Thermodynamic and Kinetic Studies on the Complexation Reactions of Copper(II) with *NN'*-Bis(β-carbamoylethyl)-*trans*-cyclohexane-1,2-diamine†

Ying-Kai Fu, Ching-Hohn Len, and Chung-Sun Chung *
Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043, Republic of China

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The interactions of *NN'*-bis(β-carbamoylethyl)-*trans*-cyclohexane-1,2-diamine (L) and copper(II) in aqueous solution have been investigated by potentiometric and spectrophotometric techniques. The log *K* values for the protonation constants of the ligand at 25.0 °C and 0.1 mol dm^{-3} $NaClO_4$ are 9.34 and 4.49. The log *K* value for the formation constant of $[Cu(L)]^{2+}$ is 12.92, and the log *K* values for the deprotonation constants of $[Cu(L)]^{2+}$ and $[Cu(H_{-1}L)]^{+}$ are −7.72 and −9.02 respectively. Electronic spectra of $[Cu(L)]^{2+}$, $[Cu(H_{-1}L)]^{+}$, and $[Cu(H_{-2}L)]$ have been recorded and are discussed. The complexation kinetics of copper(II) with this ligand have been studied under the same conditions using the stopped-flow technique. The resolved formation rate constants (in 0.10 mol dm^{-3} $NaClO_4$ at 25.0 °C) for copper(II) reacting with the unprotonated and monoprotonated ligand, L and HL^+, are 4.83×10^7 and 4.10×10^2 dm^3 mol^{-1} s^{-1} respectively. Two possible pathways for the complexation reaction are discussed.

In previous studies we have reported the thermodynamic and kinetic properties of copper(II) complexes of four closely related diamino diamides, *NN'*-bis(β-carbamoylethyl)ethylenediamine (L^1), *NN'*-bis(β-carbamoylethyl)trimethylenediamine (L^2), *NN'*-bis(β-carbamoylethyl)propylenediamine (L^3), and *NN'*-bis(β-carbamoylethyl)-2-hydroxytrimethylenediamine (L^4).[1,2] In the present study we are concerned with the thermodynamic and kinetic properties of the copper(II) complex of *NN'*-bis(β-carbamoylethyl)-*trans*-cyclohexane-1,2-diamine (L^5) in aqueous solution. A mixture of the copper(II) complexes of this ligand and its *cis* isomer has been prepared and characterized by Ojima and Nonoyama.[3]

Experimental

Reagents.—The ligand L^5 was prepared from *trans*-cyclohexane-1,2-diamine (22.8 g, 0.2 mol) and acrylamide (28.4 g, 0.4 mmol) in acetonitrile (100 cm^3) by heating the mixture under reflux for 2 h. The solution was cooled and the product filtered off, washed with acetonitrile, recrystallized from acetonitrile, and dried in air, m.p. 114—115 °C (Found: C, 56.25; H, 9.40; N, 21.80. Calc. for $C_{12}H_{24}N_4O_2$: C, 56.25; H, 9.45; N, 21.85%). The compound was 99.9% pure as determined by titration with standard base. All other chemicals used were of reagent grade from Merck. Stock solutions of copper(II) perchlorate were prepared from the twice recrystallized salt and standardized against ethylenediamine-*NNN'N'*-tetra-acetate. A saturated solution of sodium hydroxide (reagent grade) was prepared to precipitate sodium carbonate. A sample of this was diluted with freshly boiled, distilled, deionized water and stored in a Nalgene Teflon bottle. It was standardized against a weighed amount of potassium hydrogenphthalate.

Measurements.—For pH measurements a Radiometer PHM64 instrument equipped with a GK2401B combined electrode was used. The pH was standardized with NBS buffers. The hydrogen ion and hydroxide ion concentrations in 0.10 mol dm^{-3} $NaClO_4$ were calculated from $-\log [H^+] = pH - 0.11$ and $k_w = 10^{-13.78}$ [4,5] Appropriate aliquots of standard solutions of ligand or ligand and metal were titrated with a standard CO_2-free sodium hydroxide solution. In all titrations, the ionic strength was maintained relatively constant by using 0.10 mol dm^{-3} $NaClO_4$ as supporting electrolyte. The solutions were protected from air by a stream of humidified prepurified nitrogen gas and were maintained at 25.0 ± 0.1 °C during measurements. The concentrations of ligand and metal ion employed for the equilibrium work are in the range 2×10^{-3}—6×10^{-3} mol dm^{-3}. The methods of calculation were the same as reported previously.[6] The equilibrium constants were obtained by a linear least-squares fit of the data using a CDC Cyber-172 computer. A Hitachi U-3200 u.v.–visible spectrophotometer with a thermostatted cell compartment was used to record electronic absorption spectra.

Standard solutions of ligands, borate–mannitol buffers, and sodium perchlorate were prepared by weight. The kinetics of the copper(II) complex formation reactions with L^5 were studied spectrophotometrically at 320 nm, with a Union Giken RA-401 stopped-flow spectrophotometer equipped with a Union RA-415 rapid-scan attachment. For the spectrophotometric experiments the pH was controlled with a borate–mannitol buffer,[7] which was also incorporated into the reference solution. Recrystallized $NaClO_4$ was used to maintain constant ionic strength at $I = 0.10$ mol dm^{-3} in all solutions. Kinetic studies were carried out under pseudo-first-order conditions by using at least a 12-fold excess of copper(II). The concentrations of ligand and metal ion employed for the kinetic work were in the range 2.41×10^{-4}—6.88×10^{-3} mol dm^{-3}.

Results and Discussion

Protonation Constants.—A potentiometric titration of the perchlorate salt of diprotonated $(H_2L^5)^{2+}$ with standard base yielded the experimental data. The values of the protonation constants of L^5 obtained from these data using Schwargenbach's method[8] are given in Table 1 along with the corresponding values reported for L^1.[1] The first protonation constant of L^5 is much larger than the corresponding constant of L^1; however, the second protonation constant of L^5 is much smaller than that of L^1. These results indicate there must be an intramolecular hydrogen-bond formation in $(HL^5)^+$. For this ligand, the loss of internal rotational entropy due to the formation of the intramolecular hydrogen bond is very small, thus the tendency to form this bond is large.

The Composition of the Copper(II) *Complex.*—Job's method[9] of continuous variations was adopted for the determination of

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† *Supplementary data available* (No. SUP 56721, 4 pp.): observed rate constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Protonation constants of diamino diamides and equilibrium constants of their copper(II) complexes at 25.0 ± 0.1 °C and $I = 0.10$ mol dm^{-3} ($NaClO_4$)

Log K^a	L^5	$L^{1\,b}$
log K_1^H	9.34 ± 0.05	8.78 ± 0.04
log K_2^H	4.49 ± 0.08	5.82 ± 0.03
log K_f	12.92 ± 0.05	12.58 ± 0.07
log K_A	−7.72	−8.08
log K_B	−9.02	−9.33

[a] $K_1^H = [HL^+]/[H^+][L]$, $K_2^H = [H_2L^{2+}]/[H^+][HL^+]$, $K_f = [CuL^{2+}]/[Cu^{2+}][L]$, $K_A = [CuH_{-1}L^+][H^+]/[CuL^{2+}]$, $K_B = [CuH_{-2}L][H^+]/[CuH_{-1}L^+]$. [b] Data from ref. 1.

the composition of the complex. The results indicated that copper(II) forms a 1:1 complex with L^5

Equilibrium Constants for the Interactions of Copper(II) *with* L^5.—The formation reaction of copper(II) with L^5 is very fast. During titration the colour of the solution changed from blue to deep blue and finally to violet. For the 1:1 copper(II)–L^5 solution, there are two buffer regions and a definite break at $a = 2$ (here a is the number of moles of NaOH added per mole of ligand). For the 1:2 copper(II)–L^5 solution, there are two buffer regions and a definite break at $a = 1$. In the first (sloping) buffer region for each of these solutions the two protons attached to the amine groups of the ligand are dissociated by the copper(II) ion; in the second (sloping) buffer region the two amide protons are dissociated in overlapping steps. The equilibria (1)—(3)

$$Cu^{2+} + L^5 \rightleftharpoons [Cu(L^5)]^{2+} \qquad K_f = [Cu(L^5)^{2+}]/[Cu^{2+}][L^5] \quad (1)$$

$$[Cu(L^5)]^{2+} \rightleftharpoons [Cu(H_{-1}L^5)]^+ + H^+ \qquad K_A = [Cu(H_{-1}L^5)^+][H^+]/[Cu(L^5)^{2+}] \quad (2)$$

$$[Cu(H_{-1}L^5)]^+ \rightleftharpoons [Cu(H_{-2}L^5)] + H^+ \qquad K_B = [Cu(H_{-2}L^5)][H^+]/[Cu(H_{-1}L^5)^+] \quad (3)$$

were found to describe the reactions of copper(II) with this ligand. Below $a = 2$ for the 1:1 titration the formation of $[Cu(L^5)]^{2+}$ takes place. The stability constant for this complex obtained is given in Table 1 together with the corresponding value for $[Cu(L^1)]^{2+}$.

The stability constant of $[Cu(L^5)]^{2+}$ is slightly larger than that of $[Cu(L^1)]^{2+}$. Within the $[Cu(L^5)]^{2+}$ unit, the N–Cu–O bond angles are close to 180° and the CuN_2O_2 atoms are almost planar.[10] Consequently, the N_2O_2 donor set in this complex nearly matches the symmetry properties of the copper(II) orbitals; thus, a relatively stable complex is expected and found.

Deprotonation reactions of $[Cu(L^5)]^{2+}$ and $[Cu(H_{-1}L^5)]^+$ [equations (2) and (3)] take place in the region $a = 2$—4 of the 1:1 titration curve (or in the region $a = 1$—3 of the 1:2 titration curve). For these deprotonation reactions the relationship between K_A and K_B is as in equations (4)—(9) where c_{H_2L} and c_M

$$1/K_A = AK_B + B \quad (4)$$

$$A = \frac{(2 - a)c_{H_2L} + 2c_M - [H^+] + [OH^-] - \alpha'[L]}{[H^+]^2(ac_{H_2L} - 2c_{H_2L} + [H^+] - [OH^-] + \alpha'[L])} \quad (5)$$

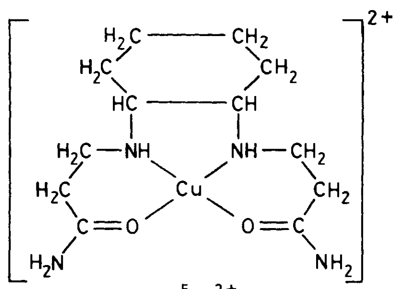
$$B = \frac{(a - 2)c_{H_2L} - c_M + [H^+] - [OH^-] + \alpha'[L]}{[H^+]\{(2 - a)c_{H_2L} - [H^+] + [OH^-] - \alpha'[L]\}} \quad (6)$$

$$\alpha = K_1^H K_2^H[H^+]^2 + K_1^H[H^+] + 1 \quad (7)$$

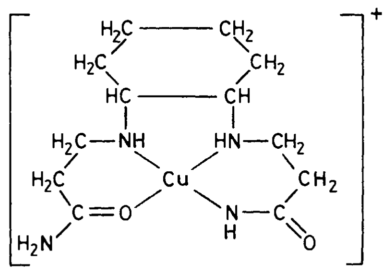
$$\alpha' = 2K_1^H K_2^H[H^+]^2 + K_1^H[H^+] \quad (8)$$

$$[L] = (c_{H_2L} - c_M)/\alpha \quad (9)$$

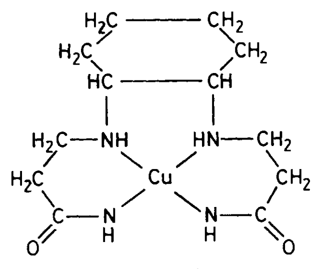
are the total concentrations of the ligand and the metal species, respectively; A and B were calculated from several sets of values of a, $[H^+]$, $[OH^-]$, c_M, and c_{H_2L} taken from each of the titration curves. The values of K_A and K_B for these copper(II) complexes, obtained by using Schwarzenbach's method,[11] are listed in Table 1.



$[Cu(L^5)]^{2+}$



$[Cu(H_{-1}L^5)]^+$



$[Cu(H_{-2}L^5)]$

The deprotonation constants of $[Cu(L^1)]^{2+}$ and $[Cu(H_{-1}L^1)]^+$ are slightly smaller than those of $[Cu(L^5)]^{2+}$ and $[Cu(H_{-1}L^5)]^+$, respectively. These sequences are presumably mainly due to the relative solvation energies of the complexes: that of $[Cu(L^1)]^{2+}$ is much larger than that of $[Cu(L^5)]^{2+}$, while that of $[Cu(H_{-1}L^1)]^+$ is slightly larger than that of $[Cu(H_{-1}L^5)]^+$. Thus, K_A for $[Cu(L^1)]^{2+}$ is smaller than that for $[Cu(L^5)]^{2+}$. The sequence of K_B, $[Cu(H_{-1}L^5)]^+ > [Cu(H_{-1}L^1)]^+$ can be explained similarly by the relative solvation energies of these complexes.

Electronic Absorption Spectra.—The electronic absorption spectra of Cu^{II}–L^5 solutions are shown in Figure 1; these spectra can be resolved into their components using equation (10). The

$$A = b(\varepsilon_{Cu^{2+}}[Cu^{2+}] + \varepsilon_{CuL^{2+}}[Cu(L^5)^{2+}] + \varepsilon_{CuH_{-1}L^+}[Cu(H_{-1}L^5)^+] + \varepsilon_{CuH_{-2}L}[Cu(H_{-2}L^5)] \quad (10)$$

Table 2. Absorption maxima for copper(II) complexes of diamino diamides in the visible region

Compound	$\lambda_{max.}$/nm	Molar absorptivity (ε/dm^3 mol^{-1} cm^{-1})
$[Cu(L^5)]^{2+}$	643	138
$[Cu(H_{-1}L^5)]^+$	576	103
$[Cu(H_{-2}L^5)]$	532	104
$[Cu(L^1)]^{2+}$	645*	126
$[Cu(H_{-1}L^1)]^+$	580*	102
$[Cu(H_{-2}L^1)]$	535*	95

* Data from ref. 2.

Table 3. Rate constants for formation (k_f) of $[Cu(L^5)]^{2+}$ at 25.0 ± 0.1 °C and I = 0.10 mol dm^{-3} ($NaClO_4$)

pH	k_f/dm^3 mol^{-1} s^{-1}	pH	k_f/dm^3 mol^{-1} s^{-1}
5.40	3.60×10^3	4.92	1.25×10^3
5.33	3.11×10^3	4.83	1.02×10^3
5.22	2.51×10^3	4.73	8.17×10^2
5.11	1.89×10^3	4.68	7.33×10^2
5.00	1.57×10^3	4.60	6.17×10^2

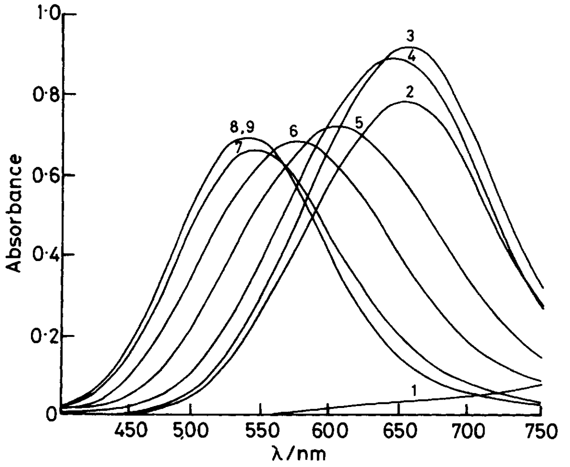


Figure 1. Visible absorption spectra of Cu^{II}–L^5 solutions. All solutions contain 0.002 41 mol dm^{-3} $Cu[ClO_4]_2$, 0.002 41 mol dm^{-3} $[H_2L^5][ClO_4]_2$, and 0.10 mol dm^{-3} sodium perchlorate. The pH values: (1) 1.33, (2) 4.23, (3) 5.78, (4) 7.51, (5) 8.54, (6) 9.28, (7) 10.21, (8) 11.67, and (9) 11.98

absorption characteristics of $[Cu(L^5)]^{2+}$, $[Cu(H_{-1}L^5)]^+$, and $[Cu(H_{-2}L^5)]$ so obtained are given in Table 2, along with the reported values for the Cu^{II}–L^1 system.

As shown in Table 2, the absorption maxim, $\lambda_{max.}$, decreases in the order $[Cu(L^1)]^{2+} > [Cu(L^5)]^{2+}$, $[Cu(H_{-1}L^1)]^+ > [Cu(H_{-1}L^5)]^+$, and $[Cu(H_{-2}L^1)] > [Cu(H_{-2}L^5)]$. These sequences can be correlated with the electron-donating power of the cyclohexylene group, which strengthens the electron-donor ability of the amino nitrogen atoms, resulting in a stronger metal–ligand interaction.

Kinetic Results.—The kinetics of the complexation reaction of copper(II) and L^5 were studied at 25 °C, I = 0.10 mol dm^{-3} ($NaClO_4$), and pH 4.60—5.40. Under these conditions, the complex formation reaction was found to proceed to completion. Kinetics studies were carried out under pseudo-first-order conditions by using at least a 12-fold excess of copper(II); the observed pseudo-first-order rate constants have been deposited (SUP 56721). Plots of $k_{obs.}$ *vs.* $[Cu^{2+}]$ give good straight lines according to equation (11) where $[\Sigma(L^5)]$

Table 4. Resolved rate constants for the formation and dissociation of copper(II) complexes of diamino diamides in aqueous solution at 25.0 ± 0.1 °C and I = 0.10 mol dm^{-3} ($NaClO_4$)

Ligand	$k_{Cu}{}^{L}$/dm^3 mol^{-1} s^{-1}	$k_{Cu}{}^{HL}$/dm^3 mol^{-1} s^{-1}	k^{CuL}/s^{-1}	$k_H{}^{CuL}$/dm^3 mol^{-1} s^{-1}
L^5	4.83×10^7	4.10×10^2	5.81×10^{-6}	0.13
L^1*	3.35×10^8	4.75×10^4	8.81×10^{-5}	7.56

* Data from ref. 1.

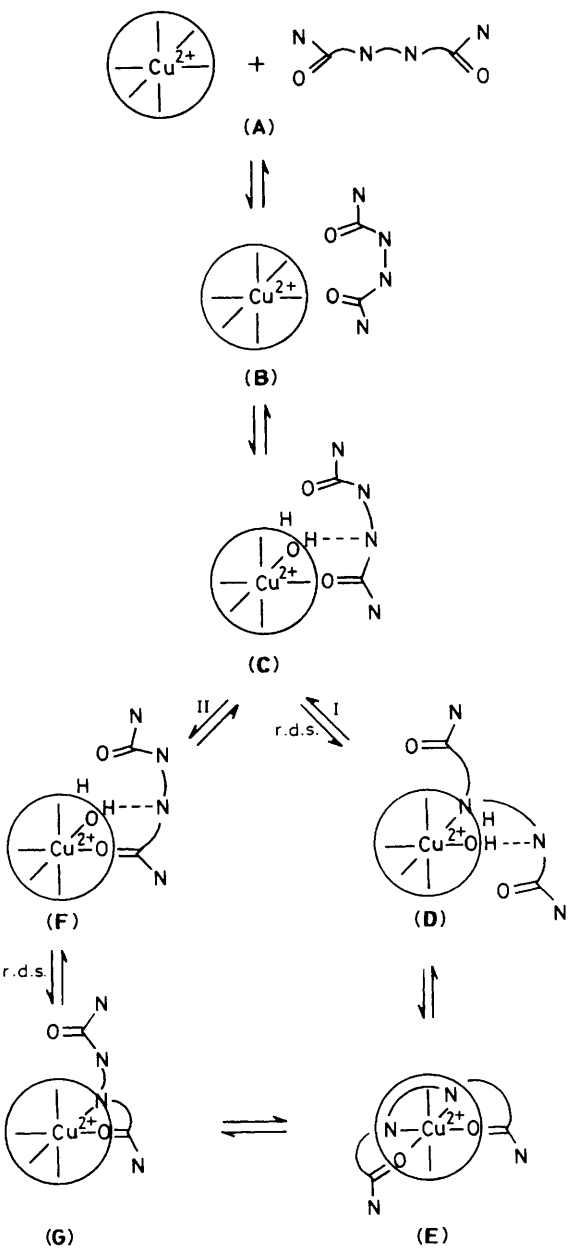


Figure 2. Possible pathways for the reaction of copper(II) with L^5. The circle represents the division between inner-sphere co-ordination and outer-sphere association (r.d.s. = rate-determining step)

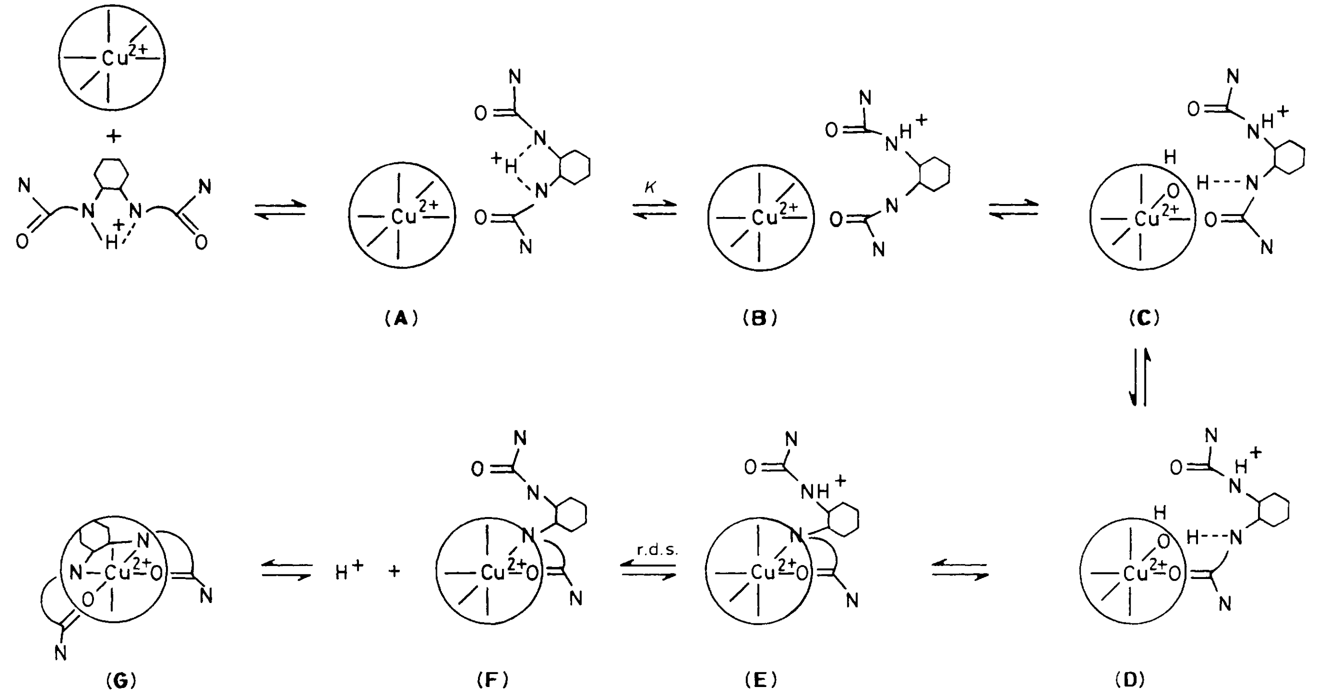


Figure 3. Possible pathways for the reaction of copper(II) with the monoprotonated ligand $(HL^5)^+$. The circle represents the division between inner-sphere co-ordination and outer-sphere association (r.d.s. = rate-determining step)

$$d[Cu(L^5)^{2+}]/dt = k_{obs.}[\Sigma(L^5)] = k_f[Cu^{2+}][\Sigma(L^5)] \quad (11)$$

represents the total concentration of all species of the uncomplexed ligand. The slopes of these plots give the values of the formation rate constants as a function of pH (Table 3).

In the pH range of this study, the predominant form of the ligand is the diprotonated $(H_2L^5)^{2+}$, and the reactive species are the unprotonated L^5 and the monoprotonated $(HL^5)^+$. Reactions of these species with Cu^{2+} to produce the chelate $[Cu(L^5)]^{2+}$ are then considered to occur, equations (12) and (13). The rate law of the formation of $[Cu(L^5)]^{2+}$ is described

$$Cu^{2+} + [HL^5]^+ \longrightarrow [Cu(L^5)]^{2+} + H^+ \quad k_{Cu}{}^{HL} \quad (12)$$

$$Cu^{2+} + L^5 \longrightarrow [Cu(L^5)]^{2+} \quad k_{Cu}{}^{L} \quad (13)$$

by equation (14); combining this with equation (11) yields

$$d[Cu(L^5)^{2+}]/dt = k_{Cu}{}^{HL}[Cu^{2+}][(HL^5)^+] + k_{Cu}{}^{L}[Cu^{2+}][L^5] \quad (14)$$

$$\frac{k_f[\Sigma(L^5)]}{[L^5]} = k_{Cu}{}^{HL}K_1{}^{H}[H^+] + k_{Cu}{}^{L} \quad (15)$$

equation (15). A plot of equation (15) gives a very good straight line and the resolved rate constants obtained are listed in Table 4 along with the corresponding values for the Cu^{II}–L^1 system.[1] The dissociation rate constants of $[Cu(L^5)]^{2+}$ obtained from the formation rate constants and the corresponding stability constants are given in Table 4 along with the reported values for $[Cu(L^1)]^{2+}$.[1]

Kinetics and Mechanism for the Formation of $[Cu(L^5)]^{2+}$—The rate constant for the complexation reaction of copper(II) with L^5 is very large because of the internal conjugate-base effect.[12,13] The essential concept of this accelerating effect is that one amino group of L^5 is presumed to hydrogen bond to a co-ordinated water molecule of the aquated copper(II) ion to give a strong outer-sphere complex and to labilize subsequent water exchange from an adjacent position of the copper(II) ion, so that the other amino or the amide group of L^5 can form an inner-sphere complex.[14]

The two possible pathways for the formation reaction of copper(II) with L^5 are shown in Figure 2. In the reaction path I, initial bonding to an amino nitrogen donor atom [(**A**) ⟶ (**B**) ⟶ (**C**) ⟶ (**D**) ⟶ (**E**)], the rate-determining step is the formation of the first co-ordination bond [(**C**) ⟶ (**D**) in Figure 2]. In the reaction path II, initial bonding to an amide oxygen donor atom [(**A**) ⟶ (**B**) ⟶ (**C**) ⟶ (**F**) ⟶ (**G**) ⟶ (**E**)], the rate-determining step is the formation of the second co-ordination bond [(**F**) ⟶ (**G**) in Figure 2]. Addition of the cyclohexane group on the central chelate ring of the ligand strongly retards the formation reaction *via* the reaction path I; however the cyclohexylene group has a less dramatic effect on the rate of the formation reaction *via* the reaction path II. If the reaction path II were the main reaction path for both the reaction of copper with L^1 and the reaction of copper with L^5, these two reactions should be at comparable rates. The results listed in Table 4 indicate that the rate for the reaction of L^1 is much faster than that of L^5. These results indicate that the reaction path I, and not II, is the main one for the reaction of L^1 with copper. Addition of the cyclohexylene group on the central chelate ring of the ligand retards the formation reaction *via* the reaction path I to such an extent that the reaction path II, the initial co-ordination of the amide oxygen donor atom, becomes a competitive pathway. Therefore, both reaction paths I and II make contributions in the reaction of copper(II) with L^5.

For the reaction of copper(II) with the monprotonated ligand, the reaction path I (initial bonding to an amino nitrogen donor atom) is strongly hindered because of the electrostatic repulsion and the loss of internal conjugate-base enhancement. Thus, the main reaction path for the reaction of copper(II) with HL^+ is the reaction path II, initial bonding to an amide oxygen donor atom

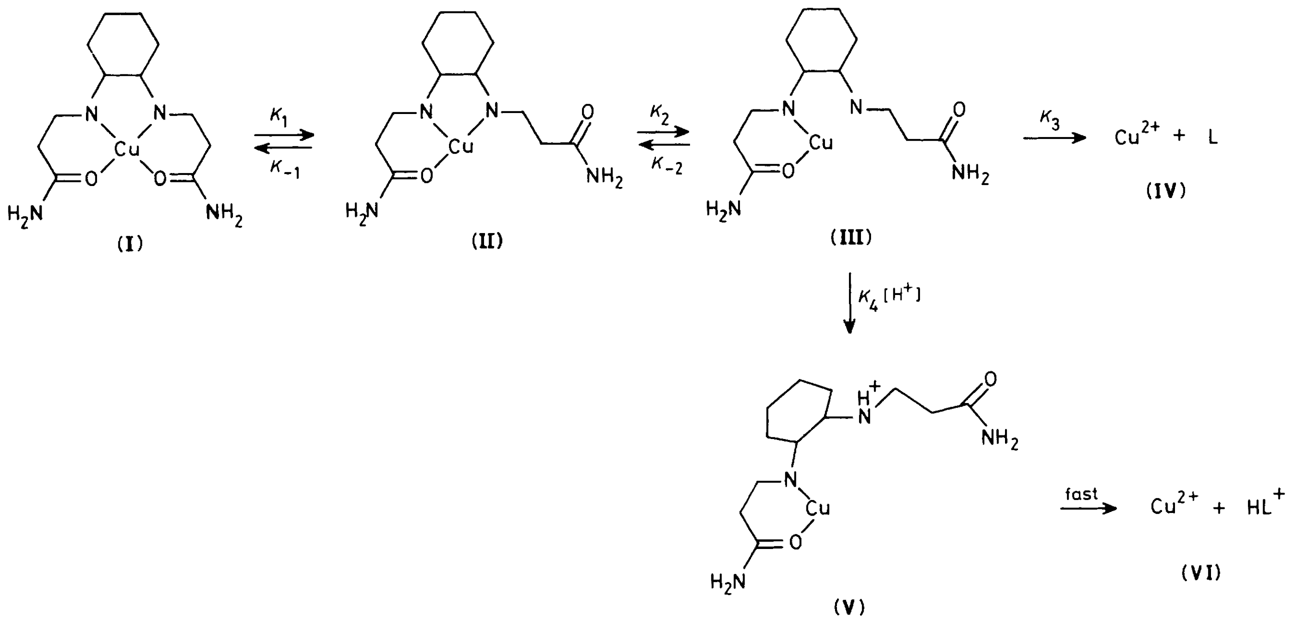


Figure 4. Proposed mechanism for the dissociation reaction of $[Cu(L^5)]^{2+}$

as shown in Figure 3. Proton loss [(**E**) ⟶ (**F**)] is the rate-limiting step for this path. As shown in Table 4, $k_{Cu}{}^{HL}$ for the reaction of $(HL^5)^+$ is smaller than that for the reaction of $(HL^1)^+$ by a factor of 116. The small rate for the reaction of $(HL^5)^+$ is due to the internal hydrogen bond in this ligand. The possible kinetically reactive species for $(HL^5)^+$ is that shown in (**B**) of Figure 3, although the thermodynamically stable species is the internal hydrogen-bonded form shown in (**A**). The equilibrium constant K for these two species in Figure 3 is expected to be small; thus the reaction of $(HL^5)^+$ is slower than that of $(HL^1)^+$.

Kinetics and Mechanism of the Dissociation Reaction of $[Cu(L^5)]^{2+}$.—The mechanism for the dissociation reaction of $[Cu(L^5)]^{2+}$ under the conditions used in this work is shown in Figure 4. In the water dissociation pathway, (**I**) ⟶ (**II**) ⟶ (**III**) ⟶ (**IV**) in this figure, the rate-determining step is the breakage of the second copper(II)–nitrogen bond [(**III**) ⟶ (**IV**)]; and the overall rate constant, $k^{CuL} = (k_1k_2/k_{-1}k_{-2})k_3$. In general, individual steps in the 'unwrapping' of diamino diamide from copper(II) are expected to be fast, but the successive equilibria leading up to the cleavage of the second copper–nitrogen bond are very unfavourable, *i.e.* $k_1k_2/k_{-1}k_{-2}$ is extremely small. Thus, a slow dissociation rate results. The fact that the rate constant k^{CuL} for the reaction of $[Cu(L^5)]^{2+}$ is much smaller than that for the reaction of $[Cu(L^1)]^{2+}$ is indicative of associative activation, *i.e.* solvation of the metal ion plays an important role in the rate-determining step [(**III**) ⟶ (**IV**) in Figure 4].

In the pH range studied in this work, an increase in the dissociation rate occurs as a result of protonation of the free amine group after the chelate ring is opened. The sequence of this proton-assisted pathway is (**I**) ⟶ (**II**) ⟶ (**III**) ⟶ (**V**) ⟶ (**VI**). The rate-determining step for this pathway is the protonation of the released amino group [(**III**) ⟶ (**V**) in Figure 4]; the overall rate constant, $k_H{}^{CuL} = (k_1k_2/k_{-1}k_{-2})k_4$. Direct protonation of the intact chelate is not important in this pH range;[15] the acid catalysis operates by H_3O^+ scavenging of the released ligand [(**III**) ⟶ (**V**)], after the copper–nitrogen bond rupture.

The rate constant $k_H{}^{CuL}$ for the reaction of $[Cu(L^5)]^{2+}$ is smaller than that for the reaction of $[Cu(L^1)]^{2+}$ by a factor of 58. In reality the proton is extensively solvated, or linked to a cluster of water molecules. Thus, the released amino group has to move far enough away from the metal ion prior to its protonation [(**III**) ⟶ (**V**) in Figure 4]. This step is hindered by the cyclohexylene group, which strongly hinders rotation of the released amino group out of the co-ordination sphere of the metal ion.

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