# Tetranuclear, Spin-coupled, Copper(II) Complexes of a Novel Octadentate Bis-diazine Ligand

**Santokh S. Tandon,**[a] **Sanat K. Mandal,**[a] **Laurence K. Thompson***[a] **and Rosemary C. Hynes**[b]

[a] *Department of Chemistry, Memorial University of Newfoundland, St John's, Newfoundland, Canada A1B 3X7*
[b] *Division of Chemistry, National Research Council, Ottawa, Ontario, Canada K1A 0R6*

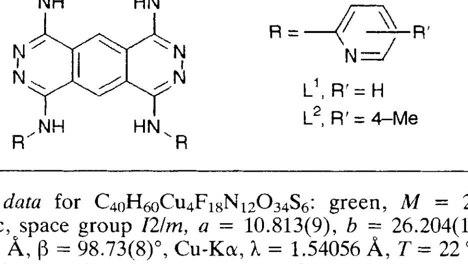
The octadentate, benzodipyridazine ligands $L^1$ and $L^2$ form tetranuclear copper(II) complexes involving hydroxide and diazine bridges and exhibit strong antiferromagnetic coupling between adjacent pairs of copper atoms, but also significant antiferromagnetic coupling across the extended, fused aromatic ring system.

Complexes in which a single ligand can organise many metals into a polynuclear cluster are not common and are dependent on particular geometric attributes of the ligand itself. The ligand 2,2′,3,3′-tetra-2-pyridyl-6,6′-biquinoxaline has been reported to form a tetranuclear ruthenium complex[1] and tetranuclear macrocyclic complexes involving template condensation of 1,3-diamino-2-hydroxypropane with 2,6-diacetylpyridine (Mn)[2] and of 1,5-diamino-3-hydroxypentane with 2,6-diformyl-4-*tert*-butylphenol (Cu) have also been reported.[3] Template condensation of 2,6-diformyl-4-methylphenol with 2,6-bis(aminomethyl)-4-methylphenol also produces tetranuclear nickel and zinc complexes.[4]

The potentially octadentate, tetranucleating ligands $L^1$ and $L^2$ were prepared from 1,2,4,5-tetracyanobenzene by ring expansion of the intermediate, tetrasubstituted benzodipyrroles[5] with hydrazine.

The tetranuclear copper(II) complex $[Cu_4(L^2)(OH)_2(H_2O)_8](CF_3SO_3)_6{\cdot}6H_2O$ **1** was obtained by reaction $L^2$ with an excess of $Cu(CF_3SO_3)_2$ in water, with stirring at room temperature for 15 h. Unreacted ligand was removed by filtration and the green filtrate concentrated to a small volume. Green crystals of **1** formed on standing at room temperature. The structure of **1** has been determined.†

The structure of $[Cu_4(L^2)(OH)_2(H_2O)_8]^{6+}$ **1** is illustrated in Fig. 1. A two-fold rotational axis passes through the fused benzene ring, while a mirror plane bisects the molecule through the bridging oxygens O(1)–O(1B). Two copper(II) ions form a binuclear centre, bridged by a hydroxide and a diazine ($N_2$) group, on each side of the essentially flat molecule with a close Cu–Cu separation of 3.302(2) Å, and a large Cu–OH–Cu bridge angle of 116.3(3)°. Cross-ligand copper–copper connections are very long, and involve eight or nine bonds depending upon the route. Each copper has a square-pyramidal geometry with two water molecules completing a $CuN_2O_3$ chromophore. The presence of just two bridge groups between coppers is in sharp contrast to related complexes involving analogous tetradentate phthalazine and pyridazine ligands, which usually form triple bridged systems.[6] However the dimensions of each binuclear half of **1** compare closely with that of the complex $[Cu_2(pap)(OH)Cl(SO_4)]$ [pap = 1,4-bis(2-pyridylamino)phthalazine], which involves an axial, bidentate, sulphate bridge (Cu–OH–Cu 115.5°, $2J = -516\ cm^{-1}$).



Complex **1** is characterized by having a low room-temperature magnetic moment [$\mu_{eff}$ = 1.24 $\mu_B$ (304 K)], indicating significant antiferromagnetic coupling between the copper(II) centres. Each $d_{x^2-y^2}$ ground-state copper is bridged equatorially by both the diazine $N_2$ group and hydroxide, thus providing two local superexchange pathways for spin exchange between the two adjacent copper centres. A variable temperature (5–304 K) magnetic study on **1** shows behaviour typical of a system with strong antiferromagnetic exchange. Fitting of the magnetic data to the Bleaney–Bowers expression for a copper dimer was only successful if a very large negative Weiss correction was employed. This clearly indicates the presence of significant interdimer coupling and consequently the data were fitted to a rectangular model (Fig. 2),[7] in which the spin-Hamiltonian involves three exchange terms [eqn. (1)]. The total susceptibility [eqn. (2)] can be

$$H_{ex} = -2[J_1(\hat{S}_1{\cdot}\hat{S}_2 + \hat{S}_{1'}{\cdot}\hat{S}_{2'}) + J_2(\hat{S}_1{\cdot}\hat{S}_{1'} + \hat{S}_2{\cdot}\hat{S}_{2'}) + J_3(\hat{S}_1{\cdot}\hat{S}_{2'} + \hat{S}_2{\cdot}\hat{S}_{1'})] \quad (1)$$

$$\chi_m^{corr} = f(J_1,J_2,J_3,g,T) + M + D + N_\alpha \quad (2)$$

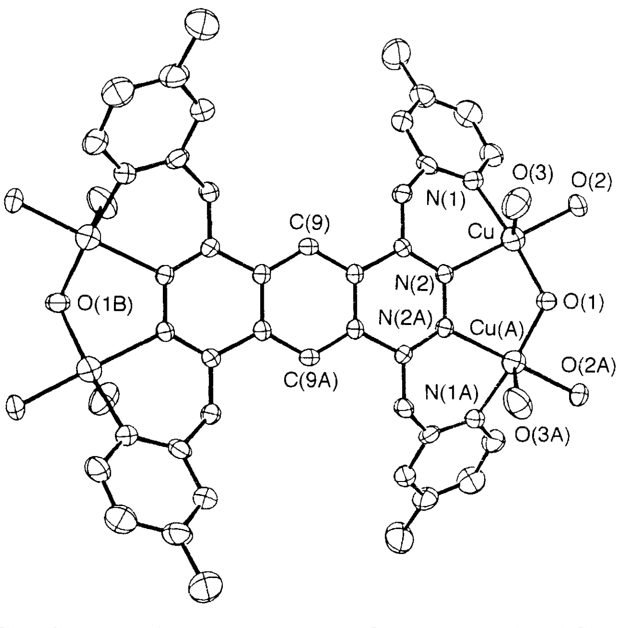


**Fig. 1** Structural view of the complex ion $[Cu_4(L^2)(OH)_2(H_2O)_8]^{6+}$ **1**. Bond lengths (Å): Cu–O(1) 1.885(3), Cu–O(2) 1.962(4), Cu–O(3) 2.473(5), Cu–N(1) 1.986(5), Cu–N(2) 2.030(4), Cu–Cu(A) 3.202(2); bond angles (°); Cu–O(1)–Cu(A) 116.3(3), Cu–N(2)–N(2A) 116.7(3), O(1)–Cu–O(2) 93.1(2), O(1)–Cu–O(3) 91.4(2), O(1)–Cu–N(1) 171.3(2), O(1)–Cu–N(2) 86.9(2), O(1)–Cu–O(3) 91.4(2), O(2)–Cu–N(1) 91.0(2), O(2)–Cu–N(2) 179.6(2), O(3)–Cu–N(1) 96.2(2), O(3)–Cu–N(2) 89.0(2), N(1)–Cu–N(2) 89.0(2).

---

† *Crystal data* for $C_{40}H_{60}Cu_4F_{18}N_{12}O_{34}S_6$: green, $M$ = 2041.47, monoclinic, space group $I2/m$, $a$ = 10.813(9), $b$ = 26.204(15), $c$ = 13.489(15) Å, β = 98.73(8)°, Cu-Kα, λ = 1.54056 Å, $T$ = 22 °C, $V$ = 3778(6) $Å^3$, $Z$ = 2, $D_c$ = 1.795 g $cm^{-3}$. The 2884 independent reflections with $2\theta < 119.8°$ were measured on a Picker diffractometer, with graphite monochromatized Cu-Kα radiation, and 2428 reflections [$I_{net} > 2.5\sigma(I_{net})$] were used in the analysis. Hydrogen atoms were located in a difference map but were not refined. Final residuals of $R$ = 0.061 and $R_w$ = 0.059 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.

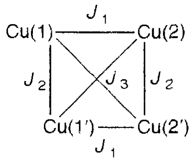


**Fig. 2** Rectangular magnetic model

corrected for monomer ($M$) and dimer ($D$) impurities and simplified by assuming that the lateral and diagonal exchange pathways are approximately the same ($J_2 = J_3$) ($N_\alpha$ = temperature independent paramagnetism). Although the inclusion of five terms did not lead to a very sensitive data analysis, it was clear that $J_2$ was not zero and that both monomer and dimer corrections were necessary. A reasonable fit of the data to eqn. (2) was obtained for $g = 2.04(2)$, $J_1 = -167(3)$ cm$^{-1}$, $J_2 = -60(5)$ cm$^{-1}$ (corrected for 6.6% monomer and 3.4% dimer impurities). The related complex $[Cu_4(L^1)(OH)_2(H_2O)_6(EtOH)_2](CF_3SO_3)_6$ has a similar structure to **1** (Cu–OH–Cu 116.0°) and comparable magnetic properties [$g = 2.01(2)$, $J_1 = -218(3)$ cm$^{-1}$, $J_2 = -36(5)$ cm$^{-1}$; 2.6% monomer and 2.6% dimer impurities]. The significant 'monomeric,' paramagnetic impurities are clearly evident in these systems from the sharp rise in susceptibility at temperatures <50 K, and presumably result from incomplete metallation of the ligand during synthesis.

The $J_1$ exchange terms clearly define the short, intradimer exchange pathways and within each binuclear half of the molecule relatively strong antiferromagnetic exchange occurs between the copper centres *via* a superexchange mechanism involving the diazine and hydroxide bridges. However this coupling is substantially weaker than that predicted for a hydroxide angle of 116.3°, based on magnetostructural correlations in a series of analogous antiferromagnetically coupled phthalazine complexes[6] ($2J = -540$ cm$^{-1}$), a situation consistent with charge delocalisation between the binuclear halves of the molecule through the fused benzene rings. This is also consistent with the observation that in structurally related pyridazine and phthalazine complexes significantly weaker antiferromagnetic coupling is observed for the phthalazine species, indicating charge delocalisation into the fused benzene ring of the phthalazine moiety.[8] The significant antiferromagnetic, cross-ring, coupling is remarkable, and occurs through distances of 12.34 and 13.72 Å across the benzodipyridazine ring system. This can be attributed to the essentially flat nature of the rectangular array of coppers relative to the heterocyclic bridge, and good overlap of the corresponding orbitals with the magnetic copper $d_{x^2-y^2}$ orbitals.

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

*Received, 12th June 1991; Com. 1/02837E*

## References

1 D. P. Rillema, R. W. Callahan and K. B. Mack, *Inorg. Chem.*, 1982, **21**, 2589.
2 V. McKee and W. B. Shepard, *J. Chem. Soc., Chem. Commun.*, 1985, 158.
3 V. McKee and S. S. Tandon, *J. Chem. Soc., Chem. Commun.*, 1988, 385.
4 M. Bell, A. J. Edwards, B. F. Hoskins, E. H. Kachab and R. Robson, *J. Am. Chem. Soc.*, 1989, **111**, 3603.
5 R. R. Gagné, W. A. Marritt, D. N. Marks and W. O. Siegl, *Inorg. Chem.*, 1981, **20**, 3260.
6 L. K. Thompson, F. L. Lee and E. J. Gabe, *Inorg. Chem.*, 1988, **27**, 39.
7 R. W. Jotham and S. F. A. Kettle, *Inorg. Chim. Acta*, 1970, **4**, 145.
8 L. K. Thompson, S. K. Mandal, J-P. Charland and E. J. Gabe, *Can. J. Chem.*, 1988, **66**, 348.