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Structure of Copper(II) Ethylenediamine Complexes in Aqueous and Neat Ethylenediamine Solutions and Solvent-Exchange Kinetics of the Copper(II) Ion in Ethylenediamine As Studied by EXAFS and NMR Methods

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The structures of copper(II) complexes with ethylenediamine (en) in aqueous and neat ethylenediamine solutions have been determined by the EXAFS (extended X-ray absorption fine structure) method. The copper(II) ion in en has an axially elongated octahedral structure with three en molecules. The Cu–N bond lengths in the four equatorial and two axial positions are 204(1) and 239(2) pm, respectively. The dynamic exchange reaction between en molecules in the bulk and en molecules bound to the copper(II) ion has been studied by the nitrogen-14 NMR line-broadening method. The rate constant and activation parameters for the ethylenediamine solvent exchange are as follows: $k_{ex} = (1.4 \pm 0.3) \times 10^7$ s^{-1} at 25 °C, $\Delta H^{\ddagger} = 9.2 \pm 2.5$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -77 \pm 10$ J mol^{-1} K^{-1}. The exchange reaction may be activated via the dissociative-interchange mechanism, followed by the formation of an intermediate with two monodentate en molecules and the occurrence of substantially fast axial–equatorial interconversion in the intermediate.

Introduction

Previously we have investigated the solvent exchange on nickel(II) ion in neat ethylenediamine and mixtures involving *N,N*-dimethylformamide (DMF) as a diluent.[2] The results have indicated that the slowest rate for solvent exchange at the nickel(II) ion studied to date is observed in ethylenediamine (en) and that the exchange reaction proceeds via a dissociative mechanism through a hexacoordinated intermediate with two equivalent monodentate ethylenediamine molecules. In this work we have extended the en exchange study to copper(II) ion. Because of the high lability of the solvated copper(II) ion, considered to be a consequence of the dynamic Jahn–Teller effect in d^9 configurations, solvated copper(II) species have been the subject of only a few mechanistic studies. Solvent exchange on the copper(II) ion is available only in water[3] and methanol.[3a,4]

First we conducted spectrophotometric measurements to characterize copper(II) ethylenediamine complexes in aqueous and neat ethylenediamine solutions. Then we investigated the solvation structure of the copper(II) ion in en as well as the structure of copper(II) complexes with en in aqueous en solutions, by the extended X-ray absorption fine structure (EXAFS) method, and the solvent exchange rate as a function of temperature by the nitrogen-14 NMR line-broadening method.

Experimental Section

Reagents. Hydrated copper(II) perchlorate was recrystallized from water for purification. Ethylenediammonium perchlorate was prepared by mixing aqueous ethylenediamine and perchloric acid solutions and recrystallized from water. *Caution*: Be careful in handling this salt because of the possibility of explosion due to dryness and/or heating! The tris(ethylenediamine)copper(II) complex was prepared by mixing hydrated copper(II) sulfate and a large excess of en and then recrystallized from water. Elemental analysis of the blue purple crystals confirmed the composition of $[Cu(en)_3]SO_4$. In addition, bis(ethylenediamine)copper(II) trifluoromethanesulfonate (triflate) was prepared as follows. Two mole equivalents of en were added to aqueous solutions of $CuSO_4 \cdot 5H_2O$. After the addition of a large excess of sodium(I) triflate the solution was concentrated to obtain the crude crystals which were recrystallized from the methanol solution. Elemental analysis of the pale blue crystals confirmed the composition of $[Cu(en)_2](CF_3SO_3)_2$. Anal. Found: C, 15.12; H, 3.29; N, 11.75. Calcd: C, 14.96; H, 3.35; N, 11.63. Dry and neat ethylenediamine was obtained by the reported procedure.[2]

Spectrophotometric Measurements. Electronic spectra of copper(II) complexes in solution were measured by a UV-2100 spectrophotometer (Shimadzu) equipped with a flow cell. The absorbance data at intervals of 1 nm over the wavelength range of 300–900 nm were recorded using a PC-9801VX computer (NEC). The flow cell with a path length of 0.5 cm was connected to a titration vessel through Teflon and glass tubes. A solution containing copper(II) perchlorate and ethylenediammonium perchlorate was titrated with a 0.5 mol dm^{-3} lithium hydroxide solution at 25.0 °C. All sample solutions contained 3 mol dm^{-3} lithium perchlorate as a supporting electrolyte. The spectrophotometric data at 40 wavelengths over the range of 400–850 nm were employed in a least-squares analysis to determine the individual spectra of copper(II) ethylenediamine complexes.

The formation of the $[Cu_p(en)_qH_r]^{(2p+r)+}$ complexes is represented by reaction 1, and the overall formation constant β_{pqr} is defined by eq 2. The

$$p\mathrm{Cu}^{2+} + q\mathrm{en} + r\mathrm{H}^+ \rightleftharpoons [\mathrm{Cu}_p(\mathrm{en})_q\mathrm{H}_r]^{(2p+r)+} \qquad (1)$$

$$\beta_{pqr} = [\mathrm{Cu}_p(\mathrm{en})_q\mathrm{H}_r{}^{(2p+r)+}][\mathrm{Cu}^{2+}]^{-p}[\mathrm{en}]^{-q}[\mathrm{H}^+]^{-r} \qquad (2)$$

absorbance, $A_{i\lambda}$, measured in solution i at a given wavelength λ is expressed by using β_{pqr} and the molar absorption coefficients $\epsilon_{pqr(\lambda)}$, $\epsilon_{\mathrm{Cu}(\lambda)}$, and $\epsilon_{\mathrm{en}(\lambda)}$ for $[Cu_p(en)_qH_r]^{(2p+r)+}$, Cu^{2+}, and en, respectively, as eq 3. The

$$A_{i\lambda} = \sum\sum\sum \epsilon_{pqr(\lambda)}\beta_{pqr}[\mathrm{Cu}^{2+}]_i{}^p[\mathrm{en}]_i{}^q[\mathrm{H}^+]_i{}^r + \epsilon_{\mathrm{Cu}(\lambda)}[\mathrm{Cu}^{2+}]_i + \epsilon_{\mathrm{en}(\lambda)}[\mathrm{en}]_i \qquad (3)$$

concentrations of Cu^{2+}, en, and H^+ are related to their total concentrations, $C_{\mathrm{Cu},i}$, $C_{\mathrm{en},i}$, and $C_{\mathrm{H},i}$ in solution i, respectively, as eqs 4–6, where K_W is

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Table I. Compositions and Mole Fractions of Sample Solutions for EXAFS Measurements

				mol fraction[b]			
soln	C_{Cu}[a]	C_{en}[a]	C_H[a]	Cu^{2+}	$Cu(en)^{2+}$	$Cu(en)_2^{2+}$	$Cu(en)_3^{2+}$
				In Ethylenediamine			
A	0.500			0	0	0	1.00
				In Water			
B	1.25	6.38		0	0	0.40	0.60
C	1.45	3.08		0	0	0.95	0.05
D	1.00	1.52	0.504	0	0.70	0.30	0
E	0.995			1.00	0	0	0

[a] In mol dm^{-3}. [b] See text.

the autoprotolysis constant of the water solvent: $-\log K_W = 13.87 \pm 0.01$ at 25.0 °C and 3 mol dm^{-3} of $LiClO_4$.[5]

$$C_{Cu,i} = [Cu^{2+}]_i + \sum\sum\sum p\beta_{pqr}[Cu^{2+}]_i^p[en]_i^q[H^+]_i^r \tag{4}$$

$$C_{en,i} = [en]_i + \sum\sum\sum q\beta_{pqr}[Cu^{2+}]_i^p[en]_i^q[H^+]_i^r \tag{5}$$

$$C_{H,i} = [H^+]_i + \sum\sum\sum r\beta_{pqr}[Cu^{2+}]_i^p[en]_i^q[H^+]_i^r - K_W[H^+]_i^{-1} \tag{6}$$

Molar absorption coefficients of the copper(II) ethylenediamine complexes were determined by minimizing the error-squares sum, $\sum(A_{i\lambda,obsd} - A_{i\lambda,calcd})^2$, on the basis of the available formation constants: $\log \beta_{110} = 11.38 \pm 0.04$ and $\log \beta_{120} = 21.35 \pm 0.09$ at 25.0 °C and 3 mol dm^{-3} of $LiClO_4$.[6]

EXAFS Measurements and Analysis. Five sample solutions of the compositions given in Table I were used for EXAFS measurements. A neat ethylenediamine solution of the copper(II) ion, solution A, was prepared in a glovebox by dissolving weighed quantities of the crystals of $[Cu(en)_3]SO_4$. Solutions B–D were prepared by dissolving copper(II) nitrate and ethylenediamine in water at a suitable mole ratio of C_{en}/C_{Cu}. Ethylenediammonium nitrate (*Caution*: Be careful in the handling because of the possibility of explosion due to heating!) was added to solution D in order to prevent hydrolysis of copper(II) ion. Solution E was an aqueous copper(II) nitrate solution.

X-ray absorption spectra were measured at the vicinity of the copper K edge (8.99 keV) using the BL10B station at the Photon Factory of the National Laboratory for High Energy Physics.[7] The white synchrotron radiations were monochromatized by an Si(311) channel-cut crystal. The incident X-ray intensity I_0 and the transmitted X-ray intensity I were simultaneously measured by ionization chambers filled with N_2 and N_2 (75%) + Ar (25%) gas, respectively. The apparent absorbance is given as $\ln(I_0/I)$.

A sample solution was contained inside a porous glass disk (radius = 2 cm, thickness = 2 mm) which was sealed with a vinyl sheet (PET film, Toray Co., Nagoya, Japan) in order to prevent evaporation of the solvent. The preparation of solution A was completely conducted in a drybox in order to prevent moisture from coming in contact with the compound.

Details of the data reduction of raw EXAFS spectra have been described elsewhere.[8–10] The EXAFS function $\chi(k)$ is given by the equation $\chi(k) = \{\mu(k) - \mu_0(k)\}/\mu_0(k)$, where k is the photoelectron wave vector ejected 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. A curve fitting procedure in the k space for the refinements of structure parameters was applied to the Fourier filtered $k^3\chi(k)_{obsd}$ values to minimize the following error-squares sum: $\sum k^6(\chi(k)_{obsd} - \chi(k)_{calcd})^2$. The model function $\chi(k)_{calcd}$ was obtained according to the single-electron and single-scattering theory.[11–14]

$$\chi(k)_{calcd} = \sum\{n_j/(kr_j^2)\}\exp(-2\sigma_j^2k^2 - 2r_j/\lambda)F_j(\pi,k)\sin(2kr_j + \alpha_j(k)) \tag{7}$$

Here for the backscattering amplitude $F(\pi,k)$ and total scattering phase shift $\alpha(k)$ were used the values reported by Teo and Lee.[15] Values of E_0 and the mean free path of a photoelectron λ were first evaluated from solution E as the standard sample involving only aquated copper(II) ion of which the structure has been well established.[16–20] The obtained values of E_0 and λ were kept constant in the course of the structural analysis of unknown samples, while the interatomic distance r, the Debye–Waller factor σ, and the number of scatters n were optimized as variable.

NMR Measurements. Six solutions for NMR measurements were prepared in a glovebox by dissolving weighed quantities of $[Cu(en)_2](CF_3SO_3)_2$ in a certain amount of freshly distilled en. The compositions of the solutions are given in Table SI (S: supplementary material). Some amounts of DMF as diluent and antifreeze were added. Samples for variable-temperature NMR measurements were introduced into 5-mm o.d. NMR glass tubes that were then flamed-sealed after degassing. The nitrogen-14 NMR measurement was performed on a JEOL JNM-GX270 FT-NMR spectrometer operating at 19.52 MHz. The temperature was measured by a substitution technique with a thermistor.

The solvent NMR line broadening caused by paramagnetic species can be expressed by eq 8,[21,22] where $\Delta\nu_{obsd}$ and $\Delta\nu_{solv}$ are the full widths

$$(T_{2P}P_M)^{-1} = \pi(\Delta\nu_{obsd} - \Delta\nu_{solv})P_M^{-1} \tag{8}$$

at half-height of the solvent NMR spectra in the presence and absence, respectively, of the paramagnetic ion, i.e., copper(II) ion, and P_M is the mole ratio of solvent bound to the copper(II) ion to free solvent in bulk.

Results and Discussion

Electronic Spectra of Copper(II) Ethylenediamine Complexes. Figure 1a shows electronic spectra measured during a titration at 25 °C and I = 3 mol dm^{-3} ($LiClO_4$) in an aqueous solution. The spectral change in Figure 1a was analyzed on the basis of the available formation constants.[6] The electronic spectra of the $[Cu(en)]^{2+}$ and $[Cu(en)_2]^{2+}$ complexes were determined with uncertainities of ca. 3% (three standard deviations) and 1%, respectively, at the peak positions and are depicted in Figure 1b together with that of the $[Cu(H_2O)_6]^{2+}$ ion. Spectrum 3 in Figure 1b was obtained from an aqueous solution containing 21.6 mmol dm^{-3} $Cu(NO_3)_2$ and 10.1 mol dm^{-3} ethylenediamine, which may correspond to that of $[Cu(en)_3]^{2+}$. This is supported by the fact that the copper(II) ion in neat ethylenediamine (solution A) exhibits virtually the same spectrum. As apparent from Figure 1, the absorption maximum and the molar absorption coefficient increase with an increase in the coordination number of en up to n = 2, while the addition of the third en results in a decrease in the energy of the absorption maximum and an increase in the intensity. Such a change in the spectra is similar to that for formation of the ammine complexes of $[Cu(NH_3)_n(H_2O)_{6-n}]^{2+}$ (n = 0–5).[23] Thus the copper(II) ion in copper(II) ethylenediamine complexes may be expected to have an axially elongated octahedral structure (vide infra).

With knowledge of the molar absorption coefficients of the individual complexes, the relative amounts of the complexes in

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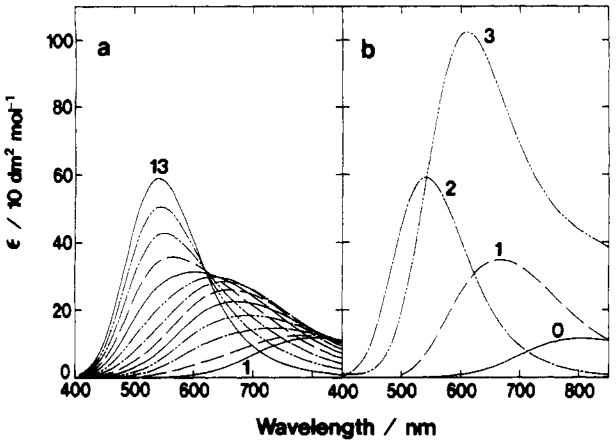

Figure 1. Electronic spectra during a titration. (a) Measured electronic spectra of copper(II) ethylenediamine solutions at 25 °C with varying hydrogen ion concentrations in the range 400–850 nm. Absorbances are normalized with a unit concentration of copper(II) ion. The individual volume of the sample solution is 30 cm^3, and initial concentrations C_{Cu}, C_{en}, and C_H are 49.91, 271.7, and 543.4 mmol dm^{-3}, respectively. Volumes of 0.5129 mol dm^{-3} LiOH titration solution added are 0 (spectrum 1), 1.0 (2), 2.0 (3), 3.0 (4), 4.0 (5), 5.0 (6), 6.0 (7), 7.0 (8), 8.0 (9), 9.0 (10), 10.0 (11), 11.0 (12), and 12.0 cm^3 (13). (b) The electronic spectra of individual copper(II) ethylenediamine complexes in aqueous solution. The numbers represent *n* in $[Cu(en)_n]^{2+}$.

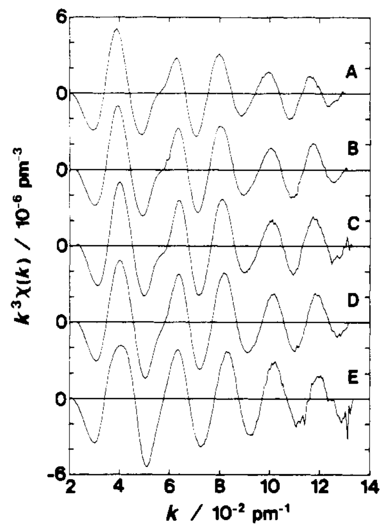

Figure 2. EXAFS spectra measured for sample solutions A–E.

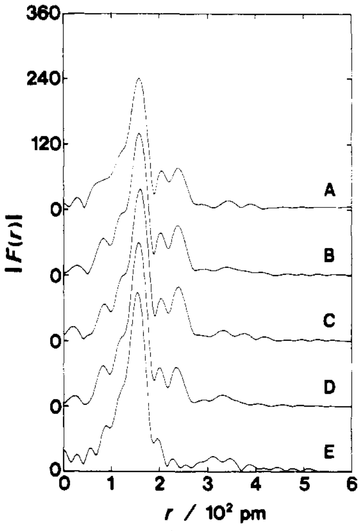

Figure 3. Fourier transforms $|F(r)|$ of the $k^3\chi(k)$ curves shown in Figure 2 uncorrected for the phase shift.

Table II. Results of the Least-Squares Refinements of Structure Parameters for Copper(II) Ethylenediamine Complexes in Ethylenediamine and Water[a]

complex	interaction	r/pm[b]	σ/pm[c]	n[d]
	In Ethylenediamine			
$[Cu(en)_3]^{2+}$	Cu–N_{eq}	204(1)	6.3(1)	4[e]
	Cu–N_{ax}	239(2)	12.5(4)	2[e]
	Cu- - -C	294(1)	7.8(2)	4[e,f]
	In Water			
$[Cu(en)_3]^{2+}$	Cu–N_{eq}	204(1)	6.2(2)	4[e]
	Cu–N_{ax}	234(2)	12.9(9)	2[e]
	Cu- - -C	294(1)	7.5(5)	4[e,f]
$[Cu(en)_2(H_2O)_2]^{2+}$	Cu–N_{eq}	202(1)	5.6(4)	4[e]
	Cu–O_{ax}	236(2)	12.1(9)	2[e]
	Cu- - -C	291(1)	7.2(6)	4[e]
$[Cu(en)(H_2O)_4]^{2+}$	Cu–N_{eq}	200(3)	5.8[e]	2[e]
	Cu–O_{eq}	198(3)	5.8[e]	2[e]
	Cu–O_{ax}	231(2)	12.8(5)	2[e]
	Cu- - -C	288(1)	6.2(6)	2[e]
$[Cu(H_2O)_6]^{2+}$	Cu–O_{eq}	197(1)	5.8(4)	4[e]
	Cu–O_{ax}	226(2)	11.9(9)	2[e]

[a] Standard deviations for the curve fitting are given in parentheses. [b] The interatomic distance. [c] The Debye–Waller factor. [d] The number of scatters. [e] The values were kept constant during the calculations. [f] The number of carbon atoms at the neighbor of the equatorial nitrogen atoms.

solutions B–D can be evaluated by the least-squares calculation. The mole fraction of species in sample solutions for the EXAFS measurements is summarized in Table I.

Solution Structure of Copper(II) Ethylenediamine Complexes. Figure 2 shows the EXAFS oscillations $\chi(k)$ weighted by k^3 of sample solutions A–E. Their Fourier transforms $|F(r)|$ (uncorrected for the phase shift) are depicted in Figure 3. The first intense peaks at 160 pm in the $|F(r)|$ curves are ascribed to the bonds between copper(II) ion and oxygen and/or nitrogen atoms in the first coordination sphere of the copper(II) ion. The intensity of the second intense peaks appearing around 240 pm gradually increases with increasing en molecules binding to the central copper(II) ion. Therefore, the peaks around 240 pm are attributed to the nonbonding interactions between the copper(II) ion and carbon atoms in the coordinated en molecule. The first intense peaks are very similar for all solutions.

The structure parameters for the copper(II) ethylenediamine complexes were determined by a least-squares calculation applied to the Fourier filtered $k^3\chi(k)$ values over the range $4.0 < k/10^{-2}$ pm^{-1} < 12.0. The E_0 and λ values were evaluated from solution E involving only the $[Cu(H_2O)_6]^{2+}$ ion of which the structure is known:[16-20] $E_0 = 9.000$ keV and $\lambda = 650$ pm. The Fourier filtering of the $|F(r)|$ values was performed over the range $0.85 < r/10^2$ pm < 2.30. The r and σ values obtained for the equatorial and axial Cu–O bonds are in excellent agreement with the literature values (r = 196 and 229 pm, σ = 6 and 14 pm).[20]

In the fitting procedure, the contribution of $[Cu(en)_2]^{2+}$ as the minor species in solutions B and D to the observed $k^3\chi(k)$ values was taken into account with knowledge of the relative amounts of the complexes. In the refinement the coordination number was fixed at a given value based on the axially elongated octahedral model. The Fourier filtering of the $|F(r)|$ values was performed over the range $0.85 < r/10^2$ pm < 3.00 and $0.85 < r/10^2$ pm < 2.30 with or without the peak due to the Cu- - -C interactions, respectively. In the case of the $[Cu(en)(H_2O)_4]^{2+}$ complex, the Debye–Waller factor (σ) of the equatorial Cu–N and Cu–O bonds was fixed at the value of 5.8 pm obtained for $[Cu(H_2O)_6]^{2+}$, while similar σ values were obtained for the equatorial Cu–N bonds in the $[Cu(en)_2(H_2O)_2]^{2+}$ and $[Cu(en)_3]^{2+}$ complexes (see Table II). The parameter values obtained in both cases including and excluding the peak due to the Cu- - -C interactions are summarized in Table II and Table SII, respectively. Both treatments obtained very similar axial bond lengths. The solid curves calculated by using the parameter values in

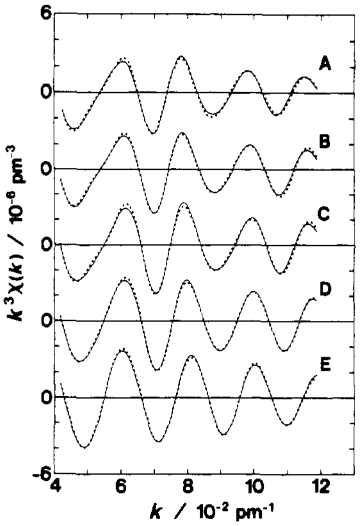

Figure 4. Fourier filtered $k^3\chi(k)$ curves of the main peak depicted in Figure 3 over the range $0.85 < r/10^2$ pm < 3.00 including the peak due to the Cu- - -C interactions. The observed values are shown by dots, and the solid lines are calculated using parameter values in Table II.

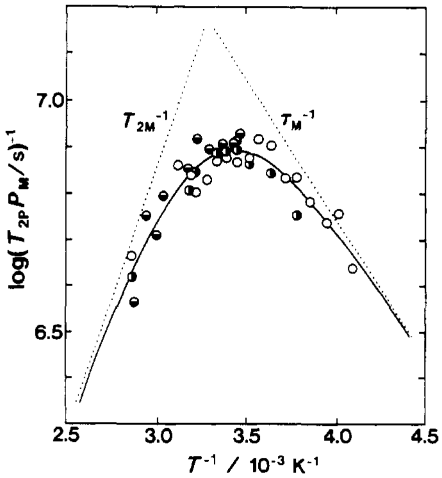

Figure 5. $(T_{2P}P_M)^{-1}$ data as a function of temperature for three different concentrations (100 (●), 70.1 (◑), 38.0% (○)) of en. The solid line was calculated using the obtained values.

Table II and Table SII reproduce well the experimental points, as shown in Figure 4 and Figure S1, respectively.

The mono-, bis-, and tris(ethylenediamine)copper(II) complexes in aqueous solution and the solvated copper(II) ion in ethylenediamine have distorted octahedral structures with two elongated bonds along the axis of the octahedron. The structure parameters for the tris complex in an aqueous solution are in excellent agreement with those for the complex in neat ethylenediamine. The structure of the $[Cu(en)_2(H_2O)_2]^{2+}$ and $[Cu(en)_3]^{2+}$ complexes in aqueous solution was determined by the X-ray diffraction method.[20] The equatorial Cu–N_{eq} and axial Cu–N_{ax} bond distances of the $[Cu(en)_3]^{2+}$ complex determined by the X-ray diffraction method are 192 and 222 pm, respectively, which are slightly shorter than those by the present EXAFS method. However, the Cu–O_{ax} bond length of the $[Cu(en)_2(H_2O)_2]^{2+}$ complex is 236(2) pm in the present EXAFS analysis, while the bond length was reported to be 292 pm by the X-ray diffraction method.[20]

Temperature Dependence of Solvent Exchange Rate. Nitrogen-14 NMR line-broadening data for $[Cu(en)_3]^{2+}$ at various temperatures are summarized in Table SIII. Figure 5 shows the $(T_{2P}P_M)^{-1}$ data for samples of three different en concentrations (weight percent of en = 100, 70.1, and 38.0%) as a function of reciprocal temperature. The transverse relaxation rate, T_{2P}^{-1}, has been confirmed to be proportional to the copper(II) ion concentration. Thus the T_{2P}^{-1} value is normalized by dividing by P_M. Under the present conditions, the modified Swift–Connick equation[24–26] is reduced to eq 9. τ_M $(=k_{ex}^{-1})$ is the residence time

$$(T_{2P}P_M)^{-1} = (T_{2M} + \tau_M)^{-1} \tag{9}$$

of a coordinated en on $[Cu(en)_3]^{2+}$ such that the exchange rate $= 3k_{ex}[Cu(en)_3^{2+}]$ related to the first-order rate constant k_{ex} for solvent exchange, and its temperature dependence may be obtained from the Eyring equation: $k_{ex} = (k_BT/h)\exp(\Delta S^{*}/R - \Delta H^{*}/RT)$. The transverse relaxation time of nitrogen-14 nucleus of coordinated en molecules, T_{2M}, can be expressed as the exponential form: $T_{2M}^{-1} = (C_M/T)\exp(E_M/RT)$.[26] The values of $(T_{2P}P_M)^{-1}$ did not vary with the degree of dilution with DMF. Thus nonlinear least-squares analyses according to eq 9 were applied to all data. Obtained values are as follows: $k_{ex} = (1.4 \pm 0.3) \times 10^7$ s^{-1} at 25 °C, $\Delta H^{*} = 9.2 \pm 2.5$ kJ mol^{-1}, $\Delta S^{*} = -77 \pm 10$ J mol^{-1} K^{-1}, $C_M = (2.5 \pm 0.5) \times 10^6$ s^{-1}, and $E_M = 19 \pm 4$ kJ mol^{-1}. Moreover, no line broadening of the ^1H and ^{14}N NMR spectra of DMF in the presence of $[Cu(en)_3]^{2+}$ has been observed. This indicates no interaction of DMF with $[Cu(en)_3]^{2+}$ in the first coordination sphere but implies the chelate-ring opening process in a dissociative activation mode (vide infra).

Ethylenediamine Exchange Mechanism on Copper(II) Ion. Poupko and Luz[3a] have estimated that the tetragonal distortion of the axially elongated octahedral structure of $[Cu(H_2O)_6]^{2+}$ and $[Cu(CH_3OH)_6]^{2+}$ alternates about x, y, and z axes such that the mean lifetime of a particularly tetragonal distortion is 1.6×10^{-11} s (25 °C) in water and 1.2×10^{-11} s (25 °C) in methanol, while the mean lifetime of a solvent molecule in $[Cu(H_2O)_6]^{2+}$ and $[Cu(CH_3OH)_6]^{2+}$ is 2×10^{-9} s and 1.4×10^{-8} s, respectively, at 25 °C. We can expect that the dynamic situation for $[Cu(en)_3]^{2+}$ should be the same as for $[Cu(H_2O)_6]^{2+}$ and $[Cu(CH_3OH)_6]^{2+}$. Thus a given en in $[Cu(en)_3]^{2+}$ experiences all orientations of the tetragonal distortion of the first coordination sphere many times prior to undergoing exchange with bulk en such that the three coordinated en molecules are kinetically indistinguishable. Therefore, accepting that the three en molecules bound to the copper(II) ion are kinetically equivalent, the values of P_M and $\tau_M = k_{ex}^{-1}$ have been estimated (vide supra). It is envisaged that en exchange occurs through the axial sites with the elongation of the axial Cu–N bond in the ground state. The activation process to the transition state involves a further lengthening of one axial bond and the penetration of an entering solvent.

The first-order rate constant (25 °C) for solvent exchange on the copper(II) ion was determined to be about 5×10^9 s^{-1} in water and 7.4×10^7 in methanol.[3a] Recently, the activation parameters for water and methanol exchange on copper(II) ion have been reported:[3b,4] $k_{ex}^{298} = 4.4 \times 10^9$ s^{-1}, $\Delta H^{*} = 11.5$ kJ mol^{-1}, and $\Delta S^{*} = -21.8$ J K^{-1} mol^{-1} for water exchange;[3b] $k_{ex}^{298} = 3.1 \times 10^7$ s^{-1}, $\Delta H^{*} = 17$ kJ mol^{-1}, $\Delta S^{*} = -44$ J K^{-1} mol^{-1}, and $\Delta V^{*} = 8.3$ cm^3 mol^{-1} for methanol exchange.[4] A slower rate of exchange is observed for ethylenediamine, which is a characteristic feature of en due to the chelate effect.[2] A mechanism has been proposed as indicated in Figure 6. One of the two axial bonds should be dissociatively elongated with the entrance of a donor nitrogen atom of an en molecule in the bulk, followed by the formation of an intermediate with two monodentate en molecules and the occurrence of substantially fast axial–equatorial interconversion in the intermediate.

Interestingly, ΔS^{*} for en exchange is a considerably large negative value in accordance with the results for methanol exchange on the copper(II) ion.[4] As pointed out in the case of

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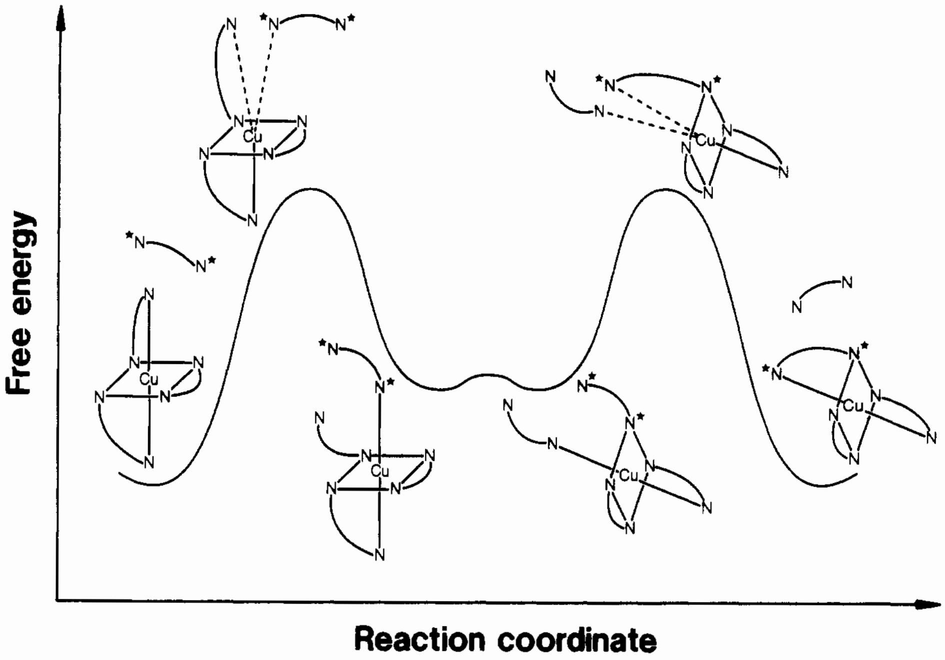

Figure 6. Proposed mechanism for ethylenediamine exchange on the copper(II) ion.

methanol exchange, any directional bonding interaction between the leaving and entering en molecules in both the first and second coordination spheres in the transition state may be expected under the rapidly alternating tetragonal distortion of $[Cu(en)_3]^{2+}$.

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Supplementary Material Available: Fourier filtered $k^3\chi(k)$ curves of the main peak depicted in Figure 3 (Figure S1), compositions of sample solutions (Table SI), results of the least-squares refinements of structure parameters for copper(II) ethylenediamine complexes in solution (Table SII), and observed NMR line-broadening data at various temperatures (Table SIII) (5 pages). Ordering information is given on any current masthead page.