ORIGINAL ARTICLE

XAFS study of the complex of an acetylacetonate-based ligand and copper ion

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Abstract An X-ray absorption fine structure (XAFS) study has been conducted to reveal the local structure and chemical state of the copper in the complex of an acetylacetonate-based ligand (**L1**) and copper ion in acetonitrile solution. The copper ion in the complex was found to be divalent from the Cu K-edge X-ray absorption near-edge structure (XANES) spectrum. The FEFF (ab initio multiple scattering calculations of XAFS) were performed with the model compounds, whose structures were optimized by using MOPAC program with AM1 Hamiltonian. The comparative study of the experimental XAFS spectra and theoretical calculations from FEFF gave the perspectives for clarifying the coordination structure of the complex of **L1** and copper ion.

Keywords Acetylacetone · Pyrene · Fluorescence · Copper · Coordination structure · XAFS

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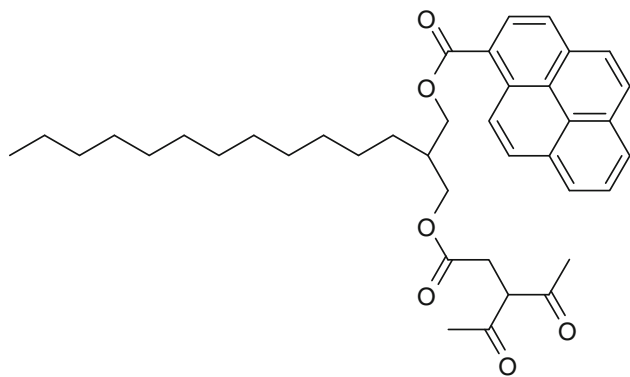
Introduction

The design and synthesis of new fluorescence sensor compounds have been widely studied in chemistry, biology and environmental sciences [1, 2]. The switching of emission property of the compounds can be achieved by metal ion, pH, redox potential etc. [3, 4]. Among them, metal ion is getting much attention as external stimulus on the view point of biological and medical interest [5]. The synthesis and structure analysis of β-diketone ligands with copper have been extensively reported on the basis of x-ray crystallography over recent years [6, 7].

In our previous study [8], we reported the fluorescence and metal-ion recognition properties of an acetylacetonate-based ligand (**L1**) as shown in Fig. 1. **L1** shows high selectivity to copper ion which promotes the fluorescence emission quenching in acetonitrile solution. From the results of Job's method and titration plot, the complex of **L1** and copper ion was found to have 1:1 stoichiometry.

It needs to be noted that the fluorescence property of **L1** appears only when used under the low concentration conditions less than 10^{-5} M. The **L1**-complex gave a brownish precipitate in methanol, ethanol and DMF. Even in acetonitrile, the precipitate was formed at higher concentrations than 10^{-5} M. The precipitate was insoluble in any solvents. It is quite important to clarify the coordination structure of the **L1**-complex because the systematic studies for such unique ligands may give further insights into the coordination chemistry and lead to a new type of sensor material.

X-ray crystallography is a powerful tool to determine the coordination structure of a complex in the solid phase, however, it does not always reflect the same structure in the solution phase, especially under the highly diluted conditions. This reminded us to use x-ray absorption fine structure (XAFS) which is one of the most reliable

Fig. 1 Molecular structure of **L1**

techniques to probe the physical and chemical structure of the compound at an atomic scale in solution and is applied to some crown ether complexes in methanol [9].

At the present work, XAFS study has been conducted to reveal the local structure and chemical state of the copper atom in the **L1**-complex in acetonitrile solution. The results were discussed with those obtained from theoretical calculations by using model compounds.

Experimental

Materials and methods

Sample preparation

All chemicals for synthesis were of available purity and used without further purification. The synthesis route and reaction procedure for **L1** are described in the literature [8]. For XAFS measurements, spectroscopic grade acetonitrile was used as the solvent, and copper nitrate (as trihydrate) was the highest grade available and was employed as received. The sample solution for XAFS measurements was prepared by mixing the same amount of acetonitrile solution of **L1** and copper nitrate. The final concentration of **L1** and copper ion was 1×10^{-5} M. The solution was filled in a polyethylene bag tightly sealed.

XAFS measurement

The Cu K-edge XAFS spectra were collected in fluorescence mode using Si(111) double crystal ($d = 0.313551$ nm) monochromator at the BL-9A station of the Photon Factory at High Energy Accelerator Research Organization (Tsukuba, Japan) with 2.5 GeV ring energy and 337.2–371.4 mA stored current. All measurements were carried out at 25 °C. Energy calibration was accomplished using copper metal foil at the Cu K-edge. The data

were treated by the program REX2000 (Rigaku) for Windows 2000. The extended XAFS (EXAFS) data were analyzed according to standard procedures. The k^3-weighted EXAFS spectra, where k represents the wave number of photoelectron, were obtained from normalized EXAFS spectra, and Fourier-transformations were performed within the range $k = 3$–12 Å^{-1} without any phase shift correction.

Theoretical calculation

The theoretical calculations by using FEFF 8 [10] were performed with the FEFF module in REX2000 using the standard parameters. The geometry optimization of the model compounds was calculated by using MOPAC 2006 in the program Scigress Explorer (FUJITSU LIMITED) with AM1 Hamiltonian [11]. The values of dielectric constant (35.94) and effective radius (3.65 in angstrom) for acetonitrile were given for the calculation. The structure of the model compounds was preliminarily optimized with MM (molecular mechanics) method. The data of Cartesian coordinates for each atom were extracted from the output file of the optimized structure and were used for the FEFF calculations.

Results and discussion

Cu K-edge XAFS study of the **L1**-complex

Figure 2 shows the XANES spectrum for the **L1**-complex in acetonitrile. To identify the chemical state of the copper ion in the **L1**-complex, the inflection point which corresponds to the edge energy (E_0) was estimated from the first
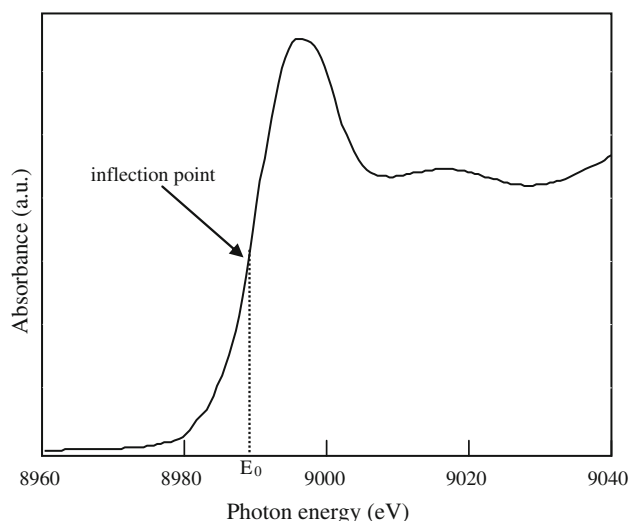

Fig. 2 XANES spectrum for the **L1**-complex in acetonitrile

derivatives of the XANES spectrum. The value of the photon energy at the inflection point for the copper ion in the **L1**-complex (8989.3 eV) was distinctly different from that for copper metal (8986.0 eV). This shows that the copper ion in the **L1**-complex is divalent. This result is in good agreement with the literature [12]. No significant change of the spectrum was observed after 5 h (data not shown), meaning that the copper ion is stable under these conditions.

On the analysis of Fourier-transformed EXAFS of the **L1**-complex, we encountered serious problems: (1) it is hard to differentiate the bonds between Cu–O and Cu–N because the bond lengths for Cu–O and Cu–N are 1.93 and 2.06 angstrom, respectively [13]; (2) the mass difference between oxygen atom and nitrogen atom is small, so that oxygen and nitrogen may give a similar signal in XAFS, especially at the first shell. In addition, since the **L1**-complex is thought to be solvated in acetonitrile solution, the bond lengths around copper atom strongly receive influence of the thermal vibration of acetonitrile at normal temperature. These problems led us to give up the curve-fitting by using empirical parameters extracted from the standard samples.

Model compounds and FEFF calculations

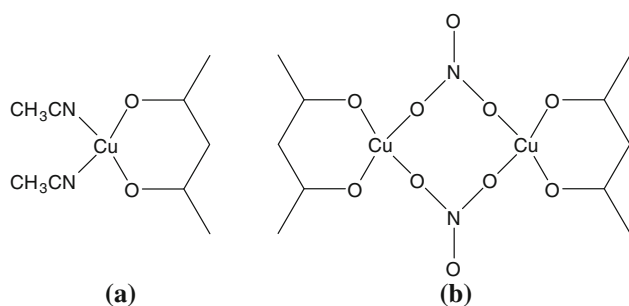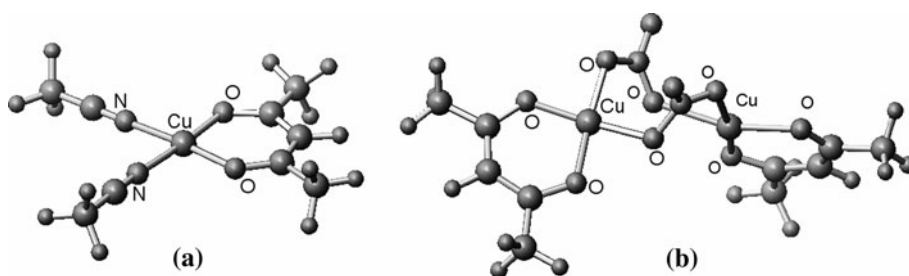In early studies, several copper complexes of β-diketone-containing ligands have been synthesized for the

Fig. 3 Model compounds for the FEFF calculations: **a** model A, acetonitrile-coordinated model; **b** model B, binuclear model. The atom charge and bond order were omitted

construction of supramolecular architectures [6, 7]. Their crystal structures have been reported in detail with respect to structure and function relationships.

Taking these studies into consideration, two model compounds were built to clarify the coordination structure of the **L1**-complex as shown in Fig. 3. These models were simplified and focused on the center metal and its coordination environment. As reported before [8], the molar ratio of **L1** and copper ion in the **L1**-complex was found to be 1, then the models that have 2:1 (ligand:copper) stoichiometry were omitted in this study. Model A has an acetonitrile-coordinated structure along with acetylacetone (Fig. 3a). Acetonitrile is known to have coordination ability to transition metals [14], then, copper ion may be stabilized by acetonitrile. The counter ion (NO_3^-) is neglected because it is difficult to locate the ion at a fixed position in the complex. Model B is one of the most plausible structures of binuclear complex that has the molar ratio of 1 (Fig. 3b). The optimized structures were shown in Fig. 4.

The FEFF 8 calculations for model compounds were carried out with the SCF option "ineffective". Since the binuclear model B is not symmetrical as shown in Fig. 4b, two data sets were obtained from the FEFF calculation, and then the mean values of the two were used for the further procedures.

Figure 5 shows the k^3-weighted EXAFS oscillations (a) for model A, model B and the **L1**-complex and their Fourier transforms (b). The similar shoulder shape can be seen in Fig. 5a-A and -Exp at ca. $k = 5.7$ Å^{-1}, however, no similar patterns were observed in the other region. There seems to be no correlation between Fig. 5a-Exp and -B in whole range of the figure. As seen in Fig. 5b-Exp there is one distinct peak at ca. $R = 2.1$ Å (R is an atomic distance from the center atom) which cannot be seen both in Fig. 5b-A and -B, meaning that the model compounds presented in this work are insufficient to elucidate the coordination structure of the **L1**-complex. From these results, there is no valuable information especially about the first-coordination shell, and then we could not achieve the determination of the coordination structure of the **L1**-complex.
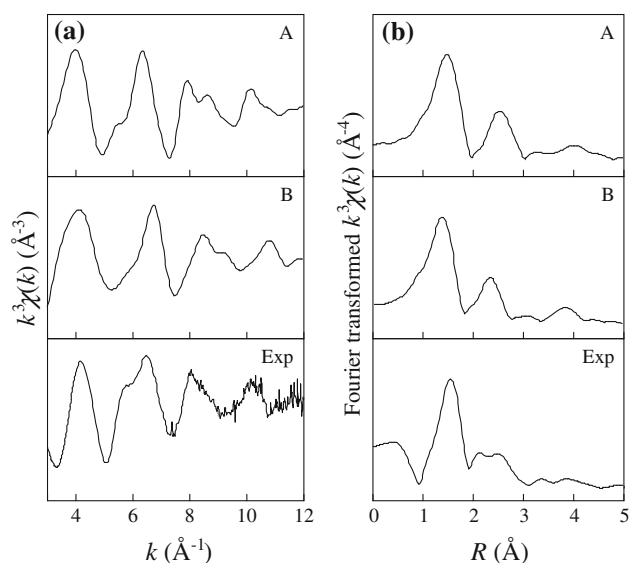
Fig. 4 Optimized structures for model compounds: **a** model A; **b** model B

Fig. 5 Simulated spectra for model A (A) and model B (B), and EXAFS spectrum for **L1**-complex (Exp). **a** $k^3\chi(k)$, **b** k^3-weighted Fourier transforms

Concluding remarks

By comparison of the values of the photon energy at the inflection point of the XANES spectra, the copper ion in the **L1**-complex was confirmed to be divalent. Two plausible models were built and their FEFF calculations were performed, but the analysis of EXAFS data gave only ambiguous results. This may suggest that the **L1**-complex has different forms other than 1:1 or 2:2 stoichiometry and exists as mixtures of them in acetonitrile and further investigations are necessary.

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