  Bull. Chem. Soc. Jpn., 56, 3287—3290 (1983)

Extended X-Ray Absorption Fine Structure Studies in Some Aqueous Copper(II) Solutions

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(Received May 23, 1983)

With a laboratory EXAFS apparatus consisting of a usual X-ray generater, an LiF crystal, and a position sensitive X-ray detector with a self-scanning photodiode array, EXAFS spectra were obtained for aqueous $[Cu(NH_3)_4]SO_4$, $[Cu(en)_2]Cl_2$ (en=ethylenediamine), and $CuSO_4$ solutions. By reference to similar spectra of the corresponding crystals, the solution spectra were analyzed by the curve-fitting method. The values obtained for the distances between the metal and its first-shell atoms in the ammine and sulfate solutions are 2.03 (±0.02) and 1.98 (±0.03) Å, in accordance with those derived from the X-ray diffraction experiments. The Cu-N distance of $[Cu(en)_2]^{2+}$ in solution is 2.02 or 2.04 (±0.02) Å. These values obtained for the solutions are very close to those of corresponding solid complexes.

The chemistry of electrolyte solutions has made a great progress with the development of new methods such as nmr and laser-Raman spectroscopies and X-ray and neutron diffractions. Extended X-ray absorption fine structure (EXAFS) has also given significant information about the species dissolved in solution and become one of the most powerful techniques to study the local environment of the concerned atom.[1-3] However, there are some experimental difficulties in an EXAFS measurement, in which the total absorption coefficient, $\mu(E)$, must be measured with high accuracy. We have developed a laboratory apparatus utilizing a position sensitive detector to measure all the absorption coefficient at one time to improve the data collection efficiency.[4-5] In our previous EXAFS study[4] of the hydrated Cu^{2+} ion using a laboratory system equipped with a position sensitive photodiode array, the spectra was of low signal-to-noise ratio and their Fourier functions were not sufficiently reliable.[6] Thus we improved the apparatus by changing the electronic circuit of the preamplifier, adjusting the timing of the AD converter, cooling the SSPA, and so on, and used it in an EXAFS study of the aqueous cyanocuprate(I) solutions.[7] This paper is concerned with the EXAFS study of some aqueous copper(II) solutions on the laboratory EXAFS apparatus with position sensitive photodiode array. The purpose of the present study is to check the accuracy of obtained structual parameters as well as to compare the bond lengths of the species in solution with the solid complexes.

X-ray diffraction studies of aqueous solutions containing a copper(II) compound have been made by Ohtaki *et al.* (perchlolate,[8] the ammine complex,[9] and the ethylenediamine complex[10]), Wertz[11] (some chloride solutions), and Magini[12] (perchlolate, sulfate, and chloride). The EXAFS study for aqueous copper(II) perchlorate solution reported by Sham *et al.*[3] gave results in agreement with those from the X-ray diffraction studies. Lagarde *et al.*[1] studied $CuBr_2$ solutions of various concentrations reported that the local order of Cu^{2+} and Br^- ions at high concentration and is close to that found in the solid.

Experimental

The laboratory EXAFS system consists of three parts: a usual X-ray generater, an LiF crystal, and a position sensitive detector with a self-scanning photodiode array (SSPA). This is schematically shown in Fig. 1. We used a tungsten sealed X-ray tube (Philips fine focus tube, 1.5 kW) as the X-ray source, which was operated with a conventional X-ray power supply (Rigaku Co. Ltd., 1.5 kW) mostly with 25 mA at 17 kV. The generated continuous X-ray beam (uncollimated) is dispersed according to the Bragg condition by the LiF(200) crystal mounted on a goniometer. The SSPA (512 K MEL Matsushita Co. Ltd.) for one-dimensional X-ray detection consists of 512 photodiodes and MOS switches without pyrex window and has the total effective length of 14.4 mm (28 μm/channel); X-rays of different wavelengths can be detected by different channels of SSPA. The analog signal from SSPA is amplified, digitalized by an AD converter (Osaka Dempa Co. Ltd.), and transferred to the memory of a micro-computer (Sord M-100 ACE IV). The same type of the laboratory EXAFS system was used in our previous study.[7] A performance test has been carried out with Cu foil; Figure 2 shows the Cu *K* absorption spectrum for one-hour measurement at the condition of 17 kV and 25 mA. Except that

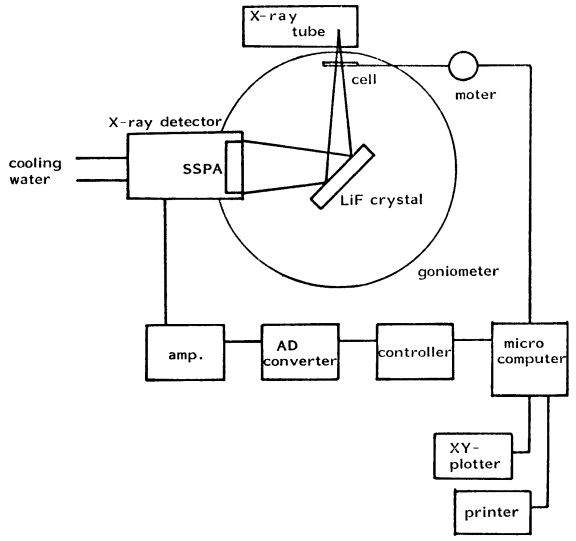

Fig. 1. The block diagram of the laboratory EXAFS system with a position sensitive photodiode array.

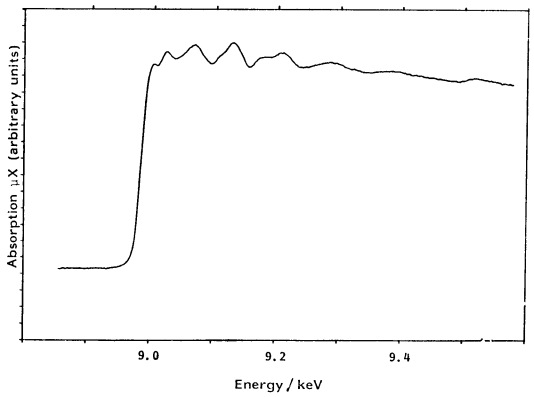

Fig. 2. X-Ray absorption spectrum of Cu-foil.

the spectrum shows a "glitch" at 9.52 keV from characteristic X-rays of W $L\beta_4$, it is comparable to that from other experiments.

The spectrum ($\mu X = \ln[(I_0 - I_d)/(I_s - I_d)]$) of each solution was obtained by measuring, in sequence and repeatedly, the beams transmitted by the sample (I_s) and by water (I_0) and the dark current without X-ray (I_d). Each step of the measurement was controlled by a micro-computer, which drives the cells at appropriate time intervals. A plastic cell contained a small volume of the sample solution between mylar windows spaced 0.6—1.0 mm apart. The solid sample was well grounded and deposited to scotch-tape.

Copper(II) sulfate and bis(ethylenediamine)copper(II) solutions were prepared by dissolving the corresponding copper salts in distilled water. The ammine solution was prepared by dissolving $[Cu(NH_3)_4]SO_4 \cdot H_2O$ in aqueous ammonia (0.14 M).† The known stability constants show that the main species contained in these solutions are $[Cu(H_2O)_6]^{2+}$ for the sulfate, $[Cu(en)_2]^{2+}$ for the ethylenediamine, and $[Cu(NH_3)_4]^{2+}$ for the ammonia solutions. The concentrations of copper ion were determined by titration with EDTA; 0.297 and 1.181 M for the sulfate, 0.321 M for the ammine, and 0.380 M for the ethylenediamine solutions.

Results and Discussion

The EXAFS spectrum $k^2\chi(k)$, in the k space, of crystalline bis(ethylenediamine)copper(II) salt ($[Cu(en)_2]Cl_2 \cdot 2H_2O$) is shown in Fig. 3 which was derived from the absorption spectrum. Fig. 4 shows the results of Fourier transformation from the k space to the r space; the transformation is applied to the $k^2\chi(k)$ values in the k range of 3.4—9.0 (Å^{-1}). The radial distribution curve shows two peaks, of which the larger one should corresponds to the N atoms of the coordinated ethylenediamine ligands and the smaller one may be due to the C atoms of the ligands.

The curve-fitting analysis was performed according to the method of Cramer *et al.*[13] using the following the formula for $k^2\chi(k)$:

$$k^2\chi(k) = c_0 N r^{-2} \exp(-c_1 k^2) k^{c_2} \sin[a_0 + (a_1 + 2r)k + a_2 k^2], \quad (1)$$

where N and r represent the coordination number and the interatomic distance, respectively, and c_0, c_1, and c_2 are the parameters for amplitude functions and

† 1 M = 1 mol dm^{-3}.

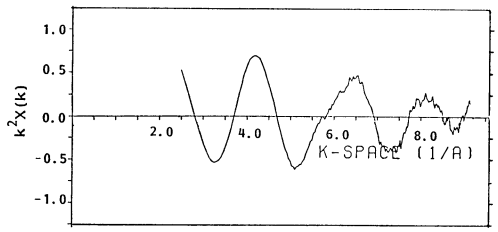

Fig. 3. EXAFS spectrum of $[Cu(en)_2]Cl_2 \cdot 2H_2O$.

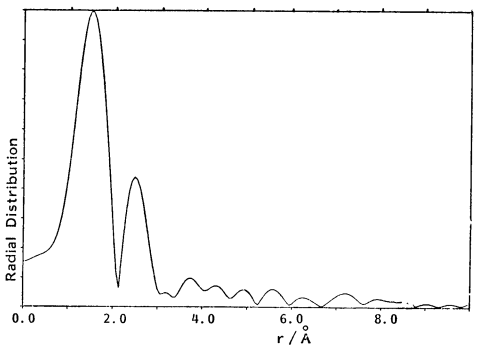

Fig. 4. Fourier transformation of the EXAFS spectrum (Fig. 3).

Table 1. Cross-check of the results of least-squares fit to EXAFS data for crystalline $[Cu(NH_3)_4]SO_4 \cdot H_2O$ and $[Cu(en)_2]Cl_2 \cdot 2H_2O$

	Coordination number	Cu-N distance / Å
$[Cu(NH_3)_4]SO_4 \cdot H_2O$	4.01±0.73 (4.0)	2.03±0.02 (2.05) a)
$[Cu(en)_2]Cl_2 \cdot 2H_2O$	3.91±0.70 (4.0)	2.04±0.02 (2.03) b)

a) Obtained with parameters derived from EXAFS of the en complex. (The values in parentheses are the results of an X-ray diffraction study.[15]) b) Obtained with parameters derived from EXAFS of the ammine complex. (The values in parentheses are the results of an X-ray diffraction study.[14])

a_0, a_1, and a_2, the phase shift parameters. To determine the parameter values, we first examined the spectra of crystalline $[Cu(NH_3)_4]SO_4 \cdot H_2O$ and $[Cu(en)_2]Cl_2 \cdot 2H_2O$ of which the structures are known ($r_{Cu-N} = 2.05$ Å[14] for ammine-N and $r_{Cu-N} = 2.03$ Å[15] for ethylenediamine-N and $N = 4$ for both complexes). With fixed N and r, we obtained two sets of six parameters by curve-fitting the Fourier-filtered spectra for the isolated Cu–N interaction. For checking the accuracy of the analysis, the least-squares fit to the EXAFS spectrum of $[Cu(en)_2]Cl_2 \cdot 2H_2O$ was carried out in the range of $k = 3.8$—8.6 (Å^{-1}) with the set of parameters obtained above from the EXAFS spectrum of $[Cu(NH_3)_4]SO_4 \cdot H_2O$; the determined coordination number (N) and atomic distances (r_{Cu-N}) are shown in Table 1. On the other hand, the N and r_{Cu-N} values of the latter complex were obtained from the analysis of its EXAFS spectrum with the set of parameter values derived from the spectrum of the former (Table 1). The obtained values are within

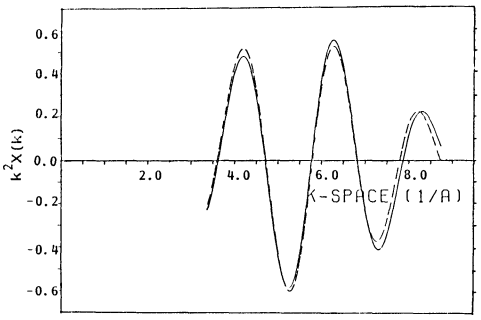

Fig. 5. First-shell fit for structure determination of an aqueous $[Cu(en)_2]^{2+}$ solution by use of a set of parameters obtained from the spectrum of solid $[Cu(NH_3)_4]SO_4 \cdot H_2O$. The solid line is the filtered EXAFS spectrum and dashed line is the least-squares fit.

Table 2. Results of curve-fitting analyses of aqueous $[Cu(NH_3)_4]^{2+}$ (0.32 M) and $[Cu(en)_2]^{2+}$ (0.38 M) solutions

	Set of parameters	Coordination number	Cu–N distance Å
$[Cu(NH_3)_4]^{2+}$	A	4.19±0.70	2.03±0.02
	B	4.24±0.71	2.02±0.02
$[Cu(en)_2]^{2+}$	A	4.59±0.72	2.04±0.02
	B	4.73±0.73	2.02±0.02

A: Parameters obtained from the spectrum of solid $[Cu(NH_3)_4]SO_4 \cdot H_2O$. B: Parameters obtained from the spectrum of solid $[Cu(en)_2]Cl_2 \cdot 2H_2O$.

the experimental error of those of X-ray diffraction analyses. This demonstrates that the analysis adopted here gives a reliable structural information.

Then we determined the structure parameters of the ammine and ethylenediamine complexes of copper(II) in aqueous solutions with both sets of parameters. The Fourier-filtered and least-squares fit curves are shown in Fig. 5 for a solution of ethylenediamine copper(II) chloride; a set of parameters obtained from the spectrum of solid $[Cu(NH_3)_4]SO_4 \cdot H_2O$ was used in the analysis. The numerical results are summarized in Table 2. Analyses with two different sets of parameters gave results in good agreement with each other. Obtained coordination numbers are about four and Cu–N distances are about 2.03 Å for both solutions;[16] these values are close to those for solid complexes. The values of ammine solution are also in good agreement with the results of Ohtaki *et al.*[9] for the concentrated aqueous solutions of ammine copper(II) salt by X-ray diffraction technique (coordination numbers of 4 and the Cu–N distances of 2.03 Å for the $[Cu(NH_3)_4]^{2+}$ solution). However, our r_{Cu-N} value (2.03 Å) for $[Cu(en)_2]^{2+}$ solutions is significantly larger than Ohtaki's (1.93 Å).[10] This inconsistency need to be further investigated by measurements of higher accuracy and precision. Generally speaking, however, the EXAFS method as applied to solutions has the advantage that it detects only the interatomic interactions in which the copper atom (or any other atom concerned) is involved, whereas the X-ray diffraction method gives a diffraction pattern which is the superposion of various diffractions by different pairs of atoms at different distances. One of the disadvantage of the EXAFS method is that the determination of interatomic distances include the estimation of the phase-shift parameter which cannot be predicted by the theory with satisfactory precision and was obtained here by an empirical method.

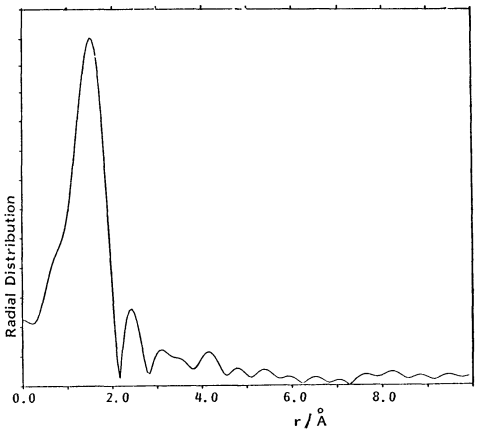

Fig. 6. Fourier transformation of the EXAFS spectrum of solid $CuSO_4 \cdot 5H_2O$.

Table 3. Results of curve-fitting analysis of aqueous $CuSO_4$ solutions

	Coordination number	Cu–O distance Å
0.30 M $CuSO_4$	4.25±0.57	1.98±0.03
1.18 M $CuSO_4$	4.13±0.57	1.98±0.03

Figure 6 shows the radial distribution from Fourier transformation of EXAFS for solid $CuSO_4 \cdot 5H_2O$, giving only one peak which corresponds to the Cu–O_{eq} interaction. Satelite at a distant position (2.3 Å) is doubtful to be a peak corresponding to Cu–O_{ax} because Fourier transformation may ripple beside the peak. Absence of the evidence for the second-nearest neighbour (O_{eq} at 2.4 Å) in the EXAFS spectrum has also been reported by Joyner.[17] To determine the Cu–O distances in solution, curve-fitting analysis was carried out using a set of parameters from solid $CuSO_4 \cdot 5H_2O$ (Cu–O=1.97 Å).[18] Table 3 shows the results for the structure parameters of two aqueous $CuSO_4$ solutions. The distance obtained is about 1.98 Å for both solutions, which generally agrees with the value from X-ray diffraction studies[8,12] within experimental error.

Concluding Remarks

An EXAFS study was carried out for aqueous solutions of some copper compounds with a position sensitive photodiode array, with which good spectra were easily obtained. The bond distance and coordination number obtained by curve-fitting method are 2.03 Å

and 4—5 for aqueous $[Cu(NH_3)_4]^{2+}$ and $[Cu(en)_2]^{2+}$ solutions. For $CuSO_4$ solutions, $Cu-O_{eq}$ is 1.98 Å and the first coordination sphere contains 4 O atoms. These results are very close to those of corresponding solid complexes.

This work was supported in part by a Grant-in-Aid from the Mitsubishi Fundation.

References

1) P. Lararde, A. Fontaine, D. Raoux, A. Sadoc, and P. Migliardo, *J. Chem. Phys.*, **72**, 3061 (1980); A. Fontaine, P. Lagarde, D. Raoux, M. P. Fontana, G. Maisano, P. Migliardo, and F. Wanderlingh, *Phys. Rev. Lett.*, **41**, 504 (1978).

2) T. K. Sham, J. B. Hastings, and M. L. Perlman, *J. Am. Chem. Soc.*, **102**, 5904 (1980).

3) J. Goulon, C. Goulon-Ginet, and M. Chabanel, *J. Solution Chem.*, **10**, 647 (1981).

4) M. Sano, K. Taniguchi, and H. Yamatera, *Chem. Lett.*, **1980**, 1285.

5) The same type of apparatus has been reported by following papers; H. Maeda, H. Terauchi, K. Tanabe, N. Kamijo, M. Hida, and H. Kawamura, *Jpn. J. Appl. Phys.*, **21**, 1342 (1982); M. Nomura, K. Asada, U. Kaminaga, T. Matsushita, K. Kohra, and H. Kuroda, *Bull. Chem. Soc. Jpn.*, **55**, 3911 (1982); K. Taniguchi, N. Yamaki, and S. Ikeda, to be published.

6) The first peak of the radial function can undoubtedly be attributed to the first H_2O shell, but the second peak was not sufficiently strong and cannot definitely be distinguished from the noise.

7) M. Sano, T. Maruo, and H. Yamatera, *Chem. Phys. Lett.*, in press.

8) H. Ohtaki, M. Maeda, and S. Ito, *Bull. Chem. Soc. Jpn.*, **47**, 2217 (1974); H. Ohtaki, T. Yamaguchi, and M. Maeda, *Bull. Chem. Soc. Jpn.*, **49**, 701 (1976).

9) T. Yamaguchi and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **52**, 415 (1979).

10) H. Ohtaki, *Rev. Inorg. Chem.*, **4**, 103 (1982).

11) J. R. Bell, J. L. Tyvoll, and D. L. Wertz, *J. Am. Chem. Soc.*, **95**, 1456 (1973); D. L. Wertz and J. L. Tyvoll, *J. Inorg. Nucl. Chem.*, **36**, 3713 (1974).

12) M. Magini, *J. Chem. Phys.*, **74**, 2523 (1981); *Inorg. Chem.*, **21**, 1535 (1982); A. Musinu, G. Paschina, G. Piccaluga, and M. Magini, *ibid.*, **22**, 1184 (1983).

13) S. P. Cramer, K. O. Hodgson, E. I. Stiefel, and N. E. Newton, *J. Am. Chem. Soc.*, **100**, 2748 (1978).

14) F. Mazzi, *Acta Crystallogr.*, **8**, 137 (1955).

15) Y. Komiyama and E. C. Lingafelter, *Acta Crystallogr.*, **17**, 1145 (1964).

16) The obtained values of coordination number, especially for the ethylenediamine case, indicate the possibility of partial five coordination of Cu^{2+} with an additional SO_4^{2-} or H_2O ligand. Further investigations are needed for the confirmation.

17) R. W. Joyner, *Chem. Phys. Lett.*, **72**, 162 (1980).

18) G. E. Bacon and N. A. Curry, *Proc. R. Soc. London*, **266**, 95 (1962).