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# Notes

## Effect of an ancillary ligand on single helix-double helix interconversion in copper complexes. Copper(I)-water bond

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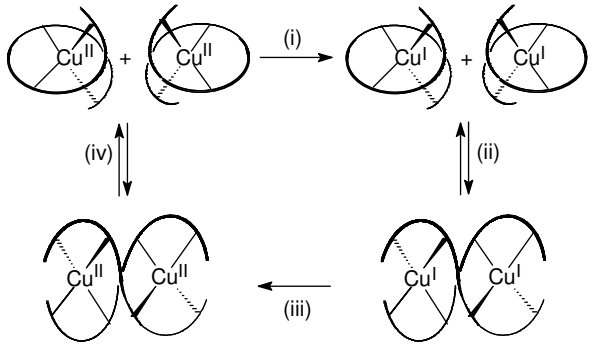
Reaction of $Cu(ClO_4)_2.6H_2O$ with the 1:2 condensate of benzildihydrazone and 2-acetylpyridine, in methanol in equimolar ratio yields a green compound which upon recrystallisation from 1:1 $CH_2Cl_2$-$C_6H_6$ mixture affords $[CuL(H_2O)](ClO_4)_2.½C_6H_6$. The complex crystallises in the space group P-1 with $a$ = 8.028(11) Å, $b$ = 12.316(17) Å, $c$ = 18.14(3) Å, $\alpha$ = 97.191(10)°, $\beta$ = 94.657(10)° and $\gamma$ = 108.039(10)°. It is single helical with the metal having a distorted trigonal bipyramidal $N_4O$ coordination sphere. The acid dissociation constant of the Cu(I) complex in $CH_3CN$ is 3.34 ± 0.19. The X band EPR spectrum of the compound is rhombic with $g_1$ = 2.43, $g_2$ = 2.10, $g_3$ = 2.02 and $A_1$ = 79.3 x $10^{-4}$ $cm^{-1}$. The Cu(II/I) potential of the complex in $CH_2Cl_2$ at a glassy carbon electrode is 0.43 V vs SCE. It is argued that the copper-water bond persists in the corresponding copper(I) species. Its implications on the single helix-double helix interconversion in copper helicates are discussed. DFT calculations at the B3LYP/ 6-311G** level shows that the binding energy of water in the single helical five-coordinate copper(I) species $[CuL(H_2O)]^+$ is ~ 40 kJ $mol^{-1}$.

**Keywords:** Coordination chemistry, copper, Helical compounds

Synthesis of metal complexes with helical topology has been a fascinating area in inorganic chemistry[1-4]. The usual strategy is to exploit the coordination properties of a metal ion to wrap around a non-helical ligand in a helical manner. For quite some time, we have been trying to synthesise helical metal complexes using ligands which are themselves helical[5-10]. Very few others have adopted such an approach[11]. In course of our studies, we have even obtained a möbius metallamacrocycle[12].

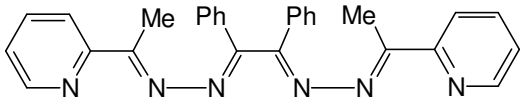
A general feature observed in the chemistry of copper(I)/copper(II) helicates is the single helix-double helix conversion triggered by electron transfer[5,13,14], as described in Scheme 1. In Scheme 1, the copper(I) and the copper(II) centers are four coordinate.

Herein we show that a fifth coordination to the metal allows only path (i) and blocks the other paths described in Scheme 1. The helical ligand used in the present study is the 1:2 condensate of benzildihydrazone and 2-acetylpyridine (L). We have previously reported its synthesis and X-ray crystal structure[8].




(i) reduction, (ii) self-assembling,
(iii) oxidation, (iv) disassembling

**Scheme 1**




L

## Experimental

Tetrabutylammonium perchlorate was purchased from Aldrich. Microanalyses were performed by a Perkin-Elmer 2400II elemental analyser. Solution conductance was measured by using a Systronics India conductivity meter 306. FTIR spectra (KBr disc, 4000-400 $cm^{-1}$) were recorded on a Shimadzu 8400S spectrophotometer, UV/vis spectra on a Shimadzu UV-160A spectrophotometer, EPR spectra with a Varian E-line Century Series spectrometer and ESI MS with a Waters Qtof Micro YA263 spectrometer. Magnetic susceptibility was determined at room temperature by a PAR 155 vibrating sample magnetometer. The magnetometer was calibrated with

$Hg[Co(SCN)_4]$ and the susceptibility data were corrected for diamagnetism using Pascal's constants. Cyclic voltammetry was performed using a EG&G PARC electrochemical analyzer (model 250/5/0) in purified dichloromethane under a dry nitrogen atmosphere in conventional three-electrode configurations. A planar EG&G PARC G0229 glassy carbon milli electrode was used as the working electrode. Under the experimental conditions used here, $E_{½}$(ferrocene-ferrocenium) is 0.48 V vs SCE.

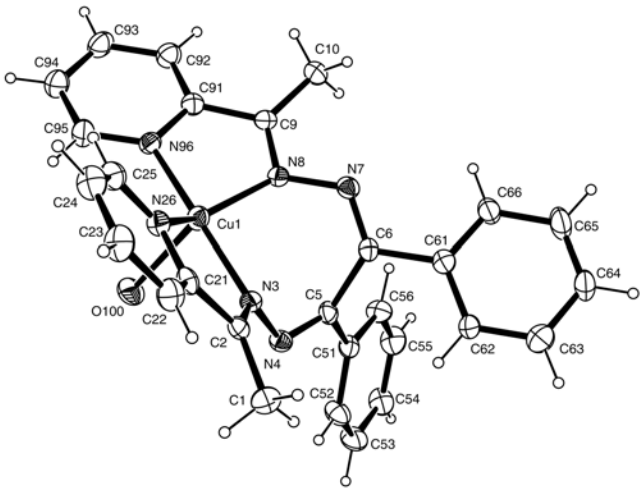
Table 1 — Crystallographic data for $[CuL(H_2O)](ClO_4)_2.½C_6H_6$ (**1**)

| | |
|---|---|
| Empirical formula | $C_{31}H_{29}N_6CuCl_2O_9$ |
| Formula weight | 764.04 |
| Crystal system | Triclinic |
| Space group | P-1 |
| $a$ (Å) | 8.028(11) |
| $b$ (Å) | 12.316(17) |
| $c$ (Å) | 18.14(3) |
| α (°) | 97.191(10) |
| β (°) | 94.657(10) |
| γ (°) | 108.039(10) |
| $U$ (Å$^3$) | 1678(4) |
| $Z$ | 2 |
| $d_{calc}$ (g cm$^{-3}$) | 1.512 |
| $\mu$ (mm$^{-1}$) | 0.873 |
| $F$ (000) | 784 |
| Unique reflections | 4894 |
| Observed reflections [$I > 2\sigma(I)$] | 3002 |
| Parameters | 445 |
| $R_1$, $wR_2$ ($I > 2\sigma(I)$) | 0.1011, 0.2698 |
| $R_1$, $wR_2$ (all data) | 0.1622, 0.3056 |
| Largest diff. peak/hole (e Å$^{-3}$) | 0.65/-0.60 |

$[CuL(H_2O)](ClO_4)_2.½C_6H_6$ (**1**) was synthesized as follows: $Cu(ClO_4)_2.6H_2O$ (0.19 g, 0.5 mmol) was added to a solution of L (0.22 g, 0.5 mmol) in 20 cm$^3$ of methanol and stirred for 2 h at room temperature. The colour of the solution changed from yellow to green and the green precipitate obtained was filtered, washed with 10 cm$^3$ of diethyl ether and dried *in vacuo* over fused $CaCl_2$. It was recrystallised from a 1:1 (*v/v*) mixture of dichloromethane and benzene to obtain green micro crystals. Yield: 0.28 g (72 %). Elemental analyses were consistent with the stoichiometry $C_{31}H_{29}N_6CuCl_2O_9$. Calc. (%): C 48.69, H 3.83, N 11.00. Found (%): C 48.58, H 3.78, N 11.06. Main FTIR bands (cm$^{-1}$): 1628(s), 1086(vs). $\mu/\mu_B$: 1.97 (at 300 K). UV-vis ($CH_2Cl_2$) λ/nm (ε /dm$^3$ mol$^{-1}$ cm$^{-1}$): 234 (32,700), 333 (34,700), 672 (130). ESI MS ($CH_2Cl_2$) *m/z*: 253.3 (15 %; **(1)** - $0.5C_6H_6$ - $H_2O$ - 2 $ClO_4^-$).

DFT calculations at the B3LYP/6-311G** level were performed by Gaussian 03W (version B.03) program[15]. The crystal structure of **(1)** was used as the input model.

Single crystals of **(1)** were grown by direct diffusion of benzene into a dilute dichloromethane solution of the complex. Data were collected with Mo-$K_\alpha$ radiation using the MARresearch Image Plate System. The crystals were positioned at 70 mm from the Image Plate. 100 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program[16]. The structure was solved using direct methods with the ShelX97 program[17]. Non-hydrogen atoms were




| *Bond lengths (Å)* | | *Bond angles (°)* | |
|---|---|---|---|
| Cu1-O100 | 2.252(6) | N3-Cu1-N8 | 94.7(2) |
| Cu1-N3 | 1.970(5) | N3-Cu1-N96 | 172.2(2) |
| Cu1-N8 | 1.996(6) | N3-Cu1-N26 | 80.1(2) |
| Cu1-N26 | 2.032(6) | N3-Cu1-O100 | 87.6(2) |
| Cu1-N96 | 1.968(6) | N8-Cu1-N96 | 81.8(2) |
| N3-N4 | 1.397(8) | N8-Cu1-N26 | 136.6(2) |
| N3-C2 | 1.245(9) | N8-Cu1-O100 | 119.9(2) |
| N4-C5 | 1.275(9) | N96-Cu1-N26 | 107.2(2) |
| N7-N8 | 1.408(9) | N96-Cu1-O100 | 88.2(3) |
| N7-C6 | 1.274(8) | N26-Cu1-O100 | 103.0(2) |

Fig. 1 — The structure of $[CuL(H_2O)]^{2+}$ in **(1)** with ellipsoids at 20 % probability. [Hydrogen atoms on the water molecule were not located].

Table 2 — Conductivity data and $pK_a$ for the complex (**1**) in acetonitrile at room temperature

| Solute conc. (mmol $dm^{-3}$) | Solution conduct. (μmho) | $\Lambda_{obs}$ (mho $cm^2$ $mol^{-1}$) | $[[CuL(H_2O)]^{2+}]^a$ (mmol $dm^{-3}$) | $[H^+]^a$ (mmol $dm^{-3}$) | $pK_a{}^b$ |
|---|---|---|---|---|---|
| 2.00 | 599 | 300 | 1.333 | 0.667 | 3.48 |
| 1.00 | 327 | 327 | 0.442 | 0.558 | 3.15 |
| 0.50 | 163 | 327 | 0.221 | 0.279 | 3.45 |
| 0.25 | 94 | 348 | 0.067 | 0.183 | 3.30 |

[a]Equilibrium concentration; [b] Average value is 3.34.

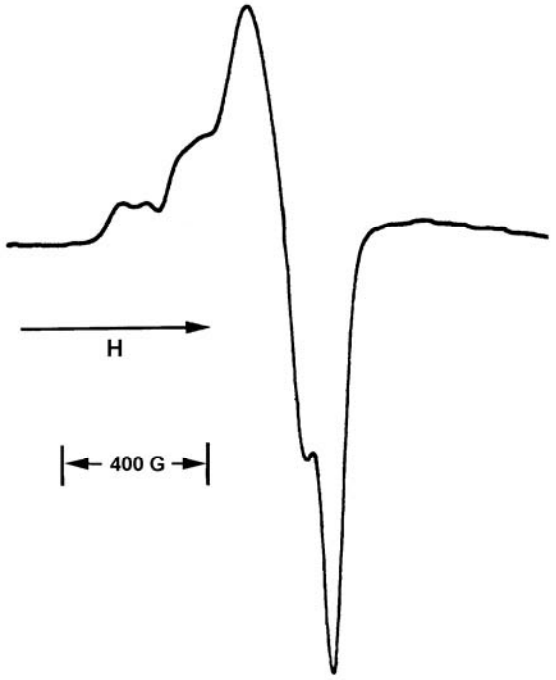



Fig. 2 — X-band EPR spectra of (**1**) in dichloromethane-toluene glass at 77 K. [$g_1 = 2.43$, $g_2 = 2.10$ and $g_3 = 2.02$; $A_1 = 79.3 \times 10^{-4}$ $cm^{-1}$].

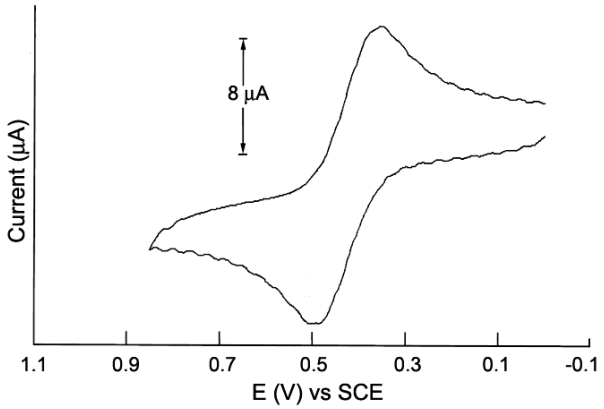



Fig. 3 — Cyclic voltammogram of (**1**) in $CH_2Cl_2$. [Cond.: dry $N_2$ atmosphere; (**1**): 1.06 mmol $dm^{-3}$; $Bu_4NClO_4$: 0.1 mol $dm^{-3}$; glassy carbon working electrode; scan rate: 50 mV $s^{-1}$].

refined with anisotropic thermal parameters. 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 attached. An empirical absorption correction was carried out using DIFABS[18]. The structure was refined on $F^2$ using Shelx97[17]. Selected crystallo-graphic data are given in Table 1.

## Results and discussion

Reaction of $Cu(ClO_4)_2.6H_2O$ with (L) in methanol in equimolar proportion gives a green compound which upon recrystallisation from 1:1 dichloro-methane-benzene mixture yields $[CuL(H_2O)](ClO_4)_2.½C_6H_6$ (**1**). In the X-ray crystal structure, complex (**1**) contains discrete $[CuL(H_2O)]^{2+}$ cations (Fig. 1) and perchlorate anions. The copper atom in $[CuL(H_2O)]^{2+}$ is five-coordinate with a geometry that can best be described as a distorted trigonal bipyramid with N(3), and N(96) being the axial and N(26), N(8) and O(100) being the equatorial atoms. The two axial nitrogen atoms form shorter bonds than the chemically equivalent equatorial nitrogen atoms; thus Cu(1)-N(3) at 1.970(5) Å is shorter than Cu(1)-N(8) at 1.999(6) Å and Cu(1)-N(96) at 1.968(6) Å is shorter than Cu(1)-N(26) at 2.032(6). The water molecule O(100) is bonded at 2.252(6) Å. The closest contact between the copper atom and a perchlorate oxygen atom is 3.15(1)Å to O(13). The conformations of the ligand moiety in the free state and in the complex cation are quite similar (Supplementary material Table S1). The only major difference is in the torsion angle of N(4)-C(5)-C(6)-N(7), which is -71.6° in the metal complex (thus facilitating the formation of a 7-membered chelate ring) and 85.9° in the free ligand. The overall topology of the cation in (**1**) is single helical.

The Cu(II)-water bond in (**1**) is somewhat long. Our BVS (bond valence sum) calculations, which correlates the oxidation state of a metal with the distances of the bonds in the coordination sphere[15], show that Cu(II)-O bond in a symmetric $CuO_5^{2+}$ core should be 2.018 Å. As revealed by electrospray

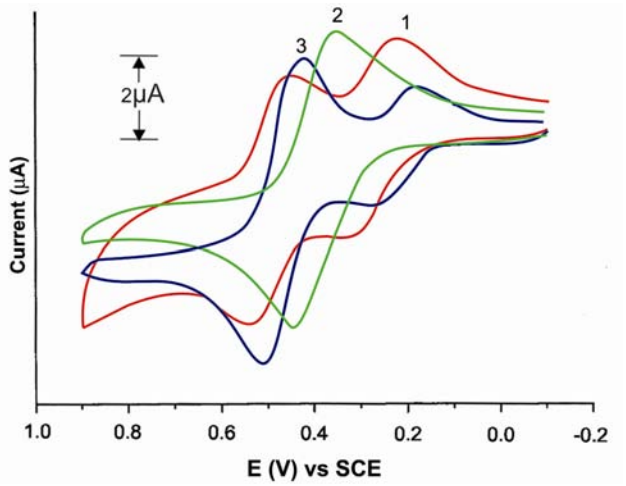



Fig. 4 — Cyclic voltammogram of $[CuL]ClO_4.0.5CH_2Cl_2$ in (1) (——) 10 ml of $CH_2Cl_2$; (2) (——) in 10 ml of $CH_2Cl_2$ + 1 ml of methanol; (3) (——) in 10 ml of $CH_2Cl_2$ + 5 ml of methanol. [Cond.: dry $N_2$ atmosphere; $[CuL]ClO_4.0.5CH_2Cl_2$: 4 mg; $Bu_4NClO_4$: 0.1 mol $dm^{-3}$; glassy carbon working electrode; scan rate: 50 mV $s^{-1}$].

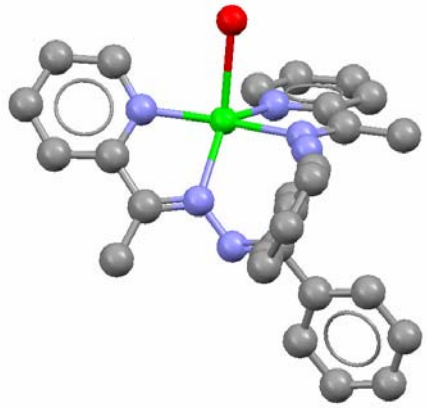


Fig. 5 – The optimized structure of $[CuL(H_2O)]^+$ in the gas phase as obtained from B3LYP/6-311G** calculations. [Colour code: green, Cu(I); red, O; blue, N; dark grey, C. The H atoms are omitted for clarity].

ionization mass spectrometry, the Cu(II)-water bond does not persist in the gas phase under mass spectrometric condition. To check whether the water molecule remains bonded to the metal in solution, we have determined the acid dissociation constant ($pK_a$) of **(1)** in acetonitrile from molar conductance. The method and the equations used are described in ref. 20. The $pK_a$ value is estimated as 3.34 ± 0.19 (Table 2).

The complex **(1)** has a magnetic moment of one unpaired electron at room temperature. Its EPR spectrum in dichloromethane-toluene glass at 77 K is sort of rhombic (Fig. 2) commensurate with its structure.

In cyclic voltammetry in $CH_2Cl_2$ at a glassy carbon electrode, complex **(1)** displays a quasireversible Cu(II/I) potential at 0.43 V vs SCE (Fig. 3). This is particularly interesting as the $[CuL]ClO_4.0.5CH_2Cl_2$, the copper(I) complex of (L) which is monomeric in the solid state gives a cyclic voltammogram characteristic of a dinuclear species (Fig. 4) in $CH_2Cl_2$[5]. It is conjectured that the coordinated water molecule in **(1)** prevents the corresponding copper(I) species from dimerisation. To test our hypothesis, we have investigated the change in the cyclic voltammogram of $[CuL]ClO_4.0.5CH_2Cl_2$ in $CH_2Cl_2$ with the addition of methanol (Fig. 4). It is found that with the increase in the proportion of methanol, the cyclic voltammogram changes to that of a mononuclear species, indicating that the coordination of methanol to the metal center prevents dimerisation in solution. Thus, the fifth coordination of copper(I) blocks the pathways (ii)-(iv) in Scheme 1. Examples of truly pentacoordinate copper(I) complexes are very rare[21-23].

In our previous publications[24,25] where we have provided X-ray crystal structures of copper(I) complexes containing a discrete Cu(I)-$OH_2$ bond, we have pointed out that coordination of water to a Cu(I) center is unusual in terms of Pearson's Hard-Soft Acid-Base theory. While Cu(I) is a "soft" acid, water is a "hard" base. Thus, the bonding between Cu(I) and water is not particularly favoured. This is supported by the experimental observation that simple $Cu^+$ ion disproportionates in water[26]. To examine whether a Cu(I)-$OH_2$ bond is feasible in combination with (L), we have performed DFT calculations at the B3LYP/ 6-311G** level on the cation $[CuL(OH_2)]^+$. For comparison, we have also carried out calculations at the same level on $[CuL(CH_3OH)]^+$. It is found that the binding of $H_2O$ and $CH_3OH$ is indeed possible to Cu(I) coordinated to (L) yielding five-coordinate Cu(I) species with a somewhat distorted trigonal bipyramidal geometry (Fig. 5). The binding energy of $H_2O$ in $[CuL(OH_2)]^+$ and that of $CH_3OH$ in $[CuL(CH_3OH)]^+$ are comparable, which is ~ 40 kJ $mol^{-1}$ with Cu(I)-O bond distances of ~ 2.6 Å. In passing we mention that recently a copper(I)-water bond has been detected in the X-ray crystal structure of the multicopper oxidase phenoxazinone synthase which catalyzes the penultimate step in the biosynthesis of the antibiotic actinomycin D by *Streptomyces antibioticus*[27]. The bond is, however, rather long, 2.92 Å.

## Supplementary data

CCDC-637423 contains the supplementary crystal data for **(1)**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Other supplementary data may be obtained from the authors on request.

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