Contribution from the Department of Chemistry,
National Tsing Hua University, Hsinchu, Taiwan 30043, Republic of China

Steric and Macrocyclic Effects in the Dissociation Kinetics of Cyclic and Open-Chain Tetraamine Complexes of Copper(II) in Strongly Acidic, Aqueous Media

Lien-Huei Chen and Chung-Sun Chung*

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In order to study the steric and macrocyclic effects upon complex dissociation rate constants, the kinetics of the dissociation reactions of (1,4,8,11-tetraazacyclotetradecane)copper(II), Cu(cyclam)$^{2+}$, and (1,5,8,12-tetraazadodecane)copper(II), Cu(3,2,3-tet)$^{2+}$, have been investigated at 25.0 °C in 0.1–5.0 M HNO_3. The reaction schemes

$$Cu(cyclam)^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cu(Hcyclam)^{3+} \xrightarrow{k_2} Cu^{2+} + (H_4cyclam)^{4+}$$

$$Cu(3,2,3\text{-tet})^{2+} \xrightarrow{k_1'} Cu^{2+} + (H_4 3,2,3\text{-tet})^{4+}$$

are given, with $k_1 = 3.15 \times 10^{-4}[H^+]\ s^{-1}\ M^{-1}$, $k_{-1} = 2.76 \times 10^{-3}\ s^{-1}$, and $k_2 = 5.10 \times 10^{-4}\ s^{-1} + 4.90 \times 10^{-5}[H^+]\ s^{-1}\ M^{-1}$ for Cu(cyclam)$^{2+}$ and $k_1' = 0.493[H^+]\ s^{-1}\ M^{-1} + 6.06\ s^{-1}$ for Cu(3,2,3-tet)$^{2+}$ at 25.0 °C and μ = 5.0 M ($NaNO_3$ + HNO_3). The possible pathways for the cleavage of the copper–nitrogen bonds, the factors influencing the dissociation rates, and the factors affecting the relative importance of each of these possible pathways are discussed.

Introduction

There has been renewed interest in the kinetic studies of the acid-catalyzed dissociation of the copper(II) and nickel(II) polyamine complexes.[1-9] Nearly all such studies support the general mechanism proposed by Margerum and co-workers.[10,11] Previously, we have reported the dissociation kinetics of the blue and red copper(II) complexes of *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, tet a (I), as well as the blue copper(II) complex of *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, tet b (II), in strongly acidic, aqueous media.[12-14] In the current investigation, we have attempted to gain more detailed understanding of the steric and macrocyclic effects on the kinetics of acid-catalyzed dissociation reactions of tetraamine complexes of copper(II). To accomplish this, we have extended our studies to the dissociation reactions of copper(II) complexes of 1,4,8,11-tetraazacyclotetradecane, cyclam (III), and 1,5,8,12-tetraazadodecane, 3,2,3-tet (IV), in 0.1–5.0 M HNO_3 (eq 1).

$$CuL^{2+} + 4H^+ \rightarrow Cu^{2+} + H_4L^{4+} \qquad (1)$$

Crystal structure determinations of both Cu(cyclam)$^{2+}$ and Cu(3,2,3-tet)$^{2+}$ have been reported,[15,16] thus providing the opportunity to elaborate the ways in which the different structures of the coordinated tetraamines (Chart I) convey properties on the dissociation kinetics of their copper(II) complexes.

Chart I

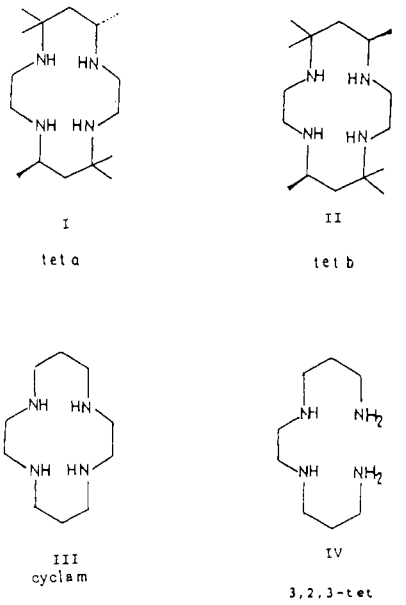

Table I. Visible Absorption Bands at μ = 5.0 M($NaNO_3$)

complex	λ_{max}, nm	ϵ_{max}, $M^{-1}\ cm^{-1}$
Cu(cyclam)$^{2+}$	500	84
Cu(3,2,3-tet)$^{2+}$	543	92

Experimental Section

Reagents. The macrocyclic complexes Cu(cyclam)$(ClO_4)_2$ and Cu(3,2,3-tet)$(ClO_4)_2$ used are the same as those reported earlier.[17] All other chemicals used in this work were of GR grade (Merck or Fluka).

Kinetic Measurements. Kinetic runs for the dissociation reactions of Cu(cyclam)$^{2+}$ were initiated by mixing a freshly prepared Cu(cyclam)$(ClO_4)_2$ 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 400–800 nm, with particular focus on 500 nm (a maximum for Cu(cyclam)$^{2+}$). A Hitachi U-3200 spectrophotometer was used and the temperature was

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Table II. Rate Constants for the Dissociation of Cu(cyclam)$^{2+}$ at 25.0 °C and μ = 5.0 M (HNO_3 + $NaNO_3$)[a]

$[HNO_3]$, M	10^4k_1,[b] s^{-1}	10^3k_{-1},[b] s^{-1}	10^4k_2,[b] s^{-1}
0.2	0.62	2.78	5.22
0.4	1.30	2.78	5.32
0.5	1.50	2.77	5.35
0.6	1.82	2.75	5.41
0.7	2.20	2.76	5.44
0.8	2.49	2.76	5.49
0.9	2.83	2.76	5.50
1.0	3.15	2.78	5.52
1.5	4.70	2.77	5.88
2.0	6.24	2.75	6.17
2.5	7.80	2.75	6.32
3.0	9.41	2.76	6.52
3.5	10.9	2.76	6.74
4.0	12.3	2.77	6.86
4.5	14.2	2.77	7.42
5.0	16.2	2.75	7.66

[a] Conditions: [Cu(cyclam)$^{2+}$] = 2.20 × 10^{-3} M; wavelength = 500 nm. [b] Mean value of at least four kinetic runs.

Table III. 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 + $NaNO_3$)

rate const	Cu(cyclam)$^{2+}$	Cu(tet a)(red)$^{2+}$
k_1	3.15 × 10^{-4}[H^+] s^{-1} M^{-1}	2.27 × 10^{-8}[H^+] s^{-1} M^{-1}
k_{-1}	2.76 × 10^{-3} s^{-1}	2.52 × 10^{-3} s^{-1}
k_2	5.10 × 10^{-4} s^{-1} + 4.91 × 10^{-5}[H^+] s^{-1} M^{-1}	1.03 × 10^{-5}[H^+] s^{-1} M^{-1} + 4.46 × 10^{-4} s^{-1}

maintained at 25.0 ± 0.1 °C for all the solutions studied. The rate constants were obtained by using the IBM 1130 computer.

The kinetics of the Cu(3,2,3-tet)$^{2+}$ dissociation reactions was studied with a Union Giken RA-401 stopped-flow spectrophotometer equipped with a Union RA-415 rapid-scan attachment, with particular focus on 543 nm (a maximum for Cu(3,2,3-tet)$^{2+}$) and the temperature maintained at 25.0 ± 0.1 °C for all the solutions studied.

Results

The visible absorption spectra were used to observe the dissociation reactions. The principal absorption band, and molar absorptivities of Cu(cyclam)$^{2+}$ and Cu(3,2,3-tet)$^{2+}$ in 5.0 M $NaNO_3$ at 25.0 °C are given in Table I. The dissociation reaction of Cu(cyclam)$^{2+}$ was found not to occur by a single stage but to take place in consecutive steps, and the simplest kinetic scheme that can accommodate the experimental results involves consecutive first-order processes with reversible steps, as given in eq 2. Here Cu(Hcyclam)$^{3+}$ is an intermediate.

$$\text{Cu(cyclam)}^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Cu(Hcyclam)}^{3+} \xrightarrow{k_2} \text{(H}_4\text{cyclam)}^{4+} + \text{Cu}^{2+} \quad (2)$$

The approximate values of the rate constants were estimated from kinetic measurements. The approximate molar absorptivity of Cu(Hcyclam)$^{3+}$, ϵ_I, was estimated from the scanning spectra. Rodiguin–Rodiguina integration[18] gave the values of the concentrations of Cu(cyclam)$^{2+}$, Cu(Hcyclam)$^{3+}$, Cu^{2+}, and H_4-cyclam^{4+} 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_I so as to obtain a minimum deviation between observed and calculated values, led to the correct rate constants. The value of ϵ_I at 500 nm evaluated by this method is 70 ± 5 cm^{-1} M^{-1}. The resulting values of the rate constants as a function of acid concentration are given in Table II. One of the experimental curves and best-fit curve in 4.0 M HNO_3, calculated with the rate constants listed in Table II, are shown in Figure 1. The other curves are very similar to this particular curve.

The results given in Table II indicate that k_1 and k_2 are [H^+] dependent. Plots of these rate constant against [H^+] give straight lines. The values for the stepwise rate constants as a function of acid concentration are tabulated in Table III. For the purpose of comparison, the corresponding values for the dissociation reaction of Cu(tet a)(red)$^{2+}$ are also given in this table.[13]

In marked contrast to the behavior of Cu(cyclam)$^{2+}$, the dissociation process of Cu(3,2,3-tet)$^{2+}$ was found to occur by a single stage, and the rate equation can be expressed as

$$\frac{-\text{d[Cu(3,2,3-tet)}^{2+}]}{dt} = k_{obsd}[\text{Cu(3,2,3-tet)}^{2+}] \quad (3)$$

The observed first-order rate constants as a function of $[HNO_3]$ are given in Table IV. A plot of k_{obsd} vs [H^+] is linear; least-squares analysis of the data gives k_{obsd} = 0.493[H^+] M^{-1} s^{-1} + 6.06 s^{-1}.

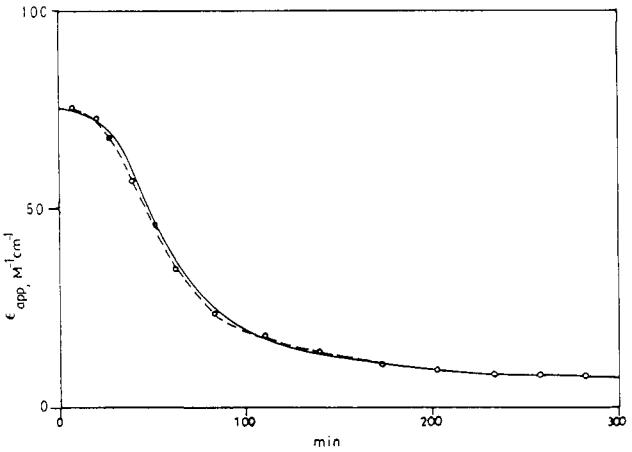

Figure 1. Apparent molar absorptivities vs time for the reaction of Cu(cyclam)$^{2+}$ in 4 M HNO_3 (μ = 5.0 M) at 500 nm and 25.0 °C. The solid line is the experimental curve, and the dashed line is the best-fit curve calculated with the constants listed in Table II, $\epsilon_{app} = A_{obsd}/bC_T$.

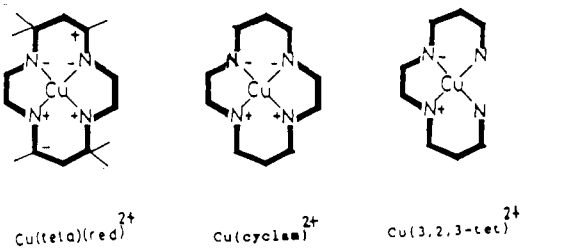

Figure 2. Configurations of the asymmetric centers and the conformations of the chelate rings of Cu(tet a)(red)$^{2+}$, Cu(cyclam)$^{2+}$, and Cu(3,2,3-tet)$^{2+}$. A plus sign at an asymmetric center indicates that the hydrogen atom of the center is above the plane of the tetraamine, and a minus sign indicates 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.

Table IV. Rate Constants for the Dissociation of Cu(3,2,3-tet)$^{2+}$ at 25.0 °C and μ = 5.0 M (HNO_3 + $NaNO_3$)[a]

$[HNO_3]$, M	k_{obsd},[b] s^{-1}	$[HNO_3]$, M	k_{obsd},[b] s^{-1}
0.10	6.10	0.75	6.44
0.15	6.13	0.80	6.45
0.20	6.16	0.90	6.50
0.25	6.19	1.00	6.58
0.30	6.20	1.25	6.67
0.35	6.23	1.50	6.78
0.40	6.25	1.75	6.92
0.50	6.32	2.00	7.04
0.60	6.35	2.25	7.17
0.70	6.40	2.50	7.30

[a] Conditions: [Cu(3,2,3-tet)$^{2+}$] = 2.01 × 10^{-3} M; wavelength = 543 nm. [b] Mean value of at least four kinetics runs.

Discussion

The X-ray crystal structure determinations of Cu(cyclam)$^{2+}$, Cu(3,2,3-tet)$^{2+}$, and Cu(tet a)(red)$^{2+}$ have been reported.[15,16,19]

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Table V. Measured and Corresponding Mechanistic Rate Constants for the Dissociation of Copper(II) Tetraamine Complexes at 25.0 °C and μ = 5.0 M (HNO_3 + $NaNO_3$)

measd rate const	mechanistic rate const	Cu(cyclam)$^{2+}$	Cu(tet a)(red)$^{2+}$ [a]	Cu(3,2,3-tet)$^{2+}$
k_{1H}	k_{12}	3.15×10^{-4} s^{-1} M^{-1}	2.27×10^{-8} s^{-1} M^{-1}	0.493
k_{1d}	k_{13}			6.06
k_{2H}	k_{45}	4.91×10^{-5} s^{-1} M^{-1}	1.03×10^{-5} s^{-1} M^{-1}	
k_{2d}	$k_{46} + k_{47}$	5.10×10^{-4} s^{-1}	4.46×10^{-4} s^{-1}	
k_{-1H}	$(k_{21} + k_{42})/k_{24}$	2.76×10^{-3} s^{-1}	2.52×10^{-3} s^{-1}	

[a] Reference 13.

As shown in Figure 2, the configurations of the asymmetric nitrogen centers of these complexes are the same. The ligands of these complexes are in planar coordination with the six-membered chelate rings in a stable chair form and the five-membered ones in a stable gauche form. Thus these complexes are expected to have similar trans-octahedral arrangements in aqueous solution with the tetraamine equatorial and the aqua groups axial.[19]

The kinetic results of the dissociation reaction of Cu(cyclam)$^{2+}$ can be explained readily by the generally accepted stepwise mechanism for the dissociation of tetraamine macrocyclic ligand complexes in strongly acidic, aqueous media (Figure 3). For the cleavage of the first copper–nitrogen bond, there are two possible pathways, the direct protonation pathway (1 → 2 → 4) and the solvation or solvent-separation pathway (1 → 3 → 4). Under the conditions used in this study, $k_{24} \gg k_{21}$ and $k_{34}[H^+] \gg k_{31}$, so that $k_1 = k_{1H}[H^+] + k_{1d} = k_{12}[H^+] + k_{13}$ and $k_{-1} = k_{-1H} + k_{-1d}/[H^+] = k_{21}k_{42}/k_{24} + k_{43}k_{31}/k_{34}[H^+]$. The measured and the corresponding mechanistic rate constants are listed in Table V. The corresponding values for the dissociation reaction of Cu(tet a)(red)$^{2+}$ are also given in this table for comparison.[13]

As shown in Figure 3, there are three types of mechanistic pathways for the cleavage of the second copper–nitrogen bond, the protonation pathway (4 → 5 → 8), the intramolecular H-bonding pathway (4 → 6 → 8) and the solvation pathway (4 → 7 → 8). In strongly acidic media, $k_{58} \gg k_{54}$, $k_{68}[H^+] \gg k_{64}$, and $k_{78}[H^+] \gg k_{74}$, so that $k_2 = k_{2H}[H^+] + k_{2d} = k_{45}[H^+] + k_{46} + k_{47}$. The measured and the corresponding mechanistic rate constants for the reactions of Cu(cyclam)$^{2+}$ and Cu(tet a)(red)$^{2+}$ are given in Table V.

For the dissociation reactions of Cu(cyclam)$^{2+}$, and Cu(tet a)(red)$^{2+}$, the cleavage of the first Cu–N bond is dominantly via the protonation pathway. The factor of 10^4 in the relative reactivity of Cu(cyclam)$^{2+}$ and Cu(tet a)(red)$^{2+}$ gives an indication of the large steric effects which *C*-methyl groups have on the dissociation kinetics. Conversely, the rate constant for the formation of this Cu–N bond, k_{-1H}, for the reaction of Cu(cyclam)$^{2+}$ is about the same as that for the reaction of Cu(tet a)(red)$^{2+}$. These results, that the rate constant k_{1H} is very sensitive to the nature of the leaving group and the rate constant k_{-1H} is very insensitive to the nature of the entering group, indicate the first Cu–N bond is fully broken in the transition state for step 1 → 2.

Like the reaction of Cu(tet a)(red)$^{2+}$, the cleavage of the second Cu–N bond of Cu(cyclam)$^{2+}$ is mainly via the intramolecular H-bonding pathway, in which Cu–N bond breaking and intramolecular H-bonding formation occur first, with rapid protonation of nitrogen donor and metal ion solvation occurring in a second step. Thus the ratio k_{2H}/k_{2d} for the cleavage of the second Cu–N bond of Cu(cyclam)$^{2+}$ is much smaller than the ratio k_{1H}/k_{1d} for the cleavage of the first Cu–N bond (Table VI).

Dissociation of the copper(II) complex of the open-chain tetraamine differs quite markedly from that of macrocyclic tetraamines. The dissociation process of Cu(3,2,3-tet)$^{2+}$ was found to occur by a single stage. The rate for the dissociation of Cu(3,2,3-tet)$^{2+}$ is much faster than that for the corresponding tetraamine macrocyclic ligand complexes of copper(II). In addition, the acid-independent solvation pathway makes the major contribution to the rate of the dissociation of Cu(3,2,3-tet)$^{2+}$ under the conditions used in this study. The proposed mechanism for the reaction of Cu(3,2,3-tet)$^{2+}$ is shown in Figure 4. In strongly acidic media, $k_{24} \gg k_{21}$, and $k_{34}[H^+] \gg k_{31}$, so that $k_1 = k_{1H}[H^+] + k_{1d} = k_{12}[H^+] + k_{13}$. The measured and the corresponding mechanistic rate constants are listed in Table V.

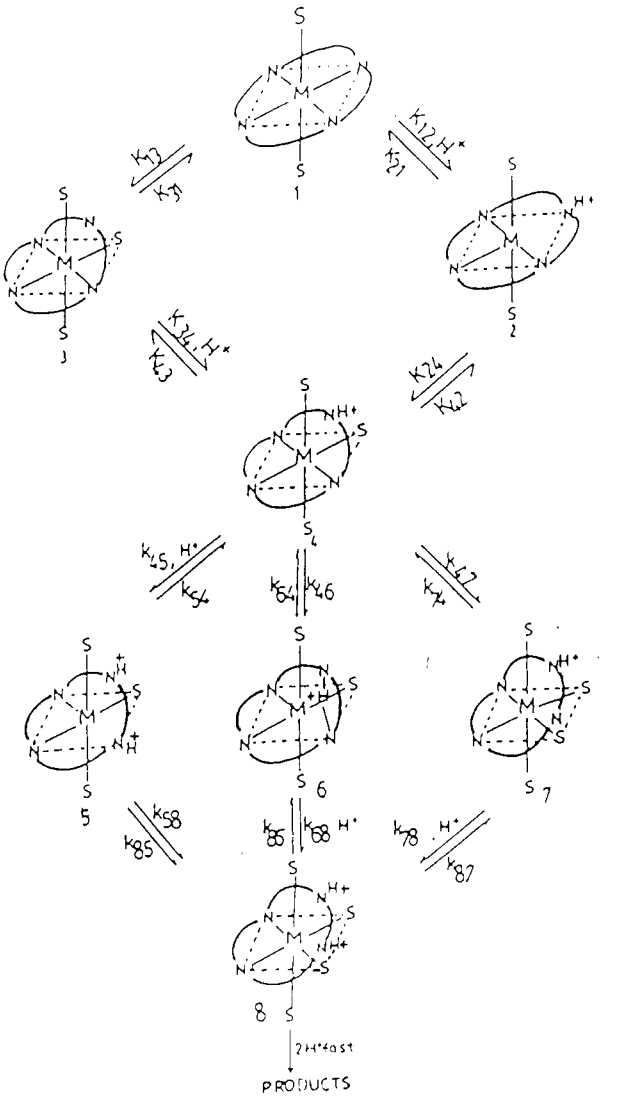

Figure 3. Proposed stepwise mechanism for the dissociation of Cu(cyclam)$^{2+}$ in strongly acidic media.

A comparison between the dissociation reactions of Cu(cyclam)$^{2+}$ and Cu(3,2,3-tet)$^{2+}$ provides an insight into the effect of ligand cyclization. The cleavage of the first Cu–N bond of Cu(cyclam)$^{2+}$, step 1 to 2 or step 1 to 3 in Figure 3, involves some angular expansion of the bond angles in two stable chelate rings. On the other hand, the cleavage of the first Cu–N bond of Cu(3,2,3-tet)$^{2+}$, step 1 to 2 or step 1 to 3 in Figure 4, involves some angular expansion of the bond angles in only one stable chelate ring. Thus, the cleavage of the first Cu–N bond of Cu(cyclam)$^{2+}$ reacts more slowly than that of Cu(3,2,3-tet)$^{2+}$ by factors of

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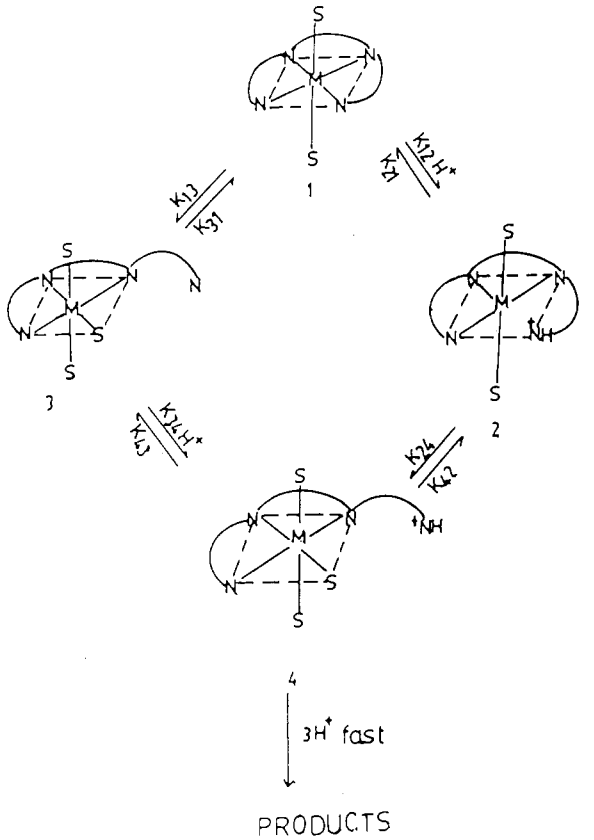

Figure 4. Proposed stepwise mechanism for the dissociation of Cu(3,2,3-tet)$^{2+}$ in strongly acidic media.

10^4–10^5 under these conditions (Tables II and IV).

The cleavage of the first Cu–N bond of Cu(cyclam)$^{2+}$ is dominantly via the protonation pathway, while the cleavage of the first Cu–N bond of Cu(3,2,3-tet)$^{2+}$ is mainly via the solvation pathway. As pointed out by Read and Margerum,[11] if the donor is unrestricted and able to move easily out of the first coordination sphere, the presence of acid has little effect. However, if the movement of the donor away from the metal ion is hindered in some way, acid can enhance the rate of dissociation. Thus the ratio k_{1H}/k_{1d} increases with the degree of restriction of the coordinate polydentate ligand, preventing the donor atom from moving out of the first coordination sphere. For the cleavage of the first Cu–N bond of Cu(cyclam)$^{2+}$, the restrictions imposed by the ligand cyclization serve to hold the donor in the first coordination sphere, making Cu(cyclam)$^{2+}$ far less susceptible to solvent attack than Cu(3,2,3-tet)$^{2+}$, which has a much smaller restriction of the chelate ring to prevent the donor from moving smoothly out of the first coordination sphere. As a result, the ratio k_{1H}/k_{1d} for Cu(cyclam)$^{2+}$ is much larger than that for Cu(3,2,3-tet)$^{2+}$, as shown in Table VI.

Table VI. Rate Constant Ratios Representing the Relative Importance of the Pathways for the Dissociation Reactions of Copper(II) Tetraamine Complexes

ML^{2+}	k_{1H}/k_{1d}, M^{-1}	k_{2H}/k_{2d}, M^{-1}
Cu(cyclam)$^{2+}$	very large	0.096
Cu(tet a)(red)$^{2+}$	very large	0.023
Cu(3,2,3-tet)$^{2+}$	0.081	

For the dissociation of Cu(3,2,3-tet)$^{2+}$, the cleavage of the first Cu–N bond involves the formation of an intermediate (4 in Figure 4) with the donor group displaced from the normal chelation position. The metal ion becomes solvated, and there is protonation and rotation of the leaving donor group. In this reaction, solvent and acid assist the dissociation by solvation and protonation of the intermediate (4 in Figure 4), and stabilize it relative to the fully coordinated form. Thus, the cleavage of the first Cu–N bond becomes rate determining at high acid concentrations. In contrast, for the reaction of Cu(cyclam)$^{2+}$, after the breaking of the first Cu–N bond, the macrocyclic ligand twists or folds instead of internally rotating the leaving group. Due to the constraints of the cyclic structure of cyclam the uncoordinated amine group and the metal ion are very close to each other, and the solvation of the metal ion and the protonated amine group is sterically hindered to a very large extent, with the result that k_{-1} is larger than k_2. Therefore, the cleavage of the second Cu–N bond becomes rate determining.

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Registry No. Cu(cyclam)$^{2+}$, 21780-12-1; Cu(3,2,3-tet)$^{2+}$, 46142-15-8.

Contribution from the Laboratoire de Chimie-Physique (UA 253 du CNRS), HEI, 13, rue de Toul, 59046 Lille Cédex, France

Identification and Characterization of Ammonium Polysulfides in Solution in Liquid Ammonia

P. Dubois, J. P. Lelieur,* and G. Lepoutre

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Ammonium polysulfides ($(NH_4)_2S_n$) in ammonia solutions have been identified by using UV–visible spectrophotometry and Raman spectroscopy. They have been prepared by reducing sulfur–ammonia solutions with hydrogen sulfide or hydrazine monohydrochloride. The radical anion S_3^- is always observed in equilibrium with S_6^{2-} for $n > 1$. The existence of S_4^{2-} in solution is shown, and it is found that this species is disproportionated. The results of this work are compared with those obtained for Li_2S_n–NH_3 solutions. For $n \leq 4$, the disproportionation of polysulfides is systematically higher for $(NH_4)_2S_n$ solutions than for Li_2S_n solutions. This results from the fact that in the presence of NH_4^+, HS^- is the most reduced species, while S^{2-} is the most reduced in the presence of Li^+. Ammonium polysulfide solutions, with $2 \leq n \leq 6$, can be prepared with concentrations at least equal to 6 M. It is shown that S_6^{2-} is the least reduced polysulfide in the medium and that the determination of the equilibrium constant between S_6^{2-} and S_3^- is the source of the difficulties which are discussed.

Introduction

The purpose of this paper is to identify the ammonium polysulfides in solution in liquid ammonia. This work also aims at giving a better characterization of chemical species in sulfur–ammonia solutions. It was recently shown[1,2] that sulfur is solubilized in liquid ammonia with a redox disproportionation mechanism. After Chivers and Lau,[3] we have observed[1,2] the oxidized species S_4N^- and the reduced species S_3^- in sulfur–ammonia solutions. It was shown[2] that S_3^- is in equilibrium with

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