Substituent effects in single helix-double helix interconversions in copper(I) complexes

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The copper(I) complex of L, the 1:2 condensate of benzil dihydrazone and 2-formylpyridine, exists as single helical \([\text{CuL}^-]\) and double helical \([\text{Cu}_2\text{L}_2]^+\) in dichloromethane solution but crystallizes only as the double helicate \([\text{Cu}_2\text{L}_2](\text{ClO}_4)_2\). In contrast, earlier [New J Chem, 27 (2003) 193] it has been found that with L', the 1:2 condensate of benzil dihydrazone and 2-acetylpyridine, only the single helical monomeric species \([\text{CuL}'^-]\) is isolable as solid. This contrasting behaviour of the copper(I) complexes of L and L' are scrutinised here by density functional calculations.

Studies on helical species are very important in order to understand the nature of some of the self-processes operative in nature. Recently Lehn and co-workers have shown that some oligomeric organic molecules undergo a dynamic single helix-double helix interconversion in solution like DNA. However, such monohelical-double helical interconversions have been known in metal helicates for quite some time; the earliest examples, reported by Constable and co-workers, involve cobalt(II) and silver(I) complexes of a quinquepyridine ligand. Very recently we have provided the first example of a copper(I) complex that is a single helix in the solid state but unfolds and coils up in solution to become a double helix [Eq. (1)]. Herein we report a copper(I) complex which exists as a single helix as well as a double helix in solution but crystallizes only as a double helicate. The results help us demonstrate a subtle control of the electronic effect in the monohelical-double helical interconversions in copper(I) helicates. The present study forms a part of our on-going research on metal helicates. The ligands involved here are L and L'.

Materials and Methods

The ligand L was synthesized as described elsewhere. Micro-analyses were performed on a Perkin-Elmer 2400II elemental analyser. UV/vis spectrum was recorded on a Shimadzu UV-160A spectrophotometer, ¹H NMR spectra (in CDCl₃) by a Brucker DPX300 spectrometer and ESI-MS on a VG-ZAB-SE instrument.

Computations

Density functional calculations were performed using the ADF program. 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). The Generalized Gradient Approximation was used with Becke88 exchange and Perdew86 correlation gradient corrections.

Synthesis and characterisation of \([\text{Cu}_2\text{L}_2](\text{ClO}_4)_2\) (1)

0.33 g (1 mmol) of freshly prepared \([\text{Cu(MeCN)}_4]\text{ClO}_4\) was added to 0.42 g (1 mmol) of L dissolved in 25 cm³ of anhydrous, degassed methanol under dry N₂ atmosphere. The reaction mixture was
stirred for 30 min at room temperature. The dark red precipitate was filtered, washed with 20 cm$^3$ of diethyl ether and dried in vacuo over fused CaCl$_2$. It was recrystallised from a 1:3 mixture of dichloromethane and n-hexane to obtain red microcrystals in 80% yield. Elemental analyses were consistent with the stoichiometry C$_{52}$H$_{40}$Cu$_2$N$_{12}$O$_8$ [Found: C 53.79, H 3.52, N 14.43, Calc: C 53.87, H 3.48, N 14.50%]. UV/Vis (CH$_2$Cl$_2$): $\lambda$nm (e/dm$^3$/mol$^{-1}$ cm$^{-1}$): 259 (51700), 313 (77500), 495 (5000).

Caution—Though while working with [Cu$_3$L$_2$(ClO$_4$)$_2$] we have not met with any incident, care should be taken in handling it as perchlorates are potentially explosive. These should not be prepared and stored in large amounts.

### X-ray crystallographic analysis of 1

Deep red single crystals of 1 were grown by direct diffusion of n-hexane into a dilute dichloromethane solution of the complex. The diffraction data were measured with MoKα radiation using the MARresearch Image Plate System at 293 K. The crystal was 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$^{11}$ to provide 4576 independent reflections. The structure was solved using direct methods with the Shelx86 program.$^{12}$ Non-hydrogen atoms were 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. Empirical absorption corrections were carried out using DIFABS.$^{13}$ The structure was refined on $F^2$ using ShelX$^{11}$ to obtain $R1 = 0.0812$, $wR2 = 0.2382$ for 2687 observed data ($I > 2\sigma(I)$) and $R1 = 0.1432$, $wR2 = 0.2835$ with 345 parameters (maximum/minimum residual electron densities = 1.06/−0.69 e Å$^{-3}$). The positional parameters along with equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table 1. CCDC-218111 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; FAX: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

### Crystal data

The cell constants and crystallographic data for 1 are: mol. formula C$_{52}$H$_{40}$Cu$_2$N$_{12}$Cl$_2$O$_8$; mol. wt. 1158.96; monoclinic C2/c; $a = 21.64(2)$ Å; $b = 11.115(14)$ Å; $c = 22.66(2)$ Å; $\beta = 107.100(10)^\circ$; $V = 5209(9)$ Å$^3$; $Z = 4$; $F(000) = 2368$; $D_m = 1.478$ g cm$^{-3}$; $\mu = 0.986$ mm$^{-1}$.

### Results and Discussion

Earlier elsewhere$^3$ we have reported the synthesis and structure of the ligand L which is a 1:2 condensate of benzildihydrazone and 2-formylpyridine. It is helical. The helical twist is brought about mainly by the torsion angle N=C(Ph)-C(Ph)=N of -99.5(3)$^\circ$ in L.
Reaction of the ligand L with [Cu(MeCN)₄]ClO₄ in anhydrous methanol in equimolar proportion under N₂ atmosphere yields a deep red compound. Recrystallisation of the compound from 3:1 n-hexane-dichloromethane mixture gives microcrystals of 1 which analyse as [CuL]ClO₄. From X-ray crystallography, 1 is found to be a dimer of the formulation [Cu₂L₂](ClO₄)₂. The structure of the cation in 1 is shown in Fig. 1. It is a double stranded helicate and has a crystallographic C₂ symmetry. Both the copper atoms are situated on the two-fold axis. Each copper atom is bonded to two nitrogen atoms from two different ligands. The independent Cu-N distances are Cu(1)-N(11) 2.038(5) and Cu(2)-N(30) 2.049(5), Cu(2)-N(3) 2.055(5), N(11)-Cu(1)-N(18) 110.8(2), N(11)-Cu(1)-N(18) 127.9(2), N(18)-Cu(1)-N(18) 129.85(18), N(18)-Cu(1)-N(18) 82.4(2), N(11)-Cu(1)-N(18) 82.4(2), N(30)-Cu(2)-N(30) 81.29(17), N(30)-Cu(2)-N(30) 129.22(18), N(30)-Cu(2)-N(30) 129.22(18). Symmetry element $S$ is $-x, y, 1/2-z$.

Earlier elsewhere we have reported that [CuL']ClO₄·½CH₂Cl₂ (2), the copper(I) complex of the ligand L' is a monomeric single helix in the solid state but a dimeric double helix in dichloromethane solution, i.e. 2 displays process (1). In electrospray ionisation mass spectrometry (positive ion) of the dichloromethane solution of 1, three peaks are observed at $m/z = 479, 480$ and 481 with the relative intensity of 1:0.33:0.51 (Fig. 2). Since for copper the natural abundance of isotope 63 is 70% and that of...
isotope 65 is 30%, for [Cu₂L₂]²⁺ (m = 958 with ⁶⁵Cu and z = 2) three peaks are anticipated at m/z = 479, 480 and 481 with a relative intensity of 1:0.39:0.43. It should be noted that no peak at m/z = 480 is expected for the monomeric cation [CuL]⁺ (mass m = 479 with ⁶⁵Cu, z = 1); ideally, two peaks should appear for [CuL]⁺ at m/z = 479 and 481 with a relative intensity of 1:0.43. That the intensity of the peak at m/z = 480 in Fig. 2 is less than that expected for a copper dimer indicates coexistence of the monomeric cation [CuL]⁺ with the dimeric one. Our calculations show that the observed isotopic distribution of the peaks at m/z = 479, 480 and 481 in Fig. 2 corresponds to ~ 1:5 molar ratio of [CuL]⁺ and [Cu₂L₂]²⁺ in dichloromethane solution. In our calculations we have assumed that the stabilities of the ions [CuL]⁺ and [Cu₂L₂]²⁺ are same under the mass spectroscopic conditions. Thus though 1 is a double helicate in the solid state, it gives rise to monomeric species also upon dissolution in dichloromethane i.e. in the case of 1, a single helix-double helix equilibrium of the type (2) [cf. Eq. (1)] exists in solution.

\[ \text{Cu}^+ + \text{Cu}^+ \leftrightarrow \text{Cu}^+ \text{Cu}^+ \ldots \text{(2)} \]

We have recorded the ¹H NMR spectra of 1 in CD₂Cl₂ at 301, 243 and 213 K. However, the spectra (Fig. 3) do not allow any clear-cut detection of the equilibrium (2). The imino protons appear as a singlet around 9.55 ppm at all the three temperatures. The pyridyl protons resonate uniformly as a doublet around 8.36 ppm and a triplet around 8.04 ppm. The phenyl protons appear in the region 7.35-6.96 ppm; these are broadened with the lowering of temperature which is not understood at present.

It is interesting to consider why in the solid state copper(I) forms a monomer with L' and a dimer with L and whether this observation has a steric or electronic basis or indeed is just a matter of crystal growth. We, therefore carried out some DFT calculations. Starting models were the two crystal structures for [CuL]⁺ and [Cu₂L₂]²⁺ and also [CuL]⁺ and [Cu₂L₂]²⁺ which were built from the crystal structure with the replacement of R = H by R = Me or vice versa. The two monomers were given C₂ symmetry and the two dimers were given D₂ symmetry which was consistent with the crystal structures and were then geometry-optimised until convergence with energies for the monomers of [CuL]⁺, [CuL']⁺ of -12.68381, -13.89170 a.u. and for the dimers [Cu₂L₂]²⁺ and [Cu₂L₂']²⁺ -25.27563, -27.68063 a.u. respectively. Taking the energy difference of 2x[Cu(ligand)]⁺-[Cu₂(ligand)₂]²⁺, the

![Fig. 3—300 MHz ¹H NMR spectra of 1 in CD₂Cl₂ at (a) 301, (b) 243 and (c) 213 K](image-url)
value for L is $-0.09199$ and for $L'$ is $-0.10277$ a.u. So in both cases equilibrium (2) in the gas phase is in favour of the monomer but more so in the case of $L'$ than L. Thus, electronically, formation of a monomer in the gas phase is favoured more in the case of $L'$. Needless to say that our DFT calculations also indicate that a single helical structure is viable for the unisolated cation $[\text{CuL}]^+$. Thus here we have shown that a change of substituent can have a significant effect on the nature of a helical species in the form of electronic factor. When we consider the complexes 1 and 2 together, we realise that there is a delicate balance in the mono- double helix interconversion. The species that will crystallise out possibly also depends on the interactions in the solid state. Similar observations have been made earlier by other workers in the area of metal helicates\(^{2-4}\). It has been often found that dissolution of a metal helicate in a solvent gives rise to a library of helical species (at times together with some non-helical ones); the relative population of the various species depends on the nature of the solvent, the metal ion(s), the anion and intra- and interligand interactions modulated by the substituent(s). For example, Hannon and co-workers\(^ {15}\) have reported very recently that the copper(I) polymer $[\text{Cu}_n(L^1)_n](PF_6)_n$, isolated in the solid state, is thought to give rise to a dinuclear double helicate, a trinuclear circular helicate and a grid-like tetranuclear species in acetonitrile. The structure of the double helicate has been realised in $[\text{Cu}_3(L^2)_2](PF_6)_2$ and that of the circular helicate in $[\text{Cu}_2(L^3)_3](PF_6)_2$. In $\left[\text{Cu}_n(L^1)_n\right](PF_6)_n$, $[\text{Cu}_2(L^2)_2](PF_6)_{2n}$ and $[\text{Cu}_3(L^3)_3](PF_6)_{2n}$, copper(I) has an N\(_4\) coordination sphere. The close similarity between Hannon’s ligands ($L^1$, $L^2$ and $L^3$) and our L and $L'$ should be noted. It is evident that because of geometric constraints, Hannon’s ligands cannot yield a mononuclear helical copper(I) species with a Cu\(_{N_4}\) chromophore. Anyway, our work independently suggests that the potential energy between single and double stranded helices is rather shallow and that electronic effect together with the packing forces occurring during crystallisation processes may dramatically affect the final edifices.

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References