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X-ray Absorption Study of the Solvated Cu(II) Ion: Transition from a Solvated Solid to the Dissolved State

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X-ray absorption spectroscopy has often been used to examine the local environment around an absorbing cation in both the solid and the liquid state.[1] However, the changes in coordination of a transition metal as it enters solution have not been investigated in depth. The lack of such studies in part reflects the difficulty of finding a single system in which the nature of ligation about the cation does not change significantly between the solid phase and solution. The few previous studies have given inconsistent results regarding structural alterations under such conditions.[2,3] Here we describe the increase in copper–oxygen bond distance and alteration of coordination for a solvated solid-state copper(II) ion as it encounters excess solvent and dissolves.

In order to examine the properties of a transition-metal ion under conditions in which the degree of solvation can be regulated, we have placed cupric ions within a smectite clay. The clay functions merely as a support for the ion into which solvent can be introduced in a controlled manner. Its presence has no effect on the X-ray absorption spectra reported here. Smectite clays consist of negatively charged sheets of aluminosilicates which are separated by an interlayer whose thickness changes upon absorption of solvent.[4] In the native clay used for these experiments, bentonite, this interlayer contains calcium cations and water molecules.[5,6] The calcium was replaced with copper by stirring the clay in a 0.1 M aqueous solution of $CuCl_2$. The copper content of the clay after ion exchange is approximately 2% by weight.

Earlier studies have demonstrated that X-ray absorption spectroscopy can be used to probe the structure of cations within clays.[7-14] For the experiments described here, Cu K-edge spectra were acquired at the National Synchrotron Light Source and Stanford Synchrotron Radiation Laboratory in both transmission and fluorescence modes. Four samples of Cu–bentonite powder, dried from water, methanol, ethanol, and ethylene glycol, were examined, as well as slurries of these samples in their respective solvents.

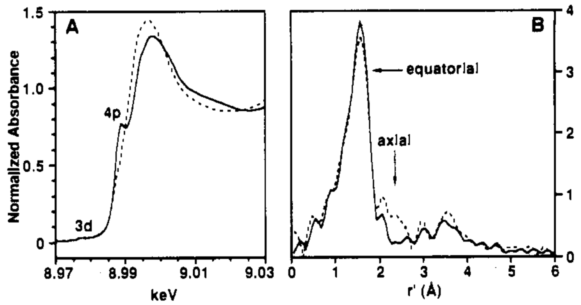

Figure 1. (A) Normalized X-ray absorption near-edge (XANES) spectra and (B) radial structure functions, $\rho_2(r')$, for Cu(II) in Cu–bentonite. Powder-dried from methanol (—) and slurry in methanol (- - -). The distribution functions are not corrected for the Cu-O phase shifts.

Figure 1 shows the normalized X-ray absorption near edge (XANES) spectra for copper ion in the Cu–bentonite dried from methanol and for the Cu–clay as a slurry in the same solvent. The spectrum of the dry material clearly shows the electronic 1s–4p transition as a resolved shoulder on the absorption edge at 8986 eV.[15-18] This transition, which is characteristic of a copper ion with square planar coordination, has broadened and almost disappeared in the slurry. The observed change suggests that as the solvent penetrates into the clay, some of the solvent molecules enter the coordination sphere of the copper(II) ion. The addition of two axial oxygen ligands shifts the coordination geometry of the Cu(II) from a square planar configuration to a distorted octahedron.[18] Similar results are observed when the solvent is ethanol or water.

The radial structure functions, $\rho_2(r')$, describing the local coordination about the copper ions in these two samples are also shown in Figure 1. The equatorial oxygen atoms, which are present for copper ions in either square planar or octahedral coordination, are the predominant feature in these functions. The axial ligands on the copper ions, whose presence in the clay slurry was deduced from the XANES spectra, are also apparent in the radial distribution for the slurried material.

There is an obvious change in the EXAFS data between the dry clay and the slurry which cannot be readily discerned by examination of the radial distributions alone. Figure 2 presents the k^2 weighted Fourier filtered EXAFS data, $k^2\chi(k)$, for the equatorial oxygen atoms about the copper atoms in the clays, powder and slurry, which were exposed to methanol. The phase of the data has clearly shifted. However, the overall amplitude of $\chi(k)$ remains approximately constant. At the first level, these results indicate that the distance between the Cu and O atoms has changed, but the number of atoms in this coordination shell remains fixed. The shift in phase is not an artifact of the presence of the axial ligands in the clay slurry. This fact is demonstrated by the third filtered $\chi(k)$ in Figure 2, which contains the contributions to the EXAFS data from both the equatorial and the axial atoms. Although inclusion of the axial atoms does affect the observed phase and amplitude of the EXAFS data slightly, the change is small compared with that observed as the copper atom dissolves. The combined EXAFS signal for the equatorial and axial oxygen atoms is dominated by the former atoms. This observation is consistent with results from other investigators,

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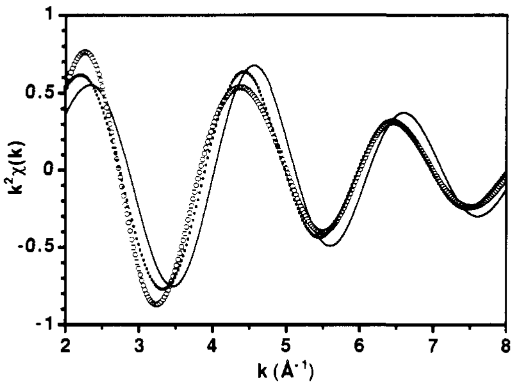

Figure 2. Fourier-filtered EXAFS data for Cu(II) in Cu–bentonite (k^2, Δk = 1.8–13 Å^{-1}). Equatorial oxygen atoms in powder-dried from methanol (Δr = 0.8–1.9 Å, —), equatorial oxygen atoms in slurry in methanol (Δr = 0.8–1.9 Å, ■), and equatorial and axial oxygen atoms in methanol slurry (Δr = 0.8–2.7 Å, ○).

Table I. Summary of Fitting Parameters for the Fluorescence EXAFS Spectra of Cu-Bentonite in Protic Solvents[a,b]

	powder			slurry		
solvent	n	r (Å)	$\Delta\sigma^2$	n	r (Å)	$\Delta\sigma^2$
methanol	4.0	1.93	0	4.3	1.96	0.0025
ethanol	3.9	1.93	–0.0002	4.2	1.96	0.0010
water	3.9	1.92	–0.0002	4.1	1.95	0.0006
ethylene glycol	3.7	1.93	0.0003	3.9	1.96	0.0009

[a] n = number of neighboring atoms; r = radial distance between absorbing and backscattering atoms in angstroms; $\Delta\sigma^2$ = difference in Debye–Waller factors between sample and reference. The errors in both absolute and relative coordination numbers (n and Δn) and radial distance (r and Δr) are ±20% of n and ±0.01 Å, respectively. [b] The values for n and $\Delta\sigma^2$ are referenced to the Cu–bentonite powder dried from methanol (n = 4, $\Delta\sigma^2$ = 0).

who have found it difficult to pinpoint the location of the axial ligands about Cu(II).[19,20]

Fit parameters obtained from the fluorescence EXAFS data for Cu–bentonite in several solvents are tabulated in Table I. The coordination numbers for the eight samples vary by 17%. For each solvent, the distance between the copper ion and the oxygen atom increases by 0.03 ± 0.01 Å as the copper atom enters solution. The Debye–Waller factors also increase, which is consistent with both the fact that the ion has moved into solution and that the bond distance between the central atom and the ligand has expanded. For comparison, we have performed the same analysis for 1 and 0.01 M solutions of $CuCl_2$ in water. The radial distance of the equatorial atoms from the Cu cations in these salt solutions, 1.965 Å, is similar to that found in the clay slurries and to values previously reported.[21,22]

These results, while clearly demonstrating that the bond distance in these copper complexes changes, do not provide the reason for this increase. The change may be inherent for copper as it shifts from square planar to octahedral coordination. Alternatively the increase may reflect an innate difference between ions in a solid-like environment and in solution. Fragmentary evidence supports the latter supposition. The XANES spectrum of the Cu–bentonite dried from ethylene glycol is intermediate between those of the other dry samples and the slurries (see supplementary material). The presence of some axial ligands in this sample is not surprising, since a greater amount of the glycol probably remains within the clay. However, the observed bond distance in this material is the same as those in the other dried clays. Studies with the copper ion under controlled conditions of temperature and humidity as well as with clays incorporating other transition-metal cations are underway in order to address this question directly.[23]

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Supplementary Material Available: Description of experimental procedures, XANES spectra for Cu–bentonite dried from ethylene glycol and the slurry of the clay in the same solvent, and the original EXAFS spectra for Cu–bentonite powder and as a slurry in methanol (6 pages). Ordering information is given on any current masthead page.

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