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EXAFS Evidence That the CuCl$_6^{4-}$ Ion in (3-Chloroanilinium)$_8$(CuCl$_6$)Cl$_4$ Has an Elongated Rather Than Compressed Tetragonal Geometry

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Introduction. Since most Cu(II) complexes have an elongated tetragonal coordination geometry, it is interesting that a recent X-ray crystal structure analysis of (3-Cl-an)$_8$(CuCl$_6$)Cl$_4$ (3-Cl-an = 3-chloroanilinium) showed the centrosymmetric CuCl$_6^{4-}$ ion to have two Cu–Cl bonds significantly shorter (2.277 Å) than the other four (2.606, 2.609 Å).[1] It was concluded that the Jahn–Teller coupling which normally produces the tetragonally elongated geometry is here associated with a ground state in which the unpaired electron is in the d$_{z^2}$ orbital.

The electron paramagnetic resonance (EPR) spectrum of (3-Cl-an)$_8$(CuCl$_6$)Cl$_4$ is, however, inconsistent with this description since it indicates a significant g shift from the free-electron value when the magnetic field is parallel to the short Cu–Cl bonds. To overcome this difficulty, it was proposed that the ground state has a significant admixture of d$_{x^2-y^2}$ due to vibronic coupling. In support of the hypothesis, it was noted that the crystallographic thermal ellipsoids of the four more distant Cl$^-$ ions are elongated along the Cu–Cl bond directions. The resulting model of the complex, including the form of the low-energy mode involved in the vibronic coupling, is shown schematically in Figure 1a.

An alternative hypothesis is that the compound contains tetragonally elongated CuCl$_6^{4-}$ ions but that there is disorder between the directions of the single pair of long Cu–Cl bonds and one of the two pairs of short Cu–Cl bonds throughout the lattice.[2] The apparent positions of the Cl$^-$ ions in the disordered bonds are then described as averages of the actual positions, and the major axes of the thermal ellipsoids lie along the bond directions because they incorporate the effects of the disorder. In this model, the complexes have a ground state with the unpaired electron in a d$_{x^2-y^2}$ orbital; in each complex, the lobes of that orbital point in the directions of the four (two ordered and two disordered) short Cu–Cl bonds. Such a structure is consistent with the observed EPR g values, provided that the two orientations are in dynamic equilibrium and that the exchange rate exceeds the difference between the frequencies of their EPR signals.[2] The dynamic equilibrium between the two orientations is illustrated in Figure 1b.

An unequivocal choice between the alternative interpretations of the X-ray crystallographic data may be made on the basis of the extended X-ray absorption fine structure (EXAFS) of the complex. The EXAFS of the complex in the crystal depends only on the local geometry of each absorber (Cu center). As shown in Figure 2, the tetragonally elongated and compressed geometries should give rise to distinctly different EXAFS patterns. We here report EXAFS measurements on (3-Cl-an)$_8$(CuCl$_6$)Cl$_4$ consistent only with a tetragonally elongated coordination geometry at the Cu atom.

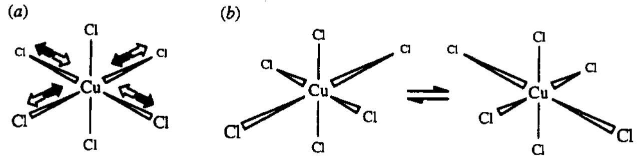

Figure 1. Alternative hypotheses to explain the properties of the CuCl$_6^{4-}$ ion: (a) The complexes are tetragonally compressed, and the geometry is perturbed by vibronic coupling. The relative motions of the Cl$^-$ ions in the low-energy mode are illustrated by means of two types of arrows. (b) The complexes are tetragonally elongated and disordered. The two long Cu–Cl bonds and one pair of short Cu–Cl bonds are in dynamic equilibrium.

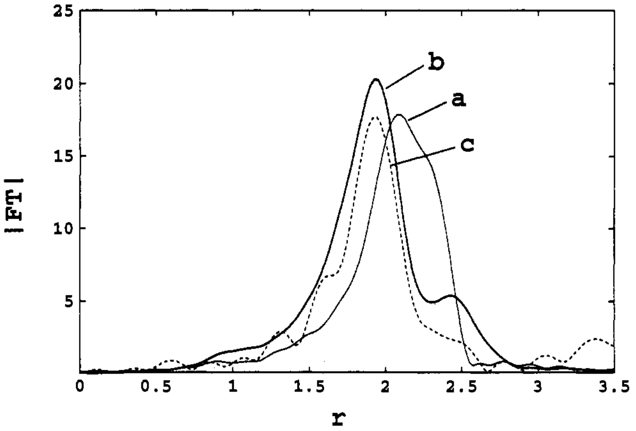

Figure 2. Fourier transforms of (a) EXAFS of CuCl$_6^{4-}$ calculated for the published tetragonally compressed geometry,[1] (b) EXAFS of CuCl$_6^{4-}$ calculated for a tetragonally elongated model with Cu–Cl = 2.277 Å (two bonds), 2.37 Å (two bonds), and 2.85 Å (two bonds), and (c) observed EXAFS of (3-Cl-an)$_8$(CuCl$_6$)Cl$_4$.

Experimental Section. The compound was prepared as yellow-green needles.[1] Elemental analyses were satisfactory (Anal. Calcd for C$_{48}$H$_{56}$Cl$_{18}$N$_8$Cu: C, 39.85; H, 3.90; N, 7.75. Found: C, 39.83; H, 3.79; N, 7.68). The sample was stored in a sealed tube which was covered with aluminum foil as a protection against light. The sample for XAS measurement was diluted with BN and the mixture ground to a fine powder. The mixture was pressed into a pellet (1.0 mm thick) supported in an Al spacer with 63.5-μm Mylar tape windows. X-ray absorption measurements were made at the Stanford Synchrotron Radiation Laboratory on an unfocused wiggler beamline (7–3) using a Si(220) double-crystal monochromator detuned 50% at 10139 eV. The storage ring delivered a current of 68–62 mA at 3 GeV. Three scans of the X-ray absorption spectrum were recorded in transmission mode using standard N$_2$-filled ionization chambers. The sample was maintained at 10 K in an Oxford Instruments CF1208 continuous-flow He cryostat. Energies were calibrated by means of a Cu foil internal standard, the first inflection point on the Cu edge being assigned as 8980.3 eV. The scans were averaged using weights based on the signal/noise ratios. A background correction was applied by fitting a polynomial to the pre-edge region, extrapolating it into the EXAFS region, and subtracting it from the data. A three-region spline was fitted to the EXAFS region and subtracted. The data were normalized to an edge jump of 1.0 and compensated for decreasing absorbance past the edge. The background-subtracted, normalized, and compensated data were converted to k-space, where k is the photoelectron wave vector $[2m_e(E - E_0)/\hbar^2]^{1/2}$ and E_0 is the threshold energy.

The EXAFS analysis was made using nonlinear least-squares

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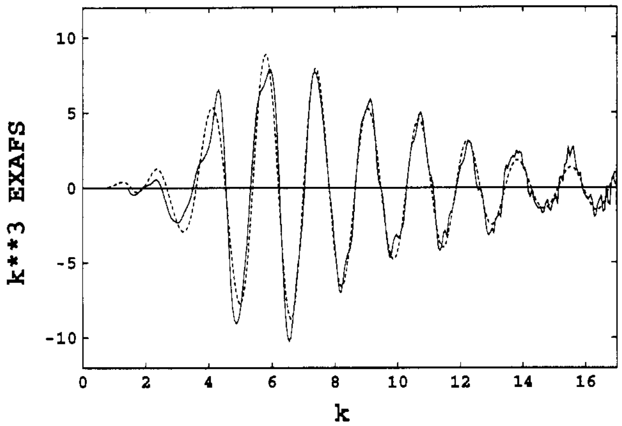

Figure 3. Observed EXAFS of (3-Cl-an)$_8$(CuCl$_6$)Cl$_4$ (continuous line) compared with EXAFS calculated from the model described in text (dashed line).

Table 1. Parameters Fitted to k^3-Weighted EXAFS Recorded from (3-Cl-an)$_8$(CuCl$_6$)Cl$_4$ at 10 K over the Range 3–17 Å^{-1} [a]

shell	occupancy N	$R_{\text{Cu–Cl}}$ (Å)	Debye–Waller factor σ^2 (Å^2)
1	2	2.276(14)	0.008(16)
2	2	2.377(18)	0.0016(22)
3	2	2.827(49)	0.0098(62)

threshold energy E_0: 8991.9(2.6) eV
scale factor $S_0{}^2$: 0.89(18)
goodness-of-fit R: 0.261

[a] Estimated standard deviations are shown in parentheses. The values of N were kept constant.

curve-fitting by means of the program xfit.[3] The phase and amplitude parameters were calculated *ab initio* using the curved-wave single-scattering EXAFS program FEFF 4.06.[4]

Three shells of Cl atoms were fitted to the observed k^3-weighted data over the range 3–17 Å^{-1} (Figure 3). The use of three rather than two shells probed the hypothesis that the geometry has a significant orthorhombic component (see Discussion, below). The parameters treated as variables were the Cu–Cl distances $R_{\text{Cu–Cl}}$, the Debye–Waller factors σ^2, the threshold energy E_0, and the scale factor $S_0{}^2$. The number of atoms in each shell, N, was fixed at 2. The goodness-of-fit parameter R was calculated as $R = [\sum(k^3(\text{data} - \text{fit}))^2/\sum(k^3(\text{data}))^2]^{1/2}$. Standard deviations, conservatively estimated as described by Lin *et al.*[5] and shown in brackets after the result to which they refer, were calculated with a filter window 0–2.65 Å, $\chi_v{}^2$ being scaled to 1 since no quantitative estimate of the uncertainties in the observations had been made. The results are shown in Table 1.

Results and Discussion. The observed EXAFS is reproduced correctly by the EXAFS calculated from a model in which each Cu^{2+} ion is surrounded by an *elongated* octahedron of Cl$^-$ ions (Figures 2 and 3). The length found for the two shortest Cu–Cl bonds, 2.276(14) Å, is in good agreement with the crystallographic values 2.277(1) Å at 293 K[1] and 2.288(2) Å at 150 K.[6] Further, the lengths of the intermediate and long Cu–Cl bonds, 2.38(2) and 2.83(5) Å, agree with the values ~2.37 and ~2.85 Å that are obtained by calculating the disorder component of the thermal parameter U for these Cl atoms if one assumes that the vibrational contribution is the same as for the nondisordered Cl.[2] Thus the apparent conflict between the EXAFS and crystallographic results is resolved.

The structure found by EXAFS was originally predicted by analyzing the optical and EPR spectra of the compound.[2] The observation of four resolved bands in the low-temperature single-crystal optical spectrum of the compound led to the conclusion that the ligand field at the Cu atom has a marked orthorhombic character. This is now confirmed by the significant differences between the short, intermediate, and long Cu–Cl distances. Bond distances close to those found by EXAFS were actually used in calculations which correctly reproduced the electronic band energies and assignments.[2]

Further evidence that (3-Cl-an)$_8$(CuCl$_6$)Cl$_4$ contains disordered tetragonally elongated CuCl$_6{}^{4-}$ complexes was adduced from the temperature dependence of the EPR spectrum. If the g shift parallel to the short Cu–Cl bonds were caused by vibronic admixture of $d_{x^2-y^2}$ into the ground state, then it should decrease significantly on cooling. The g values are, however, almost independent of temperature down to ~10 K.[2]

On several previous occasions, compounds which were initially identified on the basis of X-ray crystal structure determinations and/or EPR spectroscopy as containing tetragonally compressed Cu(II) complexes[7,8] have subsequently been found to involve the more common tetragonally elongated geometry with the long bonds and one pair of short bonds arranged in the "antiferrodistortive" manner shown in Figure 1b.[9,10] It has been shown that this behavior may be represented by calculating the potential surface of a Jahn–Teller-distorted 6-coordinate Cu(II) complex perturbed by a uniaxial lattice strain.[11,12] When the strain is modest and corresponds to a compression of the ligand field along one pair of metal–ligand bonds, a potential surface with two equivalent minima results. The wave functions associated with these minima represent equivalent orthorhombic geometries, both having the shortest metal–ligand bonds parallel to the direction of strain, but with the directions of the long and intermediate bonds interchanged in the two minima.

Behavior of just this kind has been deduced from the EPR spectrum of the complex Cu(H$_2$O)$_2$Cl$_4{}^{2-}$ formed when Cu^{2+} is doped into NH$_4$Cl at low pH. The "strain" in this example is produced by the fact that H$_2$O ligands cause a slightly stronger σ-perturbation than Cl$^-$.[12] In (3-Cl-an)$_8$(CuCl$_6$)Cl$_4$ it appears that the CuCl$_6{}^{4-}$ complex is perturbed by a lattice strain which causes compression of the ligand field along the direction of the short pair of Cu–Cl bonds. This produces a potential surface with minima which differ only in the interchange of the long and intermediate bond directions. The minima (unlike those for Cu^{2+}-doped NH$_4$Cl) are not symmetry equivalent, but the fact that the g tensor of the compound remains almost invariant between 198 and 10 K shows that the two orientations of the CuCl$_6{}^{4-}$ complex are effectively equivalent in energy. Below ~10 K the g tensor becomes orthorhombic,[2] which may indicate that the energy difference between the two orientations is not zero.

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Supplementary Material Available: A listing of observed EXAFS values for (3-chloroanilinium)$_8$(CuCl$_6$)Cl$_4$ at 10 K (2 pages). Ordering information is given on any current masthead page.

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