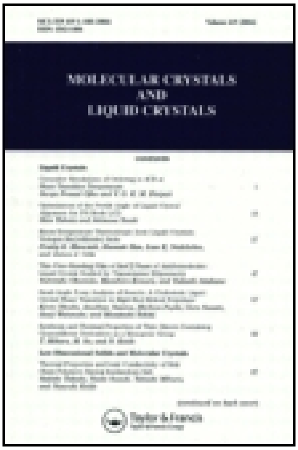

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XAFS Study on Cu(II) Complexes Stabilized in Two-dimensional Silicate Lattice, Hectorite.

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Three copper complex ions, $[Cu(en)_2]^{2+}$, $[Cu(cyclam)]^{2+}$, and $[Cu(H_2O)_4]^{2+}$ are intercalated into a layered silicate, Hectorite (Hec), by ion exchange reaction. According to the powder XRD analysis, the basal increments of 3.21Å for $[Cu(en)_2]^{2+}$-Hec, 3.81Å for $[Cu(cyclam)]^{2+}$-Hec, and 2.43Å for $[Cu(H_2O)_4]^{2+}$-Hec indicate that the local geometry around copper (II) is square planar for all the intercalates. XANES results show the characteristic peak of square planar structure due to the ligand to metal charge transfer (LMCT) effect, which is shifted to lower energy side with an order of 0.5~1.6eV but the main edges due to $1s \rightarrow 4p_\pi$ and $1s \rightarrow 4p_\sigma$ transitions are shifted to higher energy side for about 0.5~1.5eV compared to precursor depending on the ligands. From Cu K-edge EXAFS analysis, it is found that four nitrogen atoms at ~2.0Å and two oxygen atoms at ~2.4Å are coordinated with copper(II) in precursor salts, but only four nearest neighbors are coordinated to copper (II) at ~2.0Å in the intercalated complexes.

Keywords: intercalation; copper complexes; hectorite; EXAFS; XANES

INTRODUCTION

Transition metal polyaza macrocyclic ligands have attracted large scientific interest due to their significant catalytic activities in many reactions such as electrochemical, biological and photobiological processes.[1] In case of intercalation into layered host, it is expected that electronic configuration, mobility, and orientation of the complex could be altered in the interlayer surface of clays. Therefore, the characterization of chemical bonding nature as well as the local structure of transition metal complex ion within the charged layers has been one of the most attractive research problems.

Previously, we successfully carried out the X-ray absorption spectroscopic (XAS) experiments on two model Cu(II)-complexes of $[Cu(en)_2]^{2+}$ (en = ethylenediamine), and $[Cu(cyclam)]^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetra decane), in order to understand how the local structure and the ligand-filed strength could affect the electronic environment around the copper ion before and after the intercalation into dioctahedral layer silicate, montmorillonite.[2]

At the present work, we have performed the intercalation of above Cu(II)-complexes, $[Cu(en)_2]^{2+}$ and $[Cu(cyclam)]^{2+}$, into trioctahedral layer silicates, hectorite, and investigated the electronic and geometric structural change of the copper ion for both intercalates by XAS method.

EXPERIMENTAL SECTION

$[Cu(en)_2](ClO_4)_2$ and $[Cu(cyclam)](ClO_4)_2$, were prepared as previously reported.[3,4] For the formation of hectorite-copper(II) complexes, hectorite was immersed into aqueous solutions of $[Cu(en)_2](ClO_4)_2$ and $[Cu(cyclam)](ClO_4)_2$ at 65 °C for 48 hours, respectively. For comparison, the cupric ion-exchanged hectorite was prepared by treating it with 1N $CuCl_2$ solution.

X-ray absorption spectroscopic measurements were carried out with synchrotron radiation by using the EXAFS facilities installed at the beam line 10B of the Photon Factory, the National Laboratory for High Energy Physics (Tsukuba), operated at 2.5 GeV with ca. 260 ~ 370 mA of stored current. All the data were recorded in a transmission mode at room temperature.

The data analyses for experimental spectra were performed by the standard procedure as previously described.[5] In order to determine the structural parameters (coordiantion number, Debye-Waller factor, interatomic distance and threshold energy difference), a nonlinear least-squares curve fitting was performed in the *R* space of the Fourier transform(FT), using UWXAFS code[6] and *ab initio* EXAFS code FEFF6 (FT range of $\sim 2.5 \leq k \leq \sim 12.5$ Å^{-1}, Hanning window).[7]

RESULTS AND DISCUSSION

The intercalation of Cu^{2+}, $[Cu(en)_2]^{2+}$ and $[Cu(cyclam)]^{2+}$ ions into hectorite was confirmed by powder X-ray diffraction. The observed basal increment ($\Delta d = 2.43$, 3.21, and 3.81 Å) with respect to the basal spacing of the pristine hectorite (d = 9.60 Å) suggests that the copper complex are intercalated as a monolayer with their square planes parallel to the silicate layers, and the axial ligands have been replaced by silicate lattices.

Figure 1 shows the normalized Cu K-edge XANES spectra for the present compounds. The main peak B can be assigned to the $1s \rightarrow 4p$ transition, based on the dipole selection rule of $\Delta l = \pm 1$, and the shoulder peak A could be assigned to the shakedown satellite involving a $1s \rightarrow 4p_{\pi}$ transition with simultaneous ligand-to-metal charge transfer (LMCT) by means of the Cu K-edge XANES studies[8,9] for chemically well-characterized copper compounds. It is noted that the position of the peak A shifts to a lower energy site upon intercalation, indicating that the charge transfer from 2*p* orbitals of nitrogen ligand to 3*d* orbitals of copper metal occurs more effectively, and thus the Cu–N bonding character becomes more covalent, which is surely due to the modification of molecular orbital caused by the structural variation of intercalates from octahedral to square planar.[10] Moreover, whereas both copper complexes exhibit the peak A at almost the same energy position (8982.7 eV), the degree of lower shift of the peak A upon intercalation is larger for the cyclam complex (Δ = 1.4 eV) than for the ethylenediamine one (Δ = 0.6 eV), which represents that the LMCT path is more effective in the clay intercalation complexes than that in unintercalated copper complexes.

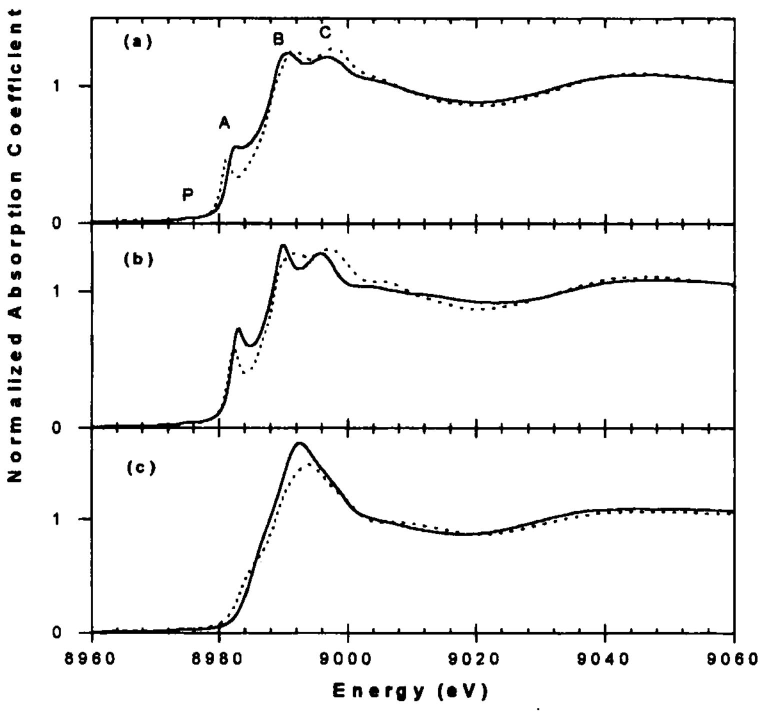

FIGURE 1 The normalized Cu K-edge XANES spectra for (a) $[Cu(cyclam)](ClO_4)_2$, (—), $[Cu(cyclam)]^{2+}$-Hec (---), (b) $[Cu(en)_2](ClO_4)_2$ (—), $[Cu(en)_2]^{2+}$-Hec (---), and (c) $[Cu(H_2O)_4]^{2+}$ (—), $[Cu(H_2O)_4]^{2+}$-Hec (---), where Hec indicates hectorite.

The main transition corresponding to 1s → $4p_\pi$ (peak B) shifts slightly to higher energy side about 0.5 eV for $Cu(en)_2$-hec and about 0.9 eV for Cu(cyclam)-hec, respectively, compared to chlorate copper complex salts. This transition is mainly affected by axial ligands and such a result is consistent with the fact that the axial liagnds of ClO_4^- are replaced by anionic clay layer.[10] On the other hand, another main transition corresponding to 1s → $4p_\sigma$ (peak C) also shifts toward high energy side with an order of 1.5 eV and 1.1 eV in $Cu(en)_2$ and Cu(cyclam), respectively, compared to precursor salts. This transition is mainly affected by equatorial ligands, and it represents that the bond strength between central metal and ligands for the intercalate becomes stronger than that for the unintercalated copper complexes, considering the MO scheme.[11]

TABLE 1 Structural parameters obtained from the best-fit for the Cu K-edge EXAFS spectra.

Compound	Atom	C.N.^{a}	R (Å)^b	σ^2 ($\times 10^{-3}$/Å^2)^c	E_0 (eV)^d
$[Cu(en)_2]^{2+}$-Hectorite	N	4	2.02	2.5	7.0
	C	4	2.88	6.1	8.9
$[Cu(en)_2]ClO_4$	N	4	2.01	5.2	4.0
	O	2	2.42	18.9	4.0
	C	4	2.89	8.4	12.4
$[Cu(cyclam)]^{2+}$-Hectorite	N	4	2.01	3.5	3.2
	C	4	2.85	5.4	
	C	4	3.00	4.9	
	C	2	3.39	3.4	
$[Cu(cyclam)]$ ClO_4	N	4	2.02	6.1	5.0
	O	2	2.42	6.7	
	C	4	2.75	3.8	
	C	4	2.93	3.6	
	C	2	3.38	3.4	

^{a}Coordination number; ^{b}Distance; ^{c}Debye-Waller factor; ^{d}Threshold energy difference

For the precursor copper complex salts and their intercalates, the multi-shell curve fittings have been performed in the region of 1 Å < R < 3.5 Å to obtain the local structural parameters. (Table. 1) According to EXAFS fitting results, it should be noted that the copper ions in the intercalation complexes do not have any axially coordinated oxygens, different from free salts state, and that the Debye-Waller factors of (Cu-N) bond in the intercalates were significantly decreased, representing that the bond strength between copper and nitrogen in intercalation complex is stronger than that of unintercalated copper complex. This result is well consistent with the XANES result.

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