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Three-Coordinate Copper(I) Amido and Aminyl Radical Complexes

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Electron transfer (ET) through proteins often utilizes copper-containing active sites as efficient one-electron relays. The type-1 active sites of the blue copper proteins are prominent examples.[1−3] It is generally thought that high ET rates through type-1 redox sites occur because the protein environments enforce unusual trigonally distorted coordination spheres to allow for minimal structural reorganization during ET.[1,4] Though large Cu^{II}/Cu^{I} self-exchange ET rate constants (k_S) in the range observed for type-1 sites have been achieved in certain synthetic monocopper systems using geometries distinct from trigonal environments,[5] ET studies have yet to be conducted in a synthetic system featuring isolated, trigonally disposed copper centers. The simplest such systems would contain a trigonal planar geometry.

Here we report the structural characterization of a trigonal planar system featuring formally Cu^{II} and Cu^{I} amido complexes related by a reversible one-electron redox event. We find in this system that ET is extremely rapid and is accompanied by a small degree of structural reorganization during redox. We propose that this structural rigidity in the absence of secondary coordination sphere effects results from significant covalency of the copper−amide linkages. In fact, a Cu^{I}−aminyl radical description of the formally Cu^{II}−amide complex may be most appropriate.

The anionic Cu^{I} amido complex $\{[Ph_2BP^{tBu}_2]Cu(NTol_2)\}\{Li(12\text{-crown-}4)_2\}$ (**1**) ($[Ph_2BP^{tBu}_2] = Ph_2B(CH_2P^tBu_2)_2$, Tol = *p*-tolyl) was synthesized by the reaction between $[Ph_2BP^{tBu}_2]Cu(pyridine)$ and $LiNTol_2$ in the presence of excess 12-crown-4[6] and isolated as a yellow, diamagnetic solid. The cyclic voltammogram of **1** features a fully reversible redox event at −0.882 V versus $FeCp_2^+/FeCp_2$ (Figure S1 in the Supporting Information). Chemical oxidation of **1** with $[FeCp_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ produced paramagnetic $[Ph_2BP^{tBu}_2]Cu(NTol_2)$ (**2**) as red needles with optical bands at 365 nm (ε = 870 M^{-1} cm^{-1}) and 480 nm (ε = 600 M^{-1} cm^{-1}).

Both **1** and **2** were studied by single-crystal X-ray crystallography (Figure 1; also see Figures S2 and S3). Immediately evident upon comparison of the two oxidation states is the minimal degree of structural rearrangement at the Cu centers upon ET (see Figure 1B for an overlay). In both structures, the Cu centers have rigorously planar coordination geometries [$\sum\angle$ = 359.97(14)° for **1** and 359.97(17)° for **2**]. The Cu−P distances, P−Cu−P angles, and P−Cu−N angles are all essentially identical in both **1** and **2**. The most notable structural difference is the Cu−N contraction seen upon oxidation from **1** [2.0019(18) Å] to **2** [1.906(2) Å]. The UV−vis spectra of **2** in benzene and acetonitrile are identical (Figure S5), consistent with **2** being three-coordinate in solution as well as in the solid state. A series of trigonal planar β-diketiminato Cu^{II} complexes synthesized by Tolman and co-workers[7] remain the only other reported examples of three-coordinate, formally Cu^{II} complexes.

Taken together, complexes **1** and **2** represent the only three-coordinate copper system to be isolated and structurally characterized in two distinct redox states.[8] Therefore, it was of interest to study the **2/1** self-exchange ET rate constant k_S. As discussed in the Supporting Information, we determined that k_S in this system is too large to measure accurately by NMR line width analysis, implying a lower limit of $k_S \geq 10^7$ M^{-1} s^{-1}.[9] For comparison, blue copper proteins typically exhibit k_S values on the order of 10^6 M^{-1} s^{-1}.[1]

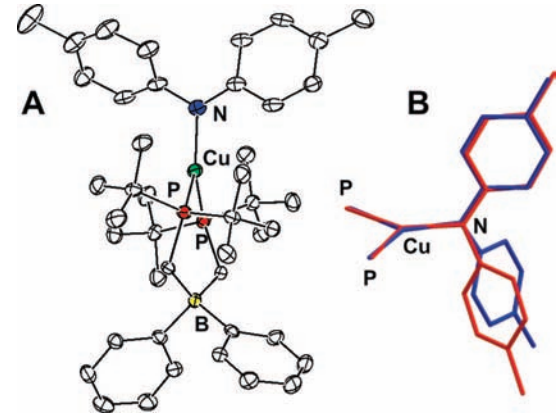

Figure 1. (A) Solid-state structure of **2**. (B) Structural overlay of anion **1** (red) and neutral **2** (blue), with only the phosphorus atoms of $[Ph_2BP^{tBu}_2]$ shown.

Spectroscopic studies of the dinuclear Cu_A ET sites in cytochrome *c* oxidase and nitrous oxide reductase have revealed significant covalency in the $Cu_2(\mu\text{-}SR)_2$ cores, resulting in significant sulfur-centered redox during ET.[10] This covalency likely contributes to the extremely efficient ET rates mediated by Cu_A,[11] and this concept has been discussed in the context of synthetic $Cu_2(\mu\text{-}X)_2$ model complexes.[9,12] It is also likely that such Cu−ligand covalency likewise plays a role in the functional properties of the type-1 active sites in blue copper proteins.[11] We therefore sought to probe the intimate electronic structures of **1** and **2**, in particular questioning whether oxidation of the amido ligand occurs during the interchange of **1** and **2**. In other words, we wondered if the Cu^{I}−aminyl radical form of **2** is an important resonance contributor. A Rh complex synthesized by Grützmacher and co-workers in 2005 was the first reported example of an isolable 1:1 aminyl radical complex of a transition metal,[13] and unlike their aryloxy radical analogues, such complexes remain quite rare.[14] To our knowledge, examples of nonchelated aminyl radical ligands have not been reported to date.

Cu K-edge X-ray absorption spectroscopy (XAS) was used to probe the effective Cu oxidation states in **1** and **2**. The Cu K-edge

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spectra for **1** and **2** in Figure 2A show a high degree of similarity in their respective pre-edge features and rising-edge energy positions, indicating practically identical Cu effective nuclear charges and ligand fields. The first electric-dipole-allowed Cu 1s → 4p transitions at 8982.2 and 8982.5 eV in **1** and **2**, respectively, are well-resolved from the rising-edge features, which is indicative of a trigonal planar coordination geometry.[15] The small shift of 0.3 eV upon oxidation of **1** indicates that **1** and **2** have similar effective oxidation states that are closer to cuprous than cupric when compared to the reference spectra for CuCl and $CuCl_2$ (Figure 2A).

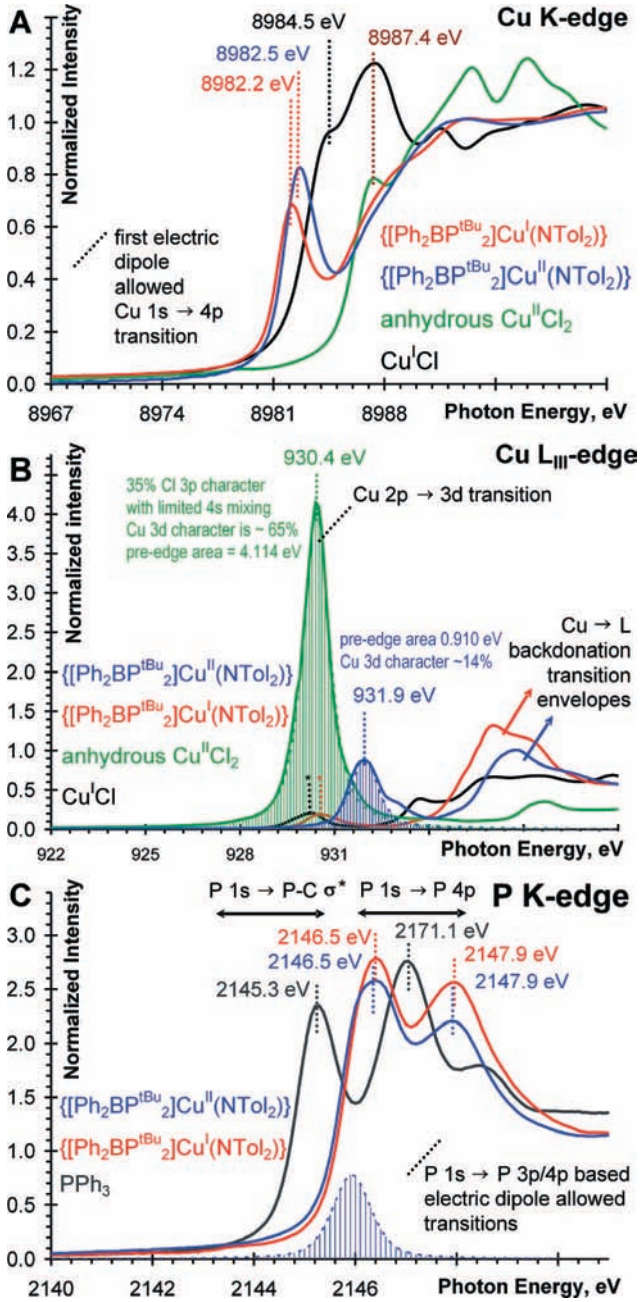

Figure 2. (A) Cu K-edge spectra, (B) Cu L_3-edge spectra, and (C) P K-edge spectra of CuCl (black), **1** (red), $CuCl_2$ (green), **2** (blue), and PPh_3 (gray). * = trace impurity.

Cu L-edge XAS was used to directly probe the Cu 3d character of the frontier orbitals in **1** and **2**. Figure 2B compares a set of features observed at the L_3 edge for complexes **1**, **2**, CuCl, and $CuCl_2$. The intense pre-edge feature at 930.4 eV for $CuCl_2$ is due to the transition of a Cu 2p electron to the unoccupied Cu 3d-based LUMO. The Cu 3d character of the LUMO is determined to be about 65% on the basis of the area under this pre-edge feature.[16] This intense feature disappears in the spectrum of CuCl.[17] The group of features between 936 and 937 eV in the spectrum of **1** arise from Cu → L back-donation. Similar but more intense features have been observed for dinuclear Cu−amidophosphine complexes.[12] Upon oxidation to **2**, a new feature at 931.9 eV appears, consistent with an electron being removed from an orbital with Cu 3d character. The proportion between the area of this feature and that of the pre-edge feature in $CuCl_2$ indicates that the redox-active molecular orbital in **2** has ∼14% 3d character and therefore that the remainder of the electron density has to be ligand-centered.

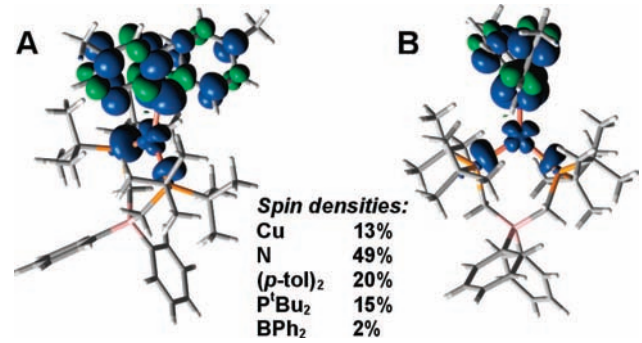

Figure 3. Atomic spin density plots[18] (0.002 isocontours) for $[Ph_2BP^{tBu}{}_2]Cu(NTol_2)$ viewed (A) parallel and (B) perpendicular to the P_2CuN plane.

To dissect the role of the phosphine ligands in the redox process, we collected P K-edge XAS data (Figure 2C). In comparison with the PPh_3 reference spectra, the spectra of **1** and **2** are shifted toward higher energy because of an increase in P effective nuclear charge for the phosphines involved in P → Cu donation. Upon oxidation, an electron hole is created in an orbital that has ∼20% phosphorus character.[16] This result and the 14% Cu 3d character clearly indicate that close to 70% of the redox-active frontier orbital of **1** and **2** must have N, C, and H character. This estimate is in good agreement with spin densities calculated using density functional theory (DFT),[18] which indicate 13% unpaired spin character on Cu, 49% on N, 15% on P, and 20% on C/H of the *p*-tolyl groups (see Figure 3 for spin density plots).

Electron paramagnetic resonance (EPR) spectra of **2** were collected at the S, X, and Q bands (Figure 4A) and are quite unusual compared with those of typical cupric complexes. The S- and X-band spectra are dominated by six lines, each with several shoulders, unlike the typical four-line pattern expected for a single cupric center. Approximate simulations were obtained using the following parameters: $(g_x, g_y, g_z) = (2.008, 2.008, 2.030)$; $(A_x^{Cu}, A_y^{Cu}, A_z^{Cu}) = (34, 34, 170$ MHz); $(A_x^{P}, A_y^{P}, A_z^{P}) = (148, 148, 173$ MHz); and $(A_x^{N}, A_y^{N}, A_z^{N}) = (24, 100, 24$ MHz).[16] Though the simulation parameters are consistent with but not proof of experimental EPR parameters, reasonable fits were obtained using the same parameters at all three bands (Figures S10−S12), lending weight to their assignments. For comparison, one of Tolman's (*β*-diketiminate)$Cu^{II}Cl$ complexes, a more typical three-coordinate Cu^{II} complex, has the parameters $g_{||} = 2.20$, $g_{\perp} = 2.05$, $A_{||}^{Cu} = 398$ MHz, $A_{\perp}^{Cu} = 52$ MHz.[7] An example of a typical nitrogen radical is di-*t*-butylnitroxide (DTBN), which exhibits anisotropic hyperfine tensor components of $A^N = 89.6$, 16.7, and 21.3 MHz.[19] The comparatively small A^{Cu} and large A_y^N values in **2**, as well as the proximity of $g_{average}$ for **2** to the value for the free electron, indicate a significant degree of spin delocalization between the Cu and N centers.

The XAS, DFT, and EPR analyses collectively suggest that **2** is better considered as a Cu^{I}−aminyl radical than a Cu^{II}−amido complex. This unusual electronic structure is also manifested in the chemical reactivity of the system. For instance, the addition of a H-atom donor such as Bu_3SnH, PhSH, or 9,10-dihydroanthracene to a solution of **2** cleanly produced $[Ph_2BP^{tBu}_2]Cu(NHTol_2)$ (**3**). The byproducts $Bu_3Sn-SnBu_3$, PhS−SPh, and anthracene were detected by ^1H NMR spectroscopy and GC−MS, and the presence of an N−H linkage in **3** was confirmed by ^1H NMR [δ(N−H) = 4.93 ppm] and IR spectroscopy [ν(N−H) = 3405 cm^{-1}]. The hydrogen-atom transfer (HAT) reactivity of **2** is to our knowledge unprecedented for the formal Cu^{II} oxidation state. Instead, HAT reactions have been observed at Cu^{III} centers[20] or alternatively at Cu^{II}−aryloxy radicals.[21] The reaction between **2** and either Bu_3SnD or Bu_3SnH provided a kinetic deuterium isotope effect of k_H/k_D = 4.8(6) at room temperature. This value is more consistent with a concerted hydrogen-atom abstraction mechanism than with rate-limiting ET followed by proton transfer, and it is within the range observed for other Cu-containing systems.[21]

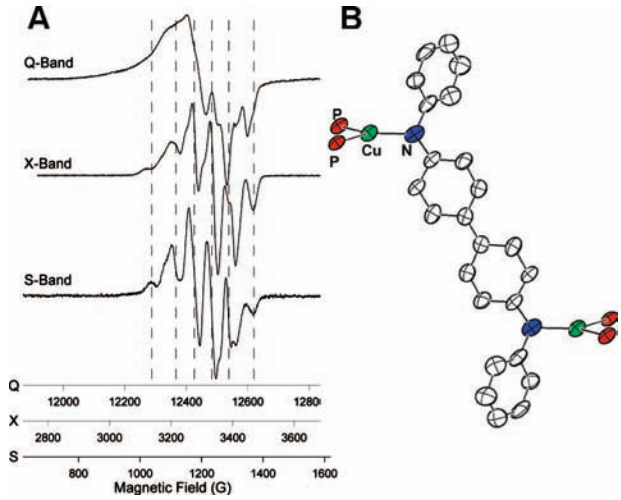

Figure 4. (A) Multifrequency EPR spectra of **2** recorded in a frozen dichloromethane/toluene glass. Microwave frequency (temperature): 35.100 GHz (123 K), 9.188 GHz (77 K), and 3.392 GHz (123 K) for the Q, X, and S bands, respectively. (B) Core structure of **5**, with only the phosphorus atoms of $[Ph_2BP^{tBu}_2]$ shown.

A further indication of radical character delocalized into the aromatic rings in **2** comes from the oxidation chemistry of $\{[Ph_2BP^{tBu}_2]Cu(NPh)_2\}\{Li(12\text{-crown-}4)_2\}$ (**4**), which lacks methyl groups para to the amido nitrogen. The reaction between **4** and $[FeCp_2][PF_6]$ produces a bright-red diamagnetic dicopper product **5** in which two diphenylamido groups have been fused together at the positions para to the N atoms (Figure 4B; also see Figure S4). The identity of **5** was established using a relatively low quality X-ray crystal structure. Nonetheless, the short length of the new C−C bond [1.399(23) Å] in **5** and the planar geometries at these carbons indicate that 2 equiv of H atoms were lost subsequent to C−C coupling. Similar ligand-centered radical coupling has been observed in an oxidized $Cu_2(\mu\text{-}NR_2)_2$ complex[12] and from a putative three-coordinate Cu^{II}−aryloxide intermediate generated by Tolman.[7]

In conclusion, we have isolated and thoroughly characterized a highly covalent, three-coordinate $Cu-NAr_2$ system in two distinct oxidation states, with the unusual oxidized form being best regarded as an aminyl radical ligated to Cu^{I}. Chemical reactivity facilitated by this electronic structure includes HAT, C−C coupling, and efficient ET, the last being reminiscent of that in protein active sites bearing similar Cu coordination geometries.

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Supporting Information Available: Synthetic, spectroscopic, computational, and EPR simulation details; ET and HAT kinetics measurements; and Cu K-, Cu L-, and P K-edge data and fits. This material is available free of charge via the Internet at http://pubs.acs.org.

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