Minimal structural reorganisation in the electrochemical oxidation of a dinuclear, double helical Cu(I) complex of a triazine-based pentadentate ligand

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A dicopper(I) double helicate oxidizes and rapidly reorganises to form a stable pentadentate dicopper(II) double helicate due to the proximity of pendant pyridyl rings as studied by electrochemical and structural analyses.

The reversible reorganisation of molecular assemblies is an attractive concept towards their application as molecular switches.[1,2] Although there are many platforms upon which to build molecular switches, transition metal ions stand out among them as external perturbation of their physical environment can change the coordination geometry of their metal–ligand complexes and hence afford a means to toggle between two or more structures.[3] As the bistability, speed and reversibility of a molecular switch is highly dependant on its translational motion, the coordination geometry of the metal–ligand complex is very important.[4] In this regard, Cu(I)/Cu(II) complexes of polypyridine ligands have been of particular interest for applications as molecular switches due to the differences in topological preferences between Cu(I) and Cu(II) cations.[5,6] For example, Cu(I) complexes of rigid pentadentate ligands such as 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (qnpy) have previously been employed to assemble dinuclear or trinuclear, double-stranded helical-type structures under anaerobic conditions (Fig. 1).[7,8] These complexes are highly sensitive to oxidation in solution and rapidly oxidise to the mixed valence form.[7,8] The mixed valent and homovalent Cu(II) complexes are stabilised as both metal and ligand requirements are satisfied through pentadentate coordination of the Cu(II) cation. To date, Cu(I) complexes of rigid pentadentate polypyridine ligands based on qnpy have not been characterised in the solid state due to the instability of the Cu(I) ion during crystallisation. In contrast, many crystal structures have been obtained for multinuclear Cu(I) complexes of rigid polypyridine ligands in which there are four or six coordinating atoms within the ligand as both ligand and metal preferences are satisfied by tetracoordinate complexation of the metal ions.[6]

Herein, the synthesis, solid state structure and electrochemical switching of a $[\mathrm{Cu}\mathbf{L1}]_2^{2+}$-type complex is described, where **L1** is a pentadentate, triazine-based heterocyclic ligand.

The synthesis of ligand **L1** was carried out by a triazine ring-forming reaction in which two equivalents of 6-cyano-2,2′-bipyridine were reacted with *p*-bromobenzoamidinate (Scheme 1).[9] $[\mathrm{Cu}\mathbf{L1}]_2^{2+}$ was synthesised by addition of $\mathrm{Cu(MeCN)_4(PF_6)}$ to a stirred solution of **L1** in acetonitrile under anaerobic conditions and was isolated as a brown solid in 80% yield.

In contrast to Cu(I) qnpy-type complexes,[7,8] the homovalent Cu(I) complex was stable in the solid state and solution for several weeks. The ^{1}H NMR spectrum of $[\mathrm{Cu}\mathbf{L1}]_2^{2+}$ supported the formation of a symmetric complex, and the presence of a binuclear Cu(I) complex with two pentadentate ligands was confirmed by high resolution ESMS.

The initial ^{1}H NMR evidence suggested that the Cu(I) centres would be bound through the peripheral 2,2′-bipyridine (bpy) motifs in a pseudo-tetrahedral arrangement which would retain the symmetry of complex leaving the triazine rings unbound. The most stable orientation would be that in which the phenyl rings point to the outside of the helix and the triazines behave similarly to

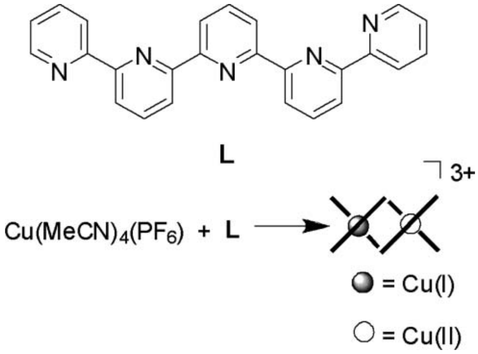
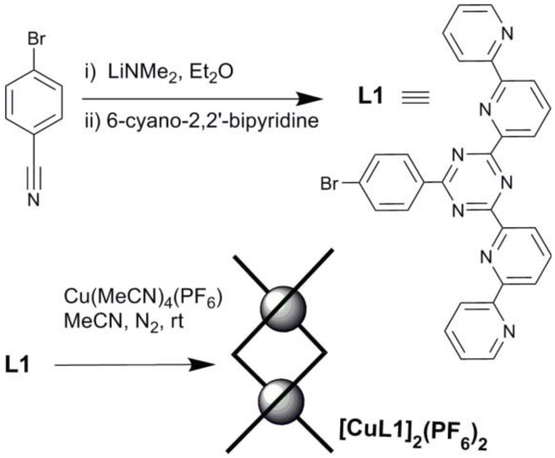


Fig. 1 Synthesis of a mixed valence $[\mathrm{CuL}]_2^{3+}$ complex based on qnpy.[7]



Scheme 1 Synthesis of binuclear, helical complex $[\mathrm{Cu}\mathbf{L1}]_2^{2+}$.

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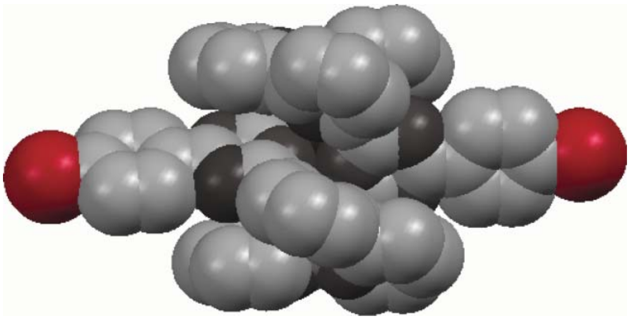

Fig. 2 Space-filling model of the calculated structure of a symmetric complex based on $[\mathrm{Cu}\mathbf{L1}]_2^{2+}$.

m-phenylene units (Fig. 2).[10,11] A model complex was generated based on the crystal structure of a dihelical Cu(I) complex incorporating a bpy substituted biphenylene unit (Fig. 2).[10,12] The energy minimized structure corroborated the ^{1}H NMR data well.

Brown crystals of $[\mathrm{Cu}\mathbf{L1}]_2^{2+}$ were obtained by slow diffusion of diethyl ether into a concentrated solution of the complex in acetonitrile.† The dinuclear complex crystallises in the monoclinic space group $P2_1/c$ with both helical enantiomers in the unit cell. The solid-state structure indicates that the ligands are in fact unsymmetric, with bpy-type coordination to one Cu(I) ion and triazine–pyridine coordination to the second Cu(I) centre (Fig. 3).

In each ligand strand a pendant pyridyl ring is positioned with its N-pyridyl atoms pointing towards the Cu(I) centres at distances of 2.693(9) and 2.510(9) Å; the remaining Cu–N distances are 2.04–2.23 Å. As expected the Cu–N distances are longer to the triazine rings than the pyridyl rings due to the poor donor ability of the triazine rings.

As the ^{1}H NMR spectrum suggested a symmetric structure, variable-temperature ^{1}H NMR studies were carried out in an effort to observe whether or not a dynamic process existed in solution. Discrepancies in the solid-state and solution behaviour of helical Cu(I) complexes of 2,2′:6′:2″-terpyridine derivatives were previously observed but dynamic processes were not observed in solution down to −80 °C in deuterated acetone.[13] The ^{1}H signals of $[\mathrm{Cu}\mathbf{L1}]_2^{2+}$ remained well resolved at low temperature within the limits of the deuterated solvents employed (CD_3CN and CD_3NO_2). The electronic absorption spectrum of the complex in acetonitrile has an absorption band trailing out to 800 nm ascribed to a Cu(I)-to-triazine ^{1}MLCT band, thus supporting triazine coordination to the Cu(I) ion. The Cu(I) to bpy ^{1}MLCT transition is around 450 nm with tailings to 600 nm, consistent with other Cu(I) polypyridine complexes.[14]

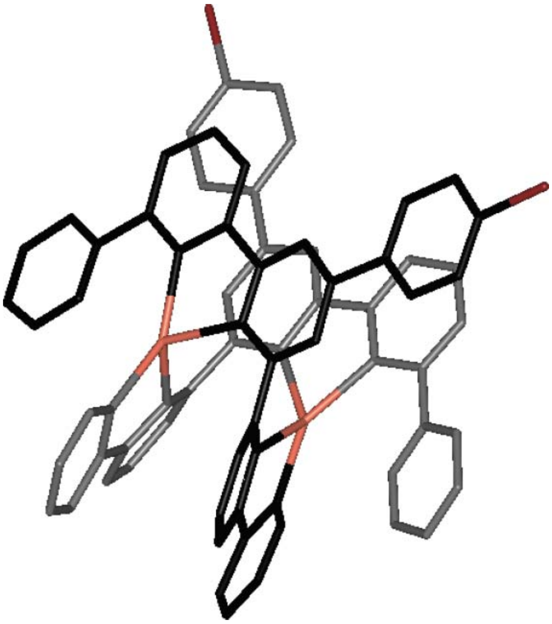

Fig. 3 Solid-state structure of $[\mathrm{Cu}\mathbf{L1}]_2^{2+}$ as a wireframe model in which the ligands have been differentiated (grey and black).

Electrochemical analysis of the complex was carried out in anhydrous acetonitrile using SCE *vs.* ferrocene as an internal reference with 0.1 M $TBAPF_6$ (Fig. 4). In the cathodic region, two initial ligand-based reversible reductions are observed at −0.92 and −1.15 V. These processes are followed by the irreversible reduction of Cu(I) to Cu(0) at −1.70 V. In the anodic region, an initial oxidation corresponding to the formation of the mixed valence complex $[\mathrm{CuL}]_2^{3+}$ is observed at 0.24 V. This first oxidation (+0.24 V) is more positive than the oxidation of $[\mathrm{Cu_3L_2}]^{3+}$ (−0.04 V),[8] where L is a qnpy-type complex, due to the increased stabilisation of the Cu(I) centre by the electron deficient triazine ring.

The chemical reversibility of the first oxidation process was analysed at two different scan rates (Fig. 4). At 25 mV s^{-1}, the anodic/cathodic peak separation is 62 mV, indicating a fully reversible process. At a scan rate of 5 V s^{-1}, the anodic/cathodic peak separation is increased to 92 mV. A second reversible oxidation is observed at 0.72 V at 25 mV s^{-1}, corresponding to the formation of the homovalent binuclear $[\mathrm{Cu}\mathbf{L1}]_2^{4+}$ complex. The

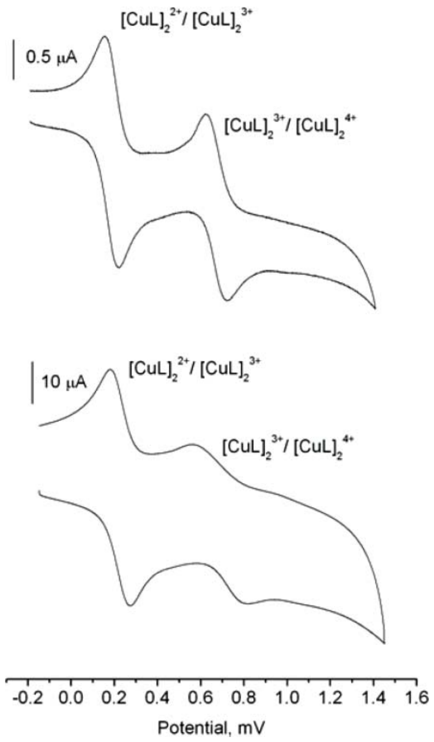

Fig. 4 Cyclic voltammogram in the cathodic region of $[\mathrm{Cu}\mathbf{L1}]_2^{2+}$ at 25 mV s^{-1} (top) and 5 V s^{-1} (bottom).

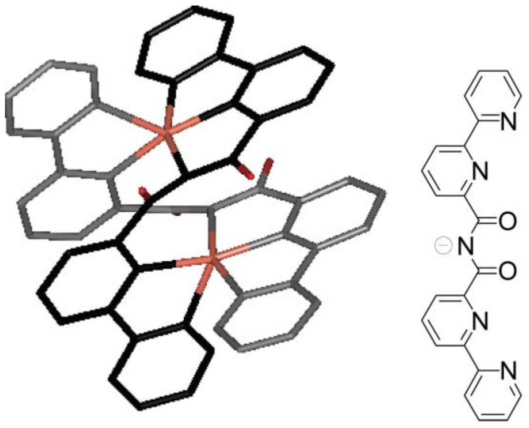

Fig. 5 Solid-state structure of $[\mathrm{Cu}\mathbf{L2}]_2^{2+}$ with ligands differentiated (left, black and gray) and the hydrolyzed ligand **L2** coordinated to the Cu(II) centres (right).

reversible behaviour of $[\mathrm{Cu}\mathbf{L1}]_2^{2+}$ at 25 mV s^{-1} is supported by the solid-state structure in that minimal structural rearrangement is required to satisfy Cu(II) ion in a pseudo square-pyramidal geometry. However, at 5 V s^{-1} the second Cu(I) oxidation is irreversible, indicating that a greater structural rearrangement is required for a reversible process to occur.

Efforts to chemically oxidise $[\mathrm{Cu}\mathbf{L1}]_2^{2+}$ to a single new species were unsuccessful employing $\mathrm{NOBF_4}$ as an oxidising agent. The oxidation process was followed by electronic absorption spectroscopy, which indicated that several species were produced by chemical oxidation. Crystallisation of an acetonitrile–ethanol solution of $[\mathrm{Cu}\mathbf{L1}]_2^{2+}$ left open to air resulted in the isolation of green crystals suitable for analysis by X-ray diffraction (Fig. 5).† The Cu(I) slowly oxidised to Cu(II) to form a dinuclear, dihelical structure in which both ligands were hydrolysed to the bis(2,2′-dipyridyl-6-carbonyl)imidate ligand **L2**. The hydrolysis of a related tridentate ligand, 2,4,6-tris(2′-pyridyl)-1,3,5-triazine (tptz), was previously observed in the synthesis of its Cu(II) complexes[15] and hydrolysis of tptz has since been observed with a number of metal ions.[16]

The Cu(II) ion is in a pseudo-square-pyramidal geometry with each Cu(II) coordinated to two bpy motifs from both ligands and the N(imido) occupying the fifth coordination site (Fig. 5). Elongated Cu–N (imido) distances (2.698(4) and 2.7038(4) Å) are observed to the imido group on the second ligand. Short intramolecular, face-to-face, π-stacking interactions are observed between the pyridyl rings adjacent to the imido group on each ligand (centroid–centroid distances of 3.37 and 3.62 Å).

We expect that the hydrolysis of **L1** to **L2** occurs after the oxidation of Cu(I) in $[\mathrm{Cu}\mathbf{L1}]_2^{2+}$ to Cu(II) and that several intermediate complexes play a role as suggested by electronic absorption spectroscopy of the oxidation process. We are currently investigating the mechanism of hydrolysis and the nature of the intermediate complexes.

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Notes and references

† *Crystal data* for $[\mathrm{Cu}\mathbf{L1}]_2(\mathrm{PF_6})_2$, $\mathrm{C_{58}H_{36}Br_2Cu_2F_{12}N_{14}P_2}$: data were collected on a Bruker APEX at 220(2) K using Cu-Kα radiation (λ = 1.54178 Å). Full-matrix, least squares refinements on F^2 using all 77402 data; M = 1505.85, monoclinic, space group $P2_1/c$, a = 17.2216(15), b = 27.920(2), c = 13.7457(12) Å, β = 98.733(4)°, U = 6532.7(10) Å^3, Z = 4, $R1$ [$I > 2\sigma(I)$] = 0.1034, $wR2$ (all data) = 0.3117.

Crystal data for $[\mathrm{Cu}\mathbf{L2}]_2(\mathrm{PF_6})_2\cdot\mathrm{EtOH}\cdot\mathrm{MeCN}$, $\mathrm{C_{50}H_{40}Cu_2F_{12}N_{12}O_5P_2}$: data were collected on a Bruker APEX at 100(2) K using Cu-Kα radiation (λ = 1.54178 Å). Full-matrix, least squares refinements on $F2$ using all 35310 data; M =1305.96, triclinic, space group $P\bar{1}$, a = 11.4580(12), b = 11.8380(12), c = 21.346(2) Å, α = 96.286(4), β = 103.165(4), γ = 110.023(4)°, U = 2592.6(4) Å^3, Z = 2, $R1$ [$I > 2\sigma(I)$] = 0.0543, $wR2$ (all data) = 0.1458.

CCDC 642096 and 642097. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b711765e

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