

Structure of copper(II)–bpy and –phen complexes: EXAFS and spectrophotometric studies on the structure of copper(II) complexes with 2,2'-bipyridine and 1,10-phenanthroline in aqueous solution

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Abstract

The structure of copper(II) complexes with 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) in aqueous solution has been studied by EXAFS and spectrophotometric methods. The EXAFS data and electronic spectra for solutions containing $[\text{Cu}(\text{bpy})]^{2+}$, $[\text{Cu}(\text{bpy})_2]^{2+}$ and $[\text{Cu}(\text{bpy})_3]^{2+}$ complexes as the main species, respectively, showed that the mono(2,2'-bipyridine)copper(II) complex has an axially elongated octahedral structure with four additional water molecules and the tris(2,2'-bipyridine)copper(II) complex also has a distorted octahedral structure. On the other hand, the bis(2,2'-bipyridine)copper(II) complex has a five-coordinate trigonal bipyramidal structure with an additional water molecule. It was also shown that the structure of the mono- and tris(1,10-phenanthroline)copper(II) complexes is axially elongated octahedral similar to the relevant 2,2'-bipyridine complexes. The structure of the bis(1,10-phenanthroline)copper(II) complex was not determinable by the present transmission mode EXAFS experiment because of its very low solubility in water.

Introduction

Complex formation reactions of metal ions with 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) have been studied extensively in water [1]. As to the copper(II) complexes, the bis-type complexes are of stereochemical interest since the complexes usually have a five-coordinate structure owing to the steric repulsion between hydrogen atoms on the carbon atoms adjacent to nitrogen atoms in one ligand and those in another [2].

Many $[\text{CuX}(\text{bpy})_2]^+$ type complexes with mono-valent anions ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$) have been isolated and their five-coordinate structure has been confirmed crystallographically [3–8]. The trigonal bipyramidal $[\text{Cu}(\text{bpy})_2(\text{H}_2\text{O})]^{2+}$ complex has also been observed in crystal [5, 9], as well as the corresponding $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})]^{2+}$ complex [10, 11]. The Cu–O bond lengths within the former complexes are 215.8 and 205.0 pm and longer distances of 218 and 223.8 pm [5, 9] have been reported for the latter [10, 11], depending on the counter anions employed. The structure determination in aqueous solution is thus desirable without any effect of the counter anions. A similar five-coordinate structure of the bis(2,2'-

bipyridine)copper(II) complex in *N,N*-dimethylformamide has been proposed on the basis of the thermodynamic quantities and electronic spectra [12].

The structure of the tris(2,2'-bipyridine)- and tris(1,10-phenanthroline)copper(II) complexes has also been investigated crystallographically [13, 14]. Both complexes have an axially elongated octahedral structure. The distortion from a regular octahedron is different between the two complexes. The equatorial Cu–N bond lengths in the two complexes are similar and are 203.1 and 204 pm, respectively. On the other hand, two axial Cu–N bonds of unequal distances of 226.6 and 245.0 pm were observed for the former [13] and of equal lengths of 233 pm for the latter [14].

Structural data of the copper(II) complexes with 2,2'-bipyridine and 1,10-phenanthroline in crystal have so far been accumulated as well as their thermodynamic quantities in aqueous solution. However, the thermodynamic quantities of the complexes will be better interpreted on the basis of their structures in aqueous solution. The structure of the mono-(2,2'-bipyridine)- and mono(1,10-phenanthroline)copper(II) complexes has never been investigated. In the present paper we report the structure of the copper(II) complexes with 2,2'-bipyridine and 1,10-phenanthroline studied by the EXAFS method

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in aqueous solution. The structure parameters of the complexes are discussed in connection with their thermodynamic quantities in aqueous solution. Spectrophotometric measurements were also carried out to obtain additional information of individual complexes present in solution. The structure of the bis(1,10-phenanthroline)copper(II) complex was not determinable by the present transmission mode EXAFS experiment because of its very low solubility in water.

Experimental

Reagents

All chemicals used were of reagent grade. Copper(II) nitrate was recrystallized once from water. 2,2'-Bipyridine, 1,10-phenanthroline and potassium nitrate were used without further purification.

Preparation of solutions

Six test solutions were prepared for EXAFS measurements. Solution NO3 was an aqueous copper(II) nitrate solution, which contains the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ion. Solutions BPY1, BPY2 and BPY3 were prepared by dissolving copper(II) nitrate and 2,2'-bipyridine in water at suitable $C_{\text{bpy}}/C_{\text{Cu}}$ mole ratios. Solutions PHEN1 and PHEN3 were similarly prepared by using 1,10-phenanthroline instead of 2,2'-bipyridine. The composition of the solutions is listed in Table 1.

EXAFS measurements

EXAFS spectra were measured around the copper K edge in transmission mode using BL10B station at the Photon Factory of the National Laboratory for High Energy Physics [15]. Monochromatized X-rays were obtained by an Si(311) channel-cut crystal.

The absorbance is obtained as $\ln(I_0/I)$, where I and I_0 are X-ray intensities with and without a sample, respectively. The intensities I_0 and I were simultaneously measured by ionization chambers filled with N_2 and $\text{N}_2(50\%) + \text{Ar}(50\%)$ gas, respectively.

A filter paper was immersed in a sample solution and then sealed in a polyethylene bag in order to

prevent evaporation of water. An effective jump at the absorption edge was obtained by changing the number of filter papers. In order to examine the reproducibility of the results, measurements were repeated twice over the whole range.

Analysis of EXAFS data

Background absorption other than that for the K edge of the copper atom was estimated by least-squares fitting Victoreen's formula [16] to the pre-edge and was subtracted from the total absorption by extrapolation. The smooth K shell absorption μ_0 due to an isolated atom was evaluated by fitting a smooth curve to the observed absorption spectrum using a sixth-order polynomial function.

The EXAFS pattern $\chi(k)$ was then extracted and normalized by the following equation

$$\chi(k) = \{\mu(k) - \mu_0(k)\} / \mu_0(k) \quad (1)$$

where k is the photoelectron wave vector ejected and given as $\{2m(E - E_0)\}^{1/2}/\hbar$. E represents the energy of the incident X-rays and E_0 is the threshold energy of a K shell electron. The E_0 value was selected as the position of the half-height of the edge jump in each sample. The $k^3\chi(k)$ values were converted to the radial distribution $F(r)$ as

$$F(r) = 1/2\pi^{1/2} \int_{k_{\min}}^{k_{\max}} k^3 [\chi(k)] [W(k)] [\exp(-2ikr)] dk \quad (2)$$

$W(k)$ is the window function of the Hanning type [17].

A curve fitting procedure in the k space for the refinements of structure parameters was applied to the Fourier filtered $k^3\chi(k)_{\text{obs}}$ values to minimize the error-square sum U .

$$U = \sum k^6 (\chi(k)_{\text{obs}} - \chi(k)_{\text{calc}})^2 \quad (3)$$

The model function $\chi(k)_{\text{calc}}$ is given by the single-electron and single-scattering theory as [18–21]

$$\chi(k)_{\text{calc}} = \sum \{n_j / (kr_j^2)\} \exp(-2\sigma_j^2 k^2 - 2r_j/\lambda) F_j(\pi, k) \times \sin(2kr_j + \alpha_j(k)) \quad (4)$$

where $F_j(\pi, k)$ is the backscattering amplitude from each of n_j scatterers j at distance r_j from the X-ray absorbing atom. σ_j^2 is the mean square displacement of the equilibrium distance r_j and λ is the mean free path of the photoelectron ejected. $\alpha_j(k)$ is the total scattering phase shift experienced by the photoelectron. The values of $F_j(\pi, k)$ and $\alpha_j(k)$ in eqn. (4) were taken from tables reported by Teo and Lee [22]. In the fitting procedures the parameters E_0 and λ were first determined from the standard sample (an aqueous copper(II) nitrate solution containing $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$) and then they were used as constants

TABLE 1. The composition (mol dm^{-3}) of sample solutions for EXAFS measurements

Solution	C_{Cu}	C_{bpy}	C_{phen}	$C_{\text{L}}/C_{\text{Cu}}$
NO3	0.995			0
BPY1	0.504	0.506		1.00
BPY2	0.193	0.396		2.05
BPY3	0.109	0.327		3.00
PHEN1	0.200		0.151	0.755
PHEN3	0.118		0.355	3.01

in the course of the structural analysis of unknown samples, while r , σ and n values were optimized as variables.

Spectrophotometric measurements

Electronic spectra were measured by a UV-2000 spectrophotometer (Shimadzu) equipped with a PC-9801VX computer (NEC), which recorded absorbance data in 1 nm intervals over the wavelength range 300–900 nm. All test solutions contained 0.1 mol dm⁻³ KNO₃ as an inert constant ionic medium. A flow cell with a pathlength of 0.5 cm was connected to a titration vessel through Teflon and glass tubes. A solution containing copper(II) nitrate was placed in a vessel and then titrated with a 0.1 mol dm⁻³ ligand (bpy or phen) solution containing 0.1 mol dm⁻³ HNO₃. Spectrophotometric data at selected 40 wavelengths over the range 350–850 nm were employed for the least-squares calculation.

Electronic spectra of sample solutions for the EXAFS measurements were also recorded by using a cell with a pathlength of 0.1 or 0.01 cm. Absorbance data at the above 40 wavelengths were used to determine the distribution of species in EXAFS sample solutions.

Analysis of spectrophotometric data

The overall formation of the [Cu_oL_pH_q]^{(2o+q)+} complex (L=bpy or phen) can be defined as eqns. (5) and (6).



$$\beta_{opq} = [\text{Cu}_o\text{L}_p\text{H}_q^{(2o+q)+}] / [\text{Cu}^{2+}]^o [\text{L}]^p [\text{H}^+]^q \quad (6)$$

The absorbance measured in the solution l at a given wavelength λ_m is expressed by using the overall formation constants β_{opq} and the molar absorption coefficients $\epsilon_{opq}(\lambda_m)$ of [Cu_oL_pH_q]^{(2o+q)+} as eqn. (7).

$$A_{lm} = \sum \sum \sum \epsilon_{opq}(\lambda_m) \beta_{opq} [\text{Cu}^{2+}]_l^o [\text{L}]_l^p [\text{H}^+]_l^q + \epsilon_{\text{Cu}}(\lambda_m) [\text{Cu}^{2+}]_l + \epsilon_{\text{L}}(\lambda_m) [\text{L}]_l \quad (7)$$

The concentrations of free Cu²⁺, L and H⁺ are related to their total concentrations, $C_{\text{Cu},l}$, $C_{\text{L},l}$ and $C_{\text{H},l}$ in the solution l by the mass-balance eqns. (8)–(10), respectively.

$$C_{\text{Cu},l} = [\text{Cu}^{2+}]_l + \sum \sum \sum o \beta_{opq} [\text{Cu}^{2+}]_l^o [\text{L}]_l^p [\text{H}^+]_l^q \quad (8)$$

$$C_{\text{L},l} = [\text{L}]_l + \sum \sum \sum p \beta_{opq} [\text{Cu}^{2+}]_l^o [\text{L}]_l^p [\text{H}^+]_l^q \quad (9)$$

$$C_{\text{H},l} = [\text{H}^+]_l + \sum \sum \sum q \beta_{opq} [\text{Cu}^{2+}]_l^o [\text{L}]_l^p [\text{H}^+]_l^q - K_w / [\text{H}^+]_l \quad (10)$$

K_w represents the autoprotolysis constant of the solvent.

Molar absorption coefficients of the complexes were determined by minimizing $\sum \sum (A_{lm,\text{obs}} - A_{lm,\text{calc}})^2$ on the basis of the formation constants reported in the literature [1].

Results and discussion

Electronic spectra

Figure 1 shows electronic spectra measured with varying both 2,2'-bipyridine and hydrogen ion concentrations in aqueous solution. In the Figure absorbances are normalized with a unit concentration of copper(II) ion. The absorbances first increase with increasing $C_{\text{bpy}}/C_{\text{Cu}}$ mole ratios and then gradually decrease with a further increase of the mole ratios. A similar pattern of the spectral change was also observed for the copper(II) 1,10-phenanthroline solutions.

The stability constants of the copper(II) 2,2'-bipyridine and 1,10-phenanthroline complexes have been critically reviewed by McBryde [1]. In the review the recommended values for the stability constants of copper(II) 2,2'-bipyridine and 1,10-phenanthroline complexes in aqueous solution at 25 °C are also

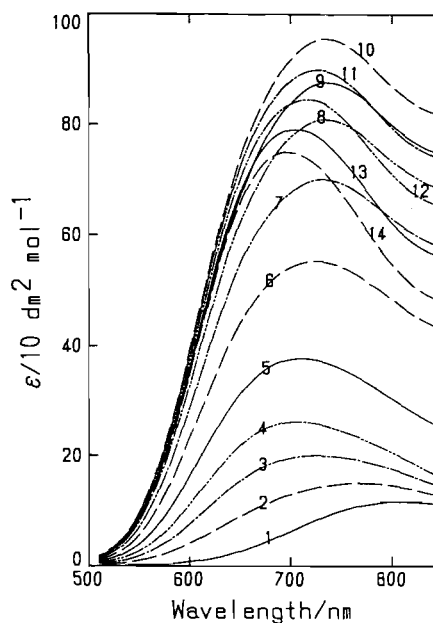


Fig. 1. Measured electronic spectra of copper(II) 2,2'-bipyridine solutions with varying bpy and hydrogen ion concentrations in the range 450–850 nm. Total concentrations C_{Cu} , C_{bpy} , C_{H} (mmol dm⁻³) in test solutions are 31.24, 0, 0 (spectrum 1); 28.92, 8.096, 7.793 (2); 26.93, 15.08, 14.51 (3); 25.19, 21.15, 20.36 (4); 23.66, 26.50, 25.50 (5); 22.31, 31.23, 30.06 (6); 21.11, 35.45, 34.12 (7); 20.02, 39.24, 37.76 (8); 19.05, 42.65, 41.05 (9); 15.31, 55.72, 53.63 (10); 33.54, 80.57, 10.79 (11); 26.69, 86.43, 30.06 (12); 20.12, 92.06, 48.55 (13); 15.39, 96.12, 61.88 (14).

given which are valid for supporting electrolyte concentration up to 0.1 mol dm^{-3} independent of electrolytes employed. Therefore, we used the values to analyze the variation of spectra. The results of the least-squares calculations and the values used are summarized in Table 2. The variation of spectra was satisfactorily reproduced as shown in the Table.

Figure 2 depicts the electronic spectra of individual copper(II) 2,2'-bipyridine and 1,10-phenanthroline complexes extracted from the measured spectral change. The absorption maxima of the $[\text{CuL}]^{2+}$ and $[\text{CuL}_3]^{2+}$ complexes become larger with increasing the number of ligand molecules within the complexes and their positions also shift to shorter wavelengths. The $[\text{CuL}]^{2+}$ and $[\text{CuL}_3]^{2+}$ complexes still show a similar spectral characteristic to that of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, suggesting that the coordination geometry around the copper(II) ion in the complexes

TABLE 2. Results of the least-squares calculation for the determination of the molar absorption coefficients of individual copper(II) 2,2'-bipyridine and 1,10-phenanthroline complexes in aqueous solution at 25°C^a

Parameters	Cu(II)-bpy	Cu(II)-phen
$\log \beta_{110}$	8.2 ^b	9.1 ^b
$\log \beta_{120}$	13.8 ^b	15.9 ^b
$\log \beta_{130}$	17.2 ^b	20.9 ^b
$\log \beta_{011}$	4.42 ^b	4.95 ^b
U^c	0.0334	0.0226
R^d	0.00795	0.0334
N^e	2000	1480

^aThe molar absorption coefficients of individual copper(II) 2,2'-bipyridine and 1,10-phenanthroline complexes were determined with uncertainties of c. 2 and 4% (three standard deviations), respectively, at peak positions. ^bTaken from ref. 1. ^cError-square sum. ^dHamilton R factor. ^eThe number of data points.

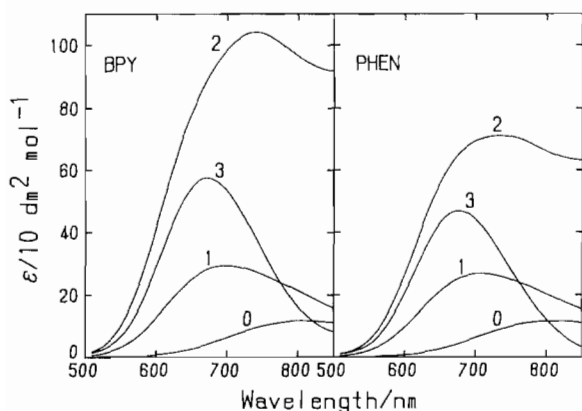


Fig. 2. Electronic spectra of individual copper(II) 2,2'-bipyridine (left side) and 1,10-phenanthroline (right side) complexes in aqueous solution. The numbers represent $[\text{CuL}_n]^{2+}$.

is similar to that in the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ion, which has an axially elongated octahedral structure [23–25]. On the other hand, the $[\text{CuL}_2]^{2+}$ complexes have a larger and broader absorption band than that for Cu^{2+} , $[\text{CuL}]^{2+}$ and $[\text{CuL}_3]^{2+}$, suggesting a different coordination structure from that of Cu^{2+} , $[\text{CuL}]^{2+}$ and $[\text{CuL}_3]^{2+}$. The structure of the bis(2,2'-bipyridine)- and bis(1,10-phenanthroline)copper(II) complexes has been reported to be five-coordinate trigonal bipyramidal with an additional water molecule in crystal [5, 9–11]. The broad band in the electronic spectra of the $[\text{CuL}_2]^{2+}$ complex is very similar to that in the reflectance spectra of the $[\text{Cu}(\text{bpy})_2(\text{H}_2\text{O})]\text{S}_5\text{O}_6$ [9] and $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})](\text{NO}_3)_2$ [10] crystals. Thus $[\text{CuL}_2]^{2+}$ in aqueous solution can be described as $[\text{CuL}_2(\text{H}_2\text{O})]^{2+}$ with a trigonal bipyramidal structure like in the solid state.

Distribution of species in sample solutions for EXAFS

On the basis of the molar absorption coefficients described in the previous section, the distribution of species present in test solutions for EXAFS measurements was correctly evaluated by a linear least-squares calculation. Absorbance data of the sample solutions for EXAFS measurements should be represented as the sum of the molar absorption coefficients of individual copper(II) complexes taking into account the mole fraction of the complexes present in solutions. A typical example for solution BPY3 is shown in Fig. 3 and the results for all solutions are summarized in Table 3.

Evidently one can expect from Table 3 that solutions BPY1, BPY2 and PHEN3 are treated as those containing only one species, i.e. the $[\text{Cu}(\text{bpy})]^{2+}$, $[\text{Cu}(\text{bpy})_2]^{2+}$ and $[\text{Cu}(\text{phen})_3]^{2+}$ complexes, respectively, since the other complexes involved are less than 10% in the solutions. The $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Cu}(\text{bpy})_3]^{2+}$ complexes should be taken into consideration as a minor species in the course of the EXAFS analyses of solutions PHEN1 and BPY3, respectively, in addition to the $[\text{Cu}(\text{bpy})_3]^{2+}$ and $[\text{Cu}(\text{phen})]^{2+}$ complexes as a predominant species in the solutions.

Structure of complexes

The EXAFS spectra weighted by k^3 of the sample solutions are shown in Fig. 4. For solutions BPY1, BPY2 and BPY3, shoulders at 4.4 and $8.5 \times 10^{-2} \text{ pm}^{-1}$ are gradually appreciable and a peak around $5.6 \times 10^{-2} \text{ pm}^{-1}$ is well separated with increasing the number of 2,2'-bipyridine molecules within the complexes. A similar trend is observable for solutions PHEN1 and PHEN3.

The Fourier transforms of the sample solutions are depicted in Fig. 5, where the first intense peaks

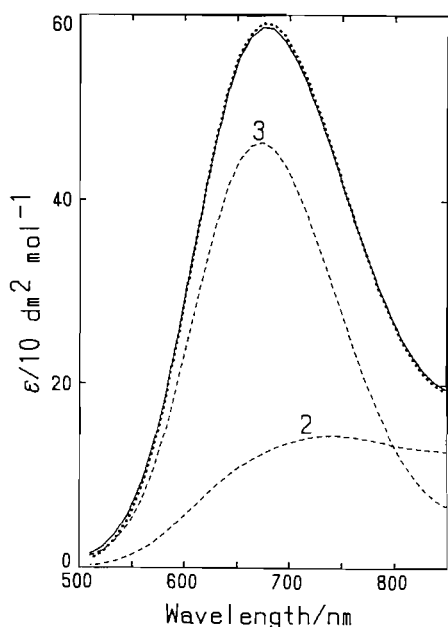


Fig. 3. Deconvolution of the electronic spectrum for solution BPY3 into those of individual species. The observed spectrum is shown by dots and calculated one by a solid line. Dashed lines indicate the absorption coefficients of individual complexes taking into account their mole fraction in solution. The numbers represent $[\text{CuL}_n]^{2+}$.

TABLE 3. Mole fraction of species in sample solutions for EXAFS measurements evaluated on the basis of the molar absorption coefficients of individual copper(II) 2,2'-bipyridine and 1,10-phenanthroline complexes ($L = \text{bpy}$ or phen)

Solution	Cu^{2+}	$[\text{CuL}]^{2+}$	$[\text{CuL}_2]^{2+}$	$[\text{CuL}_3]^{2+}$
BPY1	0.02	0.94	0.04	0
BPY2	0	0	0.94	0.06
BPY3	0	0	0.15	0.85
PHEN1	0.26	0.74	0	0
PHEN3	0	0	0.08	0.92

around 155 pm are due to the Cu–O and/or Cu–N bonds in the first coordination sphere of the copper(II) complexes. The second peaks appearing at 240 pm observed for solutions BPY1, BPY2, BPY3, PHEN1 and PHEN3 are ascribable to the non-bonding $\text{Cu} \cdots \text{C}$ interactions within the complexes similar to aqueous copper(II) pyridine solutions [26].

The structure parameters for the copper(II) 2,2'-bipyridine and 1,10-phenanthroline complexes were finally determined by a least-squares calculation applied to the Fourier filtered $k^3\chi(k)$ values. The inverse Fourier transformation of the $F(r)$ values was carried out over the range $0.85 < r$ (10^2 pm) < 3.00 . The Fourier filtered EXAFS oscillation is often distorted at both low and high values of k owing to the limited

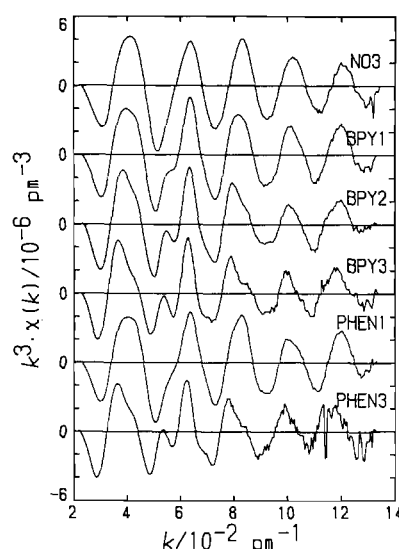


Fig. 4. The EXAFS spectra measured for sample solutions.

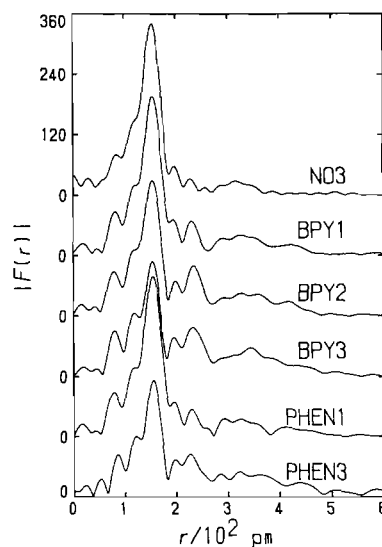


Fig. 5. The Fourier transforms $F(r)$ of the $k^3\chi(k)$ curves shown in Fig. 4 uncorrected for the phase shift.

k range of the Fourier transformation [27]. By comparing the theoretical function according to eqn. (4) with the one backfiltered by the same procedure as that employed for the experimental values, the fitting range of $4.5 < k$ (10^{-2} pm^{-1}) < 12.0 was so chosen that no distortion of the oscillation could occur. The E_0 and λ values were first evaluated from an aqueous copper(II) nitrate solution (solution NO3) containing the hexaqua copper(II) ion. The interatomic distances and Debye–Waller factors for the 2,2'-bipyridine and 1,10-phenanthroline complexes were then refined by adopting the E_0 and λ values evaluated. The contribution of the $[\text{Cu}(\text{bpy})_2]^{2+}$ and $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complexes present in solutions BPY3

and PHEN1, respectively, as a minor species to the $k^3\chi(k)$ values were taken into consideration in the fitting procedures. From the $k^3\chi(k)$ values of solutions BPY3 and PHEN1, those values of solutions NO3 and BPY2 weighted by the mole fraction of relevant species were subtracted, respectively, and the least-squares calculations were then carried out.

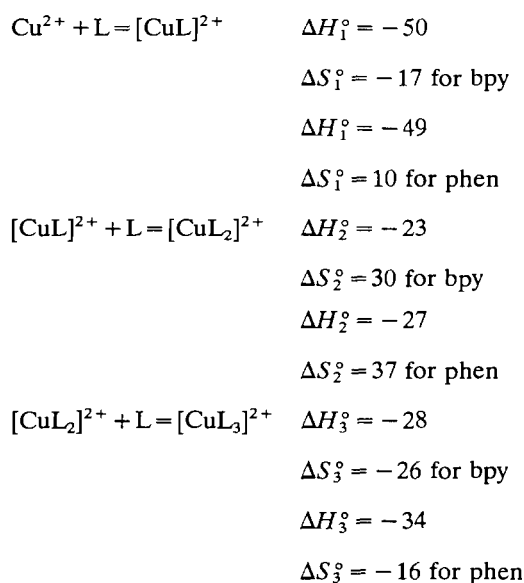
The structural models examined in the least-squares fits were based on the spectrophotometric results. An axially elongated octahedral model was assumed for the $[\text{Cu}(\text{bpy})(\text{H}_2\text{O})_4]^{2+}$, $[\text{Cu}(\text{bpy})_3]^{2+}$, $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_4]^{2+}$ and $[\text{Cu}(\text{phen})_3]^{2+}$ complexes because we have pointed out that the weak axial bonds in the distorted octahedron are in fact detectable by the EXAFS method [26]. The structure of the $[\text{Cu}(\text{bpy})_2(\text{H}_2\text{O})]^{2+}$ complex was assumed to be trigonal bipyramidal as reported in crystal [5, 9]. The numbers for the interatomic interactions were fixed on the basis of the model structure employed in the course of the calculations. The values of the Debye–Waller factors for the equatorial Cu–O and Cu–N bonds were also fixed during the refinements at the value of the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex owing to the strong correlation of parameters. No significant error could be introduced by the treatment since the similar value of 6.8 pm was obtained for the equatorial Cu–N bond in the tris(2,2'-bipyridine)- and tris(1,10-phenanthroline)copper(II) complexes. The results of the least-squares refinements are given in Table 4* and the solid curves calculated by using the parameter values in the table well reproduce the experimental points as shown in Fig. 6.

The equatorial Cu–O bond distances in the axially elongated octahedral $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Cu}(\text{bpy})(\text{H}_2\text{O})_4]^{2+}$ and $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_4]^{2+}$ complexes are slightly lengthened with increasing the number of ligand molecules within the complexes. The equatorial Cu–N bond lengths in the $[\text{Cu}(\text{bpy})(\text{H}_2\text{O})_4]^{2+}$, $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_4]^{2+}$, $[\text{Cu}(\text{bpy})_3]^{2+}$ and $[\text{Cu}(\text{phen})_3]^{2+}$ complexes are also slightly lengthened. The axial Cu–O and Cu–N distances are, on the other hand, practically the same among the complexes within the experimental uncertainties. The Cu–O distances within the trigonal bipyramidal $[\text{Cu}(\text{bpy})_2(\text{H}_2\text{O})]^{2+}$ complex is 208 pm and is longer than the equatorial Cu–O lengths within the distorted

octahedral complexes. Thus the water molecule within the $[\text{Cu}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ complex more weakly solvates copper(II) ion than that within the distorted octahedral complexes.

Relation with thermodynamic parameters

Enthalpy (ΔH_n° (kJ mol⁻¹)) and entropy (ΔS_n° (J K⁻¹ mol⁻¹)) values of stepwise formation of $[\text{CuL}_n]^{2+}$ ($n=1-3$, L=bpy or phen) in aqueous solution [28] are as follows.



Two water molecules coordinating to the copper(II) ion are replaced by a ligand molecule to form the $[\text{CuL}]^{2+}$ complex. The Cu–O and Cu–N bond distances are the same in both $[\text{Cu}(\text{bpy})(\text{H}_2\text{O})_4]^{2+}$ and $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_4]^{2+}$ complexes within experimental uncertainties. Hence, both ΔH_1° values for the 2,2'-bipyridine and 1,10-phenanthroline complexes are practically the same.

The ΔH_2° and ΔS_2° values are less negative than the ΔH_1° and ΔS_1° values in both 2,2'-bipyridine and 1,10-phenanthroline systems. Since the $[\text{CuL}]^{2+}$ and $[\text{CuL}_2]^{2+}$ complexes have a five- and six-coordinate structure, respectively, the fact may be explained in terms of the liberation of three water molecules within the six-coordinate $[\text{CuL}(\text{H}_2\text{O})_4]^{2+}$ complex followed by the formation of the five-coordinate $[\text{CuL}_2(\text{H}_2\text{O})]^{2+}$ complex. The ΔH_3° and ΔS_3° values are more negative than the ΔH_2° and ΔS_2° values in both systems, which may also be interpreted on the basis of the five- and six-coordinate structure of the $[\text{CuL}_2]^{2+}$ and $[\text{CuL}_3]^{2+}$ complexes, respectively.

The ΔH_3° value for the 2,2'-bipyridine complex is less negative than that for the 1,10-phenanthroline complex. Though the direct structural information of $[\text{Cu}(\text{phen})_2]^{2+}$ in aqueous solution could not be

*We also examined the square planar $[\text{Cu}(\text{bpy})_2]^{2+}$ structure since the σ value for the Cu–O bond in the $[\text{Cu}(\text{bpy})_2(\text{H}_2\text{O})]^{2+}$ complex is much larger than that in the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ion, indicating the rather small contribution of the interaction to the EXAFS spectra. The trigonal bipyramidal model gave the appreciably smaller error-square sum U of 2.953 than the square planar model (9.000), and thus we concluded that the Cu–OH₂ bond should not be neglected in the first coordination shell.

TABLE 4. Structure parameters with e.s.d.s in parentheses for copper(II) 2,2'-bipyridine and 1,10-phenanthroline complexes in aqueous solution^a

Complex	Parameter	Cu-O	Cu-N	Cu-O	Cu-N	Cu...C	Cu...C
[Cu(H ₂ O) ₆] ²⁺	<i>r</i> (pm)	196(1)		227(1)			
	<i>σ</i> (pm)	6.3(3)		11(1)			
	<i>n</i>	4 ^b		2 ^b			
[Cu(bpy)(H ₂ O) ₄] ²⁺	<i>r</i> (pm)	197(1)	199(1)	233(1)		292(1)	
	<i>σ</i> (pm)	6.3 ^b	6.3 ^b	12(1)		9.5(9)	
	<i>n</i>	2 ^b	2 ^b	2 ^b		4 ^b	
[Cu(bpy) ₂ (H ₂ O)] ²⁺	<i>r</i> (pm)	208(7)	200(1)			288(1)	303(1)
	<i>σ</i> (pm)	21(3)	6.3(2)			3.5(5)	4.6(5)
	<i>n</i>	1 ^b	4 ^b			4 ^b	4 ^b
[Cu(bpy) ₃] ²⁺	<i>r</i> (pm)		203(1)		227(2)	299(1)	318(2)
	<i>σ</i> (pm)		6.8(2)		12(1)	9.2(4)	8(1)
	<i>n</i>		4 ^b		2 ^b	10 ^b	2 ^b
[Cu(phen)(H ₂ O) ₄] ²⁺	<i>r</i> (pm)	197(3)	199(4)	234(1)		285(1)	
	<i>σ</i> (pm)	6.3 ^b	6.3 ^b	12(1)		10(1)	
	<i>n</i>	2 ^b	2 ^b	2 ^b		4 ^b	
[Cu(phen) ₃] ²⁺	<i>r</i> (pm)		204(1)		231(2)	300(1)	331(6)
	<i>σ</i> (pm)		6.8(2)		13(1)	11(1)	14(5)
	<i>n</i>		4 ^b		2 ^b	10 ^b	2 ^b

^a $E_0 = 8.999(1)$ keV; $\lambda = 700(70)$ pm. ^bThe values were kept constant during the calculations.

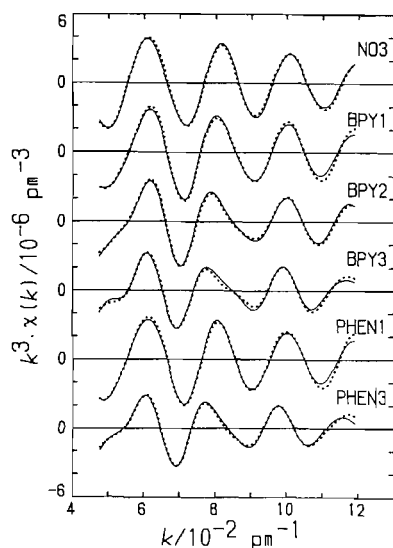


Fig. 6. The Fourier filtered $k^3\chi(k)$ curves for sample solutions. The observed values are shown by dots and calculated ones using parameter values in Table 4 by solid lines.

obtained in the present study, the Cu-O bond distances in crystals of [Cu(phen)₂(H₂O)](NO₃)₂ and [Cu(phen)₂(H₂O)](BF₄)₂ are 218 and 223.8 pm, respectively [10, 11]. These are longer than that (208 pm) of [Cu(bpy)₂(H₂O)]²⁺ in aqueous solution. On the other hand, the Cu-N lengths within the

[Cu(bpy)₃]²⁺ and [Cu(phen)₃]²⁺ complexes in aqueous solution are very similar. Therefore, the more negative ΔH_f° value in the 1,10-phenanthroline system than that in the 2,2'-bipyridine one may be ascribed to the easier dehydration in [Cu(phen)₂(H₂O)]²⁺ than in [Cu(bpy)₂(H₂O)]²⁺.

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