First dicopper(II) complex to contain bridging macrocyclic pyridazine units: structure, electrochemistry and magnetochemistry of [Cu₂L(MeCN)₂(ClO₄)₂][ClO₄]₂

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Magnetic and electrochemical studies of the structurally characterised dicopper(II) complex [Cu₂L(MeCN)₂(ClO₄)₂][ClO₄]₂ 1, the first to be bridged by two pyridazine units held within a (2 + 2) macrocyclic ligand, reveal strong antiferromagnetic exchange as well as two well separated reversible one-electron reductions at positive potentials.

Diazine-bridged dicopper(II) complexes have been the subject of many magnetostructural, redox and biochemical studies.[1] The diazine bridges can take many forms and frequently occur as part of polydentate acyclic ligands. On complexation of copper to ligands which provide 1,2-diazine bridges, for example those containing pyridazine, phthalazine, pyrazolate or triazolate moieties, it is commonly found that exogenous bridges are incorporated in addition to the diazine bridge(s): complexes with only 1,2-diazine bridges are relatively rare.[1–11] The resulting complexes typically exhibit significant magnetic exchange, and usually display one two-electron reduction step to produce a dicopper(I) species. In contrast, very few macrocyclic ligands containing 1,2-diazine moieties have been reported[2,3,7,9,12] and to date none of these have contained a pyridazine bridge between copper ions. We have prepared 3,6-diformylpyridazine as part of our programme to introduce new 'head units' into Schiff-base macrocyclic chemistry.[2,3] Reaction of this 'head unit' with 1,3-diaminopropane using lead(II) template ions results in the formation of the macrocyclic complex [Pb₂L'][ClO₄]₄ and we report here on the structure, magnetism and electrochemistry of the product of the trans-metallation with copper(II) perchlorate, [Cu₂L(MeCN)₂-(ClO₄)₂][ClO₄]₂ 1. This is the first example of a dicopper complex bridged by macrocyclic pyridazine units.

The green complex 1 was synthesised in 76% yield via transmetallation of [Pb₂L'][ClO₄]₄ with Cu(ClO₄)₂·6H₂O in acetonitrile. The IR spectrum of 1‡ showed that the Schiff-base macrocycle had remained intact. The FAB mass spectrum had a cluster of peaks consistent with the presence of [Cu₂L(ClO₄)₂]⁺, thus indicating that the original (4 + 4) Schiff-base macrocycle had ring contracted to a (2 + 2) macrocycle (Fig. 1). Such ring contractions are not unknown in Schiff-base chemistry: the reversible nature of imine bond formation allows alteration of the macrocycle size to best accommodate the particular metal salts that are being introduced.[2,13] In order to confirm that we were not simply seeing 1 fragmenting in the mass spectrometer, an X-ray structural determination was undertaken.

Single crystals were grown by diethyl ether diffusion into an acetonitrile solution of 1. The structure determination§ (Fig. 2) confirms that the Schiff-base macrocycle has indeed ring contracted from (4 + 4) to (2 + 2). The two halves of the macrocycle are related by a twofold rotation axis. The copper(II) ions have distorted square pyramidal geometries: the basal plane consists of two bridging pyridazine nitrogen donors and two imine nitrogen donors, and the copper atom lies 0.317(2) Å out of this plane towards the apical acetonitrile molecule. A perchlorate ion sits below the remaining face of the macrocyclic complex and a weak interaction between O(11) and Cu(1) is

observed. The macrocycle is fairly flat; the planes of the two pyridazine rings intersect at 29.67(7)°, and the basal planes of the two copper atoms intersect at 9.90(4)°.

The temperature dependence of the magnetic susceptibility of acetonitrile-free 1 (MeCN removed under vacuum) is typical of that expected for a strongly antiferromagnetically coupled complex. The susceptibilities, per Cu, decrease from a value of 512×10^{-6} cm³ mol⁻¹ at 300 K to 194×10^{-6} cm³ mol⁻¹ at 100 K, then increase rapidly in a Curie-like fashion on account of a small concentration of monomer 'impurity', reaching a value of 2754×10^{-6} cm³ mol⁻¹ at 4.3 K. The corresponding μ_{Cu} values decrease from 1.11 μ_B at 300 K to 0.39 μ_B at 100 K and remain almost constant at this value down to 4.3 K. An excellent fit to the Bleaney–Bowers equation yielded the parameter values $g = 2.07$, $J = -241$ cm⁻¹, fraction monomer = 0.03, TIP = 60×10^{-6} cm³ mol⁻¹. Comparison with detailed studies of Thompson et al. on acyclic μ-pyridazine compounds which also contain an exogenous bridging group, confirms the present J value in relation to the bridging geometry and Cu···Cu separation. Thus, examples of μ-pyridazine ligands which have five-membered chelating groups in the 3,6 positions, similar to those in 1, yield μ-hydroxo complexes with Cu···Cu distances of ca. 3.42 Å and J values of -380 to -390 cm⁻¹, the μ-(OH) bridge having a significant influence on the bridge geometry and on the J value.[8] The closest comparison to 1 is a planar acyclic complex also
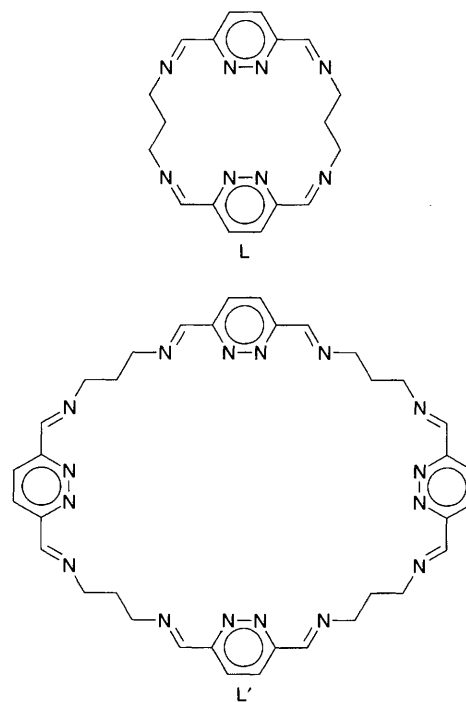

Fig. 1 Macrocyclic ligands L and L'

containing two pyridazine bridges:[4] the Cu···Cu separation of 3.760(2) Å and the Cu–N–N(pyridazine) angle of 126.8(7)° are similar to those of **1** [3.805(3) Å, 128.4(2)°], as is the J value, −268 cm⁻¹. The hydrogen-bonded oxime end groups in this complex, like the $(CH_2)_3$ lateral groups in **1**, play little part in the exchange mechanism.

Cyclic voltammetry was carried out on **1** in dry MeCN and revealed two well separated one-electron reduction waves ($E_{1/2}$ = 0.10 V and $E_{1/2}$ = 0.43 V, Fig. 3). Variation of the scan rate and analysis of peak height and separation showed that both redox processes are fully reversible. The two waves are believed to be associated with $Cu^{II}Cu^{II}$ to $Cu^{II}Cu^{I}$ and $Cu^{II}Cu^{I}$ to $Cu^{I}Cu^{I}$ reductions, respectively.[3] Similar behaviour has frequently been observed for symmetric phenolate-bridged macrocyclic dicopper complexes but with both of the one-electron reductions occurring at negative potentials.[16] In contrast, to our knowledge, none of the previous examples of symmetric pyridazine-bridged systems have exhibited two well separated one-electron reductions so complex **1** is unique in this respect. The mixed valence species is reasonably stable (K_{con} = 3.8 × 10⁵)[16] and further characterisation, using ESR and electronic spectroscopies, is therefore under way.[3]
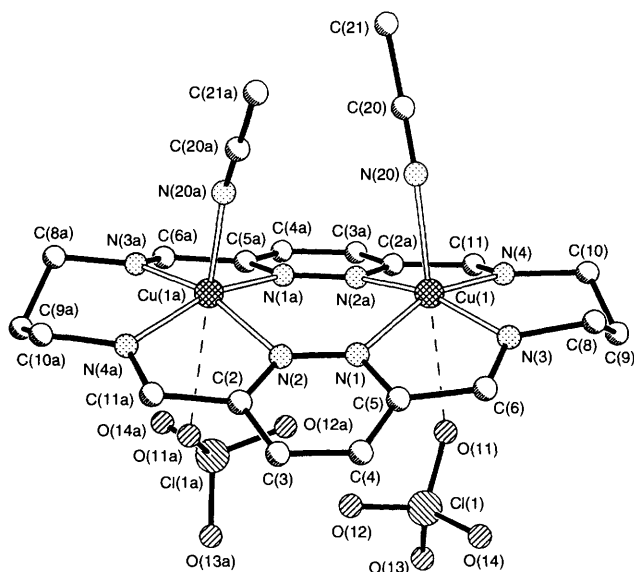

Fig. 2 Perspective view of the cation of **1**, $[Cu_2L(MeCN)_2(ClO_4)_2]^{2+}$. Selected interatomic distances (Å) and angles (°): Cu(1)–N(1) 2.041(3), Cu(1)–N(2a) 2.036(3), Cu(1)–N(3) 1.957(3), Cu(1)–N(4) 1.988(3), Cu(1)–N(20) 2.128(3), Cu(1)···O(11) 2.762(3), Cu(1)···Cu(1a) 3.805(3), N(3)–Cu(1)–N(4) 93.28(13); N(3)–Cu(1)–N(2a) 163.59(12), N(4)–Cu(1)–N(2a) 80.86(12), N(3)–Cu(1)–N(1) 80.84(12), N(4)–Cu(1)–N(1) 159.48(12), N(2a)–Cu(1)–N(1) 99.32(11), N(3)–Cu(1)–N(20) 106.09(13), N(4)–Cu(1)–N(20) 96.42(13), N(2a)–Cu(1)–N(20) 89.86(13), N(1)–Cu(1)–N(20) 104.10(12).
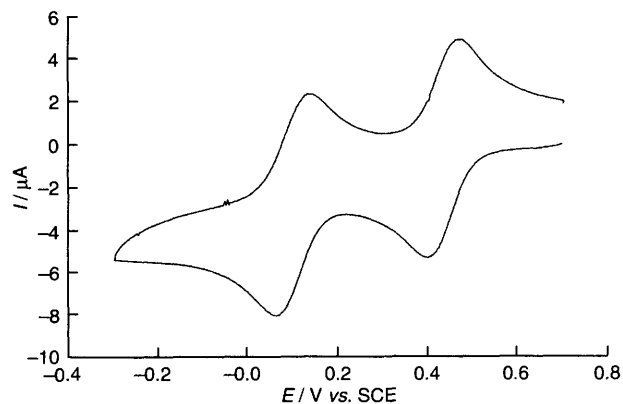

Fig. 3 Cyclic voltammogram of **1** in MeCN (100 mV s⁻¹, 1 × 10⁻³ mol dm⁻³, 0.1 mol dm⁻³ NEt_4ClO_4, platinum counter electrode *vs.* SCE)

Further development of this ligand, and related ligands based on this versatile 'head unit', will provide an excellent opportunity to systematically study the factors controlling both the redox and magnetic properties of such pyridazine-bridged complexes.[3]

Footnotes

‡ Satisfactory C, H, N, Cl analysis was obtained for acetonitrile-free **1**.

§ *Crystal data* for **1**: $C_{22}H_{26}Cl_4Cu_2N_{10}O_{16}$, green triangular prism, 0.38 × 0.17 × 0.62 mm, monoclinic, space group $C2/c$, a = 19.659(6), b = 11.792(2), c = 14.690(6) Å, β = 99.96(3)°, U = 3354(2) Å³, Z = 4, μ = 1.68 mm⁻¹. Data were collected at 130 K on a Siemens P4 four-circle diffractometer using graphite-monochromated Mo-Kα radiation. 3082 Reflections were collected in the range 4 < 2θ < 50° and the 2954 independent reflections were used in the structural analysis after a semi-empirical absorption correction had been applied. The structure was solved by direct methods (SHELXS-86)[14] and refined against all F^2 data (SHELXL-93)[15] to $R1$ = 0.039 [for 2539 F > 4σ(F); $wR2$ = 0.102 and goodness of fit = 1.04 for all 2954 F^2; 245 parameters; all non-hydrogen atoms anisotropic]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/265.

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