Conformationally dynamic copper coordination complexes†

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The interplay between oxidation state and coordination geometry dictates both kinetic and thermodynamic properties underlying electron transfer events in copper coordination complexes. An ability to stabilize both Cu(I) and Cu(II) oxidation states in a single conformationally dynamic chelating ligand allows access to controlled redox reactivity. We report an analysis of the conformational dynamics of Cu(I) complexes bearing dipicolylaniline (dpa) ligands, with ortho-aniline substituents R = H and R = OMe. Variable temperature NMR spectroscopy and electrochemical experiments suggest that in solution at room temperature, an equilibrium exists between two conformers. Two metal-centered redox events are observed which, bolstered by structural information from single crystal X-ray diffraction and solution information from EPR and NMR spectroscopies, are ascribed to the Cu(I/II) couple in planar and tetrahedral conformations. Activation and equilibrium parameters for these structural interconversions are presented and provide entry to leveraging redox-triggered conformational dynamics at Cu.

Introduction

Copper enzymes perform diverse functions that include O₂ transport, activation, and reduction, NO₂⁻ and N₂O reduction and electron transfer. Their ability to control the flow of electrons during catalysis relies on the intrinsic link between molecular and electronic structure in copper centres. The d¹⁰ Cu(I) ion has no ligand field stabilization and favours a tetrahedral coordination geometry based on steric effects. Removing one electron causes distortion of the ligand field and a tetragonal coordination geometry is energetically favoured for Cu(II). Blue copper proteins exemplify this interplay between electronic and molecular structure by holding the Cu ion in a pseudo-C₄ᵥ symmetric coordination geometry that is poised between the stable conformations of Cu(I) and Cu(II). In this way, reorganization energy for electron transfer (ET) is minimized and the blue copper proteins are able to facilitate rapid ET. In other Cu enzymes, conformational flexibility is manipulated via the protein host to impart control over ET events. Given the variation in coordination properties between ‘soft’ and tetrahedral Cu(I) versus ‘hard’ and tetragonal Cu(II), implementation of ligands capable of stabilizing both states represents a unique challenge in the synthesis and application of Cu coordination complexes.

Cu complexes capable of facilitating these changes in coordination geometry include those with macrocyclic polythiaether, tripodal tris(2-quinolylmethyl)amine, and N₄-catechylamine. Dipicolylamine (dpa) ligands have also seen widespread application in Cu coordination chemistry. In particular, homobilmetallic systems have been used as subunits in coordination polymers and as models for Cu metalloenzymes including methane monooxygenase and hemocyanin. Karlin et al. has demonstrated the flexible nature of these ligands, using derivatives in which the central amine is functionalized with aryl groups containing ortho-OMe and meta-OMe substituents to support the oxidation of Cu(I) with O₂ to form μ-1,2-peroxodicopper(II) adducts. The ability of these dpa²⁻OMe ligands to stabilize both tetrahedral and tetragonal coordination geometries of Cu caught our attention and we set out to explore the conformational dynamics of Cu(I) and Cu(II) bound to dpa²⁻OMe and dpa⁴⁻ ligands (Scheme 1).

X-ray diffraction (XRD) structures and electron paramagnetic resonance (EPR) spectroscopy support that the Cu(I) complex formed with dpa²⁻OMe, [CuCl(dpa²⁻OMe)][PF₆], adopts a square pyramidal coordination geometry in both solution and the solid state. In contrast, solution electrochemical and NMR data reveal that the Cu(II) complex formed with dpa⁴⁻OMe, CuCl(dpa⁴⁻OMe), exists in an equilibrium of two conformers consistent with monomeric tetrahedral and planar coordination geometries. Similar solution behaviour was observed for the Cu(I)
complex formed with dpaH, CuCl(dpaH), however its CuII analogue could only be prepared as the dichloride adduct. This CuCl2(dpaH) complex adopts a structure that is intermediate between square pyramidal and trigonal bipyramidal in both solid and solution phases.

A confounding factor in our analyses of the CuI conformational equilibria at play in these systems was the observation of bis(μ-Cl) dimers in the solid state structures of CuI. However, concentration dependent differential pulse voltammetry (DPV) experiments allowed us to determine that in solution, such species are only present at elevated concentrations. Under dilute solution conditions, cyclic voltammetry (CV) experiments revealed a stark contrast between the fluxional CuI states and those of CuII in which the imposition of Jahn–Teller distortions restrict conformational fluidity. [Cu IICl(dpaOMe)]+ exhibits a single reversible redox event with a peak-to-peak separation of 80 mV. In contrast, CuICl(dpaOMe) exhibits two reversible metal-centred redox events separated by over 500 mV. We ascribe these two events to the Cu II/I couple in two discrete conformations and provide both ΔG° and ΔG‡ for their interconversion. Notably, in the absence of the strategically placed ortho-substituent, oxidative and reductive features for Cu IICl2(dpaH) are separated by 440 mV, suggesting a large reorganization energy.24 The new CuCl(dpaR) complexes presented here accommodate the unique properties of both CuI and CuII and are poised to facilitate rapid redox changes.

Results

Synthesis and structural characterization

The new copper complexes prepared from known dpaR ligands,25,26 where R = H or OMe, with appropriate CuI or CuII chlorides are summarized in Scheme 1. Empirical formulations for all new complexes were examined by electrospray mass spectrometry (ESI-MS). The presence of the CuI complexes, CuCl(dpaR), were identified by parent ion peaks at m/z = 373.04 and 403.05 a.m.u. for R = H and OMe, respectively (Fig. S1 and S2†). Bulk compositions were verified by elemental analysis, where the CuCl(dpaOMe) and CuCl(dpaH) complexes form dimeric units in the solid state. The diamagnetic complexes, CuCl(dpaR), were further characterized by 1H-NMR spectroscopy in d4-DMF. The observed spectra were distinguished from free ligand by shielding of resonances from the aliphatic protons and deshielding of resonances for the aromatic protons in both pyridine and phenyl groups (Fig. S3 and S4†).

Single crystal XRD was used to establish molecular geometry in the solid state for the new coordination complexes. For CuCl(dpaOMe), single crystals suitable for diffraction were obtained under anaerobic conditions by slow diffusion of pentane into a concentrated solution of complex in dichloromethane at −36 °C to afford yellow needles in a dimeric form that contains a bridging chloride ligand, [{Cu(dpaOMe)}2(μ-Cl)] [{CuCl2}]. Single crystals of [CuCl(dpaOMe)][PF6] were obtained from vapour diffusion of pentane into a concentrated solution of complex in dichloromethane at −20 °C, yielding turquoise needles in monomeric form. Fig. 1 provides the XRD structures of [{Cu(dpaOMe)}2(μ-Cl)] [{CuCl2}] and [CuCl(dpaOMe)][PF6]. To date, attempts to obtain XRD-quality single crystals of CuCl(dpaH) have resulted in dimeric and tetrameric units of poor quality and the structure of the CuII analogue of CuCl(dpaH), CuCl2(dpaH), has been previously reported.27

Metal–ligand bond distances for [{Cu(dpaOMe)}2(μ-Cl)] [{CuCl2}] and [CuCl(dpaOMe)][PF6] are provided in Table 1. The

![Fig. 1](https://example.com/fig1.png)
Cu–N

bond distances experience a slight contraction upon metal oxidation, consistent with chelating pyridine arms bound to Cu. The Cu–N

bond distance of >2.4 Å is well above the sum of the covalent radii. Therefore, in the solid-state, there appears to be no bond between the Cu

ion and aniline (dashed bond in Fig. 1a). The bond angle between the pyridines and Cu

is 132° and larger than the 115° previously reported for the pseudo-tetrahedral [Cu

(MeCN)][B(C6F5)4].

The most notable change between the two structures is the contraction of ~0.4 Å of the Cu–N

bond distance upon oxidation. Changes in the metal oxidation state also manifest in a change in the bond angles surrounding the metal site, where the Cu

complex aligns more closely with a square pyramidal geometry with τ

value of 0.18. Notably, the coordination geometry about the Cu centre in CuCl2(dpaH) is intermediate between trigonal bipyramidal and square pyramidal with a τ

value of 0.56. Along with the change in coordination geometry, the Cu

complex also experiences a change in coordination number as the oxygen of the methoxy group is now bound to the Cu centre with a bond distance of 2.292(2) Å; within the sum of the covalent radii of the two atoms. The oxygen of the methoxy group lies above 3 Å from the copper centres in the structure of the Cu

dimer and is therefore classified as unbound.

EPR spectroscopy

Paramagnetic Cu

complexes were further characterized using X-band EPR spectroscopy. Spectra collected at 50 K on frozen solution samples are displayed in Fig. 2. The EPR spectra of [CuCl(dpaOMe)]

exhibit characteristic four-line splitting patterns resulting from the I = 3/2 nuclear spin of Cu. The [CuCl(dpaOMe)][PF6] complex displays an axial spectrum with a g

value of 2.04 and g

value of 2.25 with hyperfine interactions of A(Cu) = 24 and 464 MHz, respectively, as determined from simulations (Table S1†). Unresolved superhyperfine interactions arise from three N nuclei and have A

values spanning 40–50 MHz and A

values spanning 5–11 MHz that were required to accurately simulate the data (Fig. 2). In contrast to [CuCl(dpaOMe)][PF6], the EPR spectrum of CuCl2(dpaH) is rhombic with g values of 2.02, 2.12 and 2.25 and hyperfine coupling to the Cu nucleus displaying A(Cu) = 51, 130 and 437 MHz (Table S2†). Additionally, three N nuclei impart unresolved superhyperfine interactions of A(N) = 58–60, 54–55 and 25–35 MHz. The differences in the EPR spectra between [CuCl(dpaOMe)][PF6] and CuCl2(dpaH) are in-line with their XRD structures. It is well established that Cu

structures with tetragonal geometries display axial spectra with g

> g

> g

, as shown with [CuCl(dpaOMe)][PF6]. Distortion from tetragonal geometry introduces orbital mixing into the paramagnetic orbital and results in the rhombic signal of CuCl2(dpaH) with g

> g

> g

.†

Electrochemical analysis

CVs were collected in solutions containing 1 mM analyte and 100 mM [Bu4N][PF6] as the supporting electrolyte in DMF with a standard three electrode configuration (glassy carbon working electrode, platinum wire counter electrode, and silver wire pseudo-reference electrode, Fig. 3). All potentials are referenced to the [FeCp2]+/0 couple using an internal standard added to the cell following data collection. The black traces in Fig. 3 represent the CVs of Cu

complexes, CuCl2(dpaH). Both complexes exhibit two oxidative events. The first set (E

1) occur at −0.57 V and −0.43 V for R = OMe and R = H, respectively (Table 2). These events are both reversible and exhibit ɪ

/ɪ

1 and ɪ

/ɪ

1.4 and ɪ

/ɪ

1.1 and ɪ

/ɪ

95 mV for R = H (where E

− E

is 84 mV in the sample cell). For both complexes, the second oxidative event occurs at −0.01 V and is quasi-reversible (ɪ

/ɪ

1.5 and ɪ

/ɪ

114 mV for R = OMe, and ɪ

/ɪ

1.4 and ɪ

95 mV for R = H). There also exists a third, irreversible oxidative event for CuCl(dpaOMe) at +0.66 V (not shown) that matches the CV of free ligand (Fig. S1†), while this ligand-centred oxidation is outside the solvent window of DMF for CuCl2(dpaH).

Table 1. Selected bond distances (Å) and τ values from solid-state structures of [[CuCl(dpaOMe)]2[μ-Cl]] and [CuCl(dpaOMe)][PF6]

<table>
<thead>
<tr>
<th>Bond</th>
<th>[CuCl(dpaOMe)]2[μ-Cl]</th>
<th>[CuCl(dpaOMe)][PF6]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu−N1</td>
<td>2.020(3)</td>
<td>1.981(3)</td>
</tr>
<tr>
<td>Cu−N2</td>
<td>2.494(3)</td>
<td>2.431(3)</td>
</tr>
<tr>
<td>Cu−N3</td>
<td>1.970(3)</td>
<td>1.991(3)</td>
</tr>
<tr>
<td>Cu−Cl</td>
<td>2.286(1)</td>
<td>2.268(1)</td>
</tr>
<tr>
<td>Cu−O</td>
<td>-</td>
<td>2.292(2)</td>
</tr>
</tbody>
</table>

† τ ≅ 1/(g

⊥

+ g

∥)

= 0.18.
The CVs of the oxidized Cu$^{II}$ complexes are shown as green traces in Fig. 3. The CV of CuCl$_2$(dpaH) displays electrochemical behaviour that is similar to that of other Cu$^{II}$/I species that undergo structural reorganization during oxidation state changes. It has a large peak-to-peak separation of $E_a - E_c = 440$ mV, with reduction at $-0.49$ V and oxidation at $-0.05$ V. In contrast, the CV of [CuCl(dpaOMe)]$[PF_6]$ exhibits one primary feature, a reversible couple that aligns with $E^\circ_{1}'$ from its Cu$^I$ analogue. The oxidative event at $\sim 0.3$ V is much less intense and only appears at faster scan rates (Fig. S6†).

To probe the nature of redox events observed by CV and to assess the possibility of dimerization in solution, we performed DPV experiments as a function of concentration. Here, the concentration of CuCl(dpaR) was varied and the integrations under each curve analysed (Fig. S7 and Table S3†). At concentrations above 5 mM both complexes displayed clear broadening in the peak at $\sim -0.5$ V ($E^\circ_{p1}$ in Table S3†), and a new peak at $\sim -0.3$ V, suggesting the presence of a new species at elevated concentrations. Peak broadening is observed at concentrations as low as 2 mM, while at 1 mM and below, peaks appear sharp and symmetric. The ratio of integrations from $E^\circ_{p1}$ relative to $E^\circ_{p2}$ (the other feature observed at all concentrations) increases with increasing concentration suggesting that at elevated concentrations, complex equilibria occur involving at least three species: the monomeric conformers and a bis(μ-Cl) dimer, with at least four potentials: one for each monomer and one for each Cu$^I$ ion in the dimeric species. The overlap of features arising from these different species obscures the precise calculation of monomer/dimer equilibrium constants. However, these findings allowed us to define the conditions under which the monomeric conformers of interest predominate, namely at or below 1.5 mM.

**Variable temperature NMR spectroscopy**

To assess the solution state dynamics of the CuCl(dpaR) complexes, VT-NMR spectroscopy experiments were performed in d$_2$-dichloromethane (d$_2$-DCM). In the $^1$H-NMR spectra at 298 K shown in Fig. 4, the proton resonances for both the aromatic and aliphatic regions of the dpa$^R$ ligands are broad. These features narrow upon cooling from 298 K to 233 K until they sharpen to indicate a single symmetric species. This behaviour supports that a dynamic process is operative. The peak shape of the methylene resonances were modelled using the complete band shape method for a simple two-site degenerate exchange, over the temperature range of 233–298 K. This analysis (which is provided in the ESI†) allowed the extraction of the activation parameters reported in Table 2. Due to limited

![Fig. 3](image-url)

**Fig. 3** CVs of Cu$^I$ (black) and Cu$^{II}$ (green) complexes with dpa$^H$ (top), and dpa$^{OMe}$ (bottom). Complexes are 1 mM in DMF containing 100 mM [Bu$_4$N][PF$_6$] supporting electrolyte. Data were collected at a glassy carbon working electrode, with a platinum wire counter electrode, and a silver wire pseudo-reference electrode using a scan rate of 100 mV s$^{-1}$. Open circuit potentials are indicated by arrowhead.

![Fig. 4](image-url)

**Fig. 4** Partial $^1$H-NMR spectra (500 MHz) of CuCl(dpa$^{OMe}$) in d$_2$-DCM showing the aromatic proton resonances over the temperature range of 233–298 K.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Delta G^\circ$ (298 K) kcal mol$^{-1}$</th>
<th>$\Delta H^\circ$ kcal mol$^{-1}$</th>
<th>$\Delta S^\circ$ cal mol$^{-1}$ K$^{-1}$</th>
<th>$E^\circ_{p1}$ $^b$ V vs. Fe($^{3+}$/0)</th>
<th>$E^\circ_{p2}$ $^b$</th>
<th>$K_{eq}^{c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCl(dpa$^{OMe}$)</td>
<td>14.1</td>
<td>13.2</td>
<td>-3.0</td>
<td>-0.57</td>
<td>-0.01</td>
<td>1.0</td>
</tr>
<tr>
<td>CuCl(dpa$^H$)</td>
<td>13.0</td>
<td>7.4</td>
<td>-20.0</td>
<td>-0.43</td>
<td>-0.01</td>
<td>1.2</td>
</tr>
</tbody>
</table>

$^a$ Values determined experimentally by VT-NMR spectroscopy. $^b$ Values determined experimentally by CV at 298 K. $^c$ Values determined experimentally by DPV at concentrations ≤1.5 mM at 298 K.
solubility and limited availability of non-coordinating deuterated solvents, investigating higher temperatures to observe exchange above the coalescence point was not possible.

Discussion

With a d^{10} electron configuration, ligand field theory predicts, and experimental evidence supports that Cu_{I} complexes can be conformationally flexible and adopt multiple coordination geometries. Ronbacher et al. examined Cu complexes with flexible macrocyclic polythiaether ligands electrochemically. With increasing temperature, he observed two sets of reversible redox events and established a square scheme ascribing these events to two conformers. Analogously, and bolstered by the data presented here, we propose that the CuCl(dpa^8) complexes in the Cu_{I} state exist in an equilibrium of two conformers at room temperature (and at ≤1.5 mM). Notably, conformational rearrangement in Cu(dpa) has been previously proposed to give rise to an additional anodic peak at −0.05 V vs. [FeCp]],^{39} and the observation was not further explored. Scheme 2 shows a possible model for the structural interconversions of the monomeric Cu_{I} and Cu_{II} complexes reported here. In this model, we ascribe the two redox events observed to oxidation of Cu_{I} in two geometries (E_{°I} and E_{°II} in Scheme 2 and Table 2). Simulations of our CV data were performed using a double-step (C_{E}) approximation as the reference mechanism and are shown in Fig. S8 and Tables S4 and S5. These simulations support the proposed equilibria; when both conformational isomers are present, they can interconvert. Similar analyses have been performed to describe the dynamic behavior observed electrochemically for trans-1,2-dibromocyclohexane, where two distinct redox events report on the two conformational isomers (with axial and equatorial bromide substituents, respectively).^{37,38}

The first reductive wave observed for [Cu^{II}Cl(dpaOMe)]^{+} overlaps with E_{°I} for the corresponding Cu_{I} complex, suggesting that this feature arises from a tetragonal conformer (Scheme 2). The differences in E_{°I} for CuCl(dpaOMe) and CuCl (dpa)^{4+} indicate that the electron donating ability of the ortho-substituent on aniline directly affects the Cu redox potential. Interestingly, E_{°II} does not follow the same trend. In the model depicted in Scheme 2, E_{°II} is assigned to a tetrahedral state and its unchanged value is ascribed to decreased orbital overlap

![Scheme 2 Model for conformational equilibria observed.](Image)

relative to the planar species. These assignments are consistent with ligand field arguments in which the highest occupied orbital in a tetragonal ligand field is higher in energy than those in a tetrahedral ligand field. The model shown in Scheme 2 is consistent with our data, however, other models are possible. For example, equilibria invoking a trigonal planar coordination geometry, in which the Cu–N_{aniline} bond dissociates can also be envisioned.

The CVs of the Cu_{II} complexes provided in Fig. 2 are revealing. [CuCl(dpaOMe)][PF_{6}] displays one reversible redox event at −0.57 V at all scan rates, while the second event at −0.01 V only becomes apparent at faster scan rates. The solid-state data on this complex demonstrates the importance of the judicious choice of the –OMe substituent to bind to the Cu_{II} ion. This substituent satisfies the unique coordination properties of Cu_{II} relative to Cu_{I} and as such, locks it in place. This hemilabile chelating group enables a single, reversible redox event while its absence results in two peak potentials split by nearly 500 mV. At increased scan rates, the electrochemical process is faster than the conformational change in [CuCl(dpaOMe)][PF_{6}], and the second event at E_{°II} is again detected. In contrast to these observations, the irreversible, and highly separated redox events observed for the CuCl(dpaH) complex are reminiscent of other flexible Cu systems that undergo a structural rearrangement with a change in oxidation state.^{7,33,34,41–43} The reductive event measured at −0.49 V is attributed to the Cu_{I} reduction, where the Cu_{II} ion exists in its energetically favourable coordination geometry. Following reduction, the resultant Cu_{I} complex is then oxidized at −0.05 V. Here, the loss of a Cl\(_{-}\) ligand will undoubtedly contribute to the electrochemical irreversibility observed in this system.

Despite the dimeric coordination complex [{[CuCl(dpaOMe)]}_{2}[μ-Cl]}_{2}[CuCl\(_{3}\)] observed in the solid state, the CuCl(dpa^8) complexes appear to participate in dynamic processes in solution, which at low (<1.5 mM) concentrations, do not involve dimerization (Fig. S7 and Table S3†). Accordingly, K_{eq} in Scheme 2 can be calculated from our DPV integrations for experiments performed at low (<1.5 mM) concentrations. These integrations report directly on the relative equilibrium concentrations of the tetrahedral and planar Cu_{I} conformers. The equilibrium constants obtained from taking the ratios of these integrations are reported in Table 2 to be 1.0 and 1.2 for CuCl (dpaOMe) and CuCl(dpaH), respectively. Activation parameters obtained from VT-NMR studies also give insight into the nature of the conformational equilibria depicted in Scheme 2 as K_{eq}, ΔG at 298 K for the two complexes are similar (14.1 and 13.0 kcal mol\(^{-1}\)) for R = OMe and H, respectively. However, there is a larger entropic contribution to this value when R = H (Table 2). The presence of the ortho-OMe group likely results in twisting of the aryl group relative to the dipicolylamine chelate, lending rigidity and lowering the entropic barrier to structural interconversion. The differences in enthalpic contributions (Table 2) could have several sources. The Cu–N_{aniline} bond may exhibit hemilability as reported by Sorrell et al.\(^{44}\) Alternatively, enthalpic contributions could arise from breaking intramolecular hydrogen-bond (H-bond)
interactions between the ortho-H atoms on pyridine, and bound Cl− ligands, where the structures of CuCl2(dpa)27 and [CuCl(dpaOMe)][PF6] show intramolecular H-bonds (H⋯Cl = 2.74 and 2.75 Å). Ultimately, ΔG°2 exceeds ΔG°0 (0 and −0.2 kcal mol−1 for R = OMe and H at 298 K, respectively) in both systems, allowing for the existence of two discrete conformational states to persist in solution.

Experimental

General considerations

All manipulations were carried out using standard Schlenk-line and glovebox techniques, unless otherwise noted. Hydrocarbon and ethereal solvents were sparged with nitrogen before being deoxygenated and dried by passage through Q5 and activated alumina columns, respectively. Halogenated solvents were sparged with nitrogen and passed through two activated alumina columns. Commercially available reagents, including CuCl2(H2O)2 (Fisher Scientific), NH4PF6 (Oakwood Chemicals), were reagent grade and used as received. dpaOMe26 dpaH2,30 and CuCl2(dpaH)10 were synthesized from commercially available reagents according to procedures published in literature. CuCl (Mallinckrodt) was stirred in acetic acid, washed with ethanol followed by diethyl ether prior to use. Ferrocene (Fc0) was purified by recrystallization from hexanes and [Bu4N][PF6] (Oakwood Chemicals) was recrystallized thrice from ethanol and dried under vacuum.

Spectroscopic measurements

NMR spectra were collected on a Varian VXR 500 spectrometer in d6-DCM. Chemical shifts are referenced relative to tetramethylsilane (TMS) using the residual proton impurities of the solvent (2.50 ppm, 8.07 ppm and 5.32 ppm). All chemical shifts are reported using the standard δ notation in parts per million. Electronic absorption spectra were recorded on a Carver B500 Bruker Advance III HD NMR spectrometer at ambient temperatures unless specified in dry, degassed d6-DMSO or d6-DCM. VT-NMR spectra were collected on a Varian VXR 500 spectrometer in d6-DCM. X-ray Diffraction (XRD) data for all complexes were collected on single crystals. Perpendicular-mode X-band EPR spectra were collected using a Bruker EMX spectrometer equipped with a ER041XG microwave bridge using the following spectrometer settings: attenuation = 30 dB, microwave power = 0.2 mW, frequency = 9.35 GHz, modulation amplitude = 1.0 G, gain = 30 dB, conversion time = 11.25 ms, time constant = 10.24 ms, sweep width = 2000 G and resolution = 4000 points. The EPR spectra were modelled using EasySpin/Matlab and the natural isotopic abundances of all nuclei.21 Electrospray ionization (ESI) mass spectrometry were performed on a Waters Synapt G2-Si ESI instrument at the UIUC School of Chemical Sciences Mass Spectrometry Laboratory. CHN elemental analysis were performed on an Exeter Analytical CE 440 instrument at the UIUC School of Chemical Sciences Microanalysis Laboratory.

Electrochemical methods

Electrochemical experiments were performed on a Pine WaveDriver 10 potentiostat using a 3.0 mm glassy carbon working electrode, a platinum wire auxiliary electrode, and a silver wire pseudo-reference electrode. Data acquisition was carried out at ambient temperature (20–24 °C) in a nitrogen-filled glovebox for solution samples containing 1.0 mM of analyte and 100 mM of [Bu4N][PF6] supporting electrolyte dissolved in dry, degassed DMF. All potentials were referenced to [CP2Fe][PF6] redox couple by adding ferrocene as an internal standard at the end of each experimental run.46 The experimental CV were simulated using BASi DigiElch 8.0 software using double-step (C,E,) approximation as the reference mechanism. The simulated curves were compared directly with the experimentally obtained voltammograms and the various individual parameters were adjusted until the match between the simulated and experimental curve was optimized.

Crystallographic methods

XRD data for all complexes were collected on single crystals mounted on a glass fiber using Paratone oil. Data was acquired with a Bruker D8 Venture kappa diffractometer equipped with a Photon II CPAD detector. An Iµs microfocus sources provided the Mo Kα radiation (λ = 0.71073 Å) that was monochromated with multilayer mirrors. The collection, cell refinement and integration of intensity data were carried out using APEX2 software. Multi-scan absorption corrections were performed numerically with SADABS.47 Subsequent calculations were carried out using the SHELXL program suite.48 The structures were solved by direct methods and refined on F2 by full-matrix least-squares techniques. Analytical scattering factors for neutral atoms were used throughout the analyses. Hydrogen atoms were generated in calculated positions and refined using a riding model. ORTEP diagrams were generated using ORTEP-3 for Windows.49

Preparation of complexes

Synthesis of [CuCl(dpaOMe)][PF6]. In air, dpaOMe (100 mg, 0.35 mmol) was dissolved in a minimal amount of MeOH (3 mL) in a vial equipped with stir bar and condenser. CuCl2(H2O)2 (70 mg, 0.41 mmol) was dissolved in water (3 mL) and added dropwise to the stirred solution of ligand. This solution was allowed to stir for 4 hours at which point NH4PF6 (170 mg, 1.1 mmol) was added to immediately precipitate the product as a pale blue solid (121 mg, 66%), which was isolated via vacuum filtration. Vapor diffusion with DCM and pentane antisolvent at ~20 °C afforded turquoise crystals that were suitable for X-ray diffraction. UV-vis-NIR (DCM) λmax/nm (ε/M−1 cm−1): 260 nm (12 500), 267 nm (10 400), 281 nm (5600), 700 nm (100). MS (ESI+) m/z: 403.0 ([M]+). Anal. calcd (found) for C133H24Cl2Cu13N6O2·3H2O (%): C, 40.22 (40.43); H, 3.73 (3.50); N, 7.41 (7.29).

Synthesis of CuCl(dpaOMe). In a 20 mL scintillation vial under a nitrogen glovebox atmosphere, dpaOMe (180 mg, 0.63 mmol) was dissolved in MeCN (~3 mL) and was added
dropwise to a stirred suspension of CuCl (69 mg, 0.69 mmol) in MeCN (~3 mL). The dark yellow solution was stirred for 24 hours then filtered through a plug of Celite using a medium porous fritted funnel and washed with MeCN (15 mL). The filtrate volatiles were removed under reduced pressure. The remaining residue was redissolved in a minimal amount of DCM (~2 mL) and then pentane was added to induce precipitation. A light-yellow solid was collected, washed with 10 mL of pentane and dried under reduced pressure to afford 123 mg of product (48% yield). Single crystals of the product, suitable for diffraction, were obtained from vapor diffusion of pentane into a solution of the product in DCM at −36 °C. 1H-NMR (500 MHz, 298 K, d6-dmso) δ/ppm: 8.57 (br, 2H), 7.89–7.86 (t, J = 7.5 Hz, 2H), 7.53–7.51 (d, J = 10 Hz, 2H), 7.42–7.36 (m, 3H), 7.05–6.99 (m, 2H), 6.77–6.74 (t, J = 7.5 Hz, 1H), 4.39 (s, 4H), 3.76 (s, 3H). 13C{1H}-NMR (MHz, 298 K, d6-dmso) δ/ppm: 157.3, 154.2, 149.6, 138.2, 137.6, 125.6, 124.6, 124.2, 123.3, 120.6, 112.7, 58.0, 56.2. UV-vis-NIR (DCM) λmax/ nm (ε/M−1 cm−1): 258 nm (2500), 305 nm (shoulder), 377 (200), MS (ESI+ m/z): 403.05 ([M]+). Anal. calcld (found) for C36H34Cl3Cu3N6 (%): C, 51.01 (50.97); H, 4.04 (3.97); N, 9.91 (9.16).

Synthesis of CuCl(dpaH). In a 20 mL scintillation vial under a nitrogen glovebox atmosphere, dpaH (160 mg, 0.58 mmol) was dissolved in MeCN (~3 mL) and was added dropwise to a stirred suspension of CuCl (60 mg, 61 mmol) in MeCN (~3 mL). The dark yellow solution was stirred for 24 hours then filtered through a plug of Celite using a medium porous fritted funnel and washed with MeCN (15 mL). The filtrate volatiles were removed under reduced pressure. The remaining residue was redissolved in a minimal amount of DCM (~2 mL) and then pentane was added to induce precipitation. A light-yellow solid was collected, washed with 10 mL of pentane and dried under reduced pressure to afford 193 mg of product (89% yield). 1H-NMR (500 MHz, 298 K, d6-dmso) δ/ppm: 8.68 (br, 2H), 7.99 (br, 2H), 7.64 (br, 2H), 7.49 (br, 2H), 7.15 (br, 2H), 6.87 (br, 2H), 6.81 (br, 1H), 4.71 (br, 2H). 13C{1H}-NMR (MHz, 298 K, d6-dmso) δ/ppm: 158.2, 150.1, 149.3, 138.7, 129.5, 124.5, 124.1, 120.5, 116.5, 59.3. UV-vis-NIR (DCM) λmax/ nm (ε/M−1 cm−1): 251 nm (5000), 293 nm (shoulder), 374 (600). MS (ESI+) m/z: 373.04 ([M]+). Anal. calcld (found) for C36H36Cl3Cu3N6 (%): C, 51.01 (50.97); H, 4.04 (3.97); N, 9.91 (9.70).

Conclusions

The interplay between molecular and electronic structure for a series of CuI and CuII complexes with dpaR ligands (R = H and OMe) was explored through various spectroscopic and physical techniques. Analysis of the CuI complexes in the solid state and at concentrations ≤5 mM in solution reveal the formation of oligomers, while at concentrations ≥1.5 mM, the monomeric units predominate and exhibit conformational equilibria. Despite exhibiting Keq values close to unity for these structural interconversions, conformational changes proceed relatively slowly at room temperature due to significant activation barriers of ΔG‡ ≥ 13 kcal mol⁻¹. Through EPR, XRD, and electrochemical studies, we show that the presence of an ortho-OMe substituent on dpaOMe uniquely facilitates reversible redox changes at Cu. CV experiments support that a reversible CuI/II redox couple is assisted by this ortho-locking mechanism. Without the methoxy group, the CuI centre develops a more flexible conformation and, upon reduction to its CuII analogue, requires a large inner sphere reorganization to its more stable geometry. These findings highlight the potential utility of CuII(dpaOMe) for use in catalytic processes that are typically bottlenecked by the slow conformational changes classically associated with the CuI/II redox couple.

Conflicts of interest

There are no conflicts to declare.

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Notes and references