

Uptake of Cu(II) Ions into α -Zirconium Phosphate-Ethylamine Intercalate and their Coordination Environment in Host-guest Matrices

Isao Tomita¹, Ritsuko Inoue^{1†}, Izumi Nakai²
and Yoshitsugu Hasegawa³

¹ Department of Chemistry, Faculty of Science, Ochanomizu University, Bunkyo-ku, Tokyo, Japan

² Department of Chemistry, the University of Tsukuba, Tsukuba-shi, Ibaraki, Japan

³ Department of Industrial Chemistry, Tokyo University of Agriculture and Technology, Koganei-shi, Tokyo, Japan

(Received April 9, 1993)

Abstract

Zirconium bis (monohydrogenorthophosphate) monohydrate (α -zirconium phosphate) with relatively large particle size was prepared and employed as an intercalation host for ethylamine. Solid phases with the interlayer distances of 7.6, 9.6, 10.8, and 13.9 Å were observed as the intercalation proceeded. Further uptake of Cu(II) ions into the interlayer region of the intercalate was possible, and the coordination environment of Cu(II) ions was investigated by means of EXAFS and XANES. The results indicate that the Cu(II) ions were coordinated to O⁻ active sites rather than N atoms of the amine.

Key words: α -zirconium phosphate, ethylamine intercalation, Cu(II) uptake, EXAFS, XANES

Introduction

Zirconium bis (monohydrogenorthophosphate) monohydrate (referred to as α -ZrP, α -zirconium phosphate), $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ has been extensively studied in the past two decades, for the properties as an ion exchanger, an intercalation host, a catalyst and a solid electrolyte. The crystal structure has been solved by Troup and Clearfield [1] and was shown to be a layered structure. Each layer consists of planes of zirconium atoms bridged through phosphate groups which alternate above and below the zirconium atom planes. This layer structure enables it to accommodate metal cations and organic guest molecules.

In the present investigation, α -ZrP synthesized by the direct precipitation method [2] was intercalated with ethylamine as a guest molecule, its

[†] present address: SONY Corporation, Asahi-cho, Atsugi-shi, Kanagawa, Japan.

pH titration curve was measured by the batch method. Incorporation of Cu(II) ions into the ethylamine-intercalate was attempted and the extent of uptake was estimated. The coordination environment of Cu atoms was studied by means of EXAFS and XANES.

Experimental

Preparation of α -ZrP. Zirconium chloride oxide octahydrate, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (16.8 g) was dissolved in *ca.* 2 mol dm^{-3} hydrofluoric acid (122 ml) in a polyethylene vessel. To this mixture was added concentrated orthophosphoric acid (270 ml) with stirring and resulting solution was kept at 60°C for about 7 days with constant feeding of humidified air. Crystalline α -ZrP with a diameter up to $45 \mu\text{m}$ was precipitated, then centrifuged, washed with deionized water and air-dried. The product was identified by X-ray powder diffraction with a Shimadzu XD-610 diffractometer.

Intercalation of ethylamine. The pH titration for α -ZrP by titrant of 0.1 mol dm^{-3} ethylamine plus 0.1 mol dm^{-3} ethylammonium chloride was carried out by the batch process. The titrants have a constant ($\text{C}_2\text{H}_5\text{NH}_2 + \text{C}_2\text{H}_5\text{NH}_3\text{Cl}$) concentration with varying ratio of $\text{C}_2\text{H}_5\text{NH}_2$ to $\text{C}_2\text{H}_5\text{NH}_3\text{Cl}$, thus varying pH values from batch to batch. The ratio of titrant volume to α -ZrP weight was kept at $100 \text{ (ml g}^{-1}\text{)}$. The mixtures were shaken in stoppered Erlenmeyer flasks at 15°C for 7 days. After centrifuging, the supernatants were subjected to pH measurement. The solid phases were washed, dried and examined by X-ray powder diffraction and elemental analysis.

Uptake of Cu(II) ions to the intercalate. α -ZrP-ethylamine intercalate (0.1 g) was suspended in 20 ml of 0.05 mol dm^{-3} copper acetate solution, and stood for 24 h at 15°C . Pale blue crystallites were obtained after centrifuging and washing. Interlayer distances of the solids were measured by X-ray diffractometry. Copper content of the solids was determined by EDTA titration of the solution phases before and after the equilibration. In order to obtain the information on the first coordination sphere of copper taken up in the interlayer region, EXAFS (extended X-ray absorption fine structure) and XANES (X-ray absorption near edge structure) techniques were applied by using synchrotron radiation of the Photon Factory, KEK, Tsukuba.

Preparation of ethylamine-complex of Cu(II). Weighed amount (18.7 g) of copper perchlorate hexahydrate was dissolved in ethanol. The solution was added slowly to 20 ml of ethylamine, and bluish violet crystallites

were precipitated, its composition being $[\text{Cu}(\text{C}_2\text{H}_5\text{NH}_2)_3(\text{H}_2\text{O})](\text{ClO}_4)_2$.

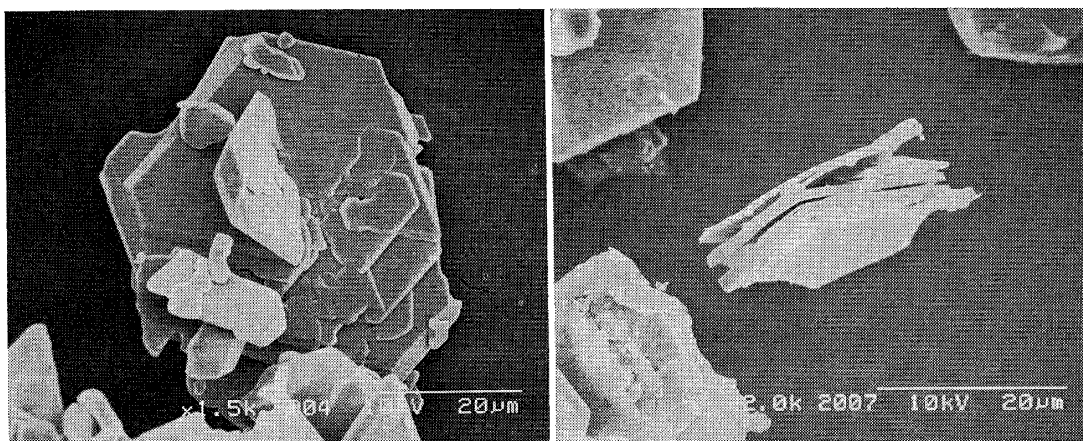
Uptake of Cu(II)-ethylamine complex into α -ZrP. The complex (2.43 g) was dissolved in 50 ml of deionized water. To this was added α -ZrP (0.3 g) and the resultant suspension stood for 24 h at 15°C. Complex-cation exchanged α -ZrP was obtained.

Observation of microcrystals with SEM. Scanning electron microscopic observation was made on α -ZrP, α -ZrP-ethylamine intercalate, and the copper-loaded intercalate with a Hitachi S-2300 scanning electron microscope.

Results and Discussion

α -Zirconium phosphate. In the preparative procedure, concentrated orthophosphoric acid was used in the present experiment. This resulted in highly crystalline, large crystals, whose SEM photograph is shown in Fig. 1a.

Intercalation of ethylamine. A pH titration curve for α -ZrP with $(\text{C}_2\text{H}_5\text{NH}_2 + \text{C}_2\text{H}_5\text{NH}_3\text{Cl})$ titrants was given in Fig. 2. The interlayer distances of solid phases estimated from X-ray powder pattern are presented in Table 1, together with pH values of the supernatant. The titration curve has been measured by Gupta and Nowell [3], and the present results essentially agreed with it. The curve has several plateaus, *i.e.*, nearly constant pH regions, as if α -ZrP had polyprotic property. It should be considered, however, that in the present system, one or more solid phases coexist with a solution phase. Assuming that the intensity of X-ray diffraction line is proportional to the amount of solid phases present, it is possible to show the variation of composition of the solids as the titration



(a) α -ZrP

(b) ethylamine-intercalate (α -ZrP/ $\text{C}_2\text{H}_5\text{NH}_2$)

Fig. 1. SEM photograph of α -ZrP and ethylamine-intercalate.

Table 1. Observed interlayer distances of the intercalates.

Sample No.	equilibrium pH	interlayer distances /Å			
1	2.60	7.54	9.50		
2	2.54	7.61	9.63		
3	2.70	7.64	9.56		
4	2.88		9.54		
5	3.40		9.59		
6	3.90		9.60	10.72	
7	4.03		9.63	10.75	
8	4.08		9.66	10.83	
9	4.20		9.60	10.72	
10	4.55			10.76	
11	5.02			10.72	
12	5.98			10.71	
13	6.24			10.80	14.33
14	6.70			10.84	14.32
15	6.76			10.76	13.54 14.18
16	6.81			10.77	13.56 14.21
17	6.97			10.82	13.62 14.28
18	7.20			10.89	13.75
19	7.30			10.84	13.70 14.36
20	7.31			11.00	13.97
21	7.32				13.70
22	7.78			10.93	13.80
23	8.63			10.85	
24	9.23				13.76 14.33
25	9.50				13.63
26	9.62			10.85	13.61
27	9.73				13.56
28	10.15				13.50 14.13
29	10.43				13.56
30	10.50				13.62 14.24

proceeded. This is shown in Fig. 3.

Correlation between the titration curve (Fig. 2) and Fig. 3 is evident at least up to the addition of ca. 4.5 mmol ethylamine. Only when a single solid phase corresponding to a single interlayer distance exists, a jump of pH value is observed. If two solid phases coexist, the plateau pH region appears. As has been discussed by Clearfield and Medina [4] for sodium ion exchange of α -ZrP, the Gibbs' phase rule can be applied to the system. Three components are necessary to describe the system: *e.g.*, ethylamine and hydrogen ion in the solution and hydrogen ion in the solid, thus $F = C + 2 - P = 5 - P$, where F is the variance, C is the number of components and P is the number of phases at equilibrium. At constant temperature and pressure, F is equal to $3 - P$. Thus, only when a single solid phase and a solution phase are present, hydrogen ion concentration can be varied. This relationship indirectly indicates that the system in interest was in

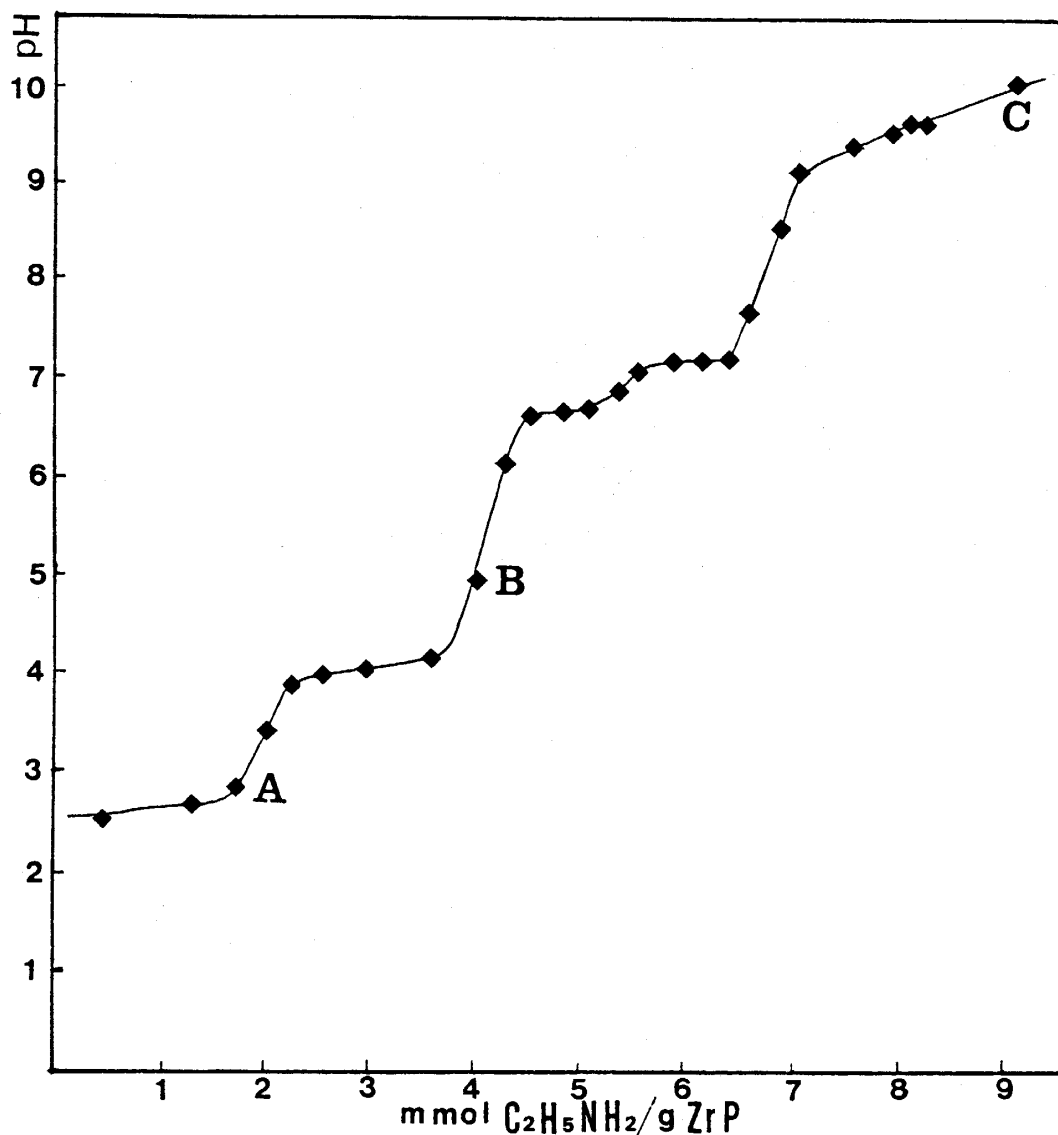


Fig. 2. pH titration curve for α -ZrP with ethylamine.

equilibrium, or close to it.

Chemical composition of ethylamine intercalates at three positions, A, B and C, in the titration curve is given in Table 2.

In the course of pH titration, exfoliation of the crystals has been observed, as has been noted for the titration with *n*-propylamine [5] (Fig. 1b). Degradation of crystallinity was seen in X-ray patterns, and a definite correlation between the titration curve and the amount of each solid phase became ambiguous.

Uptake of Cu(II) into the α -ZrP-ethylamine intercalate

Table 3 shows that the uptake of Cu(II) increased with an increase in ethylamine concentration during intercalation, although stoichiometric relation is not present between amount of both species. This may suggest

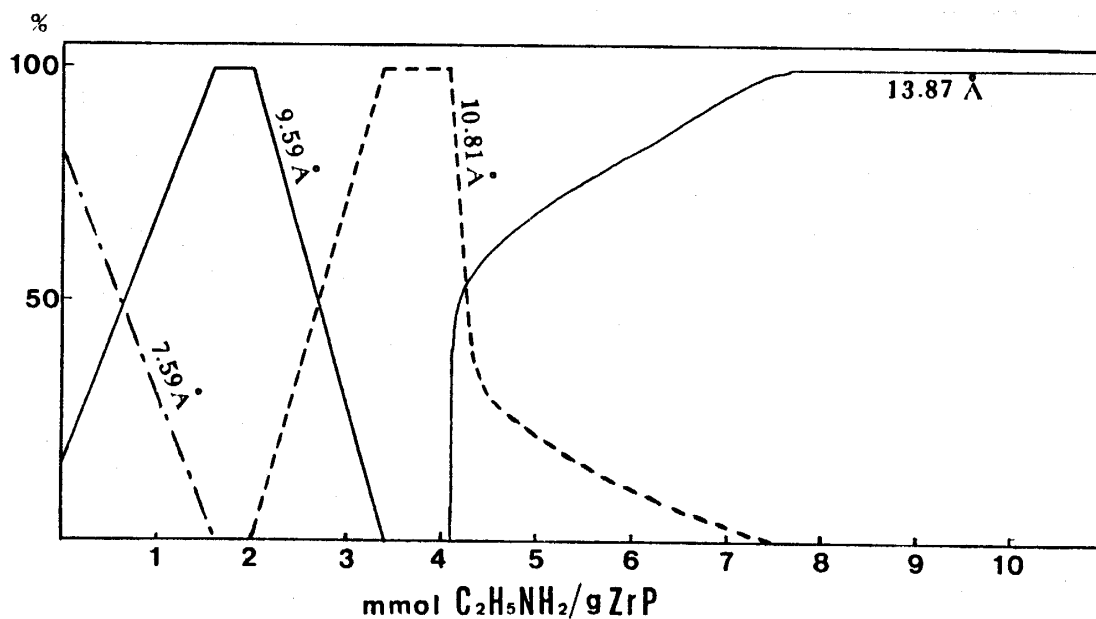


Fig. 3. Variation of composition of solid phases during titration.

Table 2. Chemical composition of intercalates at three points of the titration curve.

Point shown in the curve	Chemical composition
A	$\text{Zr}(\text{HPO}_4)_2(\text{C}_2\text{H}_5\text{NH}_2)_{0.44} \cdot 0.99\text{H}_2\text{O}$
B	$\text{Zr}(\text{HPO}_4)_2(\text{C}_2\text{H}_5\text{NH}_2)_{1.1} \cdot 0.77\text{H}_2\text{O}$
C	$\text{Zr}(\text{HPO}_4)_2(\text{C}_2\text{H}_5\text{NH}_2)_{1.6} \cdot 0.76\text{H}_2\text{O}$

Table 3. Relative uptake of Cu(II) as a function of amine amount added to α -ZrP.

Sample No.*	$\text{C}_2\text{H}_5\text{NH}_2$ amount added to α -ZrP/mmol	Relative uptake of Cu(II)
α -ZrP	0	1.00
III	1.82	1.02
VIII	4.03	1.09
XII	6.05	1.21

* Samples in this table are those of different series of experiments from Table 1.

that the pillaring of the interlayer by ethylamine is effective to some extent. On the other hand, the degree of crystallinity is degraded on uptake of the metal, and further, the interlayer distance reduced a little.

When the ethylamine complex of Cu(II) was ion-exchanged on α -ZrP, the interlayer distance expanded from 7.6 Å to 14.9 Å, whereas the diffraction pattern did not show any change in case that Cu(II) ions exchanged on α -ZrP. These observations may suggest that the Cu(II) ions taken up

into the interlayer space of the intercalate do not form the same ethylamine complex as that in aqueous solution, but ion-exchanged with remaining hydroxyl protons of phosphate groups.

In order to obtain further information on the coordination environment of Cu(II), the X-ray absorption techniques (XANES and EXAFS) have been applied. Figure 4 shows the Cu K-edge XANES spectra of four samples including N-coordinated and O-coordinated metal atoms, respectively. The profile of XANES spectra is known to be very sensitive to coordination environment of the absorber atom, in this case, copper. The spectra can be classified into two groups, *i.e.*, one is the Cu(II)-loaded intercalate (A) and the Cu(II)-loaded α -ZrP (B), another being the Cu(II)-ethylamine complex-loaded α -ZrP (C) and the pure complex (D). In the

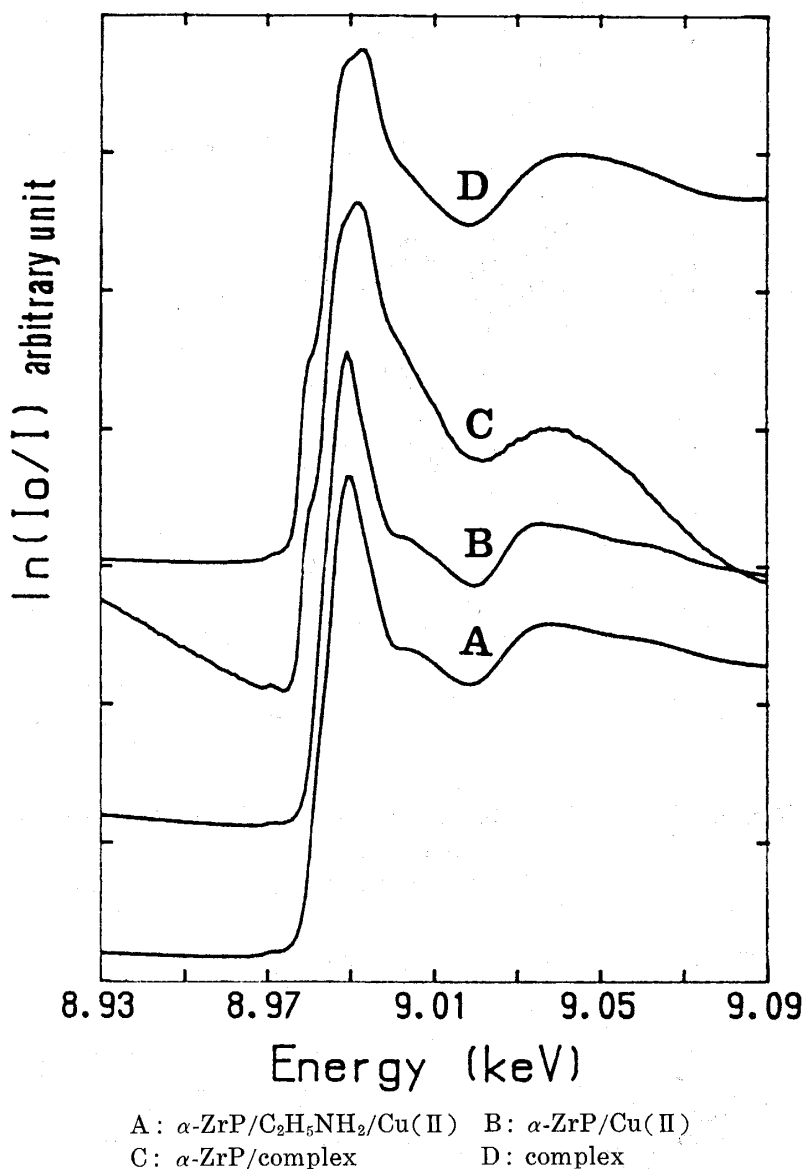


Fig. 4. Cu K-edge XANES spectra of intercalates and reference complex compound.

Cu(II)-loaded α -ZrP, Cu(II) ions are located close to O^- active sites, while in the latter group, Cu(II) ions are coordinated to N atoms of amine. XANES spectra suggest that Cu(II) ions in the Cu(II)-loaded intercalate have a similar coordination environment to those in the ion-exchanged α -ZrP.

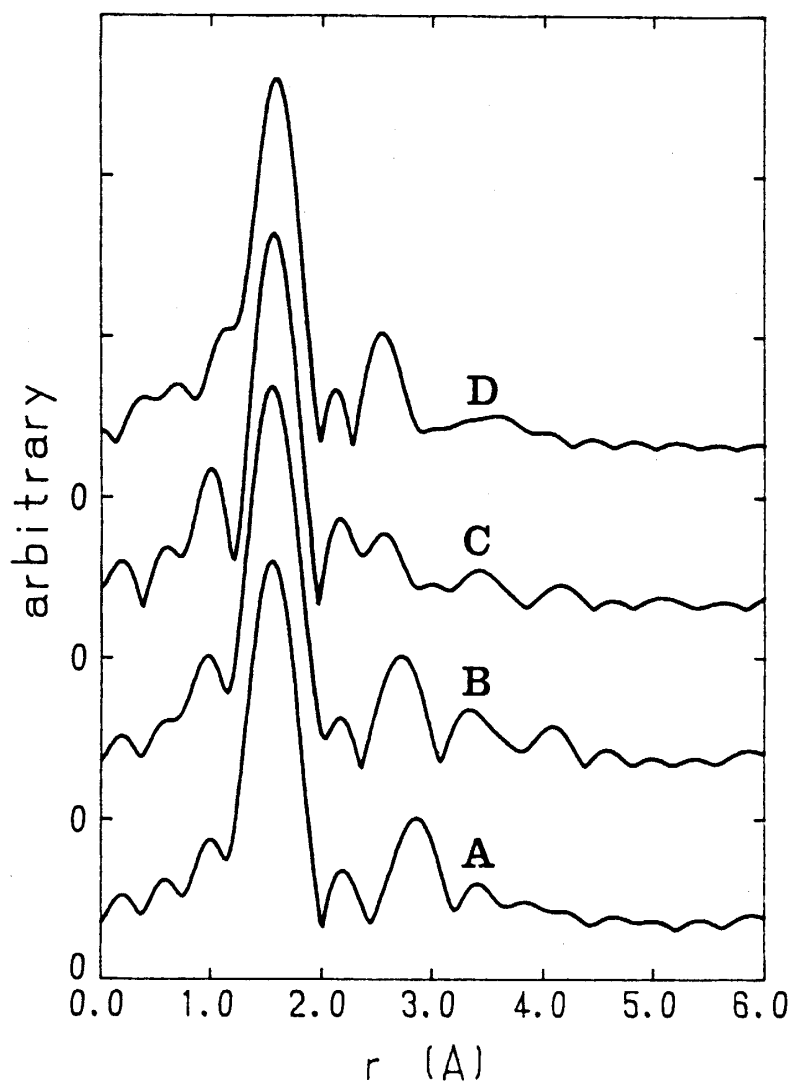


Fig. 5. Fourier transform of Cu K-edge EXAFS of intercalates and reference complex compound.

Symbols for samples are same as those in Fig. 4.

Table 4. Structure parameter obtained by curve-fitting.

Sample	$r/\text{\AA}$	σ	Bonding
α -ZrP/C ₂ H ₅ NH ₂ /Cu(II)	1.97	0.024	Cu-O
α -ZrP/Cu(II)	1.97	0.063	Cu-O
α -ZrP/Cu-C ₂ H ₅ NH ₂ complex	2.00	0.010	Cu-N
Cu-C ₂ H ₅ NH ₂ complex	2.00	0.024	Cu-N

The k^3 weighted EXAFS oscillation curve, $k^3\chi(k)$, where k is the wave number of the ejected K-shell photoelectron, was Fourier transformed, giving rise to the modified radial distribution function $F(r')$ in distance (r') space, as is given in Fig. 5. The abscissa is not corrected for the phase shifts in the figure, and the interaction shown should be read as relative values. The lowest peak is ascribed to interactions between a Cu(II) ion and the nearest neighbor atom coordinated. Coordination number of 4 was assumed for Cu(II) ions, and structural parameters of each coordination obtained by curve-fitting applied to Fourier-filtered spectra are given in Table 4. The results are reasonably interpreted as those qualitatively shown for XANES profiles, *i.e.*, the Cu(II) ions between layers of the ethylamine intercalated α -ZrP are coordinated to O⁻ active sites rather than N atoms of the amine.

Acknowledgement

The authors are deeply indebted to Mr. Kenji Matsumoto of Nissei Sangyo Co., Ltd. for his help in taking SEM photograph.

References

- [1] J. M. Troup and A. Clearfield: *Inorg. Chem.*, **16** (1977), 3311.
- [2] G. Alberti and E. Torracca: *J. Inorg. Nucl. Chem.*, **30** (1968), 317.
- [3] J. P. Gupta and D. V. Nowell: *J. Chem. Soc. Dalton*, (1979), 1178.
- [4] A. Clearfield and A. S. Medina: *J. Phys. Chem.*, **75** (1971), 3750.
- [5] G. Alberti and U. Costantino: "*Intercalation Chemistry*" (1982) ed. by M. S. Whittingham and A. J. Jacobson, Ch. 5, Academic Press.