**X-ray absorption spectroscopy study of Cu(II) coordination in the interlayer of
montmorillonite**

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Abstract—Cu(II) coordination in the interlayer of an expandable clay mineral montmorillonite is studied using X-ray absorption spectroscopy (XAS) along with electron paramagnetic resonance (EPR) and X-ray diffraction (XRD). *Ab initio* calculations are performed using FEFF code to reproduce the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) portion of the experimentally measured XAS spectra. Cu(II) coordination changes depending on the Cu(II) loading and hydration state of the interlayer. XRD shows that the Cu-saturated montmorillonite has the d_{001} -spacing values corresponding to the interlayer thickness of four and one water layer(s) for the hydrated and dehydrated interlayer,

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5 respectively. EPR shows that Cu(II) in the fully hydrated, unsaturated interlayer behaves similar
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8 to free Cu(II) ion in a bulk aqueous solution, while Cu(II) forms a square planar complex in the
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10 dehydrated interlayer. Cu(II) in the fully hydrated, Cu-saturated montmorillonite has a
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12 characteristic singlet 1st derivative XANES spectrum. FEFF calculations show that this singlet
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14 feature originates from a quasi-regular octahedral coordination of water molecules around the
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16 interlayer Cu(II) atom. All other samples and model compounds including the dry Cu-saturated
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18 montmorillonite, wet and dry unsaturated montmorillonite, aqueous Cu(II), cupric nitrate salt
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20 ($\text{Cu}(\text{NO}_3)_2 \cdot 4.5\text{H}_2\text{O}$), and Cu(II) hydroxide precipitates have doublet 1st derivative XANES
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22 spectra. FEFF calculations suggest that the doublet features arise from an axially elongated
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24 octahedral coordination under the Jahn-Teller effect or square planar coordination. FEFF
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26 calculations of the EXAFS spectra as a function of the axial oxygen bond length demonstrate
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28 that a destructive interference between backscattering from equatorial oxygen (O_{eq}) and that
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30 from axial oxygen (O_{ax}) atoms leads to an apparent coordination number (CN) less than six
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32 expected for the tetragonal coordination, with the farther, loosely bound axial oxygen atoms
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34 making a minor, yet negative contribution to the CN determined by the EXAFS analysis. This
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36 study shows that Cu(II) has interchangeable octahedral, tetragonal, and square planar
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38 coordination in the interlayer of montmorillonite, depending on Cu(II) loading and degree of
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40 hydration. The quasi-regular octahedral coordination of the interlayer Cu(II) in montmorillonite
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42 is a new finding of this study.
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54 *Key Words:* interlayer Cu(II); XAS; montmorillonite; octahedral coordination; tetragonal
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56 coordination; square planar coordination
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1. Introduction

Copper input to soil environments has been increasing from anthropogenic sources such as mining activities, agricultural applications as antibiotics and fertilizers, and industrial wastes from electrical industries, in addition to natural sources largely from the chemical weathering of Cu-containing rocks (Bhattacharyya and Gupta, 2006; El-Bayaa et al., 2009; Veli and Alyuz, 2007). As an essential element for life, its toxicity as well as deficiency may cause acute and chronic problems to humans, animals, plants, and micro-organisms (Yruela, 2009; Ryan et al., 2014; Flemming and Trevors, 1989). Clay minerals play an important role as a natural scavenger of copper in controlling its mobility and fate in soil environments (Alvarez-Puebla et al., 2004; Schlegel and Manceau, 2013; Brigatti et al., 2004).

The coordination structure of copper(II) aqua ions has been experimentally studied using diffraction methods such as X-ray and neutron diffraction. These techniques supported the widely accepted Cu(II) coordination model of an axially elongated octahedral coordination with unusually fast water exchange at the axial oxygen ligands in aqueous environments due to the $3d^9$ electronic structure and consequent Jahn-Teller distortions (Richens, 1997).

Extended X-ray absorption fine structure (EXAFS) spectroscopy has been also applied to the structural studies of Cu(II) adsorption complexes on clay and oxide minerals as well as aqueous Cu(II). However, the curve fitting involved in the data analysis has often led to structural parameters contradicting the existing body of knowledge on the local coordination environment of the adsorption complexes. For example, Cheah et al. (1998), Morton et al. (2001), Strawn et al. (2004), and Furnare et al. (2005) reported the coordination numbers (CNs) of the Cu(II) aqueous and adsorption complexes close to 4. Although a study by Pasquarello et al. (2001) suggested a five-fold coordination, the generally accepted CN of the first hydration shell of the aqueous

Cu(II) is 6 (Ohtaki and Radnai, 1993). The knowledge gap between the EXAFS-determined CN and the well-established CN value of 6 primary hydration water molecules consistent with the $3d^9$ electronic structure has not yet been satisfactorily filled.

Despite its excellence in precisely determining the local coordination environments around metal atoms, EXAFS has not been as effective in differentiating the axial oxygen atoms from equatorial oxygen atoms bound to Cu(II). In EXAFS data fitting, the axial oxygen has been either ignored or simply assumed to be present (Korshin et al., 1998). Moreover, the reported inter-atomic distance values for the axial oxygen atoms suffer from inconsistency, typically ranging from 2.1 to 2.6 Å (Pasquarello et al., 2001). Since EXAFS has not been very successful in depicting an acceptable physical picture of the well-known Cu(II) aqua ion coordination, it is even more challenging to get reliable coordination information solely by EXAFS for Cu(II) ions in the interlayer of smectite minerals. To overcome these shortcomings, theoretical calculations and structural information independently obtained from electron paramagnetic resonance (EPR) and X-ray diffraction (XRD) are used in this work to guide the X-ray absorption spectroscopy (XAS) data analysis. Using this multi-technique approach, the XAS data of Cu(II) in the interlayer of montmorillonite (SAz-1) are rigorously analyzed for montmorillonite samples with different Cu(II) loading and degree of hydration. The samples are prepared under acidic pH condition to ensure that Cu(II) is bound to the interlayer rather than the edge surfaces of the mineral.

2. Materials and Methods

2.1. Montmorillonite

Cheto montmorillonite (SAz-1) from the Source Clays Repository (The Clay Minerals Society) was used for this study. It has the reported structural formula of $(\text{Ca}_{0.39}\text{Na}_{0.36}\text{K}_{0.02})[\text{Al}_{2.71}\text{Mg}_{1.11}\text{Fe(III)}_{0.12}\text{Mn}_{0.01}\text{Ti}_{0.02}][\text{Si}_{8.00}]\text{O}_{20}(\text{OH})_4$, with most of its structural charge arising from the octahedral substitution (Fripiat et al., 1979). It has a cation exchange capacity (CEC) of 120 meq/100 g and N_2 -BET surface area of $97.42 \pm 0.58 \text{ m}^2/\text{g}$ (Fripiat et al., 1979). For the Cu adsorption experiments, it was purified and prepared in its Na exchanged form following the procedure described elsewhere (Morton et al., 2001).

2.2. Adsorption sample preparation

The adsorption samples were prepared by reacting 0.2 g montmorillonite with 200 mL cupric nitrate solution at the acidic pH of 4.0 in 250 mL PPCopolymer centrifuge bottles (Nalgene) for 10 hours. After the adsorption, the suspension was centrifuged at 10,000 rpm (19,682 g) for 20 minutes using a DuPont Sorvall RC-5B centrifuge and an RCA rotor. Then the supernatant solution was decanted and duplicate aliquots of 5 mL were collected for atomic absorption spectroscopy analysis for Cu. The slurries were either kept wet or freeze-dried for further characterization by EXAFS, EPR, and XRD. All the solutions were prepared using distilled and deionized water (18.3 M Ω -cm; Milli-Q water system).

A Cu-saturated montmorillonite (Cu-Mt) was prepared by reacting a 0.2g dry montmorillonite with a 1,000 ppm ($1.57 \times 10^{-2} \text{ M}$) Cu(II) stock solution prepared using an ACS grade $\text{Cu}(\text{NO}_3)_2 \cdot 4.5\text{H}_2\text{O}$ (Aldrich Chemical). To saturate the mineral with Cu(II), the 200 mL of supernatant after the centrifugation was replaced by the same amount of the fresh 1000 ppm Cu(II) solution and the Cu(II) loaded montmorillonite slurry was reacted with the Cu(II) solution again. This procedure was repeated for three times. The reaction pH was kept at 4.0 without

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5 added background electrolyte, to keep Cu(II) in the interlayer of the mineral rather than on the
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7 edge surfaces (Hyun et al., 2000). Montmorillonite with interlayer Na⁺ partially exchanged by
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9 Cu²⁺ (NaCu-Mt) was prepared by reacting the montmorillonite sample with a solution of 10⁻⁴ M
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11 Cu(II) in a 0.01 M NaNO₃ background electrolyte solution at pH 4.0. The final Cu(II) loading
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13 was 5.7 mg Cu(II)/g montmorillonite, corresponding to 15 % of the reported CEC value. A 1,000
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15 ppm cupric nitrate atomic absorption standard solution (Fisher Scientific) with added NaNO₃
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17 (Fisher Scientific) was used as a model compound for XAS measurements. The details of the
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19 Cu(II) samples prepared are summarized in Table 1.
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25 Other samples and reference compounds include Cu(II) precipitates and Cu(II) loaded
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27 montmorillonite prepared at pH 10. The Cu(II) precipitates were prepared by addition of 1N
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29 NaOH and consequent abrupt pH rise of the cupric nitrate stock solution. The precipitates were
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31 made to have the same Cu(II) loading as Cu-Mt by diluting the precipitates with dry Na-
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33 montmorillonite. The basic pH sample was prepared to obtain Cu(II) sorbed to the edge surfaces
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35 of montmorillonite. The spectra of the different Cu(II) loaded motnmorillonite samples and
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37 model compounds were compared to figure out the structural characteristics of Cu(II) associated
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39 under different pH, Cu(II) loading, and degree of hydration.
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46 47 **2.3. EPR**

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49 EPR is concerned with unpaired electrons and their chemical environments (Goodman and
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51 Hall, 1995). In the presence of external magnetic field, the degeneracy of the energies of
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53 electrons with different spin states is lifted, known as the Zeeman effect. When the applied
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55 electromagnetic radiation satisfies the following condition, a strong absorption or resonance
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$$h\nu = \Delta E = g\mu_B B \quad [1]$$

where ν is the frequency of the electromagnetic wave (Hz), h is Planck's constant, μ_B is the Bohr magneton (9.2731×10^{-24} J/T), and B is the applied magnetic field (Calas, 1988; Goodman and Hall, 1995). The proportionality constant g is known as the spectroscopic splitting factor or simply g -factor. It is 2.0023 for a free electron, but varies when the electron is bound in a molecule or mineral, giving information regarding the chemical environment of the unpaired electron (Goodman and Hall, 1995; Pan and Nilges, 2014).

X-band (~ 9.25 GHz) spectra of Cu(II)-loaded montmorillonite samples (NaCu-Mt) of different hydration state prepared at different degree of freeze-drying were collected using a Bruker EMX spectrometer (Department of Chemistry, University of Michigan) at room temperature. Same amounts of NaCu-Mt freeze-dried powder samples were put in quartz sample tubes (Wilmad Glass) and their EPR spectra were measured.

2.4. XRD

The 001-reflections of the Cu-saturated montmorillonite (Cu-Mt) sample before and after the freeze-drying were recorded using a Rigaku Rotaflex X-ray diffractometer with a rotating anode X-ray source (Hanawalt Lab., University of Michigan). An oriented sample of wet Cu-Mt paste was prepared by loading the paste on a glass slide. No noticeable sign of dehydration was observed during the data collection. A dry bulk powder sample of freeze-dried Cu-Mt was prepared using an aluminum sample holder. A Ni-filtered, monochromated Cu $K\alpha$ radiation generated at 40 kV/100 mA was used with a slit set of 0.5° divergent, 0.5° Soller, and 0.15 mm receiving slit. The data were collected for 1 second at each step of $0.02^\circ 2\theta$ in the range of 2° – $12^\circ 2\theta$ in a step scan mode.

2.5. XAS data collection and analysis

Cu *K*-edge (8979 eV) X-ray absorption spectra were collected at the beam lines 4-3 and 11-2 of Stanford Synchrotron Radiation Lightsource (SSRL) using a Si(220) double-crystal monochromator at the beam energy of 3.0 GeV and maximum beam current of 100 mA. Wet paste and dry powder samples were loaded in Teflon sample cells with Kapton tape windows. Fluorescence spectra were collected using a Lytle detector or 13-element Ge array detector. To minimize the contribution from the higher order harmonics, the monochromator was detuned 50 % at the highest energy position of the scan. The beam energy was calibrated using the simultaneously measured copper foil spectrum. To get improved signal to noise ratios, multiple scans (4-16) were collected.

The EXAFS can be formulated as

$$\chi(k) = \frac{\Delta\mu}{\mu_0} \approx \frac{m}{4\pi\hbar^2k} \sum_j \frac{N_j}{R_j^2} t_j(2k) e^{-2R_j/\lambda} \sin[2kR_j + 2\delta_j(k)] e^{-2k^2\sigma_j^2} \quad [2]$$

where μ_0 is the absorption coefficient without EXAFS; k is the electron wave vector $= 2\pi/\lambda_e$; N_j is the number of atoms in the j -th coordination sphere; R_j is the average radial distance to the j -th atomic shell; $t_j(2k)$ is the back-scattering amplitude for the j -th atoms; λ is the mean free path of the electron; σ_j^2 is the Debye-Waller factor due to thermal vibrations or static disorder with σ_j being the root mean square fluctuation (Sayers et al., 1971; Lytle et al., 1975; Stern, 1988).

Data analyses were performed using SixPack, EXAFSPAK, IFEFFIT, and FEFF8 code (Webb, 2002; George and Pickering, 2000; Newville, 2001; Ankudinov et al., 2002). Energy calibrated, acceptable scans were averaged and backgrounds were removed using linear fits below the absorption edge and spline fits above the edge. The background removal was

performed using the IFEFFIT code. The spectra were then converted from the energy to the frequency space using the photo electron wave vector k . The normalized, k^3 -weighted EXAFS spectra were Fourier-transformed for the k range of 3-12 and used for FEFF fitting to get structural parameters. Phase shift and amplitude functions for each backscattering path were obtained from theoretical calculations using the FEFF8 code. To obtain the optimal structural parameters, including coordination numbers and interatomic distances, the Debye-Waller factor (σ^2) and energy reference E_0 parameters were also floated during the fitting. The many-body factor S_0^2 was fixed at 0.9 to reduce the number of fitting parameters. To isolate the first shell contribution from the overall EXAFS pattern, the first shell peak on each Fourier transform function was back-transformed to get the filtered EXAFS for the first coordination shell. OPT of EXAFSPAK, the non-linear least-squares fitting subprogram, was used to obtain the best fit to the filtered EXAFS. The fitting results from the SixPack and EXAFSPAK were cross compared to each other to ensure the reliability of the results.

2.6. Theoretical XAS calculations

The XAS patterns of hypothetical, isolated $\text{Cu}(\text{O}_{\text{eq}})_4(\text{O}_{\text{ax}})_2$ coordination complex models were calculated using the FEFF8 code to simulate the experimentally measured XAS spectra of interlayer Cu(II) under different Cu loading and hydration conditions. In the calculations, the bond length between Cu and O_{eq} ($R_{\text{Cu-Oeq}}$) was fixed at 1.95 Å, while $R_{\text{Cu-Oax}}$ was allowed to vary between 2.10 Å and 2.75 Å to cover the reported range of the Cu- O_{ax} bond lengths. $R_{\text{Cu-Oax}}$ value of 1.95 Å and infinity were also calculated for the regular octahedral coordination and square planar coordination as the two extreme cases of the axially elongated tetragonal coordination. Also calculated was the XAS spectrum of the tetrahedrally coordinated CuO_4 with the bond

length of 1.95 Å. In the XANES region, full multiple scattering calculations were performed in the FEFF simulation of the Cu(II) spectra. The contributions of the backscattering from O_{eq} and O_{ax} to the overall calculated EXAFS spectra were isolated to evaluate the influence of changing coordination structures to the corresponding EXAFS patterns.

3. Results and Discussion

3.1. XRD of the Cu-saturated montmorillonite

The XRD results show that the fully hydrated and evacuated Cu-Mt have the d_{001} -spacing of 19.5 Å and 12.5 Å, respectively (Figure 1). Considering that montmorillonite with Cu as the interlayer cation has a further reduced basal spacing of 9.7 Å upon heating at 150 °C (McBride and Mortland, 1974), the basal spacing values of this study confirm that the fully hydrated and evacuated montmorillonite accommodate an average of four water layers and one water layer in the interlayer between the two adjacent tetrahedral layers. At the acidic pH of 4, the edge surfaces are positively charged and are not effective for Cu(II) adsorption due to the electrostatic repulsion. Instead, most of Cu(II) associated with montmorillonite have been shown to be in the interlayer at the similar acidic pH values (Hyun et al., 2000; Morton et al., 2001). Since the interlayers are saturated with Cu(II), the d_{001} -spacing reflects the coordination environment of Cu(II). The spacing of 19.5 Å suggests that enough water molecules are present in the fully expanded, hydrated interlayer to allow interlayer Cu(II) to keep its six hydration water molecules, as in aqueous solutions. The reduced d_{001} spacing of 12.5 Å indicates that the confined space in the dehydrated interlayer is no longer favorable for the dynamic Jahn-Teller inversion or free tumbling. The interlayer is not large enough for interlayer Cu(II) to retain its axial oxygen

ligands. Under this dehydrated condition, a square planar coordination is the most likely configuration, consistent with the one water layer thickness of the interlayer spacing. In this dehydrated interlayer, all the coordination structures except the square planar coordination would suffer from an excessive repulsion from the basal oxygen atoms since some of the O ligands would go beyond the basal O plane of the tetrahedral sheets along the *c*-axis. The one water layer thickness rules out the tetrahedral coordination of the interlayer Cu(II) (Morton et al., 2001), which requires two layers of water molecules. It can be deduced that the Cu(II) adsorption complexes should be regularly arranged such that their *z*-direction is parallel to the *c*-axis of the mineral. In conclusion, XRD suggests that a tetragonal coordination by six water molecules is possible for Cu(II) in the fully hydrated interlayer, whereas a square planar coordination by four oxygen ligands is the most likely coordination environment in the dehydrated interlayer.

3.2. EPR of interlayer Cu(II)

At room temperature, Cu(II) in the freeze-dried NaCu-Mt has two distinct EPR signals, viz., an isotropic signal with $g_{\text{iso}} = 2.170$ and an anisotropic signal with $g_{\parallel} = 2.338$, $g_{\perp} = 2.054$, and $A_{\parallel} = 142$ G (Figure 2). On the other hand, only the isotropic signal was observed for Cu(II) in the fully hydrated montmorillonite (Hyun et al., 2000). The intensity of the two signals changes with degree of dehydration of the Cu loaded montmorillonite (Figure 3). With increasing degree of dehydration, the anisotropic signal intensified while the isotropic signal decreased simultaneously. Montmorillonite itself has EPR features between ~3400 and ~3700G originating from structural Fe(III), but they neither affects or are affected by the Cu(II) adsorption or hydration state.

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6 The simultaneous observation of isotropic and anisotropic signals at room temperature
7 suggests the mixed single and multiple layers of water in the interlayers. The isotropic signal was
8 assigned as fully hydrated Cu(II) under the influence of the dynamic Jahn-Teller inversion with a
9 free tumbling motion, leading to the average-out of the orientation-dependent contributions to
10 the spin Hamiltonian, as in aqueous $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions. The observation of the isotropic signal
11 (Figure 2) indicates that Cu(II) is weakly held in the interlayer, keeping all its six water
12 molecules of the first solvation shell. This conclusion is consistent with the electron spin-echo
13 modulation (ESEM) study performed by Brown and Kevan (1988) that showed that Cu^{2+} has a
14 hydration number of 6 in an essentially aqueous environment in the hydrated interlayer of
15 montmorillonite.
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30 The observation of the anisotropic signal suggests that Cu(II) in the dehydrated interlayer is in
31 a motion-frozen state on the EPR timescale at room temperature. As the interlayer loses water,
32 interlayer Cu stops the dynamic Jahn-Teller inversion or free tumbling motion, eventually
33 reaching a motion-frozen status. The order of $g_{\parallel} > g_{\perp} > g_e$ from the Cu(II) anisotropic signal
34 indicates a D_{4h} symmetry or axially elongated octahedral coordination of Cu(II) due to the Jahn-
35 Teller effect, ruling out the possibility of tetrahedral coordination (Figure 2 and 3) (Pilbrow,
36 1990). Moreover, the $g_{\parallel}$ -value of the present study (2.338) is significantly lower than the
37 previously reported values for the aqueous Cu(II), e.g., 2.409 as reported by Bassetti et al. (1979)
38 and 2.4 by Matar et al. (1995), or the values reported for Cu(II) in the fully hydrated interlayer of
39 montmorillonite, 2.41 for Cu(II) in a Mg-montmorillonite (Brown and Kevan, 1988) and 2.420
40 for that in a Na-montmorillonite measured at 77K (Hyun et al., 2000). Consistent with the
41 reported empirical relation between $g_{\parallel}$ -value and the stability constant (Motschi, 1984), this
42 significant decrease of $g_{\parallel}$ -value compared to that of six-fold coordinated Cu(II) suggests that
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interlayer Cu(II) has lost part of its primary hydration sheath in the dehydrated interlayer. The most feasible explanation is that Cu(II) has lost the axial oxygen atoms from its first hydration shell as a result of dehydration. Loss of the longer, weaker Cu–O_{ax} bonds would result in the observed loss of fast water exchange with the neighboring water molecules. Therefore, the anisotropic signal observed in the dehydrated interlayer is assigned as Cu(II) in a square planar geometry. Consequently, the intensity change of the two signals (Figure 3) indicates the transition of Cu(II) coordination from a tetragonal to a square planar coordination with dehydration. This interpretation is also consistent with the EPR results of Cu²⁺ on various expandable layer silicates reported by McBride (1982; 1986).

3.3. XANES spectra of interlayer Cu(II)

The XANES spectra of interlayer Cu(II) in montmorillonite prepared under different Cu(II) loading and hydration conditions are plotted in Figure 4, along with those of Cu(II) model compounds. Of all the samples and model compounds, the fully hydrated Cu(II) saturated montmorillonite (Cu-Mt-w) is the only one with a singlet 1st derivative XANES spectrum. All other samples and model compounds have doublet 1st derivative XANES spectra. The position and relative intensity of the two peaks and the splitting between the two peaks change depending on Cu loading and degree of hydration. For example, Cu(II) aqua ion has the double peaks at 8988.25eV and 8992.25eV, with the pre-edge feature at 8975.75eV. The splitting between the two peaks of the doublet is 4eV. Cupric nitrate solid has the doublet at 8988.50eV and 8992.00eV with the splitting of 3.5eV. Cu-saturated, dehydrated montmorillonite (Cu-Mt-d) has the doublet at 8984.99eV and 8990.62eV with the splitting of 5.63eV.

Figure 5 shows the simulation results of the 1st derivative XANES spectra for the different Cu(II) coordination, namely, the regular octahedral, axially elongated tetragonal, and square planar coordination. The regular octahedral has a singlet feature, whereas tetragonal and square planar have doublet features. Figure 6 shows the simulation results of the 1st derivative XANES spectra for the tetragonal coordination as a function of Cu-O_{ax} distance with the fixed Cu-O_{eq} distance at 1.95 Å. The results show that the splitting between the two peaks increases with the increasing Cu-O_{ax} distance.

3.4. EXAFS spectra of interlayer Cu(II)

Two approaches were used in analyzing the EXAFS spectra of Cu(II) in aqueous solution and in the hydrated interlayer: a one-path (Cu-O) fitting with a variable coordination number (CN) and two-path (Cu-O_{eq} & Cu-O_{ax}) fitting with fixed coordination numbers of 4 and 2 for the O_{eq} and O_{ax}, respectively. The 1-path fitting was not based on any structural model. The first shell EXAFS parameters were obtained using one Cu-O path while varying both the CN and the corresponding Debye-Waller factor (σ^2). This approach gives the fewest number of fitting parameters. The 2-path fitting was based on the 4+2 coordination model where Cu(II) has the first coordination shell composed of four closer equatorial oxygen (O_{eq}) atoms and two farther axial oxygen (O_{ax}) atoms. This approach is guided by the structural information obtained from XRD, EPR, and XANES. The regular octahedral and square planar coordination can be incorporated into the 4+2 structure model as the two extreme cases. The goodness of the fit value (*R*-factor from the SixPack or *F*-factor from the OPT output data) was used as a parameter in comparing the closeness of the fitting results to the measured data: the lower is the value, the

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5 better is the fitting. The fitting results from the filtered and back-transformed first shell EXAFS
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7 were checked using the unfiltered, overall spectra.
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10 The results of the theoretical calculations of the EXAFS spectra of the hypothetical Cu(II)
11 model $\text{Cu}(\text{O}_{\text{eq}})_4(\text{O}_{\text{ax}})_2$ with different Cu- O_{ax} bond lengths in a tetragonally elongated octahedral
12 coordination are given in Figure 7. The contributions from O_{eq} and O_{ax} are not well resolved and
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14 no distinct beat pattern is observed in the overall EXAFS pattern when the two contributions are
15 combined (Figure 7). The differences in the oscillation frequency, amplitude envelope, and
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17 amplitude damping pattern between the overall EXAFS and those from O_{eq} are not distinct. In
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19 general, the relative contributions from O_{ax} to the overall EXAFS are minor and dependent on
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21 the axial bond (Cu- O_{ax}) length. The two contributions are not well resolved and a distinct,
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23 resolvable, and separable contribution from O_{ax} is not observed (Figure 7). These example
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25 calculations show that special caution is required to properly interpret the experimental EXAFS
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27 data for the aqueous and interlayer species of Cu(II). The destructive interference between the
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29 backscattering from O_{eq} and O_{ax} leads to the underestimation of the CN, close to 4 rather than 6,
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31 if analyzed using the one-path fitting without a reliable structural model. These theoretical
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33 calculations demonstrate the reason why Cu- O_{ax} bond has often been either ignored in the
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35 EXAFS fitting or reported with inconsistent bond length values in the previous studies. This
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37 result shows that an alternative EXAFS fitting strategy is needed that is guided by reliable
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39 structural information from independent sources for a better analysis of Cu(II) EXAFS data.
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54 *3.4.1. EXAFS of Cu aqua ion*

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56 The best 1-path fitting for the Cu(II) aqua ion while floating both the CN and σ^2 gives the first
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58 hydration shell of 3.3 nearest oxygen atoms located 1.964 Å from the central copper atom with
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σ^2 of 0.0039 (Table 2). The fitting underestimates the CN, compared to the generally accepted value of six solvation water molecules for Cu(II) in aqueous solutions (Ohtaki and Radnai, 1993; Richens, 1997). As the theoretical calculations in the preceding section show, the destructive contribution from the axial oxygen atoms is responsible for this significant underestimation of the CN. This deviation of the CN from the known value again demonstrates the need for a reliable fitting strategy to extract physically meaningful information from the experimental Cu EXAFS data, since the fitting without known structural information can mislead to the conclusion of ‘tetrahedral’ coordination of aqueous Cu(II) ions with the contribution from the Cu–O_{ax} path being neglected (Morton et al., 2001).

The 2-path fitting using the 4+2 structural model gives the best fit of four O_{eq} atoms at 1.969 Å with σ^2 of 0.0047 and two O_{ax} atoms at 2.138 Å with σ^2 of 0.0149 (Table 2). These EXAFS parameters are consistent with the generally accepted local coordination structure of the aqueous Cu(II) ions. The two Cu–O distances are in the reported range previously determined using XRD or ND (Pasquarello et al., 2001). The higher σ^2 value for the Cu–O_{ax} bond compared to that for Cu–O_{eq} is consistent with the physical picture of the loosely bound axial oxygen atoms under fast exchange with neighboring water molecules. The addition of the O_{ax} neighbors also improves the goodness of the fit (the *R*-factor), from 0.0420 for the 1-path fitting to 0.0372 for the 2-path fitting, even though the highly inter-dependent CN and σ^2 are both floated in the 1-path fitting significantly improving the goodness of the fitting. This comparison shows that the application of the 4+2 model with fixed CNs gives more physically reliable depiction of the coordination environment of the Cu(II) aqua ions, as well as slightly better fitting result.

Since the timescale of the EXAFS events is much shorter than the inter-conversion of the axis of elongation of the aqueous Cu(II) under the Jahn-Teller effect, EXAFS is expected to enable

the determination of a weighted average of the interatomic distances (Persson et al, 2002). However, the atomic shell-based EXAFS analysis using Eq. [2] was not efficient in exactly depicting the coordination structure including the orientation of the oxygen ligands in the shell, since the oxygen backscatterers are not evenly distributed in the shell in the tetragonal or square planar complexes. Moreover, when the two oxygen atomic ‘shells’ are too close to be resolved, which is the case for the Cu(II) aqua ion, the EXAFS analysis can lead to unreliable structural information.

3.4.2. EXAFS of interlayer Cu

The EPR and XRD results consistently suggest the tetragonal and square planar coordination for Cu(II) in the fully hydrated and dehydrated interlayer, respectively. The EXAFS data of Cu(II) in the hydrated interlayer are analyzed following the same procedure used for the Cu(II) aqua ion, i.e., 2-path fitting using the 4+2 structural model and 1-path fitting without any structural model. The fitting results are summarized in Table 2.

The 2-path model with fixed CNs gives a better fit with 4 O_{eq} atoms at 1.900 Å and 2 O_{ax} atoms at 1.955 Å ($R = 0.0138$) for Cu(II) in the wet Cu-saturated montmorillonite (Cu-Mt-w), compared to the 1-path fit with 3.2 O at 1.959 Å ($R = 0.0189$; Table 2 and Figure 8a and b). These CNs and bonding distances are supportive of the coordination close to the regular octahedral structure. The Cu- O_{eq} bond length is slightly shorter than the commonly reported ~1.95 Å, but longer than the short Cu-O bond length of 1.89843 Å for malachite (Zigan et al., 1977) and 1.87947 Å for azurite (Wyckoff, 1978), the cupric hydroxycarbonate minerals.

XRD shows that the dehydrated interlayer has only one layer of water molecules, suggesting the square planar coordination of interlayer Cu(II). The 1-path fitting gives the fitting result with

the structural parameters of 4 O at 1.941 Å with σ^2 of 0.0059 (R -factor = 0.0430), while the 2-path fitting did not converge to a set of reasonable structural parameters. The addition of a multiple scattering path of O_{eq1} -Cu- O_{eq3} at 3.92 Å improved the goodness of the fit to the measured EXAFS. Although the presence of the multiple scattering path is suggestive of square planar coordination, while discarding the possibility of tetrahedral coordination, the Fourier transform magnitude of the multiple scattering contribution in the radial structure function was not significant enough and was not included in the result presented in Table 2.

Upon wetting the dehydrated Cu-Mt by adding a small amount of water, interlayer Cu(II) immediately recovers the EXAFS parameters same as the one before dehydration or Cu-Mt-w. This observation suggests that Cu coordination reversibly and readily interchangeable between octahedral and square planar coordination depending on the availability of water molecules and the hydration state of the interlayer.

The EXAFS parameters of the first coordination shell of the interlayer Cu(II) sorbed on the fully hydrated montmorillonite with the surface Cu loading of 5.7 mg/g montmorillonite (NaCu-Mt-w) are similar to those of the Cu(II) aqua ions (Table 2 and Figure 8c and d). The 2-path fitting indicates four O_{eq} neighbors at 1.976 Å with σ^2 of 0.0050 and two O_{ax} neighbors at 2.277 Å with σ^2 of 0.0148. For the 1-path fitting the first coordination shell is composed of 3.6 oxygen atoms at 1.961 Å with σ^2 of 0.0046. The R -factor is 0.0161 for the 2-path fitting, better than 0.0278 for the 1-path fitting.

As EPR shows, interlayer Cu(II) ions cannot retain the axial oxygen atoms in the dehydrated interlayer. The 1-path fitting gives 4 O at 1.942 with σ^2 of 0.0057 and R -factor of 0.0421 for the dry NaCu-Mt (Table 2). In the present study, the estimated error for the EXAFS determination of the interatomic distance for the equatorial oxygen atoms was ± 0.006 Å for NaCu-Mt. To be

conservative, using the error value ($\pm 0.01 \text{ \AA}$) reported in literature (Korshin et al., 1998; Morton et al., 2001) for the first shell interatomic distance for Cu(II) complexes, the Cu-O_{eq} bond length in the dry interlayer ($1.942 \text{ \AA}$) is shorter than that of tetragonal coordination in the wet NaCu-Mt ($1.976 \text{ \AA}$) or Cu(II) aqua solution ($1.969 \text{ \AA}$). Consistent with the EPR results, the 2-path fitting does not converge to a physically acceptable set of structural parameters. Nor does the addition of the extra Cu-O_{ax} path improve the fitting.

3.5. Model for interlayer Cu(II) coordination

Putting together the information obtained from EPR, XRD, XANES, EXAFS, and theoretical calculations, a structural model is proposed for the coordination environment of interlayer Cu(II) in the Cu-saturated/unsaturated and hydrated/dehydrated montmorillonite (Table 3). In the fully hydrated, Cu-saturated montmorillonite (Cu-Mt-w), Cu(II) is bound to six water molecules in a close to regular octahedral coordination. This configuration is supported by the singlet 1st derivative XANES spectrum and the corresponding FEFF simulation. In the fully hydrated, Cu-unsaturated montmorillonite (NaCu-Mt-w), Cu(II) is coordinated by four closer equatorial oxygen atoms and two farther axial oxygen atoms. In this configuration, rapid water exchange at the axial oxygen atoms and change of the axis of elongation occur, as supported by EPR. Interlayer Cu(II) is bonded to four equatorial oxygen atoms in the dehydrated interlayer both in a Cu-saturated and unsaturated montmorillonite. Now Cu(II) lacks the fast water exchange or dynamic Jahn-Teller inversion, and a stronger interaction with the clay layers is expected.

The saturated interlayer has only Cu²⁺ ions and water molecules in the interlayer. The interlayer space has a difference from the aqueous solution in that it lacks the counter ions such

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5 as Cl^- , NO_3^- , ClO_4^- , and SO_4^{2-} , the common components in the aqueous solution of Cu(II) salts.
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7 The Cu-saturated interlayer has a relatively homogeneous coordination environment compared to
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9 the unsaturated interlayer. The unsaturated interlayer has Na^+ as well as Cu^{2+} . The interlayer
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11 property is largely determined by the interlayer Na^+ , affecting the Cu(II) coordination as well..
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15 The swelling phenomena of montmorillonite have long been recognized. The reversible
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17 expansion and contraction of the interlayer correspond with the conversion of copper
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19 coordination between the tetragonal and square planar configuration, suggesting that square
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21 planar Cu(II) can easily convert to the axially elongated tetragonal Cu(II) when sufficient
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23 hydration water is available. The reversible conversion of coordination is evidence by XRD,
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25 EPR, and XAS between hydrated and dehydrated montmorillonite samples as discussed in the
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27 previous (3.4.) section. Similar reversible conversion between the two configurations was also
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29 reported for Cu(II) sorbed on kaolinite (Hyun et al., 2005). The readily reversible rehydration of
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31 the interlayer rules out the likelihood of conversion to the tetrahedral configuration.
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37 This study first suggests the regular octahedral coordination of Cu(II) in the interlayer of
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39 montmorillonite. It also reports the exchangeability between octahedral, tetragonal, and square
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41 planar coordination of interlayer Cu(II) depending on the physical conditions that are readily
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43 adjustable. The findings of this study are expected to have practical implications such as in
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45 catalysts and medical applications. The analytical approaches used in this study would be
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47 expanded to probe the chemical environments of the interlayer sites in other expandable clay
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49 minerals. Further development can also be made by combining the analytical approaches with
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51 coordination theories and quantum mechanical calculations on Cu(II) coordination as a function
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53 of layer charge in a series of expandable phyllosilicate minerals.
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4. Conclusions

Complementary EPR, XRD, and XAS provided independent structural information on the Cu(II) coordination, allowing a more definitive assignment of the coordination of Cu(II) in the interlayer of montmorillonite. Interlayer Cu(II) in the Cu-saturated, fully hydrated montmorillonite has a quasi-regular octahedral coordination. Interlayer Cu(II) in unsaturated, fully hydrated montmorillonite has an axially elongated tetragonal coordination. Dehydrated montmorillonite has interlayer Cu(II) in a square planar coordination. This study newly suggests the quasi-regular octahedral coordination and shows that the different coordination structures are interchangeable depending on the hydration state and Cu(II) loading conditions.

Theoretical EXAFS calculations show that the destructive interference caused by the slight difference in the bond distance between Cu-O_{eq} and Cu-O_{ax} can confound the analysis of the experimental Cu(II) EXAFS data. EXAFS analysis based on the 4+2 structural model was able to provide physically acceptable coordination structures around interlayer Cu(II). Since the 1-path fitting could often provide fitting results comparable to the 2-path fitting in terms of the goodness of the fit, it might be considered as the better approach in terms of simplicity. However, as this study shows it is not physically acceptable when viewed in the context of the complementary EPR and XRD results. This work shows that EXAFS should be applied with caution to the study of transition metal coordination on clay minerals, particularly for metals in which multiple first shell paths are the norm in aqueous environments such as with aqua Cu(II).

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Table 1. Samples used in the present work.

Sample	pH	[Na(I)]_{tot} (mol/L)	[Cu(II)]_{tot} (mol/L)	Cu loading mg Cu/g Mont. (% CEC)
Cu solution	4.0	0	1.57×10^{-2}	-
NaCu-Mt	4.0	0.01	10^{-4}	5.7 (15 %)
Cu-Mt	4.0	0	1.57×10^{-2} three times	38 (100%)

Table 2. Structural parameters of Cu aqua ion and interlayer Cu extracted from EXAFS analysis (*C.N.*: coordination number, *R*: interatomic distance, σ^2 : Debye-Waller factor, *: fixed during fitting, *R*-factor: goodness of the fit). Numbers in bold are the selected final fitting result. Lower *R*-factor value indicates a better fitting to the measured data.

Samples		Path	<i>C.N.</i>	<i>R</i> (Å)	σ ²	<i>R</i> - factor
Aqueous Cu(II)	1-path	Cu-O	3.3	1.964	0.0039	0.0420
	2-path	Cu-O _{eq}	4*	1.969	0.0047	0.0372
		Cu-O _{ax}	2*	2.138	0.0149	
Cu-Mt-w	1-path	Cu-O	3.2	1.959	0.0038	0.0189
	2-path	Cu-O _{eq}	4*	1.900	0.0059	0.0138
		Cu-O _{ax}	2*	1.955	0.0011	
Cu-Mt-d	1-path	Cu-O	4*	1.941	0.0059	0.0430
NaCu-Mt-w	1-path	Cu-O	3.6	1.961	0.0046	0.0278
	2-path	Cu-O _{eq}	4*	1.976	0.0050	0.0161
		Cu-O _{ax}	2*	2.277	0.0148	
NaCu-Mt-d	1-path	Cu-O	4*	1.942	0.0057	0.0421

Table 3. Cu(II) coordination in the interlayer of montmorillonite

Cu(II) loading		Cu(II) saturated		Unsaturated	
Hydration state					
Hydrated	Hydrated	<ul style="list-style-type: none"> ▪ Cu-Mt-w ▪ Singlet 1st derivative XANES ▪ Close to regular octahedral coordination ▪ Homogeneous environment without counter ions ▪ 4 water layers in the interlayer 		<ul style="list-style-type: none"> ▪ NaCu-Mt-w ▪ Doublet 1st derivative XANES ▪ Isotropic EPR signal ▪ Similar to aqueous [Cu(H₂O)₆]²⁺ ▪ Axially elongated octahedral (tetragonal 4+2) structure ▪ Dynamic Jahn-Teller inversion: resonance of three orientations with different axis of elongation ▪ Rapid water exchange ▪ Free tumbling ▪ 2 water layers with the presence of Na⁺ 	
		<ul style="list-style-type: none"> ▪ Cu-Mt-d ▪ Doublet 1st derivative XANES ▪ Square planar coordination ▪ No Jahn-Teller inversion ▪ Tumbling motion frozen ▪ 1 water layer in the interlayer 		<ul style="list-style-type: none"> ▪ NaCu-Mt-d ▪ Doublet 1st derivative XANES ▪ Anisotropic EPR signal ▪ Square planar coordination ▪ No Jahn-Teller inversion ▪ Tumbling motion frozen ▪ 1 water layer in the interlayer 	

Figure Captions

Figure 1. XRD patterns of d_{001} -relection of wet and dry Cu-saturated montmorillonite (Cu-Mt).

Figure 2. EPR of the interlayer Cu(II) on montmorillonite (NaCu-Mt) after evacuation at 500mTorr.

Figure 3. EPR of interlayer Cu(II) in NaCu-Mt measured at different degree of dehydration: samples evacuated at a) 200 mTorr, b) 380 mTorr, and c) 500 mTorr, and d) simulation of 500 mTorr spectrum (c).

Figure 4. Measured 1st derivative XANES spectra of the different Cu(II) samples and model compounds (Cu-Mt-w: Cu(II)-saturated wet montmorillonite; Cu-Mt-d: Cu(II)-saturated dry montmorillonite; NaCu-Mt-w: partially Cu(II)-exchanged wet Na-montmorillonite; NaCu-Mt-d: partially Cu(II)-exchanged dry Na-montmorillonite; Cu PPT: Cu(II) oxide precipitate; Aqua Cu: Cu(II) aquatic solution).

Figure 5. Simulation results of the 1st derivative XANES spectra for the different Cu(II) coordination.

Figure 6. Simulation results of the 1st derivative XANES spectra for the tetragonal coordination as a function of Cu-O_{ax} distance at fixed Cu-O_{eq} distance of 1.95 Å.

Figure 7. FEFF calculation of hypothetical $\text{Cu}(\text{O}_{\text{eq}})_4(\text{O}_{\text{ax}})_2$ compounds: a) EXAFS and b) radial structure functions. $\text{Cu}-\text{O}_{\text{eq}}$ was fixed at 1.95 Å while $\text{Cu}-\text{O}_{\text{ax}}$ varied at 2.10 Å, 2.25 Å, 2.50 Å, and 2.75 Å.

Figure 8. EXAFS data and fitting results along with component path contributions (Data: measured data, Fit: FEFF fit results, O_{eq} : contribution from the equatorial oxygen atoms, and O_{ax} : contribution from the axial oxygen atoms). (a) k^3 -weighted $\chi(k)$ for the fully hydrated Cu-saturated montmorillonite (Cu-Mt-w), (b) Fourier transform magnitude for Cu-Mt-w, (c) k^3 -weighted $\chi(k)$ for the fully hydrated unsaturated montmorillonite (NaCu-Mt-w), and (d) Fourier transform magnitude for NaCu-Mt-w.

Figure 1

Figure 2

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Figure 8