Contribution from the Departments of Chemistry, Tunghai University, Taichung, Taiwan 400, Republic of China, and National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China

Dissociation Kinetics of the (*rac*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) (Blue) Cation in Strongly Acidic, Aqueous Media

BIH-FONG LIANG and CHUNG-SUN CHUNG*

Received June 18, 1982

In order to investigate the effects of ligand cyclization and structure variation upon complex dissociation rate constants, the kinetics of the reaction of the blue copper(II) complex of *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane has been examined spectrophotometrically in 1–5 M HNO_3. The reaction scheme

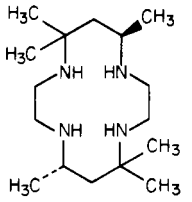
$$[Cu(tet\ b)\ (blue)]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Cu(Htet\ b)]^{3+} \xrightarrow{k_2} Cu^{2+} + (H_4tet\ b)^{4+}$$

is given, with $k_1 = 5.2\ (\pm 0.3) \times 10^{-7}\ s^{-1} + 1.42\ (\pm 0.04) \times 10^{-6}[H^+]\ s^{-1}\ M^{-1}$, $k_{-1} = 2.8\ (\pm 0.1) \times 10^{-6}\ s^{-1} + 1.1\ (\pm 0.1) \times 10^{-6}/[H^+]\ s^{-1}$ M, and $k_2 = 1.15\ (\pm 0.03) \times 10^{-5}\ s^{-1} + 1.7\ (\pm 0.1) \times 10^{-6}[H^+]\ s^{-1}\ M^{-1}$ at 25.0 °C and $\mu = 5.0$ M ($NaNO_3$ + HNO_3). Contrary to the kinetic behavior of (*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) (blue) cation, both protonation pathway and solvent-separation pathway contribute to the observed rates of the cleavages of the first and the second copper–nitrogen bonds in $[Cu(tet\ b)\ (blue)]^{2+}$. The possible mechanism for the reaction, the factors influencing the rates, and the factors affecting the relative importance of the solvent-separation pathway and the protonation pathway are considered.

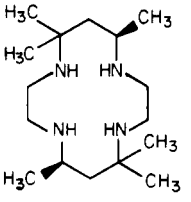
Introduction

Acid-assisted dissociation kinetics of open-chain polyamine complexes have been extensively studied,[1-9] and many of these works have been reviewed.[10] As pointed out by Margerum and co-workers,[10,11] two types of mechanistic pathways, the direct protonation and the solvent-separation pathways, make contributions to the rates of these reactions. Acid assists the dissociation of the open-chain polyamine chelate complex by direct protonation or by protonating the partially coordinated intermediate and stabilizing it relative to the fully coordinated form.[11] Thus, the ring-opening step becomes rate determining at high acid concentrations.[10,11]

The corresponding kinetics of acid-catalyzed dissociation of macrocyclic polyamine complexes have received little attention.[12-14] An earlier report from these laboratories described the kinetics of the reactions of dissociation and isomerization kinetics of the blue copper(II) complex of *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, tet a (I), in strongly acidic, aqueous media.[15] In marked contrast to the behaviors of the complexes of the open-chain polyamines, the dissociation process of this macrocyclic ligand complex was found not to occur by a single stage but to take place in consecutive and reversible steps, and the cleavage of the second metal–nitrogen bond is proposed as the rate-determining step in strongly acidic media. Furthermore the blue-to-red interconversion of $[Cu(tet\ a)\ (blue)]^{2+}$ occurred concurrently with its dissociation at high acid concentration.



I
tet a
or *meso*-1,7-CTH



II
tet b
or *rac*-1,7-CTH

In the current investigation, we have attempted to gain more detailed understanding of the effects of structure variation on the kinetics of acid-catalyzed dissociation of macrocyclic ligand complexes. To accomplish this, we have extended our studies to the reaction of the blue copper(II) complex of *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, tet b (II), in strongly acidic, aqueous media. This investigation has taken advantage of the extraordinary sluggishness of tetraamine macrocyclic ligand complex of copper(II), which is well suited for conventional quantitative kinetic study. In addition, the crystal structure determinations of both $[Cu(tet\ b)\ (blue)]^{2+}$ and $[Cu(tet\ a)\ (blue)]^{2+}$ have been reported,[16,17] thus providing the opportunity to elaborate the ways in which the different structures of the coordinated macrocyclic ligands convey properties on the dissociation kinetics of their metal complexes. In marked contrast to the behavior of $[Cu(tet\ a)\ (blue)]^{2+}$ under the same conditions, there is no isomerization of $[Cu(tet\ b)\ (blue)]^{2+}$ occurring concurrently with its dissociation at high acid concentrations. Furthermore, the dissociation rates, rate-determining step, and the relative contributions of the protonation and the solvation pathways for the reactions of these two blue copper(II) complexes are significantly different.

* To whom correspondence should be addressed at the National Tsing Hua University.

(1) Melson, G. A.; Wilkins, R. G. *J. Chem. Soc.* **1962**, 2662, 4208.
(2) Ahmed, A. K. S.; Wilkins, R. G. *J. Chem. Soc.* **1959**, 3700; **1960**, 2895, 2901.
(3) Wilkins, R. G. *J. Chem. Soc.* **1962**, 4475; *Acc. Chem. Res.* **1970**, *3*, 408.
(4) Margerum, D. W.; Rorabacher, D. B.; Clarke, J. F. G., Jr. *Inorg. Chem.* **1963**, *2*, 667.
(5) Weatherburn, D. C.; Billo, E. J.; Jones, J. P.; Margerum, D. W. *Inorg. Chem.* **1970**, *9*, 1557.
(6) Kolski, G. B.; Margerum, D. W. *Inorg. Chem.* **1969**, *8*, 1129.
(7) Childers, R. F.; Wentworth, R. A. D. *Inorg. Chem.* **1969**, *8*, 2218.
(8) Rorabacher, D. B.; Melendez-Cepeda, C. A. *J. Am. Chem. Soc.* **1971**, *93*, 6071.
(9) Turan, T. S.; Rorabacher, D. B. *Inorg. Chem.* **1972**, *11*, 288.
(10) Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. *ACS Monogr.* **1978**, *No. 174*, 1–220.
(11) Read, R. A.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 3143.
(12) Kaden, T. A. *Helv. Chim. Acta* **1970**, *53*, 617; **1971**, *54*, 2307.
(13) Cabbiness, D. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1970**, *92*, 2151.
(14) Hertli, L.; Kaden, T. A. *Helv. Chim. Acta* **1974**, *57*, 1328.
(15) Liang, B.-F.; Chung, C.-S. *Inorg. Chem.* **1981**, *20*, 2152.
(16) Bauer, R. A.; Robinson, W. R.; Margerum, D. W. *J. Chem. Soc., Chem. Commun.* **1973**, 289.
(17) Clay, R. M.; Murray-Rust, P.; Murray-Rust, J. *J. Chem. Soc., Dalton Trans.* **1979**, 1135.

0020-1669/83/1322-1017$01.50/0 © 1983 American Chemical Society

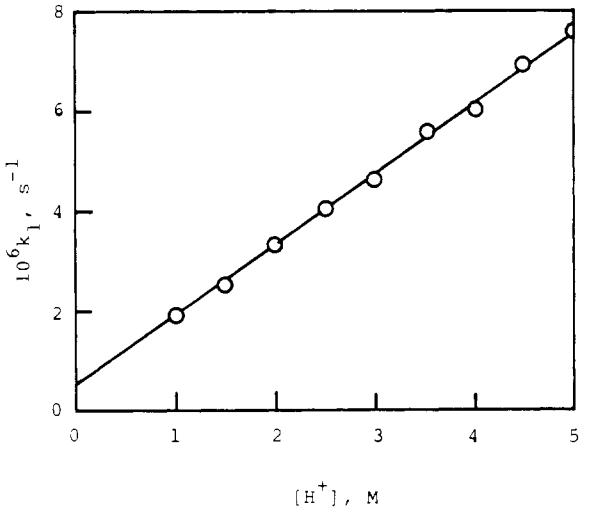


Figure 1. Plot of k_1 against $[H^+]$.

Experimental Section

Reagents. The macrocyclic ligand tet b was prepared by using the procedure described by Hay, Lawrance, and Curtis.[18] $[[Cu(tet\ b)]_2Cl](ClO_4)_3$ was prepared by using the procedure described by Bauer.[16] Anal. Calcd for $[(CuC_{16}H_{36}N_4)_2Cl](ClO_4)_3$: C, 37.32; H, 7.07; Cl, 13.77. Found: C, 37.22; H, 7.12; Cl, 13.63. All other chemicals used in this work were Merck GR grade.

Kinetic Measurements. Kinetic runs were initiated by mixing a freshly prepared $[Cu(tet\ b)\ (blue)](ClO_4)_2$ solution with a solution that contained the desired quantities of HNO_3 and $NaNO_3$. All samples were then well mixed and transferred to a thermostated quartz cell. These reactions were followed spectrophotometrically by repetitive scanning through the range 400–1000 nm, with particular focus on 520 nm (a maximum for $[Cu(tet\ b)\ (red)]^{2+}$) and 650 and 830 nm (maxima for $[Cu(tet\ b)\ (blue)]^{2+}$). A Cary 17 recording spectrophotometer was used and the temperature maintained at 25.0 ± 0.1 °C for all the solutions studied. The rate constants were obtained by using the CDC Cyber-172 computer.

Results

The electronic spectrum of $[Cu(tet\ b)\ (blue)]^{2+}$ has been reported.[19] The dissociation reaction of $[Cu(tet\ b)\ (blue)]^{2+}$ was studied spectrophotometrically in 1–5 M HNO_3. The stoichiometry is given in eq 1. This process was found not

$$[Cu(tet\ b)\ (blue)]^{2+} + 4H^+ \rightarrow Cu^{2+} + (H_4tet\ b)^{4+} \quad (1)$$

to occur by a single stage but to take place in consecutive steps. In marked contrast to the behavior of $[Cu(tet\ a)\ (blue)]^{2+}$, no red isomer was found in the reaction of $[Cu(tet\ b)\ (blue)]^{2+}$, and the simplest kinetic scheme that can accommodate these observations involves consecutive first-order processes with reversible step, as given in eq 2. Here A, B, and C are

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_2} C \quad (2)$$

respectively $[Cu(tet\ b)\ (blue)]^{2+}$, an intermediate, and the product, $Cu^{2+} + (H_4tet\ b)^{4+}$; k_1, k_{-1}, and k_2 are first-order or pseudo-first-order rate constants.

The approximate values of the rate constants were estimated from kinetic measurements. The approximate molar absorptivity of B, ϵ_B, was guessed from scanning spectra. Rodiguin and Rodiguina integration[20] would give the values of the concentrations of A, B, and C as a function of time. A comparison of the calculated values of absorbances with the observed values, followed by a variation of the rate constants and ϵ_B so as to obtain a minimum deviation between observed and calculated values, would lead to the best fitted rate constants. Resulting values of these rate constants are given in Table I.

The results given in this table indicate that all of these stepwise rate constants are $[H^+]$ or $[H^+]^{-1}$ dependent. Plots

Table I. Consecutive First-Order Rate Constants for the Dissociation of $[Cu(tet\ b)\ (blue)]^{2+}$ at 25.0 °C and μ = 5.0 M (HNO_3 + $NaNO_3$)

$[HNO_3]$, M	10^6k_1, s^{-1}	10^6k_{-1}, s^{-1}	10^6k_2, s^{-1}
1.0	1.9	3.8	13.3
1.5	2.5	3.5	14.1
2.0	3.3	3.3	15.2
2.5	4.0	3.2	16.1
3.0	4.6	3.1	16.6
3.5	5.6	3.1	17.8
4.0	6.0	3.0	18.3
4.5	6.9	3.0	19.2
5.0	7.6	2.9	20.2

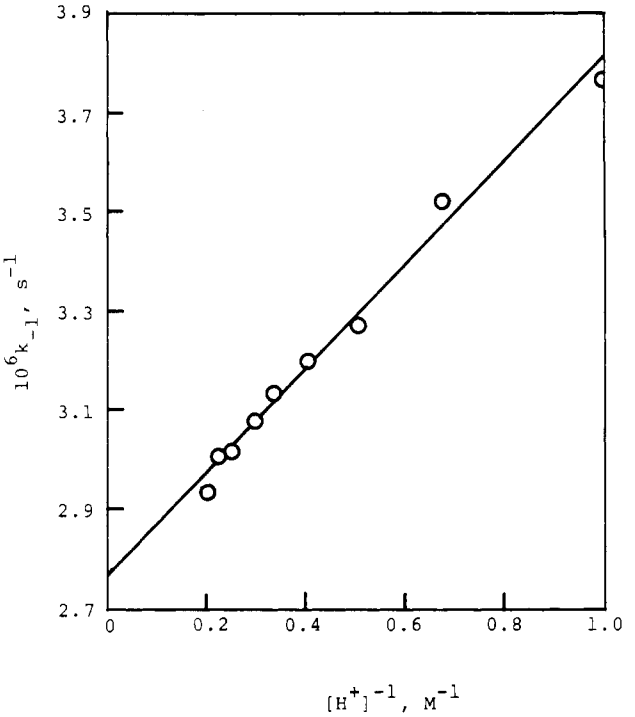


Figure 2. Plot of k_{-1} against $[H^+]^{-1}$.

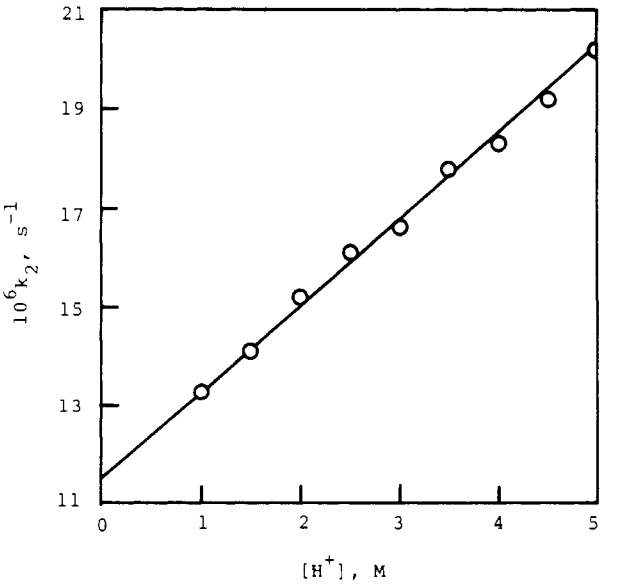


Figure 3. Plot of k_2 against $[H^+]$.

(18) Hay, R. W.; Lawrance, G. A.; Curtis, N. F. *J. Chem. Soc., Perkin Trans. 1* **1975**, 591.
(19) Liang, B.-F.; Chung, C.-S. *J. Chin. Chem. Soc. (Taipei)* **1979**, *26*, 93.
(20) Rodiguin, N. M.; Rodiguina, E. N. "Consecutive Chemical Reactions"; Van Nostrand: Princeton, NJ, 1964.

Table II. Pseudo-First-Order Rate Constants for the Acid Dissociation Reactions of Copper(II) Macrocyclic Tetraamine Complexes as a Function of Acid Concentration at 25.0 °C and μ = 5.0 M (HNO_3 + $NaNO_3$)

pseudo-first-order rate const	[Cu(tet b) (blue)]$^{2+}$	[Cu(tet a) (blue)]$^{2+}$ [a]
k_1	5.2 (±0.3) × 10^{-7} s^{-1} + 1.42 (±0.04) × 10^{-6} [H^+] s^{-1} M^{-1}	2.6 (±0.3) × 10^{-4} [H^+] s^{-1} M^{-1}
k_{-1}	2.8 (±0.1) × 10^{-6} s^{-1} + 1.1 (±0.1) × 10^{-6}/ [H^+] s^{-1} M	1.4 (±0.1) × 10^{-3} s^{-1}
k_2 (k_3[a])	11.5 (±0.3) × 10^{-6} s^{-1} + 1.7 (±0.1) × 10^{-6} [H^+] s^{-1} M^{-1}	4.6 (±0.2) × 10^{-4} s^{-1}

[a] See ref 15.

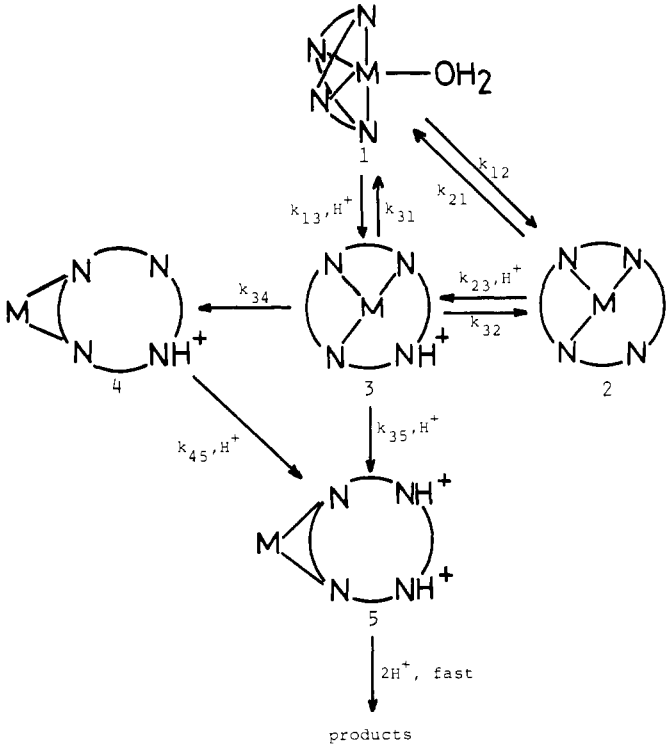


Figure 4. Proposed stepwise mechanism for the dissociation of [Cu(tet b) (blue)]$^{2+}$ in strongly acidic media.

of these stepwise rate constants vs. [H^+] or [H^+]$^{-1}$ give straight lines as shown in Figures 1–3. The values for these stepwise rate constants as a function of acid concentration at 25.0 °C and μ = 5.0 M (HNO_3 + $NaNO_3$) are listed in Table II, along with the reported rate constants of [Cu(tet a) (blue)]$^{2+}$ for the purpose of comparison.[15]

Discussion

The experimental results listed in Table II can readily be explained by the generally accepted stepwise mechanism pictured in Figure 4,[10] where species **1** and **3** are [Cu(tet b) (blue)]$^{2+}$ and intermediate **B**, respectively. As shown in Table II, both the water dissociation pathways and the protonation pathways make contributions to the rate. In the protonation pathway, proton attack occurs prior to or during copper–nitrogen bond rupture, as the **1** → **3** and the **3** → **5** steps in Figure 4. In the water dissociation pathway, the proton scavenges the released amine after spontaneous or water-induced copper–nitrogen bond rupture, as the **1** → **2** → **3** and **3** → **4** → **5** steps in Figure 4. In strongly acidic media, k_{23}[H^+] >> k_{21}, so that $k_1 = k_{13}$[H^+] + k_{12}, $k_{-1} = k_{21}k_{32}/k_{23}$[$H^+$] + k_{31}, and $k_2 = k_{35}$[H^+] + k_{34}. The values for the resolved rate constants are listed in Table III.

Table III. Resolved Rate Constants for the Dissociation of [Cu(tet b) (blue)]$^{2+}$ at 25.0 °C and μ = 5.0 M (HNO_3 + $NaNO_3$)

$k_{12} = 5.2\ (\pm 0.3) \times 10^{-7}\ s^{-1}$
$k_{13} = 1.42\ (\pm 0.04) \times 10^{-6}\ s^{-1}\ M^{-1}$
$k_{31} = 2.8\ (\pm 0.1) \times 10^{-6}\ s^{-1}$
$k_{21}k_{32}/k_{23} = 1.1\ (\pm 0.1) \times 10^{-6}\ s^{-1}\ M^{-1}$
$k_{34} = 11.5\ (\pm 0.3) \times 10^{-6}\ s^{-1}$
$k_{35} = 1.7\ (\pm 0.1) \times 10^{-6}\ s^{-1}\ M^{-1}$

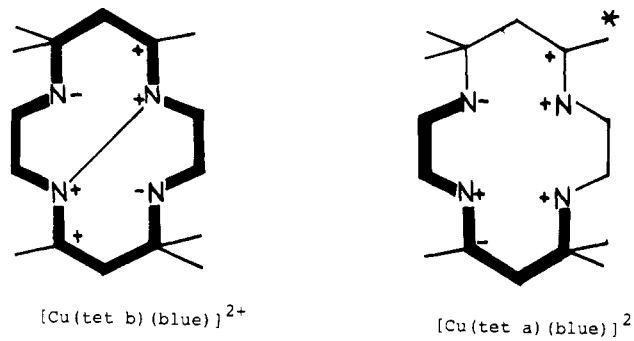


Figure 5. Configurations of the asymmetric centers and the conformations of the chelate ring of [Cu(tet b) (blue)]$^{2+}$ and [Cu(tet a) (blue)]$^{2+}$. A plus sign at an asymmetric center indicates that the hydrogen atom of the center is above the plane of the macrocycle, and a minus sign, that is below. Gauche conformations of the five-membered chelate rings and chair conformations of the six-membered chelate rings are indicated by heavier lines. The axial C(7) methyl group is indicated with an asterisk.

The crystal structure determinations of these two blue copper(II) complexes have been reported.[16,17] The blue tet b complex has been isolated as [[Cu(tet b)]$_2$Cl](ClO_4)$_3$, which contains five-coordinate trigonal-bipyramidal copper. 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 as shown in Figure 5.[16] Chloride ion, which occupies one of the positions in the trigonal plane in the solid, 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.[21,22] Crystallographic study of [Cu(tet a) (blue)]-(ClO_4)$_2$ indicates that the gross geometry is an approximately tetragonally distorted, octahedrally coordinated, copper with the macrocycles equatorial and perchlorates axial.[17] The ligand is in a distorted planar configuration with two stable chelate rings and two unstable chelate rings as shown in Figure 5. Conductivity and spectroscopic data suggest that both ClO_4^- ions, which are coordinated in the solid, are replaced by solvent.[17]

Important factors influencing the rates of dissociation of metal complexes have been studied by Wilkins and co-workers.[1-3] One of these important factors is the relative stabilities of the chelate rings. The gauche five-membered chelate ring is more stable than the eclipsed five-membered chelate ring. Therefore, the activation energy for the cleavage of the copper–nitrogen bond in a gauche ring is greater than that for the cleavage of the copper–nitrogen bond in an eclipsed ring. Similar arguments can be made for six-membered chair vs. skew-boat rings. The resulting relative reactivity for the cleavage of the ring Cu–N bond is given in eq 3, where E is

$$(E5, SB6) > (G5, SB6) > (E5, C6) > (G5, C6) \quad (3)$$

eclisped, 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

(21) Margerum, D. W.; Bauer, R. A., unpublished results.
(22) Chung, C.-S.; Huang, S.-T. *J. Chin. Chem. Soc. (Taipei)* **1976**, *23*, 139.

Table IV. Rate Constants of Solvation and Protonation Pathways for the Dissociation Reactions of Copper(II) Macrocyclic Tetraamine Complexes and Ratio Representing the Relative Importance of the Two Pathways

ML^{2+}	k_{1d}, s^{-1}	k_{1H}, s^{-1} M^{-1}	k_{1H}/k_{1d}, M^{-1}	k_{2d}, s^{-1} M^{-1}	k_{2H}, s^{-1} M^{-1}	k_{2H}/k_{2d}, M^{-1}
[Cu(tet b) (blue)]$^{2+}$	5.2×10^{-7}	1.42×10^{-6}	2.7	11.5×10^{-6}	1.7×10^{-6}	0.15
[Cu(tet a) (blue)]$^{2+}$ [a]		2.6×10^{-4}	very large	4.6×10^{-4}		very small

[a] Reference 15.

of the methyl groups in the macrocyclic ligands are taken into account, then the relative reactivities for the cleavage of the ring Cu–N bond are given in eq 4 in terms of the ring con-

$$\begin{bmatrix}\text{E5}\\ \text{2 axial Me}\\ \text{on SB6}\end{bmatrix} > \begin{bmatrix}\text{G5}\\ \text{2 axial Me}\\ \text{on SB6}\end{bmatrix} > \begin{bmatrix}\text{E5}\\ \text{2 axial Me}\\ \text{on C6}\end{bmatrix} > \begin{bmatrix}\text{E5}\\ \text{1 axial Me}\\ \text{on SB6}\end{bmatrix} \simeq \begin{bmatrix}\text{G5}\\ \text{2 axial Me}\\ \text{on C6}\end{bmatrix} > \begin{bmatrix}\text{G5}\\ \text{1 axial Me}\\ \text{on SB6}\end{bmatrix} > \begin{bmatrix}\text{E5}\\ \text{1 axial Me}\\ \text{on C6}\end{bmatrix} > \begin{bmatrix}\text{G5}\\ \text{1 axial Me}\\ \text{on C6}\end{bmatrix} \quad (4)$$

formations and the number of axial methyl groups.

The cleavage of the first M–N bond in [Cu(tet b) (blue)]$^{2+}$ starts with a gauche five-membered ring and chair six-membered ring containing one axial methyl group. This is a relatively low energy state, and the rate of the cleavage of this M–N bond is much slower than in the case for the cleavage of the first M–N bond in [Cu(tet a) (blue)]$^{2+}$, which starts with an eclipsed five-membered ring and skew-boat six-membered ring containing two axial methyl groups.[17]

Another significant difference between these two blue copper(II) complexes is that the five-coordinated [Cu(tet b) (blue)]$^{2+}$ is open to solvent attack, while the tetragonally distorted, octahedrally coordinated [Cu(tet a) (blue)]$^{2+}$ is not. The metal–solvent bond formation provides energetic assistance to the metal–nitrogen bond rupture, thereby enhancing the dissociation rate. In general, proton attack at the amine nitrogen and solvent attack at the metal ion can accelerate the dissociation of metal complexes. If the complex is open to solvent attack, the presence of acid has little effect and the ratio k_{nH}/k_{nd} is relatively small. However, if the solvent attack at the metal ion is hindered, acid can enhance the rate of dissociation and the ratio k_{nH}/k_{nd} is large.

As pointed out by Read and Margerum,[11] the relative rate of dissociation by the protonation and the solvation pathways, represented by the ratio k_{nH}/k_{nd}, is of interest and is significant. The ratios for the open-chain polyamine complexes of nickel(II) have recently been discussed.[11] The values of the ratios for these macrocyclic tetraamine ligand complexes of copper(II) are tabulated in Table IV. For the cleavage of the first metal–nitrogen bond, the restrictions imposed by the ligand cyclization served to hold the donor in the first coordination sphere, making the macrocyclic complex more susceptible to acid attack than the corresponding open-chain complex, which has smaller restriction of the chelate ring to prevent the donor from moving smoothly out of the first coordination sphere. The extremely large ratio k_{1H}/k_{1d} of the reaction of [Cu(tet a) (blue)]$^{2+}$ lends support to this view. As mentioned previously, [Cu(tet b) (blue)]$^{2+}$ is more susceptible to solvent attack, and this associative mode of activation reflected in the small value of the ratio for [Cu(tet b) (blue)]$^{2+}$ is shown in Table IV.

The other factors that affect the value of the ratio k_{nH}/k_{nd} are the Coulombic factor and the tendency toward intramolecular hydrogen bonding. The magnification in the electrostatic effect exhibited between the protonated intermediate, [Cu(HL)]$^{3+}$, and H^+ relative to the reactant, [CuL]$^{2+}$, and H^+, as well as the large tendency for an intramolecular hydrogen bond to form within the ring,[23,24] leads to a small ratio

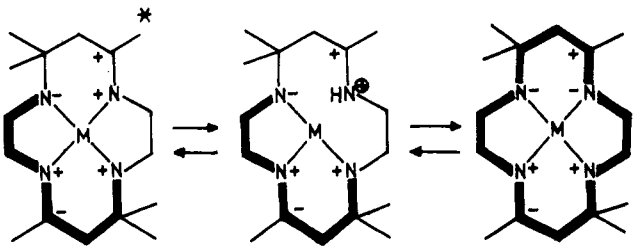


Figure 6. Configurational conversions of [Cu(tet a) (blue)]$^{2+}$ in strongly acidic media. A plus sign at an asymmetric center indicates that the hydrogen atom of the center is above the plane of the macrocycle, and a minus sign, that is below. Gauche conformations of the five-membered chelate rings and chair conformations of the six-membered chelate rings are indicated by heavier lines. The axial C(7) methyl group is indicated with an asterisk.

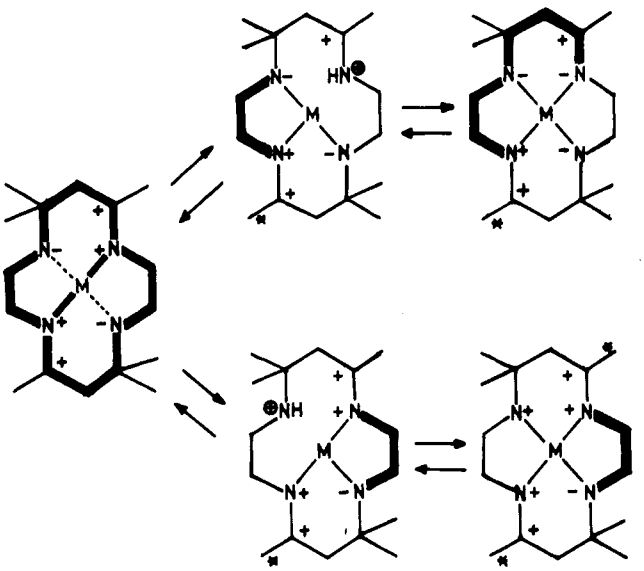


Figure 7. Cleavage, nitrogen inversion, and recombination of each of the copper–nitrogen bonds in [Cu(tet b) (blue)]$^{2+}$ in strongly acidic media. A plus sign at an asymmetric center indicates that the hydrogen atom of the center is above the plane of the macrocycle, and a minus sign, that is below. Gauche conformations of the five-membered chelate rings and chair conformations of the six-membered chelate rings are indicated by heavier lines. The axial C(7) methyl group is indicated with an asterisk.

k_{2H}/k_{2d} for the cleavage of the second copper–nitrogen bond of the macrocyclic complex as shown in Table IV.

Another interesting difference between the reactions of these two blue copper(II) macrocyclic tetraamine complexes is that the blue-to-red interconversion of [Cu(tet a)]$^{2+}$ occurs concurrently with its dissociation in strongly acidic media, while there is no such isomerization observed in the reaction of [Cu(tet b) (blue)]$^{2+}$ under the same conditions. The X-ray structure determinations indicate the blue species of [Cu(tet a)]$^{2+}$ differs from the stable red species only in the configuration of a single chiral nitrogen center.[17] In strongly acidic media, the cleavage, nitrogen inversion, and recombination of the copper–nitrogen bond in [Cu(tet a) (blue)]$^{2+}$ lead to the formation of the stable isomer, [Cu(tet a) (red)]$^{2+}$, as shown

(23) Luo, C.-L.; Chin, C.-H.; Chung, C.-S. *J. Chin. Chem. Soc. (Taipei)* **1979**, *26*, 61.

(24) Whimp, P. O.; Bailey, M. F.; Curtis, N. F. *J. Chem. Soc. A* **1970**, 1956.

in Figure 6. On the other hand, the cleavage, nitrogen inversion, and recombination of each of the copper–nitrogen bonds in [Cu(tet b) (blue)]$^{2+}$ lead to the formation of extremely unstable isomers as shown in Figure 7. The existence of each of these extremely unstable species is highly unlikely. Presumably this is the reason that there is no blue-to-red interconversion occurring concurrently with its dissociation in strongly acidic media. In addition to [Cu(tet b) (blue)]$^{2+}$, tet b forms two relatively stable red complexes with copper(II). Each of these two complexes differs from [Cu(tet b) (blue)]$^{2+}$ in the configurations of two chiral nitrogen centers.[25,26] The lack of the blue-to-red interconversion of [Cu(tet b)]$^{2+}$ in strongly acidic media agrees with the postulate that the cleavage of the third copper–nitrogen bond is much faster than the recombination of the second copper–nitrogen bond as shown in Figure 4.

Acknowledgment. This work was supported by a grant from the Chemistry Research Center, National Science Council of the Republic of China, to which the authors wish to express their thanks.

Registry No. II, 74112-91-7.

(25) Liang, B.-F.; Margerum, D. W.; Chung, C.-S. *Inorg. Chem.* **1979**, *18*, 2001.

(26) Liang, B.-F. Ph.D. Dissertation, National Tsing Hua University, 1980.

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Crystal and Molecular Structure of the Copper(III)–Tripeptide Complex of Tri-α-aminoisobutyric Acid

LEONARD L. DIADDARIO, WILLIAM R. ROBINSON, and DALE W. MARGERUM*

Received July 17, 1982

The crystal structure of the thermally stable copper(III)–deprotonated-peptide complex of tri-α-aminoisobutyric acid, $Cu^{III}(H_{-2}Aib_3)\cdot 2H_2O\cdot 1.5NaClO_4$, has been determined. The crystal was found to be monoclinic with lattice parameters of a = 20.638 (7) Å, b = 9.250 (6) Å, c = 11.362 (5) Å, β = 92.80 (3)°, and Z = 4. The structure was solved and refined in the centrosymmetric space group $P2/c$ with final residual values of R = 0.050 and R_w = 0.055. The Cu^{III}–N(amino), the two Cu^{III}–N(peptide), and the Cu^{III}–O(carboxyl) bond lengths are 1.898 (5), 1.801 (4), 1.804 (5), and 1.826 (3) Å, respectively. The copper(III)–ligand bond lengths are 0.12–0.17 Å shorter than the equivalent copper(II) bonds and 0.02–0.04 Å shorter than the corresponding nickel(II) bonds. The copper(III) is four-coordinate with the four donor atoms coplanar within ±0.06 Å and in a nearly square-planar geometry. The bond angles for the chelate rings average 87.3° for the copper(III)– compared to 85.1° for nickel(II)– and 83° for copper(II)–peptide complexes. There appears to be no axial coordination for $Cu^{III}(H_{-2}Aib_3)$ as the closest contact distance is 2.91 Å for a perchlorate oxygen.

Introduction

Peptide complexes of copper(III) have been shown to be relatively stable in aqueous solution.[1-5] Extensive knowledge of the copper(II)– and nickel(II)–peptide structures, which are largely the result of the work of Freeman and co-workers,[6] and of the solution chemistry of the copper(III)–peptide complexes has inferred many of the structural features of these copper(III) complexes. However, the present work is the first determination of a crystal structure for a copper(III)–peptide complex.

Reactions of the copper(III)–peptide complexes[1-4] with acids and nucleophiles are slow compared to the fast substitution reactions observed for the copper(II)–peptide complexes.[7-11] Sluggish substitution reactions are characteristic of known d^8 square-planar complexes of nickel(II), palladium(II), and platinum(II).

The copper(III/II) reduction potentials for a variety of peptide complexes have been measured and have been found to span a potential range of 0.37–1.2 V (vs. SHE).[5,12] The reduction potentials are affected by the number and type of donors bound to the copper and by the substituents on the α-carbons. The deprotonated-peptide nitrogen is a stronger σ donor than either an amine nitrogen or a carboxylate oxygen. As the number of deprotonated-peptide or deprotonated-amide nitrogen donor groups is increased, the trivalent oxidation state of copper is stabilized.

Alkyl substituents on the α-carbons increase the electron-donating ability of the coordinated nitrogens and further stabilize copper(III). The reduction potentials[5] for the peptide complexes containing leucyl, valyl, and isoleucyl residues are lower than those of alanyl-containing peptides even though the electron-donating abilities of all these α-substituents are approximately the same.

Entropy changes for the reduction reactions of several copper(III/II)–peptide complexes have been determined from cyclic voltammetric measurements of the $E_{1/2}$ as a function of temperature in a nonisothermal cell.[13] A large negative

(1) Margerum, D. W.; Chellappa, K. L.; Bossu, F. P.; Burce, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 6894.
(2) Burce, G. L.; Paniago, E. B.; Margerum, D. W. *J. Chem. Soc., Chem. Commun.* **1975**, 261.
(3) Kirksey, S. T., Jr.; Neubecker, T. A.; Margerum, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 1631.
(4) Rybka, J. S.; Kurtz, J. L.; Neubecker, T. A.; Margerum, D. W. *Inorg. Chem.* **1980**, *19*, 2791.
(5) Bossu, F. P.; Chellappa, K. L.; Margerum, D. W. *J. Am. Chem. Soc.* **1977**, *99*, 2195.
(6) Freeman, H. C. *Adv. Protein Chem.* **1967**, *22*, 257.
(7) Cooper, J. C.; Wong, L. F.; Venezky, D. L.; Margerum, D. W. *J. Am. Chem. Soc.* **1974**, *96*, 7560.
(8) Wong, L. F.; Cooper, J. C.; Margerum, D. W. *J. Am. Chem. Soc.* **1976**, *98*, 7268.
(9) Raycheba, J. M. T.; Dukes, G. R.; Margerum, D. W. *Inorg. Chem.* **1978**, *17*, 2449.
(10) Rybka, J. S.; Margerum, D. W. *Inorg. Chem.* **1980**, *19*, 2784.
(11) Youngblood, M. P.; Margerum, D. W. *Inorg. Chem.* **1980**, *19*, 3072.
(12) Hamburg, A. W.; Margerum, D. W., to be submitted for publication.

0020-1669/83/1322-1021$01.50/0 © 1983 American Chemical Society