera-

[†] Crystal data for $\text{C}_{84}\text{H}_{69}\text{O}_{52}\text{N}_{36}\text{Cu}_8$: green, hexagonal plate, $M = 2923.05$. Monoclinic, space group $P2_1/c$ (No. 14), $a = 13.346(4)$, $b = 37.71(1)$, $c = 21.519(6)$ Å, $\beta = 91.04(2)^\circ$, Mo-K α , $\lambda = 0.71069$ Å, $T = -80^\circ\text{C}$, $V = 10829(6)$ Å³, $Z = 4$, $D_c = 1.793$ g cm^{-3} . The 10338 independent reflections with $2\theta < 44.9^\circ$ were measured on a Rigaku AFC6S diffractometer, with graphite-monochromatized Mo-K α radiation, and 5958 reflections [$I_{\text{net}} > 2.50\sigma(I_{\text{net}})$] were used in the analysis. Hydrogen atoms were located in a difference map but were not refined. Final residuals of $R = 0.063$ and $R_w = 0.058$ were obtained for significant reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[‡] PAP = 1,4-bis(2'-pyridylamino)phthalazine, PAP4Me = 1,4-bis(4'-methyl-2'-pyridylamino)phthalazine.

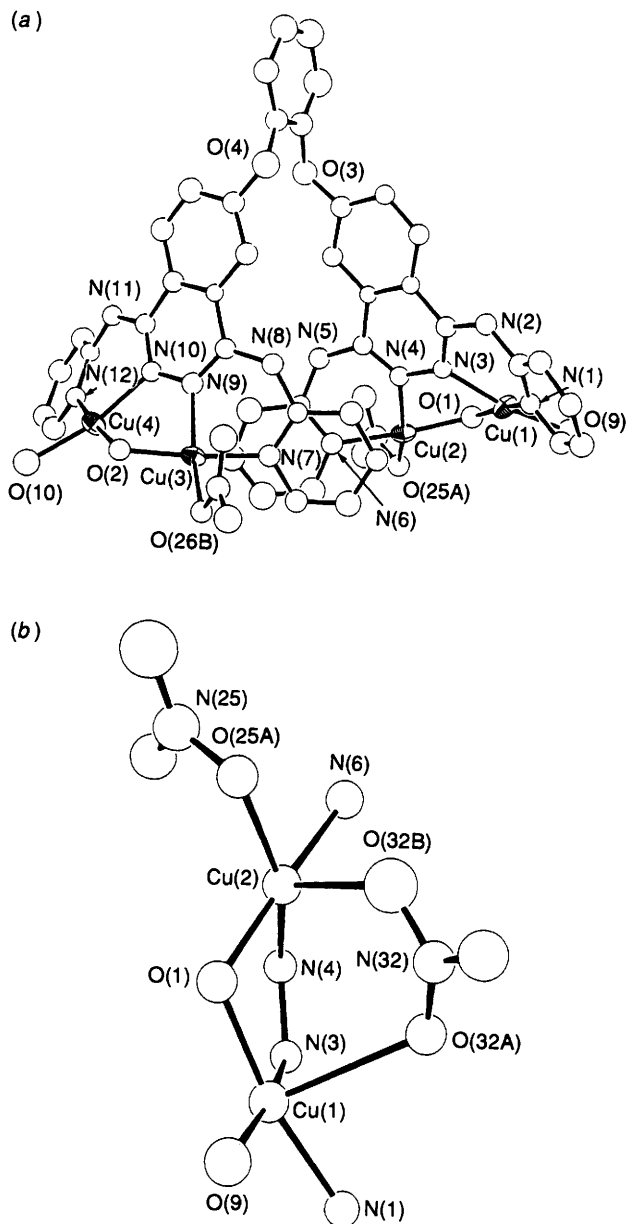


Fig. 2 Structural views of $[\text{Cu}_4(\text{L})(\mu_2\text{-OH})_2(\mu_2\text{-NO}_3)_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]^{2+} \cdot 1$. Bond lengths (Å): Cu(1)–O(1) 1.904(9), Cu(2)–O(1) 1.897(9), Cu(3)–O(2) 1.906(9), Cu(4)–O(2) 1.897(9), Cu(5)–O(5) 1.887(9), Cu(6)–O(5) 1.89(1), Cu(7)–O(6) 1.886(9), Cu(8)–O(6) 1.880(9), Cu(1)–Cu(2) 3.163(3), Cu(3)–Cu(4) 3.122(3), Cu(5)–Cu(6) 3.122(3), Cu(7)–Cu(8) 3.188(3). Bond angles: Cu(1)–O(1)–Cu(2) 112.6(5), Cu(3)–O(2)–Cu(4) 110.4(4), Cu(5)–O(5)–Cu(6) 111.4(5), Cu(7)–O(6)–Cu(8) 116.7(5).

ture (5–304 K) magnetic study on **1** shows behaviour typical of a system with strong antiferromagnetic intradinuclear exchange. Fitting of the magnetic data to the Bleaney–Bowers equation¹⁹ (1) (θ is a corrective term to account for possible

$$X_m = \frac{N\beta^2 g^2}{3k(T-\theta)} [1 + 1/3e^{-2J/kT}]^{-1} (1-\rho) + \frac{[N\beta^2 g^2] \rho}{4kT} + N\alpha \quad (1)$$

interdimer association and ρ represents the fraction of paramagnetic impurity; other terms have their usual meaning, for a copper(II) dimer gave best fit parameters $g = 2.04(7)$, $-2J = 535(18) \text{ cm}^{-1}$, $N\alpha = 65 \times 10^{-6} \text{ emu}$, $\theta = 0$, $\rho = 0.02$, which indicates strong, local intradimer antiferromagnetic coupling, and that coupling between the pairs of binuclear centres through the ligand framework is non-exis-

tent. This is corroborated by a variable temperature magnetic study on the dinuclear Cu^{II} complex of the bis-isoindoline ligand L' $[\text{Cu}_2(\text{L}')\text{Br}_4]$, for which $-2J < 2 \text{ cm}^{-1}$.¹⁵

The redox chemistry of **1** was studied by cyclic voltammetry [dimethylformamide (DMF)–tetraethylammonium perchlorate, Pt, standard sodium calomel electrode (SSCE)]. It exhibits one non-reversible redox wave at $E_4 = 0.377 \text{ V}$ ($\Delta E_p = 542 \text{ mV}$), which is associated with $\text{Cu}^{\text{II}}-\text{Cu}^{\text{I}}$ reduction. The positive E_4 is consistent with results for other dinuclear copper(II) complexes with similar N_4 monomeric, dinucleating diazine ligands.^{18,20}

The synthetic strategy of multiplying dinucleating N_4 -phthalazine ligand units has been extended in the same manner to produce hexanucleating and octanucleating ligands by using glycerol and pentaerythritol substrates. Initial studies indicate that hexanuclear and octanuclear copper(II) complexes can be successfully synthesized and that the copper pairs are strongly coupled magnetically within each dinuclear fragment. The magnetic and electrochemical properties and potential catecholase activity of all these systems will be examined. The scope of this study will be limited largely by the availability of poly-alcoholic substrates, and we are currently attempting to extend the coordinating capacity of ligands of this sort to exceed eight metals per ligand.

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