Crystallographic, Spectroscopic and Theoretical Studies of an Electron-delocalized Cu(1.5)–Cu(1.5) Complex

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The mixed-valence complex $[Cu_2L]^{3+}$ 1 (L = {$N[CH_2CH_2N(H)CH_2CH_2N(H)CH_2CH_2]_3N$}) has been shown from EPR, visible spectroscopic, and single-crystal X-ray diffraction measurements to possess an unpaired electron delocalized over a short Cu(1.5)–Cu(1.5) bond in both the hydrated nitrate [2.364(2) Å] and acetate [2.415(2) Å] salts: Fenske–Hall MO analysis reveals direct σ-bonding interactions between the copper centres.

As part of an ongoing investigation of the binding properties of the macrobicyclic octaaza cryptand ligand {$N[CH_2CH_2$-$N(H)CH_2CH_2N(H)CH_2CH_2]_3N$} (L),[†,1] we have isolated an

intriguing air-stable mixed-valence complex of L, $[Cu_2L]^{3+}$ 1 which contains a single unpaired electron delocalized over a short Cu–Cu bond. Previous reports concerning the valence, stoichiometry and spectroscopic characteristics of dicopper complexes of this ligand[2] and the analogous Schiff base complex, $[Cu_2\{N(CH_2CH_2N=CHCH=NCH_2CH_2)_3N\}]^{3+}$ 2[3,4] have been complicated by impure and/or unstable materials and the absence of definitive crystallographic characterization. We herein report unambiguous structural

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† The Schiff base precursor of L was synthesized via a non-template modification (50% yield) of the method published by Hunter et al. (ref. 4). The reduced form, L was prepared by reduction of the Schiff base compound with excess LiAlH$_4$ in THF.

characterization of **1** [as the acetate (**a**) and nitrate (**b**) salts]‡ along with preliminary spectroscopic data of the purifed material. This complex exhibits spectroscopic properties which, while analogous to those observed for the normal bridged mixed-valence copper compounds, are fundamentally unique to a directly bonded electron-delocalized system.

The complex **1** is formed from reaction of excess Cu^{II} salts with L in methanol.§ Over the course of several days, the blue colour of the solution became progressively more intense, indicating slow formation of the mixed-valence complex. The $[Cu_2L]^{3+}$ cation of **1b**·$2H_2O$ (Fig. 1) exhibits a Cu–Cu distance of 2.364(1) Å. This distance is much less than is found in dicopper(II) complexes and is even shorter than most Cu^L–Cu^I bonding distances,¶,[5,6] such as is found in the dicopper(I) analogue of **2**.[3] Each Cu atom is in a trigonal bipyramidal environment,[7] with very similar apical and equitorial Cu–N distances of 2.056(5)–2.080(4) Å. The $[Cu_2L]^{3+}$ cation of **1a**·$6H_2O$ (Fig. 2) possesses a slightly elongated ligand structure and an increased Cu–Cu distance of 2.415(1) Å. The observed structural differences between **1a** and **1b** are presumably due to the strong hydrogen-bonding interactions

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‡ *Crystal data* for **1b**·$2H_2O$: $[Cu_2(C_{18}H_{42}N_8)][NO_3]_3$·$2H_2O$, M = 719.7, triclinic, $P\bar{1}$ (no. 2), a = 8.853(2), b = 10.606(2), c = 15.688(3) Å, α = 83.79(2), β = 84.32(2), γ = 88.95(2)°, V = 1457.1(6) Å³, Z = 2, D_c = 1.64 g cm⁻³, $F(000)$ = 754, Mo-Kα radiation, μ = 15.3 mm⁻¹, T = 203 K. Intensity data for 3829 unique reflections (5° < 2θ < 45°) was collected using ω scans on a Siemens R3m/V diffractometer. All non-hydrogen atoms were refined anisotropically, except for C(9) which was refined isotropically. Amine hydrogen atoms were located at physically meaningful positions, and all hydrogen atoms were inserted at idealized positions and treated as fixed-atom contributors in the final stages of refinement. For 2645 reflections with $F > 4\sigma(F)$, refinement converged with R = 0.0409 and wR = 0.0384.

Crystal data for **1a**·$6H_2O$: $[Cu_2(C_{18}H_{42}N_8)][CH_3CO_2]_3$·$6H_2O$, M = 782.9, trigonal, R-3 (no. 148), a = 15.550(2), c = 25.563(5), V = 5353(2) Å³, Z = 6, D_c = 1.46 g cm⁻³, $F(000)$ = 2502, Mo-Kα radiation, μ = 1.24 mm⁻¹, T = 203 K. Intensity data for 2324 unique reflections (5° < 2θ < 55°) was collected using ω scans on a Siemens R3m/V diffractometer. All non-hydrogen atoms were refined anisotropically. Amine hydrogen atoms were located at physically meaningful positions, and all hydrogen atoms were inserted at idealized positions and treated as fixed-atom contributors in the final stages of refinement. For 1690 reflections with $F > 4\sigma(F)$, refinement converged with R = 0.0351 and wR = 0.0471.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ L-$2H_2O$ (0.15 g, 0.37 mmol) was added to a solution of $Cu[CH_3CO_2]_2$ (0.20 g, 1.1 mmol) in 20 cm³ methanol. The pale blue solution slowly became more intensely coloured and was allowed to sit until no further colour change was observed (4 days). Ragunathan and Bharadwaj (ref. 2) followed a similar procedure, but stopped the reaction after 30 min; this relatively short reaction time accounts for their characterization of the bulk material as a dicopper(II) salt, and their reported spectroscopic anomalies were presumably caused by minor amounts of the mixed-valence complex. The methanol was removed under vacuum, and **1a** was extracted into $CHCl_3$. Crystals for X-ray and magnetic susceptibility analyses were recrystallized from ethyl acetate. Magnetic susceptibility measurements of powdered crystalline material show that the complex conforms to Curie–Weiss behaviour (T = 5–350 K, μ = 1.8 μ_B, θ = −8 K). The room temperature solution susceptibility of μ = 1.7 μ_B is as expected for a complex with a single unpaired electron. The nitrate salt, **1b**, was similarly formed from stoichiometric amounts of $Cu(NO_3)_2$ (aq) (6.50 cm³, 0.75 mmol; 0.115 mol dm⁻³) and L-$2H_2O$ (0.15 g, 0.37 mmol) in methanol. Crystals for X-ray analysis were recrystallized from methanol.

¶ Preliminary evidence suggests that the complex discussed could contain a Cu(1.5)–Cu(1.5) bond.

observed between the acetate counterions and the secondary amines of L. In both structures, however, the two copper atoms are pulled towards each other, out of the plane defined by the three equitorial nitrogen atoms (0.143 and 0.118 Å in **1a** and 0.138 and 0.141 Å in **1b**), indicating a net bonding

Fig. 1 $[Cu_2L]^{3+}$ cation of **1b**·$2H_2O$: Cu(1)–Cu(2) 2.364(1), Cu(1)–N(1) 2.068(5), Cu(2)–N(2) 2.065(5), Cu(1)–N(eq) 2.056(5)–2.080(4), Cu(2)–N(eq) 2.065(5)–2.075(5) Å
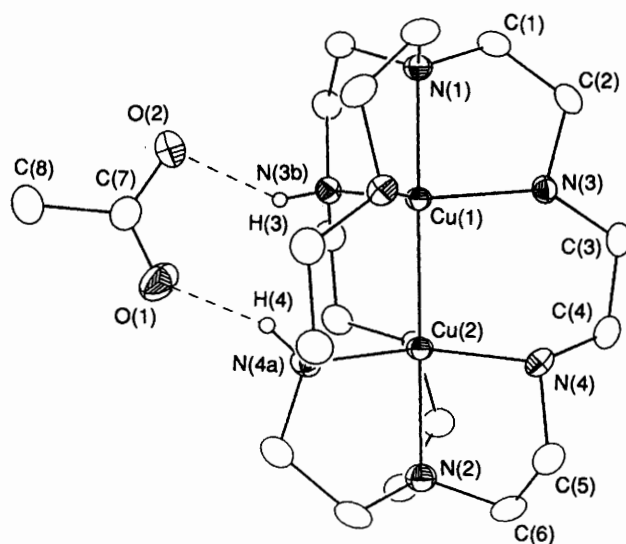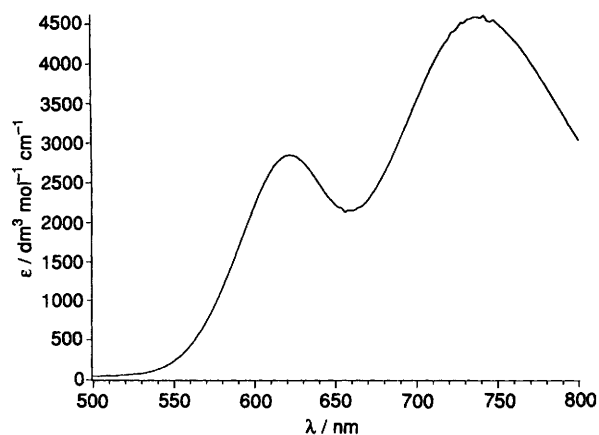

Fig. 2 $[Cu_2L]^{3+}$ cation of **1a**·$6H_2O$: Cu(1)–Cu(2) 2.415(1), Cu(1)–N(1) 2.060(4), Cu(2)–N(2) 2.068(4), Cu(1)–N(3) 2.085(3), Cu(2)–N(4) 2.045(3) Å. The cation sits on a crystallographic threefold axis. The acetate anions (only one independent anion is shown for clarity) are hydrogen-bound to the secondary amines [O(1)–N(4) 2.915, O(2)–N(3) 3.033 Å] and to the H_2O molecules of solvation.

Fig. 3 Visible absorbance spectrum of **1a** (MeOH: $\lambda = 736$ nm, $\varepsilon = 4500$ dm^3 mol^{-1} cm^{-1}; $\lambda = 622$ nm, $\varepsilon = 2900$ dm^3 mol^{-1} cm^{-1})
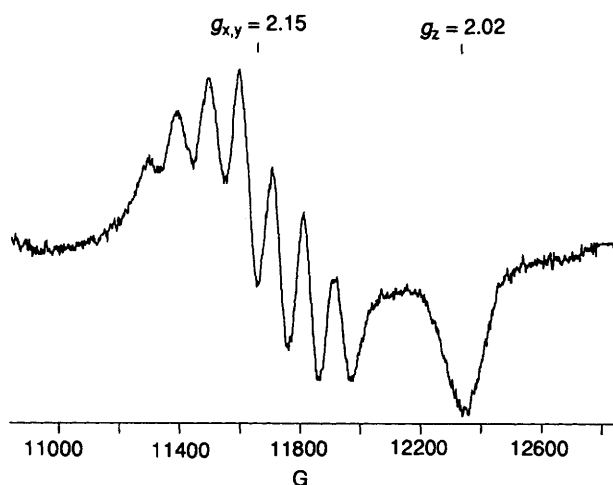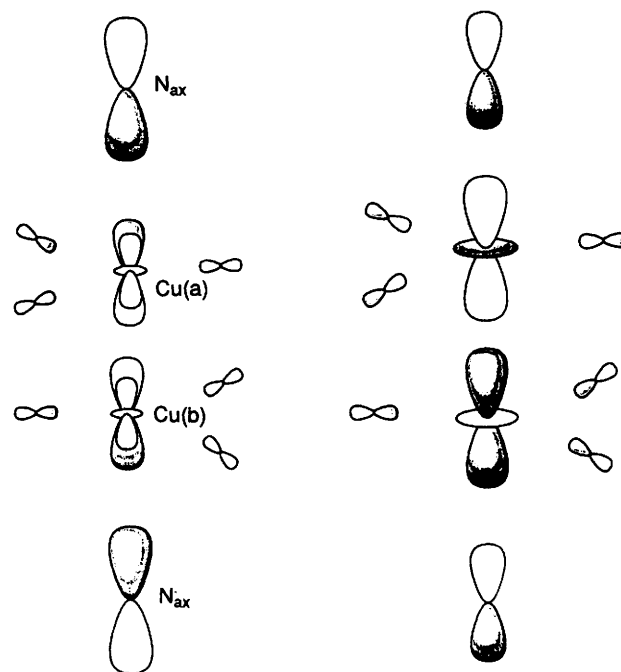

Fig. 4 Q-band EPR spectrum of **1a** in frozen methanol ($g_{x,y} = 2.15$, $A_{x,y} = 104 \times 10^{-4}$ cm^{-1}; $g_z = 2.02$, $A_z \sim 20 \times 10^{-4}$ cm^{-1}). The z vector is collinear with the Cu–Cu bond.

SHOMO –21.19 eV
12%, 11% Cu 4p$_z$
8%, 8% Cu 3d$_z{}^2$
21%, 19% N$_{ax}$ 2p$_z$
11% (total) N$_{eq}$ 2p$_z$
Cu–Cu bonding

HOMO –18.39 eV
21%, 20% Cu 3d$_z{}^2$
14%, 15% N$_{ax}$ 2p$_z$
17% (total) N$_{eq}$ 2p$_z$
Cu–Cu antibonding
Cu–N$_{ax}$ antibonding

interaction between the copper centres. All C–C and C–N bond lengths and their associated angles are as expected for a saturated, neutral amine ligand.

The visible-region electronic spectra of **1** (Fig. 3) exhibits two intense absorbance maxima. These signals are both sharper and more intense than those reported for bridged mixed-valence copper complexes[8] and are comparable to the absorbance reported for **2** ($\lambda = 756$ nm, $\varepsilon = \sim5000$ dm^3 mol^{-1} cm^{-1}), which Harding et al.,[3] attribute to a charge transfer within the Cu(1.5)–Cu(1.5) centre. The less intense signals reported by Ragunathan and Bharadwaj[2] are similar to those observed prior to formation of the mixed-valence system, **1**.

The room temperature solution EPR spectrum of **1** displays an isotropic 7-line signal (9.46 G, CHCl$_3$, 300 K, $g = 2.12$, $A = 75 \times 10^{-4}$ cm^{-1}). This signal becomes asymmetric when frozen due to overlapping $g_\perp$ and $g_\parallel$ signals, but remains essentially unchanged down to 20 K. The similarity of EPR parameters for **1** and **2**, which contain very different coordina-

tion sites (amine vs. imine, respectively), supports the hypothesis that these signals arise from direct electron transfer between the two copper centres. The Q-band EPR spectrum (Fig. 4) clearly shows that the well-resolved seven-line signal cannot be due to overlapping signals from isolated Cu^{II} centres. While the experimental hyperfine couplings are somewhat larger than is observed for mixed-valence complexes where the electron delocalization occurs via a bridging ligand,[7] they are comparable to one-half the hyperfine splitting values reported for Cu(ethylenediamine)$_2{}^{2+}$.[9]

Fenske–Hall[10] MO calculations indicate that the half-filled HOMO consists primarily of Cu d$_{z^2}$–Cu d$_{z^2}$ and Cu d$_{z^2}$–N p$_z$(apical) σ^* combinations. As found with Hoffmann's calculations for Cu^I–Cu^I systems,[11] the 4s and 4p orbitals of the copper atoms serve to stabilize both the bonding and antibonding σ interactions, and the 'removal' of one electron from the σ^* HOMO correlates with the observed shorter Cu–Cu distance in **1** relative to Cu^I systems. The SHOMO consists primarily of strong Cu 4p$_z$–Cu 4p$_z$, Cu d$_{z^2}$–Cu d$_{z^2}$ and Cu 4p$_z$–N p$_z$(apical) σ-bonding interactions.

While L and similar cryptands usually bind a single atom in their cavities, some ligands are capable of encapsulating two or more ions, although usually at non-bonding distances.[12] Presumably, the cavity of L is too small to comfortably accommodate two Cu^{II} ions or a long Cu^{II}–Cu^{II} bond, thus a mixed-valence dimer is favoured in order to minimize charge repulsion. The mechanism and kinetics for the reduction of two Cu^{II} ions to the Cu(1.5)–Cu(1.5) moiety in aqueous and non-aqueous media are the subject of another paper,[13] and full spectroscopic and theoretical analyses are slated for future publication.

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