Spectroscopic Studies on the Average-Valence Copper Site $[Cu_2]^{3+}$

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The electron-transfer site "Cu_A" is believed to be common to both nitrous oxide reductase and a number of cytochrome *c* oxidases.[1,2] Mounting spectroscopic and analytical evidence[2–5] that this center contains mixed-valence dicopper has rekindled interest in small-molecule models incorporating $[Cu^{1.5}Cu^{1.5}]$.

This site is not spontaneously formed without steric enforcement but is achievable within a host which constrains the copper bonding orbitals to approach bonding distance (~2.4 Å) in a symmetric coordination environment which is acceptable to both +1 and +2 oxidation states. Trigonal bipyramidal coordination geometry is particularly favorable, in terms of both redox preference considerations and effective overlap of the d_{z^2} orbitals when collinear. Ideal hosts[6,7] for such purposes are azacryptand ligands[8] L^1 and L^2 whose dicopper cryptates, $[Cu_2L^1]^{3+}$ (**1**) and $[Cu_2L^2]^{3+}$ (**2**) are, on the basis of low-temperature EPR spectra,[9] described as *average-* rather than mixed-valence complexes. **1** and **2** have been structurally characterized;[10,11] here we present the X-ray crystal structure of a third variant, $[Cu_2L^3]^{3+}$ (**3**) (synthesized by a Cu(I) template method, followed by Ag^+ oxidation). In addition to the structure, we present spectroscopic data which enable a comparative analysis of the unusual electronic properties of **1**–**3**.

The X-ray crystallographic study of **3**[14] confirms the close approach of the copper nuclei within the cryptate ligand cage (Figure 1) with a Cu–Cu distance of 2.419(1) Å, compared with 2.448 Å in **1**[10] and 2.415(1) Å in **2**.[11] Apart from some variation in the torsion angle (N3–Cu1–Cu2–N4), where **2** has 43.6°, **1** has 17°, and **3** has 56.3°, there is remarkably similar C_3 symmetry in the structures of the three complexes.

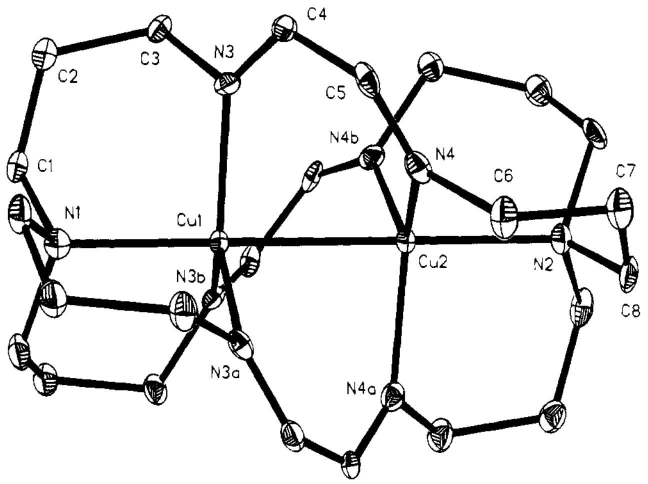

Figure 1. $[Cu_2L^3]^{3+}$ cation (50% ellipsoids). Selected bond distances (Å) and angles (deg): Cu1–N1 = 2.051(11), Cu1–N3 = 2.015(4), Cu2–N2 = 2.059(10), Cu2–N4 = 2.029(4); N1–Cu1–N3 = 92.7(1), N3–Cu1–Cu2 = 87.2(1), N2–Cu2–N4 = 94.7(1), N4–Cu2–Cu1 = 85.3(1).

The similarity of structures **1**–**3** provides the basis for comparative interpretation of the observed electronic spectra. Each cryptate shows an intense ultraviolet absorption, around 300 nm, together with further intense features in the visible/near-IR region. This longer wavelength absorption consists of a band around 600–650 nm, $\epsilon_{max} \sim$ 1500–3500 M^{-1} cm^{-1}, and a more intense band in the region 750–850 nm, $\epsilon_{max} \sim$ 5000 M^{-1} cm^{-1}, the asymmetric profile of which suggests the presence of several components. **1** and **2** also exhibit a broad low-intensity shoulder around 1000 nm, possibly masked by the tail of the 840 nm band of **3**. In MCD, there is remarkable similarity between the spectra of complexes **1** and **2**, with that of **3** being obviously related although additional weak bands between 300 and 700 nm are observed. All MCD bands exhibit temperature dependence, indicating that they arise from a paramagnetic ground state.[17] In the region 600–1100 nm, MCD bands with different resolution and signs are observed for each of the complexes. Those between 600 and 950 nm correspond to the intense electronic absorption bands in Figure 2. Most surprising however is the appearance of an intense positive MCD band between 1000 and 1100 nm, where absorption is weak. A number of less intense transitions are observed between 400 and 600 nm, with the greatest complexity observed for complex **3**. Below 400 nm the highest energy electronic absorption band gives rise to two oppositely signed *C* terms[17] in the MCD spectra of **1** and **2** and a number of unresolved transitions in the MCD spectrum of **3**.

The similarity of the MCD and optical spectra, irrespective of ligand unsaturation, suggests that neither metal-to-ligand charge transfer nor the opposite is involved. Hence we can assign the spectrum to transitions within a manifold of mainly d orbitals delocalized over the Cu_2^{3+} dimer. Preliminary molecular orbital calculations on **1** show that the unpaired

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(8) L^1 is $N(CH_2CH_2N{=}CH{-}CH{=}NCH_2CH_2)_3N$, L^2 is the saturated version $N(CH_2CH_2NH{-}CH_2{-}CH_2{-}NHCH_2CH_2)_3N$, and L^3 has a longer alkyl chain $N(CH_2CH_2CH_2N{=}CH{-}CH{=}NCH_2CH_2CH_2)_3N$.

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(14) Crystal data for **3**: $C_{24}H_{42}Cl_3Cu_2N_8O_{12}$, green-brown dichroic plate, dimensions 0.52 × 0.48 × 0.08 mm, rhombohedral, a = 9.999(1) Å, c = 57.153(4) Å, V = 4948.6(8) $Å^3$, space group $R3c$, Z = 6, $F(000)$ = 2682. The structure was solved by direct methods,[15] and refined on F^2 as a racemic twin using SHELXL-93.[16] Refinement converged with wR2 = 0.0552 (all data) (conventional R1 = 0.0221 for $I > 2\sigma(I)$), GOOF = 0.935, and twin component 0.54(5).

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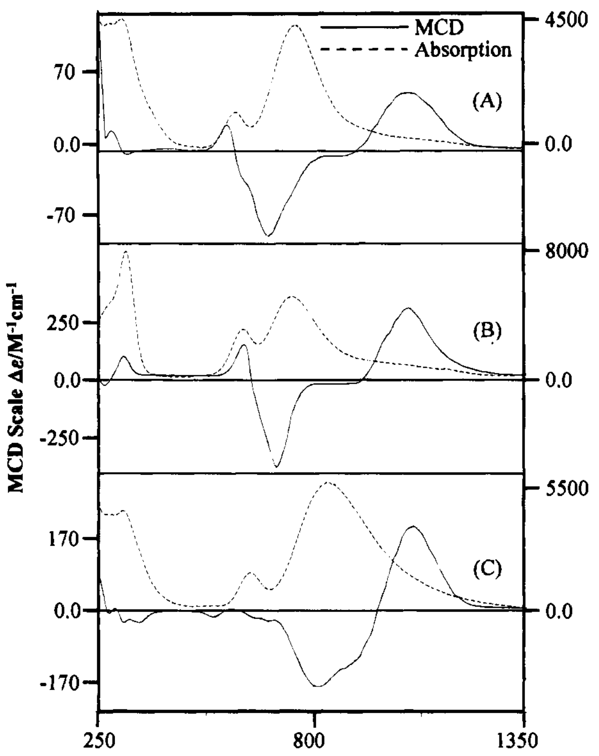

Figure 2. Room-temperature absorption (- - -) and 4.2 K MCD (—) spectra of **1**–**3** (traces A–C, respectively) with 1:1 H_2O:ethanethiol used as inert glassing agent. MCD spectra were measured[13] at 5 T; $\Delta\epsilon$ values are $\epsilon_L - \epsilon_R$, the molar extinction coefficients for left and right circularly polarized light, respectively, based on the spin concentration determined[12] from the EPR spectrum. The spectra are not normalized for magnetic field.

electron of the mixed-valence complex is in the antibonding d_{z^2}-based molecular orbital; under C_3 symmetry, transitions from this orbital will give rise to a number of allowed electric dipole transitions with oppositely signed MCD bands.[18] As a consequence, these transitions are intense. The MCD band at 1050 nm quite clearly exhibits a vibrational progression around 180 cm^{-1}, consistent with RR results indicating a contribution of Cu–Cu orbital overlap in the molecular orbital involved in this transition. Full assignment of the optical and MCD spectra must await the more detailed theoretical analysis in progress.[18]

Vibrational features below 1000 cm^{-1} in the RR[19] spectra of **1**–**3**, excited within the intense near-IR, are all polarized (Figure 3). Excitation profiles in the region 700–900 nm for several of the modes of **2** are shown in Figure 4. Totally symmetric low-frequency modes involving motion of copper nuclei, either Cu–Cu or Cu–N, are expected to be enhanced by excitation within electronic transitions involving orbitals based on those nuclei. The results suggest that at least two distinct vibronic transitions contribute to the absorption intensity over the 700–900 nm region, in agreement with the MCD results. RR bands in the region 240–490 cm^{-1} can be assigned[20] to symmetric ν(Cu–N) stretches, while those corresponding primarily to a Cu–Cu stretch are expected at frequencies below 200 cm^{-1}. In these coupled oscillators, however, no vibrational modes can be expected to be pure, least of all those involving collinear nuclei.

These average-valence systems are unusual in that the cations are directly linked, in contrast to others[21] which involve the intermediacy of a bridging ligand. Despite the apparent simplicity of the interaction, some observations remain unexplained, among them the anomalous intensity of the 1050 nm MCD feature and its extensive vibrational progression. One conclusion is justified however, on the basis of the combined RR and MCD data: the characteristic intense near-IR absorption originates in vibronic transitions associated with a significant degree of motion of both copper nuclei.

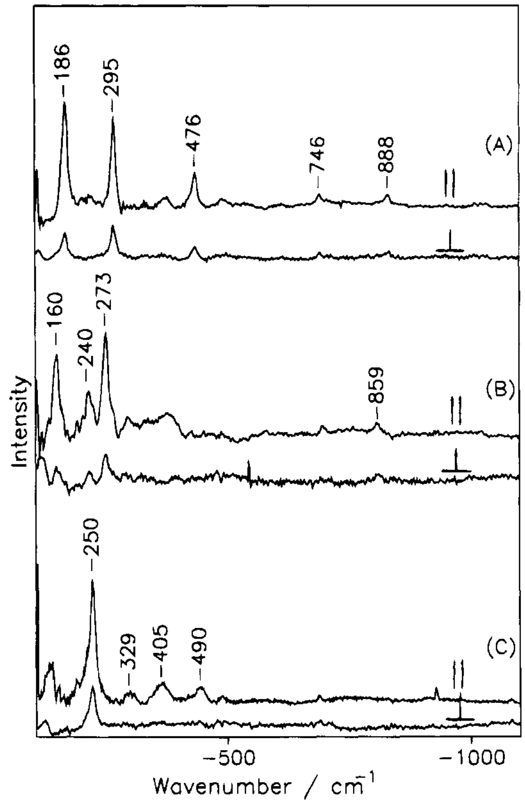

Figure 3. Resonance Raman (RR) spectra of mM aqueous solns of **1**–**3** (traces A–C, respectively) at 840 nm excitation achieved using an Ar^+-pumped Ti-sapphire laser. The mode at 185 cm^{-1} in **3** was enhanced at longer excitation wavelengths.

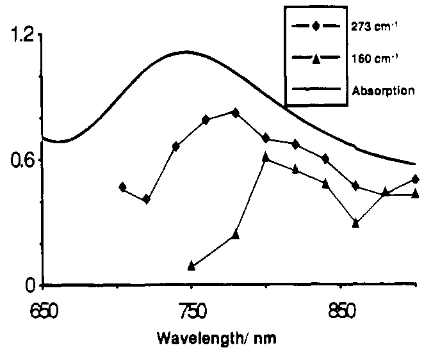

Figure 4. RR excitation profiles for complex **2**. Spectra were recorded at excitation wavelengths in the range 700–900 nm, using the 1050 cm^{-1} band of $NaNO_3$ as internal standard.

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Supplementary Material Available: Tables listing crystal data, atomic coordinates, bond distances and angles, hydrogen atom coordinates and temperature factors (6 pages). Ordering information is given on any current masthead page.

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