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Effect of Coordinated Anion in Configurational Conversion of a Tetraamine Macrocyclic Ligand Complex of Copper(II)

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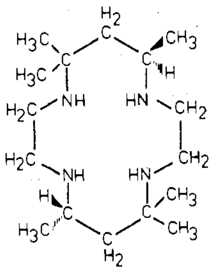
For an investigation of the effect of a coordinated anionic ligand in the configurational conversion of a tetraamine macrocyclic ligand complex of copper(II), the kinetics of the blue-to-red interconversion of the copper(II) complex of *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane in the presence and absence of anionic ligands has been examined at 25 °C by using spectrophotometric techniques. This reaction is catalyzed by base, and the coordinated base which contains another lone pair in the vicinity of the amine hydrogen is much more reactive than free base. A concerted mechanism is proposed. The reactivity order for the blue-to-red interconversion of $[Cu(tet\,a)L(blue)]^+$ is $[Cu(tet\,a)(OH)(blue)]^+ > [Cu(tet\,a)(SH)(blue)]^+ > [Cu(tet\,a)(OAc)(blue)]^+ > [Cu(tet\,a)(NO_2)(blue)]^+ >> [Cu(tet\,a)Cl(blue)]^+$, $[Cu(tet\,a)Br(blue)]^+$, $[Cu(tet\,a)I(blue)]^+$, $[Cu(tet\,a)(SCN)(blue)]^+$, and $[Cu(tet\,a)N_3(blue)]^+$. The important factors determining the reactivity of these complexes are considered.

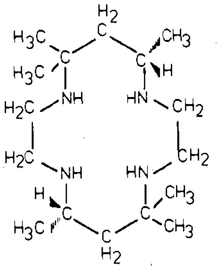
Introduction

The macrocyclic ligand 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane exists as two isomers, tet a (I) and tet b (II).[1,2] In neutral or slightly acidic solution, each



(I)

tet a



(II)

tet b

of these isomers reacts with copper(II) to form initially a blue complex which is readily converted into the more thermodynamically stable red isomer at higher pH (eq 1 and 2).[3,4]

$$[Cu(tet\,a)(blue)]^{2+} \rightarrow [Cu(tet\,a)(red)]^{2+} \tag{1}$$

$$[Cu(tet\,b)(blue)]^{2+} \rightarrow [Cu(tet\,b)(red)]^{2+} \tag{2}$$

In a previous paper we have reported the kinetics of blue-to-red interconversion of the copper(II) complex of tet b (eq 2).[5] The present paper concerns the kinetics of the blue-to-red interconversion of $[Cu(tet\,a)]^{2+}$ (eq 1). The crystal structure determinations of the blue and red complexes of $[Cu(tet\,a)]^{2+}$ have recently been completed.[6] Therefore, it is possible to be quite specific about the rearrangements which accompany the color change with $[Cu(tet\,a)]^{2+}$. The equilibrium constants of the complexation reactions of $[Cu(tet\,a)(blue)]^{2+}$ with anionic ligands represented by eq 3 were recently reported.[7,8]

$$[Cu(tet\,a)(blue)]^{2+} + L^- \rightleftarrows [Cu(tet\,a)L(blue)]^+ \tag{3}$$

With such information at hand, it seems desirable to study the effect of coordinated anions in the blue-to-red interconversion of this complex.

Table I. First-Order Rate Constants for Conversion of $[Cu(tet\ a)(blue)]^{2+}$ to $[Cu(tet\ a)(red)]^{2+}$ as a Function of Hydroxide Ion Concentration at 25.0 °C and $\mu = 0.10$ M ($NaNO_3$ + NaOH)

$[OH^-]$, M	k_{obsd}, s^{-1}	$[OH^-]$, M	k_{obsd}, s^{-1}
5.62×10^{-7}	1.13×10^{-4}	7.89×10^{-4}	0.18
1.26×10^{-6}	3.21×10^{-4}	1.30×10^{-3}	0.32
3.16×10^{-6}	6.61×10^{-4}	1.80×10^{-3}	0.49
8.32×10^{-6}	1.77×10^{-3}	2.80×10^{-3}	0.66
1.44×10^{-5}	2.85×10^{-3}	3.80×10^{-3}	0.77
1.82×10^{-5}	3.95×10^{-3}	1.13×10^{-2}	2.07
2.29×10^{-5}	4.32×10^{-3}	2.38×10^{-2}	3.02
3.16×10^{-5}	6.13×10^{-3}	3.63×10^{-2}	3.67
5.01×10^{-5}	1.06×10^{-2}	4.98×10^{-2}	4.17
8.51×10^{-5}	1.55×10^{-2}	1.49×10^{-1}	5.40
1.99×10^{-4}	3.92×10^{-2}	2.49×10^{-1}	5.60
2.09×10^{-4}	4.57×10^{-2}	4.99×10^{-1}	5.73
2.98×10^{-4}	0.06		

Experimental Section

Reagents. The macrocyclic ligand tet a was prepared by using the procedure described by Hay, Lawrance, and Curtis.[9] $[Cu(tet\,a)(blue)](ClO_4)_2$ was prepared by using the procedure described by Hay and Clark.[10] This complex has a band maximum at 650 nm with ϵ value of 210 M^{-1} cm^{-1}. Anal. Calcd for $CuC_{16}H_{36}N_4 \cdot 2ClO_4$: C, 35.13; H, 6.59; N, 10.25; Cl, 12.99. Found: C, 35.33; H, 6.72; N, 10.23; Cl, 12.90. $[Cu(tet\,a)(red)](ClO_4)_2$ was prepared by the procedure given by Cabbiness.[11] This complex has a band maximum at 512 nm with ϵ value of 135 M^{-1} cm^{-1}. Anal. Calcd: C, 35.13; H, 6.59; N, 10.25; Cl, 12.99. Found: C, 34.98; H, 6.66; N, 10.37; Cl, 13.00. All other chemicals used in this work were of GR grade of Merck.

Instrumentation. A Cary 17 spectrophotometer with a thermostated cell compartment was used to measure absorption spectra and to follow the slow reactions. Rate data for faster reactions were obtained by using a Durrum D-115 stopped-flow spectrophotometer. For pH measurements, a Radiometer PHM 64 equipped with a GK 2401 B combined electrode was used. The pH was standardized with NBS buffers, and the readings were corrected to give the hydroxide ion concentration. The hydroxide ion concentration in 0.1 M $NaNO_3$ solution is calculated from $K_w = 10^{-13.78}$ and $-\log [H^+] = pH - 0.11$. Above pH 13, standard NaOH was used to give the hydroxide ion concentration. The rate constants and equilibrium constants were obtained by a linear least-squares fit of the data by using the IBM 1130 computer.

Kinetic Measurements. All reaction were measured at 650 nm and studied under conditions which were first order in the blue form of the copper complex. Plots of ln ($A - A_\infty$) vs. time were linear and

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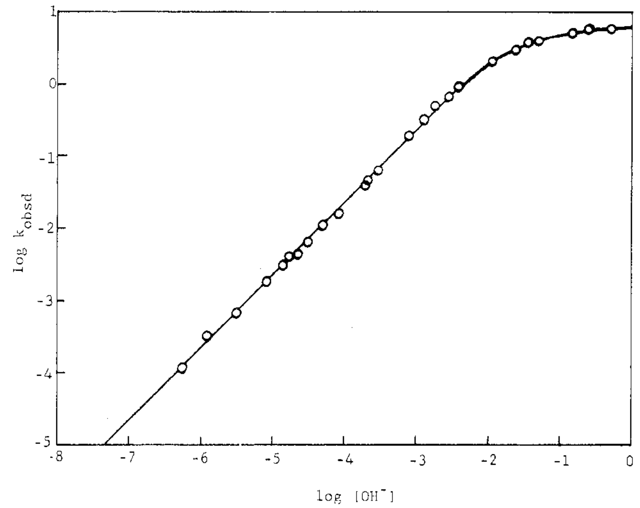

Figure 1. Rate constants for the formation of $[Cu(teta)(red)]^{2+}$ from $[Cu(teta)(blue)]^{2+}$ as a function of hydroxide ion concentration at 25.0 °C and $\mu = 0.10$ M. The solid line is calculated from $k_{obsd} = k_{OH}K_{OH}[OH^-]/(1 + K_{OH}[OH^-])$ where $k_{OH} = 5.7\ s^{-1}$ and $K_{OH} = 50.3\ M^{-1}$.

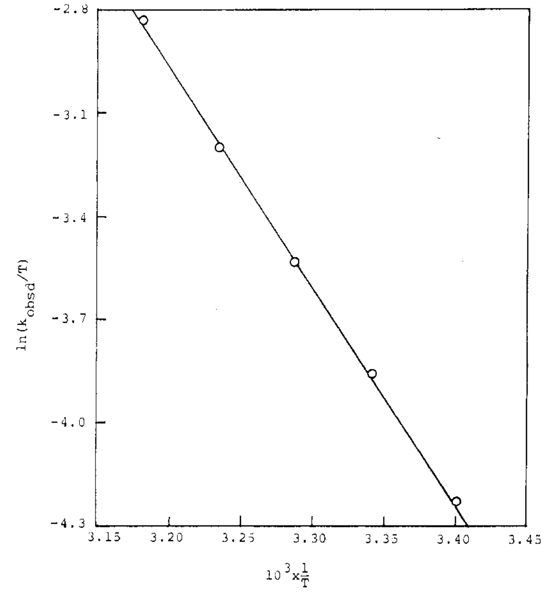

Figure 2. Graphical resolution of the activation parameters of reaction of the formation of the red form from $[Cu(teta)(OH)(blue)]^+$.

gave the k_{obsd} values reported. The A_∞ values for the absorbance were measured after 10 half-lives. A 10-cm cell was used. The average percent standard deviation for rate constants from individual runs is ±2% for k_{obsd}. The deviation of pH measurement is ±0.02 on the pH scale. Temperature control was maintained within ±0.1 °C. Ionic strength was controlled at 0.10 M by using $NaNO_3$.

Results

The blue isomer of $[Cu(teta)]^{2+}$ is stable in dilute acidic solution, but in neutral or slightly basic solution it converts very slowly to the stable red isomer. The rate of the blue-to-red interconversion increases as the concentration of hydroxide ion increases up to 1 M, after which the rate becomes nearly constant with log $[OH^-]$ as shown in Figure 1. The observed rate constants (from a first-order dependence on the concentration of the blue form) are given in Table I. In the presence of anionic ligands, the observed rate constants are significantly different from those in the absence of these ligands as shown in Table II. The temperature dependence of the blue-to-red interconversion was studied at high hydroxide concentration where the $[Cu(teta)(OH)(blue)]^+$ species is fully formed as shown in Table III. The plot of ln (k_{obsd}/T) against $1/T$ in Figure 2 gives $\Delta H^\ddagger = 12.9 \pm 0.8$ kcal/mol and $\Delta S^\ddagger = -11.9 \pm 0.8$ eu.

Table II. First-Order Rate Constants for the Conversion of $[Cu(tet\ a)(blue)]^{2+}$ to $[Cu(tet\ a)(red)]^{2+}$ as a Function of Ion Concentration at 25.0 °C and $\mu = 0.10$ M ($NaX + NaNO_3$)

[L], M	$[OH^-]$, M	k_{obsd}, s^{-1}
	L = Cl^-	
0.000	1.51×10^{-5}	3.56×10^{-3}
0.034	1.51×10^{-5}	3.25×10^{-3}
0.051	1.51×10^{-5}	2.95×10^{-3}
0.069	1.51×10^{-5}	2.68×10^{-3}
0.087	1.51×10^{-5}	2.47×10^{-3}
	L = Br^-	
0.000	1.58×10^{-5}	3.60×10^{-3}
0.034	1.58×10^{-5}	3.20×10^{-3}
0.051	1.58×10^{-5}	2.85×10^{-3}
0.069	1.58×10^{-5}	2.57×10^{-3}
0.087	1.58×10^{-5}	2.32×10^{-3}
	L = I^-	
0.000	1.48×10^{-5}	3.55×10^{-3}
0.017	1.48×10^{-5}	3.34×10^{-3}
0.026	1.48×10^{-5}	3.09×10^{-3}
0.034	1.48×10^{-5}	2.90×10^{-3}
0.043	1.48×10^{-5}	2.70×10^{-3}
	L = N_3^-	
0.000	8.5×10^{-5}	1.81×10^{-2}
0.040	8.5×10^{-5}	7.90×10^{-3}
0.060	8.5×10^{-5}	6.20×10^{-3}
0.080	8.5×10^{-5}	4.75×10^{-3}
0.100	8.5×10^{-5}	3.97×10^{-3}
	L = SCN^-	
0.000	1.26×10^{-5}	2.74×10^{-3}
0.034	1.26×10^{-5}	1.25×10^{-3}
0.051	1.26×10^{-5}	9.75×10^{-4}
0.069	1.26×10^{-5}	7.74×10^{-4}
0.087	1.26×10^{-5}	6.30×10^{-4}
	L = OAc^-	
0.060	4.27×10^{-8}	1.84×10^{-5}
0.080	5.75×10^{-8}	2.42×10^{-5}
0.100	7.41×10^{-8}	3.02×10^{-5}
	L = NO_2^-	
0.060	4.47×10^{-7}	1.16×10^{-4}
0.080	7.58×10^{-6}	1.61×10^{-3}
0.100	3.63×10^{-6}	7.45×10^{-4}
	L = SH^-	
9.5×10^{-4}	5.62×10^{-6}	2.12×10^{-3}
1.0×10^{-3}	1.07×10^{-5}	3.25×10^{-3}
1.05×10^{-3}	1.74×10^{-5}	4.70×10^{-3}

Table III. First-Order Rate Constants for the Conversion of $[Cu(tet\ a)(blue)]^{2+}$ to $[Cu(tet\ a)(red)]^{2+}$ as a Function of Temperature at $[OH^-] = 1.0$ M

temp, °C	k_{obsd}, s^{-1}	temp, °C	k_{obsd}, s^{-1}
21.0	4.28	36.0	12.6
26.0	6.30	41.0	18.5
31.0	8.89		

Discussion

As shown in Figure 1, the rate of the blue-to-red interconversion increases as log $[OH^-]$ increases up to log $[OH^-] = -0.3$, after which the rate become nearly constant with hydroxide ion concentration. A reaction mechanism consistent with the hydroxide ion dependence is given in eq 4 and 5.

$$[Cu(teta)(blue)]^{2+} + OH^- \overset{K_{OH}}{\rightleftharpoons} [Cu(teta)(OH)(blue)]^+ \tag{4}$$

$$[Cu(teta)(OH)(blue)]^+ \xrightarrow{k_{OH}} [Cu(teta)(red)]^{2+} + OH^- \tag{5}$$

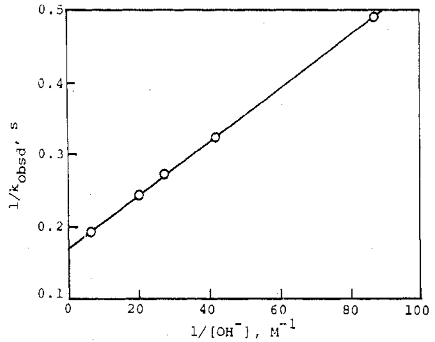

Figure 3. Double-reciprocal dependence of the observed rate constant of the blue-to-red conversion of $[Cu(tet\,a)]^{2+}$ and the concentration of hydroxide ion at 25.0 °C and $\mu = 0.10$ M.

Table IV. Stability Constants and Resolved Rate Constants of Adduct Formation of $[Cu(tet\,a)(blue)]^{2+}$ with Monodentate Ligands at 25.0 °C and $\mu = 0.10$ M ($NaNO_3$ + NaL)

	stability const, M^{-1}		
L	spectro-photometric[a]	kinetic	resolvd rate const, s^{-1}
Cl^-	7.0 ± 0.5	7.3 ± 0.6	*b*
Br^-	9.5 ± 0.5	9.5 ± 0.8	*b*
I^-	11.3 ± 0.6	10.9 ± 0.7	*b*
OH^-	50.3 ± 4.5	47.6 ± 6.0	5.7 ± 0.5
SCN^-	48.1 ± 1.8	49.1 ± 2.0	*b*
N_3^-	45.3 ± 2.1	46.2 ± 2.5	*b*
OAc^-	1.4 ± 0.3	1.3 ± 0.4	$(1.2 \pm 0.2) \times 10^{-4}$
NO_2^-	4.0 ± 0.4	3.5 ± 0.5	$(9.5 \pm 1.0) \times 10^{-5}$
SH^-	218 ± 10	225 ± 15	$(4.9 \pm 0.3) \times 10^{-3}$

[a] From ref 7 and 8. [b] The value of the constant is zero or extremely small.

The resulting rate expression is given in eq 6 where $[Cu(tet\,a)(blue)]_{total}$ refers to the sum of $[[Cu(tet\,a)(blue)]^{2+}]$ and $[[Cu(tet\,a)(OH)(blue)]^+]$.

$$d[[Cu(tet\,a)(red)]^{2+}]/dt = k_{obsd}[Cu(tet\,a)(blue)]_{total} = k_{OH}K_{OH}[OH^-][Cu(tet\,a)(blue)]_{total}/(1 + K_{OH}[OH^-]) \quad (6)$$

The k_{obsd} values given in Table I are equal to $k_{OH}K_{OH}[OH^-]/(1 + K_{OH}[OH^-])$. The reciprocal of k_{obsd} has a linear dependence on the reciprocal of the hydroxide ion concentration in accord with eq 7 as plotted in Figure 3.

$$\frac{1}{k_{obsd}} = \frac{1}{k_{OH}} + \frac{1}{k_{OH}K_{OH}}\left[\frac{1}{[OH^-]}\right] \quad (7)$$

The values found are $k = 5.7 \pm 0.5\ s^{-1}$ and $K_{OH} = 50.3 \pm 4.5\ M^{-1}$ which are in excellent agreement with the reported constants obtained by spectrophotometric measurements as shown in Table IV.

The blue species of $[Cu(tet\,a)]^{2+}$ differs from the red species only in the configuration of a single chiral nitrogen center. The nitrogen which inverts in the blue-to-red interconversion starts with an eclipsed five-membered ring and a skew-boat six-membered ring. This is a relatively high energy state, and the inversion rate is much greater than the inversion rate for the analogous reaction of $[Cu(tet\,b)(blue)]^{2+}$.[5] The nitrogen which inverts in the reaction of $[Cu(tet\,b)(blue)]^{2+}$ starts with a stable five-membered ring in a gauche form and a stable six-membered ring in a chair form.[12] Similarly, the $\Delta H^{\ddagger}$ value for the interconversion of $[Cu(tet\,a)(OH)(blue)]^+$ is 12.9 kcal/mol smaller than that for the corresponding reaction of $[Cu(tet\,b)(OH)(blue)]^+$.[5]

The negative $\Delta S^{\ddagger}$ value of the blue-to-red interconversion of $[Cu(tet\,a)(OH)(blue)]^+$ is consistent with a concerted mechanism which requires solvent molecules on both sides of the nitrogen undergoing inversion. The configurational entropy of the gauche form is smaller than that of the eclipsed form of the five-membered chelate ring.[13] This fact and a statistical effect account in part for the positive $\Delta S^{\ddagger}$ value for the $[Cu(tet\,b)(OH)(blue)]^+$ reaction, but it is not clear why the $[Cu(tet\,a)(OH)(blue)]^+$ reaction should have a $\Delta S^{\ddagger}$ value which is 21 eu more negative, unless it requires more water molecules to reach the transition state.

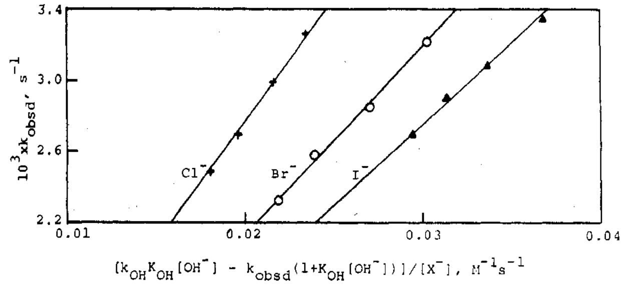

Figure 4. Plot of eq 13 to resolve the rate constant and stability constant for the reactions of $[Cu(tet\,a)(blue)]^{2+}$ in the presence of Cl^-, Br^-, and I^- at 25.0 °C and $\mu = 0.10$ M.

Addition of the anionic ligand, L^-, to the aqueous solution of $[Cu(tet\,a)(blue)]^{2+}$ results in the formation of $[Cu(tet\,a)L(blue)]^+$. The equilibrium constants of these reactions have been reported in the previous papers.[7,8] In the presence of Cl^-, Br^-, I^-, NCS^-, or N_3^-, the rate of the blue-to-red interconversion is significantly smaller than that in the absence of these ions. The fact that halide or pseudohalide ion complexes inhibit the interconversion reaction by blocking hydroxide ion from the coordination site is additional supporting evidence for the importance of coordinated hydroxide ion in this reaction, where the inversion of one of the nitrogen atoms is required. In the presence of SH^-, NO_2^-, or OAc^-, the rate constants are significantly larger than those in the presence of halide or pseudohalide ions.

A reaction mechanism consistent with these observations is given in eq 8–11.

$$[Cu(tet\,a)(blue)]^{2+} + L^- \overset{K_L}{\rightleftharpoons} [Cu(tet\,a)L(blue)]^+ \quad (8)$$

$$[Cu(tet\,a)(blue)]^{2+} + OH^- \overset{K_{OH}}{\rightleftharpoons} [Cu(tet\,a)(OH)(blue)]^+ \quad (9)$$

$$[Cu(tet\,a)L(blue)]^+ \xrightarrow{k_L} [Cu(tet\,a)(red)]^{2+} + L^- \quad (10)$$

$$[Cu(tet\,a)(OH)(blue)]^+ \xrightarrow{k_{OH}} [Cu(tet\,a)(red)]^{2+} + OH^- \quad (11)$$

The resulting rate expression is given by eq 12 where $[Cu(tet\,a)(blue)]_{total}$ refers to the sum $[[Cu(tet\,a)(blue)]^{2+}] + [[Cu(tet\,a)(OH)(blue)]^+] + [[Cu(tet\,a)L(blue)]^+]$.

$$d[[Cu(tet\,a)(red)]^{2+}]/dt = k_{obsd}[Cu(tet\,a)(blue)]_{total} = (k_{OH}K_{OH}[OH^-] + k_LK_L[L^-])[Cu(tet\,a)(blue)]_{total}/(1 + K_{OH}[OH^-] + K_L[L^-]) \quad (12)$$

The k_{obsd} values given in Table II are equal to $(k_{OH}K_{OH}[OH^-] + k_LK_L[L^-])/(1 + K_{OH}[OH^-] + K_L[L^-])$. A plot of k_{obsd} vs. $(k_{obsd}K_{OH}[OH^-] - k_{obsd}(1 + K_{OH}[OH^-]))/[L^-]$ gives a straight line with slope $1/K_L$ and intercept k_L for each of these anionic ligands as plotted in Figures 4–9 in accord with eq 13.

$$k_{obsd} = (1/K_L) \times (k_{OH}K_{OH}[OH^-] - k_{obsd}(1 + K_{OH}[OH^-]))/[L^-] + k_L \quad (13)$$

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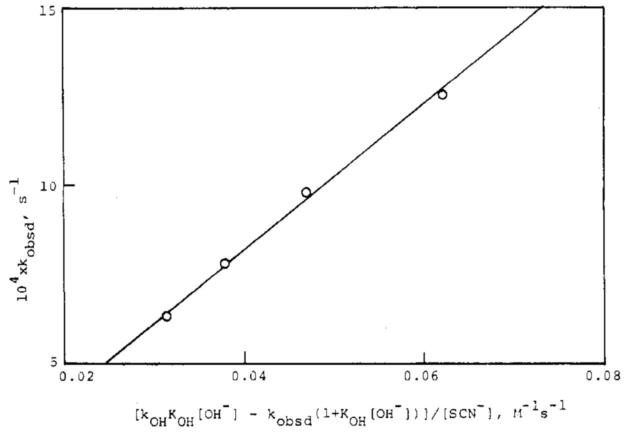

Figure 5. Plot of eq 13 to resolve the rate constant and stability constant for the reaction of [Cu(tet a)(blue)]$^{2+}$ in the presence of SCN$^-$ at 25.0 °C and μ = 0.10 M.

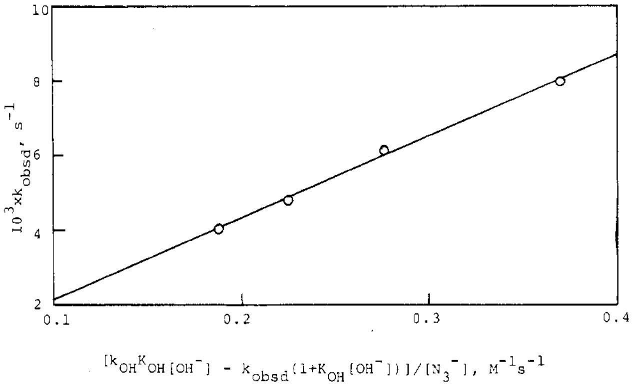

Figure 6. Plot of eq 13 to resolve the rate constant and stability constant for the reaction of [Cu(tet a)(blue)]$^{2+}$ in the presence of N$_3^-$ at 25.0 °C and μ = 0.10 M.

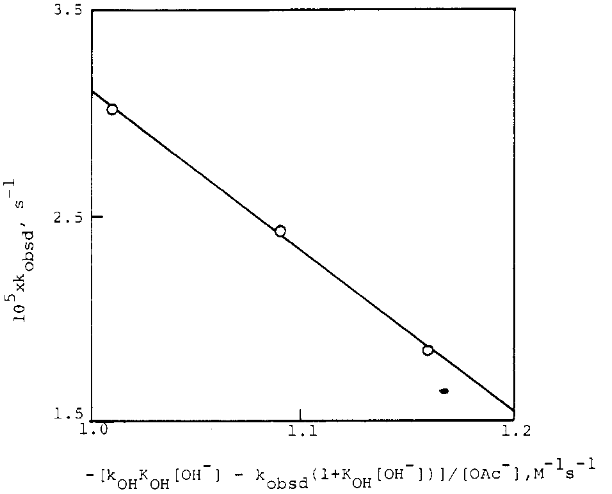

Figure 7. Plot of eq 13 to resolve the rate constant and stability constant for the reaction of [Cu(tet a)(blue)]$^{2+}$ in the presence of OAc$^-$ at 25.0 °C and μ = 0.10 M.

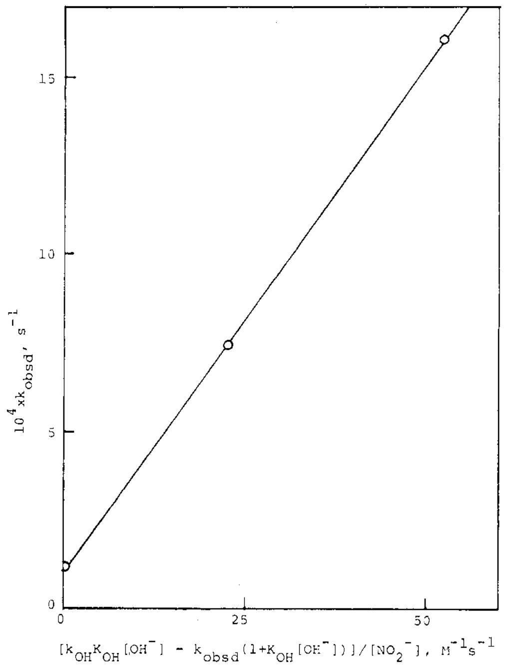

Figure 8. Plot of eq 13 to resolve the rate constant and stability constant for the reaction of [Cu(tet a)(blue)]$^{2+}$ in the presence of NO$_2^-$ at 25.0 °C and μ = 0.10 M.

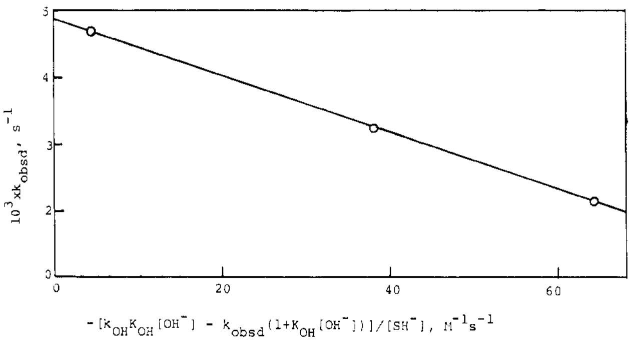

Figure 9. Plot of eq 13 to resolve the rate constant and stability constant for the reaction of [Cu(tet a)(blue)]$^{2+}$ in the presence of SH$^-$ at 25.0 °C and μ = 0.10 M.

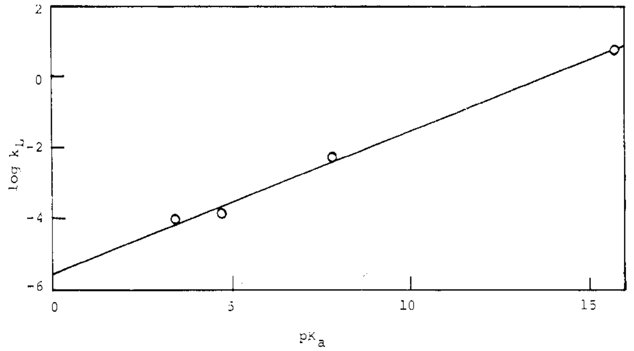

Figure 10. A Brønsted plot for the blue-to-red interconversion of [Cu(tet a)L]$^+$.

The equilibrium constants, K_L, evaluated from the kinetic data by using eq 13 were in excellent agreement with the reported constants obtained by spectrophotometric measurements under equilibrium conditions as shown in Table IV. Thus, these seem to be good evidence that coordinated base provides the best pathway to initiate the inversion of the macrocyclic nitrogen atom and gives the subsequent changes needed for the blue-to-red interconversion. For the same reason mentioned in the previous paper,[5] a preequilibrium step with the formation of low concentration of deprotonated nitrogen bonded to copper would not depend on the source of the base. Thus, a strong preference for the reaction of coordinated base over free base suggests a concerted mechanism in which intramolecular hydrogen bonding, nitrogen inversion, and ring conformational changes occur.

The resolved rate constants, k_L, evaluated from the kinetic data by using eq 13 were given in Table IV. As preliminary observations on these constants, we note that those coordinated anions that fail to catalyze the blue-to-red interconversion of

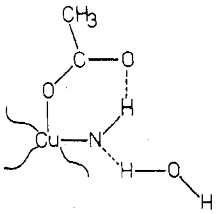

Figure 11. Proposed intramolecular hydrogen bonding and concerted inversion of nitrogen in $[Cu(tet\,a)(OAc)(blue)]^+$.

the copper(II) complex are of two types: (1) those that are weak bases such as Cl^-, Br^-, and I^- and (2) those coordinated ligands such as N_3^- and NCS^-, which lack another lone pair in the vicinity of the N–H group. The latter contains lone pairs, which are too far away to react with the N–H group that must be inverted during the blue-to-red reaction.

In the case of the coordinated anions that contain another lone pair in the vicinity of the amine hydrogen, the value of the resolved rate constant k_L increases as the basicity of the anionic ligand increases as shown by the data given in Table IV. The trend, $k_{NO_2} < k_{OAc} < k_{SH} < k_{OH}$, led us to think that there must be a relation between the proton basicity factors and the resolved rate constants of the anions. Plotting the basicity constant defined as log $([HL]/[H^+][L^-])$ or pK_a as abscissa and log k_L as ordinate, we obtain a straight line relationship as shown in Figure 10. The magnitude of the slope, 0.40, suggests that the hydrogen is partially removed from the nitrogen to the coordinated base in the activated complex as shown in Figure 11. The hydrogen-bonded ring structure may be important in helping to maintain an activated species long enough to permit the five-membered and six-membered rings to twist and the nitrogen to attract a proton from a solvent molecule on the opposite site of the coordinated base, thus leading to the inversion.

On the basis of these results we are able to conclude that the kinetics shows a strong preference for the reaction of coordinated bases which contain another lone pair in the vicinity of the amine hydrogen over free bases. The hydrogen is partially removed from the nitrogen in the activated complex. A concerted mechanism is proposed in which intramolecular hydrogen bonding, nitrogen inversion, and ring conformation changes occur.

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Registry No. $[Cu(tet\,a)(blue)]^{2+}$, 73464-68-3; $[Cu(tet\,a)(red)]^{2+}$, 73464-69-4; $[Cu(tet\,a)(OH)(blue)]^+$, 73464-70-7; $[Cu(tet\,a)(SH)(blue)]^+$, 73395-63-8; $[Cu(tet\,a)(OAc)(blue)]^+$, 73384-40-4; $[Cu(tet\,a)(NO_2)(blue)]^+$, 73384-33-5; $[Cu(tet\,a)Cl(blue)]^+$, 73464-66-1; $[Cu(tet\,a)Br(blue)]^+$, 73464-67-2; $[Cu(tet\,a)I(blue)]^+$, 73493-86-4; $[Cu(tet\,a)(SCN)(blue)]^+$, 73384-34-6; $[Cu(tet\,a)N_3(blue)]^+$, 73384-35-7; OH^-, 14280-30-9; Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5; N_3^-, 14343-69-2; SCN^-, 302-04-5; OAc^-, 71-50-1; NO_2^-, 14797-65-0; SH^-, 15035-72-0.

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Effects of Axial Ligation on Molecular Oxygen Binding by Donor Atoms Built in Saturated Macrocycles. Equilibrium and Kinetic Study with Cobalt(II) Complexes of Macrocyclic Pentaamines and Oxatetraamine

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Cobalt(II) complexes of two 16-membered macrocyclic homologues 1,4,7,10,13-pentaazacyclohexadecane (L^2) and 1-oxa-4,7,11,14-tetraazacyclohexadecane (L^3) are capable of coordinating molecular oxygen at pH $\sim$5 to form μ-peroxo-bridging complexes $(CoL)_2O_2$. A comparison with a 14-membered tetraamine L^5 suggests that an extra ligation at an axial position with the fifth N or O donor atom built in the macrocyclic structure appreciably promotes the rates and equilibrium of O_2 uptake, in particular with the N donor. The equilibrium and kinetic results for L^2 are compared with the relevant data reported for a linear pentaamine homologue L^4.

The modes and capabilities by which cobalt(II)–tetraamine (N_4) complexes bind molecular oxygen[2] are subjected to characteristic modification by the tetraamine ligand cyclization and the cyclized ring size.[3] Although the ring closure of triethylenetetramine (trien)[4,5] with ethylene (into 12-membered N_4) or propylene (into 13-membered N_4) does not alter the stoichiometry of the μ-dioxygen-μ-hydroxo products (represented by $(CoL)_2O_2OH$), it introduces stereochemical constraint to make the O_2 uptake less favorable kinetically and thermodynamically.[3] A most dramatic consequence of the cyclized structure occurs at 14-membered homologue 1,4,8,11-tetraazacyclotetradecane (L^5), where the oxygenation product takes a different $(CoL)_2O_2$ structure lacking a μ-hydroxo bridge.[3,6,7] This implies that rigid planarity around Co(II) is imposed by the 14-membered cyclic structure with one of the axial positions used for interaction with O_2 and the remaining axial site left open (or more likely, for interaction with H_2O solvent). The oxygenation product and the kinetics leading to it (first order in $[CoL^{2+}]$ and in $[O_2]$) for the saturated 14-membered N_4 are analogous to those for unsaturated 16-membered macrocyclic N_4 porphyrins.[8,9] Because of the "nonfrilled" structure, L^5 offers excellent advantages for the study of properties associated with the macrocyclic structure characterizing the natural macrocyclic ligands.

This paper continues the oxygenation study promoted by cobalt(II) complexes of macrocyclic ligands, 1,4,7,10,13-pentaazacyclopentadecane (L^1), 1,4,7,10,13-pentaazacyclohexadecane (L^2), and 1-oxa-4,7,11,14-tetraazacyclohexadecane

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