of biogenetic considerations.[1-3] The foregoing synthetic route to (+)-**1** is generally highly stereoselective and convergent, affording (+)-**1** in ~21 steps from the known lactolide (+)-**6**.

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Highly Delocalized Cu(I)/Cu(II): A Copper-Copper Bond?

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The need for efficient long-distance electron transfer, for example, in the emerging field of molecular electronics,[1] has refueled interest in the electron transfer process and consequently in mixed-valence compounds.[2] The systematic study of electron transfer requires data over a wide range of internuclear separations[3] as well as from as large as possible a selection of metal cations. Thus although (d^5/d^6) second and third transition series ions such as ruthenium and osmium continue to be well-represented in the mixed-valence literature,[4] scant attention has been paid to the less well-behaved first transition series where the phenomenon not only exists but is of biological importance.[5] In particular, mixed-valence copper model systems are of interest in assisting the characterization of the half-met derivatives of coupled dicopper sites,[6] which are spectroscopically more informative than the fully oxidized or reduced states. A valuable study[7] describes the conversion of class II[8] mixed-valence dicopper molecules from EPR-localized to EPR-delocalized as a function of temperature. However, none of these models exhibits EPR delocalization at temperatures as low (77 K) as does the half-met site, and the investigators note that "it would take a remarkable binucleating ligand to obtain a mixed-valence $Cu^{II}Cu^{I}$ site where the frequency of electron exchange between copper sites remains high at very low temperatures."

By means of template condensations of tris(2-ethylamino)amine (tren) with glyoxal upon a labile group II cation template, we have[9] obtained a macrobicyclic octaaza ligand,[10] L, which although normally mononucleating can accommodate copper ions either singly or in pairs. Transmetalation of $[ML]^{2+}$ (**1**) with an excess of $Cu(MeCN)_4ClO_4$ yields dark brown hexagonal crystals of $Cu_2L(ClO_4)_2$ (**2**); when Cu(II) is used, a finely crystalline blue-green product, $[Cu_2LH]X_4$ (X = ClO_4 (**3**), $CF_3SO_3^-$ (**4**)), is obtained. Rapid titration of an aqueous solution of **3** with 5×10^{-3} M NaOH solution indicates a buffering capacity similar to that of NH_4^+ ($pK_a = 9.3$) and greater than that of $(C_2H_5)_3NH^+$ ($pK_a = 10.6$), although no inflexion point is observed in any of these titrations.

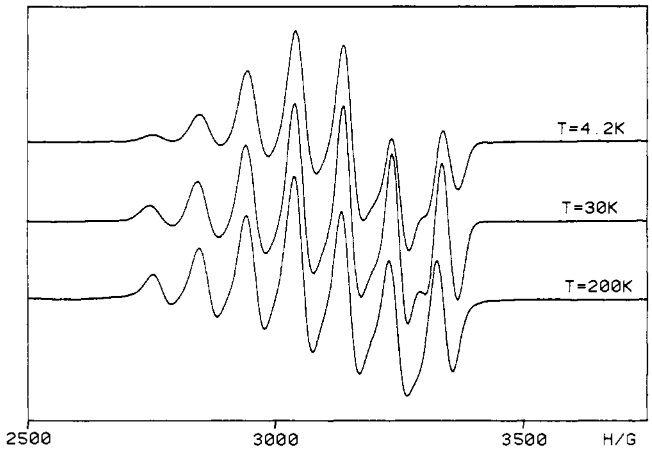

Figure 1. X-band EPR spectra of **3** as DMF glass at T = 200, 30, and 4.2 K (g = 2.137, A = 100 × 10^{-4} cm^{-1}).

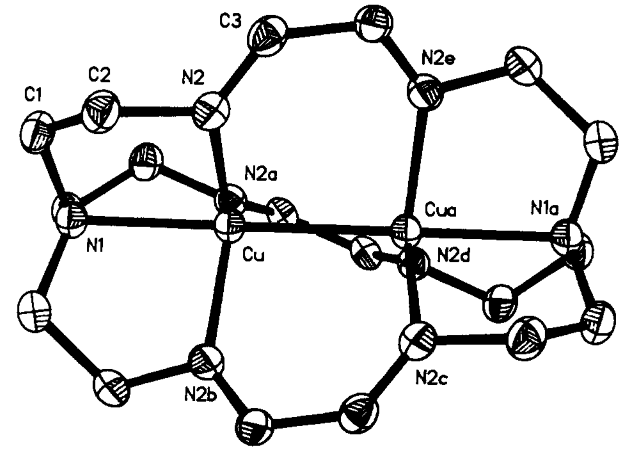

Figure 2. Structure of **2**. For crystallographic data see ref 14.

It is clear that the magnetic and spectroscopic properties of **3** and **4** are not those of dicopper(II). In the temperature range 4–300 K, Curie law behavior is observed (μ = 1.9 BM per formula unit at 300 K) for **3** and **4** and both frozen and freshly made fluid dmf solution EPR spectra take the form of a near-isotropic 7-line signal retained with little change of shape (Figure 1) down to 4 K.[11] Both Nujol mull and solution electronic spectra are dominated by an intense near-infrared absorption (λ = 756 nm, ϵ = 5000 M^{-1} cm^{-1}, $\Delta\nu_{1/2}$ = 2500 cm^{-1}). The decay of the spectra exhibits several isosbestic features and obeys first-order kinetics with half-life ranging from 1–3 min in organic solvents to ~3 h in H_2O, betraying solution instability of this presumably mixed-valence species. The half-life is also pH dependent, decreasing by a factor of 50 for a pH change from 2 to 10.

X-ray crystallographic structure determination of **2** (Figure 2) shows a 2.448-Å separation of Cu^+ ions, on the lower limit of

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(10) $2N(CH_2CH_2NH_2)_3 + 3OCH{\cdot}CHO \xrightarrow{M^{2+}} N(CH_2CH_2N{=}C{-}C{=}N\text{-}CH_2CH_2)_3N$.

(11) Freezing of the DMF solution within 1 s of preparation failed to remove entirely lines that appear as shoulders on this 7-line spectrum.

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Cu–Cu distances so far reported.[12] This occurrence of such a short Cu–Cu distance unsupported by a bridge exemplifies Hoffmann's "weak soft interaction[13]" between d^{10} ions. In this connection we note that the Cu(I) ions are pulled slightly (0.182 Å) out of the trigonal plane toward each other, an observation which is at least consistent with the existence of bonding interaction between Cu(I) ions. While we failed (presumably on account of solution instability) to grow crystals of **3** or **4** of sufficient size for X-ray crystallography, we did succeed in obtaining a crystal of **2** quite heavily (~30% as judged by intensity of the near-IR absorption) doped with a mixed-valence species. This *blue* crystal exhibits a 7-line EPR spectrum in the polycrystalline state, as is typical of magnetically dilute, doped species. X-ray diffraction measurements showed it to be isomorphous[14] with **2**, a finding which rules out any significant change of internuclear distance or coordination geometry in $[Cu_2L]^{3+}$ as vs $[Cu_2L]^{2+}$.

Cyclic voltammetry of **2** in dmf solution shows two almost reversible waves, one at −1160 mV (ΔE = 60 mV) vs Ag/AgCl attributable to ligand- or metal-based reduction and the other at +310 mV (ΔE = 110 mV) vs Ag/AgCl corresponding to Cu(I) oxidation.[15] Quantitative chemical oxidation of **2** with $AgClO_4$ confirms that this is a one-electron process and the electronic spectrum of the oxidized solution is identical with that of **3**. There is no sign of any oxidation wave at potentials more positive than 310 mV, although following application of potentials above +1900 mV, an irreversible cathodic peak appears at −536 mV, demonstrating severe chemical change consequent on this further oxidation.

The intense near-infrared absorption of **3** and **4** is exceptional in several respects. It is solvent independent and unusually narrow, with an intensity greater by an order of magnitude than any so far observed for mixed-valence copper, comparable, indeed, with that observed[16] for the intervalence transfer band of the most highly delocalized mixed-valence ruthenium example, the Creutz–Taube ion. However, for class III average-valence species the IT description of electronic absorption becomes invalid. The near-infrared absorption presumably originates in an allowed transition between ground and excited state orbitals of the $Cu^{1.5}Cu^{1.5}$ assembly; more precise assignment must await the results of our spectroscopic experiments, now in an early stage.

Acknowledgment. We thank Professors N. S. Hush and D. N. Hendrickson for helpful discussions and SERC for support (to V. McKee).

Note Added in Proof. By adjustment of the pH in the preparation of the perchlorate salt, we have succeeded in isolating a mixed-valence complex with the formula $[Cu_2L](ClO_4)_3$. The spectroscopic (EPR and electronic) properties of this complex are nearly identical with those of **3**.

Registry No. 2, 137040-30-3; **3**, 137040-32-5; **4**, 137040-33-6; Cu-$(MeCN)_4ClO_4$, 14057-91-1; Cu, 7440-50-8.

Supplementary Material Available: Tables of atomic coordinates, bond lengths, bond angles, anisotropic displacement coefficients, H-atom coordinates, and isotropic displacement coefficients, and a table of analytical data for **2** and **3** (2 pages); listing of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

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[14] Crystal data for **2**: $[Cu_2(GT)](ClO_4)_2$, $C_{18}H_{30}Cl_2N_8O_8$, brown crystal with dimensions 0.5 × 0.6 × 0.2 mm, rhombohedral, space group $R32$, a = 8.804 (4) Å, c = 30.95 (2) Å, V = 2078 (2) $Å^3$, Z = 3, λ (Mo Kα) = 0.71069 Å, μ = 1.7 mm^{-1}. Intensities of 641 unique reflections ($4 < 2\theta < 55°$) were measured at room temperature on a Siemens R3v diffractometer and were corrected for Lorentz, polarization, and absorption effects. The structure was solved by direct methods (TREF: Sheldrick, G. M. SHELXS 86, A Program for Crystal Structure Solution, University of Göttingen, 1986). Anisotropic thermal parameters were assigned to all non-hydrogen, atoms and hydrogen atoms were inserted at calculated positions except for that on C3, which was located from a difference Fourier map and not refined. Least-squares refinement using SHELX76 (Sheldrick, G. M. SHELX 76, A Program for Crystal Structure Determination, Cambridge University, 1976) and SHELXTL-PC (Sheldrick, G. M., Siemens Analytical X-ray Instruments Inc., Madison, WI 53719, 1990) on 559 reflections with $I > 3\sigma(I)$ converged with R = 0.023, wR = 0.037, and no residual peaks greater than ±0.20 e $Å^{-3}$. A blue-green plate with dimensions 0.5 × 0.4 × 0.06 mm was found to be isomorphous with **2**. Reflection data were collected as for **2**. The final atomic coordinates obtained for **2** were used as a starting point and the refinement on 403 reflections with $I > 3\sigma(I)$ converged with R = 0.040 and wR = 0.049.

[15] This relatively positive potential for Cu(I)/Cu(II) redox reflects the low oxidation state stabilization characteristic of this ligand, originating in the "soft" character of the 6 imino donors, enhanced by the distorted tetrahedral site geometry which favors the Cu(I) rather than the Cu(II) state. Such positive potentials characterize blue Cu proteins such as Pc, Az, where a similar lack of alteration of site geometry on redox change generates fast electron transfer kinetics: Shepard, W. E. B.; Anderson, B. F.; Lewandoski, D. A.; Norris, G. E.; Baker, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 7817–7819. Guss, J. M.; Harrowell, P. R.; Murata, M.; Norris, V. A.; Freeman, H. C. J. *J. Mol. Biol.* **1986**, *192*, 361–387.

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Specific, Multiple-Point Binding of ATP and AMP to a Guanidinium-Functionalized Monolayer

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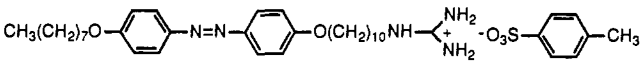
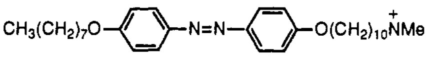
Multiple-point interaction between host and guest systems is a key element for molecular recognition. It amplifies the host-guest binding energy and provides orientational effects between the interacting bodies that result in highly specific recognition.[1] We have detected strong, specific binding of ATP and AMP with the monolayer of guanidinium-functionalized **1**.[2]



1



2

The guanidinium moiety is an important interaction unit for many biological receptors,[3] in particular those for RNA.[4] Its

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[2] The synthesis of **1** will appear in a future publication. Crystalline **1**: golden yellow flakes; mp 165–168 °C. ^1H NMR spectra were obtained on a JEOL JNM-GSX 400 spectrometer (DMSO): δ 7.82 (dd, J = 2.1, 8.8 Hz, 4 H, azobenz), 7.49 (d, J = 7.93 Hz, 2 H, PTS aromatic), 7.12 (d, J = 7.93 Hz, 2 H, PTS aromatic), 7.09 (dd, J = 1.22, 8.3 Hz, 4 H, azobenz), 4.06 (t, J = 6.41 Hz, 4 H, CH_2O), 3.08 (br t, 2 H, $C\mathit{H}_2NH$), 2.29 (s, 3 H, PTS-$C\mathit{H}_3$), 1.74 (m, 4 H, $C\mathit{H}_2CH_2O$), 1.43 and 1.28 (m, 24 H, alkyl tail and spacer), 0.87 (t, J = 7.01 Hz, 3 H, CH_3). IR (KBr): 3178, 2920, 1677, 1631, 1600, 1580, 1246, 1146, 840 cm^{-1}. Anal. Calcd for $C_{38}H_{57}N_5O_5S$: C, 65.58; H, 8.26; N, 10.06. Found: C, 65.50; H, 8.24; N, 10.05.

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