Thermodynamic and Kinetic Studies on the Complexation Reactions of Aqua(*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) (blue) with Neutral Monodentate Ligands†

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In order to study the charge effects of the entering and leaving groups in substitution reactions of five-co-ordinate complexes, the equilibrium constants (K) of the complexation reactions of a trigonal-bipyramidal complex, aqua(*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II), $[CuL(H_2O)]^{2+}$ (blue isomer), with eight neutral monodentate ligands (L′), ammonia, methyl-, dimethyl-, trimethyl- and ethyl-amine, aniline, pyridine and piperidine, as well as the rate constants for the formation (k_f) and the aquation (k_{aq}) of $[CuL(L')]^{2+}$ have been determined in 0.20 mol dm^{-3} $NaClO_4$ at 25.0 °C. The formation rate constants are discussed in relation to a combination of the basicity, the softness and the size of the entering group. A plot of log k_f against log K gives a straight line with a slope of 0.98. The kinetic results are consistent with an associative-interchange, I_a, mechanism.

Previously we have reported the kinetics and mechanism of the reactions of the blue[1] and red[2] isomers of aqua(*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)-copper(II) $[CuL(H_2O)]^{2+}$ with uninegative ligands, Cl^-, Br^-, I^-, N_3^-, SCN^-, O_2CMe^- and CN^-, in aqueous solution. In the current investigation, we have attempted to study the charge effects of the entering and leaving groups in these reactions. To accomplish this we have extended our studies to the equilibria and kinetics of reactions of the blue isomer with neutral monodentate ligands L′ containing nitrogen-donor atom, namely ammonia, methyl-, dimethyl-, trimethyl- and ethyl-amine, aniline, pyridine and piperidine, in aqueous solution [equation (1)].

$$[CuL(H_2O)]^{2+} + L' \underset{k_{aq}}{\overset{k_f}{\rightleftharpoons}} [CuL(L')]^{2+} + H_2O; \quad K = k_f/k_{aq} \qquad (1)$$

The crystal structure of the reactant $[CuL(H_2O)]^{2+}$ has been reported.[3] As shown in Fig. 1, this complex ion is a suitable trigonal-bipyramidal copper(II) substrate with a non-removable tetradentate ligand and the equatorially co-ordinated aqua group replaceable by a variety of neutral monodentate ligands.

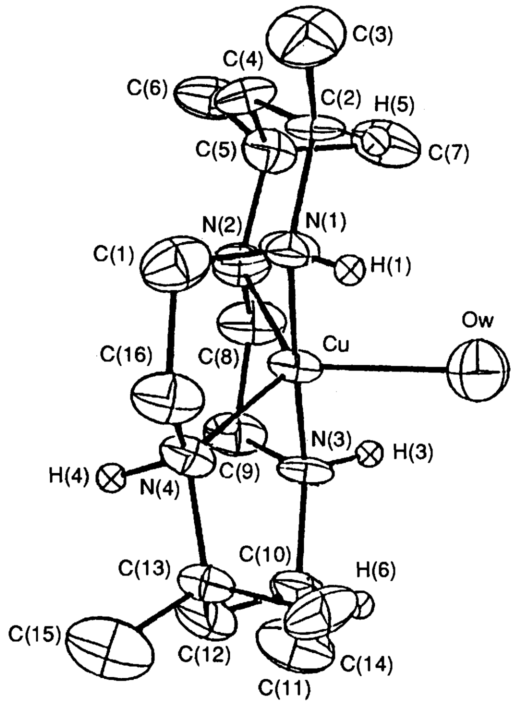

Fig. 1 Crystal structure of $[CuL(H_2O)]^{2+}$

Experimental

Reagents.—The macrocyclic ligand L was prepared using the procedures described by Curtis.[4] In order to prepare $[CuL(H_2O)][ClO_4]_2$, cold aqueous 10^{-3} mol dm^{-3} L (200 cm^3) and cold aqueous 10^{-3} mol dm^{-3} $Cu(ClO_4)_2$ (200 cm^3) were mixed rapidly with 5 mol dm^{-3} NaOH (8 cm^3). After 10 s, 5 mol dm^{-3} $HClO_4$ (10 cm^3) was added to acidify and quench the reaction. The salt $NaClO_4 \cdot H_2O$ (10 g) was dissolved in the solution and after cooling a blue precipitate was obtained. The solution was filtered and the crystals were washed with small amounts of 10^{-4} mol dm^{-3} $HClO_4$. The blue solid was recrystallized twice from 10^{-4} mol dm^{-3} $HClO_4$. Other chemicals used were of reagent grade from Merck or Fluka.

Instrumentation.—A Hitachi U-3200 UV/VIS spectrophotometer with a thermostatted cell compartment was used to measure absorption spectra. Kinetic data were obtained by using a Union Giken RA-401 stopped-flow spectrophotometer equipped with a Union RA-415 rapid-scan attachment. The temperature was maintained within 25.0 ± 0.1 °C. The rate constants and equilibrium constants were obtained by a linear least-squares fit of the data by using a CDC Cyber-172 computer. A Radiometer automatic titration assembly, consisting of titrator (TTT 85), autoburette (ABU 80), pH meter (PHM 82) equipped with a GK 2401B combined electrode and

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† *Supplementary data available* (No. SUP 56826, 23 pp.): plots of molar absorption coefficients and of pseudo-first-order rate constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

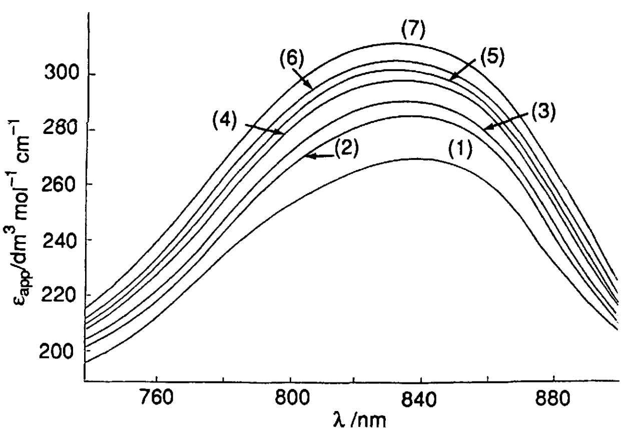

Fig. 2 Electronic spectra of copper(II) complexes at various concentrations $[NH_3]_T$. All solutions contain 4.21×10^{-4} mol dm^{-3} copper(II) complexes, $[CuL(H_2O)]^{2+}$ + $[CuL(NH_3)]^{2+}$, at pH 9.79, 25.0 ± 0.1 °C and I = 0.20 mol dm^{-3} ($NaClO_4$). The total concentration of NH_3, $[NH_3]$ + $[NH_4^+]$, is as follows. (1) 0, (2) 0.0089, (3) 0.0118, (4) 0.0244, (5) 0.0342, (6) 0.0497 and (7) 0.0907 mol dm^{-3}

Table 1 Equilibrium constants for the reaction $[CuL(H_2O)]^{2+} + L' \rightleftharpoons [CuL(L')]^{2+} + H_2O$ at 25.0 ± 0.1 °C and I = 0.20 mol dm^{-3} ($NaClO_4$)

L'	K/dm³ mol⁻¹
C_5H_5N	0.791 ± 0.036
NH_2Ph	5.33 ± 0.11
NMe_3	66.7 ± 5.6
NH_3	84.1 ± 0.9
NH_2Me	405 ± 29
NH_2Et	417 ± 27
$NHMe_2$	513 ± 41
$C_5H_{10}NH$	1240 ± 90

a K401 calomel electrode was used to prepare solutions at constant pH.

Equilibrium Constant Determinations.—The spectrophotometric measurements were carried out as described in previous papers.[5–8] The ionic strength was maintained constant at I = 0.20 mol dm^{-3} ($NaClO_4$) for all solutions. The pH was standardized with NBS buffers. The hydrogen-ion and hydroxide-ion concentrations in I = 0.20 mol dm^{-3} ($NaClO_4$) were calculated from $-\log[H^+]$ = pH -0.14 and $K_w = 10^{-13.73}$ mol² dm^{-6}.[9]

Kinetic Measurements.—The kinetics of the complexation reactions of $[CuL(H_2O)]^{2+}$ with ammonia, methyl-, dimethyl-, trimethyl- and ethyl-amine were studied at 834 nm, those with aniline, pyridine and piperidine were studied at 840 nm, with a Union Giken RA-401 stopped-flow spectrophotometer equipped with a Union RA-415 rapid-scan attachment. The pH of the solution was adjusted by using a pH-stat and borate buffer. No difference was detectable in reactions with and without borate buffer. The ionic strength was maintained constant at I = 0.20 mol dm^{-3} ($NaClO_4$) for all solutions. Kinetic studies were carried out under pseudo-first-order conditions by using at least a 15-fold excess of L' over the complex concentration (4.21×10^{-4} mol dm^{-3}).

Results

Composition of the Copper(II) *Complexes.*—Job's method of continuous variations[10] was used to determine the composition of the copper(II) complexes (see SUP 56826). The results indicate that $[CuL]^{2+}$ forms a 1:1 complex with each of these neutral monodentate ligands.

Equilibrium Constants.—Addition of a solution of the neutral monodentate ligand L' to a solution of $[CuL(H_2O)]^{2+}$ resulted in a simple equilibrium (1) involving the replacement of the co-ordinated aqua group. The values of the apparent molar absorption coefficients obtained by using equation (2) have been

$$\varepsilon_{app} = A/l[M]_T \qquad (2)$$

deposited (SUP 56826). Here l is the length of the cell and $[M]_T$ is the total concentration of the copper(II) complexes, $[CuL(H_2O)]^{2+}$ + $[CuL(L')]^{2+}$. The electronic spectra of the complexes at various total concentrations of NH_3 are shown in Fig. 2.

For the reaction of $[CuL(H_2O)]^{2+}$ with NH_3, NH_2Me, $NHMe_2$, NMe_3, NH_2Et, NH_2Ph and $C_5H_{10}NH$, the equilibrium constants are large. The molar absorptivities of the products of these reactions were measured (see SUP 56826). The values of $[L']$ as a function of the total concentration of L' obtained by using equation (3) have also been deposited. Here $[L']_T$ is the

$$[L'] = \frac{1}{1 + K_a[H^+]}\left\{[L']_T - \frac{(\varepsilon_{CuL} - \varepsilon_{app})[M]_T}{(\varepsilon_{CuL} - \varepsilon_{CuLL'})}\right\} \qquad (3)$$

total concentration of L', K_a is the protonation constant of L';[11] ε_{CuL} and $\varepsilon_{CuLL'}$ are the molar absorptivities of $[CuL(H_2O)]^{2+}$ and $[CuL(L')]^{2+}$, respectively (SUP 56826). For the reaction of $[CuL(H_2O)]^{2+}$ with C_5H_5N, $[L']_T$ is much larger than $[M]_T$, therefore $[L'] = [L']_T/(1 + K_a[H^+])$.

For each of these reactions, a plot of ε_{app} against $(\varepsilon_{app} - \varepsilon_{CuL})/[L']$ gives a straight line in accordance with equation (4).[5]

$$\varepsilon_{app} = -\frac{1}{K}\left(\frac{\varepsilon_{app} - \varepsilon_{CuL}}{[L']}\right) + \varepsilon_{CuLL'} \qquad (4)$$

These plots have been deposited. The values of the equilibrium constants obtained from their slopes are listed in Table 1. The values of $\varepsilon_{CuLL'}$ obtained from the intercepts are in excellent agreement with those obtained by spectrophotometric measurements.

Rate Constants.—The pseudo-first-order rate constants obtained under the condition that $[L']_T$ is much larger (> 15-fold) than $[CuL(H_2O)^{2+}]$ are listed in Table 2. Since the equilibrium constants of equation (1) are relatively small in aqueous solution, $[CuL(L')]^{2+}$ is only incompletely formed at ordinary concentrations of X. Reaction (1) is therefore reversible. The observed pseudo-first-order rate constants have been plotted *vs.* the concentration of X, which is equal to $([L']_T - [CuL(L')^{2+}])/(1 + K_a[H^+])$, and obey equation (5).

$$k_{obs} = k_{aq} + k_f[L'] \qquad (5)$$

The results have been deposited (see SUP 56826). The rate constants of complexation (slope) and of aquation (intercept) are listed in Table 3. The equilibrium constants calculated from the rate constants by using equation (6) and listed in Table 3 are

$$K = k_f/k_{aq} \qquad (6)$$

in excellent agreement with those obtained by spectrophotometric measurements under equilibrium conditions.

Discussion

Equilibrium Constants.—As listed in Table 1, the equilibrium constants increase in the order $C_5H_5N < NH_2Ph < NMe_3 < NH_3 < NH_2Me < NH_2Et < NHMe_2 < C_5H_{10}NH$. This sequence can be explained by a combination of the basicity,[11] the softness, and the steric effect of the ligand. A plot of log K against log K_a of the ligands is shown in Fig. 3. The ligands NH_3, NH_2Me, $NHMe_2$, NH_2Et and $C_5H_{10}NH$, classified as hard bases,[12] obey the equation log K = 0.62 log K_a − 3.9. The ligands C_5H_5N and NH_2Ph, which are softer than NH_3,[12] lie

Table 2 Observed pseudo-first-order rate constants, k_{obs}/s^{-1},[a] for the reaction $[CuL(H_2O)]^{2+} + L' \rightleftharpoons [CuL(L')]^{2+} + H_2O$ at 25.0 ± 0.1 °C and I = 0.20 mol dm^{-3} ($NaClO_4$)

L′	$10^2[L']_T$/mol dm^{-3}	$10^2[L']$/mol dm^{-3}	k_{obs}/s^{-1}	L′	$10^2[L']_T$/mol dm^{-3}	$10^2[L']$/mol dm^{-3}	k_{obs}/s^{-1}
NH_3[b]	1.00	0.64	2.49 ± 0.03	NH_2Et[c]	1.00	0.07	2.16 ± 0.03
	2.00	1.27	3.34 ± 0.04		2.00	0.13	2.51 ± 0.04
	4.00	2.55	5.05 ± 0.04		4.00	0.27	3.51 ± 0.04
	6.00	3.82	7.37 ± 0.06		6.00	0.40	4.31 ± 0.04
	8.00	5.09	8.54 ± 0.06		8.00	0.54	5.39 ± 0.04
NH_2Me[d]	1.00	0.07	2.11 ± 0.03	$C_5H_{10}NH$[e]	1.00	0.02	2.25 ± 0.04
	2.00	0.14	2.46 ± 0.03		2.00	0.05	3.20 ± 0.04
	4.00	0.27	3.38 ± 0.03		4.00	0.10	4.06 ± 0.05
	6.00	0.41	4.25 ± 0.05		6.00	0.14	5.21 ± 0.05
	8.00	0.50	5.17 ± 0.05		8.00	0.19	6.31 ± 0.06
$NHMe_2$[f]	1.00	0.06	2.23 ± 0.03	C_5H_5N[g]	1.00	1.00	2.09 ± 0.04
	2.00	0.11	2.71 ± 0.03		2.00	2.00	2.11 ± 0.04
	4.00	0.23	3.62 ± 0.04		4.00	4.00	2.14 ± 0.05
	6.00	0.34	4.68 ± 0.05		6.00	6.00	2.17 ± 0.05
	8.00	0.45	5.62 ± 0.06		8.00	8.00	2.20 ± 0.05
NMe_3[h]	1.00	0.37	1.86 ± 0.03	NH_2Ph[i]	1.00	1.00	2.06 ± 0.03
	2.00	0.73	2.24 ± 0.04		2.00	2.00	2.22 ± 0.04
	4.00	1.46	2.81 ± 0.05		4.00	4.00	2.42 ± 0.04
	6.00	2.19	3.86 ± 0.05		6.00	6.00	2.60 ± 0.04
	8.00	2.92	4.27 ± 0.06		8.00	8.00	2.84 ± 0.06

[a] $[CuL(H_2O)^{2+}]_T = 4.21 \times 10^{-4}$ mol dm^{-3}; mean value of five kinetic runs. [b] pH 9.79 ± 0.02, log K_a = 9.40. [c] pH 9.60 ± 0.02, log K_a = 10.6. [d] pH 9.71 ± 0.02, log K_a = 10.7. [e] pH 9.72 ± 0.02, log K_a = 11.2. [f] pH 9.72 ± 0.02, log K_a = 10.8. [g] pH 9.72 ± 0.02, log K_a = 5.24. [h] pH 9.70 ± 0.02, log K_a = 9.80. [i] pH 9.73 ± 0.02, log K_a = 4.65.

Table 3 Rate constants for substitution by L′(k_f) of $[CuL(H_2O)]^{2+}$ and for aquation (k_{aq}) of $[CuL(L')]^{2+}$ and equilibrium constants* for the complexation reactions of $[CuL(H_2O)]^{2+}$ with L′ at 25.0 °C and I = 0.20 mol dm^{-3} ($NaClO_4$)

L′	k_f/dm^3 mol^{-1} s^{-1}	k_{aq}/s^{-1}	K*/dm^3 mol^{-1}
C_5H_5N	1.55 ± 0.04	2.08 ± 0.01	0.745 ± 0.020
NH_2Ph	10.7 ± 0.5	1.98 ± 0.03	5.40 ± 0.27
NMe_3	98.0 ± 7.3	1.51 ± 0.15	65.1 ± 8.1
NH_3	141 ± 7	1.59 ± 0.27	88.5 ± 15.7
NH_2Me	648 ± 37	1.62 ± 0.13	399 ± 39.4
NH_2Et	687 ± 15	1.64 ± 0.06	419 ± 18
$NHMe_2$	846 ± 18	1.73 ± 0.06	489 ± 20
$C_5H_{10}NH$	2325 ± 103	1.86 ± 0.14	1250 ± 110

* Kinetically determined value = k_f/k_{aq}.

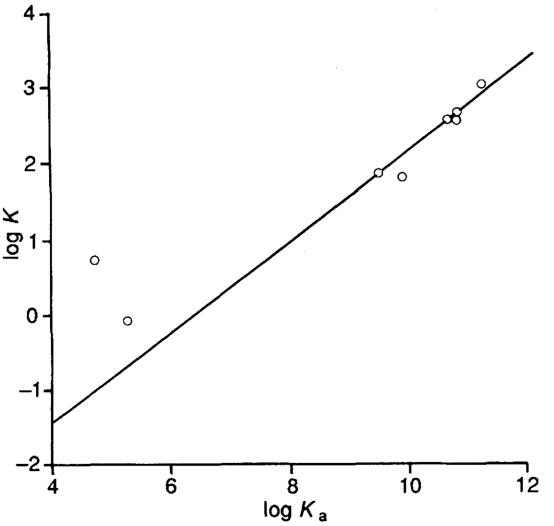

Fig. 3 Correlation of the equilibrium constants, K, for reaction (1) at 25.0 °C and I = 0.20 mol dm^{-3} ($NaClO_4$) with the protonation constants of the ligands L′

significantly above this line, indicating that $[CuL]^{2+}$ is a soft acid. On the other hand, the large hard ligand NMe_3 lies slightly below this line due to steric effects.

Rate Constants.—Like the reactions of $[CuL(H_2O)]^{2+}$ with uninegative ligands,[1] the rate constants for the complexation reactions of $[CuL(H_2O)]^{2+}$ with these neutral ligands are very sensitive to the nucleophilic character of the entering ligand, and vary over some three orders of magnitude (Table 3). These results indicate that bond formation plays a significant role on going from the reactants to the activated complex. On the other hand, the rate constants of the aquation reactions of $[CuL(L')]^{2+}$ are approximately the same. These results indicate that the aquation reactions are extremely insensitive to the nature of the leaving group, L′; in other words, extremely little or no Cu–L′ bond dissociation has developed in the transition state. It is thus apparent that these reactions take place *via* an associative-intimate mechanism. The five-co-ordinated complexes $[CuL(H_2O)]^{2+}$ and $[CuL(L')]^{2+}$ (ref. 3) are trigonal bipyramidal and are readily subject to nucleophilic attack by the incoming ligand as shown in Fig. 1.

The sequence of k_f, $C_5H_5N < NH_2Ph < NMe_3 < NH_3 < NH_2Me < NH_2Et < NHMe_2 < C_5H_{10}NH$, indicates that the basicity, the softness and the size of X are important in determining the reactivity of the nucleophilic reagent. Fig. 4 shows a plot of log k_f against log K_a of the ligand. For the hard ligands, NH_3, NH_2Me, NH_2Et, $NHMe_2$ and $C_5H_{10}NH$, there is a fairly good fit to the equation $\log k_f = 0.63 \log K_a - 0.38$. The slope of this line, 0.63, is significant and can be used as a measure of the sensitivity of the reaction rate to the basicity of the ligand. Softer ligands, such as C_5H_5N and NH_2Ph,[12,13] lie above this line; the large hard ligand NMe_3 lies below it.

According to the principle of hard and soft acids and bases,[13] C_5H_5N and NH_2Ph are borderline bases; the other six ligands are hard bases. The large deviations of the rate constants of C_5H_5N and NH_2Ph in Fig. 4 indicate that $[CuL(H_2O)]^{2+}$ is very sensitive to the softness of the base. In aqueous solution, copper(II) ion is on the borderline between hard and soft. Addition of four basic amines softens the copper(II) and makes it a soft acid, in accord with the symbiosis pointed out by Jørgensen.[14]

Trimethylamine is significantly larger than the other seven ligands studied in this work. As a consequence, its rate constant is slower than that estimated from its basicity. This steric retardation is indicative of associative activation.

The values of the nucleophilic reactivity constant n°_{Pt} for NH_3, $C_5H_{10}NH$, NH_2Ph and C_5H_5N are very similar;[15] however,

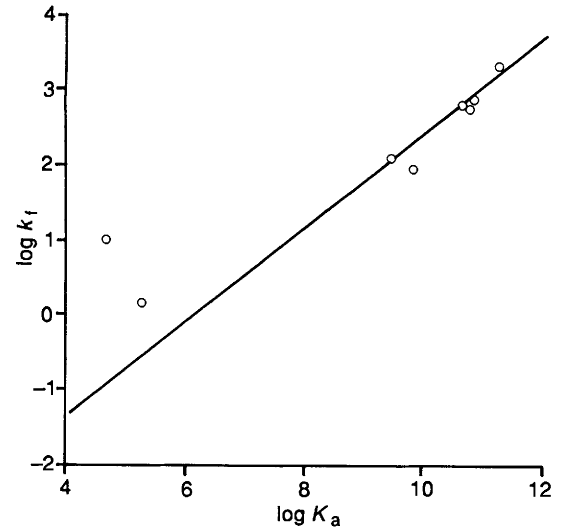

Fig. 4 Correlation of the formation rate constants k_f for reaction (1) at 25.0 °C and $I = 0.20$ mol dm^{-3} ($NaClO_4$) with the protonation constants of the ligands, L′

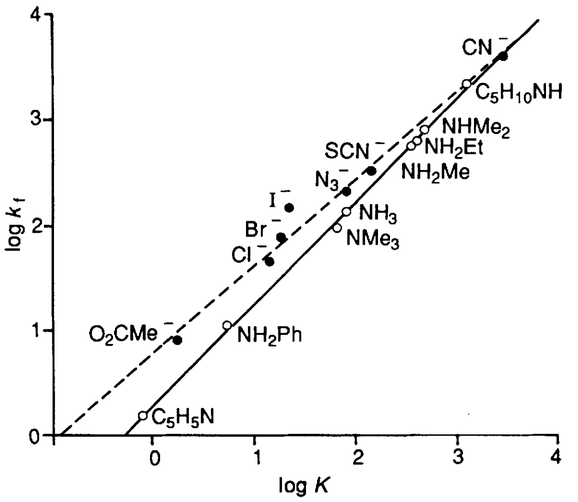

Fig. 5 Plot of log k_f *vs.* log K for the reactions of $[CuL(H_2O)]^{2+}$ with X^{n-} (○), $n = 0$ (●) $n = 1$: ——, least-squares equation log $k_f = 0.98$ log $K + 0.28$; – – –, least-squares equation log $k_f = 0.82$ log $K + 0.80$

the values of k_f for these ligands span some three orders of magnitude. These results indicate that the reactions of $[CuL(H_2O)]^{2+}$ with these ligands are more sensitive to the proton-basicity factor of the incoming ligand than is the analogous reaction of *trans*-$[Pt(C_5H_5N)_2Cl_2]$.[15]

A plot of log k_f *vs.* log K for these neutral ligands yields a straight line according to the equation log $k_f = 0.98$ log K + 0.28 as shown in Fig. 5. The slope of this line, 0.98, indicates that the nature of L′ in the transition state is virtually the same as that in the product. In other words, the entering group L′ is completely bound to the copper(II) centre in the transition state.

Stoichiometric Mechanism.—Careful examination of the kinetic results indicated that no six-co-ordinated intermediate builds up during the course of these reactions. Thus the results suggest that the species $[CuL(L')(H_2O)]^{2+}$ is an activated complex, not an intermediate. Therefore these formation and aquation reactions are regarded provisionally as proceeding *via* an associative interchange (I_a) mechanism [equations (7) and (8)]. The first step (7) is a diffusion-controlled association of

$$[CuL(H_2O)]^{2+} + L' \overset{K_{os}}{\rightleftharpoons} [CuL(H_2O)]^{2+}, L' \quad (7)$$

Table 4 Rate constants for substitution by X⁻ (k_f) of $[CuL(H_2O)]^{2+}$ and for aquation (k_{aq}) of $[CuL(X)]^+$ and equilibrium constants (K) for complexation reactions of $[CuL(H_2O)]^{2+}$ with X⁻ at 25.0 °C and $I = 0.10$ mol dm^{-3} ($NaNO_3$ + NaX)*

X⁻	k_f/dm^3 mol^{-1} s^{-1}	k_{aq}/s^{-1}	K/dm^3 mol^{-1}
Cl⁻	41.4	2.60	15.5
Br⁻	80.0	3.81	18.1
I⁻	150.6	5.41	22.2
SCN⁻	346	2.87	147
N_3^-	221	2.41	84.5
O_2CMe^-	8.1	4.52	1.8
CN⁻	4080	1.40	2950

* From ref. 1.

$$[CuL(H_2O)]^{2+}, L' \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [CuL(L')]^{2+} + H_2O \quad (8)$$

the reactants to form an outer-sphere complex $[CuL(H_2O)]^{2+}$, L′; the second step (8) is an associative interchange of H_2O and L′ within the outer-sphere complex. The rate law for this mechanism is as in equation (9). Here the subscript T

$$d[CuL(L')^{2+}]/dt = k_{obs}[CuL(H_2O)^{2+}]_T = (k_1K_{os}[L'] + k_{-1})[CuL(H_2O)^{2+}]_T \quad (9)$$

indicates the total concentration of the copper(II) complexes, $[CuL(H_2O)^{2+}]_T = [CuL(H_2O)^{2+}] + [CuL(H_2O)^{2+}, L']$. This equation is the same as (5), where $k_f = k_1K_{os}$ and $k_{aq} = k_{-1}$.

The Charge Effects of Entering and Leaving Groups.—In a previous paper[1] we have reported the equilibrium and the rate constants for the reactions of $[CuL(H_2O)]^{2+}$ with uninegative ligands [equation (10)]. These constants are summarized in

$$[CuL(H_2O)]^{2+} + X^- \underset{k_{aq}}{\overset{k_f}{\rightleftharpoons}} [CuL(X)]^+ + H_2O; \quad K = k_f/k_{aq} \quad (10)$$

Table 4. As shown in Fig. 5, a plot of log k_f *vs.* log K for these uninegative ligands yields a straight line according to the equation log $k_f = 0.82$ log $K + 0.80$, which is significantly different from that for the reactions of the neutral ligands. The different values of the slopes of these two lines indicate that the rates of the complexation reactions of $[CuL(H_2O)]^{2+}$ are more sensitive to the change in the nucleophilic character of the neutral ligand than in that of the uninegative ligand. In other words, the degree of bond making in the transition state for the reaction of the neutral ligand is larger than that for the reaction of the uninegative ligand.

The values of k_{aq} for the reactions of $[CuL(X)]^+$ differ by a factor of *ca.* 4 (Table 4), but the aquation rates for the reactions of $[CuL(L')]^{2+}$ are all about the same (Table 3). These results indicate that the degree of bond breaking in the transition state for the aquation of $[CuL(L')]^{2+}$ is smaller than that for the aquation of $[CuL(X)]^+$.

Acknowledgements

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