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Letter

A novel copper(I) complex that is a monomeric single helix in solid state but a dimeric double helix in solution

Shubhamoy Chowdhury,[a] Peter B. Iveson,[b] Michael G. B. Drew,[b] Derek A. Tocher[c] and Dipankar Datta*[a]

[a] *Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India. E-mail: icdd@mahendra.iacs.res.in*
[b] *Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK*
[c] *Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK*

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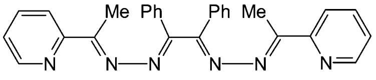
Single helical $[Cu^IL]ClO_4{\cdot}12CH_2Cl_2$ (L = 1:2 condensate of benzil dihydrazone and 2-acetylpyridine) unfolds and coils up in CH_2Cl_2 solution to generate double helical $[Cu^I{}_2L_2]^{2+}$.

Helicity continues to receive considerable attention as it allows for a greater understanding of the self-assembly processes involved in supramolecular chemistry.[1,2] Many examples of both single- and double-stranded architectures have now been reported.[1–3] While there have been many studies made on the interconversion between single- and double-stranded DNA,[4] there has so far been only a single report of such a process in a synthetic model.[1a] In this unique system, Lehn *et al.* described the dynamic interconversion between a single and double helical structure in solution by a family of oligomeric organic species. Herein we describe an inorganic example that exists as a monomeric single helicate in the solid state but converts to a dimeric double helicate in solution.

As a part of our on-going studies on metal helicates,[5–7] we wanted to synthesise double helical copper(I) complexes with the ligand L, which is a 1:2 condensate of benzil dihydrazone and 2-acetylpyridine. Elsewhere we have reported the X-ray crystal structure of the 1:2 condensate of benzil dihydrazone and 2-formylpyridine, which is helical.[8] Reaction of L with $[Cu(CH_3CN)_4]ClO_4$ in anhydrous methanol in equimolar proportion under N_2 atmosphere yields a deep red copper(I) compound that upon recrystallisation from a 3:1 *n*-hexane–dichloromethane mixture give micro crystals of $[CuL]ClO_4{\cdot}\frac{1}{2}CH_2Cl_2$ (**1**). Complex **1** is indefinitely stable in air in the solid state as well as in solution.



(L)

The solid state structure of the cation in **1** as determined by X-ray crystallography is shown in Fig. 1. There are two cations in the asymmetric unit but they have essentially similar structures. On the whole, the cation in **1** can be described as a single-stranded helix with the metal having a somewhat flattened tetrahedral N_4 coordination sphere. The average dihedral angle (τ) between the two CuN_2 coordination planes is 49.2° (for D_{2d} symmetry, τ is 90°).

The cyclic voltammetry of complex **1**, performed at a glassy carbon electrode in purified dichloromethane, is characteristic of a dimer of the type $[Cu_2L_2]^{2+}$. Two quasi-reversible oxidative cyclic responses with equal current heights are observed (Fig. 2), which can be ascribed to electrode processes (1a) and (1b). The redox potentials of the couples (1a) and (1b) are respectively 0.27 and 0.50 V *vs.* a saturated calomel electrode (SCE).

$$[Cu^{II}Cu^IL_2]^{3+} + e^- \rightleftharpoons [Cu^I{}_2L_2]^{2+} \qquad (1a)$$

$$[Cu^{II}{}_2L_2]^{4+} + e^- \rightleftharpoons [Cu^{II}Cu^IL_2]^{3+} \qquad (1b)$$

The difference of 0.23 V in the redox potentials of the two couples is indicative[9] of considerable antiferromagnetic exchange in the species $[Cu^{II}{}_2L_2]^{4+}$. Attempts to do coulometry at 0.75 V *vs.* SCE at a platinum wire gauge electrode in dichloromethane under dry N_2 atmosphere gave rise to a continuous slow accumulation of charge.[10] This means that the oxidised species is unstable in solution. The involvement of one electron in each of the couples (1a) and (1b) has been established by comparing the cyclic voltammetric peak currents with those of the ferrocene–ferrocenium couple under the same experimental conditions.

Since the cyclic voltammetry results suggest that the cationic part of **1** actually exists as $[Cu_2L_2]^{2+}$ in dichloromethane medium, we have investigated the positive ion electrospray ionisation mass spectrum (ESIMS) of a dichloromethane solution of **1**. Three peaks are observed at m/z = 507.26, 508.25 and 509.26 with an intensity ratio of 1:0.41:0.47. Since for copper the natural abundance of isotope 63 is 70% and that of isotope 65 30%, for $[Cu_2L_2]^{2+}$ (molecular weight with ^{63}Cu = 1015.06) the relative intensities of these peaks are calculated as 1:0.39:0.43. Thus, we assign these 3 peaks to the dimeric species $[Cu_2L_2]^{2+}$. For the monomeric cation $[CuL]^+$ (molecular weight with ^{63}Cu = 507.53 and that with ^{65}Cu = 509.53), no peak at m/z = 508 with the intensity being as high as that observed is expected. Consequently, the ESIMS results also hint at the existence of a dimeric cation in solution.

To examine whether dissolution of **1** in dichloromethane leads to a mixture of species, we have studied the ^1H NMR spectra of **1** in CD_2Cl_2 at 298 and 213 K. At both temperatures, the methyl protons appear as a sharp singlet at 2.48 ppm (Fig. 3). However, some broadening of the aromatic proton resonances occurs at 298 K (Fig. 3). The observation of a single signal for the methyl protons at both temperatures possibly means that we have a single species in a dichloromethane solution of **1**.

That we have only the dimeric species in dichloromethane solution is implicated from cyclic voltammetry also. Fig. 2

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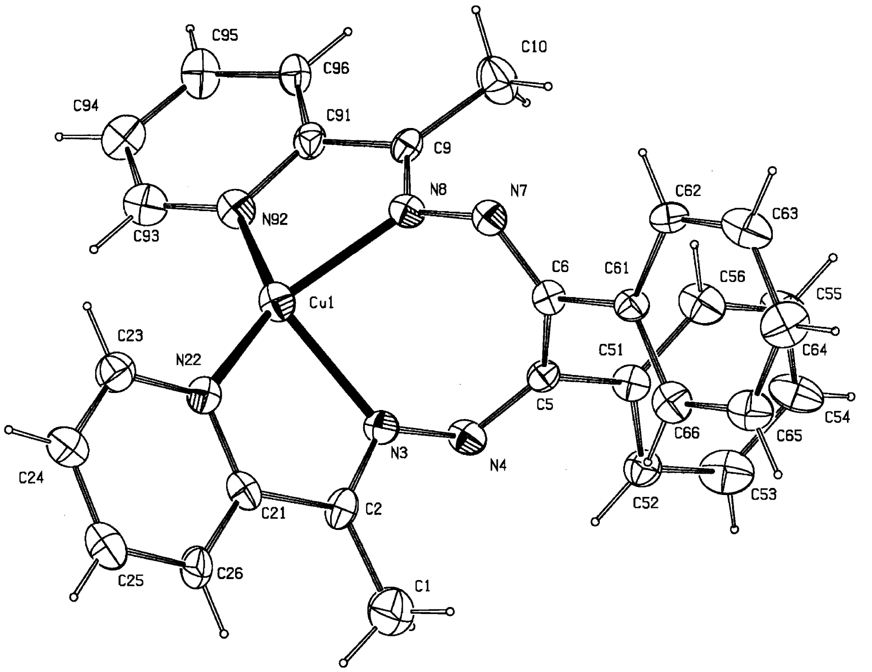


Fig. 1 The structure of the cation in **1** with ellipsoids at 20% probability. In one of the cations (see text): Cu1–N22 1.973(7), Cu1–N92 2.012(8), Cu1–N8 2.064(7), Cu1–N3 2.110(7) Å, N22–Cu1–N3 80.5(3), N3–Cu1–N8 84.9(3), N8–Cu1–N92 80.1(3), N92–Cu1–N22 144.0(3), τ (see text) 47.9° and in the other cation: Cu1–N22 1.995(7), Cu1–N92 1.995(7), Cu1–N8 2.093(7), Cu1–N3 2.123(8) Å, N22–Cu1–N3 79.6(3), N3–Cu1–N8 83.7(3), N8–Cu1–N92 79.8(3), N92–Cu1–N22 135.5(3), τ 50.6°.

shows that when the scan rate is increased from 50 to 500 mV s^{-1}, the two waves remain "pseudo" reversible, indicating that the dimer is present to start off with. One possibility is that the monomer is initially present, but the formation of the Cu(II) complex causes ligand rearrangement and formation of dimer; the second oxidation can then occur. If this were the case, the second oxidation wave would be very dependent on the scan rate.

Hints to the possible structure of the $[Cu_2L_2]^{2+}$cation are provided by the X-ray crystal structure of $[Ag_2L_2]^{2+}$ (Fig. 4) in the deep yellow $[Ag_2L_2](ClO_4)_2 .4H_2O$ (**2**) complex, which has been synthesised by reacting hydrated $AgClO_4$ with L in ethanol. The cation in **2** is found to be a double-stranded helicate with C_2 symmetry and the metal having a distorted tetrahedral N_4 coordination sphere (τ = 76.6°). The helical twist in **2** is brought about by the torsion angle of −103.3° around the N(7)–C(6)–C(5)–N(4) bonds although the C(9)–N(8)–N(7)–C(6) and C(5)–N(4)–N(3)–C(2) torsion angles of −144.5° and −166.9°, respectively, also contribute. Our density functional theory (DFT) calculations[11] using the ADF program[12] clearly show that in the gas phase a double

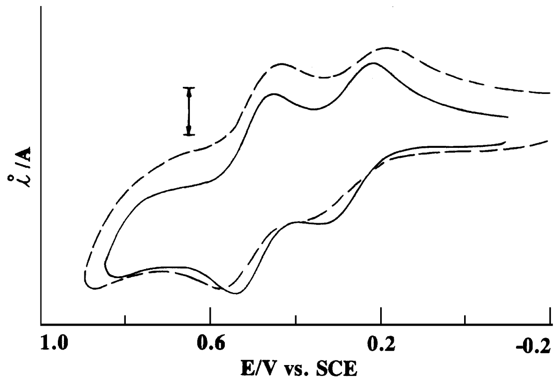


Fig. 2 Cyclic voltammograms of **1** in CH_2Cl_2 at scan rates (v) of 50 (—) and 500 (---) mV s^{-1}. The current scale is 2 μA for v = 50 mV s^{-1} and 3.5 μA for v = 500 mV s^{-1}. Conditions: dry N_2 atmosphere, 0.975 mmol dm^{-3} **1**, 0.1 mol dm^{-3} Bu_4NClO_4, glassy carbon working electrode. Under the same conditions, $E_{\frac{1}{2}}$(ferrocene–ferrocenium) is 0.48 V *vs.* SCE.

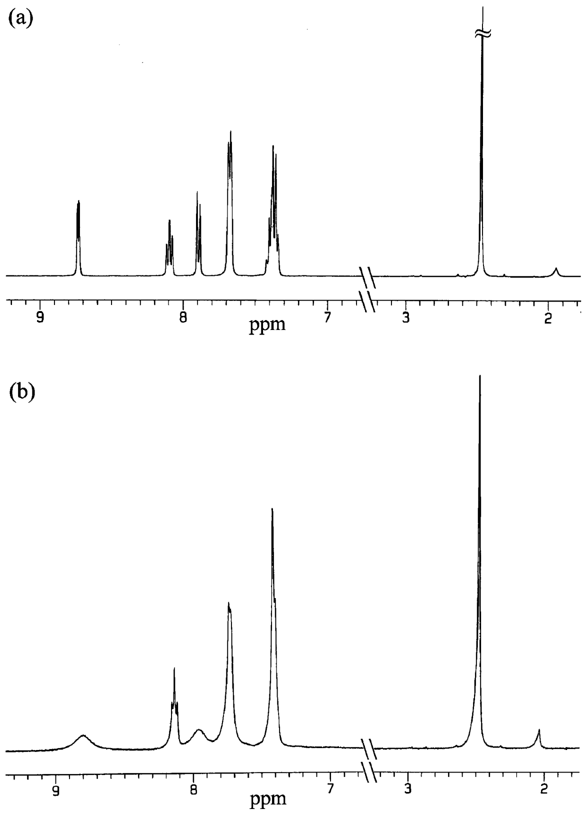


Fig. 3 400 MHz ^1H NMR spectrum of **1** in CD_2Cl_2: (a) at 213 K, (b) at 298 K. Relative intensities of the signals from left to right is 1:1:1:3:3:3.

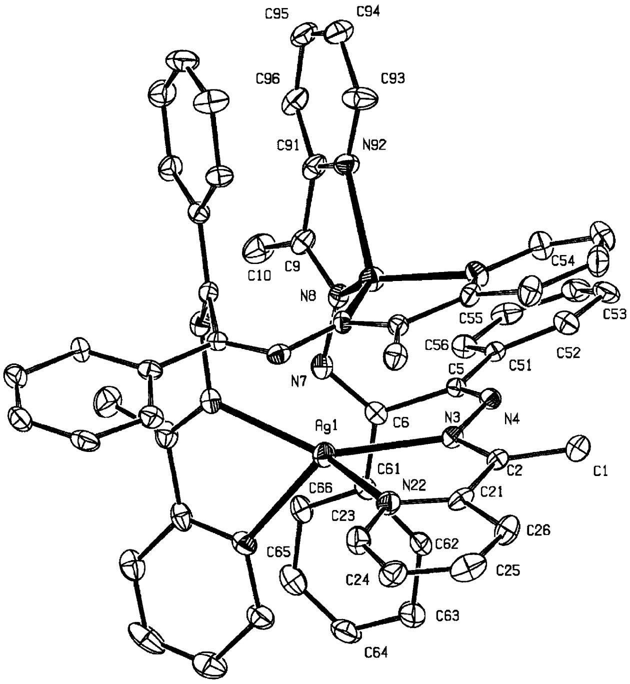
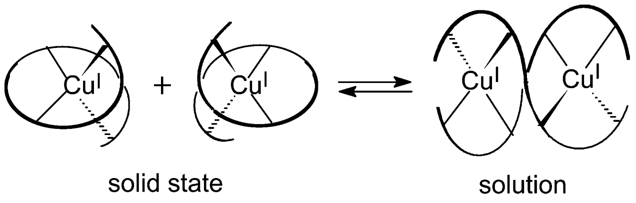


Fig. 4 The structure of the cation in **2** with ellipsoids at 20% probability. Selected bond lengths (Å) and angles (°): Ag1–N22 2.289(8), Ag1–N3 2.384(8), Ag1–N92* 2.331(7), Ag1–N8* 2.340(7), Ag···Ag 3.315(5), N3–Ag1–N22 72.1(3), N92*–Ag1–N8* 70.1(3), τ 76.6. * refers to symmetry element $-x$, y, $3/2-z$.

helical structure similar to that of the $[Ag_2L_2]^{2+}$ cation in **2** would be possible for $[Cu_2L_2]^{2+}$. Thus a process like (2) is implicated for $[CuL]^+$.



(2)

In a dichloromethane solution, we have a double helix that upon crystallisation decoils and folds into two single helices.[13] Such an observation is truly novel in the chemistry of helicates.

Experimental

L was synthesised as described elsewhere.[8] All measurements on **1** were done with its single crystals. Purification of dichloromethane used for electrochemistry is as follows. Two hundred and fifty milliliters of commercial dichloromethane was thoroughly washed three times with 100 ml of 5% Na_2CO_3 solution. Then it was washed thoroughly with water and stored over fused $CaCl_2$ overnight. The filtrate was distilled over fused $CaCl_2$. The fraction at 40–41 °C was collected.

Syntheses

[CuL]ClO$_4$·12CH$_2$Cl$_2$ (1). Freshly prepared $[Cu(CH_3CN)_4]ClO_4$ (0.33 g, 1 mmol) was added to L (0.44 g, 1 mmol) dissolved in anhydrous, degassed methanol (25 ml) under dry N_2 atmosphere. The reaction mixture was stirred for 30 min at room temperature. The dark red precipitate was filtered, washed with diethylether (20 ml) and dried *in vacuo* over fused $CaCl_2$. It was recrystallised from a 1:3 mixture of dichloromethane and *n*-hexane to obtain red micro crystals of **1** in 80% yield. Single crystals were grown by direct diffusion of *n*-hexane into a dilute dichloromethane solution of **1**. Anal. found (calcd): C 52.51 (52.64), H 3.91 (3.88), N 12.97 (12.93%). UV/VIS (CH_2Cl_2) λ_{max}/nm (ε/dm^3 mol^{-1}cm^{-1}): 261 (28 950), 290 (30 700), 420 (7350), 525 (1650).

[Ag$_2$L$_2$](ClO$_4$)$_2$·4H$_2$O (2). $AgClO_4 \cdot xH_2O$ (0.33 g) was added to L (0.44 g, 1 mmol) dissolved in ethanol (25 ml) and stirred for 30 min at room temperature. The deep yellow precipitate was filtered, washed with diethylether (20 ml) and dried *in vacuo* over fused $CaCl_2$. It was recrystallised from a 1:3 dichloromethane–*n*-hexane mixture to obtain deep yellow micro crystals of **2** in 70% yield. Single crystals were grown by direct diffusion of *n*-hexane into a dilute dichloromethane solution of **2**. Anal. found (calcd): C 48.94 (48.87), H 4.07 (4.10), N 12.19 (12.22%). UV/VIS (CH_2Cl_2) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 295 sh (79 400), 320 (49 800).

X-Ray crystallography

The data were collected at 295 K with MoKα radiation using the MARresearch image plate system. The crystals were positioned at 70 mm from the image plate. One hundred frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program[14] and structure solution with SHELXS-86 program.[15] The non-hydrogen atoms were refined anisotropically and remaining atoms isotropically. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were bonded. Both structures contained disordered perchlorate anions and solvent molecules. In **2**, there were six solvent water molecules, each refined with 0.3333 occupancy; hydrogen atoms were not locatable. Empirical absorption corrections were carried out using DIFABS.[16] The structures were refined on F^2 using SHELXL.[17] Final R values: for **1** with observed data $I > 2\sigma(I)$, $R_1 = 0.0907$ and $wR_2 = 0.1916$ and for all data $R_1 = 0.2344$ and $wR_2 = 0.2517$; for **2** with observed data $I > 2\sigma(I)$, $R_1 = 0.0756$ and $wR_2 = 0.2224$ and for all data $R_1 = 0.1298$ and $wR_2 = 0.2586$.

CCDC reference numbers 157534–5. See http://www.rsc.org/suppdata/nj/b2/b207057j/ for crystallographic files in CIF or other electronic format.

Crystal data for 1. $C_{28.5}H_{25}Cl_2CuN_6O_4$: $M_w = 649.65$, monoclinic, space group $P2_1/a$, $a = 15.32(3)$, $b = 20.70(3)$, $c = 18.71(3)$ a, $\beta = 96.19(1)°$, $U = 5900(15)$ Å^3, $Z = 8$, $\mu = 0.966$ mm^{-1}; 13 624 reflections collected, 10 667 unique/independent reflections, R(int) = 0.054.

Crystal data for 2. $C_{56}H_{56}Ag_2Cl_2N_{12}O_{12}$: $M_w = 1375.76$, monoclinic, space group $C2 2/c$, $a = 28.01(4)$, $b = 15.30(2)$, $c = 20.37(3)$ Å, $\beta = 127.94(1)°$, $U = 6888(16)$ Å^3, $Z = 4$, $\mu = 0.707$ mm^{-1}; 6929 reflections collected, 4502 unique, R(int) = 0.0307.

Acknowledgements

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10 **1** (12.71 mg) taken in 25 ml of dichloromethane was electrolysed. There was a continuous slow accumulation of charge; after 3 h of electrolysis, 2.65 coulombs had been collected, to compare to the theoretical coulomb count of 1.89.

11 Slater-type orbital basis sets of triple zeta quality for the valence orbitals were employed with polarisation functions on the ligand atoms (2p for H, and 3d for C and N) and additional valence p orbitals on the metal atom. The Generalised Gradient Approximation was used with Becke88 exchange and Perdew86 correlation gradient corrections. The starting model was the crystal structure of $[Ag_2L_2]^{2+}$ in **2** (with Cu replacing Ag) with imposed D_2 symmetry, which was then geometry-optimised successfully until convergence.

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