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Substitution Reactions of Five-Coordinate Complexes. 2. Formation and Aquation Kinetics of the (Acido)(*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) (Red) 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) (red) complexes, [Cu(tet b)Y(red)]$^+$ (Y^- = Cl^-, Br^-, I^-, SCN^-, N_3^-, O_2CMe^-, CN^-), have been determined between 15.0 and 40.0 °C at μ = 0.10 M ($NaNO_3$ + NaY) by the stopped-flow method. These complexes present a square-pyramidal geometry with Y^- or H_2O in the apical position. The equilibrium constants, K_Y, for the complexation reactions of [Cu(tet b)(H_2O)(red)]$^{2+}$ 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 0.94. The kinetic results are consistent with an associative-interchange, I_a, mechanism.

Introduction

In aqueous solution, *C*-*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, tet b, reacts with copper(II) to form initially a blue complex, which is readily converted into the more thermodynamically stable red isomer.[1,2] A previous paper has dealt with the formation and aquation kinetics of the (acido)(*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) (blue) complexes, [Cu(tet b)Y(blue)]$^+$ (Y^- = Cl^-, Br^-, I^-, N_3^-, SCN^-, O_2CMe^-, CN^-), in aqueous solution.[3] In the present study we are concerned with the kinetic and mechanism of the formation and aquation of [Cu(tet b)Y(red)]$^+$ in aqueous solution (eq 1).

$$[\mathrm{Cu(tet\ b)(H_2O)(red)}]^{2+} + \mathrm{Y}^- \rightleftarrows [\mathrm{Cu(tet\ b)Y(red)}]^+ + \mathrm{H_2O} \quad k_f,\ k_{aq},\ K_Y \quad (1)$$

In this reaction structures have been determined for crystalline forms of the reactant [Cu(tet b)(H_2O)(red)](ClO_4)$_2$[4] and of the product [Cu(tet b)(SCN)(red)](ClO_4)·$2H_2O$.[5,6] Each of these complexes contains a slightly distorted square-pyramidal Cu^{2+} with the macrocycle equatorial and the unidentate ligand axial as shown in Figure 1. The macrocyclic tet b ligand is in a planar configuration with both six-membered chelate rings in a stable chair form and both five-membered chelate rings in an unstable twist form. Each of these red complexes has the 1*SR*,4*RS*,8*SR*,11*RS* configuration of the four chiral nitrogen centers; and the 7*RS*,14*RS* configuration of the two chiral carbon centers. As shown in Figure 1, all C atoms lie on the lower side of the four-nitrogen plane, while the Cu atom deviates slightly upward from the four-nitrogen plane toward the monodentate ligand. Bonding of another ligand in the other axial position does not occur even in the presence of a strong coordinating monodentate ligand. As shown in Figure 1, the two bulkly axial methyl groups as well as the protons attached to carbon atoms lie below the metal ion and hinder the axial position opposite the coordinate monodentate ligand. Thus, [Cu(tet b)(H_2O)(red)]$^{2+}$ is a suitable square-pyramidal copper(II) substrate, with the tet b acting as a nonremovable tetradentate ligand and the axially coordinated aqua group replaceable by a variety of monodentate ligands.

Table I. Equilibrium Constants (M^{-1}) for the Reaction [Cu(tet b)(H_2O)(red)]$^{2+}$ + Y^- ⇄ [Cu(tet b)Y(red)]$^+$ + H_2O as a Function of Temperature at μ = 0.10 M ($NaNO_3$ + NaY)

temp, °C	Y^-						
	$Cl^{-\,b}$	$Br^{-\,b}$	$I^{-\,b}$	$N_3^{-\,b}$	$SCN^{-\,b}$	$O_2CMe^{-\,c}$	$CN^{-\,d}$
15	1.93	3.40	7.16	9.38	10.2	0.260	415
20	1.88	3.32	6.80	9.01	9.80	0.254	347
25[e]	1.81	3.17	6.48	8.62	9.29	0.247	297
30	1.78	3.13	6.19	8.35	9.02	0.244	247
40	1.73	3.03	5.66	7.78	8.35	0.240	180

[a] [[Cu(tet b)(H_2O)(red)]$^{2+}$] = 1.10 × 10^{-3} M. [b] 3.0 × 10^{-2} < [Y^-] < 1.0 × 10^{-1} M. [c] 2.5 × 10^{-2} < [Y^-] < 1.0 × 10^{-1} M. [d] 2.5 × 10^{-3} < [Y^-] < 1.0 × 10^{-2} M. [e] From ref 11.

Table II. Thermodynamic Data for the Complexation Reactions of [Cu(tet b)(H_2O)(red)]$^{2+}$ with Anions at 25.0 °C and μ = 0.10 M ($NaNO_3$ + NaY)

Y^-	$\Delta H_r°$,[a] kcal/mol	$\Delta S_r°$,[b] eu	Y^-	$\Delta H_r°$,[a] kcal/mol	$\Delta S_r°$,[b] eu
Cl^-	−0.78	−1.90	N_3^-	−1.60	−0.44
Br^-	−0.65	−0.48	O_2CMe^-	−0.56	−4.90
I^-	−1.80	−2.20	CN^-	−6.80	−9.80
SCN^-	−1.23	−0.20			

[a] Standard deviation ±0.15 kcal/mol. [b] Standard deviation ±0.2 eu.

Experimental Section

Reagents. The complex [Cu(tet b)(H_2O)(red)](ClO_4)$_2$ used was the same as that reported earlier.[4] 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 made 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.[7-10] The method of calculation was the same as described previously.[7-10]

Kinetic Measurements. The formation and aquation reactions of [Cu(tet b)Cl(red)]$^+$ was measured at 525 nm; the formation and aquation reactions of [Cu(tet b)Br(red)]$^+$, [Cu(tet b)SCN(red)]$^+$, [Cu(tet

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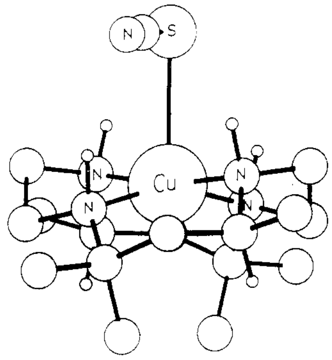

Figure 1. Crystal structure of [Cu(tet b)(SCN)(red)]$^+$.

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

$10^2[Y^-]$, M	k_{obsd}, s^{-1} *t* = 15 °C	*t* = 20 °C	*t* = 25 °C	*t* = 30 °C	*t* = 40 °C
			Y^- = Cl^-		
3.0	44.9	63.3	76.3	103	161
6.0	47.3	66.7	80.3	108	169
7.5	48.5	68.4	82.3	111	173
8.6	49.4	69.5	83.7	112	176
10	50.6	71.2	85.6	115	179
			Y^- = Br^-		
3.0	50.5	71.8	85.8	117	178
6.0	55.1	78.3	93.4	127	193
7.5	57.5	81.6	97.2	132	200
8.6	59.1	83.7	100	136	205
10	61.4	87.0	103	141	212
			Y^- = I^-		
3.0	62.7	87.8	106	141	214
6.0	73.7	103	123	163	245
7.5	79.3	110	132	173	260
8.6	83.4	115	138	182	272
10	88.5	122	146	193	287
			Y^- = N_3^-		
3.0	55.2	78.0	93.6	125	191
6.0	67.3	94.6	113	151	227
7.5	73.4	103	122	164	246
8.6	77.8	108	130	174	259
10	83.5	117	139	185	276
			Y^- = SCN^-		
3.0	58.5	83.5	99.0	134	201
6.0	72.2	103	121	162	242
7.5	79.1	112	132	176	262
8.6	84.2	118	140	187	276
10	90.5	128	150	220	295
			Y^- = O_2CMe^-		
2.5	49.7	71.3	87.6	115	181
5.0	50.0	71.7	88.2	116	182
6.0	50.2	71.9	88.4	116.7	182.6
7.5	50.4	72.3	89.0	117	184
10	50.7	72.6	89.3	118	184
			Y^- = CN^-		
0.25	69.9	92.8	106	137	173
0.5	105	136	151	189	226
0.6	120	153	169	210	248
0.75	141	179	196	241	280
1.0	177	222	240	293	334

[a] [[Cu(tet b)(H_2O)(red)]$^{2+}$] = 1.10 × 10^{-3} M; mean value of at least four kinetic runs.

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

temp, °C	k_f, M^{-1} s^{-1}	k_{aq}, s^{-1}	equilibrium const K_Y, M^{-1} kinetic[a]	spectrophotometric[b]
		Y^- = Cl^-		
15	81.8	42.2	1.94	1.93
20	113	59.9	1.89	1.88
25	133	72.3	1.84	1.81
30	176	97.7	1.80	1.78
40	265	153	1.73	1.73
		Y^- = Br^-		
15	156	45.8	3.41	3.40
20	217	65.3	3.32	3.32
25	253	78.2	3.24	3.17
30	339	107	3.17	3.13
40	495	163	3.04	3.03
		Y^- = I^-		
15	369	51.6	7.15	7.16
20	496	72.9	6.80	6.80
25	574	88.6	6.48	6.48
30	737	119	6.19	6.19
40	1036	183	5.66	5.66
		Y^- = N_3^-		
15	404	43.1	9.37	9.38
20	553	61.4	9.01	9.01
25	644	74.3	8.67	8.62
30	843	101	8.35	8.35
40	1206	155	7.78	7.78
		Y^- = SCN^-		
15	457	44.8	10.2	10.2
20	633	64.6	9.80	9.80
25	725	77.2	9.39	9.29
30	947	105	9.02	9.02
40	1344	161	8.35	8.35
		Y^- = O_2CMe^-		
15	12.8	49.4	0.259	0.260
20	18.0	70.8	0.254	0.254
25	21.8	87.4	0.249	0.247
30	28.3	115	0.246	0.244
40	43.2	180	0.240	0.240
		Y^- = CN^-		
15	14228	34.4	414	415
20	17256	49.7	347	347
25	17923	61.4	292	297
30	20872	84.5	247	247
40	21480	119	180	180

[a] Kinetically determined value k_f/k_{aq}. [b] From ref 7.

b)N_3(red)]$^+$, [Cu(tet b)I(red)]$^+$, [Cu(tet b)O_2CMe(red)]$^+$ and [Cu(tet b)CN(red)]$^+$ were measured at 600 nm. When a more than 15-fold excess of Y^- was mixed with the [Cu(tet b)(H_2O)(red)]$^{2+}$ solution, reaction 1 was first order in the red 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 is ±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. The equilibrium constant for the reaction of [Cu(tet b)(H_2O)(red)]$^{2+}$ and the anionic ligand Y^- was determined by measuring the apparent absorbance, ϵ_{app}, at 600 nm, which had a linear dependence on $(\epsilon_{app} - \epsilon_{Cu(tet\ b)(H_2O)})/[Y^-]$ in accordance with eq 2.[11] The values of equilibrium constants are

$$\epsilon_{app} = -1/K_Y(\epsilon_{app} - \epsilon_{Cu(tet\ b)(H_2O)})/[Y^-] + \epsilon_{Cu(tet\ b)Y} \quad (2)$$

listed in Table I. $\Delta H_Y°$ and $\Delta S_Y°$ values for the reaction of [Cu(tet b)(H_2O)(red)]$^{2+}$ with Y^- are listed in Table II.

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Table V. Activation Parameters for Formation and Aquation of $[Cu(tet\ b)Y(red)]^+$ 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^-	7.70	−23.2	8.48	−21.6
Br^-	7.56	−22.1	8.39	−21.7
I^-	6.69	−23.4	8.36	−21.5
N_3^-	7.13	−21.7	8.46	−21.5
SCN^-	6.98	−22.0	8.42	−21.6
O_2Me^-	7.96	−25.7	8.51	−21.1
CN^-	2.30	−31.4	8.26	−22.6

[a] Standard deviation ±0.3 kcal/mol. [b] Standard deviation ±1.0 eu.

Rate Constants. The pseudo-first-order rate constants obtained under the condition that $[Y^-]$ is much larger (>15-fold) than $[[Cu(tet\ b)(H_2O)(red)]^{2+}]$ are listed in Table III. Since the equilibrium constants of eq 1 are relatively small in aqueous solution, $[Cu(tet\ b)Y(red)]^+$ is only incompletely formed at ordinary concentrations of Y^-. Reaction 1 is therefore a reversible reaction. The observed pseudo-first-order rate constants are plotted vs. the actual concentration of Y^- and follow eq 3. The results

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

are deposited as supplementary material (Figures 1S-7S). The rate constants of formation (slope) and of aquation (intercept) are listed in Table IV. The equilibrium constants, calculated from the rate constants by using eq 4, are in excellent agreement with

$$K_Y = k_f/k_{aq} \qquad (4)$$

those obtained by spectrophotometric measurements under equilibrium conditions as shown in this table.

Activation Parameters. Plots of ln (k_f/T) against $1/T$ and plots of ln (k_{aq}/T) against $1/T$ are deposited as supplementary material (Figures 8S and 9S). The activation parameters obtained from these figures are listed in Table V.

Discussion

Thermodynamic Data. In general, the axial ligation constant increases as the softness and the basicity of the anion increase. The results given in Table I indicate the tendency to form $[Cu(tet\ b)Y(red)]^+$ depends heavily on the softness or polarizability of the anion. The very large ligation tendency of CN^- is attributed to its large softness and high basicity. It is interesting to note that the ligation tendencies of SCN^- and N_3^- are about the same. The softness of N_3^- is smaller than that of SCN^-; however, the basicity toward proton of N_3^- is $10^{5.4}$ times that of SCN^-. The fact that O_2CMe^- has the least ligation tendency indicates that the copper macrocyclic complex is a soft acid. In addition, the sequence of the tendency to form $[Cu(tet\ b)Y(red)]^+$, $O_2CMe^- < Cl^- < Br^- < I^- < N_3^- < SCN^- < CN^-$ also indicates that this copper(II) macrocyclic complex is a soft acid. At 25 °C, the equilibrium constants can be quantitatively correlated by the Edwards equation,[12,13] $\log (K_Y/K_0) = 1.51E_n + 0.026H$, where H is a proton basicity factor defined by $H = 1.74 + \text{pka}$; E_n is a redox factor defined by $E_n = E° + 2.60$, here $E°$ is the standard oxidation potential for the process, $2Y^- \rightleftarrows Y_2 + 2e^-$. Both definitions are arranged so that $H = 0$ and $E_n = 0$ for water at 25 °C. K_0 is therefore the constant when the monodentate ligand is water.[14-16]

For $[Cu(tet\ b)Y(red)]^+$, Y^- is in the axial position; on the other hand, for the blue isomer $[Cu(tet\ b)Y(blue)]^+$, Y^- is in the equatorial position. The axial Cu–Y distance in $[Cu(tet\ b)Y(red)]^+$ is longer than the equatorial Cu–Y distance in $[Cu(tet\ b)Y(blue)]^+$. As a result, the equilibrium constant of the reaction of $[Cu(tet\ b)(H_2O)(red)]^{2+}$ with Y^- is smaller than that of the analogous reaction of $[Cu(tet\ b)(H_2O)(blue)]^{24}$.

Table VI. Softness Parameter[a] and Basicity toward Proton[b]

Y^-	softness param	pK_a	Y^-	softness param	pK_a
Cl^-	1.65	−4	N_3^-	2.19	4.7
Br^-	2.79	−7	O_2CMe^-	*c*	4.7
I^-	4.03	−10	CN^-	7.14	9.1
SCN^-	4.26	−0.7			

[a] Reference 14. [b] Reference 15. [c] Hard.

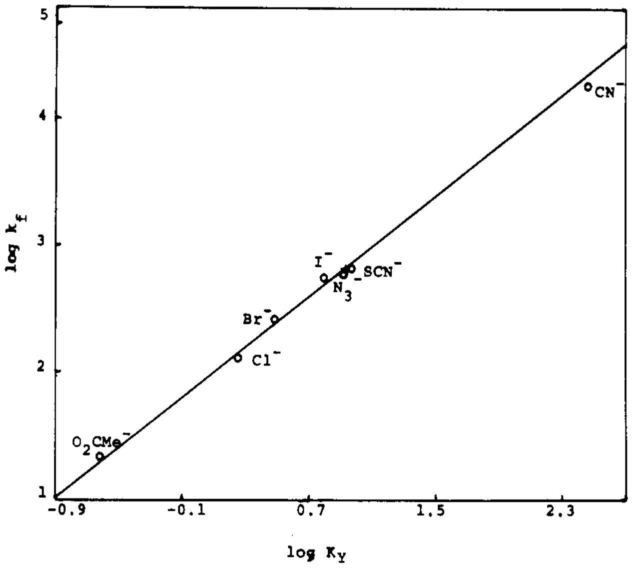

Figure 2. Correlation of the formation rate constants with the equilibrium constants in the reaction $[Cu(tet\ b)(H_2O)(red)]^{2+} + Y^- \rightleftarrows [Cu(tet\ b)Y(red)]^+ + H_2O$ at 25.0 °C and $\mu = 0.10$ M ($NaNO_3 + NaY$).

As shown in Table II, these axial ligation reactions are characterized by negative values of $\Delta H_Y°$, promoting the complex formation, and negative values of $\Delta S_Y°$, counteracting it. These negative $\Delta S_Y°$ values imply more order in the products. As in the case of the analogous reactions of $[Cu(tet\ b)(H_2O)(blue)]^{2+}$ with these anions, the negative $\Delta S_Y°$ values are due to a solvation cage effect produced by a more ordered cage in the vacinity of coordinated Y^- ligand.[17,18] The $\Delta H_Y°$ values of these reactions are less negative than those of the analogous reactions of $[Cu(tet\ b)(H_2O)(blue)]^{2+}$. This is probably due to the difference Cu–Y bond distances in these complexes. The Cu–Y distance in $[Cu(tet\ b)Y(red)]^+$ is longer than that in $[Cu(tet\ b)Y(blue)]^+$. Thus $\Delta H_Y°$ values for the formation of $[Cu(tet\ b)Y(red)]^+$ are less negative than those of $[Cu(tet\ b)Y(blue)]^+$.

Formation Rate Constants. As shown in Table IV, the rate for the formation reactions of $[Cu(tet\ b)(H_2O)(red)]^{2+}$ is very sensitive to the nucleophilic character of the entering group. The rate constants of these reactions span 3 orders of magnitude. The values of these formation constants indicate the substitution reactions take place via an associative mechanism, in which bond formation plays a significant role on going from the reactant to the activated complex.

In general, the formation rate constant increases as the polarizability and the basicity of the anion increase. The entering-group reactivity order for the Cu(II) substitution reactions, $CN^- > SCN^- > N_3^- > I^- > Br^- > Cl^- > O_2CMe^-$, indicates that $[Cu(tet\ b)(red)]^{2+}$ is a soft center. In aqueous solution, copper(II) ion is on the borderline between soft and hard. Addition of four basic amines softens the copper(II) and makes it a soft acid, in accord with the symbiosis pointed out by Jørgensen.[19,20]

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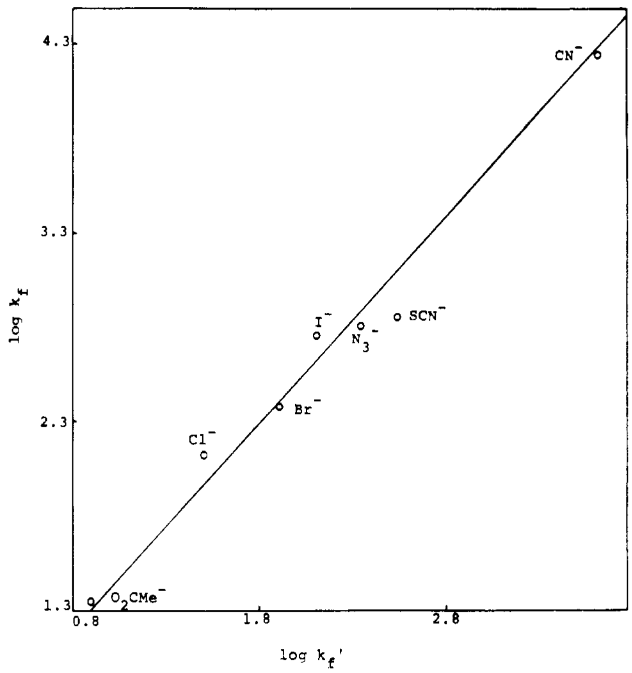

Figure 3. Correlation of log k_f^r for substitution by Y^- of $[Cu(tet\ b)(H_2O)(red)]^{2+}$ at 25.0 °C and μ = 0.10 M ($NaNO_3$ + NaY) vs. log k_f^b for substitution by Y^- of $[Cu(tet\ b)(H_2O)(blue)]^{2+}$ under the same conditions.

The softness parameters of these anionic ligands and the pK_a values of the conjugate acids of these anionic ligands are listed in Table VI. Although N_3^- is less soft than Br^- or I^-, the basicity toward H^+ of N_3^- is about 10^{12} times that of Br^- or 10^{15} times that of I^-. As it turns out, the formation rate constant varies in the order $Br^- < I^- < N_3^-$. This sequence indicates that not only the polarizability or softness but also the inherent base strength of the entering group affect the formation rate of $[Cu(tet\ b)Y(red)]^+$. The very large reactivity of CN^- is attributed to its large softness and high basicity.

Figure 2 gives a plot of log k_f for formation versus log K_Y. The linearity is good. The slope of this straight line, 0.94, indicates that the nature of Y^- in the transition state is virtually the same as that in the product, namely Y^- bound to the metal. Hence, these reactions take place via an associative-intimate mechanism.

Kinetics of substitution reactions of platinum(II) complexes have been studied extensively.[21-23] The nucleophilic reactivity order observed for Pt(II) substitution reactions is different from that of Cu(II) reactions observed in this work.[24] A detailed study of the relative reactivities of Pt(II) and Cu(II) complexes indicates that the Pt(II) complexes are more sensitive to the polarizability of the entering group than $[Cu(tet\ b)(H_2O)(red)]^{2+}$,[25] while $[Cu(tet\ b)(H_2O)(red)]^{2+}$ is more sensitive to the inherent basicity of the entering group than the Pt(II) complex.

The formation reactions of both $[Cu(tet\ b)Y(red)]^+$ and $[Cu(tet\ b)Y(blue)]^+$ take place via an associative mechanism. A plot of log k_f^r for the formation of $[Cu(tet\ b)Y(red)]^+$ against log k_f^b for the formation of $[Cu(tet\ b)Y(blue)]^+$ is linear (Figure 3), and these formation rate constants can be correlated by

$$\log k_f^r = 1.08(\log k_f^b) + 0.47 \qquad (5)$$

Aquation Rate Constants. The rate constants of aquation reactions of $[Cu(tet\ b)Y(red)]^+$ (Table V) are about the same,

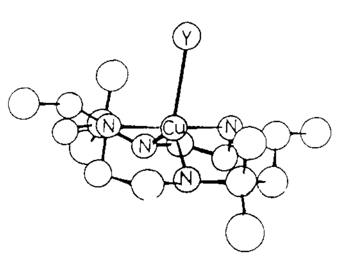

Figure 4. Crystal structure of $[Cu(tet\ b)Y(blue)]^+$.

indicating extremely little or no Cu–Y bond dissociation has developed in the transition state. It is thus apparent that these ligand substitution reactions take place via an associative-intimate mechanism.

Although the rates of equation reactions of both $[Cu(tet\ b)Y(red)]^+$ and $[Cu(tet\ b)Y(blue)]^+$ are not sensitive to the nature of the leaving ligand, they are very sensitive to the conformation of the inert macrocyclic ligand. The aquation rates of $[Cu(tet\ b)Y(blue)]^+$ are much slower than those of $[Cu(tet\ b)Y(red)]^+$. Crystal structure determinations of both $[Cu(tet\ b)(H_2O)(red)]^{2+}$ and $[Cu(tet\ b)(H_2O)(blue)]^{2+}$ have been reported.[4,26] Like $[Cu(tet\ b)(SCN)(red)]^+$ shown in Figure 1, $[Cu(tet\ b)(H_2O)(red)]^{2+}$ is open to nucleophilic attack. On the other hand, the two bulky axial methyl groups of $[Cu(tet\ b)(H_2O)(blue)]^{2+}$ hover above the macrocyclic ligand and block access to the central metal as shown in Figure 4. The relatively slow aquation rate of $[Cu(tet\ b)Y(blue)]^+$ is attributed to the steric effect and the hydrophobic nature of the two bulky axial methyl groups of $[Cu(tet\ b)Y(blue)]^+$. These results suggest that there is substantial Cu–OH_2 bond making in the transition states for the aquation reactions of $[Cu(tet\ b)Y(red)]^+$ and $[Cu(tet\ b)Y(blue)]^+$.

Activation Parameters. Both formation and aquation reactions of $[Cu(tet\ b)Y(red)]^+$ are characterized by the relatively small ΔH values and large negative $\Delta S^{\ddagger}$ values. These results suggest that bond formation is dominant in the transition state for both the formation and the aquation reactions. The facts that both $\Delta H_{aq}^{\ddagger}$ and $\Delta S_{aq}^{\ddagger}$ for the aquation reactions are extremely insensitive to the nature of the leaving group indicate that no or extremely little Cu–Y bond dissociation has developed in the transition state. In conclusion, the activated complex of the formation and the aquation reactions is a six-coordinate species $[Cu(tet\ b)Y(H_2O)(red)]^+$.

Proposed Mechanism. In these formation and aquation reactions, no six-coordinate intermediate has been detected. Careful examination of the kinetic results indicated that no six-coordinate intermediate built up during the courses of these reactions. As pointed out above, the six-coordinate species $[Cu(tet\ b)Y(H_2O)(red)]^+$ is the activated complex. Therefore these reactions are regarded provisionally as an associative interchange (Ia) mechanism:

$$[Cu(tet\ b)(H_2O)(red)]^{2+} + Y^- \overset{K_{os}}{\rightleftharpoons} [Cu(tet\ b)(H_2O)(red)^{2+},Y^-] \qquad (6)$$

$$[Cu(tet\ b)(H_2O)(red)^{2+},Y^-] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Cu(tet\ b)Y(red)]^+ + H_2O \qquad (7)$$

In this interchange Ia mechanism, the first step (eq 6) is the diffusion-controlled association of the ions to form an outer-sphere complex $[Cu(tet\ b)(H_2O)(red)^{2+},Y^-]$; the second step (eq 7) is an associative interchange of H_2O and Y^- within the ion pair. The rate law for this mechanism is

$$d[[Cu(tet\ b)Y(red)]^+]/dt = (k_1K_{os}[Y^-] + k_{-1})[Cu(tet\ b)(H_2O)(red)^{2+}]_T \qquad (8)$$

Here the subscript T indicates the total concentration of the species, $[Cu(tet\ b)(H_2O)(red)^{2+}]_T = [Cu(tet\ b)(H_2O)(red)^{2+}] +$

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$[Cu(tet\ b)(H_2O)(red)^{2+},Y^-]$. Hence

$$k_{obsd} = k_1K_{os}[Y^-] + k_{-1} \qquad (9)$$

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

As shown in Figure 1, the copper(II) of $[Cu(tet\ b)Y(red)]^{2+}$ is in a very slightly distorted square pyramid with the macrocycle equatorial and the oxygen atom of the aqua group axial. All C atoms lie on the lower side of the four-nitrogen plane, while the Cu atom deviates upward from the plane toward the coordinated monodentate ligand. Two bulky axial methyl groups as well as the protons of the macrocyclic ligand lie below the metal ion and hinder the axial position opposite to the coordinated monodentate ligand. Thus the coordination of the sixth ligand to this axial position (trans attack) is inhibited sterically by the "picket fence". On the other hand, $[Cu(tet\ b)Y(red)]^+$ is open to cis attack, in which both the entering group and the leaving group are on the same side of the coordinated macrocyclic ligand in the the transition state.

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

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Reinvestigation of the Pressure Effect on the Outer-Sphere Electron-Transfer Reaction between Aquapentaamminecobalt(III) and Hexacyanoferrate(II) in Aqueous Solution

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The pressure effect on kinetics of the outer-sphere electron-transfer reaction between $[Co^{III}(NH_3)_5(H_2O)]^{3+}$ and $[Fe^{II}(CN)_6]^{4-}$ was reexamined very carefully under the following conditions: $[Co^{III}] = 5.0 \times 10^{-5}$ M, $[Fe^{II}] = (1.7–9.2) \times 10^{-3}$ M, $I = 0.5$ M ($NaClO_4$), pH 3.8–3.9 (0.05 M acetate buffer), 25 °C. The ion-pair formation constant (194 ± 4 M^{-1} at atmospheric pressure) decreases with increase in pressure at 25–100 MPa, whereas the opposite trend was reported by van Eldik and Kelm. The electron-transfer step within the encounter complex ((9.31 ± 0.13) × 10^{-2} s^{-1} at atmospheric pressure) has $\Delta V_e^* = +37.6 \pm 1.2$ cm^3 mol^{-1} (reported value +26.5 cm^3 mol^{-1}). Other kinetic parameters for the electron-transfer process are $\Delta H_e^* = 115 \pm 2$ kJ mol^{-1} and $\Delta S_e^* = +122 \pm 7$ J K^{-1} mol^{-1} (obtained at 25.0–46.3 °C).

Introduction

Outer-sphere electron-transfer reactions between highly and oppositely charged reactants often give the rate law (1), in which K_{OS} is the formation constant of an outer-sphere encounter complex (ion pair) and k_e the electron-transfer rate constant within it.[2-8] Such reactions enable us to obtain individual values of K_{OS}

$$k_{obsd} = k_eK_{OS}[X]/(1 + K_{OS}[X]) \qquad (1)$$

$$X = \text{reactant used in excess}$$

and k_e. We have examined the pressure effect on these terms for three outer-sphere electron-transfer reactions[9,10] and found positive ΔV_{OS} and ΔV_e^* values. The positive ΔV_{OS} values were interpreted to be due to a decrease in electrostriction at the outer-sphere solvation sheath by partial charge cancellation. van Eldik and Kelm reported a negative value of ΔV_{OS} for the outer-sphere electron-transfer reaction (2).[11] Since a negative ΔV_{OS} value is not in line with our results, we have investigated further details of the pressure effect on reaction 2.

$$[Co^{III}(NH_3)_5(H_2O)]^{3+} + [Fe^{II}(CN)_6]^{4-} \overset{K_{OS}}{\rightleftharpoons} \text{encounter complex} \xrightarrow{k_e} \text{products} \qquad (2)$$

Experimental Section

Materials. Aquapentaamminecobalt(III) perchlorate hydrate, $[Co^{III}(NH_3)_5(H_2O)](ClO_4)_3 \cdot H_2O$, was prepared by the known method.[12] All other materials, including $Na_4[Fe^{II}(CN)_6] \cdot 10H_2O$, disodium dihydrogen ethylenediaminetetraacetate (EDTA),[13] diethylenetriaminepentaacetic acid (DTPA),[13] ascorbic acid, sodium perchlorate, and sodium acetate, were obtained commercially and recrystallized once or twice from water. Acetic acid (reagent for microanalytical use) was used as received.

Kinetic Runs. All the kinetic studies were carried out by the stopped-flow method with the iron complex in at least 40-fold excess over the cobalt complex. A solution of the cobalt(III) complex containing the appropriate buffer component and DTPA was mixed with a solution of $[Fe^{II}(CN)_6]^{4-}$ to start kinetic runs. Most runs were monitored at 420 nm, where the $[Fe^{III}(CN)_6]^{3-}$ ion has a strong absorption peak ($\epsilon = 1023$ mol^{-1} dm^3 cm^{-1}).[14] The $[Fe^{II}(CN)_6]^{4-}$ ion is oxidized slowly in air, and the rate is greater at lower pH. About 10% of it was oxidized after 2 h ($[Fe^{II}] = 6.0 \times 10^{-3}$ M) at pH 3.6, and hence the kinetic studies (mostly at pH 3.8–3.9) are not disturbed by the air oxidation. Reaction temperature was carefully controlled within ±0.1 °C. The pressure was monitored by a Toyo Baldwin HT-3500 pressure cell connected to a Unipulse AM10 DC amplifier and is subject to uncertainty by ca. 5%.

Measurements. Kinetic runs at ambient pressure were carried out by use of a Union-Giken RA-401 stopped-flow spectrophotometer. A Hikari Koatsu FIT-3A high-pressure apparatus[15] was connected to the spec-

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