

Reporting a Unique Example of Electronic Bistability Observed in the Form of Valence Tautomerism with a Copper(II) Helicate of a Redox-Active Nitrogenous Heterocyclic Ligand

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S Supporting Information

ABSTRACT: Valence tautomeric compounds involving nondioxolene-type ligands are rare. The triple-helicate copper(II) complex $[\text{Cu}^{\text{II}}_2(\text{L})_3](\text{ClO}_4)_4 \cdot 3\text{CH}_3\text{CN}$ (**1**) containing a redox-active N-heterocyclic ligand (L) has been prepared and displays VT equilibrium in solution, as established by electronic spectroscopy, electron paramagnetic resonance spectroscopy, and cyclic and differential pulse voltammetry carried out at variable temperatures. The process involves intramolecular transfer of an electron from one of the L ligands to a copper(II) center, leading to the oxidation of L to an $\text{L}^{\bullet+}$ radical with concomitant reduction of the Cu^{II} center to Cu^{I} , as shown by the equilibrium $[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}\text{L}^{\bullet+}\text{L}_2]^{4+} \rightleftharpoons [\text{Cu}^{\text{II}}_2\text{L}_3]^{4+}$.

The design and synthesis of molecules that exhibit intramolecular electron-transfer (ET) phenomena prompted by external stimuli are currently under close scrutiny both for applications and for theoretical reasons.¹ The possibility of inducing reversible interconversion between two energetically close-lying electronic states has motivated chemists to use such species for information storage and retrieval and in the development of molecular-sized devices such as switching and display systems.^{2,3} Valence tautomeric (VT) complexes consisting of redox-active metal centers coordinated by one or more non-redox-innocent ligands and capable of shifting electronic charge distribution reversibly under equilibrium conditions are potential candidates for such purposes.^{4,5}

Most of the VT compounds reported to date are based on dioxolene-type ligands.^{3a,4a,6–8} A few examples involving Schiff base,⁹ phenoxy,¹⁰ porphyrin,¹¹ enolate,¹² dithiolate,¹³ and polychlorotriphenylmethyl radical-based ligands¹⁴ have also been reported in recent times. Although several VT complexes containing quinone derivatives as principal ligands and N-heterocyclic derivatives as ancillary ligands are known,^{5b,15,16} we are not aware of any compound in which the N-heterocyclic derivative acts as the principal redox-active ligand.

We recently reported¹⁷ the synthesis of the N-heterocyclic compound 3,3'-dipyridin-2-yl-[1,1']bi[imidazo[1,5-a]pyridinyl]

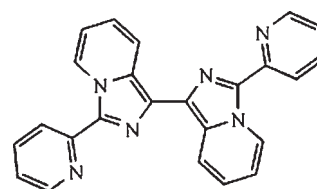


Figure 1. 3,3'-Dipyridin-2-yl-[1,1']bi[imidazo[1,5-a]pyridinyl] (L).

(L) (Figure 1), which contains a pair of biologically relevant imidazo[1,5-a]pyridine moieties.¹⁸ Compound L is redox-active and undergoes two one-electron oxidations (as confirmed by constant-potential coulometric experiments) in *N,N*-dimethylformamide (DMF) at $E_{1/2} = 0.63$ and 0.89 V vs Ag/AgCl [Figure S1 in the Supporting Information (SI)].

Compound L acts as a bis-bidentate ligand during its coordination to a transition-metal ion, causing the central C–C bond (see Figure 1) to experience twisting and bending to the extent required by the stereoelectronic demand of the central metal ion, generating a helical topology. Herein we report the synthesis and characterization of the triple-helicate copper(II) complex $[\text{Cu}^{\text{II}}_2(\text{L})_3](\text{ClO}_4)_4 \cdot 3\text{CH}_3\text{CN}$ (**1**) to provide the first example of a VT compound in which this redox-active chelating N-heterocyclic ligand participates directly in the intramolecular ET process.

Compound **1** was obtained as a brown crystalline product by reacting the ligand L with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in a 3:2 molar ratio in acetonitrile. Details of the synthesis are given in the SI. Compound **1** is fairly soluble in acetonitrile and DMF but practically insoluble in other common organic solvents. Crystals suitable for X-ray diffraction analysis were obtained by diffusing toluene into an acetonitrile solution of **1**. Compound **1** crystallized in the monoclinic space group $C2/c$ ¹⁹ and adopted a triple-stranded helical structure, as shown in Figure 2. A labeled ORTEP view of the molecule is displayed in Figure S2. In this structure, the three bis-bidentate ligands are twisted by 68.59, 77.13, and 68.59° about their central C–C bonds. The presence of a crystallographic inversion center implies the equivalence of the two copper(II)

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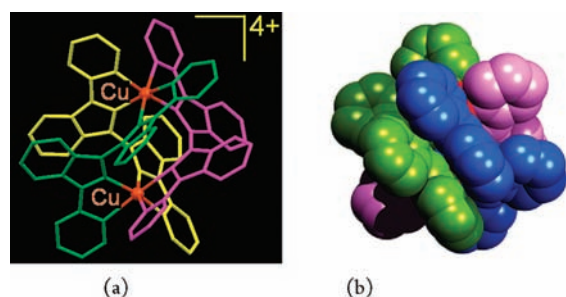


Figure 2. (a) Wire-frame and (b) space-filling representations of the triple-helical structure of the cation in **1**. Each ligand is shown in a different color.

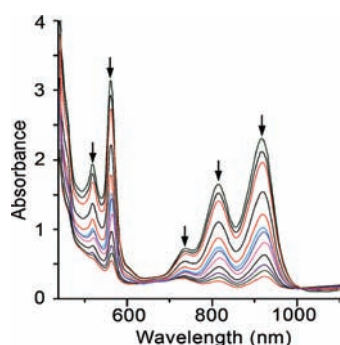


Figure 3. Variable-temperature (298–203 K) electronic absorption spectra of **1** in CH_3CN (1×10^{-3} M). The absorbances of the MLCT bands (marked by arrows) decreased with decreasing temperature.

centers, each of which obtains a distorted octahedral geometry $[\text{CuN}_6]$. The trans angles in the basal plane, $\text{N}(2)\text{--Cu--N}(7)$ [$168.17(9)^\circ$] and $\text{N}(6)\text{--Cu--N}(8)$ [$163.95(8)^\circ$] are somewhat compressed and force the copper atom out of the least-squares basal plane by 0.030 \AA toward the axial donor $\text{N}(1)$. The remaining trans angle, $\text{N}(1)\text{--Cu--N}(4)$ [$173.50(8)^\circ$], is close to linearity. The equatorial Cu(II)--N distances [$2.028(2)\text{--}2.091(2) \text{ \AA}$] are considerably shorter than their axial counterparts [$2.297(2)$ and $2.338(2) \text{ \AA}$], as expected in this case because of the Jahn–Teller effect. The two copper(II) centers, which are 5.070 \AA apart, are magnetically almost noninteracting, as shown by variable-temperature (1.8–300 K) magnetic susceptibility measurements (Figure S3).

The electronic absorption spectrum of **1** is quite interesting, showing multiple absorption bands in the vis/near-IR region that are susceptible to change with changes in solvent or temperature. Thus, in acetonitrile at room temperature, **1** displays a medium-intensity d–d band at 660 nm in the form of a shoulder along with a broad absorption feature at 1150 nm ($\epsilon = 110 \text{ L mol}^{-1} \text{ cm}^{-1}$) (Figure S4). Similar absorption characteristics are known to be exhibited by copper(II) complexes with distorted trigonal structures.²⁰ In addition to these d–d bands, five more intense bands ($\epsilon = 750\text{--}3000 \text{ L mol}^{-1} \text{ cm}^{-1}$) that appear to be of charge-transfer (CT) origin were also observed at $521, 563, 734, 817,$ and 919 nm . Importantly, as shown in Figure 3, the intensities of all five CT bands decreased uniformly as the temperature of the solution was lowered from 298 to 203 K . The lowering of temperature has the visual effect of a color change of the solution from deep-red (298 K) to brown (203 K). It is of interest to note that the absorption profiles pass through an isosbestic point at ca.

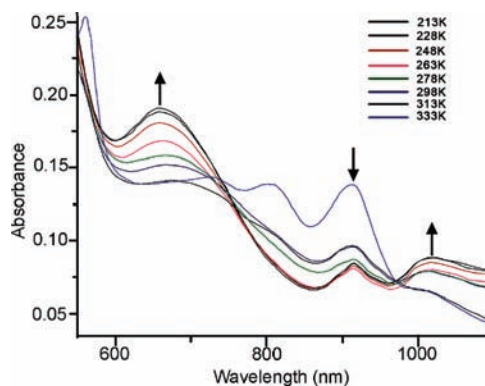
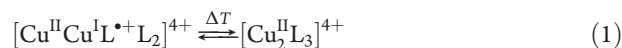


Figure 4. Variable-temperature (333–213 K) electronic absorption spectra of **1** in DMF (1×10^{-3} M). The arrows indicate the trends in absorbance changes with decreasing temperature.

1000 nm , accompanied by a slow gain in absorption intensity beyond this point. Reversal of the thermal effect retraces the absorption features with no displacement of the absorption peaks or the isosbestic point. Clearly, the observed phenomenon indicates the occurrence of a reversible thermally induced equilibrium process. We believe that a VT reaction equilibrium is established in solution,^{4a,5c,21} initiated by intramolecular ET from one of the L ligands to a copper(II) center that leads to the oxidation of L to L^{*+} with concomitant reduction of the Cu^{II} center to Cu^{I} , as shown by eq 1. The Cu^{I} species becomes more prevalent from ambient to higher temperatures. The CT bands thus observed seem to be of $\text{Cu}^{\text{I}} \rightarrow \text{L}^{*+}$ metal-to-ligand charge transfer (MLCT) origin.



The VT equilibrium under consideration is very much solvent-dependent. For example, in DMF, the MLCT transitions are prominent at higher temperatures ($>330 \text{ K}$), while at near- or subambient temperatures, the spectra (Figure 4) are dominated by the ligand-field transitions appearing at 665 and 1020 nm along with a residual CT peak at 920 nm , with ϵ_{max} of $160, 85,$ and $95 \text{ L mol}^{-1} \text{ cm}^{-1}$, respectively, at 298 K . These results indicate that $[\text{Cu}_2^{\text{II}}(\text{L})_3]^{4+}$ is the dominant species in DMF at subambient temperatures, a contention which gained further support from cyclic voltammetry measurements.

Variable-temperature cyclic voltammograms (CVs) of **1** in DMF are shown in Figure 5. The CV at room temperature exhibited three oxidation processes at $E_{1/2} = 0.35 \text{ V}$ (process I), 0.62 V (process II), and 0.86 V (process III) (Figure 5a). The current height for process I diminished rapidly with decreasing temperature and disappeared almost completely at 233 K (Figure 5b). This was further corroborated by differential pulse voltammetry measurements (Figures S5 and S6). Since the free ligand L is electroactive and undergoes two successive one-electron oxidations (Figure S1) at comparable potentials in DMF, we believe that oxidation processes II and III observed for **1** are both ligand-based. The corresponding zinc(II) complex $[\text{Zn}^{\text{II}}_2(\text{L})_3](\text{ClO}_4)_4$ also displayed two one-electron oxidations at 0.64 and 0.91 V under identical experimental conditions. On the other hand, process I is believed to originate from oxidation of the Cu^{I} center generated in solution through valence tautomerism. As may be noted in Figure 5a, at 338 K the $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ couple appears to be

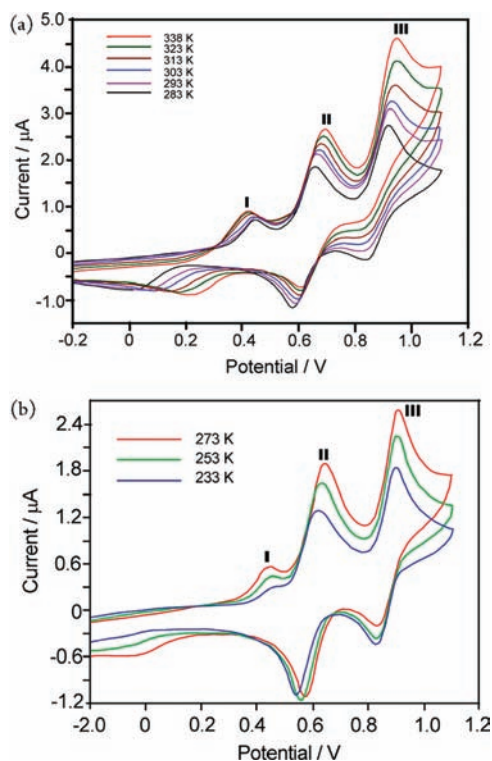


Figure 5. Variable-temperature CVs of **1** in DMF (0.1 M TBAP) at (a) 338–283 K and (b) 273–233 K (glassy carbon electrode; scan rate = 100 mV s⁻¹; potentials vs Ag/AgCl).

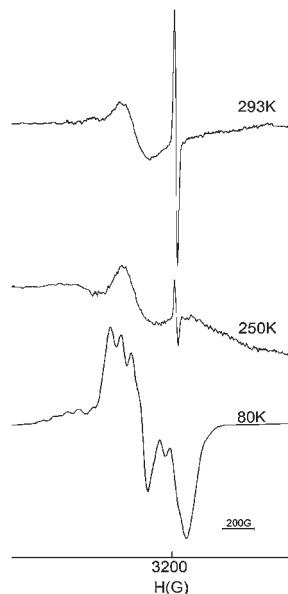


Figure 6. Variable-temperature X-band EPR spectra of **1** in 1:10 (v/v) DMF/acetonitrile.

quasireversible in nature ($\Delta E_p = 200$ mV) with $E_{1/2} = 0.32$ V. The complete disappearance of process I at 233 K (Figure 5b) lends further support to the existence of a VT equilibrium (eq 1) in solution, as indicated by the electronic spectral studies.

Temperature-dependent electron paramagnetic resonance (EPR) spectra often provide diagnostic evidence in favor of the shift in spin from the metal to the ligand center and vice versa in a

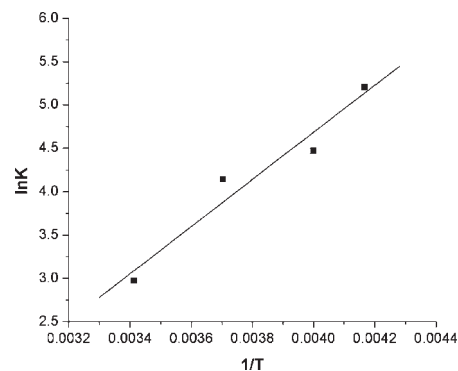


Figure 7. Plot of $\ln K$ vs $1/T$ for compound **1** using data calculated from the EPR spectra.

VT compound.²² EPR spectra recorded for **1** in 1:10 (v/v) DMF/acetonitrile showed an interesting variation with temperature. The spectrum at 293 K contained a sharp, strong signal at $g = 2.003$ together with a broad feature at $g = 2.138$ (Figure 6). While the former signal can be assigned to an $L^{\bullet+}$ radical species generated in solution through valence tautomerism, the latter broad feature seems to originate from a combination of signals arising from the residual dinuclear species $[\text{Cu}^{\text{II}}_2(\text{L})_3](\text{ClO}_4)_4$ present in the equilibrium together with the background spectrum from the remaining Cu^{II} center in $[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}L^{\bullet+}L_2]^{4+}$ that is not involved in ET. As the temperature decreased, the Cu^{II} signal in the spectrum progressively gained intensity at the cost of the radical signal (Figure 6, 250 K) and ultimately showed up as a pure rhombic spectrum (characteristic of Cu^{II}) at 80 K. The low-temperature spectrum also revealed fine structure due to nuclear hyperfine splitting ($^{63,65}\text{Cu}$, $I = 3/2$) of the highest- g component, $g_3 = 2.21$ ($A_3 = 58 \times 10^{-4}$ cm⁻¹), with unresolved features for the remaining g -tensor components ($g_2 = 2.12$ and $g_1 = 1.97$). From the EPR experiments, ratios of the concentrations of $[\text{Cu}^{\text{II}}_2\text{L}_3]^{4+}$ and the radical form $[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}L^{\bullet+}L_2]^{4+}$ were obtained over the temperature range 295–240 K by integration of the areas under the characteristic peaks. A plot of $\ln K$ versus $1/T$ (Figure 7), based on the equation $\ln K = -\Delta H/RT + \Delta S/R$, provides an estimate of the ΔH (-22.6 kJ mol⁻¹) and ΔS (-52 J mol⁻¹ K⁻¹) values for the equilibrium $[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}L^{\bullet+}L_2]^{4+} \rightleftharpoons [\text{Cu}^{\text{II}}_2\text{L}_3]^{4+}$. The results clearly indicate that the formation of $[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}L^{\bullet+}L_2]^{4+}$ species in solution is an entropy-driven process.

In conclusion, we have prepared the new compound $[\text{Cu}_2(\text{L})_3](\text{ClO}_4)_4 \cdot 3\text{CH}_3\text{CN}$ (**1**) with a triple-stranded helical structure, as confirmed by single-crystal X-ray diffraction analysis.¹⁹ In solution, **1** demonstrates electronic bistability^{5b,9a} in the form of valence tautomerism involving $[\text{Cu}^{\text{II}}_2\text{L}_3]^{4+}$ and $[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}L^{\bullet+}L_2]^{4+}$ species in equilibrium (eq 1), as established by variable-temperature electronic spectroscopy, cyclic and differential pulse voltammetry, and EPR studies. To the best of our knowledge, the result reported herein constitutes the first example of a VT compound in which an N-heterocyclic ligand is the electron donor. Incidentally, all the copper complexes showing valence tautomerism reported to date have only dioxolene-type ligands as electron donors.^{6a,b,d,22}

■ ASSOCIATED CONTENT

S Supporting Information. Synthesis and characterization details of **1**, metrical parameters (Table S1), Figures S1–S6, and

crystallographic data for **1** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (19) Crystal data for **1**: refined formula, C₇₈H₅₇Cl₄Cu₂N₂₁O₁₆; M_r = 1813.33; crystal dimensions, 0.15 mm × 0.10 mm × 0.03 mm; monoclinic, C2/c; a = 23.4418(19) Å, b = 12.9048(10) Å, c = 26.735(2) Å, β = 90.821(2)°; V = 8086.8(11) Å³; Z = 4; d_{calcd} = 1.489 g cm⁻³; T = 193(2) K; λ = 0.77490 Å; reflns collected/unique = 38713/10337; R_{int} = 0.0521; R₁ = 0.0558, wR₂ = 0.1681 [I ≥ 2σ(I)]; R₁ = 0.0613, wR₂ = 0.1742 (all data); GOF = 1.029.
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