The activation parameters for the acid-hydrolysis path of the Ru(III) organonitrile complexes shown in Table IV are very similar to one another. There may be a compensation of more favorable ΔH^{*} values by less favorable ΔS^{*} values, as expected for reactions with the same mechanism, especially in cases where bond formation is important, but experiments over a larger temperature range would be necessary to substantiate this effect.

The relative rates for the benzonitrile, acetonitrile, and 1-adamantylcarbonitrile reactions (3.4×10^{-5}, 1.2×10^{-5} and 7.2×10^{-6} s^{-1}) are consistent with the ideas previously advanced for the base-hydrolysis reactions,[1,2] i.e., that the metal atom catalyzes hydrolysis by withdrawing electron density from the nitrile group when the nucleophile attacks and that substituents on the nitrile group can retard the reaction by donating electron density. As previously found for the base-hydrolysis reactions, the acid hydrolysis of organonitriles coordinated to Co(III) and Ru(II) appears to be much slower.

With regard to electron-transfer reactions of organonitrile complexes of Ru(III) and Co(III), the hydrolysis of the Ru(III) nitrile moiety can be predicted quite readily and the extent can be ascertained readily from the visible absorption spectrum of the complex. The half-lives of such reactions at 25 °C are sufficiently long to allow sample preparation without an unacceptable loss of concentration of the desired nitrile complex. Upon reduction of Ru(III) to Ru(II), hydrolysis is greatly for retarded (by a factor of at least 10^6 for the base-hydrolysis path and undetected for the acid-hydrolysis path), posing no significant limitation to the study of reactions of Ru(II)-Co(III) bimetallic complexes.

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Registry No. $Ru(NH_3)_5NCCH_3^{3+}$, 44819-54-7; $Ru(NH_3)_5NCC_6H_5^{3+}$, 46343-59-3; $Ru(NH_3)_5NCR^{3+}$ (R = adamantane), 87518-03-4; $Ru(NH_3)_5(C_{10}H_{15}CONH)^{2+}$, 87518-04-5; Ru, 7440-18-8; acetonitrile, 75-05-8; benzonitrile, 100-47-0; 1-adamantylcarbonitrile, 23074-42-2.

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Proton-Promoted Chelate-Ring Opening in Copper(II) Polyamine Complexes

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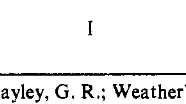
Kinetic studies of the acid aquation of Cu(II) complexes of a structurally related series of polyamines have been made as a function of $[H_3O^+]$, temperature, and presence of a general acid for catalysis of the chelate-ring opening reaction. The polyamines studied include en, dien, trien, tren, dach, and [9]aneN_3. Activation parameters are reported for a rate-limiting reorganization step; the rates of all ligands in the series for the dissociation of the CuL^{2+} complex saturate in $[H_3O^+]$ except the strained ligand dach. $Cu(dach)(H_2O)_4^{2+}$ dissociates with a strictly first-order law in $[H_3O^+]$. The mechanism for chelate-ring opening via a distorted intermediate, CuL^{*2+}, for ligands of this series is compared to the reported ligand dissociation reactions for analogous Ni(II) complexes where comparable data exist. It is concluded that the more rapidly dissociating Cu(II) complexes proceed to products predominantly via intermediates in which protonation of a partially ruptured Cu-N bond is assisted by H_3O^+ as an ion pair with an electrolyte anion. However with $Cu(tren)(H_2O)^{2+}$, two different intermediates are required to explain two different kinetically active paths that saturate in $[H_3O^+]$ at 3 s^{-1} (pH 3.0-5.0) and 500 s^{-1} ($[H_3O^+] > 0.050$ M). The path saturating at 3 s^{-1} has activation parameters like those of other straight-chain polyamines. This path is independent of counteranion, ClO_4^- or Cl^-. The one at 500 s^{-1} has an 8.3 kcal/mol lower activation enthalpy in Cl^- solution than for $Cu(en)(H_2O)_4^{2+}$ at 12.0 ± 1.8 kcal/mol (NO_3^- medium). The more rapidly dissociating intermediate is described as one in which an H_3O^+,X^- pair intercepts a partially ruptured Cu-N bond of $Cu(tren)(H_2O)^{2+}$ prior to the time for the rupturing ring to rotate out of the first coordination sphere of Cu(II). The rate of this path is counteranion dependent. Cl^- provides an additional lowering of the barrier by ca. 2.0 kcal/mol vs. ClO_4^-. The $Cu(tren)(H_2O)^{2+}$ dissociation in acetate buffers (pH 3.0-5.0) exhibits approximately the same general-acid acceleration as recently reported for $Ni(en)(H_2O)_4^{2+}$. The influence of increasing chain length or a modification of the CuL^{2+} structure that increases strain for the dissociation step is discussed for complexes of the above series.

Introduction

Dissociation of a chelate ligand, such as ethylenediamine, is much slower than the analogous loss of monodentate ligands of the same donor type (NH_3 for en) from a metal ion center. Acid can accelerate the dissociation of chelate rings by several orders of magnitude. Wilkins and co-workers observed the acid acceleration in their early mechanistic studies of the dissociation of $Ni(en)(H_2O)_4^{2+}$ and $Cu(en)(H_2O)_4^{2+}$.[1-6] Their conclusions have largely held up to the test of time for most of the labile-ion transition-metal systems that have been examined mechanistically.[7] Most of the mechanistic conclusions have been drawn from studies of Ni(II) complexes because the rates with Ni(II) are slower (albeit kinetically rapid) than with most other ions of interest of the first-row transition metal ions. The Ni(II) cases are therefore more amenable to kinetic methods.

Ahmed and Wilkins suggested in their earliest studies of chelate-ring openings with Ni(II) and Cu(II) complexes that H^+ might be involved in the direct attack of the shared electron pair between ligand and metal ion center.[6]



I

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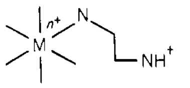
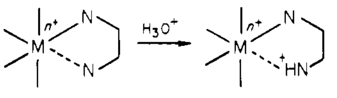
This view has usually been rejected on electrostatic grounds—that H^+ in the vicinity of the charged metal ion site would be too acidic to compete successfully for the lone electron pair of the basic ligand in a three-center bond configuration. The explanation that has been generally accepted to account for proton acceleration of chelate-ring opening from metal ion complexes is that protonation of the pendant (monodentate) form stabilizes the partially coordinated intermediate II and prevents ring closure. Intermediate II can



II

then only dissociate to products.[7] The case for $Ni(en)(H_2O)_4^{2+}$ was very recently reexamined by Read and Margerum.[8] These workers observed that dissociation of en is accelerated both by specific-acid (H_3O^+) and by general-acid catalysis as long as the general acid possesses a second site of attachment such as a carbonyl group of a carboxylic acid, but not by acids such as pyridinium ion that have no additional lone-pair sites on the molecule.[8] Of the two catalytic paths, general-acid catalysis gives the larger enhancement with $Ni(en)(H_2O)_4^{2+}$. Margerum has explained the specific-acid term in the rate law for ring opening of $Ni(en)(H_2O)_4^{2+}$ as due to protonation of the N-base of en prior to the time that en can be displaced or rotate out of the first coordination sphere. That is to say, acid attack at the amine nitrogen occurs prior to or during solvent replacement of the donor.[8] The general-acid catalysis path requires the donor acid to be placed adjacent to the ring–opening site for efficient proton transfer, either by hydrogen bonding to water in the first coordination sphere of Ni(II) or by displacement of a cis water molecule by the second donor atom of the active general acid. Margerum has described the intermediate involved in enhanced activity at high acid concentration as one with reduced coordination by the amine functionality but not completely removed from the first coordination sphere of Ni(II)—one whose bond is largely broken with a lone pair available for protonation[8] (intermediate III). III is then rapidly scavenged by protons, yielding IV,



III IV

which converts to the final products rapidly. It can be seen that IV differs only slightly in conceptual nature from I.

There remains the question of how general the case of Ni(II) is in describing the chelate-ring-opening phenomena as accelerated by acid. For example, the biologically important Cu(II) case, which in certain systems enzymatically interacts via chelation to dopamine and catechol substrates, has received only limited attention in mechanistic studies due to experimental difficulties. Also, little attention has been given even for Ni(II) in terms of obtaining activation parameters in the mechanistic investigations of chelate-ring openings. In spite of experimental difficulties, it seems that activation parameter studies are likely to be essential if any discernment of mechanistic cases is to be realized. It may be inferred from substitution reactions of $(NH_3)_5RuOH_2^{2+}$ with the protonated forms of pyridine and imidazole[9] that the restriction suggested by the involvement of proton–cationic metal center–ligand base, as mentioned above, is not correct in general for the periodic table. By the law of microscopic reversibility, a direct attack of H^+ during the ligand dissociation of $(NH_3)_5RuL^{2+}$ (L = py or ImH) would be required if protonated forms are active for substitution and *indeed* the rate laws for loss of LH^+ in these systems are first order in $[H_3O^+]$.[9,10] It is likely that the more electron-rich metal centers are able to avail themselves of filled d-orbital protonation in the transition state and that these paths are less likely for the first row, where size increases the electrostatic repulsion influence. By contrast to the Ru(II) systems loss of monodentate donors such as NH_3 from Ni(II) or Cu(II) are thought to be independent,[6] or least far less sensitive to H_3O^+ acceleration.[8]

We wish to report here kinetic studies of the acid aquation involving various structurally related polyamines (en, dien, trien, tren, dach, piperazine, and [9]aneN_3) coordinated to Cu(II). The work has been carried out over a range of temperature and acid conditions that allow conclusions to be drawn concerning the mechanism of the acid-accelerated dissociation. The key cases of tren and [9]aneN_3 as ligands reveal that the residual structure of a molecule is also important for the ring-opening process. In the case of $Cu(tren)(H_2O)^{2+}$ we observe that two different kinetic pathways both saturate in $[H_3O^+]$. It is our conclusion that in this one molecule, $Cu(tren)(H_2O)^{2+}$, both types of intermediates involving acid assistance (direct attack of H_3O^+ on a distorted bond as in IV and the protonation of a pendant, opened ring as in II) are observed. It is also rewarding to note that since activation parameters were obtained in this work for the rapid dissociations of some of these ligands, the values for rate constants at 25 °C reported by Wilkins[5] and by Kustin[11] for the straight-chain polyamines were reproduced in our laboratory with good agreement. Evidence points to a stabilization of the transition state for the direct attack of H_3O^+ by the presence of an anion influence on the kinetic barrier to ring opening.

Experimental Section

Kinetic Experiments. Data were collected on a Durrum (Dionex) D-110 stopped-flow spectrophotometer. Data analysis was carried out in an on-line fashion with a DEC 11/03 interfaced computer using appropriate first-order kinetic programs on floppy magnetic disks. Temperature control was ±0.1 °C provided by a Forma bath unit. Ionic strength was controlled with either NaCl, LiCl, $LiClO_4$, or $NaCH_3CO_2/NaCl$ and $NaCH_3CO_2/LiClO_4$. In the cases of lower [acid] conditions for the tren systems, acetate buffer was used with acetate ion concentration of 0.050 M. For the acetate-dependence studies $[NaCH_3CO_2] + [NaCl] = 0.25$. Buffers were produced by adding HCl so that $\mu = 0.25$ was retained and the buffer ratio established a desired pH. True acetate concentration was calculated from known K_a values. In higher [acid] cases, $HClO_4$ was used as the source of H_3O^+ and ionic strength was adjusted with LiCl. HNO_3 was used only in the case of $Cu(en)^{2+}$ in order to reproduce the conditions of Kustin[11] for comparison; the electrolyte salt was NaCl to keep ionic strength constant.

UV–Visible Spectra. Spectra were obtained on a Varian-Cary 118C spectrophotometer with a thermostated samples compartment, and quartz cells were used. In all kinetic runs, spectra were taken before and after the addition of acid. In every case, spectra matched with that of $Cu(H_2O)_6^{2+}$ after the addition of acid.

Reagents. tren [tris(2-aminoethyl)amine] was obtained from Tridom chemicals. Other ligands such as en (ethylenediamine), dien (diethylenetriamine), trien (triethylenetetraamine), dach (1,4-diazacycloheptane), ImH (Imidazole), $1\text{-}CH_3ImH$ (1-methylimidazole), and NH_2CH_3 (methylamine) and all other starting materials for synthesis of [9]aneN_3 were obtained from Aldrich and were used without further purification.

Synthesis of [9]aneN_3. Preparation of [9]aneN_3 was taken from ref 12 with two modifications to improve the yield. During the cyclization step as 1,2-dibromoethane is added dropwise to a hot

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Table I. Acid-Catalyzed Dissociation of Straight-Chain Polyamines from Cu(II)

complex	k_1,[a] s^{-1}	k_2/k_{-1},[a] M^{-1}	λ, nm
$Cu(en)^{2+}$	126	32.8	590
$Cu(dien)^{2+}$	348	9.0	625
$Cu(trien)^{2+}$	296	20.0	575
$Cu(en)^{2+}$	121[b]		
$Cu(en)^{2+}$	115[c]		

[a] $T = 25.0$ °C; $[CuL^{2+}]_i = 4.425 \times 10^{-3}$ M in the dien and trien cases, 1.45×10^{-3} M in all en cases; $[H_3O^+] = 0.005$–0.150 M in the cases of $Cu(en)^{2+}$ and 0.075–0.175 M in the cases of $Cu(dien)^{2+}$ and $Cu(trien)^{2+}$; $\mu = 0.10$ M in $Cu(en)^{2+}$ case, salt was NaCl, H_3O^+ source was HNO_3; $\mu = 0.25$ M in $Cu(dien)^{2+}$ and $Cu(trien)^{2+}$ cases, salt was LiCl, H_3O^+ source was $HClO_4$. [b] At 0.064 M $[H_3O^+]$; ref 11. [c] At 0.15 M $[H_3O^+]$; ref 5.

Table II. Temperature Dependence of Calculated Kinetic Parameters in Electrolyte Medium

system	counterion	T, °C	k_1, s^{-1}	k_2/k_{-1}, M^{-1}
$Cu(en)^{2+}$	NO_3^-, Cl^-	20.0	108	32.5
		22.8	120	31.9
		24.8	133	31.9
		27.5	172	24.9
		29.6	195	24.7
		31.9	241	25.9
	ClO_4^-	15.0	55.9	50.7
		17.2	75.6	36.1
		19.8	85.5	42.9
		23.0	103	39.3
		25.1	139	29.0
$Cu(dien)^{2+}$	Cl^-	19.9	264	7.4
		23.0	302	9.3
		25.0	348	9.9
		27.4	386	10.7
		30.4	397	13.1
		33.0	500	10.7
	ClO_4^-	15.8	181	12.6
		19.5	230	12.4
		23.0	296	11.5
		25.0	334	12.4
		27.2	375	12.1
$Cu(tren)^{2+}$ [a]	Cl^-	18.4	413	4.2
		21.5	437	4.3
		23.7	480	4.3
		26.3	496	4.6
	ClO_4^-	17.8	418	1.4
		19.4	500	1.2
		20.4	532	1.1
		22.4	559	1.2
		28.0	637	1.7
$Cu(tren)^{2+}$ [b]	Cl^-	20.2	2.5	1.4×10^4
		22.6	2.7	1.4×10^4
		25.0	3.0	1.2×10^4
		28.2	3.7	1.3×10^4
		31.3	4.2	1.4×10^4
	ClO_4^-	19.8	1.70	1.24×10^4
		22.5	2.00	1.24×10^4
		25.0	2.24	1.31×10^4
		27.5	2.62	1.09×10^4
$Cu(dach)^{2+}$	Cl^-	20.4	14.1[c]	
		22.8	13.3[c]	
		25.6	16.8[c]	
		29.1	23.2[c]	
		33.3	24.7[c]	
		36.6	29.5[c]	
$Cu([9]aneN_3)^{2+}$	Cl^-	16.6	45.7	0.63
		18.0	36.1	0.79
		22.8	72.0	0.52
		24.6	36.2	1.2
		25.5	42.8	1.3
		29.8	58.8	0.93
		33.0	59.5	1.2
$Cu(trien)^{2+}$	ClO_4^-	14.3	19.0	37.6
		16.8	21.8	41.7
		19.0	31.0	43.0
		21.3	35.8	35.4
		23.4	38.5	11.0
		25.9	34.3	4.2

[a] Higher [acid] condition. [b] Lower [acid] condition. [c] k_2 values.

solution of diethylenetriamine-*N,N′,N″-p*-tosylate and anhydrous potassium carbonate in DMF, the temperature must be kept constant at 100 °C. If the temperature is higher or lower, the yield is substantially reduced or even eliminated. The second necessary modification step requires water to be added in order to precipitate a white gummy solid after waiting a period of 3–4 days.

Synthesis of $[Cu_2(tren)_2(Im)](ClO_4)_3$. $[Cu_2(tren)_2(Im)](ClO_4)_3$ was synthesized according to the published procedure.[13]

Results and Dicussion

Specific-Acid Catalysis for Polyamine Dissociation from Cu(II). When complexes of Cu(II) polyamines are rapidly mixed with acid solution, the ligand dissociation reaction (1)

$$CuL^{2+} + nH_3O^+ \rightarrow Cu(H_2O)_6{}^{2+} + LH_n{}^{n+} \quad (1)$$

is observed (L = en, dien, trien, tren, dach, $[9]aneN_3$). The rate laws conform to the mathematical form of eq 2. Other

$$\frac{-d[CuL^{2+}]}{dt} = \frac{a[H_3O^+][CuL^{2+}]}{b + c[H_3O^+]} \quad (2)$$

workers, who have studied a more limited set of conditions,[5,11] have reported first-order behavior in $[H_3O^+]$, which is consistent with eq 2 with $k_{obsd} = a/b$. For all the polyamines listed above *except* tren, only one absorbance decrease according to eq 2 is observed in the stopped-flow spectrophotometric trace. The relaxations were examined at the appropriate d–d transition (see Table I) for loss of the CuL^{2+} complex. In the case of $Cu(tren)(H_2O)^{2+}$ two different saturation limits and decay times, depending on whether the $[H_3O^+]$ is in the range of 10^{-5}–10^{-3} M or is greater than 5×10^{-2} M, are found at 675 nm.

Data for the dissociation of $Cu(en)^{2+}$, $Cu(dien)^{2+}$ and $Cu(trien)^{2+}$ at 25.0°C are shown in Table I under conditions and concentrations matching those of Wilkins[5] and Kustin[11] to facilitate comparison of results. As can be seen from Table I, Wilkin's stopped-flow experiments and one of Kustin's temperature-jump measurements were carried out near the saturation limit in $[H_3O^+]$ as measured in our laboratory.

The dependence for the chelate dissociations shown by eq 2 is consistent with the simplest mechanism shown by Scheme I. In Scheme I, CuL^{*2+} represents an active intermediate

Scheme I

$$CuL^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CuL^{*2+}$$

$$CuL^{*2+} + H_3O^+ \xrightarrow{k_2} Cu(H_2O)_6{}^{2+} + HL^+$$

$$HL^+ + (n-1)H_3O^+ \overset{\text{rapid}}{\rightleftharpoons} LH_n{}^{n+} + (n-1)H_2O$$

that can react rapidly with H_3O^+, followed by rapid loss of the protonated ligand. CuL^{*2+} can be any of the precursors for intermediates I, II, and III described in the Introduction. Indeed, it would appear that some systems utilize intermediates more like III and at least one intermediate like II, as explained later. The values recorded in the tables for k_1, k_{-1}, and k_2 refer to the steps shown in Scheme I. A plot of $1/k_{obsd}$ for the spectrophotometric decay to the final products vs. $1/[H_3O^+]$ yields $1/k_1$ as the intercept and k_{-1}/k_1k_2 as the slope. These

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Table III. Temperature Dependence of Saturation Rates for Systems Generating $[Cu(tren)(H_2O)]^{2+}$ at Low [Acid] (Chloride Medium)

system	$\Delta H_1^\ddagger$, kcal/mol	$\Delta S_1^\ddagger$, eu
$[Cu(tren)(H_2O)]^{2+}$	8.26 ± 0.20	−28.58 ± 0.65
$[Cu(tren)(1\text{-}CH_3ImH)]^{2+}$	8.38 ± 0.87	−29.04 ± 2.92
$[cu(tren)(CH_3NH_2)]^{2+}$	8.58 ± 0.78	−27.69 ± 2.62
$[Cu_2(tren)_2Im]^{3+}$	9.43 ± 0.63	−24.78 ± 2.11

Table IV

A. Temperature Dependence of Saturation Rate Constants, k_1

system	counterion	$\Delta H_1^\ddagger$, kcal/mol	$\Delta S_1^\ddagger$, eu
$Cu(en)^{2+}$	NO_3^-, Cl^-	12.02 ± 1.75	−8.4 ± 5.9
	ClO_4^-	13.30 ± 1.75	−4.3 ± 5.4
$Cu(dien)^{2+}$	Cl^-	7.51 ± 0.82	−27.8 ± 2.7
	ClO_4^-	10.60 ± 0.27	−11.5 ± 0.9
$Cu(trien)^{2+}$	ClO_4^-	9.66 ± 2.62	−18.9 ± 8.9
$Cu(tren)^{2+}$ [a]	Cl^-	3.70 ± 0.63	−33.9 ± 2.1
	ClO_4^-	5.71 ± 1.51	−26.7 ± 5.1
$Cu(tren)^{2+}$ [b]	Cl^-	8.26 ± 0.20	−28.6 ± 0.7
	ClO_4^-	8.74 ± 0.43	−27.6 ± 1.5
$Cu(dach)^{2+}$	Cl^-	8.46 ± 1.91	−24.6 ± 6.4
$Cu([9]aneN_3)^{2+}$	Cl^-	2.93 ± 3.18	−41.0 ± 10.7

B. Eyring Treatment of the Ratio k_2/k_{-1} for Chloride Medium Systems

	$\Delta H_2^\ddagger - \Delta H_{-1}^\ddagger$, kcal/mol	$\Delta S_2^\ddagger - \Delta S_{-1}^\ddagger$, eu
$Cu(en)^{2+}$	8.9 ± 2.3	−21.9 ± 7.7
$Cu(dien)^{2+}$	5.3 ± 1.9	−36.2 ± 6.4
$Cu(tren)^{2+}$ [a]	1.4 ± 0.8	−51.0 ± 2.7
$Cu(tren)^{2+}$ [b]	−1.9 ± 1.3	−46.0 ± 4.0
$Cu([9]aneN_3)$	3.83 ± 3.73	−39.1 ± 12.5

[a] Higher [acid], $[H_3O^+] > 0.050$ M. [b] Lower [acid], pH 3.00–5.00, $\mu = 0.25$. All other systems are higher [acid] data.

values were used to evaluate k_1 and k_2/k_{-1} for the tables; cf. Table II. Repeating the studies of the saturation profiles at various temperatures allows for evaluation of activation parameters for the reorganizational step, k_1, and the discrimination ratio of productive to unproductive events, k_2/k_{-1}. The application of Eyring rate theory to $-\ln(k_1/T)$ vs. $1/T$ allows the evaluation of $\Delta H_1^\ddagger$ and $\Delta S_1^\ddagger$ for the reorganization step. Treatment of the ratio of k_2/k_{-1} yields $(\Delta H_2^\ddagger - \Delta H_{-1}^\ddagger)$ and $(\Delta S_2^\ddagger - \Delta S_{-1}^\ddagger)$; however, the errors associated with these estimates seem too large to be of particular value. The temperature and $[H_3O^+]$ dependence of ligands studied in chloride medium in this work are collected in Table VI as follows (ligand, table section): en, A; dien, B; tren (high $[H_3O^+]$), C; tren (low $[H_3O^+]$), D; dach, E; [9]aneN$_3$, F. Several systems that generate $Cu(tren)(H_2O)^{2+}$ on mixing at low $[H_3O^+]$ are also reported in Table VI as follows: $Cu(tren)(NH_2CH_3)^{2+}$, G; $[Cu_2(tren)_2(Im)]^{3+}$, H; $Cu(tren)(1\text{-}CH_3ImH)^{2+}$, I. In Table II we have given the values obtained by the double-reciprocal plot for k_1 and k_2/k_{-1} at various temperatures.

Kinetics studies carried out in ClO_4^- medium are given in Table VII as follows: dien, A; tren (high $[H_3O^+]$), B; tren (low $[H_3O^+]$), C; trien, D; en, E. Data from other tables are derived from kinetic treatment of the primary data in Tables VI and VII.

A number of studies were carried out with $Cu(tren)L'^{2+}$ ($L' = H_2O$, NH_2CH_3, 1-methylimidazole ($1\text{-}CH_3ImH$), $(Im)Cu(tren)^+$). It was our original goal to measure the rate of dissociation of L' from $Cu(tren)^{2+}$ in the pH range of 3–5. It became apparent that reaction 3 occurs rapidly on the

$$Cu(tren)L'^{2+} + H_3O^+ \rightarrow Cu(tren)(H_2O)^{2+} + HL'^+ \quad (3)$$

$$Cu(tren)(H_2O)^{2+} + H_3O^+ \rightarrow Cu(H_2O)_6^{2+} + H(tren)^+ \quad (4)$$

stopped-flow time scale (on mixing) and that any spectral change for the systems under study were those of reaction 4. This is confirmed by the report that rates of dissociation of L' are in the temperature-jump regime.[14] We have given the values of $\Delta H_1^\ddagger$ and $\Delta S_1^\ddagger$ for these systems that form $Cu(tren)(H_2O)^{2+}$ on mixing in Table III because the results reflect on the reproducibility of the activation parameter data we report and on the low sensitivity of the measured rates to the presence of the acid form of noncoordinating buffer ions. As shown in Table III, the activation parameters obtained for the k_1 step with $Cu(tren)(H_2O)^{2+}$ at low acid concentration are in close agreement, irrespective of the source in solution, with $\Delta H_1^\ddagger = 8.66 \pm 0.62$ kcal/mol and $\Delta S_1^\ddagger = -27.5 \pm 1.4$ eu for average values in $\mu = 0.25$ chloride medium.

However, if $Cu(tren)(H_2O)^{2+}$ solutions are rapidly mixed at higher [acid] conditions (0.20–1.0 M), a more rapid loss of the tren ligand occurs. The kinetic studies reveal that the decay to products also exhibits saturation at high acid concentration, but at a significantly higher rate plateau (ca. 500 s^{-1}) compared to the saturation plateau near 3 s^{-1} (chloride medium) for dissociation of $Cu(tren)(H_2O)^{2+}$ at the lower [acid] range (pH 3–5). The saturation kinetics at high acid concentration exhibit activation parameters of $\Delta H_1^\ddagger = 3.70 \pm 0.63$ kcal/mol and $\Delta S_1^\ddagger = -33.9 \pm 2.1$ eu. The activation parameter data for all ligands examined in this work are listed in Table IV.

General-Acid Catalytic Influence. Because most of the rate studies of this report were carried out in a range of $[H_3O^+]$ above 0.050 M, no common buffer species were present and the influence of general acids HA, for example CH_3COOH, was not examined. However, in the case of $Cu(tren)(H_2O)^{2+}$ in the low [acid] range (pH 3–5) the pH was controlled by the acetate/acetic acid buffer system. Since Read and Margerum had noted the general-acid catalysis for ring opening with $Ni(en)(H_2O)_4^{2+}$,[8] it was thought to be prudent to examine the influence of the protonated form of the acetate buffer, CH_3COOH, on the rate of ring opening of $Cu(tren)(H_2O)^{2+}$. The water position of $Cu(tren)(H_2O)^{2+}$ exchanges rapidly as shown by NMR[15] and the rapid dissociation of nitrogen base ligands, L′, has been noted for eq 3 above.[14] Data were obtained only at 25.0 °C, $\mu = 0.25$. Saturation in rate as a function of $[H_3O^+]$ was observed throughout the range of buffer concentration for 0.05–0.25 M. *Rates in the acetate buffer region were shown to be independent of electrolyte anions.* This is described later in the text. The saturation-limited step, k_1', was measured as a function of the total amount of the buffer species present. The observed saturation k_1' was found to obey the relationship shown in eq 5. The

$$k_1' = k_1 + k_{HOAc}[CH_3COOH]_{tot} \quad (5)$$

data for the influence of $[CH_3COOH]_{tot}$ are given in Table V. The values obtained for a least-squares fit to the data of Table V yield $k_1 = 1.78 \pm 0.14$ s^{-1} and $k_{HOAc} = 9.25 \pm 1.29$ M^{-1} s^{-1}. The data reported for the ring opening at low buffer concentration of 0.050 M are listed in Table II. Some buffer species had to be present to control the pH for the study of $Cu(tren)(H_2O)^{2+}$ at low [acid]. At 0.050 M buffer less than 18% of the total value of k_1' may be attributed to the general-acid term.

The uncertainties in kinetic runs on different days, and therefore the meaning of the intercept eq 5, represent ±10% uncertainty at low buffer concentrations. Therefore, we have

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Table V. Observed Kinetic Parameters As Influenced by the General Acid CH_3COOH

$[CH_3COOH]_{tot}$	$10^2[CH_3COOH]$, M (midrange true concn ± max dev)[a]	k_1',[b] s^{-1}
0.010	0.946 ± 0.099	1.50
0.025	2.37 ± 0.25	2.01
0.050	4.73 ± 0.49	2.43
0.075	7.10 ± 0.74	2.56
0.100	9.46 ± 0.99	2.79
2.250	23.7 ± 2.5	3.85

[a] Minimum value at pH 4.0; maximum value at pH 3.0; effective concentration for eq 5 taken as the mean with ±10.5% uncertainty. [b] $T = 25.0\ °C$, $\mu = 0.25$, $[Cu(tren)(H_2O)^{2+}]_i = 4.30 \times 10^{-3}$ M.

neglected correcting the activation parameter measurements at low $[H_3O^+]$ in the dissociation of $Cu(tren)(H_2O)^{2+}$ for the small correction needed for the general-acid term in eq 5. The magnitudes of the values for $\Delta H_1^\ddagger$ and $\Delta S_1^\ddagger$ for $Cu(tren)(H_2O)^{2+}$ in the range pH 3–5 (Table IV) are clearly different enough from comparison values that the general-acid correction will not alter the conclusions that can be reached for this system relative to the others where no general-acid competition may exist.

Structural Aspects and Comparisons of Reaction Medium. Copper(II) complexes are well-known to be Jahn–Teller distorted with four stronger bonds to the ligands in the plane perpendicular to the elongated axis. This geometry is well-known for the complexes of en, dien, and trien, of the ligands studied here. Like en, dach will adopt coordination with its two nitrogen donors along one edge of the 4-coordinate plane of Cu(II). The ligand dach appears to be strained on coordination to Cu(II), as shown by its 3.15 log unit lower association constant with Cu(II) than for en or 2.95 units lower than that for the related daco ligand.[18] dach has an additional three-carbon saturated bridge between terminal N donors that is absent for en. Piperazine, which like dach has two saturated carbon tethers between the N donors but two carbons long rather than three, forms no chelated Cu(II) complex. Apparently the strain is too severe to allow chelation of piperazine. When $Cu(dach)(H_2O)_4^{2+}$ is mixed with acid solutions, no saturation effect is observed up to 1.00 M in $[H_3O^+]$, but rather strictly first-order behavior is found for the dissociation of dach accelerated by H_3O^+. This behavior and the absence of a $Cu(piperazine)(H_2O)_4^{2+}$ analogue complex suggest that $Cu(dach)(H_2O)_4^{2+}$ is already substantially strained—virtually like CuL^{*2+} of Scheme I. The strain effect appears in the activation parameters for $Cu(dach)(H_2O)_4^{2+}$ compared to those for $Cu(en)(H_2O)_4^{2+}$. The activation enthalpy for dach is about 4.8 kcal/mol lower than that for en while the activation entropy is approximately 20 eu more negative. About 1 kcal of this difference is due to chloride and nitrate counterions compared to ClO_4^- medium. The entropy effect for dach vs. en is almost certain to involve the conformational entropy cost for dach to rotate away from the Cu(II) center compared to the lesser hindered end of en. The activation parameters for dach are similar to those for the dissociation of tren at low [acid] or dien at high [acid] with Cl^- present. Both of the latter systems must have some stress from the rest of the coordinated part of tren or dien as the first en-like fragment begins to dissociate. Hence, comparable entropies of activation are anticipated. One might have thought that $\Delta H^\ddagger$ would be lower for dach than for tren (low [acid]) or dien. However, the enhancement in rate due to a lower activation enthalpy due to strained rings actually is manifest in all of the complexes $Cu(tren)(H_2O)^{2+}$, $Cu(dien)(H_2O)_3^{2+}$, and $Cu(dach)(H_2O)_4^{2+}$ relative to $Cu(en)(H_2O)_4^{2+}$. The activation enthalpy barrier for dissociation of en is about 3.4 kcal/mol higher while the cost in entropy is more positive by ca. 20 eu. These results are consistent with what one normally assumes concerning the costs to achieve structures for intermediates such as II or III. The similarity of the activation parameters, accounting for the strain differences among ligands, for dissociation of en, dien, and tren (at low $[H_3O^+]$) suggests a common mechanism and a related set of intermediates for this path. In the absence of other information any of the intermediates—I, II, or III—might suffice. At higher $[H_3O^+]$ the activation enthalpy for dissociation of tren is 8.3 kcal/mol lower than the barrier for en and 5.0 kcal/mol lower than its own barrier in the pH 3–5 range. The activation entropy for $Cu(tren)(H_2O)^{2+}$ at high $[H_3O^+]$ is more negative by 6 eu than its own barrier at low $[H_3O^+]$. If two pathways to product exist for $Cu(tren)(H_2O)^{2+}$ during acid-induced ring opening, these cannot have the same intermediate. Clearly the pathway at high $[H_3O^+]$ is compensated in activation enthalpy and destablized somewhat in entropy. The logical candidate for the high [acid] dissociation of tren is therefore one like intermediate III, which is attacked directly by H_3O^+, forming one like IV. Bond making to the proton can be used to compensate the bond-breaking barrier for $Cu(tren)(H_2O)^{2+}$ in the high $[H_3O^+]$ range.

The case for different kinetic pathways involving intermediates of different structures is unambiguously drawn out by studies of the activation parameters in the presence of ClO_4^- vs. Cl^- for both paths. The dissociation of $Cu(tren)(H_2O)^{2+}$ in low [acid] is clearly independent of ClO_4^- or Cl^- as shown in Table IVA. Yet the high [acid] dissociation shows that $\Delta H^\ddagger$ decreases from 5.71 ± 1.51 kcal/mol in ClO_4^- medium to 3.70 ± 0.63 kcal/mol in Cl^- solution. The entropies are about the same for activation by either path, either anion. $Cu(dien)^{2+}$ also exhibits an anion sensitivity. $\Delta H^\ddagger$ decreases from 10.60 ± 0.27 kcal/mol (ClO_4^-) to 7.51 ± 0.82 kcal/mol (Cl^-), again by 3.0 kcal/mol compared to 2.0 for the tren high [acid] path. In the $Cu(dien)^{2+}$ dissociation in ClO_4^- the activation entropies are more discriminated by counterion effects, becoming more negative in Cl^- vs. ClO_4^- medium by about 16 eu. In fact, the values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the $Cu(dien)^{2+}$ reaction and $Cu(trien)^{2+}$ reaction in ClO_4^- medium are very comparable, suggesting that the entropy difference is more clearly drawn for the more flexible chain polyamines whereas tren requires a very negative $\Delta S^\ddagger$ near −30 eu by any pathway such that any anion serves about equally well in its counterion interactions with the activated complex. It is logical that a direct H_3O^+ attack pathway should be more sensitive to the nature of electrolyte anions than a path through intermediate II. Protonation forming II happens after the main event of bond rupture between Cu^{2+} and the N donor, and at a distance remote from the Cu^{2+} site. With a direct attack route, approach of H_3O^+ should be assisted by forming ion pairs, H_3O^+,X^-. This would lower the electrostatic repulsion as H_3O^+ attacks the rupturing bond. If it is assumed that some protonation of the lone pair lowers $\Delta H^\ddagger$ by a direct attack path, it is also likely that $\Delta S^\ddagger$ will be a more sensitive function of the nature of X^- if the proper orientation of approach of the H^+ to be transferred is considered. Therefore, it is completely reasonable that although $\Delta H^\ddagger$ becomes less positive, $\Delta S^\ddagger$ will also be more negative even with the compensation of electrostatic attraction, due to orientational factors. This seems to be borne out by the $Cu(dien)^{2+}$ dissociation. Therefore, the high [acid] dissociations of $Cu(tren)^{2+}$ and straight-chain polyamines appear to have the common character of type III intermediates (direct attack of H_3O^+ with anion assistance) while the slower saturating rate of $Cu(tren)^{2+}$ at low [acid]

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Table VI. Acid Dissociation Observed Rate Constants for Cu(II) Polyamine Complexes in Chloride Medium[a]

A. en

	k_{obsd} at T °C					
$[H_3O^+]$, M	20.0	22.8	24.8	27.5	29.6	31.9
0.016	38.2	41.8	45.9	49.1	55.8	72.5
0.033	52.2	59.3	67.9	81.4	90.2	106.5
0.061	70.4	79.0	82.2	101.0	117.9	152.9
0.100	82.9	91.8	104.2	119.9	137.7	161.1
0.330	105.2	113.6	125.4	151.5	169.3	

$\mu = 0.10$; $[CuL_2]_i = 2.90 \times 10^{-3}$ M

B. dien

	k_{obsd} at T °C					
$[H_3O^+]$, M	19.9	23.0	25.0	27.4	30.4	33.0
0.10	111.6	145.7	173.0	199.0	225.9	260.4
0.20	160.0	197.1	229.2	265.6	287.3	326.8
0.30	180.8	213.4	263.3	284.7	307.1	383.8
0.40	197.1	240.3	276.5	312.7	337.5	414.9
0.50	205.9	251.6	289.5	331.2	349.9	

$\mu = 0.25$; $[CuL]_i = 8.85 \times 10^{-3}$ M

C. tren (High $[H_3O^+]$ Condition)

	k_{obsd} at T °C			
$[H_3O^+]$, M	18.4	21.5	23.7	26.3
0.20	122.2	131.6	144.5	155.2
0.40	190.0	194.9	216.3	248.4
0.60	217.0	247.3	266.6	293.4
0.80	262.6	275.5	308.9	318.1
1.00	290.4	302.1	331.4	337.1

$\mu = 0.50$; $[CuL]_i = 4.425 \times 10^{-3}$ M

D. tren (Lower $[H_3O^+]$ Condition)

	k_{obsd} at T °C				
pH	20.2	22.6	25.0	28.2	31.3
3.94	1.56	1.71	1.67[b]	2.19	2.58[c]
3.80	1.69	1.88	1.94	2.44	2.91
3.60	1.91	2.11	2.20	2.76	3.28
3.38	2.12	2.35	2.42	3.08	3.62
3.24	2.23	2.46	2.69	3.28	3.73

$\mu = 0.25$; $[CuL]_i = 4.425 \times 10^{-3}$ M; [buffer] = 0.050 M

E. dach

	k_{obsd} at T °C					
$[H_3O^+]$, M	20.4	22.8	25.6	29.1	33.3	36.6
0.10	19.9	23.4	27.6	33.5	43.5	51.6
0.20	21.2	24.9	29.1	35.2	45.5	54.2
0.30	22.3	26.0	30.2	37.6	47.2	56.9
0.40	23.8	27.1	32.2	39.8	49.9	60.3
0.50	25.6	29.0	34.5	42.8	52.6	63.2

$\mu = 0.25$; $[CuL]_i = 8.85 \times 10^{-3}$ M

F. $[9]aneN_3$

	k_{obsd} at T °C						
$[H_3O^+]$, M	16.6	18.0	22.8	24.6	25.5	29.8	33.0
0.20	5.20	4.88	6.82	6.96	8.45	8.80	11.4
0.30	7.85	6.94	9.70	10.6		14.1	17.2
0.40	9.29	9.05	12.8	12.9	15.0	17.6	19.3
0.50	11.5	10.3	15.3	13.9		19.1	22.6
0.60	12.3	11.5	16.5	14.7	18.0	20.0	24.8
0.70		12.3		15.8		20.3	26.4
0.80					20.7		
1.00					19.6		

$\mu = 0.50$; $[CuL]_i = 8.85 \times 10^{-3}$ M

G. $Cu(tren)(NH_2CH_3)^{2+}$ (Low $[H_3O^+]$ Condition)

	k_{obsd} at T °C				
pH	20.0	22.7	25.0	28.0	31.1
4.01	1.26	1.42	1.51	1.64	2.16
3.80	1.49	1.63	1.76	1.90	2.56
3.60	1.70	1.88	2.13	2.44	2.91
3.41	1.85	2.06	2.36	2.72	3.19
3.20	2.00	2.23	2.54	2.96	2.80

$\mu = 0.25$; $[CuL]_i = 4.425 \times 10^{-3}$ M

H. $Cu_2(tren)_2(Im)^{3+}$ (Low $[H_3O^+]$ Condition)

	k_{obsd} at T °C				
pH	20.9	23.8	25.2	28.3	30.5
3.98	1.58	1.98	1.95[b]	2.56	2.85
3.78	1.77	2.20	2.19	2.87	3.16
3.60	1.90	2.39	2.36	3.03	3.40
3.39	2.04	2.52	2.52[d]	3.20	3.56
3.21	2.16	2.63	2.65[e]	3.38	3.75

$\mu = 0.25$; $[CuL]_i = 4.425 \times 10^{-3}$ M

I. $Cu(tren)(1\text{-}CH_3ImH)^{2+}$ (Low $[H_3O^+]$ Condition)

	k_{obsd} at T °C				
pH	20.1	23.2	24.8	28.2	30.2
3.97	1.16	1.40	1.32[b]	1.81	1.90
3.77	1.26	1.53	1.50[f]	1.97	2.07
3.60	1.36	1.64	1.65[g]	2.12	2.25
3.40	1.42	1.72	1.71	2.20	2.34
3.25	1.49	1.80	1.80	2.31	2.48

$\mu = 0.25$; $[CuL]_i = 4.425 \times 10^{-3}$ M

[a] All k_{obsd} values are the average of three runs; a deviation of ±3% in k_{obsd} was the difference in runs. Units of k are s^{-1}. Accuracy is implied to three significant figures only. [b] pH 4.00. [c] pH 3.98. [d] pH 3.40. [e] pH 3.25. [f] pH 3.80. [g] pH 3.61.

conditions shows the results anticipated for type II systems (ring rupture is complete at the time of protonation).

The cyclic amine, $[9]aneN_3$, has three nitrogen base sites, each linked by ethylene bridges. If tethering of sites manifests strain for straight-chain polyamines, one would anticipate a large effect for $[9]aneN_3$. Because the coordination of $[9]aneN_3$ must occur by facial coordination of three positions of a distorted octahedron on Cu(II) rather than in a meridonal manner, as for $Cu(dien)(H_2O)_3{}^{2+}$, one would anticipate activation parameters for dissociation of $Cu([9]aneN_3)(H_2O)_3{}^{3+}$ that are very different from those for $Cu(en)(H_2O)_4{}^{2+}$. The results presented in Table IV bear out these anticipated results. The activation enthalpy for the geometrical reorganization needed to make CuL^{*2+} is very small, *virtually zero, within experimental error*. However the greatly reduced enthalpy barrier to Cu(II)–N bond rupture does not result in an extremely more rapid dissociation of $[9]aneN_3$ relative to the normal polyamines as there must also be a very negative activation entropy associated with tethering of the dissociating nitrogen group to two adjacent bound nitrogen sites. The additional strain associated with breaking a nitrogen base away from Cu(II) in $Cu([9]aneN_3)(H_2O)_3{}^{2+}$ represents ca. 20 eu more negative entropy than feedback from nonadjacent ethylene-bridged nitrogen sites as in $Cu(tren)(H_2O)^{2+}$ or $Cu(dien)(H_2O)_3{}^{2+}$, when Cl^- solution systems are compared for each case. In $[9]aneN_3$ the ring-opening event is entropy controlled. The strain presented by two two-carbon tethers between the *same* adjacent N donor sites is so severe that piperazine cannot coordinate in the bidentate fashion as shown by the absence of such a complex, and the influence is only

Table VII. Acid Dissociation Rate Constants for Cu(II) Polyamine Complexes in Perchlorate Medium[a]

A. dien

	k_{obsd} at T °C				
$[H_3O^+]$, M	15.8	19.5	23.0	25.0	27.2
0.10	102.2	129.9	161.2	184.6	206.0
0.20	123.9	154.0	195.2	237.7	263.6
0.30	142.3	186.1	230.0	268.3	294.7
0.40	156.2	195.5	245.8	272.6	305.6
0.50	157.7	201.1	261.2	288.4	328.2

$\mu = 0.25$ ($LiClO_4$); $[CuL] = 8.85 \times 10^{-3}$ M

B. tren (High $[H_3O^+]$ Condition)

	k_{obsd} at T °C				
$[H_3O^+]$, M	17.8	19.4	20.4	22.4	28.0
0.20	89.5	96.1	98.3	108.8	161.5
0.40	142.3	144.5	167.5	176.3	257.0
0.60	191.8	220.6	216.3	237.7	324.8
0.80	211.6	242.0	248.4	275.0	366.0
1.00	249.2	277.6	284.3	308.0	396.4

$\mu = 0.50$ ($LiClO_4$); $[CuL]_i = 4.425 \times 10^{-3}$ M

C. tren (Lower $[H_3O^+]$ Condition)

	k_{obsd} at T °C			
pH	19.8	22.5	25.0	27.5
4.08	0.91	1.06	1.25	1.33
3.83	1.09	1.27	1.43	1.59
3.61	1.24	1.45	1.65	1.85
3.42	1.40	1.62	1.87	2.12
3.17	1.57	1.83	2.12	2.40

$\mu = 0.25$ ($LiClO_4$); $[CuL]_i = 4.425 \times 10^{-3}$ M

D. trien

	k_{obsd} at T °C					
$[H_3O^+]$, M	14.3	16.8	19.0	21.3	23.4	25.9
0.01	5.61	6.75	10.16	10.27	10.62	11.11
0.02	5.87	7.93	11.44	11.51	8.29	12.23
0.03	9.86	10.83	15.52	16.66	12.53	18.05
0.04	13.67	15.86	22.37	24.56	17.40	25.03
0.05	15.37	17.42	27.73	30.20	18.69	28.57

$\mu = 0.05$ ($LiClO_4$); $[CuL]_i = 4.425 \times 10^{-3}$ M

E. en

	k_{obsd} at T °C				
$[H_3O^+]$, M	15.0	17.2	19.8	23.0	25.1
0.0164	25.3	28.4	35.4	40.1	43.8
0.0328	35.6	40.2	49.3	59.3	73.8
0.0606	41.5	51.1	61.1	73.7	88.1
0.100	45.7	58.0	71.4	79.3	101.6
0.330	53.6	73.8	79.0	96.0	119.7

$\mu = 0.10$ ($LiClO_4$); $[CuL]_i = 2.90 \times 10^{-3}$ M; $[CuL_2]_i = 3.80 \times 10^{-4}$ M

[a] All k_{obsd} values are the average of three runs; a deviation of ±3% in k_{obsd} was the difference in runs. Units of k are s^{-1}. Accuracy is implied to three significant figures only.

Table VIII. Formation Constant of $CuL(H_2O)_n{}^{2+}$

L	log of assn const	conditions	ref
en	10.76	$\mu = 0.5$ (KNO_3), 25 °C	15
dien	16.0	$\mu = 0.10$ (KCl), 20 °C	16
trien	20.1	$\mu = 0.1$ (KCl), 25 °C	17
[9]aneN_3	15.5	$\mu = 0.1$ (KNO_3), 25 °C	12
daco	10.56	$\mu = 0.10$, 25 °C	18
tren	18.8	$\mu = 0.1$, 25 °C	19
dach	7.61	$\mu = 0.5$ (KNO_3), 25.4 °C	23

partially relaxed by expansion of the tether by one carbon unit in dach, such that the mechanism in Scheme I is short-circuited through step 2 for $Cu(dach)(H_2O)_4{}^{2+}$.

Since only one acid-dependent spectral change is observed for dissociation of the Cu(II) polyamines, the rupture of the first Cu(II)–N bond appears to be rate determining. This contrasts to the Ni(II) case, where sequential changes are often detected.[7] Once partial coordination of the LH^+ ligand is achieved for Cu(II), dissociation of the next N center in the polyamine is accelerated by the charge of the cationic ligand such that the rates for breaking sequential Cu(II)–N bonds are more rapid than that that for breaking the first unit. Kodama and Kimura have measured the rate of formation of $Cu([9]aneN_3)(H_2O)_3{}^{2+}$ by the stopped-flow method.[20] These workers report that in acidic solution only the monoprotonated form of [9]aneN_3 is reactive for formation of the complex. If one combines the formation constant of $Cu([9]aneN_3)(H_2O)_3{}^{2+}$ (1.70×10^{16})[21] with the first pK_a of [9]aneN_3 (10.59),[21] together with the rate of formation of the LH^+ species (6.8×10^6 M^{-1} s^{-1}) as found by Kodama and Kimura,[20] a value of 12 M^{-1} s^{-1} is calculated for the second-order acid dissociation of $[9]aneN_3H^+$ from $Cu([9]aneN_3)(H_2O)_3{}^{2+}$. Under the conditions of the Kodama and Kimura study of the formation reaction, no saturation or dependence on $[H_3O^+]$ was reported. Their conditions are analogous to the part of the acid dissociation kinetic curve where dissociation is approximately first-order in $[H_3O^+]$. The lowest value of $[H_3O^+]$ in our experiments for dissociation of [9]aneN_3 from Cu(II) was 0.20 M. At this $[H_3O^+]$ one calculates an apparent first-order rate constant of 2.4 s^{-1}. Our experimental value of 5.0 s^{-1}, obtained at an ionic strength different from that used to measure the formation constant of $Cu([9]aneN_3)(H_2O)_3{}^{2+}$, is still quite close to the calculated result.

Rorabacher's group has recently investigated the dissociation of NH_3 from $Cu(NH_3)(H_2O)_5{}^{2+}$ and these workers report $\Delta H^{\ddagger} = 9.6$ kcal/mol, $\Delta S^{\ddagger} = -7$ eu, and $k_{298} = 2 \times 10^4$ s^{-1} for the process.[22] As with $Ni(NH_3)(H_2O)_5{}^{2+}$, Rorabacher has not observed an acceleration of the rate by H_3O^+. With his value for comparison, the activation enthalpy to open a chelate ring even by the H_3O^+-accelerated path is greater than the enthalpy to rupture the monodentate group by 3 kcal/mol. The result is the same effect found for $Ni(en)(H_2O)_4{}^{2+}$ vs. $Ni(NH_3)(H_2O)_5{}^{2+}$ although in the Cu(II) case the chelate ring vs. monodentate donor has a smaller $\Delta\Delta H^{\ddagger}$ of 1–2 kcal/mol than for the Ni(II) case. The factor of about 10^2 faster ligand loss for monodentate vs. chelate is also retained for Cu(II).

If one examines the data in Tables I and II for trends in the values of k_1, it is observed that for a given ligand k_1 increases at most a factor of 2 from 18 to 33 °C. The following order is also noted in comparing ligands at 25 °C for k_1 in chloride medium:

$$\begin{array}{llllllll} \text{tren (high }[H_3O^+]) & > & \text{dien} & > & \text{trien} & > & \text{en} & > \\ 496\ s^{-1} & & 348\ s^{-1} & & 295\ s^{-1} & & 126\ s^{-1} & \end{array}$$

$$\begin{array}{lll} [9]aneN_3 & > & \text{tren (low }[H_3O^+]) \\ 36\ s^{-1} & & 3.0\ s^{-1} \end{array}$$

The first ring opening of the analogous Ni(II) complexes follows the order reported for dissociation as follows:

$$\begin{array}{lllllll} \text{tren} & > & \text{dien} & \sim & \text{trien} & > & \text{en} \\ 66\ s^{-1} & & 14\ s^{-1} & & 15\ s^{-1} & & 0.15\ s^{-1} \end{array}$$

The order appears to be the same for Ni(II) and Cu(II) excluding the entry for [9]aneN_3 and tren at low $[H_3O^+]$. Since the rate of substitution at $Cu(H_2O)_6{}^{2+}$ by neutral

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polyamine ligands is rapid and approaches the diffusion limit (ca. 10^8 s^{-1}), one normally anticipates that the dissociation rate would parallel the inverse of the formation constant for the CuL^{2+} complex. The order given directly above does not follow the predicted inverse order on this basis as shown by the stability constants given in Table VII. Such a predicted order would be valid only for dissociation of the neutral amine and not the protonated form as has been studied in this work. A likely explanation for the change in dissociation order when the protonation of the leaving group is involved is that a different degree of stretching of the Cu–N bond is involved when H_3O^+ intercepts the leaving nitrogen donor than when one obtains a calculated rate constant based on the dissociation of a neutral nitrogen donor, requiring larger Cu–N displacement to become the broken structure.

Even with the short series above, the influence of increasing the polyamine chain length and building up ring strain with increasing number of chelate rings is observed for both Cu(II) and Ni(II). Considering the difference in coordination geometry for $Cu([9]aneN_3)(H_2O)_3^{2+}$ and $Cu(tren)(H_2O)^{2+}$ relative to the linear amines, a decrease in k_1 is noted as the ground-state structure departs from distorted octahedral and is least for the 5-coordinate system. This analysis is made complicated by changes in mechanism for the later entries of the series.

Examination of the ratio of productive to unproductive events, k_2/k_{-1}, also establishes a trend:

tren (low $[H_3O^+]$) > en > trien > dien >
1.2×10^4 32 20 10
tren (high $[H_3O^+]$) > $[9]aneN_3$
4.6 1.2

The temperature dependence of k_2/k_{-1} is only slightly increasing for a general ligand (nearly constant for both paths with tren) and decreases very slightly for en in the range 18–33 °C. Since the ratio involves two rate constants, it is difficult to factor out definitively what the trend shown above might mean. The ratio for k_2/k_{-1} is *significantly larger* for tren at low [acid] conditions than any of the other ligand dissociations. Since the frequency to achieve the transition state is lower for tren at low [acid] (ca. 3 s^{-1}), a greater degree of bond distortion is likely implied in the step k_1. Once the geometry is achieved, however, the tendency to proceed to product relative to return to the ground state is more favored than for the lesser strained straight-chain amines. The difference in the k_2/k_{-1} ratio again supports a different type of intermediate for the $Cu(tren)(H_2O)^{2+}$ dissociation at low [acid]. If the low [acid] path involves II, then again the other systems must be more likely III. As the ligand structure becomes more complicated at the right-hand side of the series, the ratio approaches unity. Folding of the ligand structure becomes equally difficult for complete rupture of the Cu–N bond or its return.

Conclusion

It appears that for ring opening of polyamine donors on Cu(II) the intermediates are very similar to those described in the literature for Ni(II). However, with tren as a ligand, Ni(II) remains 6-coordinate while Cu(II) changes to coordination number 5.[15] This subtle change appears to be responsible for more than one set of geometries that favor the ultimate dissociation of the ligand for the Cu(II) complex. One intermediate, presumably similar to III, can be protonated at higher values of $[H_3O^+]$ with compensation in the bond breaking. Another intermediate geometry is obtained at a rate nearly 250 times slower. This intermediate behaves differently from the intermediates achieved for dissociation of straight-chain polyamines such as en and dien in terms of sensitivity to anions in the medium. Since this intermediate is achieved more slowly than the one intercepted only at high $[H_2O^+]$ for $Cu(tren)(H_2O)^{2+}$, the more slowly formed intermediate appears to be most closely related to intermediate II in which protonation of the pendant ligand prevents ring closure, while the others show features required for a direct attack pathway involving III.

We have only examined the influence of the general-acid catalysis of acetic acid for $Cu(tren)(H_2O)^{2+}$ in the pH range 3–5. A modest increase of 18% in the rate at 0.05 M buffer was observed. Margerum's values for the dissociation of $Ni(en)(H_2O)_4^{2+}$ show a 12% increase at the same concentration of free acetic acid with $k_{1d} = 0.108 \pm 0.008$ s^{-1} and $k_{HOAc} = 0.30 \pm 0.01$ M^{-1} s^{-1}.[8] Both terms in the rate law given by eq 5 are larger for Cu(II), by about 17- and 30-fold, respectively. The percent changes for a given amount of buffer species are rather comparable. It would appear that the Cu(II) systems are amenable to about the same degree of general-acid catalysis as are ring openings of polyamines on Ni(II).

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