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Delocalized Mixed-Valence Bi- and Trinuclear Complexes with Short Cu–Cu Bonds

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Two mixed-valence copper complexes were synthesized with ligands *N*-(2-pyridylmethyl)acetamide (Hpmac) and *N*,*N*′-(2-methyl-2-pyridylpropan-1,3-diyl)bis(acetamide) ($H_2pp(ac)_2$). Dimer $[Cu_2(pmac)_2]OTf$ and trimer $[Cu_3(pp(ac)_2)_2]\cdot NaOTf$ both contain fully delocalized, mixed-valence $Cu^{1.5}Cu^{1.5}$ moieties.

Multinuclear Cu sites in metalloproteins are of key importance in a wide range of functions, including oxygen transport (hemocyanin),[1] electron transfer (Cu_A from cytochrome *c* oxidase [C*c*O] and nitrous oxide reductase [N_2OR]),[2,3] oxidases and oxygenases (catechol oxidase, ascorbate oxidase, and particulate methane monooxygenase [pMMO], for example),[4,5] and the reduction of nitrous oxide to dinitrogen (Cu_Z from N_2OR).[3] Particularly, germane to the complexes reported herein are the binuclear mixed-valence Cu_A center, the binuclear Cu center in pMMO, and the trinuclear centers of multicopper oxidases. The Cu_A center found in C*c*O and N_2OR was characterized as a dithiolate-bridged, type III,[6] delocalized mixed-valence ($Cu^{1.5}Cu^{1.5}$) Cu center with a close Cu−Cu distance of ∼2.6 Å.[2,7] Synthetic analogues of these mixed-valence Cu centers are limited to a few examples with a variety of ligands including (*N*-thioethyl)daco,[8] μ-1,3-carboxylato ligands XDK and PXDK,[9–11] octaazacryptand,[12,13] and tripodal ureayl ligands.[14] The binuclear Cu center in pMMO has also been implicated as having a mixed-valence oxidation state and a short (2.52−2.65 Å) Cu−Cu distance.[15] Finally, the trinuclear clusters in multicopper oxidases, although displaying larger Cu−Cu distances (3.66−3.90 Å),[5] have been shown to have multiple oxidation states.

We recently reported the synthesis of pyridylmethylamide ligands with different substituent groups on the amide side arm,[16] as well as the synthesis and characterization of a variety novel Zn^{II}, Cu^{II}, and Cu^{I} complexes with these ligands.[17,18] Herein we present two new mixed-valence complexes synthesized with pyridylamide ligands *N*-(2-pyridyl-

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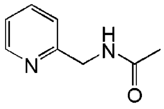
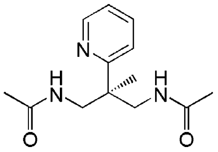
methyl)acetamide (Hpmac) and *N*,*N′*-(2-methyl-2-pyridylpropan-1,3-diyl)bis(acetamide) ($H_2pp(ac)_2$). $[Cu_2(pmac)_2]OTf$ (**1**) is a fully delocalized mixed-valence dimer structurally and spectroscopically similar to a mixed-valence Cu dimer reported by Borovik et al.,[14] while $[Cu_3(pp(ac)_2)_2]{\cdot}NaOTf$ (**2**) is an unprecedented mixed-valence $Cu^{1.5}Cu^{1.5}Cu^{I}$ trimer.



Hpmac



$H_2pp(ac)_2$

The addition of elemental S to a CH_2Cl_2 solution of Hpmac, Et_3N, and $[CuOTf]_2{\cdot}C_6H_6$ affords a dark-green solution, from which **1** was crystallized in 42% yield.[19] Et_3N deprotonates Hpmac to the $pmac^-$ anion, and charge balance in **1** requires the Cu ions be of mixed valence. While we did not isolate any sulfide or disulfide products, the S presumably acts as the oxidizing agent. $H_2pp(ac)_2$, which consists of a pyridyl ring connected to two amide arms, was synthesized by condensing 2-methyl-2-(2-pyridinyl)-1,3-diaminopropane with acetic anhydride.[19] After deprotonation of $H_2pp(ac)_2$ with NaH, the addition of an acetonitrile solution of Cu(OTf)$_2$ led to the initial formation of a dark-green solution that turned purple after about 2 h, from which **2** was isolated in 28% yield.[19] NaH serves the dual role of base and reducing agent, producing deprotonated $pp(ac)_2^{2-}$ anions and reducing half of the Cu^{II} to Cu^{I}. Complex **1** was similarly synthesized with NaH but with poorer yields. For **2**, charge balance requires a mixed-valence oxidation state of $Cu^{II}Cu^{I}_2$.

The electronic absorption spectrum of **1** is dominated by an intense band around 677 nm with weaker bands at 440 and 1060 nm. This spectrum is similar to the spectra of the fully delocalized mixed-valence Cu species reported by Borovik et al.[14] and Barr et al.[12] (Figure 1). In contrast, the electronic absorption spectrum of **2** is blue-shifted with respect to **1**, displaying an intense peak at 525 nm and a near-IR peak at 937 nm. The electronic absorption spectrum of **2** is remarkably similar to the mixed-valence Cu dimers with ligands XDK and PXDK reported by Lippard et al.[9,10] For type III mixed-valence Cu complexes, these intense bands with $\epsilon > 500\ M^{-1}\ cm^{-1}$ were assigned as $\psi \rightarrow \psi^*$ transitions from the $Cu^{1.5}Cu^{1.5}$ manifold.[7,10,20] Given that the Cu−Cu distance is shorter in **1** than in **2** (vide infra), it is surprising that the $\psi \rightarrow \psi^*$ transitions occur at lower energy in **1**.

Another indicator of a mixed-valence Cu system is a seven-line Cu hyperfine splitting pattern resulting from the unpaired electron being delocalized over both $I = {}^3/_2$ Cu nuclei. Both **1** and **2** display seven-line Cu hyperfine splitting at 77 and 296 K (Figures 1 and S1 in the Supporting Information). The *g* and *A* parameters for **1** and **2**, determined by simulations,[21] are quite typical for type III mixed-valence Cu complexes.[10,14] The seven-line pattern in **2**, as opposed to a 10-line pattern expected for an electron delocalized over three Cu nuclei, clearly indicates that the unpaired electron is only delocalized over two Cu nuclei.

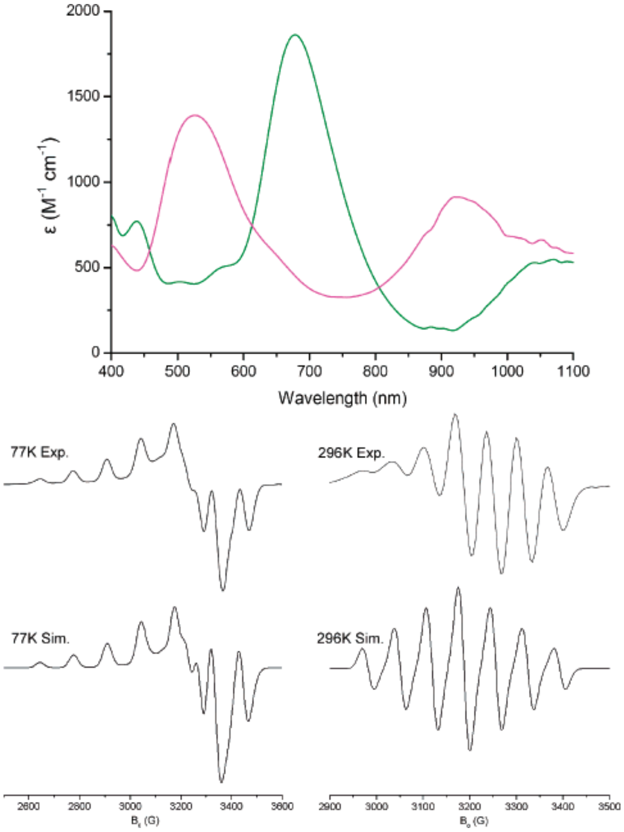


Figure 1. Electronic absorption spectra (top) of **1** in CH_2Cl_2 (green) and **2** in CH_3CN (purple). X-band EPR spectra and simulations of **2** (bottom) in a frozen CH_2Cl_2 solution at 77 K (left) and in CH_2Cl_2 at room temperature (right). EPR parameters for **2** at 77 K (9.436 MHz, 6.41 mW, mod. amp. 21 G): $g_1 = 2.0324$; $g_2 = 2.0816$; $g_3 = 2.2163$; $A_1 = 15$ G; $A_2 = 45$ G; $A_3 = 133$ G. EPR parameters for **2** at 296 K (9.432 MHz, 2.00 mW, mod. amp. 6 G): $g_{iso} = 2.1137$; $A_{iso} = 65$ G.

The X-ray crystal structure[22] of **1** reveals that the N atoms from the pyridyl and amidate groups coordinate to one Cu ion while the O atom of the amidate group coordinates to a second Cu via a μ-1,3-(κN:κO)-amidate bridging mode (Figure 2, top), similar to that seen in Borovik et al.'s complexes.[14] Both Cu atoms have identical coordination environments and are square-planar, with the N atom of the amidate group trans to the O atom from the other ligand's amidate group and the N atom from the pyridyl group trans

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(19) See the Supporting Information for synthetic details and characterization.

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(22) X-ray data collection was performed on a Bruker Apex CCD diffractometer with Mo Kα radiation (0.710 73 Å) at 120 K for **2a** and 100 K for **2a** and **2b**. X-ray data for **1**: $C_{17}H_{18}Cu_2F_3N_4O_5S$, $M = 574.49$, monoclinic, space group $C2/c$, $a = 27.741(6)$ Å, $b = 11.365(2)$ Å, $c = 13.468(3)$ Å, $\beta = 102.735(2)°$, $V = 4141.7(14)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.843$ g/cm^3, R1 = 0.0566, wR2 = 0.0820, GOF = 1.030. X-ray data for **2a**: $C_{31}H_{44}Cu_3F_3N_6NaO_8S$, $M = 931.39$, orthorhombic, space group *Pccn*, $a = 22.117(3)$ Å, $b = 15.280(2)$ Å, $c = 21.380(3)$ Å, $V = 7225.3(17)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.712$ g/cm^3, R1 = 0.0284, wR2 = 0.0770, GOF = 1.005. X-ray data for **2b**: $C_{31}H_{44.97}Cu_3F_3N_6NaO_9S$, $M = 948.37$, monoclinic, space group $P2_1/n$, $a = 12.633(3)$ Å, $b = 19.231(5)$ Å, $c = 15.626(5)$ Å, $\beta = 93.685(9)°$, $V = 3788.4(18)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.663$ g/cm^3, R1 = 0.0567, wR2 = 0.1140, GOF = 1.002.

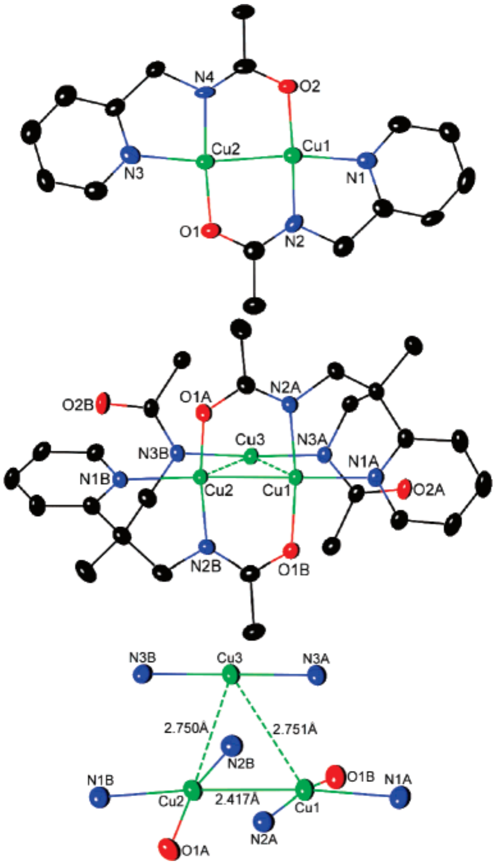

Figure 2. X-ray crystal structure of the cationic portion of **1** (top) with H atoms removed for clarity and thermal ellipsoids at the 50% probability level. X-ray crystal structure of **2a** (middle) with NaOTf, Et_2O, and all H atoms removed for clarity and thermal ellipsoids at the 50% probability level. Central coordination sphere of **2a** (bottom) with only Cu and coordinated ligand atoms shown. Selected bond distances (Å) and angles (deg) for **1**: Cu1−Cu2, 2.3756(9); Cu1−N1, 2.031(4); Cu1−N2, 1.886(3); Cu1−O2, 1.872(3); Cu2−N3, 2.012(4); Cu2−N4, 1.853(4); Cu2−O1, 1.884(3); N1−Cu1−Cu2, 170.47(11); N2−Cu1−O2, 174.74(14); N3−Cu2−Cu1, 171.78(11); N4−Cu−O1, 176.01(16). Selected bond distances (Å) and angles (deg) for **2a**: Cu1−Cu2, 2.4168(5); Cu1−Cu3, 2.7506(4); Cu2−Cu3, 2.7503(4); Cu1−N1A, 2.0593(17); Cu1−N2A, 1.8969(16); Cu1−O1B, 1.8925(14); Cu3−N3A, 1.8752(17); O1B−Cu1−N2A, 166.64(7); N1A−Cu1−Cu2, 175.40(5); N1A−Cu1−Cu3, 120.52(4); N3B−Cu3−N3A, 176.53(7); Cu2−Cu3−Cu1, 52.124(11).

to the second Cu ion. The square-planar geometry is illustrated by the nearly linear N1A−Cu1−Cu2 and N2A−Cu1−O1B bond angles and the average geometry index, τ_4 (a metric for four-coordinate geometry),[18] of 0.08, which is close to 0 for perfect square-planar geometry.

The short Cu−Cu distance of 2.3756(9) Å in **1** suggests the presence of a Cu−Cu bond. This Cu−Cu distance is shorter than those of most reported $Cu^{1.5}Cu^{1.5}$ complexes, which vary from 2.39 to 2.73 Å,[9−11,13,14] but slightly longer than the shortest reported Cu−Cu distance of 2.364(2) Å, reported for a Cu_2 species with a cryptate ligand.[12] The entire cation in **1** is planar, with a mean deviation of all non-H atoms from the least-squares plane of only 0.0453 Å. The packing structure of **1** (Figure S2 in the Supporting Information) shows that the Cu dimers are coplanar, with an interplanar spacing of about 3.35 Å, which falls in the range of weak van der Waals interactions (∼3.4 Å).

Complex **2** crystallizes in two polymorphic forms that differ in their packing structures, depending on crystallization conditions: **2a** was crystallized from CH_3CN and **2b** from tetrahydrofuran.[23] The Cu1 and Cu2 atoms in **2** have the same coordination environment as the Cu atoms in complex **1**, but with a distorted metal site geometry and a slightly longer Cu−Cu distance [2.4168(5) Å for **2a** and 2.4282(9) Å for **2b**; see Figure 2]. Because of the geometric and bonding constraints of $pp(ac)_2^{2-}$, the N_{amide}−Cu bonds for Cu1 and Cu2 twist away from the pyridyl ring plane, resulting in a distorted square-planar geometry for both Cu centers and an average τ_4 value of 0.11. The second amidate side arm of each ligand reaches over the same side of the Cu1−Cu2 unit to coordinate to the third Cu atom in **2**, forming a two-coordinate, nearly linear “handle” above the mixed-valence Cu1−Cu2 “basket”, similar in concept to “picnic basket” porphyrins.[24] The relatively short Cu−Cu distances (average $Cu^{1.5}\cdots Cu^{I}$ distance of 2.758 Å for **2a** and 2.750 Å for **2b**) suggest the possibility of orbital overlap between the mixed-valence moiety and the Cu^{I}. The only other structurally characterized mixed-valence Cu trimer, reported by Setsune et al., has Cu−Cu distances of 2.51−2.60 Å.[25] Ward et al. reported a Cu^{I}_3 trimer with Cu−Cu distances of 2.92−3.61 Å that could be oxidized to a mixed-valence species.[26] Both of these complexes exhibit temperature-dependent delocalization behavior, making them type II mixed-valence species.

The electron paramagnetic resonance (EPR), electronic absorption, and structural evidence support **2** as a fully delocalized mixed-valence $Cu^{1.5}Cu^{1.5}Cu^{I}$ complex. Electrochemical and computational studies on **1** and **2**, as well as the syntheses, structures, and characterization of related mixed-valence species with related ligands are underway and will be published as a full paper.

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Supporting Information Available: Full syntheses and characterization of $H_2pp(ac)_2$, **1**, and **2**, the EPR spectra and simulations for **1**, and the packing diagrams for **1**, **2a**, and **2b** (PDF); X-ray structural information for **1**, **2a**, and **2b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Polymorph **2a** is comprised of double-stranded chains of Cu trimers linked via the amidate O atoms and Na cations (Figure S3 in the Supporting Information), while **2b** forms 2D sheets of trimers connected via amidate O atoms to NaOTf nodes (Figure S4 in the Supporting Information).

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