an oxygen atom transfer to the metal from the ligand is also consistent with the second weight loss step of a similar magnitude for $\mathrm{Mo(dcq)_4}$ at about 350 °C, which would give $\mathrm{MoO_2(dcq)_2}$ at the end of the two steps. The loss of dichloroquinoline in the $\mathrm{Mo(dcq)_3(pic)}$ complex is interesting and consistent with the stronger metal to oxygen bond in the better nucleophile ($\mathrm{dcq^-}$) and the suggested loss of quinoline derivatives (as opposed to quinolinol derivatives). The weaker donor ability of the carboxylate also indirectly strengthens the metal–oxygen bond of at least one dichloroquinolinolate to the extent that the decomposition temperature is lowered by 40 °C relative to $\mathrm{Mo(dcq)_4}$. As noted above, the weight losses for $\mathrm{Mo(dbq)_4}$ and $\mathrm{Mo(dcq)_3(nq)}$ suggest bromoquinoline and quinoline, respectively. Why or how the dibromoquinoline transfers a bromine or the nitroquinoline transfers a nitro group is pure speculation at this point and needs mass spectral verification. The fate of the quinoline radicals is also unknown for these species.

Conclusions. By the use of anionic eight-coordinate quinolinolate and picolinate donors, complete substitution of the chlorides of $\mathrm{MoCl_4}$ occurs and allows the preparation of $\mathrm{MoL_4}$ complexes.[15] Since the neutral ligands only allow partial substitution, specific two-step routes to mixed-ligand eight-coordinate chelates are now possible. Even isomers of the 2:2 complexes have been observed, although they do not appear to undergo the twist isomerization noted for the tungsten analogues; instead, substitution and oxidative decomposition occur. Ligand scrambling is more prevalent in the molybdenum complexes, and decomposition occurs more readily. In fact, some of the tungsten complexes have been prepared at or near the decomposition temperatures of the molybdenum complexes.

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Registry No. $\mathrm{Mo(dcq)_4}$, 87739-33-1; $\mathrm{Mo(dbq)_4}$, 87854-58-8; $\mathrm{Mo(dcq)_3(pic)}$, 88027-25-2; $\mathrm{Mo(dcq)_3(nq)}$, 88005-42-9; $\mathrm{Mo(dcq)_2(pic)_2}$, 87854-59-9; $\mathrm{Mo(dcq)_2(nq)_2}$, 87854-60-2; $\mathrm{Mo(dcq)_3(q)}$, 92901-38-7; $\mathrm{Mo(q)_4}$, 87854-61-3; $\mathrm{Mo(dcq)(pic)_3}$, 74594-59-5; $\mathrm{Mo(pic)_4}$, 18307-05-6; $\mathrm{Mo(dcq)_3Cl}$, 74620-90-9; $\mathrm{Mo(dbq)_3Cl}$, 87739-31-9; $\mathrm{Mo(dcq)_2Cl_2}$, 74594-57-3; $\mathrm{Mo(pic)_3Cl}$, 87739-32-0.

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(15) We had been able to prepare $\mathrm{Mo(pic)_4}$ by the reaction shown as eq 1; cf.: Donahue, C. J.; Archer, R. D. *Inorg. Chem.* **1978**, *17*, 1677. Its properties are consistent with those in this study.

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Substitution Reactions of Five-Coordinate Complexes. 1. Formation and Aquation Kinetics of the (Acido)(*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) (Blue) Cation

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Rate constants for the formation (k_f) and the aquation (k_{aq}) of seven different (acido)(*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) (blue) complexes, $[\mathrm{Cu(tet\ b)Y(blue)}]^+$ ($\mathrm{Y^-} = \mathrm{Cl^-}, \mathrm{Br^-}, \mathrm{I^-}, \mathrm{SCN^-}, \mathrm{N_3^-}, \mathrm{O_2CMe^-}, \mathrm{CN^-}$), have been determined between 15.0 and 40.0 °C at $\mu = 0.10$ M ($\mathrm{NaNO_3 + NaY}$) by the stopped-flow method. These complexes present a trigonal-bipyramidal geometry with $\mathrm{Y^-}$ or $\mathrm{H_2O}$ in equatorial position. The equilibrium constants, K_Y, for the complexation reactions of $[\mathrm{Cu(tet\ b)(H_2O)(blue)}]^{2+}$ with these anions obtained by spectrophotometric measurements under equilibrium conditions are in excellent agreement with kinetically determined values (k_f/k_{aq}). A graph of log k_f against log K_Y gives a slope of 0.85. The kinetic results are consistent with an associative-interchange, $\mathrm{I_a}$, mechanism.

Introduction

An examination of substitution in five-coordinated complexes merits attention since they represent an intermediate case, in both a kinetic and steric sense, between the four-coordinated complexes, which are open to nucleophilic attack, and the six-coordinated systems, which are not.[1] Clearly, both associative and dissociative mechanisms are possible, since a five-coordinate complex can potentially either added or lose a unidentate ligand.[2] In order to expand the knowledge in this area, we have initiated a systematic kinetic study of ligand substitution in five-coordinated complexes $[\mathrm{MLX}]^{(2-n)+}$ (eq 1), where M is a bivalent metal ion, L is a macrocyclic quadridentate ligand, and X^{n-} and Y^{m-} are unidentate ligands. In this reaction, the four coordination positions are rendered inert by using the strongly complexing macrocyclic ligand, and the unidentate ligand exchanges with each other. Equilibrium constants of some of these reactions have been reported.[3-6]

$$\mathrm{MLX}^{(2-n)+} + \mathrm{Y}^{m-} \rightleftarrows \mathrm{MLY}^{(2-m)+} + \mathrm{X}^{n-} \qquad (1)$$

The present paper is concerned with the kinetics of the formation and aquation of (acido)(*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) (blue) complexes, $[\mathrm{Cu(tet\ b)Y(blue)}]^+$ ($\mathrm{Y^-} = \mathrm{Cl^-}, \mathrm{Br^-}, \mathrm{I^-}, \mathrm{N_3^-}, \mathrm{SCN^-}, \mathrm{O_2CMe^-}, \mathrm{CN^-}$), in aqueous solution (eq 2).

$$[\mathrm{Cu(tet\ b)(H_2O)(blue)}]^{2+} + \mathrm{Y^-} \rightleftarrows [\mathrm{Cu(tet\ b)Y(blue)}]^+ + \mathrm{H_2O} \quad k_f,\ k_{aq},\ K_Y \qquad (2)$$

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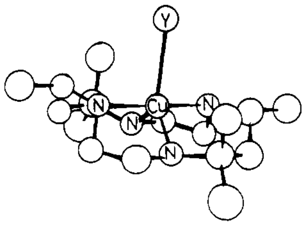

Figure 1. Crystal structure of [Cu(tet b)Y(blue)]$^+$.

Crystal structure determinations of a few of these five-coordinate copper(II) complexes, [[Cu(tet b)(blue)]$_2$Cl]$^{3+}$,[7] [Cu(tet b)(NO$_3$)(blue)]$^+$,[8] and [Cu(tet b)(H$_2$O)(blue)]$^{2+}$[9] have been reported. Each of these complexes contains trigonal-bipyramidal coordinate Cu^{2+} as shown in Figure 1. The macrocyclic tet b ligand is in its stable, folded configuration with both six-membered chelate rings in a chair form and both five-membered chelate rings in a gauche form. The unidentate ligand occupies one of the positions in the trigonal plane. Each of these blue complexes has the *RRRR*(*SSSS*) configuration of the chiral nitrogen centers, which is normally seen in folded macrocyclic tetraamine complexes.[10] This complex ion is a suitable trigonal-bipyramidal copper(II) substrate, with the tet b acting as a nonremovable tetradentate ligand and the equatorially coordinated aqua group replaceable by a variety of monodentate ligands (eq 2).

Experimental Section

Reagents. Complexes [Cu(tet b)(H$_2$O)(blue)](ClO$_4$)$_2$ and [Cu(tet b)(NO$_3$)(blue)](ClO$_4$) used are the same as those reported earlier.[8,9] All other chemicals used were of GR grade (Merck or Fluka).

Instrumentation. A Cary 17 spectrophotometer with a thermostated 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 rate constants and equilibrium constants were obtained by a linear least-squares fit of the data by using the Apple II minicomputer or the CDC Cyber 172 computer.

Equilibrium Constant Determinations. The spectrophotometric measurements were carried out as described in previous papers.[5,11] The method of calculation was the same as described previously.[5,11]

Kinetic Measurements. The formation and aquation reactions of [Cu(tet b)Cl(blue)]$^+$, [Cu(tet b)Br(blue)]$^+$, [Cu(tet b)SCN(blue)]$^+$, [Cu(tet b)N$_3$(blue)]$^+$, and [Cu(tet b)O$_2$CMe(blue)]$^+$ were measured at 680 nm; the formation and aquation reactions of [Cu(tet b)I(blue)]$^+$ and [Cu(tet b)CN(blue)]$^+$ were measured at 665 nm. When a more than 15-fold excess of Y$^-$ was mixed with the [Cu(tet b)(H$_2$O)(blue)]$^{2+}$ solution, reaction 2 was first order in the blue copper complex. A plot of ln ($A_e - A$) vs. time was linear and gave the k_{obsd} value reported. A 1-cm cell was used. The mean percentage standard deviation for rate constants from individual runs are ±2% for k_{obsd}. Temperature control was maintained within ±0.1 °C. Ionic strength was controlled at 0.10 M by using NaNO$_3$.

Results

Thermodynamic Data. Addition of a solution of a monodenate ligand (Y$^-$) to a solution of [Cu(tet b)(H$_2$O)(blue)]$^{2+}$ resulted in the setting up of complex equilibria, involving the replacement of coordinated water by the monodentate ligand Y$^-$ according to eq 2. The values of the equilibrium constants as a function of temperature obtained by spectrophotometric methods are listed in Table I.

Table I. Equilibrium Constants (M^{-1})[a] for the Reaction [Cu(tet b)(H$_2$O)(blue)]$^{2+}$ + Y$^-$ $\rightleftarrows$ [Cu(tet b)Y(blue)]$^+$ + H$_2$O as a Function of Temperature at μ = 0.10 M (NaNO$_3$ + NaY)

temp, °C	Y$^-$						
	Cl$^-$ [b]	Br$^-$ [b]	I$^-$ [b]	SCN$^-$ [b]	N$_3^-$ [b]	O$_2$CMe$^-$ [c]	CN$^-$ [d]
15	18.5	21.0	28.8	203	121	1.98	4740
20	17.5	19.5	25.2	172	107	1.85	3720
25[e]	15.5	18.1	22.2	147	85	1.80	2950
30	15.1	16.8	19.6	126	84	1.76	2350
40	12.9	14.6	15.5	94	67	1.68	1530

[a] [[Cu(tet b)(H$_2$O)(blue)]$^{2+}$] = 8.31 × 10^{-4} M. [b] 1.0 × 10^{-2} M < [Y$^-$] < 8.0 × 10^{-2} M. [c] 1.0 × 10^{-2} M < [Y$^-$] < 1.0 × 10^{-1} M. [d] 1.0 × 10^{-3} M < [Y$^-$] < 8.0 × 10^{-3} M. [e] From ref 6.

Table II. Thermodynamic Data for the Complexation Reactions of [Cu(tet b)(H$_2$O)(blue)]$^{2+}$ with Anions at 25.0 °C and μ = 0.10 M (NaNO$_3$ + NaY)

Y$^-$	$\Delta H_Y°$,[a] kcal/mol	$\Delta S_Y°$,[b] eu	Y$^-$	$\Delta H_Y°$,[a] kcal/mol	$\Delta S_Y°$,[b] eu
Cl$^-$	−1.9	−0.8	N$_3^-$	−4.3	−5.3
Br$^-$	−2.7	−3.2	O$_2$CMe$^-$	−0.8	−1.6
I$^-$	−4.5	−8.8	CN$^-$	−8.1	−11.4
SCN$^-$	−5.5	−8.5			

[a] Standard deviation ±0.2 kcal/mol. [b] Standard deviation ±0.4 eu.

Plots of ln K_Y against $1/T$ are shown in Figure 2 (supplementary material); $\Delta H_Y°$ and $\Delta S_Y°$ values for the reaction of [Cu(tet b)(H$_2$O)(blue)]$^{2+}$ with Y$^-$ obtained from this figure are listed in Table II.

Rate Constants. The pseudo-first-order rate constants obtained under the condition that [Y$^-$] is in much larger (>15-fold) concentration than [Cu(tet b)(H$_2$O)(blue)]$^{2+}$ are listed in Table III. Since the equilibrium constants of eq 2 are relatively small in aqueous solution, [Cu(tet b)Y(blue)]$^+$ is only incompletely formed at ordinary concentration of Y$^-$. Reaction 2 is therefore a reversible reaction. The observed pseudo-first-order rate constants are plotted in Figures 3–9 (supplementary material) vs. the actual concentration of Y$^-$ and follow eq 3. The rate constants of formation (slope) and

$$k_{obsd} = k_{aq} + k_f[Y^-] \tag{3}$$

of aquation (intercept) are listed in Table IV. The equilibrium constants, at 25.0 °C calculated from the rate constant by using eq 4, are in excellent agreement with those obtained by

$$K_Y = k_f/k_{aq} \tag{4}$$

spectrophotometric measurements under equilibrium conditions as shown in Table V.

Activation Parameters. Plots of ln (k_f/T) against $1/T$ and plots of ln (k_{aq}/T) against $1/T$ are shown in Figures 10 and 11, respectively. The activation parameters obtained from these figures are listed in Table VI.

Discussion

Thermodynamic Data. The equilibrium constant varies in the order O$_2$CMe$^-$ < Cl$^-$ < Br$^-$ < I$^-$ < N$_3^-$ < SCN$^-$ < CN$^-$. This trend of ligation tendency indicates that [Cu(tet b)(H$_2$O)(blue)]$^{2+}$ is a soft acid. 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.[12,13]

Although the softness parameter of N$_3^-$ is smaller than that of Br$^-$ or I$^-$, N$_3^-$ has a larger complexation tendency with [Cu(tet b)(H$_2$O)(blue)]$^{2+}$ than these halide ions. This se-

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Table III. Observed Pseudo-First-Order Rate Constants, k_{obsd} (s^{-1}),[a] for the Reaction $[Cu(tet\ b)(H_2O)(blue)]^{2+} + Y^- \rightleftarrows [Cu(tet\ b)Y(blue)]^+ + H_2O$ as a Function of Temperature at $\mu = 0.10$ M ($NaNO_3$ + NaY)

	k_{obsd}, s^{-1}				
$10^2[Y^-]$, M	t = 15 °C	t = 20 °C	t = 25 °C	t = 30 °C	t = 40 °C
$Y^- = Cl^-$					
1.0	1.63	1.96	3.04	4.31	9.91
2.0	1.88	2.26	3.64	5.04	11.06
4.0	2.03	2.64	4.44	6.13	13.54
6.0	2.87	3.63	5.16	7.11	15.53
8.0	3.08	3.92	5.98	8.62	18.51
$Y^- = Br^-$					
1.0	2.14	3.04	4.63	6.54	14.82
2.0	2.41	3.11	5.06	7.51	17.06
4.0	2.98	4.88	7.14	9.31	20.83
6.0	3.44	5.06	8.72	11.14	23.81
8.0	3.51	6.21	10.20	13.85	28.54
$Y^- = I^-$					
1.0	2.81	6.21	6.81	10.16	23.24
2.0	3.66	4.14	8.37	12.42	26.47
4.0	4.44	5.77	11.34	17.20	35.25
6.0	6.42	6.82	15.40	19.88	41.23
8.0	8.56	10.11	17.44	25.61	51.24
$Y^- = SCN^-$					
1.0	2.51	4.88	5.31	8.84	16.64
2.0	4.85	7.74	9.81	15.06	27.16
3.0	5.66	9.17	13.40	18.26	33.81
4.0	8.88	13.14	16.71	21.98	44.16
6.0	12.66	17.31	23.52	32.24	59.41
$Y^- = N_3^-$					
1.0	2.43	3.12	4.83	6.84	13.18
2.0	2.58	4.91	6.85	10.12	20.14
4.0	5.61	7.94	11.58	16.47	30.06
6.0	7.64	11.51	15.71	22.30	43.32
8.0	10.12	14.89	20.08	28.91	52.31
$Y^- = O_2CMe^-$					
1.0	1.89	2.14	4.50	7.46	16.84
2.0	1.96	2.22	4.66	7.58	17.03
4.0	2.03	2.41	4.78	7.61	17.01
6.0	2.16	2.66	5.02	7.79	18.02
10.0	2.23	2.89	5.18	8.22	19.11
$Y^- = CN^-$					
0.1	3.14	4.24	5.84	7.88	16.71
0.2	5.43	7.22	9.81	13.54	22.44
0.4	9.26	14.71	15.21	22.53	36.41
0.6	15.61	20.62	22.25	33.82	54.43
0.8	10.53	26.88	33.50	42.31	70.62

[a] $[[Cu(tet\ b)(H_2O)(blue)]^{2+}] = 8.31 \times 10^{-4}$ M; mean value of at least three kinetic runs.

Table IV. Rate Constants for Substitution by Y^- (k_f) of $[Cu(tet\ b)(H_2O)(blue)]^{2+}$ and for Aquation (k_{aq}) of $[Cu(tet\ b)Y(blue)]^+$ as a Function of Temperature at $\mu = 0.10$ M ($NaNO_3$ + NaY)

temp, °C	k_f, $M^{-1}\ s^{-1}$	k_{aq}, s^{-1}	temp, °C	k_f, $M^{-1}\ s^{-1}$	k_{aq}, s^{-1}
$Y^- = Cl^-$					
15	19.0	1.48	30	59.5	3.93
20	28.1	1.70	40	120.6	8.63
25	41.4	2.61			
$Y^- = Br^-$					
15	34.3	1.63	30	98.5	5.82
20	49.3	2.54	40	188.4	13.06
25	80.0	3.81			
$Y^- = I^-$					
15	77.0	2.10	30	206.1	8.56
20	108.6	3.44	40	377.5	20.11
25	150.6	5.41			
$Y^- = SCN^-$					
15	186	1.13	30	466	4.36
20	255	1.82	40	818	10.26
25	346	2.87			
$Y^- = N_3^-$					
15	313	1.01	30	305	3.77
20	289	1.14	40	561	8.62
25	221	2.41			
$Y^- = O_2CMe^-$					
15	3.4	1.80	30	15.3	7.06
20	5.3	2.21	40	27.2	24.74
25	8.1	4.52			
$Y^- = CN^-$					
15	2670	0.51	30	5180	2.31
20	3940	0.86	40	8070	5.71
25	4080	1.40			

Table V. Rate Constants for Substitution by Y^- (k_f) of $[Cu(tet\ b)(H_2O)(blue)]^{2+}$ and for Aquation (k_{aq}) of $[Cu(tet\ b)Y(blue)]^+$ and Equilibrium Constants for the Complexation Reactions of $[Cu(tet\ b)(H_2O)(blue)]^{2+}$ with Y^- at 25.0 °C and $\mu = 0.10$ M ($NaNO_3$ + NaY)

			stability const, M^{-1}	
Y^-	k_f, $M^{-1}\ s^{-1}$	k_{aq}, s^{-1}	kinetic[a]	spectrophotometric[b]
Cl^-	41.4	2.60	15.9	15.5
Br^-	80.0	3.81	20.5	18.1
I^-	150.6	5.41	26.0	22.2
SCN^-	346	2.87	125	147
N_3^-	221	2.41	84.5	84.5
O_2CMe^-	8.1	4.52	1.8	1.8
CN^-	4080	1.40	2914	2950

[a] Kinetically determined value k_f/k_{aq}. [b] From ref 6.

Table VI. Activation Parameters for Formation and Aquation of $[Cu(tet\ b)Y(blue)]^+$ at 25.0 °C and $\mu = 0.10$ M ($NaNO_3$ + NaY)

Y^-	$\Delta H_f^{\ddagger}$,[a] kcal/mol	$\Delta S_f^{\ddagger}$,[b] eu	$\Delta H_{aq}^{\ddagger}$,[a] kcal/mol	$\Delta S_{aq}^{\ddagger}$,[b] eu
Cl^-	12.6	−8.8	14.5	−7.8
Br^-	11.4	−11.1	14.6	−7.3
I^-	10.5	−12.4	14.9	−5.3
SCN^-	10.1	−13.3	15.4	−5.1
N_3^-	10.9	−11.3	15.0	−6.4
O_2CMe^-	14.4	−6.5	15.2	−4.8
CN^-	7.8	−16	15.9	−4.6

[a] Standard deviation ±0.3 kcal/mol. [b] Standard deviation ±0.9 eu.

quence indicates that not only the softness but also the inherent base strength of the anion affects its complexation tendency with $[Cu(tet\ b)(H_2O)(blue)]^{2+}$. The softness parameters and the pK_a values of the conjugate acids of these anions in aqueous solution[14,15] are listed in Table VII. The very large complexation tendency of CN^- is attributed to its large softness and high basicity. At 25 °C, these equilibrium constants can be quantitatively correlated by the Edwards equation,[6,16] $\log (K/K_0) = 2.189E_n + 0.033H$, where K_0 is the constant for a reference base (for example, water), H is a proton basicity factor, and E_n is a redox factor.[17]

The reactions of these anions with $[Cu(tet\ b)(H_2O)(blue)]^{2+}$ are characterized by the negative $\Delta H_Y°$ values, which promote the complex formations, and the relatively small negative $T\Delta S_Y°$ values, which counteract them as shown in Table II. The negative $\Delta S_Y°$ values of these reactions are probably due to the fact that these anions are structure-breaking ligands.[18,19]

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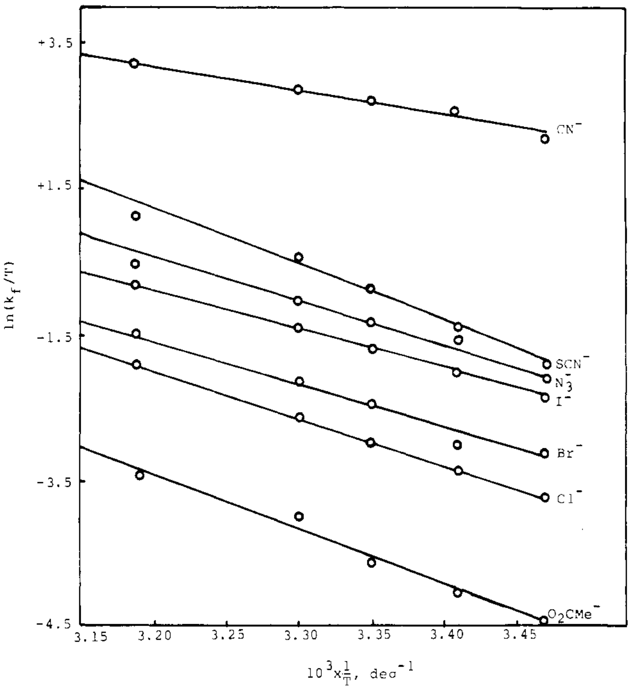

Figure 10. Graphical resolution of the activation parameters for substitution by Y^- of $[Cu(tet\ b)(H_2O)(blue)]^{2+}$ at $\mu = 0.10$ M ($NaNO_3 + NaY$).

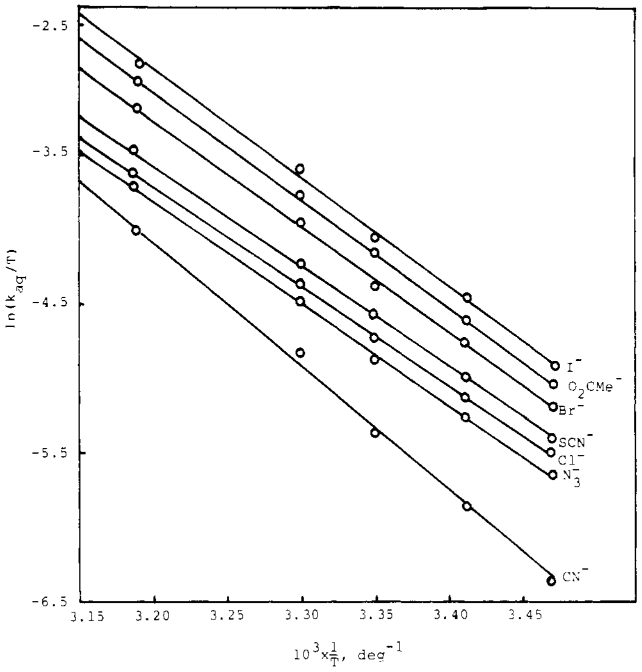

Figure 11. Graphical resolution of the activation parameters for the aquation reaction of $[Cu(tet\ b)Y(blue)]^+$ at $\mu = 0.10$ M ($NaNO_3 + NaY$).

Table VII. Softness Parameter[a] and Basicity toward Proton[b] at 25.0 °C

Y^-	softness parameter	pK_a	Y^-	softness parameter	pK_a
Cl^-	1.65	−4	N_3^-	2.19	4.7
Br^-	2.79	−7	O_2CMe^-		4.7
I^-	4.03	−10	CN^-		9.1
SCN^-	4.26	−0.7			

[a] Ref 14. [b] Ref 15.

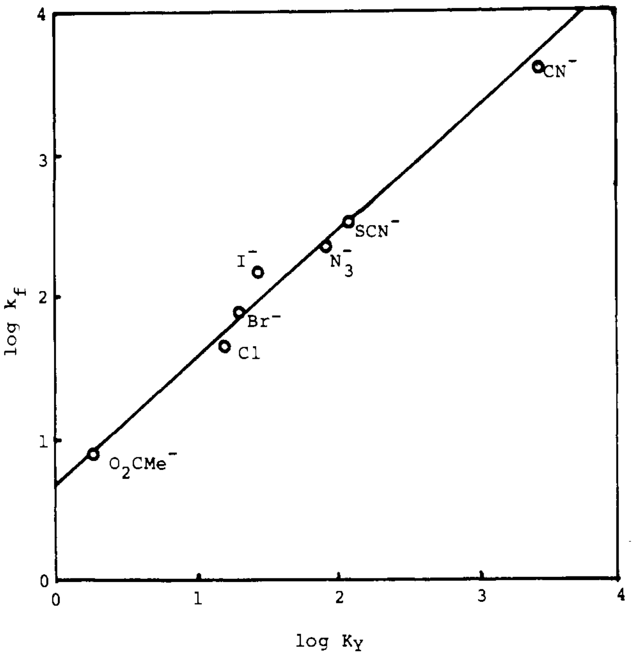

Figure 12. Correlation of the formation rate constants with the equilibrium constants in the reaction $[Cu(tet\ b)(H_2O)(blue)]^{2+} + Y^- \rightleftarrows [Cu(tet\ b)Y(blue)]^+ + H_2O$ at 25.0 °C and $\mu = 0.10$ M ($NaNO_3 + NaY$).

This implies more order in the products. The reason $\Delta S° < 0$ is probably due to a solvation cage effect produced by a more ordered cage in the vacinity of coordinated Y ligands.

Effect on Rates of Entering and Leaving Ligands. The rate constants for the substitution by Y^- of $[Cu(tet\ b)(H_2O)(blue)]^{2+}$ listed in Table V depend heavily on the nature of Y^-, the entering group, and vary over some 3 orders of magnitude. It is necessary that bond making plays a significant role on going from the reactant to the activated complex. On the other hand, the rates of aquation of $[Cu(tet\ b)Y(blue)]^+$ listed in Table V are very insensitive to the nature of Y^-, the leaving group. Clearly, there is no substantial bond breaking in the process of going from reactants to activated complex. Hence, these reactions take place via an associative-intimate mechanism.

A remarkable feature of the formation reactions is the existence of a correlation between rate constants and equilibrium constants: more thermodynamically favored reactions proceed faster. Figure 12 shows a plot of log k_f as a function of log K_Y. The slope of this plot, 0.85, is considered evidence of an associative-intimate mechanism in which the transition state resembles the product in having Y^- bound to the metal. In contrast, the order of rate constants of aquation reactions does not parallel the order of aqueous solution instabilities of these complexes; that is, the order in increasing k_{aq} values is $[Cu(tet\ b)CN(blue)]^+ < [Cu(tet\ b)N_3(blue)]^+ < [Cu(tet\ b)Cl(blue)]^+ < [Cu(tet\ b)SCN(blue)]^+ < [Cu(tet\ b)Br(blue)]^+ < [Cu(tet\ b)O_2CMe(blue)]^+ < [Cu(tet\ b)I(blue)]^+$; whereas the order in decreasing K_Y values is $K_{CN} > K_{SCN} > K_{N_3} > K_I > K_{Br} > K_{Cl} > K_{O_2CMe}$.

The entering-group reactivity order, $CN^- > SCN^- > N_3^- > I^- > Br^- > Cl^- > O_2CMe^-$, indicates that both the polarizability and the basicity of the nucleophile are important in determining the reactivity. This relative order of reactivity seems to be similar to that obtained with platinum(II) complexes[20] and leads us to think that there may be a relationship between the values of log k_f and the values of the $n_{Pt}°$ index for these nucleophiles. A plot of log k_f against $n_{Pt}°$ is shown

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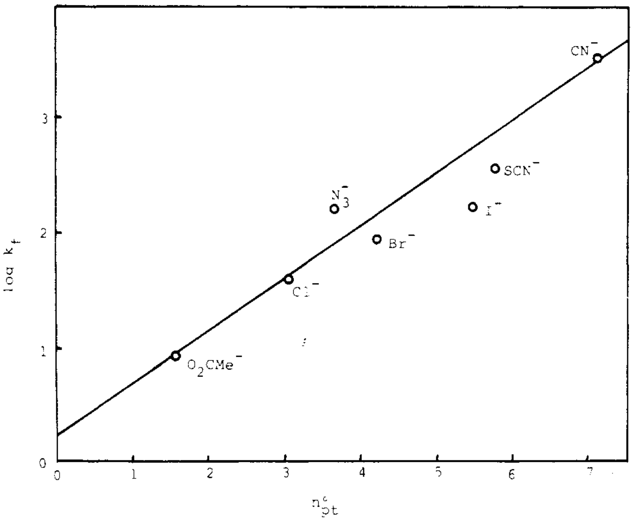

Figure 13. Correlation of log k_f for reaction 2 at 25.0 °C and μ = 0.10 M ($NaNO_3$ + NaY) with the standard *trans*-$Pt(py)_2Cl_2$ for different nucleophiles.

in Figure 13. However, the values for some of them do not lie on a straight line in this plot. Although CN^-, Cl^-, and O_2CMe^- obey the equation log $k_f = 0.45n_{Pt}{}^\circ + 0.2$, N_3^- is more reactive, whereas I^-, Br^-, and SCN^- are less reactive than expected by this equation. These deviations indicate that the sequence of the sensitivity to the proton basicity factor is $[Cu(tet\ b)(H_2O)(blue)]^{2+}$ > *trans*-$Pt(py)_2Cl_2$, while the sequence of the sensitivity to the softness of the entering group is *trans*-$Pt(py)_2Cl_2$ > $[Cu(tet\ b)(H_2O)(blue)]^{2+}$.

Activation Parameters. Examination of the activation parameters listed in Table VI reveals three important features. The first is that an increase in rate of the formation reaction of $[Cu(tet\ b)Y(blue)]^+$ is largely due to a decrease in $\Delta H_f{}^\ddagger$. The second is that all of the formation and the aquation reactions are attended by negative values of $\Delta S^\ddagger$. The third is that the enthalpies and the entropies of activation for aquation reactions remain about the same.

The negative entropies and the rather small enthalpies of activation indicate that bond formation is dominant in the transition state for both the formation and the aquation reactions of $[Cu(tet\ b)Y(blue)]^+$. The fact that both $\Delta S_{aq}{}^\ddagger$ and $\Delta H_{aq}{}^\ddagger$ for the aquation reaction are very insensitive to the nature of the leaving group indicates that extremely little Cu–Y bond dissociation has developed in the transition state, although the Y^- group has moved to allow the Cu–OH_2 bond to develop.

Proposed Mechanism. No six-coordinate intermediate $[Cu(tet\ b)Y(H_2O)(blue)]^+$ has been detected in these formation and aquation reactions. Careful examination of the kinetic results indicated that no six-coordinate intermediate built up during the course of these reactions. So these reactions are regarded provisionally as I_a:

$$[Cu(tet\ b)(H_2O)(blue)]^{2+} + Y^- \overset{K_{os}}{\rightleftharpoons} [Cu(tet\ b)(H_2O)(blue)]^{2+}, Y^- \quad (5)$$

$$[Cu(tet\ b)(H_2O)(blue)]^{2+}, Y^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Cu(tet\ b)Y(blue)]^+ + H_2O \quad (6)$$

The outer-sphere complexation (eq 5) is very rapid and is always at equilibrium. The rate law for this mechanism is

$$d[Cu(tet\ b)Y(blue)^+]/dt = (k_1K_{os}[Y^-] + k_{-1})[Cu(tet\ b)(blue)(H_2O)^{2+}]_T \quad (7)$$

therefore

$$k_{obsd} = k_1K_{os}[Y^-] + k_{-1} \quad (8)$$

This equation is the same as expressed in eq 3, where $k_f = k_1K_{os}$ and $k_{aq} = k_{-1}$.

Conclusions

The evidence developed in this work indicates that the formation and aquation reactions of $[Cu(tet\ b)Y(blue)]^+$ proceed via an associative-interchange, I_a, mechanism. The five-coordinated complexes, $[Cu(tet\ b)(H_2O)(blue)]^{2+}$ and $[Cu(tet\ b)Y(blue)]^+$ are trigonal bipyramidal and readily are subject to nucleophilic attack by incoming groups. Considerable Cu–Y bond formation has developed in the transition state for the formation reaction of $[Cu(tet\ b)Y(blue)]^+$. In agreement with this conclusion, extremely little Cu–Y bond dissociation has developed in the transition state for the aquation reaction. A linear relationship between log k_f and log K_Y was obtained.

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Registry No. $[Cu(tet\ b)Cl(blue)]^+$, 92282-27-4; $[Cu(tet\ b)Br(blue)]^+$, 92282-28-5; $[Cu(tet\ b)I(blue)]^+$, 92282-29-6; $[Cu(tet\ b)(SCN)(blue)]^+$, 92187-26-3; $[Cu(tet\ b)(N_3)(blue)]^+$, 92282-30-9; $[Cu(tet\ b)(O_2CMe)(blue)]^+$, 92282-31-0; $[Cu(tet\ b)(CN)(blue)]^+$, 92282-32-1.

Supplementary Material Available: Figures 2–9, showing plots of ln K_Y vs. $1/T$ and k_{obsd} vs. $[Y^-]$ (8 pages). Ordering information is given on any current masthead page.