Redox Cycling of Segmented Copper Helicates

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In the past decade many wondrous examples of metallohelicates have been described.[3] Although these architectures are fascinating to behold, few applications have been found for metallohelicates or related structures and most attention has focused on their relevance to supramolecular chemistry.[4] In particular, because dissociation of the helicate competes with reversible redox cycling,[5] useful catalytic functions have not been identified despite the close proximity of redox-active metal centers.[4] With copper(I) helicates, for example, oxidative dissociation is promoted by the need to change the geometry around the metal center from tetrahedral[6] to a 5- or 6-coordinate ligand field.[7] Even the binuclear mixed-valence copper helicate formed from quinquepyridine,[8] which shows reversible one-electron oxidation and reduction steps in cyclic voltammetry, changes nuclearity on reduction to the copper(I) species. We now introduce a simple strategy, based on a multitopic ligand able to satisfy the coordination demands of both copper(I) and copper(II) cations, that allows self-assembly of binuclear copper helicates displaying exceptional redox stability. It might be anticipated that such systems will display useful catalytic functions.[9]

$[Cu_2L_2](BF_4)_2$, $\mathbf{1}^{2+}$, was prepared in 96% yield by treating the free ligand **L** (Figure 1) in CH_2Cl_2 with copper(I) tetrafluoroborate in acetonitrile at 20 °C. The X-ray crystal structure shows that the two copper(I) cations are separated by 3.278 Å and that the complex is a helicate (Figure 2A). Each metal center, having pseudotetrahedral geometry, is coordinated to N atoms provided by a single imino (I_N) function and three pyridine (P_N) residues, with the two cations being equivalent. The free I_N atom that resides 2.629 Å from the copper(I) cation is unlikely to be coordinated to the metal even if the cis conformation is indicative of some electronic interaction.[10] In solution, however, ^{15}N-HMBC NMR spectroscopy resolves only three distinct N atoms. This suggests that the two bound ligands glide across the metal centers, causing their equivalence on the NMR time scale, so that the complex persists in a state of dynamic fluctuation in solution (Figure 1). A similar conclusion is reached from FT-IR and both ^{1}H and ^{13}C NMR spectra recorded in solution where only a single imino group can be resolved.

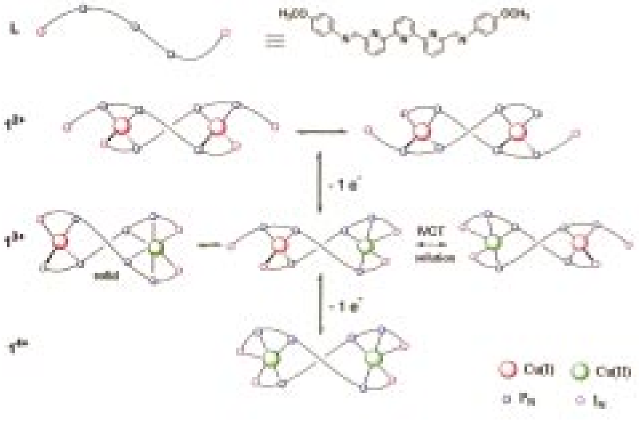

Figure 1. Schematic representation of the changes in coordination and/or structure at each stage of oxidation of the binuclear copper helicate.

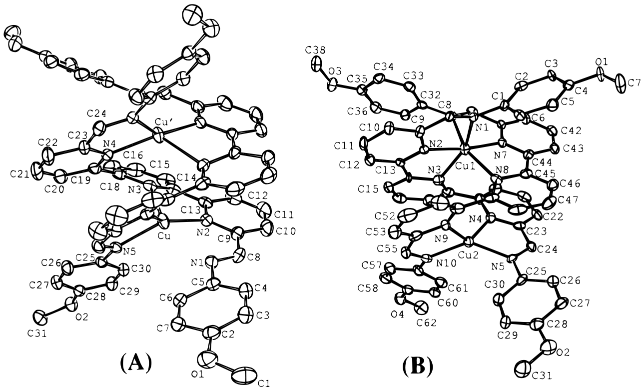

Figure 2. (A) ORTEP view of the X-ray crystal structure of the binuclear copper(I) complex $\mathbf{1}^{2+}$ showing the helical arrangement of the ligands **L** with the uncoordinated imino functions residing in the cis conformation. (B) ORTEP view of the crystal structure of the mixed-valence species $\mathbf{1}^{3+}$ showing coordinative asymmetry in the solid state.

Cyclic voltammetry studies made in acetonitrile show, in addition to several quasi-reversible reduction processes associated with the ligands ($E_{1/2} = -1.18 \pm 0.02$ V, $\Delta E_p = 69$ mV; $E_{1/2} = -1.42 \pm 0.02$ V vs SCE, $\Delta E_p = 103$ mV), two successive, quasi-reversible oxidation steps. Controlled potential coulommetry showed each oxidation step corresponds to removal of a single electron. Consequently, the first process ($E_{1/2} = 0.15 \pm 0.01$ V vs SCE, $\Delta E_p = 78$ mV) forms the mixed-valence species $\mathbf{1}^{3+}$ while the second step ($E_{1/2} = 0.87 \pm 0.02$ V vs SCE, $\Delta E_p = 84$ mV) generates the binuclear copper(II) complex $\mathbf{1}^{4+}$. The difference in potential between removal of the first and second electrons ($\Delta E_{1/2} = 720$ mV) is due, in part, to the Coulombic effect associated with the increased charge since the metal centers must remain in close proximity. That the two metal centers are electronically coupled is apparent from the appearance of a Gaussian-shaped, intervalence charge-transfer (IVCT) absorption band centered at 1400 nm ($\epsilon_{max} \approx 37 \pm 5$ M^{-1} cm^{-1}; $\Delta\nu_{1/2} \approx 1950 \pm 100$ cm^{-1}). Spectroelectrochemistry made at fixed potentials of 0.50 and 1.10 V vs Ag°, respectively, showed no detectable loss of either $\mathbf{1}^{3+}$ or $\mathbf{1}^{4+}$ over 5 min standing while the IVCT absorption band of $\mathbf{1}^{3+}$ was stable over many days. This stability is in marked contrast to most other metallohelicates which undergo substantial structural rearrangement during redox cycling.[4,5,8,11]

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[10] All X-ray structural data reported for structurally relevant imines show a trans conformation while MO calculations made at the PM3 level indicate that a trans configuration is the more stable structure for **L**.

[11] A further example of a redox stable copper helicate has been reported: Ho, P. K. K.; Peng, S. M.; Wong, K. Y.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1996**, 1829.

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Chemical oxidation of $\mathbf{1}^{2+}$ with ferrocenium cations formed the mixed-valence species with a bimolecular rate constant of $(4.5 \pm 0.6) \times 10^5$ M^{-1} s^{-1} in acetonitrile containing ammonium tetrafluoroborate (0.1 M). Immediately after one-electron oxidation, we propose that the ancillary imino N atom coordinates to the newly formed copper(II) center, giving a 5-coordinate species (Figure 1). Isolated crystals of $\mathbf{1}^{3+}$, however, show that the copper(II) center is 6-coordinate in the solid state with the ligand field being supplied by two I_N and four P_N atoms (Figure 2B). There is a concomitant shift in the ligand field around the copper(I) center from three P_N and one I_N atoms to two P_N and two I_N atoms. The solid-state structure clearly demands a substantial internal rearrangement. This is not the case in solution, however, where the IVCT absorption band indicates that the two metal centers must possess similar coordination shells. Analyzing the IVCT band in terms of an asymmetric structure[12] gives an electronic coupling matrix element (H_{MM}) of ca. 140 cm^{-1} but requires the energy difference between the terminals to be only ca. 0.2 eV. This is considered too small to reflect the markedly disparate terminals seen in the crystal structure. Conversely, analyzing the IVCT band as a symmetric system[13] requires the metal centers to be strongly coupled ($H_{MM} \approx 3570$ cm^{-1}) with full electron delocalization, and this is consistent with their close spacing. The high reversibility encoded in the cyclic voltammograms also indicates that oxidation in solution is not accompanied by large-scale structural reorganization. This hypothesis was confirmed by EPR spectroscopy made in frozen solution where the spectral pattern[14] corresponds to a $d_{x^2-y^2}$ ground state having a distorted 5-coordinate environment around the copper(II) cation.[15] These various findings indicate that the 5-coordinate species is favored in solution but not in the solid (Figure 1).

Oxidation of both $\mathbf{1}^{2+}$ and $\mathbf{1}^{3+}$ with phenoxathiin hexachloroantimonate in CH_3CN/CH_2Cl_2 (4/1) resulted in quantitative formation of the fully oxidized product $\mathbf{1}^{4+}$ under conditions where it was stable for about 1 h. Formation of $\mathbf{1}^{4+}$ could restore the molecular symmetry, giving two identical 5-coordinate copper(II) cations, or polarize the molecule into 4- and 6-coordinate terminals. The various kinetic spectroscopic studies show no indication of a large-scale transformation accompanying oxidation, and it is concluded that the metal centers in $\mathbf{1}^{4+}$ adopt 5-coordinate structures. Consequently, we attribute the remarkable redox stability of the metallohelicate to the presence of a terminal imino function that can readily provide the coordination demands of the copper(II) cation. Indeed, without the accessory, imine oxidation of the copper(I) helicate causes rapid dissociation into mononuclear copper(II) species.[16] Treatment of $\mathbf{1}^{3+}$ and $\mathbf{1}^{4+}$ with hydrazine restored the original copper(I) helicate in essentially quantitative (>95%) yield.

The overall stability constant for $\mathbf{1}^{2+}$ was measured by titration of **L** with Cu^+ in acetonitrile ($\log \beta = 18.5$) and by dissociative titration[17] with 2,9-dimethyl-1,10-phenanthroline ($\log \beta = 20.3$). Stepwise formation of the copper(I) helicate is not cooperative since the individual stability constants do not increase progressively:

$$\mathbf{L} + Cu^+ \rightarrow Cu(\mathbf{L})^+ \qquad \log K_1 = 7.05$$

$$\mathbf{L} + Cu(L)^+ \rightarrow Cu(\mathbf{L})_2{}^+ \qquad \log K_2 = 3.55$$

$$Cu(\mathbf{L})_2{}^+ + Cu^+ \rightarrow Cu_2(\mathbf{L})_2{}^{2+} \qquad \log K_3 = 7.90$$

The difficult step involves attachment of a second ligand to the mononuclear fragment $Cu(\mathbf{L})^+$, possibly for stereochemical reasons. A dissociative titration made with 2,9-dimethyl-1,10-phenanthroline after chemical oxidation with phenoxathiin hexachloroantimonate established that $\mathbf{1}^{4+}$ was considerably less stable ($\log \beta = 9.80$) than $\mathbf{1}^{2+}$. The mixed-valence species $\mathbf{1}^{3+}$ does not disproportionate in CH_3CN while adding an equimolar amount of $\mathbf{1}^{2+}$ to a solution of $\mathbf{1}^{4+}$ shows that the equilibrium lies firmly on the side of the mixed-valence species with the comproportionation constant being ca. 1×10^{12}. Quantitative analysis of the resultant absorption spectral profile shows $\mathbf{1}^{3+}$ ($\log \beta \gg 26.4$) to be the more stable complex, as expected from the cyclic voltammetry results.

The present system has two copper cations ca. 3.3 Å apart and can cycle reversibly over four redox levels spanning some 2.3 eV. In solution, a symmetrical 5-coordinate geometry around the copper(II) center(s) is favored over the asymmetrical 6-coordinate geometry preferred in the solid state. Such structures are made possible by the segmented nature of **L** and because the I_N atoms coordinate strongly to the metal center. Computer molecular modeling studies suggest that access to the metal centers is partially blocked by the terminal anisole groups and this could exaggerate the preference for a 5-coordinate arrangement. The internal flexibility, especially at the copper(I) level, and the ambivalent binding properties of **L** provide the foundation for the kinetic inertness in solution, and this might provide a means by which to design catalytically active copper helicates.

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Supporting Information Available: The synthesis and characterization of $\mathbf{1}^{2+}$ and $\mathbf{1}^{3+}$, UV−vis absorption spectra for the helicates, cyclic voltammograms, spectroelectrochemical changes, an EPR spectrum recorded for the mixed-valence species, analysis of IVCT absorption band, and methodology used to determine stability constants (22 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[13] For the IVCT absorption band the oscillator strength (f) is 0.00033, the dipole strength (M) is 0.066 Å, the degree of electron delocalization (α^2) is 0.0004, and the amount of charge transferred ($1 - 2\alpha^2$) is unity.

[14] The main EPR parameters are: g (parallel) = 2.010, A (parallel) = 122 G, g (perpendicular) = 2.25, A (perpendicular) = 42 G. A distorted 5-coordinate geometry is supported by the observation that {g (parallel)/A (parallel) = 176 cm^{-1}}.

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