Coordination Polymerisation of a Binuclear Copper(II) Macrocyclic Cation Through Self-assembly

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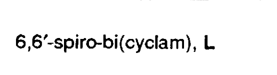
The newly prepared binuclear cation $[Cu_2Cl(\mathbf{L})]^{3+}$ [**L** = 6,6′-spiro-bi(cyclam) where cyclam = 1,4,8,11-tetraazacyclotetradecane] self-assembles into a μ-chloro-bridged one-dimensional polymer; the crystal structure and preliminary spectroscopic features are reported.

Polymeric copper(II) complexes involving macrocyclic ligands are extremely rare.[1,2] Although a number of dimeric, oligomeric and polymeric copper(II) complexes involving polydentate ligands have been identified,[3–6] very few polymeric complexes have been characterised by single crystal X-ray crystallography.[7–9] Two important aspects of such species are the nature of bridging ligand and the relative orientation of metal ions, the latter having important consequences in terms of studying magnetic interactions.[10] We report here the structure of a one-dimensional chloro-bridged polymeric copper(II) complex in which the ligand structure plays a crucial role in facilitating participation of the chloride ion in the self-assembling process. UV–VIS and ESR data provide evidence for the persistence of the polymeric chain structures in solution.



6,6′-spiro-bi(cyclam), **L**

The polymeric species $[Cu_2Cl(\mathbf{L})]_n(ClO_4)_{3n}(EtOH)_n$ (**A**) was prepared by the reaction of the hydrochloride salt of the ligand 6,6′-spiro-bi(cyclam) (**L**) with copper(II) perchlorate in 1:2 ratio in the presence of sodium hydrogen carbonate. Crystals of the navy blue polymeric species **A** were obtained in yields above 90% by diluting the reaction mixture with absolute ethanol [$\lambda_{max}(H_2O)$ 521–530 nm, concentration dependent]. However, the binuclear monomeric species $[Cu_2(\mathbf{L})](ClO_4)_4$ (**B**) was the only product [$\lambda_{max}(H_2O)$ 498 nm; ε = 138 dm^3 mol^{-1} cm^{-1}] isolated when the hydrochloride salt of the ligand was replaced with either the free ligand or its perchlorate salt.[11] Satisfactory microanalytical data were obtained for both **A** and **B**.

X-Ray-quality crystals of the polymeric species **A** were obtained by recrystallisation from a solution in aqueous

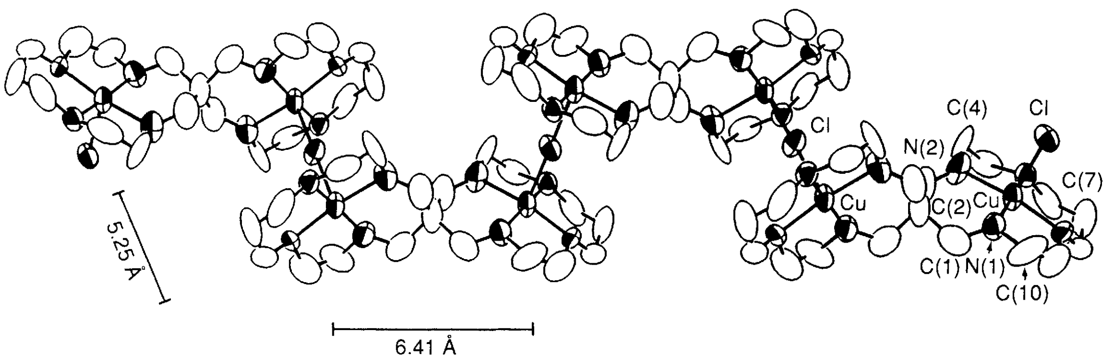


Fig. 1 ORTEP diagram of a portion of the polymeric chain consisting of μ-chloro-bridged [Cu_2(**L**)] units with atomic labelling and running parallel to the *c* axis

ethanol layered with diethyl ether.† The crystal structure is composed of polymeric chains of [Cu_2(**L**)Cl]$^{3+}$ cations. Each cation is associated with three perchlorate ions and a molecule of ethanol as solvent of crystallisation. An ORTEP diagram of a portion of the polymeric structure is shown in Fig. 1. The chloride ion symmetrically bridges the copper centres in adjacent cations with Cu–Cl = 2.627(2) Å. The average Cu–N distance is 2.01 Å and the average chelate angles for the five- and six-membered chelate rings are 86.9 and 92.7°, respectively, similar to those found in Cu^{II} complexes of cyclam and its derivatives.[12,13] The copper ion is only 0.15 Å above the plane described by the four nitrogen donors and the coordination geometry around each copper(II) ion can be described as square pyramidal.

The zigzag propagation of the chain results primarily from the ligand structure where the quaternary carbon in the ligand plays a crucial role and controls the relative orientation of each macrocyclic plane defined by the CuN_4 unit. The angle between these planes is 86.9° and the distance between the Cu atoms that are not bridged through a chloride ion is 6.41 compared to 5.25 Å between the chloro-bridged Cu atoms. The polymeric structure results from the alternate linkages formed by the bridging chloride and the quaternary carbon in the ligand structure.

ESR spectra of **A** and **B** are compared in Fig. 2. In principle, in the case of species **A**, both a weak through-space interaction and a strong interaction through the chloro-bridge can be expected between the Cu^{II} centres. The polymeric species **A** shows two features at g = 2.045 and 2.121 without any hyperfine structures suggesting that the unpaired electron does not interact with either the copper or the chlorine nuclei. The non-polymeric species **B** shows a complex multiplet due to dipole–dipole interaction.[14–16] This difference in ESR spectra and the concentration-dependent UV–VIS spectral data suggest that the polymeric species persist even on dissolution in a solvent. Similar anion-dependent behaviour has been observed in other complexes of **L**[17] and the homobinuclear Ni^{III} and the heterobinuclear mixed-valent Cu^{II}–Ni^{III} complexes of **L**, in which the metal ions are Jahn–Teller distorted, show evidence for the formation of polymeric species.[18] Anion-induced self-assembly of these cations is of interest from the perspective of synthesising molecular materials that could find use in the construction of molecular magnets, non-linear optical systems and solid-state ionic conductors.

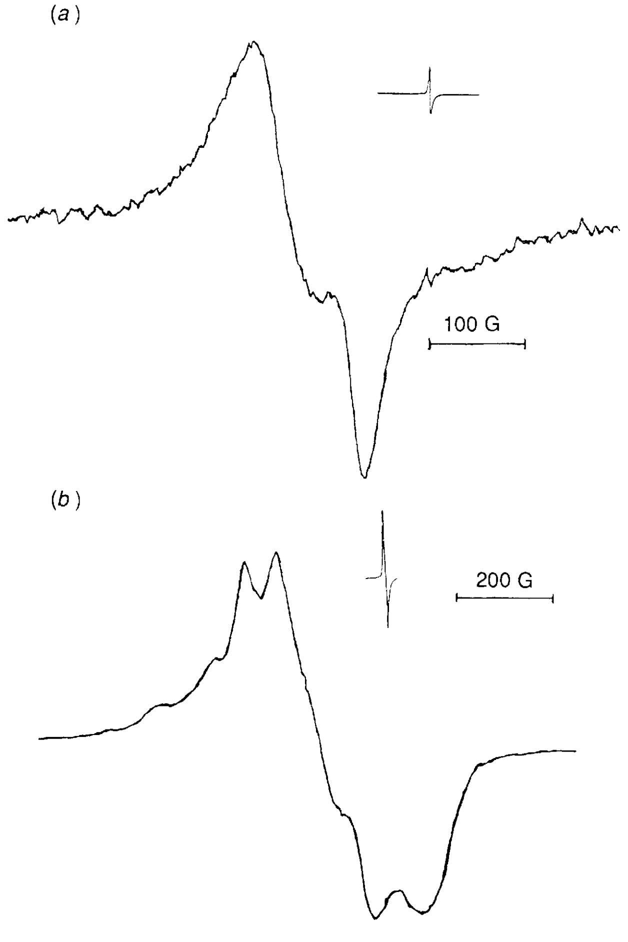


Fig. 2 ESR spectra of (*a*) the polymeric species **A** and (*b*) the non-polymeric species **B** (dimethylformamide glass at 77 K referenced to diphenylpicrylhydrazyl; 1 G = 10^{-4} T)

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† *Crystal data*: $Cu_2Cl_4O_{12}C_{19}H_{44}\cdot C_2H_5OH$, M = 890.8, monoclinic, dimensions: 0.2 × 0.5 × 0.6 mm; space group $I2/a$, a = 15.730(9), b = 14.368(6), c = 16.434(4) Å, β = 101.51(3)°, U = 3640(3) Å^3, D_c = 1.63 Mg m^{-3}, Mo-Kα radiation (λ = 0.70930 Å). The intensity data were collected using an Enraf–Nonius CAD4 diffractometer. 1067 absorption-corrected reflections with $I > 2.5\sigma(I)$ of the unique 2387 reflections were used to solve the structure using the PC version of the NRCVAX program. The ethanol molecule of solvation was found disordered. The final R values were R = 0.079 and R_w = 0.062. 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.

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