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(33) See ref 9 and footnote 17 referred to therein.

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Role of Coordinated Hydroxide Ion in Configurational Conversions of Tetraamine Macrocyclic Ligand Complexes of Copper(II)

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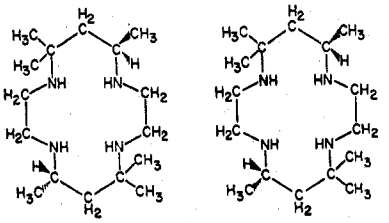
Blue-to-red interconversion of the copper(II) complex of tet b (II) is base catalyzed due to the required inversion of nitrogen atoms in the complexes. Coordinated hydroxide ion is much more reactive than free hydroxide ion and a concerted mechanism is proposed in which intramolecular hydrogen bonding, nitrogen inversion, and ring conformational changes occur.

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).[2,3] Each of these isomers forms a blue complex



I II

as well as red complexes with copper(II).[4,5] The present paper concerns the kinetics of the blue-to-red interconversion of $[Cu(tet\ b)]^{2+}$ (eq 1) and the important contribution of the

$$[Cu(tet\ b)(blue)]^{2+} \rightarrow [Cu(tet\ b)(red)]^{2+} \qquad (1)$$

coordinated hydroxide ion in the reaction, where inversions of the nitrogen atoms are required. The blue-to-red reaction is much faster than the rates of dissociation of the macrocyclic ligands from copper(II).[5] Hence there is no doubt that the configurational conversion occurs while the ligand is coordinated. In this reaction structures have been determined for crystalline forms of the reactant[6] and of the product.[7] Therefore, it is possible to be quite specific about the rearrangements which accompany the color change with $[Cu(tet\ b)]^{2+}$. The blue tet b complex has been isolated as $[Cu(tet\ b)]_2Cl(ClO_4)_3$ which contains five-coordinate (trigonal-bipyramidal) copper as shown in Figure 1. The ligand is in its most stable, folded configuration with both six-membered chelate rings in a symmetrical chair form and both five-membered chelate rings in a gauche form.[6] Chloride ion, which occupies one of the positions in the trigonal plane, dissociates from the copper in dilute solution but the electronic spectral characteristics of the complex in aqueous solution are similar to those of the crystals.[8]

The structure of $[Cu(tet\ b)(red)](ClO_4)_2$ is shown in Figure 2.[7] The copper is four-coordinate with a very slightly distorted square-planar arrangement of the four nitrogens of tet b. The six-membered chelate rings are in the chair form but the five-membered chelate rings are in an eclipsed (or partially eclipsed) form rather than the gauche form. The diagrams of structures III and IV in Figures 1 and 2 indicate the relative positions of the hydrogen atoms on the four nitrogens. It can be seen that two of the four nitrogens must be inverted during the blue-to-red reaction. Inversion reactions of uncomplexed amines have been studied extensively[9] and a few reactions of various polyamine complexes with the metal ions Co(III),[10,16] Pt(II),[11] Pt(IV),[12] Pb(II),[13] Ni(II),[14,15] and Cu(II)[14] have been investigated. It is not surprising that hydroxide ion assists the inversion reaction in eq 1, but it is most interesting that the main reaction pathway is via hydroxide ion which is coordinated to the copper. Poon and Tobe[16] studied the cis to trans isomerization of *cis*-$[Co(cyclam)Cl_2]^+$ in aqueous solution and also suggested an intramolecular proton transfer from nitrogen to oxygen in the *cis*-$[Co(cyclam)(OH)(H_2O)]^{2+}$ cation.

Table I. Visible and Near-Infrared Absorption Bands

complex	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}
$[Cu(tet\ b)(red)]^{2+}$	525	174
$[Cu(tet\ b)(blue)]^{2+}$	833	269
	680 sh	172
$[Cu(tet\ b)Cl(blue)]^{2+}$	840	324
	670	316

Experimental Section

Reagents. The macrocyclic ligand tet b was prepared by using the procedure described by Hay, Lawrance, and Curtis.[17] $\{[Cu(tet\ b)]_2Cl\}(ClO_4)_3$ was prepared by using the procedure described by Bauer.[6] Anal. Calcd for $2CuC_{16}H_{36}N_4Cl\cdot3ClO_4$: C, 37.32; H, 7.07; Cl, 13.77. Found: C, 37.22; H, 7.12; Cl, 13.63. $[Cu(tet\ b)(red)](ClO_4)_2$ was prepared by the procedure given by Bauer.[8] Anal. Calcd for $CuC_{16}H_{36}N_4\cdot2ClO_4$: C, 35.14; H, 6.63; Cl, 12.96. Found: C, 35.05; H. 6.84; Cl, 13.10. 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 reactions. A Durrum D-115 stopped-flow spectrophotometer was used to measure the absorbance jump after stopped-flow mixing of base with $[Cu(tet\ b)(blue)]^{2+}$ solutions. 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 stability constants were obtained by a linear least-squares fit of the data by using the IBM 1130 computer.

Kinetic Measurements. All reactions were measured at 840 nm and studied under conditions which were first order in the blue form

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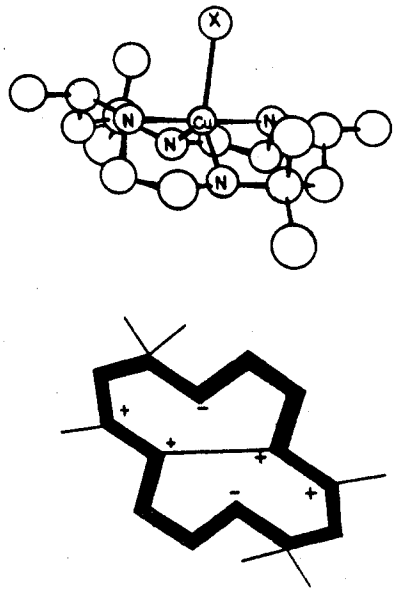
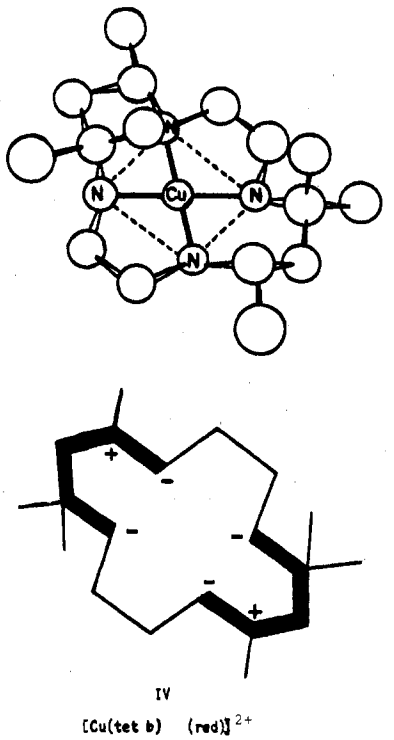


III

[Cu(tet b)X (blue)]$^+$

Figure 1. Crystal structure of [Cu(tet b)(blue)]$^{2+}$ and a representation of the configurations of the asymmetric centers and the conformations of the chelate rings of tet b in this complex. A plus sign at an asymmetric center indicates that the hydrogen atom of the center is above the plane of the macrocycle and a minus sign that it is below. Gauche conformations of the five-membered chelate rings and chair conformations of the six-membered chelate rings are indicated by heavier lines.



IV

[Cu(tet b) (red)]$^{2+}$

Figure 2. Structure of [Cu(tet b)(red)]$^{2+}$ and a representation of the configurations of the asymmetric centers and the conformations of the chelate rings of tet b in this complex. A plus sign at an asymmetric center indicates that the hydrogen atom of the center is above the plane of the macrocycle and a minus sign that it is below.

of the copper complexes. Plots of ln $(A - A_\infty)$ vs. time were linear and 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 are ±1% for k_{obsd}. The deviation of pH measurement is ±0.02 pH

Table II. Apparent Molar Absorptivities at 670 nm for [Cu(tet b)(blue)]$^{2+}$–X^- Systems as a Function of Halide and Hydroxide Ion Concentration at 25.0 ± 0.1 °C, μ = 0.10 M ($NaNO_3$ + NaX), Where X Is Halide or Hydroxide Ions

$[Cl^-]$, M	ϵ_{app}, M^{-1} cm^{-1}	$[Br^-]$, M	ϵ_{app}, M^{-1} cm^{-1}
0.010	186	0.010	209
0.020	201	0.020	239
0.040	222	0.040	283
0.060	238	0.060	311
0.080	249	0.080	330
0.100	258	0.100	346

$[I^-]$, M	ϵ_{app}, M^{-1} cm^{-1}	$[OH^-]$, M	ϵ_{app},[a] M^{-1} cm^{-1}
0.010	279	0.005 12	13331
0.012	297	0.015 12	5127
0.014	313	0.035 12	2355
0.016	329	0.065 12	1283
0.018	343	0.095 12	879
0.020	357		

[a] Measured at 840 nm.

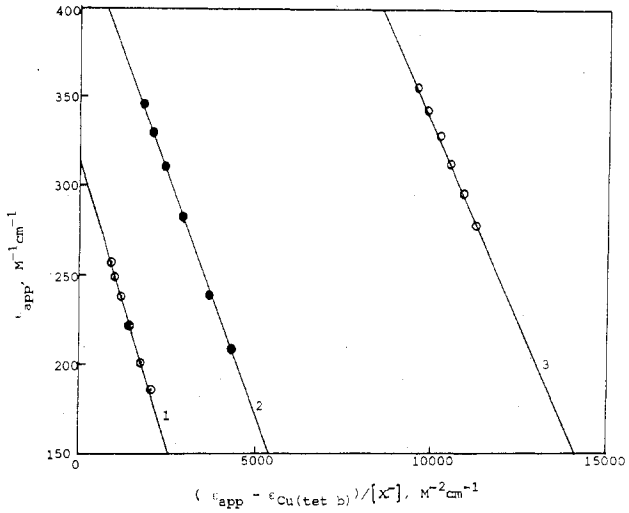


Figure 3. Spectrophotometric determination of the equilibrium constants of [Cu(tet b)(blue)]$^{2+}$ with halide ions at 25.0 °C and μ = 0.10 M. Curves 1, 2, and 3 are for [Cu(tet b)(blue)]$^{2+}$–Cl^-, [Cu(tet b)(blue)]$^{2+}$–Br^-, and [Cu(tet b)(blue)]$^{2+}$–I^- systems, respectively.

scale. Temperature control was maintained within ±0.1 °C.

Results

Spectral Data. The visible and near-infrared absorption spectra were used to observe the reactions. The principal absorption bands and molar absorptivities of the complexes in aqueous acidic solution are given in Table I. Apparent molar absorptivities are given in Table II.

Equilibrium Constants. Addition of the solution of halide ion to an aqueous solution of [Cu(tet b)(blue)]$^{2+}$ resulted in the setting up of complex equilibria, involving the replacement of coordinated water by halide ion according to eq 2. Sodium

$$[Cu(tet\ b)(blue)]^{2+} + X^- \rightarrow [Cu(tet\ b)X(blue)]^+ \quad (2)$$

nitrate was added to control the ionic strength of the solutions. The apparent molar absorptivities at 670 nm, which were used to calculate the stability constants of the five-coordinate species according to eq 2, were obtained by using the equation

$$\epsilon_{app} = A/lC_T \quad (3)$$

where A is the absorbance at 670 nm, l is the length of the cell, and C_T is the total concentration of the copper(II) complexes, [[Cu(tet b)(blue)]$^{2+}$] + [[Cu(tet b)X(blue)]$^+$].

Table III. Stability Constants of Halide and Hydroxide Ions with $[Cu(tet\ b)(blue)]^{2+}$ at 25.0 ± 0.1 °C, μ = 0.10 M ($NaNO_3$ + NaX)

X^-	spectrophotometric measurmt, M^{-1}	kinetic measurmt, M^{-1}
Cl^-	15.5 ± 0.3	15.5 ± 0.2
Br^-	18.1 ± 0.2	19.5 ± 1.8
I^-	22.2 ± 0.1	22.0 ± 0.2
OH^-	508 ± 5	506 ± 10

Table IV. First-Order Rate Constants for the Conversion of $[Cu(tet\ b)(blue)]^{2+}$ to $[Cu(tet\ b)(red)]^{2+}$ as a Function of Hydroxide Ion Concentration at 25.0 ± 0.1 °C, μ = 0.10 M ($NaNO_3$ + NaX)

pH	$[OH^-]$, M	k_{obsd}, s^{-1}
7.39	4.07×10^{-7}	1.26×10^{-6}
7.79	1.02×10^{-6}	3.80×10^{-6}
8.36	3.80×10^{-6}	1.15×10^{-5}
8.75	9.33×10^{-6}	2.69×10^{-5}
9.12	2.19×10^{-5}	6.60×10^{-5}
9.44	4.57×10^{-5}	1.46×10^{-4}
9.62	6.92×10^{-5}	2.07×10^{-4}
10.09	2.04×10^{-4}	6.44×10^{-4}
10.21	2.69×10^{-4}	8.39×10^{-4}
10.41	4.31×10^{-4}	1.14×10^{-3}
10.61	6.76×10^{-4}	1.64×10^{-3}
10.71	8.51×10^{-4}	1.88×10^{-3}
10.85	1.17×10^{-3}	2.32×10^{-3}
11.07	1.95×10^{-3}	3.04×10^{-3}
11.31	3.39×10^{-3}	3.91×10^{-3}
11.46	4.90×10^{-3}	4.31×10^{-3}
11.62	6.92×10^{-3}	4.90×10^{-3}
11.80	1.05×10^{-2}	5.27×10^{-3}
11.93	1.41×10^{-2}	5.49×10^{-3}
12.03	1.78×10^{-2}	5.76×10^{-3}
12.33	3.55×10^{-2}	6.23×10^{-3}
12.61	6.76×10^{-2}	6.71×10^{-3}
12.96	1.79×10^{-1}	7.36×10^{-3}[a]
13.22	3.98×10^{-1}	7.83×10^{-3}[a]
13.37	6.03×10^{-1}	8.39×10^{-3}[a]

[a] Ionic strength is equal to the concentration of NaOH.

The solubility of $[Cu(tet\ b)X(blue)]^+$ in an aqueous solution of Br^- or I^- is very low. So the spectrum of $[Cu(tet\ b)X(blue)]^+$ cannot be obtained directly in aqueous solution.

The apparent molar absorptivity of the solution, ϵ_{app}, had a linear dependence on $(\epsilon_{app} - \epsilon_{Cu(tet\ b)})/[X^-]$ in accordance with eq 4 as plotted in Figure 3. The values of stability

$$\epsilon_{app} = \frac{-1}{K_x} \frac{\epsilon_{app} - \epsilon_{Cu(tet\ b)}}{[X^-]} + \epsilon_{Cu(tet\ b)X} \qquad (4)$$

constants calculated from the slopes of the straight lines in Figure 3 are given in Table III.

The equilibrium constant for the reaction of $[Cu(tet\ b)(blue)]^{2+}$ and OH^- was determined by measuring the absorbance jump after stopped-flow mixing of base with $[Cu(tet\ b)(blue)]^{2+}$ solution. A plot of ϵ_{app} against $-(\epsilon_{app} - \epsilon_{Cu(tet\ b)})/[OH^-]$, where $[OH^-] = [OH^-]_T - [[Cu(tet\ b)(OH)(blue)]^+]$, gives a straight line of slope $1/K_{OH}$, as shown in Figure 4. The values of $[OH^-]$ were calculated by an iterative procedure in which an estimated value of K_{OH} was used to calculate values of $[OH^-]$ and then these were used to obtain a new value of K_{OH} until the least-squares deviation in the plot of ϵ_{app} vs. $-(\epsilon_{app} - \epsilon_{Cu(tet\ b)})/[OH^-]$ reached a minimum value. The measured value of K_{OH} is 508 M^{-1}.

Kinetics Data. The blue isomer of $[Cu(tet\ b)]^{2+}$ is stable in dilute acidic solutions, but in slightly basic solutions it converts very slowly to the red isomer. The rate of the blue-to-red interconversion increases as the pH increases up to pH 12, after which the rate becomes nearly constant with pH as shown in Figure 5. The observed rate constants from a first-order dependence on the concentration of the blue form are given in Table IV. Chloride ion, bromide ion, and iodide ion diminish the ability of hydroxide ion to catalyze the interconversion reaction as shown in Table V. The temperature

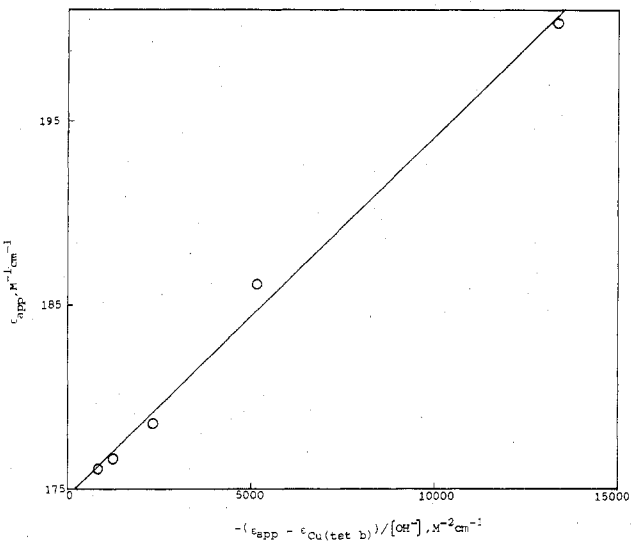


Figure 4. Spectrophotometric determination of the equilibrium constant of $[Cu(tet\ b)(blue)]^{2+}$ with hydroxide ion at 25.0 °C and μ = 0.10 M.

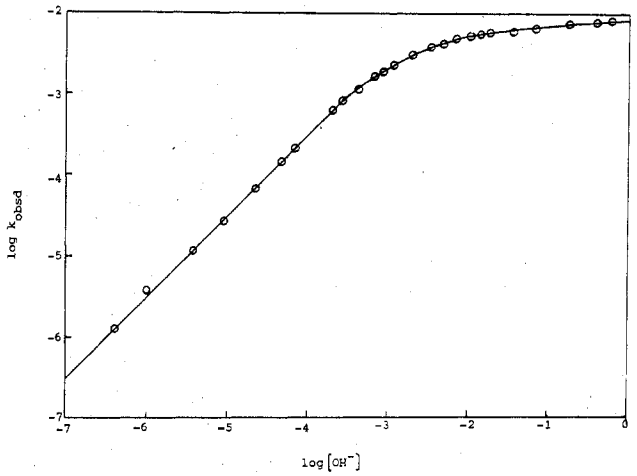


Figure 5. Rate constants for the formation of $[Cu(tet\ b)(red)]^{2+}$ from $[Cu(tet\ b)(blue)]^{2+}$ as a function of hydroxide ion concentration at 25.0 °C and μ = 0.10 M. The solid line is calculated from $k_{obsd} = kK_{OH}[OH^-]/(1 + K_{OH}[OH^-])$ where $k = 6.22 \times 10^{-3}$ s^{-1} and $K_{OH} = 506$ M^{-1}.

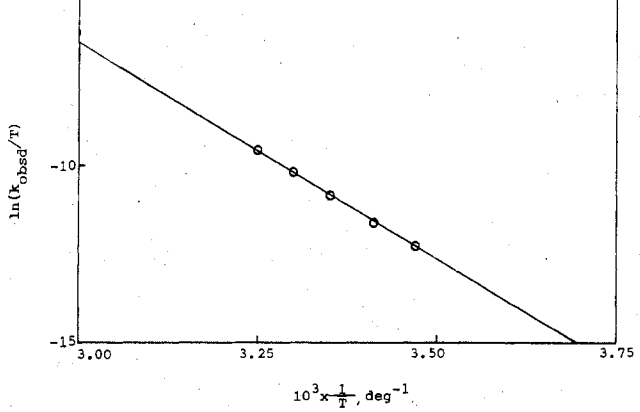


Figure 6. Graphical resolution of the activation parameters of reaction of the formation of the red form from $[Cu(tet\ b)(OH)(blue)]^+$.

Table V. First-Order Rate Constants for the Conversion of $[Cu(tet\ b)(blue)]^{2+}$ to $[Cu(tet\ b)(red)]^{2+}$ as a Function of Hydroxide Ion Concentration and Halide Ion Concentration at 25.0 ± 0.1 °C, μ = 0.10 M ($NaNO_3$ + NaX)

$[X^-]$, M	pH	k_{obsd}, s^{-1}
	Cl^-	
0.000	10.70	1.89×10^{-3}
0.010	10.70	1.66×10^{-3}
0.020	10.70	1.52×10^{-3}
0.040	10.70	1.28×10^{-3}
0.080	10.70	9.70×10^{-4}
0.020	10.31	7.17×10^{-4}
0.020	10.99	2.39×10^{-3}
0.020	11.13	2.87×10^{-3}
	Br^-	
0.000	10.62	1.67×10^{-3}
0.010	10.62	1.40×10^{-3}
0.020	10.62	1.27×10^{-3}
0.040	10.62	9.74×10^{-4}
0.080	10.62	7.64×10^{-4}
0.100	10.62	6.85×10^{-4}
0.020	10.31	6.62×10^{-4}
0.020	10.99	2.33×10^{-3}
0.020	11.13	2.81×10^{-3}
	I^-	
0.000	10.78	2.08×10^{-3}
0.010	10.78	1.81×10^{-3}
0.020	10.78	1.60×10^{-3}
0.040	10.78	1.30×10^{-3}
0.050	10.78	1.19×10^{-3}
0.010	10.33	7.97×10^{-4}
0.010	10.99	2.50×10^{-3}
0.010	11.11	2.91×10^{-3}

Table VI. First-Order Rate Constants for the Conversion of $[Cu(tet\ b)(blue)]^{2+}$ to $[Cu(tet\ b)(red)]^{2+}$ as a Function of Temperature at $[OH^-]$ = 0.095 ± 0.001 M and $[NaNO_3]$ = 0.005 ± 0.001 M

temp, °C	k_{obsd}, s^{-1}
15.0	1.41×10^{-3}
20.0	2.84×10^{-3}
25.0	6.01×10^{-3}
30.0	1.13×10^{-2}
35.0	2.07×10^{-2}

dependence of the blue-to-red interconversion was studied at high pH where the $[Cu(tet\ b)(OH)(blue)]^+$ species is fully formed as shown in Table VI. The plot of ln (k/T) against $1/T$ in Figure 6 gives $\Delta H^{\ddagger}$ = 23.3 ± 0.5 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 9.3 ± 0.3 eu.

Discussion

The absorption spectra of $[Cu(tet\ b)(blue)]^{2+}$ and $[Cu(tet\ b)Cl(blue)]^+$ in solution both have two bands in the visible region (Table I) indicating the same type of trigonal-bipyramidal structure as that found in the crystalline blue complex, where tet b is folded and a chloride ion or water molecule is in the equatorial position.[6,8]

The equilibrium of adduct formation between $[Cu(tet\ b)(blue)]^{2+}$ and halide ions has been studied recently.[18] The study resulted in smaller values of K_X for data at 0.4 M ionic strength. The decrease in K_X is consistent with the behavior expected from the extended Debye–Hückel expression. The fact that the halide complexes of $[Cu(tet\ b)(blue)]^{2+}$ are more stable than those of $[Cu(aquo)]^{2+}$, while the opposite is the case for the hydroxide complexes, suggests that the coordinated tetraamine macrocyclic ligand softens the borderline acid, copper(II) ion.

The visible spectrum of $[Cu(tet\ b)(red)]^{2+}$ in solution has a single absorption peak at 525 nm and this also agrees with the spectrum of the crystalline red complex indicating a square-planar (or slightly distorted square-planar) complex.

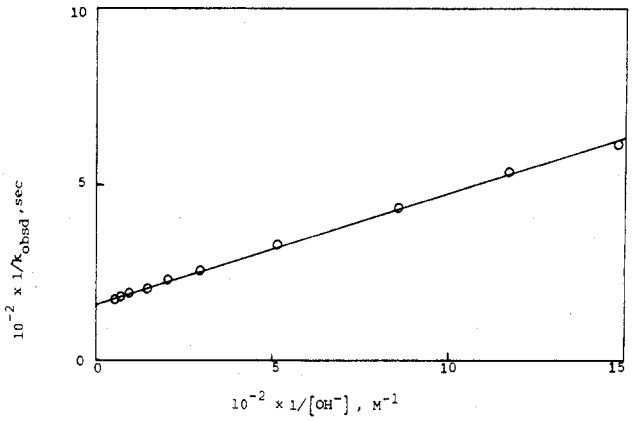


Figure 7. Double-reciprocal dependence of the observed rate constant of the blue-to-red conversion of $[Cu(tet\ b)]^{2+}$ and the concentration of hydroxide ion at 25.0 °C and μ = 0.10 M.

A reaction mechanism consistent with the hydroxide ion dependence and halide ion inhibition of the blue-to-red interconversion of $[Cu(tet\ b)]^{2+}$ is given in eq 5, 6, and 7.

$$[Cu(tet\ b)(blue)]^{2+} + X^- \underset{}{\overset{K_X}{\rightleftharpoons}} [Cu(tet\ b)X(blue)]^+ \quad (5)$$

$$[Cu(tet\ b)(blue)]^{2+} + OH^- \overset{K_{OH}}{\rightleftharpoons} [Cu(tet\ b)(OH)(blue)]^+ \quad (6)$$

$$[Cu(tet\ b)(OH)(blue)]^+ \xrightarrow{k} [Cu(tet\ b)(red)]^{2+} + OH^- \quad (7)$$

The resulting rate expression is given in eq 8 where [Cu(tet b)(blue)]$_{total}$ refers to the sum of $[[Cu(tet\ b)(blue)]^{2+}]$ + $[[Cu(tet\ b)(OH)(blue)]^+]$ + $[[Cu(tet\ b)(X)(blue)]^+]$.

$$d[Cu(tet\ b)(red)^{2+}]/dt = k_{obsd}[Cu(tet\ b)(blue)]_{total} = \frac{kK_{OH}[OH^-][Cu(tet\ b)(blue)]_{total}}{1 + K_{OH}[OH^-] + K_X[X^-]} \quad (8)$$

The k_{obsd} values given in Table IV are equal to $kK_{OH}[OH^-]/(1 + K_{OH}[OH^-] + K_X[X^-])$. In the absence of halide ions, the reciprocal of K_{obsd} has a linear dependence on the reciprocal of the hydroxide ion concentration in accord with eq 9 as plotted in Figure 7.

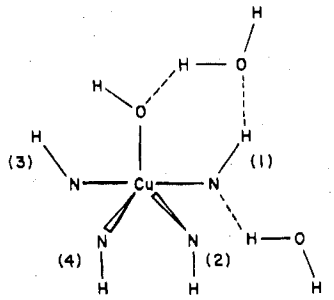
$$\frac{1}{k_{obsd}} = \frac{1}{k} + \frac{1}{kK_{OH}}\frac{1}{[OH^-]} \quad (9)$$

The values found are $k = (6.22 \pm 0.10) \times 10^{-3}$ s^{-1} and K_{OH} = 506 ± 10 M^{-1} which is in excellent agreement with the constant obtained by spectrophotometric measurements as shown in Table III.

Data for halide ion inhibition of the $[Cu(tet\ b)(blue)]^{2+}$ interconversion reaction are given in Table V. The stability constants of the halide complexes, K_X, were evaluated from the kinetic data by using eq 10 and were in excellent agreement with constants evaluated by spectrophotometric measurements under equilibrium conditions as shown in Table III.

$$K_X = \frac{1}{[X^-]}\left(\frac{kK_{OH}[OH^-]}{k_{obsd}} - 1 - K_{OH}[OH^-]\right) \quad (10)$$

Thus, the formation of the halide complexes, $[Cu(tet\ b)(X)(blue)]^+$, prevents or reduces the extent of the formation of the hydroxide ion complex, $[Cu(tet\ b)(OH)(blue)]^+$, and the latter provides the best pathway for the blue-to-red reaction. The coordinated hydroxide ion assists in the inversion



V

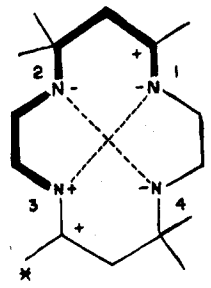
Figure 8. Proposed intramolecular proton-transfer and concerted inversion of N(1) in [Cu(tet b)(OH)(blue)]$^+$. The inversion is accompanied by ring conformational changes to give a distorted planar coordination geometry for the four nitrogens around copper.

of the nitrogen atoms. As can be seen in Figures 1 and 2, two of the nitrogen atoms must invert for the blue-to-red reaction.

The mechanism proposed for the blue-to-red interconversion of the tet b complex is via the [Cu(tet b)(OH)(blue)]$^+$ species. Measurements of the absorbance jump after stopped-flow mixing of base with [Cu(tet b)(blue)]$^{2+}$, as well as the equilibrium study, show the existence of a hydroxide adduct to the blue form. The pH dependence of the kinetics data, with a first-order OH^- dependence at lower pH changing to an almost zero-order OH^- dependence at higher pH, shows the importance of the hydroxide adduct in the interconversion mechanism. The fact that halide ion complexes inhibit the interconversion reaction by blocking hydroxide ion from the coordination site is additional supporting evidence for the importance of [Cu(tet b)(OH)(blue)]$^+$. It is reassuring that the spectrally measured equilibrium constants for [Cu(tet b)X(blue)]$^+$ agree with those measured on the basis of the rate data and proposed mechanism (Table III). Thus, there seems to be good evidence that the coordinated hydroxide ion provides the best pathway to initiate the inversion of the macrocyclic nitrogen atom and give the subsequent changes needed for the blue-to-red interconversion.

Why should a coordinated hydroxide ion be more effective than a free hydroxide ion in these reactions? In dilute base the concentration of OH^- in the vicinity of the N–H group is greatly increased due to coordination. However, the basicity of the hydroxide ion (pK_b = 2.70 for [Cu(tet b)(OH)(blue)]$^+$) is reduced in direct proportion to its tendency to become coordinated. If the reaction mechanism had a simple proton transfer process as the rate-determining step, then the relative concentrations and basicities of coordinated vs. free hydroxide ion should cancel one another. Similarly, a preequilibrium step with the formation of low concentrations of deprotonated trigonal nitrogen bonded to copper would not depend on the source of the base. On the other hand, a concerted process of proton transfer and inversion with rearrangements of the ring conformations as well as the coordination geometry could be enhanced by a coordinated hydroxide ion and this mechanism will be considered.

The positions of the amine hydrogens in [Cu(tet b)(OH)(blue)]$^+$ are shown in Figure 8. Two water molecules are included in the vicinity of H(1) to indicate how they might assist in the proton transfer and inversion reactions. H(1) and H(3) will have a much greater chance of reacting with the coordinated OH^- (via a water molecule) than H(2) and H(4). The latter are more distant and the other atoms of tet b make it almost impossible for them to interact with the coordinated hydroxide group. Since structure III is the structure of the reactant and IV is the structure of the product, two nitrogens must invert in the overall reaction and the only pathway from III to IV is via the inversion of N(1) and N(3). The inversion



VI

Figure 9. Configuration of [Cu(tet b)]$^{2+}$ after the inversion of N(1) in V and ring conformational changes to a tetrahedrally distorted square-planar structure. The axial C(7) methyl group is indicated with an asterisk. A plus sign at an asymmetric center indicates that the hydrogen atom of the center is above the plane of the macrocycle and a minus sign that it is below.

of N(2) and N(4) will give a different isomer in which the four NH's are on the same side of the N_4 plane as the CH's on chiral carbons. With the use of the configurational diagrams previously proposed[20] the result of inverting N(1) or N(3) and shifting from a folded to a slightly distorted planar form is shown in Figure 9. The dashed lines in VI indicate a tetrahedrally distorted square-planar structure.

It is possible to estimate the relative activation energies of the various possible configurational inversions. The gauche chelate ring is more stable than the eclipsed five-membered chelate ring and microscopic reversibility requires the same transition state for their interconversions. Therefore, the activation energy for the inversion of a nitrogen atom in a gauche ring is greater than for a nitrogen atom in an eclipsed ring. Similar arguments can be made for six-membered chair vs. skew-boat rings. The resulting relative reactivity for inversion of the ring nitrogen atoms is given in eq 11 where E

$$(E5, SB6) > (G5, SB6) > (E5, C6) > (G5, C6) \qquad (11)$$

is eclipsed, G is gauche, SB is skew-boat, C is chair, and 5 and 6 represent a five-membered chelate ring and a six-membered chelate ring, respectively. If, in addition, the steric interactions of the methyl groups in the macrocyclic ligands are taken into account, then the relative reactivities for the inversion of the ring N atoms are given in eq 12 in terms of the ring conformations and the number of axial methyl groups.

$$\begin{bmatrix}\text{E5}\\ \text{2 axial Me}\\ \text{on SB6}\end{bmatrix} > \begin{bmatrix}\text{G5}\\ \text{2 axial Me}\\ \text{on SB6}\end{bmatrix} > \begin{bmatrix}\text{E5}\\ \text{2 axial Me}\\ \text{on C6}\end{bmatrix} > \begin{bmatrix}\text{E5}\\ \text{1 axial Me}\\ \text{on SB6}\end{bmatrix} \simeq$$

$$\begin{bmatrix}\text{G5}\\ \text{2 axial Me}\\ \text{on C6}\end{bmatrix} > \begin{bmatrix}\text{G5}\\ \text{1 axial Me}\\ \text{on SB6}\end{bmatrix} > \begin{bmatrix}\text{E5}\\ \text{1 axial Me}\\ \text{on C6}\end{bmatrix} > \begin{bmatrix}\text{G5}\\ \text{1 axial Me}\\ \text{on C6}\end{bmatrix} \qquad (12)$$

Figure 10 shows the reaction pathway in terms of the required ring configurational changes for the copper–tet b complex, where (a) is [Cu(tet b)(blue)]$^{2+}$, (b) is the proposed unstable reaction intermediate VI, (c) is the structure (IV) found for [Cu(tet b)(red)]$^{2+}$, and (d) is the structure (VII) for a second red form which may be present in very small concentrations in solution. The main reaction pathway appears to be from (a) to (b) to (c). The forward rate constant derived from a steady-state treatment of species (b), neglecting (d), is $k_{ab}k_{bc}/(k_{ba} + k_{bc})$, but the relative reactivities for the inversion reactions indicate that $k_{bc} \gg k_{ba}$. This is because in eq 12 k_{bc} corresponds to the second condition from the left and k_{ba} corresponds to the next to last position on the right. If hydroxide ion catalysis of the inversion reactions has the same

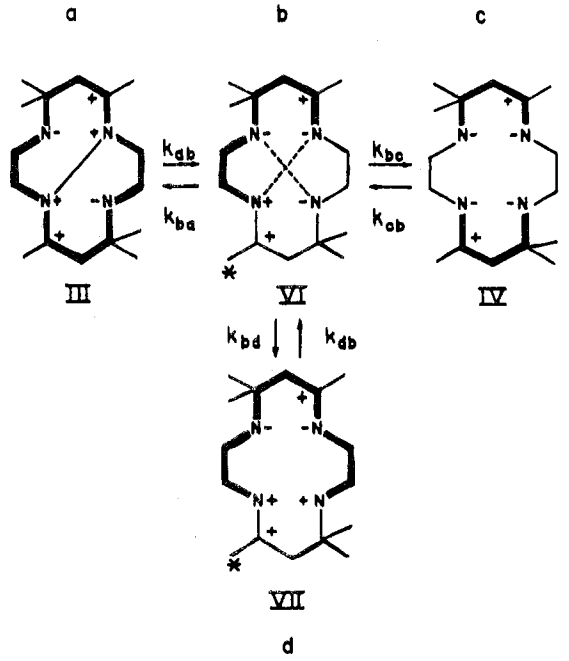


Figure 10. Proposed inversion and ring conformational changes in the reaction of $[Cu(tet\ b)]^{2+}$ where (a) is $[Cu(tet\ b)(blue)]^{2+}$, (b) is an unstable reaction intermediate, (c) is the main red product, and (d) is a second red product present in small concentrations. The axial C(7) methyl group is indicated with an asterisk. A plus sign at an asymmetric center indicates that the hydrogen atom of the center is above the plane of the macrocycle and a minus sign that it is below.

relative effect on k_{bc} and k_{ba}, then the rate-determining step of the overall reactions is k_{ab}.

Poon and Tobe[16] proposed an intramolecular proton transfer mechanism for *cis*-$[Co(cyclam)(OH)(H_2O)]^{2+}$ in the cis to trans isomerization of this Co(III) complex. The monohydroxide complex is a weak base ($pK_b = 9$) which makes it less suitable than $[Cu(tet\ b)(OH)(blue)]^+$ as an intramolecular proton acceptor, but the Co^{III}–NH group should be a stronger acid than the Cu^{II}–NH group. According to their preferred reaction scheme, the bis(hydroxide) complex, *cis*-$[Co(cyclam)(OH)_2]^+$, is less reactive in the isomerization reaction than the mono(hydroxide) complex despite the fact that it is a better base ($pK_b = 6$). An alternative reaction scheme with free hydroxide ion causing the inversion would require an unacceptable difference of 4 orders of magnitude in the reaction of free OH^- with *cis*-$[Co(cyclam)(H_2O)_2]^{2+}$ compared to *cis*-$[Co(cyclam)(OH)(H_2O)]^+$. The detailed mechanism suggested by Poon and Tobe avoids this problem but does not adequately explain the greatly reduced reactivity (by a factor of 10^2) of the bis(hydroxide) complex compared to the mono(hydroxide) complex. However, a concerted mechanism of the type we propose for the $[Cu(tet\ b)(OH)(blue)]^+$ reaction will account for this behavior. The octahedral cobalt(III) complexes must lose either an H_2O molecule or an OH^- ion in order to isomerize (note that a dissociation reaction is not a requirement for the Cu(II) reaction). If inversion occurs prior to the dissociation reaction, then there is no reason for the bis(hydroxide) species to be slow because the intramolecular proton transfer should convert one OH^- to H_2O which could then dissociate as easily as in the mono(hydroxide) complex. Any additional proton loss from Co^{III}–OH_2 prior to the rate step would be equivalent to the reaction of free OH^- rather than an intramolecular mechanism. A second path which they also consider has the nitrogen inversion taking place in a tetragonal-pyramidal five-coordinate intermediate, but this would require the loss of an OH^- group prior to the rate step in the case of the *cis*-$[Co(cyclam)(OH)_2]^+$. This would cause a $1/[OH^-]$ dependence which is contrary to their data.

On the other hand, a concerted mechanism of the type we suggest for the Cu(II) macrocyclic ligands would explain the behavior observed in the Co(III) reactions. One OH^- group in *cis*-$[Co(cyclam)(OH)_2]^+$ could assist the inversion via a hydrogen-bonded ring structure to an amine hydrogen while the other OH^- group dissociates from Co^{III} in order to permit the cis to trans reaction. Hydroxide ion is more difficult to dissociate from Co^{III} than is H_2O and hence *cis*-$[Co(cyclam)(OH)_2]^+$ is less reactive than *cis*-$[Co(cyclam)(OH)(H_2O)]^{2+}$. Poon and Tobe also found chloride ion inhibition in the isomerization studies.

The small $\Delta S^{\ddagger}$ value for the blue-to-red interconversion of $[Cu(tet\ b)(OH)]^+$ is in marked contrast to large positive $\Delta S^{\ddagger}$ values which have been found for the inversion of nitrogen centers in Co(III) complexes where free hydroxide ion causes the reaction. Thus, the $\Delta S^{\ddagger}$ values for the racemization at asymmetric nitrogen centers are +30 for $[Co(NH_3)_4(N\text{-}Me(en))]^{3+}$ and +21 for $[Co(NH_3)_4sar]^{2+}$.[10] The large positive $\Delta S^{\ddagger}$ are consistent with the desolvation steps which occur in the reaction of OH^- with these positive ions. No coordination position is available for the hydroxide ion. The racemization of $[Co(NH_3)_4(N\text{-}Me(en))]^{3+}$ needs to invert only one gauche five-membered ring, yet the $\Delta H^{\ddagger}$ for the reaction with free hydroxide ion is 23.8 kcal/mol[10] compared to a $\Delta H^{\ddagger}$ value of 23.3 kcal/mol for $[Cu(tet\ b)(OH)(blue)]^+$ which has to invert two adjacent stable chelate rings (one gauche five-membered and one chair six-membered with three methyl groups). The larger $\Delta H^{\ddagger}$ values may also reflect the desolvation which takes place in the reaction with free hydroxide ion.

In conclusion, the kinetics of the configurational conversion of a $[Cu(tet\ b)(blue)]^{2+}$ shows a strong preference for the reaction of coordinate hydroxide ion over free hydroxide ion. The probable reaction mechanism can be described in detail because structures of the main reactants and products have been determined. The relative rate of inversion of the macrocyclic nitrogen, predicted in accordance with the conformations of adjacent rings and the number of axial methyl groups, helps to show the probable mechanism. A concerted mechanism is proposed for the reaction of coordinated hydroxide ion with amine hydrogens.

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Registry No. $[Cu(tet\ b)(red)]^{2+}$, 53447-11-3; $[Cu(tet\ b)(OH_2)(blue)]^{2+}$, 70024-12-3; $[Cu(tet\ b)Cl(blue)]^+$, 66139-47-7; $[Cu(tet\ b)Br(blue)]^+$, 66139-48-8; $[Cu(tet\ b)I(blue)]^+$, 70024-13-4; $[Cu(tet\ b)OH(blue)]^+$, 70024-14-5; OH^-, 14280-30-9; Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5.

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Mechanism of Complex Formation: Kinetics and Equilibria of the Nickel(II)–Salicylate Ion System

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Rate and equilibrium measurements have been performed on the nickel(II)–salicylate ion system in the pH range between 6 and 7.2 at 25 °C and at an ionic strength 0.1 M. Under the experimental conditions a 1:1 chelate complex is formed with release of a proton. The equilibrium constant of the reaction is 1.4×10^{-6}. Temperature-jump experiments show that two parallel paths involving Ni^{2+} and $NiOH^+$ ions, respectively, are operative. The rate constant of the path involving Ni^{2+} ion (70 M^{-1} s^{-1}) lies ca. 3 orders of magnitude below the value predicted by the Eigen mechanism whereas the species $NiOH^+$ reacts with a rate constant of 6.3×10^4 M^{-1} s^{-1}. The results are discussed in terms of an attack by the two species of Ni(II) at the internally hydrogen-bonded carboxylic oxygen of salicylate ion.

Introduction

The kinetics of formation of nickel(II) complexes have been so widely investigated that it is conceivable that Ni(II) will take over the central role in inorganic reaction mechanisms which has been occupied by Co(III) in the past. These reactions are in general discussed in terms of the Eigen mechanism[1,2] according to which the rate-determining step is solvent loss from the inner solvation shell of the metal after an external ion pair between metal and ligand has been formed.

Values of the second-order rate constants different from those expected on the basis of the simple S_N1_{ip} model are sometime obtained when the ligand is a chelating agent.[3] These deviations from the normal behavior are often ascribed to rate-determining ring closure[3] and in some cases to the presence in the ligand of internal hydrogen bonds which make the reaction site blocked by a proton.[3-5] In a previous paper[6] on rates of complexation of nickel(II) with anthranilate, salicylate, and sulfosalicylate ions the abnormally low rates have been explained with the possibility of a steric-controlled mechanism.

In this study of the equilibria and kinetics of the nickel(II)–salicylate system we present different conclusions.

Experimental Section

All chemicals were analytical grade reagents. Nickel perchlorate and salicylic acid were crystallized twice from water. Conductivity water was used to prepare the solutions and as a reaction medium. The desired acidities were obtained by adding to the solutions small amounts of $HClO_4$ or NaOH, and pH was measured with a Metrohm E 388 pH meter. Buffers of NaH_2PO_4–Na_2HPO_4 or trisethanolamine were avoided because we found that they reacted with Ni(II).

The ionic strength was 0.1 M ($NaClO_4$) in all kinetic runs and 0.3 M in the equilibrium measurements. The temperature was 25 °C.

Equilibrium results were obtained at 340 and 330 nm with a Perkin-Elmer 200 spectrophotometer and kinetic results at 615 nm by using a temperature-jump apparatus (Messanlagen-Studiengesellschaft, Göttingen). Blank experiments with solutions containing only nickel ion and indicator showed no relaxation effects in the time range of the experiments. The values of the relaxation times obtained from replicated runs exhibited a spread of ±10% at most. The concentrations of the reactants were changed from 10^{-3} to 10^{-2} M, and the indicator, bromothymol blue, was present in concentrations (1.5 or 3) $\times 10^{-5}$ M.

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Results

Equilibrium Constant. Evidence for formation of a complex between nickel(II) and salicylate ion has been obtained both by potentiometry and by spectrophotometry.

Titration curves have been performed with salicylic acid alone and in the presence of an equivalent concentration of nickel perchlorate. The comparison showed that complex formation begins at pH 6, and the degree of complexation increases with decreasing the hydrogen ion concentration. Above pH 7.7 subsequent additions of dilute NaOH did not lead to further increase of pH but to formation of a precipitate which was immediately revealed by a nonconstant instrument signal and became clearly visible after few minutes. Great care was taken to avoid local formation of precipitate since this is difficult to dissolve.

In the wavelength range between 310 and 350 nm the absorbance, A, of a mixture of salicylic acid and nickel perchlorate is higher than the sum of the contributions of the two components. If we ascribe this to formation of 1:1 complexes, it is possible to define an equilibrium ratio[5] (eq 1),

$$K = [NiL_T][H^+]/[Ni_f][L_f] \quad (1)$$

where $[L_f]$ and $[Ni_f]$ are the sum of concentrations of all uncomplexed forms of ligand and nickel(II), respectively, and $[NiL_T]$ is the sum of the concentrations of all possible 1:1 complexes. The salicylate ion concentration, C_L, was 8×10^{-4} M, and the nickel concentration, C_{Ni}, was changed between 0.050 and 0.091 M with pH varying between 6 and 7.2. Under these conditions it is assumed that $[H_2L] \ll [HL^-] \simeq [L_f]$ and that $[NiOH^+] \ll [Ni^{2+}] \simeq [Ni_f] \simeq C_{Ni}$, and the relationship between the absorbance, A, and the concentrations can be written in the form of eq 2, where $\Delta\epsilon = \epsilon_{NiL} - \epsilon_L - \epsilon_{Ni}$.

$$\frac{C_L}{A - \epsilon_L C_L - \epsilon_{Ni} C_{Ni}} = \frac{1}{\Delta\epsilon} + \frac{1}{\Delta\epsilon}\frac{1}{K}\frac{[H^+]}{C_{Ni}} \quad (2)$$

The three ϵ values are mixed coefficients formed by the contributions of differently protonated forms of the components of the system and might therefore depend on pH. ϵ_L and ϵ_{Ni} have been independently determined and at the investigated acidities. Plots of the left-hand-side member of eq 2 against $[H^+]$ at different, constant, C_{Ni} yield straight lines with a common intercept and the same K.

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