Kinetics of Aquocopper(II) Ion Reacting with Polyamines and Poly(amino alcohols). Evidence for Rapid Jahn–Teller Inversion

D. B. Moss, Chin-tung Lin, and D. B. Rorabacher*[1]

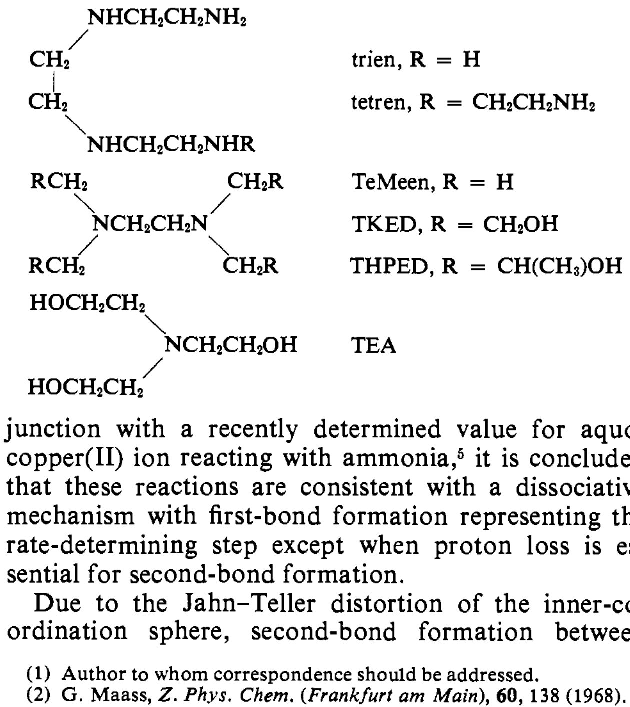
Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received November 10, 1972*

Abstract: The kinetics of aquocopper(II) ion reacting with *N,N,N',N'*-tetramethyl(ethylenediamine), triethylenetetramine, tetraethylenepentamine, triethanolamine, *N,N,N',N'*-tetrakis(2-hydroxyethyl)ethylenediamine, and *N,N,N',N'*-tetrakis(2-hydroxypropyl)ethylenediamine have been studied at 25°, $\mu = 0.1$ *M*, using the stopped-flow and temperature-jump techniques. By comparison to the corresponding Ni(II) rate constants, it is concluded that the formation of these Cu(II) ligand complexes proceeds by a mechanism which is essentially dissociative in nature. The kinetic behavior of the poly(amino alcohol) reactions further implies that Jahn–Teller inversion of a singly bonded complex species is rapid even under conditions where first-bond formation involves a weakly bonding donor atom.

For ligand substitution on aquocopper(II) ion, both dissociative and associative mechanisms have been proposed. In the formation of 1:1 Cu(II) complexes, dissociative behavior has generally been assumed although ligand dependent rate constants have been observed both for unidentate[2] and bidentate ligands.[3]

Evidence of associative behavior would be expected to be most evident in reactions with ligands containing strongly nucleophilic donor atoms and has been suggested in the study with ethylenediamine.[3,4] In the first part of the current investigation, therefore, we have studied the kinetics of $Cu(H_2O)_6^{2+}$ reacting with three polyamine ligands: *N,N,N',N'*-tetramethylethylenediamine (TeMeen), triethylenetetramine (trien), and tetraethylenepentamine (tetren) (see Chart I). In conjunction with a recently determined value for aquocopper(II) ion reacting with ammonia,[5] it is concluded that these reactions are consistent with a dissociative mechanism with first-bond formation representing the rate-determining step except when proton loss is essential for second-bond formation.

Chart I. Structure of Ligands Included in This Work



Due to the Jahn–Teller distortion of the inner-coordination sphere, second-bond formation between Cu(II) and a multidentate ligand must involve the replacement of a water molecule which was initially equatorial. Within the concept of the dynamic Jahn–Teller effect, when first-bond formation involves a strong donor atom, as in the polyamines, immediate rapid inversion should occur to place that donor atom in the equatorial plane accompanied by the elongation of two copper–water bonds. However, if the initial bond formed involves a weak donor atom, slow inversion (or no inversion) might be anticipated.

In the second part of the current work we have attempted to obtain information on the rate of the inversion process by means of kinetic studies on $Cu(H_2O)_6^{2+}$ reacting with three poly(amino alcohols): triethanolamine (TEA), *N,N,N',N'*-tetrakis(2-hydroxyethyl)ethylenediamine (TKED), and *N,N,N',N'*-tetrakis(2-hydroxypropyl)ethylenediamine (THPED) (see Chart I). As has been shown in earlier studies on the latter two ligands reacting with Ni(II) and Co(II),[6] the initial bond formation with these ligands is *via* a weakly coordinating alcoholic oxygen (the tertiary nitrogen donor atoms being sterically hindered[7]), with the second-bond formation to a nitrogen donor atom representing the rate-determining step. Thus, assuming that with Cu(II) the alcoholic oxygen will substitute initially for an axial water, the rate-determining step presumably involves or follows either (i) the direct loss of an equatorial water or (ii) a Jahn–Teller inversion in which the weakly coordinating alcoholic oxygen donor atom is incorporated into the equatorial plane while a stronger copper–water bond is elongated. Despite the seeming unfavorability of either process, substitution still appears to be relatively rapid.

Experimental Section

Reagents. The crystallization and purification of TKED and THPED as the perchlorate salts[6] and of tetren as the sulfate salt[8] have been previously described. The commercially available sulfate salt of trien (reagent grade, J. T. Baker) was neutralized with NaOH in a minimal volume of water and the neutral trien layer

---

[1] Author to whom correspondence should be addressed.

[2] G. Maass, *Z. Phys. Chem.* (*Frankfurt am Main*), **60**, 138 (1968).

[3] L. J. Kirschenbaum and K. Kustin, *J. Chem. Soc. A*, 684 (1970).

[4] R. F. Pasternack, P. R. Huber, U. M. Huber, and H. Sigel, *Inorg. Chem.*, 11, 276 (1972).

[5] H. Diebler and P. Rosen, *Ber. Bunsenges. Phys. Chem.*, **76**, 1031 (1972).

[6] (a) D. B. Rorabacher, T. S. Turan, J. A. Defever, and W. G. Nickels, *Inorg. Chem.*, **8**, 1498 (1969); (b) D. B. Rorabacher and D. B. Moss, *ibid.*, **9**, 1314 (1970).

[7] T. S. Turan and D. B. Rorabacher, *Inorg. Chem.*, 11, 288 (1972).

[8] D. W. Margerum, D. B. Rorabacher, and J. F. G. Clarke, Jr., *Inorg. Chem.*, **2**, 667 (1963).

which separated upon standing was drawn off and vacuum distilled (110° at 2 Torr) to yield the pure *colorless* polyamine as confirmed by gas chromatography. TeMeen (J. T. Baker) was distilled over BaO (119–121°) as previously described.[7] TEA (Eastman) was vacuum distilled (170° at 5 Torr) to yield the pure product as confirmed by thin layer chromatography.[9]

All ligand solutions were standardized by potentiometric acid-base titrations. For trien and tetren spectrophotometric mole ratio plots were also run with primary standard $Cu(NO_3)_2$ solution.[8] $NaClO_4$ and $Cu(ClO_4)_2$ (G. F. Smith Chemical Co.) were recrystallized from hot, aqueous solution, filtered, washed with ether (until the washings were neutral to wet litmus), and allowed to air dry. Cu(II) solutions were standardized by titration with EDTA using pyrocatechol violet as indicator with pyridine buffer. Distilled deionized water was used to prepare all solutions.

Kinetics. Kinetic measurements on the reactions of aquocopper(II) ion with TKED and THPED were made using a Durrum stopped-flow spectrophotometer while the reactions with TeMeen, trien, and tetren were followed with an Aminco-Morrow stopped-flow mixing device mounted on a Beckman DU-2 spectrophotometer. In view of the buffer interferences noted in other Cu(II) kinetic studies, several potential nonnucleophilic buffers were investigated including sterically hindered pyridines and diamines. None was found suitable for our studies due to limited solubility, short-term stability, or incorrect pH range. Therefore, the borate-mannitol buffer system utilized in previous Ni(II) studies[6-8] was finally selected for the current study. Due to limitations of the mannitol solubility, however, the lowest pH conveniently obtainable was about pH 4.5 (equivalent to approximately 0.4 *M* mannitol).

Although a slow-forming blue copper-mannitol complex, $\text{mann}_2[\text{Cu(OH)}_3]^{2-}$, has been observed to form at high pH,[10] there have been no reports of similar complex formation with aquocopper(II) at low pH, and difference spectra fail to reveal any evidence of interaction between Cu(II) and the borate-mannitol buffers over the pH range studied.

For all stopped-flow studies the temperature was maintained at 25.0 ± 0.4° with the ionic strength controlled at $\mu = 0.1$ *M* using $NaClO_4$. The TKED and THPED reactions were monitored at 290 nm while 260 nm was used for the polyamine reactions. At these wavelengths the Cu(II) absorbance increases with increasing pH above pH 5 due to the formation of small amounts of the highly absorbing species, $CuOH^+$. Owing to the lack of a reliable value for the protonation constant of this latter species, no attempt was made to resolve the individual molar absorptivity values for $Cu(aq)^{2+}$ and $CuOH^+$, but, instead, calibration curves of the "apparent" molar absorptivity of Cu(II) *vs.* pH were constructed for each wavelength used. For the copper complexes, the molar absorptivity values were determined at 290 nm ($\epsilon_{\text{Cu(tetren)}}$ 2870, $\epsilon_{\text{CuTHPED}}$ 2980) and 260 nm ($\epsilon_{\text{CuTeMeen}}$ 5430; $\epsilon_{\text{Cu(trien)}}$ 4860, $\epsilon_{\text{Cu(tetren)}}$ 5238).

The reaction between Cu(II) and TEA was studied using a temperature-jump relaxation spectrometer (Messanlagen Studiengesellschaft mBH, Goettingen, Germany) equipped with a Tektronix Type 549 storage oscilloscope as previously described.[11,12] Methyl red was used as a coupled indicator. Blank solutions of this indicator with Cu(II) or TEA exhibited no observable relaxation effects within the time range of the instrument (>5 μsec). For this system the solutions were unbuffered with the pH of the final solutions being adjusted to within ±0.01 of the desired pH value by dropwise addition of $HClO_4$ or NaOH solutions. Owing to the necessity for higher reactant concentrations to obtain suitable data, ionic strength was controlled at 0.3 *M* ($NaClO_4$) with the final temperature following the jump being calibrated at 25.0 ± 0.2°.

All pH measurements and potentiometric titration curves in this study were made using a Corning Model 12, Sargent Model DR, or Radiometer Model TTT 1c pH meter with the saturated calomel electrode outfitted with a KCl-impregnated agar bridge to prevent the precipitation of $KClO_4$ at the junction.

Results

Protonation Constants. Since all of the ligands included in this investigation are highly protonated in the pH region studied, accurate protonation constants were essential to the proper resolution of the kinetic data. Such values have been previously determined by us for TEA,[9] TKED,[6] THPED,[6] and TeMeen[7] which are in good agreement with literature values. These values are listed in Table I as mixed-mode protonation constants (charges on species omitted)

$$K_{\mathrm{H}_j}{}^{\mathrm{m}} = [\mathrm{H}_j\mathrm{L}]/a_{\mathrm{H}}[\mathrm{H}_{j-1}\mathrm{L}] \qquad (1)$$

For trien and tetren much discrepancy exists among the available values.[13] The values cited by most workers are considerably lower than are consistent with values which we have recently obtained in water and methanol-water solvents.[14] Considering the care taken in the purification of these ligands in our work, the number of replicate determinations, and the thoroughness of the data resolution, as well as the consistent trends as a function of solvent composition, we are strongly inclined to favor the higher values as listed in Table II. As will be noted later, however, the

Table I. Mixed-Mode Protonation Constants and Copper Complex Stability Constants for TeMeen and the Poly(amino alcohol) Ligands at 25°, $\mu = 0.1$ *M* ($NaClO_4$)

Ligand	Log $K_{\mathrm{H1}}{}^{\mathrm{m}}$	Log $K_{\mathrm{H2}}{}^{\mathrm{m}}$	Log K_{CuL}	Log K_{OH}
TeMeen	9.14	5.94	7.20[a]	
TKED	8.35	4.29	8.52[b]	
THPED	8.70	4.12	9.46[c]	
TEA	7.88[d]		3.9[e]	−5.7[f]

[a] R. L. Gustafson and A. E. Martell, *J. Amer. Chem. Soc.*, **81,** 525 (1959). [b] Value listed is for $\mu = 0.5$ *M:* J. L. Hall, W. E. Dean, and E. A. Pacofsky, *J. Amer. Chem. Soc.*, **82,** 3303 (1960). [c] Value listed is for $\mu = 0.5$ *M:* J. L. Hall, F. R. Jones, C. E. Delchamps, and C. W. McWilliams, *J. Amer. Chem. Soc.*, **79,** 3361 (1957). [d] Value listed for $\mu = 0.1$ *M* is presumed valid at higher ionic strength as well: J. Bjerrum and S. Refn, *Suom. Kemistilehti B*, **29,** 68 (1956). [e] G. Douheret, *Bull. Soc. Chim. Fr.*, 2915 (1965). [f] Defined as $K_{\mathrm{OH}} = [\mathrm{CuOHL}][\mathrm{H}^+]/[\mathrm{CuL}]$ as calculated from $K_{\mathrm{CuOHL}}{}^{\mathrm{OH}} = [\mathrm{CuOHL}]/[\mathrm{CuL}][\mathrm{OH}^-] = 2 \times 10^8\ M^{-1}$: B. Skrifvars and A. Ringbom, unpublished results cited in A. Ringbom, "Complexation in Analytical Chemistry," Wiley, New York, N. Y., 1963, Table A.2c.

Table II. Mixed-Mode Protonation Constants and Copper Complex Stability Constants for Trien and Tetren at 25°, $\mu = 0.1$ *M* ($NaClO_4$) (from ref 14)

	Trien	Tetren
Log $K_{\mathrm{H1}}{}^{\mathrm{m}}$	10.09	10.36
Log $K_{\mathrm{H2}}{}^{\mathrm{m}}$	9.31	9.65
Log $K_{\mathrm{H3}}{}^{\mathrm{m}}$	6.75	8.50
Log $K_{\mathrm{H4}}{}^{\mathrm{m}}$	3.39	4.70
Log $K_{\mathrm{H5}}{}^{\mathrm{m}}$		2.40
Log K_{CuL}	20.4[a,c]	22.9[b,c]

[a] 20.0°, $\mu = 0.1$ *M* KCl: G. Schwarzenbach, *Helv. Chim. Acta*, **33,** 974 (1950). [b] $\mu = 0.1$ *M* KNO_3: C. N. Reilley and J. N. Holloway, *J. Amer. Chem. Soc.*, **80,** 2917 (1958). [c] *Cf.* D. B. Rorabacher, B. J. Blencoe, and D. W. Parker, *Anal. Chem.*, **44,** 2339 (1972).

---

(9) D. B. Rorabacher and R. B. Cruz, to be submitted for publication.

(10) (a) T. Takahashi and H. Shirai, *Kogyo Kagaku Zasshi*, **64,** 515 (1961); *J. Electroanal. Chem.*, **3,** 330 (1962); G. B. Fridman and T. L. Nuterman, *Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhnol.*, **8,** 162 (1965); G. Floret and M. V. Massa, *Ann. Pharm. Fr.*, **24,** 201 (1966).

(11) W. J. MacKellar and D. B. Rorabacher, *J. Amer. Chem. Soc.*, **93,** 4379 (1971).

(12) D. B. Rorabacher and C. A. Melendez-Cepeda, *J. Amer. Chem. Soc.*, **93,** 6071 (1971).

(13) D. B. Rorabacher and F. R. Shu, manuscript in preparation.

(14) D. B. Rorabacher, W. J. MacKellar, F. R. Shu, and M. Bonavita, *Anal. Chem.*, **43,** 561 (1971).

primary consideration is that consistent protonation constant values be utilized when making comparisons between various kinetic studies with the same ligand species.

Literature values for the stability constants of the 1:1 copper complexes were used in all cases as a first approximation in treating the kinetic data. These values are listed in Tables I and II. Corroboration of these values and the protonation constants was obtained by checking the molar absorptivity constants at varying pH as previously described.[6,7]

Kinetics. All reactions studied were of the form

$$\mathrm{Cu(aq)^{2+} + H_{\mathit{j}}L^{\mathit{j}+} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} CuL^{2+} + \mathit{j}H^+} \qquad (2)$$

The pH range accessible for the reaction systems studied by the stopped-flow method was limited to a lower value of 4.5 by the borate–mannitol buffer system used to maintain constant pH. The upper limit was arbitrarily set at about 5.3 in order to minimize the possibility of kinetic interference by $CuOH^+$ or precipitation of $Cu(OH)_2$. Within this pH range, the independence of the kinetic data from any contribution by $CuOH^+$ was specifically established in the study on the TEA reaction (where the presence of only one reactive ligand species simplified this analysis).

In the pH range studied the conditional stability constants were lowered by ligand protonation to the extent that the reactions did not generally proceed to completion but were found to obey the mixed second- and first-order reversible rate equation

$$d[\mathrm{CuL}]/dt = k_f\,[\mathrm{Cu^{2+}}][\Sigma \mathrm{L}] - k_d[\mathrm{CuL^{2+}}] \qquad (3)$$

where k_f and k_d represent the observed overall formation and dissociation rate constants, respectively, and $[\Sigma L]$ represents the total concentration of uncomplexed ligand in both protonated and unprotonated forms.[14] These observed overall rate constants were calculated using the integrated form of eq 3 as previously described.[6] The values thus obtained for the formation rate constants as listed in Table III–VII show consistent trends which parallel changes in pH. With the exception of the TeMeen study, the experimental dissociation rate constants were too erratic to be useful and are not considered further.

Table III. Observed Rate Constants for the Reaction of Aquocopper Ion with TKED[a]

pH	$k_f \times 10^{-4}$, M^{-1} sec^{-1}	pH	$k_f \times 10^{-4}$, M^{-1} sec^{-1}
5.21	5.73	4.84	5.97
5.18	6.55	4.80	4.52
5.03	6.00	4.73	4.02
4.97	6.35	4.67	4.56
4.94	4.66, 5.58	4.62	3.89
4.86	5.54	4.50	3.23

[a] At 25°, $\mu = 0.1\ M$, $[Cu^{2+}] = 3.854 \times 10^{-4}\ M$, [TKED] = $1.869 \times 10^{-5}\ M$.

Table IV. Observed Rate Constants for the Reaction of Aquocopper Ion with THPED[a]

pH	$k_f \times 10^{-4}$, M^{-1} sec^{-1}	pH	$k_f \times 10^{-4}$, M^{-1} sec^{-1}
5.29	3.95	4.79	3.57
5.19	4.51	4.71	3.54
5.11	4.28	4.67	3.66
4.93	3.89	4.60	3.40
4.85	4.15, 3.71	4.51	2.99

[a] At 25°, $\mu = 0.1\ M$, $[Cu^{2+}] = 3.854 \times 10^{-4}\ M$, [THPED] = $1.605 \times 10^{-5}\ M$.

Table V. Observed Rate Constants for the Reaction of Aquocopper Ion with TeMeen at 25°, $\mu = 0.1\ M$

pH	$[Cu^{2+}]$, mM	[TeMeen], mM	$k_f \times 10^{-2}$, M^{-1} sec^{-1}	k_d, sec^{-1}
5.52	1.052	0.0535	114	(12.1)
5.46	1.052	0.0535	81.3	(14.3)
5.36	1.052	0.0535	65.1	18.3
5.19	1.052	0.0535	30.0	15.3
4.92	1.474	0.0748	9.83	13.1
4.84	1.474	0.0748	7.55	12.3
4.76	2.10	0.1069	4.00	12.1
4.69	2.10	0.1069	3.72	12.2
4.53	2.10	0.1069	1.93	12.3

Table VI. Observed Rate Constants for the Reaction of Aquocopper Ion with trien[a]

pH	$k_f \times 10^{-5}$, M^{-1} sec^{-1}	pH	$k_f \times 10^{-5}$, M^{-1} sec^{-1}
5.27	2.20	4.79	0.920
5.15	1.99	4.69	0.771
5.07	1.79	4.65	0.695
4.90	1.31	4.57	0.604
4.83	0.921	4.53	0.563

[a] At 25°, $\mu = 0.1\ M$, $[Cu^{2+}] = 3.85 \times 10^{-4}\ M$, [trien] = $1.27 \times 10^{-5}\ M$.

Table VII. Observed Rate Constants for the Reaction of Aquocopper Ion with tetren[a]

pH	$k_f \times 10^{-4}$, M^{-1} sec^{-1}	pH	$k_f \times 10^{-4}$, M^{-1} sec^{-1}
5.31	7.20	4.84	6.98
5.21	7.81	4.79	6.30
5.14	8.03	4.77	6.23
4.98	7.04, 7.08	4.64	5.94
4.90	6.37		

[a] At 25°, $\mu = 0.1\ M$, $[Cu^{2+}] = 3.85 \times 10^{-4}\ M$, [tetren] = $1.13 \times 10^{-5}\ M$.

For the reactions involving TKED, THPED, and TeMeen, the formation rate constants were found to be dependent on both the unprotonated and monoprotonated ligand species for which the specific rate constants were then resolved by plotting the expression[6,7]

$$k_f\frac{[\Sigma \mathrm{L}]}{[\mathrm{L}]} = k_{\mathrm{Cu}}{}^{\mathrm{L}} + k_{\mathrm{Cu}}{}^{\mathrm{HL}}K_{\mathrm{H1}}{}^{\mathrm{m}}a_{\mathrm{H}} \qquad (4)$$

For the THPED plot the intercept is not significantly different from zero so that the rate constant involving the unprotonated ligand species cannot be established. On the other hand, the scatter of the data for the TeMeen reaction reveals considerably uncertainty in the value of $k_{Cu}{}^{HL}$ as determined from the slope.

In the case of the trien and tetren systems, several protonated species are available for reaction with the metal ion. However, detailed analyses of the experimental data reveal that, in each case, two protonated species are predominantly contributing to the observed kinetics in the pH range studied; *viz.*, the di- and triprotonated species of trien and the tri- and tetraprotonated species of tetren. The specific rate constants were, therefore, obtained by plotting the following equations: for trien

$$k_f\frac{[\Sigma L]}{(a_H)^2[L]} = k_{Cu}{}^{H_2L}\ \beta_{H2}{}^{m} + k_{Cu}{}^{H_3L}\ \beta_{H3}{}^{m}a_H \tag{5}$$

for tetren

$$k_f\frac{[\Sigma L]}{(a_H)^3[L]} = k_{Cu}{}^{3H_3L}\beta_{H3}{}^{m} + k_{Cu}{}^{H_4L}\beta_{H4}{}^{m}a_H \tag{6}$$

where

$$\beta_{H_j}{}^{m} = K_{H1}{}^{m}K_{H2}{}^{m}\ \ldots\ K_{H_j}{}^{m}$$

The plots of the kinetic data according to these equations exhibit some scatter, but this affects mainly the slopes, *i.e.*, the rate constant values for the more protonated species. The rate constants for H_2trien^{2+} and $H_3tetren^{3+}$, as determined from the intercepts, are determined within about ±10%. The tetren data are comparable to previous results reported for this system.[15]

Due to the lower basicity of TEA, this ligand was not as highly protonated in the pH region studied, resulting in a shorter reaction lifetime. Since only the last 15–20% or less of the reaction was observable on the stopped flow, this particular reaction was studied using the temperature-jump method. This approach permitted this reaction to be studied in the absence of a buffer, thereby permitting a comparison of the kinetic behavior of Cu(II) reacting with similar poly(amino alcohol) ligands with and without the borate–mannitol buffer present.

The reactant concentrations required to obtain satisfactory relaxation curves necessitated the use of a higher ionic strength ($\mu = 0.3\ M$) than that used for the other studies. Since TEA is uncharged, however, this should have no significant effect on the formation rate constant.[12]

The use of methyl red as a monitoring indicator coincidentally limited the pH range of the TEA study to that imposed previously by the borate–mannitol buffer, *viz.*, pH 4.5–5.3, since higher or lower pH values yielded relaxation amplitudes which were too small to be experimentally resolved with precision. A single relaxation process was observed for this system which was interpreted to reflect the contributions of four coupled reactions

$$Cu(aq)^{2+} + L \underset{k^{Cu-L}}{\overset{k_{Cu}{}^{L}}{\rightleftharpoons}} CuL(aq)^{2+} \tag{7}$$

$$CuL(aq)^{2+} \overset{K_{OH}}{\rightleftharpoons} Cu(OH)L^{+} + H^{+} \tag{8}$$

$$H^{+} + L \overset{K_H}{\rightleftharpoons} HL^{+} \tag{9}$$

$$H^{+} + In^{-} \overset{K_I}{\rightleftharpoons} HIn \tag{10}$$

A fifth coupled reaction involving $CuOH^+$ was also considered

$$CuOH^{+} + L \rightleftharpoons Cu(OH)L^{+} \tag{7a}$$

but was not found to contribute significantly to the observed relaxation in the pH range studied. (Although $CuOH^+$ has been reported to react much more rapidly than $Cu(aq)^{2+}$,[16] the kinetic contribution of the hydroxy species appears to be significant only at pH values above those included in this study.) Bis-complex formation is also insignificant under the conditions used.[17]

Since the proton transfer processes represented in eq 8–10 are presumed to be much faster than the metal complex formation reaction in this reaction scheme,[18] the former may be considered to be at equilibrium at all times. The reciprocal relaxation time, τ^{-1}, can then be related directly to the rate constants for reaction 7, *viz.*[19]

$$\tau^{-1} = k_{Cu}{}^{L}\{([Cu^{2+}]A) + ([L]B)\} + k^{Cu-L} \tag{11}$$

where $[Cu^{2+}]$ and [L] are the equilibrium concentrations of aquocopper(II) ion and uncomplexed, unprotonated ligand, respectively, which are present in the experimental solution at 25°. In eq 11, A and B are defined as

$$A = -\partial[L]/\partial[CuL] = \frac{K_{OH}K_H[L] + [Cu(OH)L^+] + ([H^+] + K_{OH}) \times \left(\dfrac{1 + K_I[H^+] + K_I[In^-]}{1 + K_I[H^+]}\right)}{[H^+]\left\{K_H[Cu(OH)L^+] + K_H[L] + (1 + K_H[H^+]) \times \left(\dfrac{1 + K_I[H^+] + K_I[In^-]}{1 + K_I[H^+]}\right)\right\}} \tag{12}$$

$$B = -\partial[Cu]/\partial[CuL] = \frac{1}{[H]^{+}\left\{1 + \left(\dfrac{K_I[In^-]}{1 + K_I[H^+]}\right) + K_H[L]\right\}} \times \left\{([H^+ + K_{OH})\left(1 + \frac{K_I[In^-]}{1 + K_I[H^+]} + K_H[L]\right) + [Cu(OH)L^+] - A(K_H[H^+][Cu(OH)L^+])\right\} \tag{13}$$

The experimental relaxation data, as summarized in Table VIII, show no pH dependence other than that accounted for by the ligand protonation. The ratio of these rate constants is nearly identical with the thermodynamic stability constant listed in Table I.

Table VIII. Experimental Rate Data for the Reaction of Aquocopper Ion with TEA at 25°, $\mu = 0.3\ M$

pH	$[\Sigma Cu^{2+}]$, mM	$[\Sigma L]$, M	τ^{-1}, μsec
4.5	2.06	0.128	141
	3.13	0.255	118
	4.13	0.127	108
4.9	2.15	0.053	123
	5.60	0.209	69
	7.90	0.319	66[a]
5.3	1.90	0.042	133
	3.80	0.043	129
	8.00	0.107	87
	11.5	0.161	59
	15.0	0.215	48

[a] $\mu > 0.3\ M$.

---

(15) R. E. Shepherd, G. M. Hodgson, and D. W. Margerum, *Inorg. Chem.*, 10, 989 (1971).

(16) D. W. Margerum, B. A. Zabin, and D. L. Janes, *Inorg. Chem.*, 5, 250 (1966).

(17) See Table I, footnote *e*.

(18) M. Eigen, W. Kruse, G. Maass, and L. DeMaeyer, *Progr. React. Kinet.*, 2, 287 (1964).

(19) D. B. Rorabacher, *Inorg. Chem.*, 5, 1891 (1966).

All rate constants resolved for the six systems included in this investigation are tabulated in Table IX.

Table IX. Resolved Rate Constants for Aquocopper Ion Reacting with Polyamine and Poly(amino alcohol) Ligands at 25°, $\mu = 0.1\ M$

Ligand	$k_{\mathrm{Cu}}{}^{\mathrm{L}}$, $M^{-1}\ \mathrm{sec}^{-1}$	$k^{\mathrm{Cu-L}}$, sec^{-1}
TeMeen	$1.7\ (\pm 0.1) \times 10^{8}$	$13\ (\pm 2)$
$\mathrm{HTeMeen}^{+}$	$1.0\ (\pm 0.5) \times 10^{3}$	
$\mathrm{H_2trien}^{2+}$	$7.5\ (\pm 0.6) \times 10^{6}$	
$\mathrm{H_3trien}^{3+}$	$1.6\ (\pm 0.4) \times 10^{4}$	
$\mathrm{H_3tetren}^{3+}$	$9.0\ (\pm 0.5) \times 10^{4}$	
$\mathrm{H_4tetren}^{4+}$	$3.3\ (\pm 0.5) \times 10^{4}$	
TEA	$3.0\ (\pm 0.3) \times 10^{7}$ [a]	$5.0\ (\pm 0.9) \times 10^{3}$ [a]
TKED	$3.5\ (\pm 1.6) \times 10^{7}$	
HTKED^{+}	$5.4\ (\pm 0.4) \times 10^{4}$	
HTHPED^{+}	$5.3\ (\pm 0.2) \times 10^{4}$	

[a] $\mu = 0.3\ M$.

As noted earlier, only the TEA system was studied in the absence of the borate–mannitol buffer. Therefore, in determining whether the rate constants determined for the other five systems are influenced by the buffer, it is particularly significant that the resolved rate constants for Cu(II) reacting with unprotonated TEA and TKED are essentially identical despite the presence of buffer in the latter system. As noted in the Discussion section, the corresponding rate constants for Ni(II) show a similar agreement. Since the kinetic behavior of Ni(II) has been shown to be independent of the borate–mannitol buffer,[6,8] the similar behavior of Cu(II) and Ni(II) with these ligands is taken as strong confirmatory evidence that Cu(II) is also unaffected by the borate–mannitol buffer.

Of additional significance to the question of buffer interference is the observation that our raw kinetic data on the copper–tetren reaction at the lowest pH value studied (where the mannitol concentration was at a maximum equivalent to approximately 0.4 *M*) are in good agreement with the corresponding raw data obtained by Margerum and coworkers in the absence of buffer.[15] The observed rate constant differences between the two studies amount to no more than 20% in this pH region (our value being the lower). Thus, even under the most unfavorable circumstances the buffer influence appears to be within experimental error limits.

Discussion

As illustrated in Figure 1, the mechanism for first-bond formation between a ligand and the tetragonally distorted aquocopper(II) ion, whether associative or dissociative, can be considered to involve a three-step process: (i) diffusion of the reactants together to form a contact ion pair or outer-sphere complex (species II), (ii) substitution of the ligand for an axial inner-sphere water to produce species III, and (iii) subsequent tetragonal inversion to place the ligand in an equatorial position (species IV).[20]

If a dissociative mechanism applies, the value of k_1 (as represented in Figure 1) can be presumed to approximate the rate constant value for solvent exchange on aquocopper(II) ion[19,20] for which values ranging from 2×10^{8} to $8 \times 10^{9}\ \mathrm{sec}^{-1}$ have been variously reported.[2,21] Since k_{-0} for an outer-sphere complex involving a neutral ligand should be about $4 \times 10^{10}\ \mathrm{sec}^{-1}$ in the absence of external interactions, it would appear that $k_{-0} > k_1$. Thus, if tetragonal inversion is rapid, the observed formation rate constants for copper complexes should be approximated by the relationship

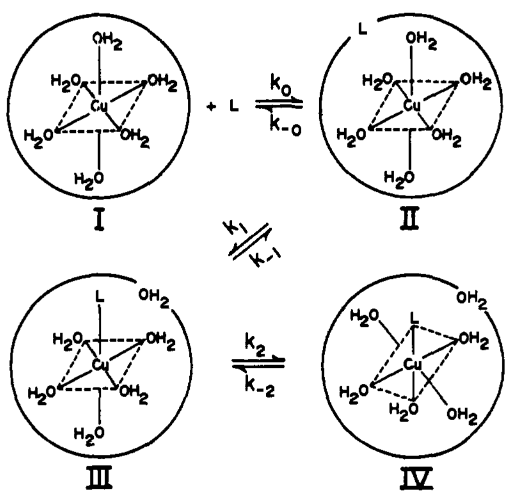


Figure 1. Schematic representation of the dissociative mechanism for ligand substitution on $\mathrm{Cu(H_2O)_6}^{2+}$ with subsequent Jahn–Teller inversion. The circle surrounding the aquocopper ion is intended to represent the next layer of solvent molecules surrounding the inner-coordination sphere.

$$k_f = K_{os}k_1 \tag{14}$$

where $K_{os} = k_0/k_{-0} \approx 0.15\ M^{-1}$ for a system involving a neutral ligand.

For octahedrally coordinated metal ions, eq 14 has been utilized to test the applicability of a dissociative mechanism for various ligand substitution reactions. For aquocopper(II) ion, however, the uncertainty in the k_1 value makes this approach infeasible.

As an alternative approach, we have chosen to compare the Cu(II) rate constants obtained in this study to the corresponding values for Ni(II).[22] Since these two metal ions are of the same charge and approximate size, electrostatic and steric factors are presumed to be identical leading to identical values of K_{os}. Furthermore, extensive evidence exists to support a dissociative mechanism for Ni(II) ligand substitution reactions.[23] Thus, consistency in the ratio of the rate constants for these two metal ions may be interpreted as strong evidence for a dissociative mechanism for Cu(II) as well. As a corollary, variations in this ratio should provide evidence for differentiating behavior which can be examined in light of the variation in the properties between these two metal ions.

The comparative rate constant values are tabulated in Table X for the ligands included in this study along with literature values for ammonia and ethylenediamine. Where available, values for Co(II) are also listed for additional comparison.

Polyamines. As shown in Table X, the rate con-

---

[20] M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963); *Ber. Bunsenges. Phys. Chem.*, **67**, 753 (1963).

[21] (a) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962); (b) R. E. Connick, Symposium on Relaxation Techniques, Buffalo, N. Y., Jan 1965; (c) C. W. Meredith, Ph.D. Dissertation, University of California at Berkeley, 1965.

[22] R. G. Wilkins, *Pure Appl. Chem.*, **33**, 583 (1973).

[23] (a) R. G. Wilkins, *Accounts Chem. Res.*, **3**, 408 (1970); (b) K. Kustin and J. Swinehart, *Progr. Inorg. Chem.*, **13**, 107 (1970).

Table X. Comparative Logarithmic Rate Constants for Ligand Substitution on Co(II), Ni(II), and Cu(II) at 25°, $\mu = 0.1\ M$ (All rate constant values in M^{-1} sec^{-1})

Ligand species	Co(II)	Ni(II)	Cu(II)	Log ($k_{\mathrm{Cu}}{}^{\mathrm{L}}/k_{\mathrm{Ni}}{}^{\mathrm{L}}$)	Cu remarks
H_2O	$5.9^{a,b}$	$4.5^{a,b}$	$\sim 9.2^{a,c}$	~ 4.7	Normal
NH_3	5.0^{b}	3.7^{b}	8.3^{d}	4.6	Normal
en		5.6^{e}	9.6^{f}	4.0	ICB; diffusion-lim
Hen$^+$		2.3^{e} (2.9^{g})	$5.2^{f,h}$	2.9	H$^+$ loss RDS
TeMeen		2.6^{e}	8.2^{j}	5.6	ICB
HTeMeen$^+$		-0.7^{e}	3.0^{j}	3.7	H$^+$ loss RDS
H(trien)$^+$		4.1^{k}			
H_2trien^{2+}		1.9^{k}	6.9^{j}	5.0	Normal
H_3trien^{3+}		$\sim 1.0^{k}$	4.2^{j}	~ 3.2	H$^+$ loss RDS
H_2tetren^{2+}		3.0^{k}	$(7.6)^{l}$	4.6	Normal
H_3tetren^{3+}		0.5^{k}	5.0^{j} (5.2^{l})	4.5	Normal
H_4tetren^{4+}			4.5^{j} (4.1^{l})		
TEA		2.5^{i}	7.5^{j}	5.0	See text
TKED	4.8^{m}	2.4^{n}	7.5^{j}	5.1	See text
HTKED$^+$	2.9^{m}	0.9^{n}	4.7^{j}	3.8	See text
THPED	4.4^{m}	2.2^{n}			
HTHPED$^+$	2.4^{m}	0.4^{n}	4.7^{j}	4.3	See text

[a] First-order rate constants (units sec^{-1}). [b] Reference 19. [c] Calculated from ligand substitution reactions (see text). [d] Reference 5. [e] Reference 7. [f] Reference 3. [g] J. C. Cassatt and R. G. Wilkins, *J. Amer. Chem. Soc.*, **90**, 6045 (1968); *cf.* ref 7, Table V, footnote *a*. [h] Reference 27. [i] Reference 9. [j] This work. [k] Reference 13 (values shown are reevaluated from ref 8). [l] Reference 15 (these authors used much lower protonation constants in resolving their kinetic data). [m] Reference 6b. [n] Reference 6a.

stants for ammonia substitution on the three aquometal ions parallel the values listed for water exchange although, in the case of Cu(II), the value we have chosen to tabulate for the water exchange rate constant is influenced by the ammonia substitution rate data[5] as well as corresponding data on glycinate and acetate substitution rate constants.[24] Nonetheless, the logarithmic ratio of $k_{\mathrm{Cu}}{}^{\mathrm{L}}/k_{\mathrm{Ni}}{}^{\mathrm{L}} = 4.7$ obtained for these two ligands is assumed to represent "normal" behavior and will be used as the standard for comparison. Deviations of ±0.3 log unit from this value will not be considered to be experimentally significant in view of the errors inherent in the Cu(II) measurements.

We note first of all that the ratio for the ethylenediamine rate constants is abnormally low. The anomalously large rate constant for this ligand reacting with Ni(II) has already been attributed by us to an "internal conjugate base" (ICB) mechanism in which, in the outer-sphere complex, one strongly basic donor atom of the ligand is presumed to hydrogen bond to a coordinated water molecule, thereby slowing the dissociation of the outer-sphere complex (*i.e.*, decreasing k_{-0}) and possibly labilizing subsequent water loss from the inner-sphere.[19,25] Loss of a cis water then permits the rapid substitution of the adjacent donor atom followed by collapse of the hydrogen bond.

In discussing their results for copper–ethylenediamine, Kirschenbaum and Kustin[3] have suggested that the ICB mechanism may also account for the anomalously rapid reaction of Cu(II) with en although they have also pointed out that an associative (SN2) mechanism would provide an equally satisfactory explanation. In referring to Kirschenbaum and Kustin's data and corresponding rate constants for related reactions with Cu(II), Pasternack and coworkers[4] imply that the ICB mechanism does not provide as satisfactory an explanation for the observed rate constants as does the SN2 mechanistic proposal.[26]

Indeed, one could well argue that the greater acidity of the coordinated waters on Cu(II) relative to Ni(II) should result in a greater rate enchancement for the former ion relative to the 100-fold enhancement observed for Ni(II)[7,25] if an ICB mechanism is operative whereas the observed rate constant ratio is low. However, the reaction of Cu(II) with en appears to have reached the diffusion limit—a fact which can be accounted for in terms of the ICB mechanism by a lowering of the k_{-0} value as a result of the hydrogen bond formation[25] and the possible increase in k_1 induced by imparting a partial hydroxide character to the coordinated water involved in the hydrogen bonding.[19,25] As a result, k_1 may exceed k_{-0} such that the reaction becomes diffusion controlled, *i.e.*, $k_f = k_0$. For a neutral ligand species we obtain $k_0 \approx 6 \times 10^9\ M^{-1}$ sec^{-1} at 25° which is clearly within the experimental error of the reported value of $4 \times 10^9\ M^{-1}$ sec^{-1}. This same explanation applies to the anomalous ligand dependence observed by Maass in studying Cu(II) reacting with acetate and sulfate. Our recalculations indicate that for the dianionic sulfate ion, k_{-0} will again be reduced to the point where the reaction becomes diffusion controlled whereas acetate has not reached this limit.

Consistent with this interpretation is the observation that the ratio of formation rate constants for TeMeen, as determined in this study, is seen to be abnormally large. This ligand is much less basic than is en (log $K_{\mathrm{H}} = 9.1$[7] as compared to 10.0 for en[14]) so that the ICB rate enhancement should be diminished.[19] Therefore, the diffusion limit may not be exceeded for Cu(II) reacting with this ligand (although the number of effective collisions may be reduced by steric hindrance for both Ni(II) and Cu(II)[7]). It should be cautioned, however, that a strict interpretation of the ratio of these formation rate constants as being reflective of a greater ICB effect for Cu(II) relative to Ni(II) is tenuous since it has recently been concluded with Ni(II) that the rate-determining step with TeMeen may be the second-bond formation.[7]

Of the protonated polyamine species, the rate constant ratio for Cu(II) compared to Ni(II) is essentially "normal" for H_2trien^{2+}, H_2tetren^{2+}, and H_3tetren^{3+}. For Hen$^+$, HTeMeen$^+$, and H_3trien^{3+}, however, the ratios are smaller than normal. In all three cases, proton loss must precede ring closure. As has already been suggested for Hen$^+$ [3] and several other protonated ligand species,[24,27] these low ratios probably reflect diminished rate constant values for Cu(II) resulting from a shift in the rate-determining step to the point of the proton loss preceding second-bond formation.

Poly(amino alcohols). As implied in the foregoing

---

(24) A. F. Pearlmutter and J. Stuehr, *J. Amer. Chem. Soc.*, **90**, 858 (1968).

(25) R. W. Taylor, H. K. Stepien, and D. B. Rorabacher, *Inorg. Chem.*, submitted for publication.

(26) It is apparent in ref 4 that the term SN2 is intended to convey the concept that bonding by the incoming ligand (en) is in the lead over ligand loss (*i.e.*, an associative interchange).

(27) V. S. Sharma and D. L. Leussing, *Inorg. Chem.*, **11**, 138 (1972).

discussion, the kinetic behavior of the polyamine reactions with $Cu(H_2O)_6{}^{2+}$ is consistent with a mechanism in which the first donor atom is conceived to bond at an axial position in the inner-sphere followed by rapid Jahn–Teller inversion of the inner-sphere in which the axial bonds are contracted while the bonds along an equatorial axis are lengthened in a concerted process,[20] thus defining a new equatorial plane containing the ligand donor atom (Figure 1). If this were not the case, second-bond formation between Cu(II) and a multidentate ligand would require the direct loss of an equatorial water molecule, a process which is presumed to be kinetically sluggish.[28]

For the polyamine reactions, the initial bond formed involves a donor atom (amine nitrogen) which is stronger than the water molecule replaced in the substitution process—making the subsequent inversion a thermodynamically favorable process.[29] For the poly(amino alcohol) ligands, however, studies on Ni(II) have previously established that the tertiary nitrogen donor atoms are too sterically hindered to permit direct bonding to the metal ion.[7] Thus, the reaction mechanisms of these ligands with Ni(II) and Co(II) involve first-bond formation with an alcoholic oxygen donor atom followed by nitrogen bond formation as the rate-determining step.[6] The steric requirements for this ligand suggest that the same mechanism must prevail for Cu(II).

For both Co(II) and Ni(II), solvation[30] and kinetic[11,31] evidence supports the contention that the alcoholic oxygen involved in the first-bond formation with the poly(amino alcohols) results in a weaker coordinate bond than that provided by the displaced water molecule, and the same situation may be presumed to exist for Cu(II). In fact, related Cu(II) solvation data indicate that, whereas the displacement of water by alcoholic oxygen occurs readily in the axial positions, there is no evidence of significant displacement in the equatorial positions even as the bulk solvent approaches anhydrous conditions.[32] Thus, it must be concluded that in the reactions of Cu(II) with the poly(amino alcohols), the Jahn–Teller inversion, which normally precedes the second-bond formation step, *must be very unfavorable from a thermodynamic standpoint.* Yet, as noted above, the only alternative route to second-bond formation would appear to involve the direct loss of an equatorial water (which has been predicted to proceed with a rate constant of only about 10^4 sec^{-1}).[28]

Based on the foregoing statements, it is surprising to note that the rate constant ratios for the Ni(II) and Cu(II) reactions with unprotonated TEA and TKED are "normal" or slightly above normal. The possibility that an ICB effect might be compensating for otherwise sluggish behavior with Cu(II) is discounted on the basis of recent evidence that the ICB effect is not a significant factor with these ligands[33] (the previous evidence to the contrary[6] having arisen from ligand conformational effects).[7] Thus, no evidence of sluggish inversion is apparent.

This behavior is particularly significant in view of the recent report by Noack, Kokoszka, and Gordon[34] that the dynamic Jahn–Teller effect is inhibited for Cu(II) when the inner-coordination sphere is inhomogeneous. Moreover, these authors noted that such inhomogeneous species were readily generated by the addition of ethanol to aqueous Cu(II) solutions giving rise to species corresponding to our presumed intermediate. In critically examining the apparent discrepancy between their observations and our kinetic data, we note that the epr measurements of Noack, *et al.*, were dependent upon variations in apparent tumbling correlation times caused by the inversion process. Since these times are in the subnanosecond region (10^{-11}–10^{-10} sec), the inversion time could still be rapid on our time scale without being observable in their measurements. Moreover, a shift in the tetragonal equilibria, which must accompany inhomogeneous ligand fields,[29] might diminish the contribution of this phenomenon to the epr signal such that it would no longer be apparent. Therefore, we conclude that a consistent explanation for both the epr and kinetic observations is provided if the inversion relaxation time for our intermediate is in the time range of 10^{-10}–10^{-8} sec. The implied decrease in the k_2/k_{-2} ratio (Figure 1) would then presumably be compensated by the increase in the k_1/k_{-1} ratio (alcohol *vs.* water) for Cu(II) relative to Ni(II) as is implied by the solvation studies.[30,32]

As with the highly protonated polyamines, the monoprotonated species of TKED and THPED exhibit low rate constant ratios which might be interpreted to indicate that proton loss is the rate-determining step. Unlike the protonated polyamines, however, the formation of the first chelate ring in $HTKED^+$ and $HTHPED^+$ does not require proton loss. (No kinetic contribution is observable for monoprotonated TEA, for which proton loss would be required prior to ring closure.) This may imply the interesting possibility that, in the reactions of Cu(II) with $HTKED^+$ and $HTHPED^+$, the rate-determining step is shifted to a point following the closure of the first chelate ring—a seemingly rare occurrence in metal complexation reactions.

Acknowledgment. This work was supported by the National Institute of General Medical Sciences under Grant GM-12596. The authors wish to thank Professor Tokuji Kimura of this department for the use of his Durrum stopped-flow spectrophotometer for a portion of this study.

---

[28] D. B. Rorabacher and D. W. Margerum, *Inorg. Chem.*, **3**, 382 (1964) (*cf.* ref 16a cited therein).

[29] L. E. Orgel and J. D. Dunitz, *Nature (London)*, **179**, 462 (1957).

[30] R. F. Pasternack and R. A. Plane, *Inorg. Chem.*, **4**, 1171 (1965).

[31] D. B. Rorabacher and R. W. Taylor, Abstracts, 3rd International Conference on Non-Aqueous Solvents, East Lansing, Mich., July 1972.

[32] N. J. Friedman and R. A. Plane, *Inorg. Chem.*, **2**, 11 (1963).

[33] D. B. Rorabacher, R. B. Cruz, C. T. Lin, and D. B. Moss, Proceedings of the XIVth International Conference on Coordination Chemistry, Toronto, June 1972.

[34] M. Noack, G. F. Kokoszka, and G. Gordon, *J. Chem. Phys.*, **54**, 1342 (1971).