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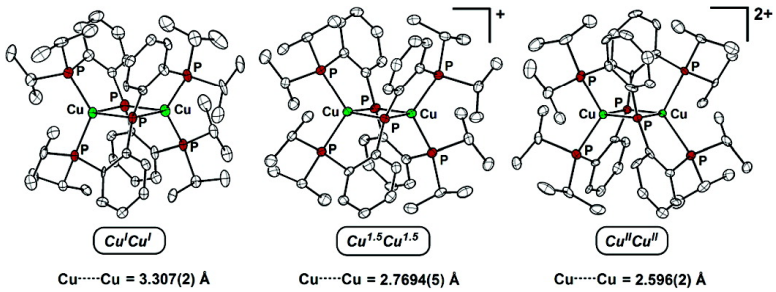

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Structural Snapshots of a Flexible Cu_2P_2 Core that Accommodates the Oxidation States Cu^ICu^I, $Cu^{1.5}Cu^{1.5}$, and $Cu^{II}Cu^{II}$

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Understanding how nature controls electron transfer (ET) rates in copper-containing proteins, such as the "blue copper" protein family, has provided impetus for theoretical, biochemical, and small molecule model studies.[1] It is generally accepted that structural reorganization as a function of ET needs to be minimized if rapid rates are to be achieved,[2] and that this can be difficult to accomplish in synthetic copper systems due to ligand rearrangement, loss, and exchange processes.[3] Recently, we described an amido-bridged Cu_2N_2 system, $\{(SNS)Cu\}_2$ (**1**) ($[SNS]^-$ = bis(2-*tert*-butylsulfanylphenyl)amide),[4] that shares the diamond core structural motif of the Cu_A site[5] and reversibly accommodates rapid ET via low overall structural reorganization.[6] Because the copper centers in **1** possess geometries intermediate between tetrahedral and square planar (coined *pseudotetrahedral* herein), we thought ligand modification might provide reversible access to a third, formally $Cu^{II}Cu^{II}$ species. Furthermore, we have described a highly luminescent Cu_2N_2 system, $\{(PNP)Cu\}_2$ (**2**) ($[PNP]^-$ = bis(2-di-*iso*-butylphosphinophenyl)amide), that mediated two fully reversible redox events according to CV data.[7,8] We thus sought to replace the amide bridging ligands in **2** with more electron-releasing phosphides to further stabilize the doubly oxidized species and to afford us the possibility of isolating and structurally analyzing the system across the oxidation states Cu^ICu^I, $Cu^{1.5}Cu^{1.5}$, and $Cu^{II}Cu^{II}$.

Here we describe the characterization of a phosphido-bridged dicopper system, $\{(PPP)Cu\}_2$ (**3**) ($[PPP]^-$ = bis(2-di-*iso*-propylphosphinophenyl)phosphide), in which each Cu center maintains a highly distorted tetrahedral geometry across these three oxidation states. While the overall topology of each structure is very similar to those Cu_2N_2 systems we have described previously, the Cu_2P_2 system displays remarkable flexibility at the phosphide hinge to allow for dramatic changes in both the Cu···Cu distance and the Cu−P_μ−Cu angle as a function of oxidation state. Dicopper systems that can reversibly access three discrete oxidation states were essentially unknown prior to this study. Indeed, a complete set of structural data for any such transition metal system is rare. Most relevant to the current study is an aryloxide-bridged Fe_2O_2 system that was structurally characterized in the oxidation states $Fe^{II}Fe^{II}$, $Fe^{II}Fe^{III}$, $Fe^{III}Fe^{III}$.[9] The structural analyses of systems supported by redox-active ligands across three oxidation states have also been described.[10]

To prepare the dicopper system of interest to us (Scheme 1), a chlorophosphine precursor of (PPP)H was synthesized by *ortho*-lithiation of 2-di-*iso*-propylphosphinophenyl bromide with *n*-butyllithium, followed by addition of 0.5 equiv of PCl_3. Subsequent reduction of the resulting diarylchlorophosphine by $LiAlH_4$ gave (PPP)H as a colorless oil. The reaction of (PPP)H with mesitylcopper(I) gave diamagnetic red−orange **3** (^{31}P NMR (ppm): 34.0 (br, 4P), −21.0 (br, 2P)) with concomitant formation of mesitylene. XRD analysis of suitable crystals of **3** confirmed its dimeric diamond-core structure (Figure 1). The most striking difference between the structure of **3** and previously characterized Cu_2N_2 systems[4,7] is its much longer Cu···Cu distance (3.307(2) Å for **3** vs 2.5989(3) Å for **1** and 2.6245(8) Å for **2**) resulting from the larger phosphide bridging groups. The Cu−X−Cu angles are likewise expanded (Cu−P_μ−Cu (avg) = 90.63° for **3** vs Cu−N−Cu (avg) = 75.72° for **1** and 74.07° for **2**).

Scheme 1

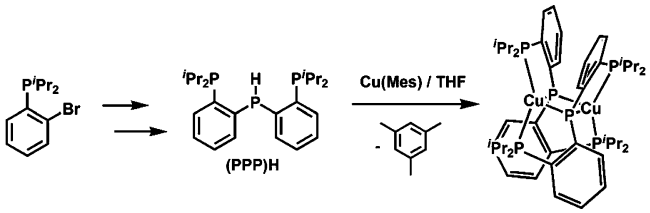
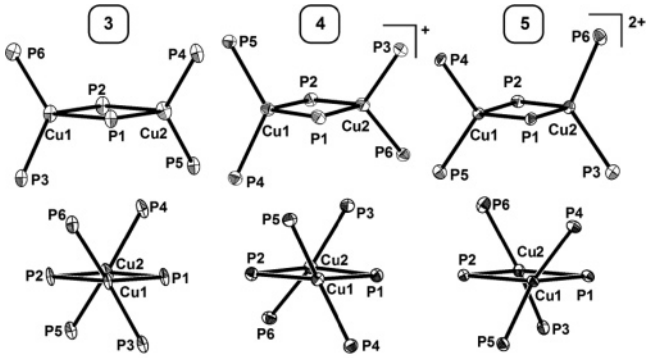


Figure 2a compares the cyclic voltammetry of **3** and its Cu_2N_2 relative **2**. Two fully reversible redox events are observed for each system. There is a large cathodic shift of approximately 600 mV for each redox couple of the phosphide-bridged system **3**. Its



	Cu^ICu^I	$Cu^{1.5}Cu^{1.5}$	$Cu^{II}Cu^{II}$
Cu···Cu	3.307(2) Å	2.7694(5) Å	2.596(2) Å
Cu-P_{bridge}(avg)	2.326 Å	2.2740 Å	2.244 Å
Cu-$P_{terminal}$(avg)	2.231 Å	2.2827 Å	2.286 Å
Cu-(μ-P)-Cu (avg)	90.63°	75.02°	70.71°

Figure 1. Pertinent X-ray data for complexes **3**, **4**, and **5**.

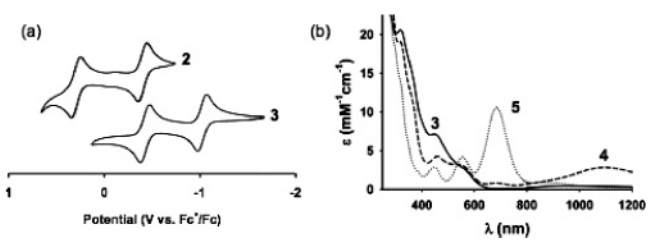


Figure 2. (a) Cyclic voltammograms of **2** and **3** (THF, 0.35 M $[^nBu_4N][PF_6]$, 200 mV/s) vs Fc^+/Fc. (b) Optical spectra for **3** (solid), **4** (dashed), and **5** (dotted).

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$Cu^{1.5}Cu^{1.5}/Cu^{I}Cu^{I}$ couple is assigned at $E^{\circ\prime} = -1.02$ V, and its $Cu^{II}Cu^{II}/Cu^{1.5}Cu^{1.5}$ couple is assigned at $E^{\circ\prime} = -0.42$ V.

Chemical oxidation of **3** with 1 equiv of $[FeCp_2][BPh_4]$ yielded the red−purple paramagnetic species $[\{(PPP)Cu\}_2][BPh_4]$ (**4**). The X-band EPR spectrum of **4** at 10 K showed an isotropic $S = 1/2$ signal. The complex hyperfine splitting pattern features components from the two Cu centers and the phosphide bridges (see Supporting Information). These data, along with a signature low-energy intervalence charge-transfer band at 1095 nm ($\epsilon = 2800$ M^{-1} cm^{-1}, Figure 2b), suggest that **4** be described as a delocalized mixed-valence system.[11]

This electronic structure for **4** was at first surprising to us given the unusually long Cu···Cu distance present in **3**, but XRD analysis revealed that one-electron oxidation of **3** also resulted in a huge Cu−Cu contraction (Cu···Cu = 2.7694(5) Å in **4**, see Figure 1). This 0.538 Å contraction is accompanied by a dramatic compression of the average $Cu-P_{\mu}-Cu$ angle from 90.63° in **3** to 75.02° in **4**. While modest distortions of a similar nature are observed upon one-electron oxidation of **1**,[4] the Cu_2P_2 system is unexpectedly flexible. Despite the structural compression that occurs upon oxidation, there is complete retention of the pseudotetrahedral Cu centers and the dimeric topology.

Two-electron oxidation of **3** with 2 equiv of $[FeCp_2][BAr^F{}_4]$ ($Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$) yielded $[\{(PPP)Cu\}_2][BAr^F{}_4]_2$ (**5**), a deep blue−purple compound with an intense LMCT absorption at 683 nm ($\epsilon = 10\,600$ M^{-1} cm^{-1}, Figure 2b). ^1H, ^{13}C, ^{19}F, and ^{31}P NMR resonances were observed for **5**, consistent with population of an $S = 0$ ground state at room temperature. $^{31}P\{^1H\}$ NMR resonances occur at 266.1 (2P) and 37.3 ppm (4P) in CD_2Cl_2. The extreme downfield chemical shift of the bridging phosphide resonance of **5** is likely the result of the large change in bond angles at the bridging phosphides.[12,13]

Though suitable single crystals of **5** proved elusive, using $AgSbF_6$ instead of $[FeCp_2][BAr^F{}_4]$ afforded the more readily crystallized salt $[\{(PPP)Cu\}_2][SbF_6]_2$. Its molecular structure reveals two SbF_6 anions per dimeric unit, and it is gratifying to observe that the Cu_2P_2 diamond core is maintained along with retention of pseudotetrahedral geometries at each copper center (Figure 1). Close examination of the bond parameters reveals a further contraction of the Cu···Cu distance (2.596(2) Å) and further compression of the average $Cu-P_{\mu}-Cu$ angle (70.71°). Although the onset of a direct bonding interaction between the two 17-electron centers upon oxidation cannot be dismissed, it is plausible that the Cu···Cu contraction is a consequence of an optimized bridging angle that facilitates exchange coupling between the Cu centers.[14] Indeed, the simplest oxidation state description for **5** involves two strongly antiferromagnetically coupled Cu^{II} centers. The prototypical $Cu_2Cl_6^{2-}$ dianion, whose structure is very similar to that of **5**, also features two Cu^{II} centers that are either ferromagnetically or antiferromagnetically coupled depending on the choice of counterion and the resulting perturbations in bond angles.[14c] The structure of **5** is distinctive because small-molecule Cu^{II} ions residing in pseudotetrahedral coordination environments are rare.[15] Moreover, few examples of Cu^{II} phosphine complexes are known,[16] and only one previous example has been structurally characterized.[16a]

A ramification of the elasticity of the Cu_2P_2 core manifests itself in the luminescence behavior of **3**. Excitation into the low-energy absorptions of **3** ($\lambda_{ex} = 500$ nm) afforded an emission spectrum with $\lambda_{max} = 687$ nm. This emission band is much broader and quite red-shifted compared to that of the amide derivative **2**.[7] The reorganizational energy upon excitation, which can be estimated using the width of an emission band,[17] is accordingly higher for **3** (ca. 3250 cm^{-1}) relative to **2** (ca. 2600 cm^{-1}). In addition, while **2** is known to have an extremely high quantum yield ($\phi = 0.67(4)$) and a long excited-state lifetime ($\tau = 10.9(4)$ μs) in THF at 298 K,[7] corresponding emission measurements for **3** reveal significantly lower values ($\phi = 0.013(3)$ and $\tau = 0.6(3)$ μs). It seems most likely that this attenuation in emission is related to a greater degree of structural reorganization upon MLCT in **3** than in **2**.

To summarize, we have shown that synthetic dicopper centers bridged in the diamond-core structural motif become unusually redox active, in this case sampling the oxidation states $Cu^{I}Cu^{I}$, $Cu^{1.5}Cu^{1.5}$, and $Cu^{II}Cu^{II}$. The auxiliary ligand preserves a geometry that is midway between square planar and tetrahedral about each copper center, yet is flexible enough to accommodate pronounced changes in the Cu···Cu distance as a function of ET.

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Supporting Information Available: Experimental and characterization data; crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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