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An X-Ray Diffraction Study on the Structures of Bis- and Tris(ethylenediamine)copper(II) Complexes in Solution

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The structure of copper(II) complexes with ethylenediamine (en) in solution has been determined by means of X-ray diffraction. The measurements were performed at 25 °C for aqueous ethylenediamine solutions of copper(II) nitrate, the mole ratio (en/Cu) in the solutions being 2.09 and 5.14. In the former solution the bis(ethylenediamine)copper(II) complex was contained as the main species, while the tris(ethylenediamine)copper(II) complex was predominantly formed in the latter solution. The analysis of the X-ray scattering data of the solutions showed that in the bis-complex four nitrogen atoms of the two ethylenediamine molecules coordinated to the central metal ion at the distance of 1.93 Å in a planar form and oxygen atoms of two water molecules were located at 2.92 Å above and below the plane. Since the axial Cu-OH_2 bond distance is very long, the structure of the bis-complex can be regarded as square-planar. In the tris-complex the equatorial Cu-N bond length was 1.92 Å, which was practically the same as that within the bis-complex. The axial Cu-N distance was 2.22 Å.

There exist nine electrons in the d-orbital of a copper(II) ion, and thus, a hexacoordinated copper(II) complex tends to have a distorted octahedral structure. Structures of copper(II) complexes have been extensively studied by the spectroscopic analysis of solutions, as well as by the crystallographic method. The distortion of the structure of the $[Cu(OH_2)_6]^{2+}$ complex was first investigated by the X-ray crystal analysis, and it was found that the equatorial Cu–O bond distance within the complex comparatively shortened to be 2.16 Å, while the axial Cu–O bond length was 2.2—2.5 Å.[1–5] The distorted octahedral structure of the $[Cu(OH_2)_6]^{2+}$ complex was also found in solution by the X-ray diffraction method.[6–8] Ohtaki and his coworkers[7,8] reported that the equatorial and axial Cu–O bond lengths within the $[Cu(OH_2)_6]^{2+}$ complex were 1.94 and 2.43 Å, respectively, in a copper(II) perchlorate solution.

Yamaguchi and Ohtaki[9] reported the structures of the $[Cu(NH_3)_4(OH_2)_2]^{2+}$ and $[Cu(NH_3)_5X]^{2+}$ ($X=NH_3$ or H_2O) complexes by means of X-ray diffraction in solution. The Cu–N_{eq} and Cu–O_{ax} distance within the former were 2.03 and 2.33 Å, respectively, whereas the Cu–N_{eq}, Cu–N_{ax}, and Cu–X_{ax} were 1.93, 2.30, and 2.30 Å, respectively, in the latter.

The structures of the copper(II)–ethylenediamine complexes have been investigated by the ESR spectroscopy[10] and the X-ray diffraction method in crystal. In the tris(ethylenediamine)copper(II) sulfate, the CuN_6 moiety of the complex has an octahedral structure in which all the Cu–N bond distances are 2.15 Å.[11] The indifferent bond length within the complex was explained in terms of the dynamic Jahn-Teller effect. Since the angle of the N–Cu–N bond within the complex was not 90 °, the symmetry of the complex was not O_h but D_3.[11]

A regular octahedral structure was also found for $K_2Pb[Cu(NO_2)_6]$ in which all the Cu–N distances were 2.11 Å.[12] However, most of the hexacoordinated copper(II) complexes have distorted octahedral structures with two elongated bonds along the axis of the octahedron. The tris-complexes of copper(II) ion containing 2,2′-bipyridine and 1,10-phenanthroline were distorted octahedral.[13,14] In the tris(2,2′-bipyridine)-copper(II) complex, the equatorial Cu(II)–N bond distance was 2.031 Å, but the axial Cu–N bond lengths were 2.450 and 2.226 Å.[13] On the other hand, in the tris(1,10-phenanthroline)copper(II) complex the two axial Cu–N bond lengths were the same to be 2.33 Å, the equatorial Cu–N distance being 2.05 Å.[14]

Bertini *et al.*[15] investigated the effect of counter anions on the distortion of the octahedral structure of the tris(ethylenediamine)copper(II) complex in crystal containing various counter anions by using the ESR spectroscopy. They showed that the degree of the distortion varied with the counter anions.[15] The shape of the ESR spectra of the sulfate and nitrate salts was different and they suggested that the structure of the $[Cu(en)_3]^{2+}$ ion of the nitrate may be octahedrally distorted. On the contrary, the distortion of the structure of the $[Cu(en)_3]^{2+}$ ion in the sulfate was suggested to be small, which had also been studied crystallographically by Cullen and Lingafelter.[11]

The structure of the bis(ethylenediamine)copper(II) complex has been extensively investigated by the spectroscopic and crystallographic methods and it has been found that the complex ion has a distorted octahedral structure with counter anions or water molecules at the axial positions. The equatorial bond length within the bis-complex was about 2.05 Å, which was almost the same as that within the tris-complex.[14,16] When water molecules bound to the central copper(II) ion at the axial position, the Cu–OH_2 bond length remarkably changed from 2.22 Å to 2.89 Å depending on counter anions. The bond distance between the central copper ion and a thiocyante ion within the $[Cu(ClO_4)(NCS)(en)_2]$ complex was determined to be 2.73 Å by means of X-ray diffraction in the crystal.[17] Thus, the structure can be practically regarded as square-planar.

Although the structure of the $[Cu(en)_3](NO_3)_2$ compound has been assumed to be a distorted octahedron by a spectroscopic measurement,[15] the structure has not been determined by the X-ray diffraction method in crystal or in solution. In the present study, we have attempted to determine the structures of the bis-and tris(ethylenediamine)copper(II) complexes in aqueous solutions and to compare them with the structures of copper-ammine complexes,[9)] as well as those of ethylenediamine complexes of zinc(II),[18)] cadmium(II),[19)] and nickel(II)[20)] in solution.

Experimental

Preparation and Analysis of Sample Solutions. Ethylenediamine was purified by the method previously reported.[18)] Copper(II) nitrate of reagent grade was purchased from Wako Pure Chemicals Co., Osaka, and recrystallized twice from water. The sample solutions were prepared by dissolving copper(II) nitrate into aqueous ethylenediamine solutions by the similar way to that described in previous papers.[18–20)]

Concentrations of copper(II) ions in the test solutions were determined by electrogravimetry. The concentration of nitrate ions was calculated from the stoichiometry of copper(II) nitrate. The density of the test solutions was measured pycnometrically. The composition of the test solutions is given in Table 1.

Method of Measurements and Treatment of X-Ray Scattering Data. The method of measurements and the apparatus used were essentially the same as those employed in the previous works.[7,8,18–20)] Mo $K\alpha$ radiation (λ=0.7107 Å) was used for the measuremets over the range $1°<\theta<70°$ (2θ is the scattering angle). The data were recorded twice over the whole angle range. Corrections and analysis of the scattering data were performed in the same ways as those previously reported. Coherent and reduced intensities of the solutions are given in Figs. 1 and 2, respectively. The radial distribution function $D(r)$ was calculated by the following equation:

$$D(r) = 4\pi r^2\rho_0 + \frac{2r}{\pi}\int_0^{s_{\max}} s\cdot i(s)\cdot M(s)\cdot\sin(rs)\mathrm{d}s, \qquad (1)$$

where ρ_0 is the average scattering density in the stiochiometric volume V of the solution per Cu atom and $s_{\max}$ denotes the maximum s-value attained in the measurements ($s_{\max}=16.7$ Å^{-1}). $M(s)$ represents the modification function[21)] and the reduced intensities $i(s)$ are given by

$$i(s) = I^{\mathrm{coh}}(s) - \sum \mathrm{n}_i\{(f_i(s)+\Delta f_i')^2+(\Delta f_i'')^2\}, \qquad (2)$$

where n_i is the number of atom i and $f_i(s)$ denotes the scattering factor of atom i at s. $\Delta f_i'$ and $\Delta f_i''$ represent the real and imaginary parts of the anomalous dispersion, respectively.

Table 1. Composition of solutions A and B (mol dm^{-3})

	A	B
Cu	1.460	1.230
N	9.011	15.10
C	6.091	12.64
O	49.73	37.82
H	106.3	111.5
ρ/g cm^{-3}	1.195	1.159
V/Å	1267	1350
en/Cu	2.09	5.14

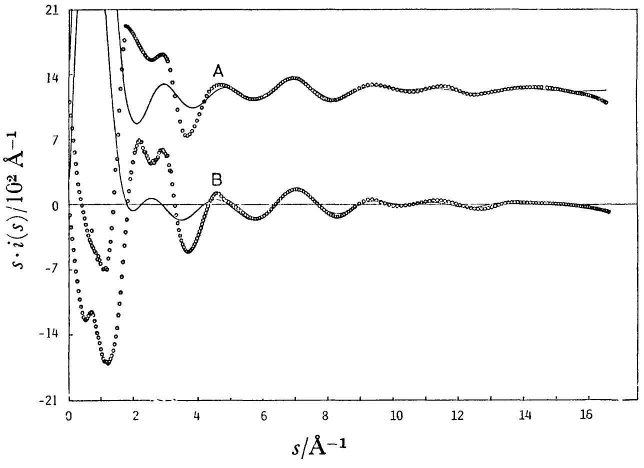

Fig. 2. The reduced intensities multiplied by s for solutions A and B. The observed $s\cdot i(s)$ curves are shown by circles and calculated ones by solid lines.

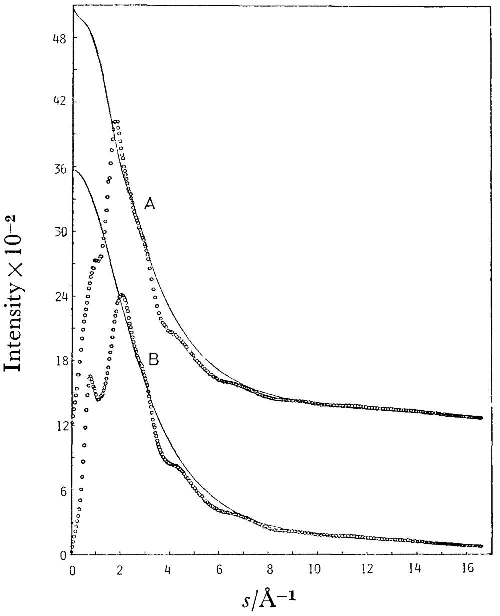

Fig. 1. Coherent scattering intensities of the sample solutions A and B. Experimentally obtained intensities I^{coh} are shown by circles and calculated independent scattering intensities by solid lines.

The theoretical scattering intensities due to atom-pairs of all possible combinations were obtained as follows:

$$i_{\mathrm{calcd}}(s) = \sum_{i}\sum_{\substack{j\\ i\neq j}} n_{ij}\{(f_i(s)+\Delta f_i')(f_j(s)+\Delta f_j') + (\Delta f_i'')(\Delta f_j'')\}\frac{\sin(r_{ij}s)}{(r_{ij}s)}\cdot\exp(-b_{ij}s^2), \qquad (3)$$

where r_{ij}, b_{ij}, and n_{ij} denote the distance, the temperature factor and the frequency factor of the atom-pair i-j, respectively.

Calculations were mainly carried out with the computer M 160 and M 180 using NLPLSQ[21)] and KURVLR[22)] programs at the Tokyo Institute of Technology and partly with the computer M 200H at the Instituse for Molecular Science in Okazaki.

Results

According to the stability constants so far reported,[23)] the bis(ethylenediamine)copper(II) complex is contained as the main species in solution A.

The stability constant of the tris(ethylenediamine)-copper(II) complex is comparatively small ($\log K_3 \simeq 1$[23)]), and thus, the tris-complex can only exist in a solution containing a large excess of ethylenediamine. In solution B in which the mole ratio of ethylenediamine to copper(II) ion is 5.14, the tris(ethylenediamine)-copper(II) complex is expected to be formed as the predominant species. The coexistence of the bis-complex with the tris-complex in solution B must also be taken into account in the course of the analysis of the scattering data.

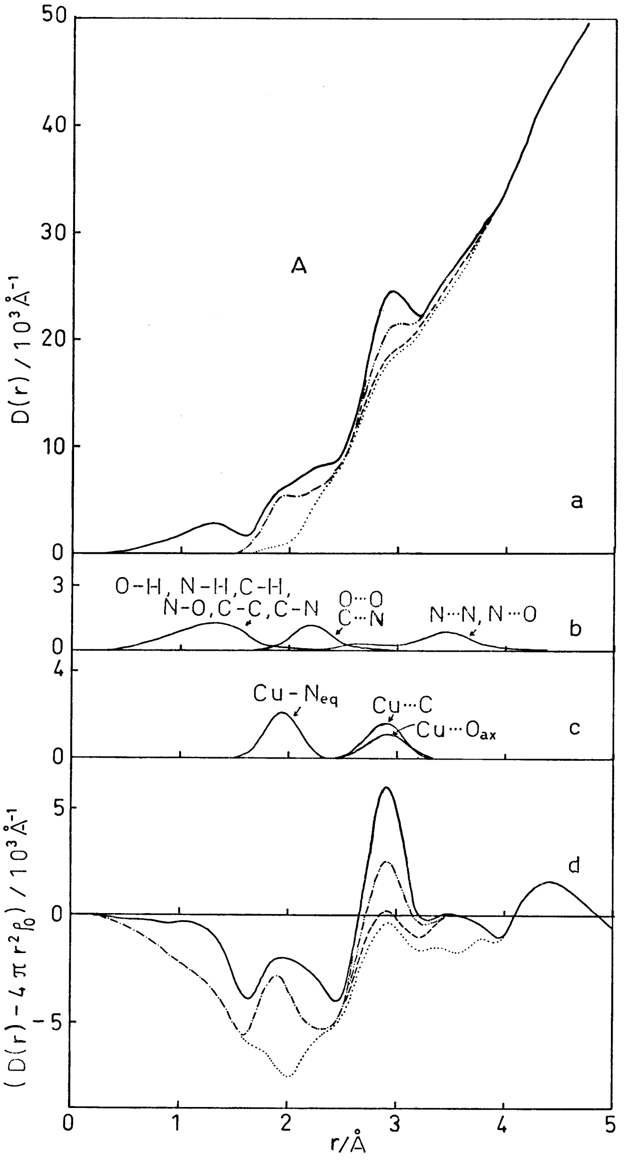

Fig. 3. (a); The $D(r)$ curve for solution A. The chain line (·—·—) shows the residual curve after subtraction of the theoretical peaks shown in b except for N···N and N···O interactions. The chain line (—··—··) shows the residual curve after subtraction of the theoretical peak shape due to the Cu···C interaction. Furthermore, after subtraction of the theoretical curve of the Cu-O$_{ax}$ interaction, the dashed line is obtained. After subtraction of the theoretical peaks due to the Cu-N$_{eq}$, N···N, and N···O interactions the dotted line is obtained. (b) and (c); The theoretical peak shapes of each atom pair. (d); The corresponding $D(r)-4\pi r^2\rho_0$ curve to (a).

Solution A. From the corrected diffraction intensities (Fig. 1A) the $s \cdot i(s)$ curve was obtained (Fig. 2A), and thus, the radial distribution and differential radial distribution curves (Fig. 3, a and d, respectively) were calculated. In the radial distribution curve of solution A, five peaks were observed in the region 1—5 Å (see Fig. 3, a and d).

A broad and small peak at about 1.2 Å is composed of peaks due to the O–H bond within water molecules, the N–H, C–H, C–C, and C–N bonds within ethylenediamine molecules and the N–O bond within nitrate ions in the solution (see Fig. 3, b). The second peak appearing at about 2.0 Å may be attributed to the Cu–N bond within the metal complex, the O···O pair within nitrate ions and the C···N interaction within ethylenediamine molecules. The third peak around 2.9 Å may be ascribed to the nonbonding Cu···C interactions within the complex and the O···O interactions in the bulk water. The O···O pairs within nitrate ions may also contribute to this peak. The Cu–OH$_2$ bond, if it exists, can be expected to be included in this peak. A broad peak around 4 Å must include some longer intramolecular interactions, as well as intermolecular interactions between ions in the solution. The fifth peak at about 5 Å might consist of much longer intermolecular interactions, which will not be taken into consideration in the present analysis.

At the first step of analysis of the radial distribution curve, the theoretical peaks of the intramolecular interactions within ethylenediamine molecules and nitrate ions were subtracted from the original $D(r)$ curve, and then the curve expressed by the chain line (·—·—·) was obtained. The analysis of the residual curve revealed that the Cu–N$_{eq}$ bond distance and its temperature factor were 1.93 Å and 0.002 Å^2, respectively. The frequency factor (n) of the Cu–N$_{eq}$ bond was evaluated to be four from the area under the peak at 1.93 Å. The nonbonding Cu···C distance was estimated to be about 2.85 Å by using a suitable structure model of ethylendiamine and the Cu–N$_{eq}$ distance estimated. After subtraction of the theoretical peak due to the Cu···C interactions, a double-dotted chain line (··—··—··) was obtained. A peak still remaining at about 2.9 Å was larger and sharper than that expected from the contribution of the only bulk water. Therefore, we assumed that the interaction between the central copper(II) ion and water molecules at the axial position may be included in the peak besides the H$_2$O···H$_2$O and NO$_3$···H$_2$O interactions. After subtraction of the Cu–O$_{ax}$ interactions, the distance of which was assumed to be 2.95 Å, the dotted line (······) with no appreciable peak was obtained in the region of 1.5—2.5 Å (Fig. 3, a and d). The N···N and N···O distances were estimated from the Cu–N$_{eq}$ and Cu–O$_{ax}$ lengths within the bis-complex on the basis of the structural model employed in the calculation mentioned above. Subtraction of the theoretical curve for the Cu–O$_{ax}$ interaction, as well as the N···N and N···O interactions led to a smooth back-ground curve shown by the dotted line. A broad peak still left at about 2.9 Å could be ascribed to the adjacent O···O interactions in the bulk water and hydrated nitrate ion, which were not taken into account in the calculation examined here. The parameter values were finally refined by the least-squares method by using the $s\cdot i(s)$ data of the high-angle region.

Solution B. An analytical procedure similar to that employed in the previous section was performed on the scattering data obtained from solution B. Subtraction of the theoretical peaks due to the O–H bond within H_2O, the N–H, C–H, C–C, C–N and C···N interactions within ethylenediamine molecules, and the N–O and O···O interactions within NO_3^- from the radial distribution curve of solution B led to a residual curve shown by a chain line (·—·—·) (Fig. 4, a and d). Two peaks observed at 1.9 and 2.2 Å in the residual curve may be identified to be due to the Cu–N_{eq} and Cu–N_{ax} bonds within the tris-complex. The area under the former and latter peaks corresponded to four and two Cu–N interactions, respectively. The former peak at 1.9 Å was, therefore, ascribed to the equatorial Cu–N bond. The temperature factors were estimated to be 0.002—0.0025 Å^2 to the former interaction and 0.003—0.0035 Å^2 to the latter. The peak obtained at 2.85 Å may partly be attributed to the nonbonding Cu···C interaction, and therefore, the double-dotted chain line (··—··—··) was obtained by subtracting the peak due to the nonbonding Cu···C interaction. A further subtraction of the peak due to the intramolecular N···N pairs within the tris-complex gave a dotted-line (······) (Fig. 4, a and d). The parameter values were refined by using the least-squares procedure.

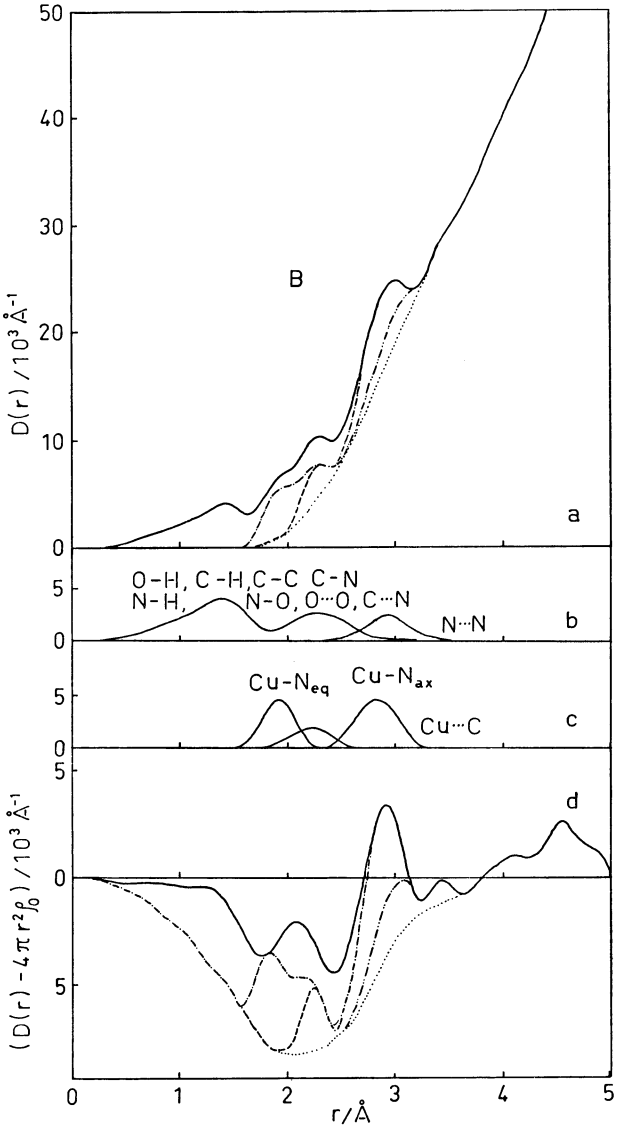

Fig. 4. (a); The $D(r)$ curve for solution B. The chain line (·—·—) shows the residual curve after subtraction of the theoretical peak shapes in (b) except for the N···N interaction from the original curve (solid line). After subtraction of the theoretical peak shape due to the Cu–N_{eq} bond from the chain line (·—·—·), the dashed line is obtained. The chain line (··—··—) shows the residual curve of the theoretical peak shape of the Cu···C interaction. After subtraction of the theoretical peak shapes of the Cu–N_{ax} and N···N interactions, the dotted line is obtained as the residual curve. (b) and (c); The theoretical peak shapes of atom-pairs indicated in the figure. (d); The corresponding $D(r)-4\pi r^2\rho_0$ curve to (a).

Least-squares Refinements. The $s\cdot i(s)$ data obtained in a high-angle region where $s>5$ Å^{-1} for solutions A and B were used for the least-squares refinement of the structure parameters of the bis- and tris-complexes in the solutions. In order to avoid introduction of errors by neglecting long-range intermolecular interactions in the solutions in the course of the refinements, the lower limit of the s-value was changed from 4.5 Å^{-1} to 7 Å^{-1}. In the least-squares calculations for solution A, in which the bis(ethylenediamine)copper(II) complex was predominantly formed, two types of calculations, I and II, were carried out. In type I, frequency factors n of all atom-pairs within the bis-complex were floated as well as the bond distances r and temperature factors b. In type II, on the other hand, the frequency factors were fixed and the only distances and temperature factors were refined. Throughout these refinements, the structure of the bis(ethylenediamine)copper(II) complex was assumed to be octahedral (Table 2).

The contribution from the O–H bond within water molecules was taken into account by using the structural parameters reported in the literature.[7,8,16,24] Structural parameters of the atom-pairs within ethylenediamine molecules were quoted from the work by Yokozeki and Kuchitsu[25] determined in the gas phase, as have been done in the previous studies.[18–20] The parameter values of the N–O pairs within NO_3^- were taken from the work by Caminiti *et al.*[26] and Maeda *et al.*[27] Contributions of all the atom-pairs were comparatively small in the s-region where we refined the structural parameters of the intramolecular interactions within the bis(ethylenediamine)copper(II) complex in the solution.

The parameter values for the O···O (NO_3^-), C···N (en), Cu···O_{ax}, Cu···C, and N···N ($Cu(en)_2(H_2O)_2$) atom-pairs were refined as independent variables. The change in the s-region in the course of the refinements did not practically affect the parameter values. The refined parameter values obtained by both I and II

Table 2. Least-squares refinements for solution A obtained over various s ranges
The parameter values, r=distance (Å), b=temperature factor (Å^2), and n=frequency factor, were refined. The values in parentheses are their standard deviations.

Inter-action	Parameter	4.5 Å$^{-1}<s<$16.7 Å^{-1}		5.0 Å$^{-1}<s<$16.7 Å^{-1}		6.0 Å$^{-1}<s<$16.7 Å^{-1}		7.0 Å$^{-1}<s<$16.7 Å^{-1}	
		I	II	I	II*	I	II	I	II
O···O (NO_3^-)	r	2.21(3)	2.22(3)	2.22(3)	2.22(3)	2.20(4)	2.20(4)	2.20(3)	2.20(3)
C···N (en)	r	2.26(8)	2.25(8)	2.17(6)	2.18(6)	2.3(1)	2.3(1)	2.32(7)	2.18(6)
$Cu(en)_2^{2+}$									
Cu–N_{eq}	r	1.943(7)	1.948(7)	1.934(7)	1.934(6)	1.93(1)	1.94(1)	1.922(7)	1.924(7)
	b	0.0028(5)	0.0033(5)	0.0025(4)	0.0027(4)	0.0025(6)	0.0028(5)	0.0023(3)	0.0025(3
	n	3.8(1)	4a)	3.81(9)	4a)	3.6(2)	4a)	3.9(1)	4a)
Cu···O_{ax}b)	r	2.92(4)	2.92(4)	2.92(3)	2.92(3)	2.91(5)	2.91(5)	2.90(3)	2.90(4)
	n	1.8(1)	2a)	1.9(1)	2a)	2.3(3)	2a)	2.6(2)	2a)
Cu···Cc)	r	2.89(2)	2.88(2)	2.89(2)	2.89(2)	2.89(3)	2.90(3)	2.88(2)	2.89(2)
	n	3.9(2)	4a)	4.0(2)	4a)	4.5(4)	4a)	4.7(3)	4a)
N···Nd)	r	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7
	b	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.006
	n	4a)	4a)	4a)	4a)	4a)	4a)	4a)	4a)
N···Od)	r	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
	b	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.006
	n	8a)	8a)	8a)	8a)	8a)	8a)	8a)	8a)

a) Fixed. b) The temperature factor of the interaction was fixed at 0.006 Å^2. c) The temperature factor of the interaction was fixed at 0.006 Å^2. d) The bond length, temperature factor, and frequency factor were fixed. *The calculated $s \cdot i(s)$ curve in Fig. 2 was obtained by using the parameter values given here.

types of calculations were almost consistent. The frequency factors of the Cu–N_{eq} and Cu–O_{ax} interactions obtained by the I-type calculation were close to four and two, respectively, and the frequency factor of the nonbonding Cu···C interaction was approximately four. Therefore, the distorted octahedral structure of the bis(ethylenediamine)copper(II) complex was thus confirmed from the least-squares calculations.

The Cu–N_{eq}, Cu–O_{ax}, and Cu···C distances were 1.93, 2.92, and 2.89 Å, respectively. Since the temperature factors of intramolecular interactions within the bis-complex except for the temperature factor of the Cu–N_{eq} bond were estimated to be about 0.006 Å^2 from the analysis of the radial distribution curve, they were assumed to be constant at 0.006 Å^2 in the course of the least-squares calculations.

The least-squares refinements of the parameter values of the tris(ethylenediamine)copper(II) complex were carried out by the similar way to that employed in the case of the bis-complex (Table 3). In the I-type calculation frequency factors n of all atom-pairs within the tris-complex were allowed to vary. In the II-type calculation frequancy factors of the atom-paris within the tris-complex were fixed by assuming the structure of the tris-complex to be distorted octahedral. In the III-type calculation the intramolecular N..N distance was also fixed. Throughout these calculations the temperature factors were kept constant at 0.003, 0.006, and 0.007 Å^2 for Cu–N_{ax}, Cu···C, and N···N interactions, respectively.

The frequency factors of the Cu–N_{eq}, Cu–N_{ax}, and Cu···C interactions found were practically four, two and six, respectively, in the I-type calculation. The Cu–N_{eq} distance within the tris-complex was almost the same as that of the bis-complex. In the analysis of the $s \cdot i(s)$ curve of solution B, the coexistence of the bis-complex together with the predominant tris-complex was taken into account. However, the experimental $s \cdot i(s)$ values were well reproduced by the structure model of the only tris-complex, and the contribution of the minor species of the bis-complex did not practically improve the result. Therefore, the values shown in Table 4 obtained by the least-squares method were those calculated on the assumption of the existence of the only bis-complex in solution A and the only tris-complex in solution B.

The final values for the distances of the Cu–N_{eq}, Cu–N_{ax}, Cu–O_{ax}, and Cu···C pairs of the bis- and tris-complexes are summarized in Table 4.

Discussion

In crystals the length of the axial Cu–OH_2 bond is affected by ligand molecules coordinated at the equatorial positions, counter ions and crystal structures (see Table 5). In copper(II) complexes in which nitrogen atoms are coordinated to the central copper(II) ion in the equatorial plane while two water molecules are located at the axial position, the shorter the equatorial Cu–N bond distance becomes, the longer the axial Cu–OH_2 bond length is[14] (Fig. 5, see also Tables 5 and 6). The Cu–N_{eq} distance (1.92 Å) within the tris(ethylenediamine)copper(II) complex in solution is shorter than that in other tris-complexes observed in

TABLE 3. LEAST-SQUARES REFINEMENTS FOR SOLUTION B OVER VARIOUS s RANGES
The parameter values, r=distance (Å), b=temperature factors (Å^2), and n=frequency factor, were refined. The values in parentheses are their standard deviations.

Interaction	Parameter	4.5 Å^{-1}<s<15.5 Å^{-1}			5.0 Å^{-1}<s<15.5 Å^{-1}	
		I	II	I	II	III*
O···O (NO_3)	r	2.21(4)	2.23(4)	2.20(2)	2.20(2)	2.22(2)
C···N (en)	r	2.27(4)	2.24(4)	2.33(2)	2.31(2)	2.28(2)
$Cu(en)_3^{2+}$						
Cu-N$_{eq}$	r	1.909(7)	1.924(8)	1.911(4)	1.916(5)	1.919(5)
	b	0.0017(4)	0.0023(5)	0.0023(3)	0.0025(3)	0.0027(3)
	n	4.1(1)	4$^{a)}$	4.04(6)	4$^{a)}$	4$^{a)}$
Cu-N$_{ax}$$^{b)}$	r	2.21(2)	2.23(3)	2.20(8)	2.21(2)	2.22(2)
	n	2.8(1)	2$^{a)}$	2.52(8)	2$^{a)}$	2$^{a)}$
Cu···C$^{c)}$	r	2.81(2)	2.80(2)	2.83(1)	2.83(1)	2.829(9)
	n	5.3(2)	6$^{a)}$	5.7(1)	6$^{a)}$	6$^{a)}$
N···N	r	2,85(5)	2.97(5)	2.90(2)	2.944(6)	2.93$^{a)}$

Interaction	Parameter	5.5 Å^{-1}<s<15.5 Å^{-1}			6.0 Å^{-1}<s<15.5 Å^{-1}	
		I	II	I	II	III
O···O (NO_3)	r	2.20(2)	2.20(2)	2.20(2)	2.20(2)	2.20(2)
C···N (en)	r	2.36(2)	2.33(2)	2.36(2)	2.33(2)	2.32(2)
$Cu(en)_3^{2+}$						
Cu-N$_{eq}$	r	1.904(4)	1.908(4)	1.903(5)	1.906(4)	1.905(5)
	b	0.0026(3)	0.0029(2)	0.0026(3)	0.0029(3)	0.0029(3)
	n	3.92(6)	4$^{a)}$	3.89(9)	4$^{a)}$	4$^{a)}$
Cu-N$_{ax}$$^{b)}$	r	2.205(9)	2.21(1)	2.20(1)	2.21(1)	2.20(1)
	n	2.47(9)	2$^{a)}$	2.47(9)	2$^{a)}$	2$^{a)}$
Cu···C$^{c)}$	r	2.842(9)	2.844(9)	2.84(1)	2.84(1)	2.83(9)
	n	6.3(1)	6$^{a)}$	6.4(2)	6$^{a)}$	6$^{a)}$
N···N$^{d)}$	r	2,87(2)	2.87(2)	2.87(3)	2.87(3)	2.93$^{a)}$

Interaction	Parameter		7.0 Å^{-1}<s<15.5 Å^{-1}	
		I	II	III
O···O (NO_3)	r	2.20(2)	2.20(2)	2.20(2)
C···N (en)	r	2.38(3)	2.31(2)	2.29(2)
$Cu(en)_3^{2}$				
Cu-N$_{eq}$	r	1.899(6)	1.903(6)	1.904(6)
	b	0.0025(3)	0.0030(3)	0.0030(3)
	n	3.8(1)	4$^{a)}$	4$^{a)}$
Cu-N$_{eqb)}$	r	2.21(9)	2.20(2)	2.20(2)
	n	2.8(1)	2$^{a)}$	2$^{a)}$
Cu···C$^{c)}$	r	2.84(1)	2.85(1)	2.83(1)
	n	6.6(2)	6$^{a)}$	6$^{a)}$
N···N$^{d)}$	r	2,86(4)	2.87(3)	2.93$^{a)}$

a) Fixed; b) Fixed (b=0.003 Å^2), c) Fixed (b=0.006 Å^2); d) Fixed (b=0.007 Å^2). *The calculated $s{\cdot}i(s)$ curve shown in Fig. 2 was obtained by using the parameter values of this type.

crystals (Table 7), but it is compared with the Cu–O$_{eq}$ distance within the $[Cu(OH_2)_6]^{2+}$ complex.[7,8] On the contrary, the Cu–N$_{ax}$ distance within the tris(ethylenediamine)copper(II) complex (2.22 Å) is shorter than the Cu–O$_{ax}$ distance within the $[Cu(OH_2)_6]^{2+}$ complex, which has been reported to be 2.43 Å.[7,8]

In the $[Cu(NH_3)_4(OH_2)_2]^{2+}$ complex in solution, the Cu–N$_{eq}$ and Cu–O$_{ax}$ distances are 2.03 and 2.33 Å, respectively.[9] In the bis(ethylenediamine)copper(II) complex, the equatorial Cu–N bond is shorter than that within the tetraamminecopper(II) complex, which indicates a stronger Cu–N(en) interaction than

Table 4. Final parameter values for the bis- and tris-(ethylenediamine)copper(II) complexes[a] (Å)

	Bis-complex	Tris-complex
Cu-N_{eq}	1.934(6)	1.919(5)
Cu-N_{ax}	—	2.22(2)
Cu-O_{ax}	2.92(3)	—
Cu···C	2.89(2)	2.829(9)
Structure	Distorted octahedral	

a) The values in parentheses are their standard deviations.

Table 5. Crystal data for axial Cu-OH_2 distance (Å)

Compound	Cu-OH_2	Author
$[Cu(NH_3)_4]SO_4{\cdot}H_2O$	2.59, 3.37	a)
$[Cu(C_5H_8N)_2]{\cdot}2H_2O$	2.52	b)
$[Cu(en)_2(OH_2)Cl]Cl$	2.68	c)
	2.62	d)
$[Cu(en)_2(OH_2)Br]Br$	2.78	e)
$[Cu(C_6H_9O_2N_3)_2](NO_3)_2{\cdot}(H_2O)_2$	2.461, 2.778	f)
$[Cu(CH_2COO)_2NH]{\cdot}2H_2O$	2.410	g)
$4[Cu(en)_2]{\cdot}Si_8O_{20}{\cdot}38H_2O$	2.64, 2.74	h)
	2.60, 3.04	
$[Cu(en)_2(OH_2)]{\cdot}[Cu_2(CN)_2(SeCN)_2]$	2.483	i)
$[Cu(C_6H_6N_4)(OH_2)_4]{\cdot}(SO_4)(H_2O)$	2.384	j)
$[Cu(en)_2(OH_2)_2]^{2+}$	2.92	This work (in solution)

a) F. Mazzi, *Acta Crystallogr.*, **8**, 137 (1955). b) A.McL. Mathieson and H. K. Welsh, *Acta Crystallogr.*, **5**, 599 (1952). c) F. Mazzi, *R. C. Soc. Miner. Ital.*, **9**, 148 (1953). d) R. D. Ball, D. Hall, C. E. F. Richard, and T. N. Waters, *Inorg. Phys. Theor.*, **1967**, 1435. e) F. Mazzi, *R. C. Soc. Miner. Ital.*, **9**, 148 (1953). f) B. Evertson, *Acta Crystallogr., Sect. B*, **25**, 30 (1969). g) A. Podder, J. K. Dattagupta, N. N. Sana and W. Saenger, *Acta Crystallogr., Sect. B*, **35**, 53 (1979). h) Yu. I. Smolin, Yu. F. Shepelov, and I. K. Butikova, *Sov. Phys.-Crystallogr.*, **17**, 10 (1972). i) V. Vrabel and J. Garaj, *Acta Crystallogr., Sect. B*, **35**, 357 (1979). j) E. Sletten and E. Voland, *Acta Crystallogr., Sect. B*, **35**, 840 (1979)

the Cu–N(NH_3) one. On the other hand, the Cu–O_{ax} distance within the former complex becomes longer than that within the latter. Therefore, the bis(ethylenediamine)copper(II) complex is more distorted than the tetraamminecopper(II) complex owing, probably, to a higher electron density at the copper(II) atom of the bis(ethylenediamine)copper(II) complex by a stronger electron donation from the coordinated ethylenediamine molecules, and thus, a more weakened Cu–OH_2 interaction along the axis results.

In the bis(ethylenediamine)copper(II) complex, the axial Cu–OH_2 distance is so long (2.92 Å) that the complex can be regarded as square-planar.

In the CuN_4O_2-type complexes in solution the ratio of the axial bond length to the equatorial one is smaller than that in crystal (see Fig. 5). The enhanced lengthening in the Cu–O_{ax} bond in crystal may be caused by interactions of the coordinated oxygen atom with another copper(II) ion (*e.g.*, in the case of $[Cu(NH_3)_4]SO_4{\cdot}H_2O$) or anions.

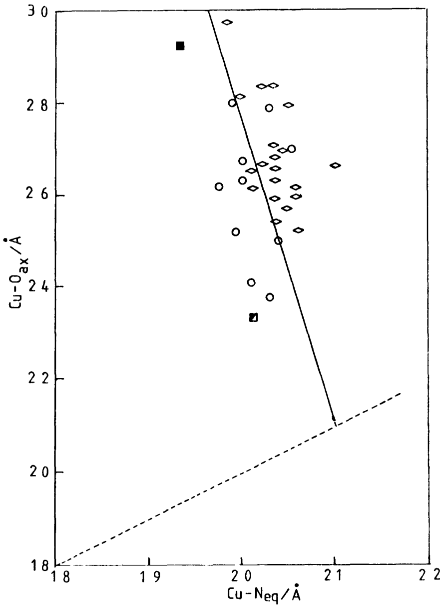

Fig. 5. A relationship between the equatorial Cu-N and axial Cu-O bond lengths of the CuN_4O_2 type complexes. ○: Complex containing only neutral ligands in crystal,[14] ◇: Complex containing neutral and anionic ligands in crystal,[14] ■: $[Cu(en)_2(OH_2)_2]^{2+}$ in solution, ◩: $[Cu(NH_3)_4(OH_2)_2]^{2+}$ in solution.[23]

Table 6. Crystal data for Cu-N distance (Å) in bis(ethylenediamine)copper(II) complexes

Compound	Cu-N	Author
$[Cu(en)_2](BF_4)_2$	2.02	a)
$[Cu(en)_2(SCN)(ClO_4)]$	2.02	b)
$4[Cu(en)_2]{\cdot}Si_8O_{20}{\cdot}38H_2O$	1.96—2.06	c)
$[Cu(en)_2(SCN)_2]$	1.99—2.01	d)
$[Cu(en)_2(OH_2)Cl]Cl$	1.98—2.02	e)
$[Cu(en)_2(OH_2)]{\cdot}[Cu_2(CN)_2(SeCN)_2]$	2.02—2.08	f)
$[Cu(en)_2](NO_3)_2$	2.01—2.04	g)
$[Cu(en)_2][Si(C_6H_4O_2)_3]$	1.990—2.018	h)
$[Cu(en)_2](ClO_4)_2$	2.03—2.05	i)
$[Cu(en)_2][Hg(SCN)_4]$	2.08—2.17	j)
$[Cu(en)_2(OH_2)Br]Br$	1.97—1.98	k)
$[Cu(en)_2(OH_2)_2]^{2+}$	1.93	This work (in solution)

a) D. S. Brown, J. D. Lee, and B. G. Melson, *Acta Crystallogr., Sect. B*, **24**, 730 (1968). b) M. Cammas, G. Carta, and G. Marongiu, *J. Chem. Soc., D*, **1971**, 1462; *J. Chem. Soc., Dalton Trans.*, **1973**, 251. c) Yu. I. Smolin, Yu. F. Shepelev, and I. K. Butikova, *Sov.Phys.-Crystallogr.*, **17**, 10 (1972). d) D. W. Brown and E. C. Lingafelter, *Acta Crystallogr.*, **17**, 254 (1964). e) R. D. Ball, D. Hall, C. E. F. Richard, and T. N. Waters, *Inorg. Phys. Theor.*, **1967**, 1435. f) V. Vrabel and J. Garaj, *Acta Crystallogr., Sect. B*, **35**, 357 (1979). g) K. Komiyama and E. C. Lingafelter, *Acta Crystallogr.*, **17**, 1145 (1964). h) V. D. Sackerer and G. Nagorsen, *Z. Anorg. Allg. Chem.*, **437**, 188 (1977). i) A. Pajunen, *Suomen Kem.*, **40**, 32 (1967). j) H. Scomloudi, *Acta Crystallogr.*, **6**, 148 (1953). k) F. Mazzi, *Rand. Soc. Miner. Ital.*, **9**, 148 (1953).

TABLE 7. CRYSTAL DATA FOR Cu-N_{eq} AND Cu-N_{ax} DISTANCES (Å) IN THE TRIS-COMPLEX CONTAINING BIDENTATE LIGANDS

Compound	Cu-N_{eq}	Cu-N_{ax}	Ref
$[Cu(en)_3]SO_4$	2.15	2.15	a)
$[Cu(bipy)_3](ClO_4)_2$	2.031	2.450, 2.226	b)
$[Cu(phen)_3](ClO_4)_2$	2.05	2.33	c)
$[Cu(en)_3]^{2+}$	1.92	2.22	This work[d)]

a) D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, **9**, 1858 (1970). b) Q. P. Anderson, *J. Chem. Soc.*, **1972**, 2597. c) Q. P. Anderson, *J. Chem. Soc., Dalton Trans.*, **1973**, 1237. d) In solution.

Only a few crystal structures of the CuN_6-type complexes have been reported so far (Table 7). In the X-ray analysis of the $[Cu(en)_3]SO_4$ in crystal, the structure was regularly octahedral. On the contrary, the tris(ethylenediamine)copper(II) ion in solution was concluded to have a distorted octahedral structure. The symmetrical structure of the $[Cu(en)_3]^{2+}$ ion in the $[Cu(en)_3]SO_4 \cdot H_2O$ crystal has been explained in terms of the dynamic Jahn-Teller effect.[11)] In the solution, on the other hand, the distorted octahedral structure of the $[Cu(en)_3]^{2+}$ ion is clearly seen by the X-ray diffraction method, because such a dynamic distortion in the structure of a species is not observable but it is recognized as a random distribution of a distorted species in the analysis of scattering data in solution.

The $[Zn(en)_2]^{2+}$ ion has a regular tetrahedral structure with the Zn–N bond length of 2.131 Å.[18)] A similar tetrahedral structure is kept in the $[Cd(en)_2]^{2+}$ complex, in which the Cd–N distance is found to be 2.339 Å.[19)] The structure of the $[Ni(en)_2]^{2+}$ ion has an almost regular octahedral structure by combining with additional two water molecules in the coordination sphere.[20)] The Ni–N distance, as well as the Ni–O distance, within the complex is 2.10 Å.[20)] The bis(ethylenediamine)copper(II) complex is square-planar. The $[Zn(en)_3]^{2+}$ complex is regular octahedral, and the Zn–N bond length is 2.276 Å,[18)] which is larger than the Ni–N distance within the $[Ni(en)_3]^{2+}$ complex (2.202 Å[20)]). In the $[Cu(en)_3]^{2+}$ complex the Cu–N_{eq} bond is much smaller than the Zn–N and Ni–N distances of the relevant tris-complexes. The Cu–N_{ax} bond, on the contrary, is longer than the Ni–N bond within the $[Ni(en)_3]^{2+}$ ion, although the Cu–N distance is slightly shorter than the Zn–N bond length within the $[Zn(en)_3]^{2+}$ complex. Obviously the Cu–N bond length within the $[Cu(en)_3]^{2+}$ complex is shorter than the Cd–N distance within the $[Cd(en)_3]^{2+}$ ion, because Cd^{2+} ion has a much larger ionic size than Cu^{2+} ion.

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