labilizing effect on the leaving X. Then, X can leave the first coordination sphere without help from the entering H_2O ligand. In the transition state of reaction 5, the entering H_2O is not included in the first coordination sphere (D mechanism). In contrast, $CoX(NH_3)_5^{2+}$ has no such ligand of labilizing power. In this case, X leaves the first coordination sphere only when prompted by the simultaneous intrusion of the H_2O ligand into the first coordination sphere. In the transition state of reaction 1, the entering H_2O would be included in the first coordination sphere to some extent (I mechanism). Along this line of argument, the acid-independent aquations of *cis*-$CoX(NH_3)_4(H_2O)^{2+}$ (reaction 14) should proceed through the I mechanism, since neither H_2O nor NH_3 ligand has labilizing power, whereas aquations of *cis*-$Co(OH)X(NH_3)_4^+$ might proceed through a mechanism intermediate between I and D, since the OH^- ligand has a labilizing power, which may not be so strong as for NH_2^-.

In conclusion, the mechanistic information obtained from the volume profiles clearly coincided with the mechanistic expectation drawn from the labilizing power consideration. An important factor for this success may be that the complexes dealt with in this work have similar structures. They contain only simple molecular monodentate ligands, four of which are NH_3.

Registry No. *cis*-$CoCl(NH_3)_4(H_2O)^{2+}$, 18460-69-0; *cis*-$CoBr(NH_3)_4(H_2O)^{2+}$, 44433-46-7; *cis*-$Co(NO_3)(NH_3)_4(H_2O)^{2+}$, 104194-91-4.

Supplementary Material Available: Table A, giving the individual values of k_{obsd} (3 pages). Ordering information is given on any current masthead page.

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Complexation Kinetics of Diamino Diamides with Copper(II) in Aqueous Solution

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Equilibrium constants are determined for the protonation and metal complexation of the copper(II) complexes with *N,N'*-bis(β-carbamoylethyl)ethylenediamine (BCEN), *N,N'*-bis(β-carbamoylethyl)trimethylenediamine (BCTN), *N,N'*-bis(β-carbamoylethyl)-1,2-propylenediamine (BCMEN), and *N,N'*-bis(β-carbamoylethyl)-2-hydroxytrimethylenediamine (BCHTN) in 0.10 M $NaClO_4$ at 25.0 °C. The stability constants in 0.10 M $NaClO_4$ at 25.0 °C for the complexes $Cu(BCEN)^{2+}$, $Cu(BCTN)^{2+}$, $Cu(BCMEN)^{2+}$, and $Cu(BCHTM)^{2+}$ are $\log k_f = 12.58$, 10.27, 12.62, and 10.07, respectively. The formation kinetics of these copper(II) complexes have been studied under the same conditions with use of the stopped-flow technique. The resolved formation rate constants ($M^{-1}\ s^{-1}$ in 0.10 M $NaClO_4$ at 25.0 °C) for copper(II) reacting with the unprotonated and monoprotonated ligands BCEN, $HBCEN^+$, BCTN, $HBCTN^+$, BCMEN, $HBCMEN^+$, BCHTN, and $HBCHTN^+$ are 3.35×10^8, 4.75×10^4, 1.48×10^8, 9.21×10^4, 2.23×10^8, 3.76×10^4, 7.80×10^8, and 4.78×10^5, respectively. Three possible pathways for the complexation reactions of copper(II) with these ligands are discussed. The first metal–nitrogen bond formation is proposed as the rate-determining step for the reactions of copper(II) with the unprotonated ligands; proton loss is the rate-limiting step in the reactions of copper(II) with the monoprotonated ligands. Similarly, in dissociation reactions of these copper(II) complexes, the rate-determining step for the water dissociation pathway is the breakage of the second copper–nitrogen bond; the rate-determining step for the proton-assisted pathway is the protonation of the released amino group. The reactivity order for the dissociation reaction is $[Cu(BCHTN)]^{2+} > [Cu(BCTN)]^{2+} > [Cu(BCEN)]^{2+}$, $[Cu(BCMEN)]^{2+}$. The important factors determining the reactivity of these complexes are considered. The kinetic results of the formation and dissociation reactions of these complexes are consistent with a dissociative mechanism.

Introduction

In a previous contribution we report the formation and dissociation kinetics of nickel(II) complexes of four closely related diamino diamides.[1] These four ligands are depicted in Chart I. Three possible pathways for the reactions of nickel(II) ion with these ligands have been described and discussed. It is proposed that each of these diamino diamides reacts with nickel(II) ion by the stepwise formation of coordinate bonds, where the rate-determining step is the formation of the first nickel–nitrogen bond and the subsequent bonding is rapid.

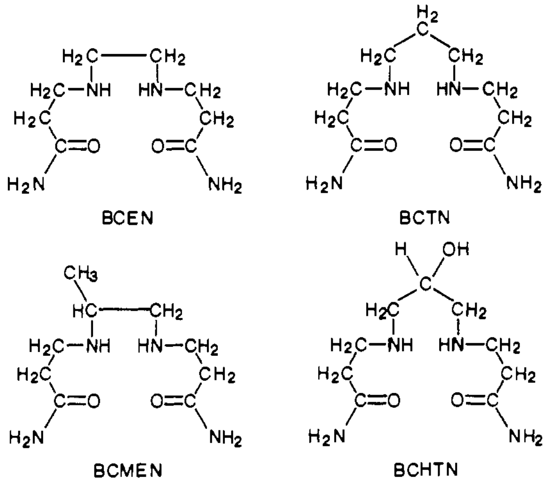
In the present contribution we present kinetic results obtained by stopped-flow measurements on the formation reactions of these four ligands with copper(II) ion (eq 1), where *n* is 0–2. Here L represents the diamino diamides depicted in Chart I.

$$Cu^{2+} + H_nL^{n+} \xrightarrow{k_f} CuL^{2+} + nH^+ \qquad (1)$$

Experimental Section

Reagents. The ligands BCEN, BCTN, BCMEN, and BCHTN were the same as those reported previously.[2-4] All other chemicals used were of GR grade from Merck or Fluka.

Chart I



Measurements. For pH measurements a Radiometer PHM64 instrument equipped with a GK2401B combined electrode was used. The pH was standardized with NBS buffers. The hydrogen ion and hydroxide ion concentrations in 0.10 M $NaClO_4$ were calculated from $-\log [H^+] = pH - 0.11$ and $k_w = 10^{-13.78}$.[5-7] Appropriate aliquots of standard solutions of ligand or ligand and metal were titrated with a standard CO_2-free sodium hydroxide solution. In all titrations the ionic strength

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0020-1669/86/1325-3890$01.50/0

Table I. Protonation Constants of Diamino Diamides and Stability Constants of Their Copper(II) Complexes[a] at 25.0 ± 0.1 °C and μ = 0.10 M ($NaClO_4$)

log K	BCEN	BCTN	BCMEN	BCHTN
log $K_1^{H\,b}$	8.78 ± 0.04	9.22 ± 0.06	8.84 ± 0.05	8.53 ± 0.06
log $K_2^{H\,b}$	5.82 ± 0.03	6.89 ± 0.04	5.54 ± 0.04	6.60 ± 0.06
log K_f	12.58 ± 0.07	10.20 ± 0.08	12.62 ± 0.08	10.07 ± 0.08

[a] $K_1^H = [HL^+]/([H^+][L])$, $K_2^H = [H_2L^{2+}]/([H^+][HL^+])$, $K_f = [CuL^{2+}]/([Cu^{2+}][L])$. [b] Reference 1.

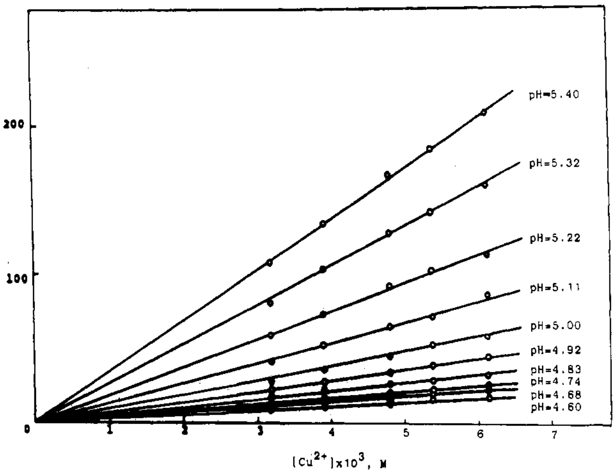

Figure 1. Observed first-order rate constants (k_{obsd}) as a function of $[Cu^{2+}]$ for the formation of $[Cu(BCEN)]^{2+}$ at 25.0 ± 0.1 °C and μ = 0.10 M ($NaClO_4$).

was maintained relatively constant by using 0.10 M $NaClO_4$ as supporting electrolyte. The solutions were protected from air by a stream of humidified prepurified nitrogen and were maintained at 25.0 ± 0.1 °C during measurements. The concentrations of ligand and metal ion employed for the equilibrium work are in the range of 3×10^{-4}–1×10^{-2} M. The methods of calculations are the same as reported previously.[8,9] The equilibrium constants were obtained by a linear least-squares fit of the data by using the CDC Cyber-172 computer.

Standard solutions of ligands, borate–mannitol buffers, and sodium perchlorate were prepared by weight. The copper(II) ion concentration was standardized by EDTA titration. The kinetics of the copper(II) complex formation reactions with BCEN, BCTN, BCMEN, and BCHTN were studied spectrophotometrically at 252, 258, 252, and 255 nm, respectively, with a Union Giken RA-401 stopped-flow spectrophotometer equipped with a Union RA-415 rapid-scan attachment. For the spectrophotometric experiments the pH was controlled with a borate–mannitol buffer,[10] which was also incorporated into the reference solution. Recrystallized $NaClO_4$ was used to maintain constant ionic strength at μ = 0.10 M in all solutions. Kinetic studies were carried out under pseudo-first-order conditions by using at least a 10-fold excess of copper(II). The concentrations of ligand and metal ion employed for the kinetic work are in the range of 2×10^{-4}–7×10^{-3} M.

Results

Job's method of continuous variations was adopted for the determination of the composition of the complex. The results are deposited as supplementary material and indicated that copper(II) forms a 1:1 complex with each of these diamino diamides. The stability constants of the copper(II) complexes with these diamino diamides at 25.0 °C and 0.10 M $NaClO_4$, $K_f = [CuL^{2+}]/([Cu^{2+}][L])$, obtained in this work are listed in Table I. The values of these constants are virtually the same as those at 0.10 M $NaNO_3$ reported previously.[11]

The kinetics of the reactions of copper(II) and these ligands were studied at 25 °C, μ = 0.10 M, and pH 4.60–5.40. Under these conditions, the complex formation reactions were found to proceed to completion. Kinetic studies were carried out under pseudo-first-order conditions by using at least a 10-fold excess of copper(II). The observed pseudo-first-order rate constants are given in Tables II–V. Plots of k_{obsd} vs. $[Cu^{2+}]$ give straight lines according to eq 2 (Figures 1–4), where $[\sum L]$ represents the total

$$d[CuL^{2+}]/dt = K_f[Cu^{2+}][\textstyle\sum L] \qquad (2)$$

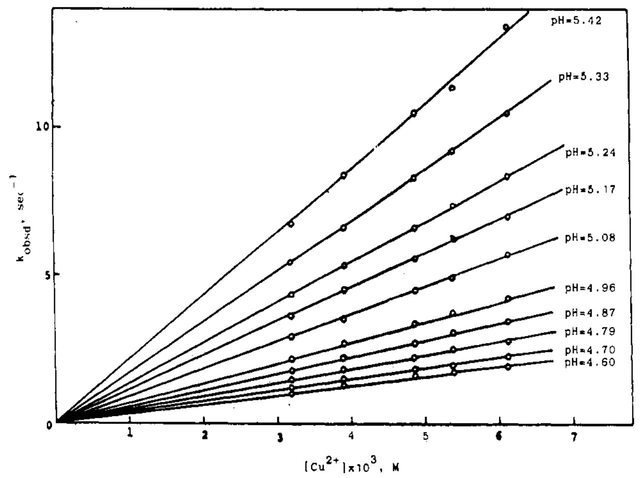

Figure 2. Observed first-order rate constants (k_{obsd}) as a function of $[Cu^{2+}]$ for the formation of $[Cu(BCTN)]^{2+}$ at 25.0 ± 0.1 °C and μ = 0.10 M ($NaClO_4$).

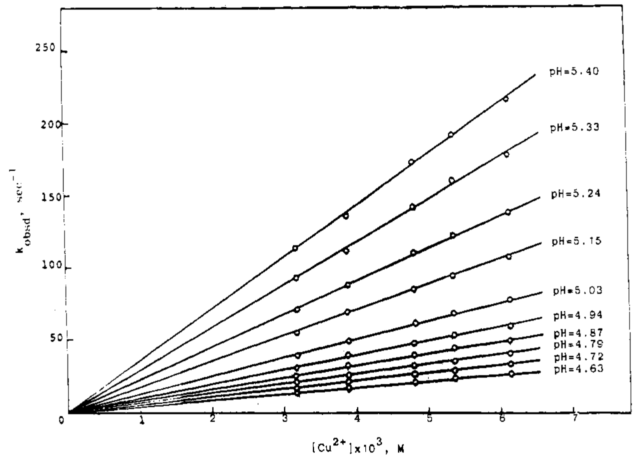

Figure 3. Observed first-order rate constants (k_{obsd}) as a function of $[Cu^{2+}]$ for the formation of $[Cu(BCMEN)]^{2+}$ at 25.0 ± 0.1 °C and μ = 0.10 M ($NaClO_4$).

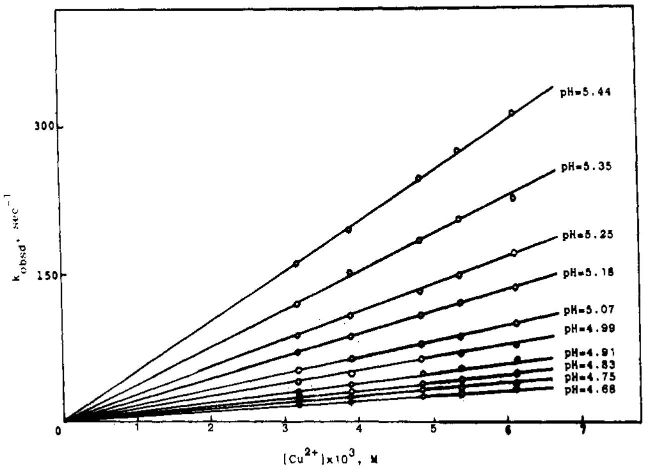

Figure 4. Observed first-order rate constants (k_{obsd}) as a function of $[Cu^{2+}]$ for the formation of $[Cu(BCHTN)]^{2+}$ at 25.0 ± 0.1 °C and μ = 0.10 M ($NaClO_4$).

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Table II. Experimental Observed Rate Constants for Reaction of the Copper(II) Ion with BCEN at 25.0 ± 0.1 °C and μ = 0.1 M ($NaClO_4$)

pH	10^4[BCEN], M	$10^3[Cu^{2+}]$, M	k_{obsd}, s^{-1}	pH	10^4[BCEN], M	$10^3[Cu^{2+}]$, M	k_{obsd}, s^{-1}
5.40	2.45	3.18	108	4.92	2.45	3.18	22.5
		3.92	134			3.92	28.6
		4.88	167			4.88	35.5
		5.39	184			5.39	39.3
		6.12	208			6.12	44.6
5.32	2.45	3.18	81.4	4.83	2.45	3.18	17.4
		3.92	104			3.92	21.5
		4.88	128			4.88	27.1
		5.39	142			5.39	29.8
		6.12	160			6.12	33.4
5.22	2.45	3.18	58.7	4.74	2.45	3.18	13.5
		3.92	73.8			3.92	16.7
		4.88	91.9			4.88	20.8
		5.39	102			5.39	22.8
		6.12	113			6.12	26.2
5.11	2.45	3.18	40.9	4.68	2.45	3.18	11.2
		3.92	52.8			3.92	15.1
		4.88	64.4			4.88	17.5
		5.39	71.5			5.39	20.2
		6.12	80.6			6.12	23.1
5.00	2.45	3.18	29.5	4.60	2.45	3.18	9.05
		3.92	36.7			3.92	11.5
		4.88	45.5			4.88	13.9
		5.39	50.1			5.39	16.1
		6.12	57.2			6.12	17.2

concentration of all species of uncomplexed ligand. The slopes of these plots give the values of the formation rate constants (Table VI).

In the pH range of this study, the predominant form of the ligand is H_2L^{2+}, and the reactive species are L and HL^+, where L and HL^+ represent the unprotonated and monoprotonated diamino diamides, respectively. Reactions of these species with Cu^{2+} to produce the chelate CuL^{2+} is then considered to occur as in eq 3.

$$H_2L^{2+} \rightleftarrows HL^+ + H^+ \qquad 1/K_2^H = [HL^+][H^+]/[H_2L^{2+}]$$

$$HL^+ \rightleftarrows L + H^+ \qquad 1/K_1^H = [L][H^+]/[HL^+]$$

$$Cu^{2+} + HL^+ \rightarrow CuL^{2+} + H^+ \qquad k_{Cu}{}^{HL}$$

$$Cu^{2+} + L \rightarrow CuL^{2+} \qquad k_{Cu}{}^{L} \tag{3}$$

A rate law of a form that involves the predominant species is described by eq 4.[12,13]

$$d[CuL^{2+}]/dt = k[Cu^{2+}][H_2L^{2+}]/[H^+] + k'[Cu^{2+}][H_2L^{2+}]/[H^+]^2$$

Combining this and eq 2 yields

$$k_f[\Sigma L]/[L] = k[H_2L^{2+}]/[H^+] + k'[H_2L^{2+}]/[H^+]^2 \tag{4}$$

or

$$k_f[\Sigma L] = kK_1{}^HK_2{}^H[H^+] + k'K_1{}^HK_2{}^H \tag{5}$$

Here $[\Sigma L]$ represents the total concentration of all species of uncomplexed ligand. Plots of $k_f[\Sigma L]/[L]$ against $[H^+]$ are shown in Figures 5 and 6. From (5), the intercept gives a value for $k'K_1{}^HK_2{}^H$ and the slope equals $kK_1{}^HK_2{}^H$. The values of $k_{Cu}{}^L$ and $k_{Cu}{}^{HL}$ obtained respectively as $k'K_1{}^HK_2{}^H$ and $kK_2{}^H$ are listed in Table VII. The dissociation rate constants obtained from the formation rate constants and the corresponding stability constants are given in Table VII.

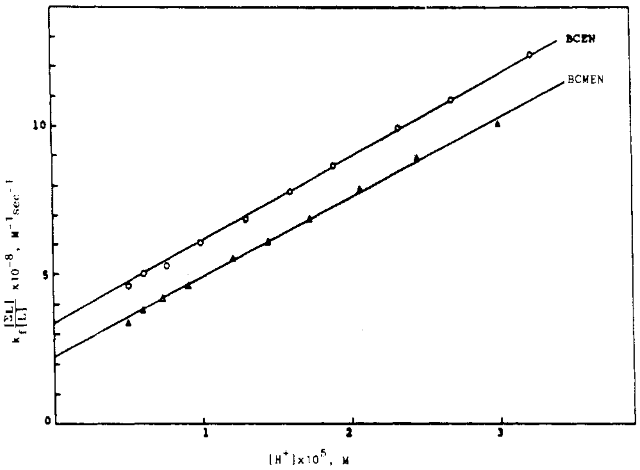

Figure 5. Resolution of the formation rate constants for copper(II) reacting with unprotonated and monoprotonated diamino diamides at 25.0 ± 0.1 °C and μ = 0.10 M ($NaClO_4$). Plots of eq 5: (○) BCEN; (△) BCMEN.

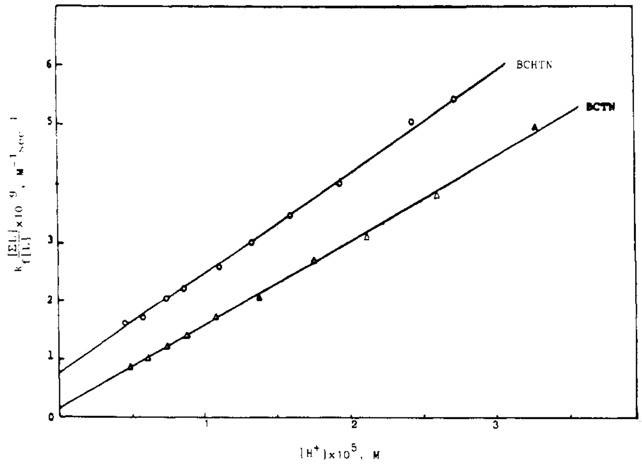

Figure 6. Resolution of the formation rate constants for copper(II) reacting with unprotonated and monoprotonated diamino diamides at 25.0 ± 0.1 °C and μ = 0.10 M ($NaClO_4$). Plots of eq 5: (○) BCHTN; (△) BCTN.

Discussion

The formation rate constants for copper(II) reacting with these diamino diamides listed in Table VII are very insensitive to the nature of the entering ligand. These constants span less than a factor of 7. In contrast, the resolved dissociation rate constants of these complexes depend heavily on the nature of the diamino

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Table III. Experimental Observed Rate Constants for Reaction of the Copper(II) Ion with BCTN at 25.0 ± 0.1 °C and μ = 0.10 M ($NaClO_4$)

pH	10^4[BCTN], M	10^3[Cu^{2+}], M	k_{obsd}, s^{-1}	pH	10^4[BCTN], M	10^3[Cu^{2+}], M	k_{obsd}, s^{-1}
5.42	2.44	3.18	6.78	4.96	2.44	3.18	2.18
		3.92	8.46			3.92	2.72
		4.88	10.5			4.88	3.37
		5.39	11.3			5.39	3.73
		6.12	13.4			6.12	4.22
5.33	2.44	3.18	5.43	4.87	2.44	3.18	1.78
		3.92	6.69			3.92	2.21
		4.88	8.34			4.88	2.72
		5.39	9.22			5.39	3.04
		6.12	10.5			6.12	3.45
5.24	2.44	3.18	4.36	4.79	2.44	3.18	1.48
		3.92	5.35			3.92	1.85
		4.88	6.66			4.88	2.25
		5.39	7.41			5.39	2.51
		6.12	8.36			6.12	2.80
5.17	2.44	3.18	3.65	4.70	2.44	3.18	1.21
		3.92	4.55			3.92	1.51
		4.88	5.61			4.88	1.82
		5.39	6.27			5.39	1.98
		6.12	7.02			6.12	2.32
5.08	2.44	3.18	2.94	4.60	2.44	3.18	1.03
		3.92	3.57			3.92	1.31
		4.88	4.50			4.88	1.61
		5.39	4.93			5.39	1.78
		6.12	5.71			6.12	1.94

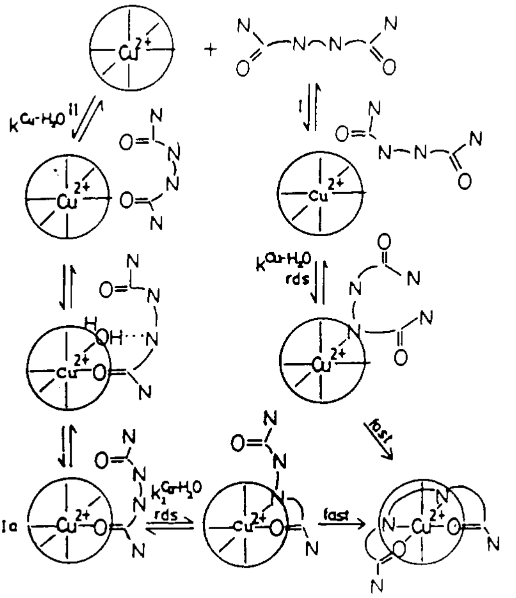

Figure 7. Possible pathways for the reaction of copper(II) with BCEN, BCTN, or BCMEN. The circle represents the division between inner-sphere coordination and outer-sphere association.

diamide, the leaving group, and vary over some 3 orders of magnitude. Clearly, these reactions are much more sensitive to the kind of bond being broken than to the kind being formed. Hence, these reactions take place via a dissociative-intimate mechanism. A similar effect of entering and leaving ligands on rate is also found in the formation and dissociation reactions of nickel(II) complexes of these diamino diamides,[1] suggesting a common mechanism, in which hydrogen-bond formation in the outer-sphere complex between an amino nitrogen atom and a proton of one of the coordinated water molecules increased the values of the outer-sphere association constant, K_{os}, and the rate constant for water exchange of aquated metal ion, K^{M-H_2O},[14,15] resulting in relatively large formation rate constants.

For the formation reactions of copper(II) with unprotonated and monoprotonated BCEN, BCMEN, and BCTN, there are two alternate pathways, initial bonding to an amino nitrogen donor atom and initial bonding to an amide oxygen donor atom (Figure 7). For the reactions of copper(II) with unprotonated and monoprotonated BCHTN, a third pathway, initial bonding to an alcoholic oxygen donor atom, must be taken into consideration (Figure 8). As has been shown in the earlier study on these four ligands reacting with nickel(II),[1] the first metal-nitrogen bond formation is proposed as the rate-determining step for the copper(II) reaction with the unprotonated diamino diamides. Unlike the formation reactions of nickel(II) complexes, proton loss is the rate-limiting step in the reactions of monoprotonated diamino diamides with copper(II).[16,17]

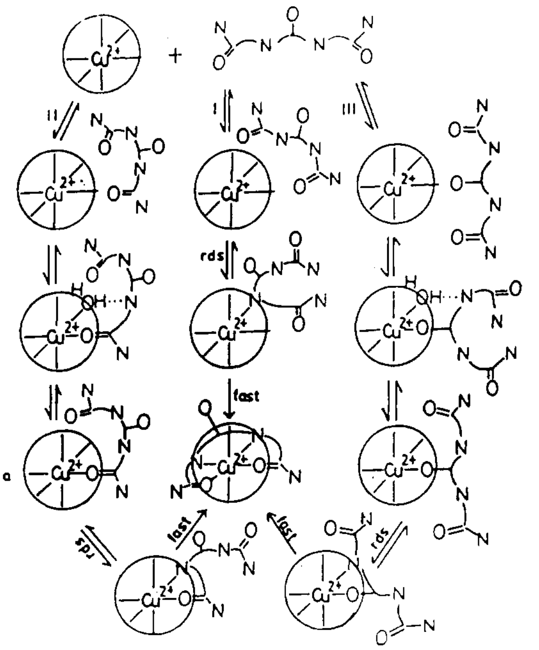

Figure 8. Possible pathways for the reaction of copper(II) with BCHTN. The circle represents the division between inner-sphere coordination and outer-sphere association.

An important aspect of the chemistry of these complexes is the ability of the amide group to deprotonate and coordinate through

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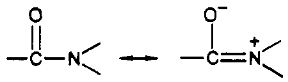
Table IV. Experimental Observed Rate Constants for Reaction of the Copper(II) Ion with BCMEN at 25.0 ± 0.1 °C and μ = 0.10 M (NaClO$_4$)

pH	10^4[BCMEN], M	10^3[Cu^{2+}], M	k_{obsd}, s^{-1}	pH	10^4[BCMEN], M	10^3[Cu^{2+}], M	k_{obsd}, s^{-1}
5.40	2.56	3.18	114	4.94	2.56	3.18	31.2
		3.92	136			3.92	38.5
		4.88	173			4.88	47.9
		5.39	192			5.39	53.1
		6.12	216			6.12	59.8
5.33	2.56	3.18	92.5	4.87	2.56	3.18	25.8
		3.92	112			3.92	32.1
		4.88	142			4.88	39.7
		5.39	160			5.39	44.1
		6.12	177			6.12	49.8
5.24	2.56	3.18	71.4	4.79	2.56	3.18	20.8
		3.92	88.1			3.92	25.9
		4.88	110			4.88	32.1
		5.39	123			5.39	35.4
		6.12	138			6.12	40.4
5.15	2.56	3.18	55.6	4.72	2.56	3.18	17.3
		3.92	68.7			3.92	21.7
		4.88	85.5			4.88	26.7
		5.39	94.1			5.39	29.8
		6.12	107			6.12	33.6
5.03	2.56	3.18	39.5	4.63	2.56	3.18	14.1
		3.92	49.4			3.92	17.8
		4.88	61.3			4.88	21.2
		5.39	68.1			5.39	24.5
		6.12	77.2			6.12	27.1

Table V. Experimental Observed Rate Constants for Reaction of the Copper(II) Ion with BCHTN at 25.0 ± 0.1 °C and μ = 0.10 M (NaClO$_4$)

pH	10^4[BCHTN], M	10^3[Cu^{2+}], M	k_{obsd}, s^{-1}	pH	10^4[BCHTN], M	10^3[Cu^{2+}], M	k_{obsd}, s^{-1}
5.44	2.43	3.18	160	4.99	2.43	3.18	41.2
		3.92	195			3.92	50.5
		4.88	247			4.88	62.3
		5.39	275			5.39	69.2
		6.12	312			6.12	78.3
5.35	2.43	3.18	119	4.91	2.43	3.18	32.5
		3.92	152			3.92	40.1
		4.88	184			4.88	49.8
		5.39	205			5.39	54.2
		6.12	227			6.12	62.5
5.25	2.43	3.18	87.5	4.83	2.43	3.18	26.1
		3.92	108			3.92	33.2
		4.88	134			4.88	40.0
		5.39	149			5.39	43.8
		6.12	171			6.12	50.5
5.18	2.43	3.18	71.5	4.75	2.43	3.18	21.2
		3.92	88.2			3.92	25.5
		4.88	109			4.88	32.3
		5.39	120			5.39	36.1
		6.12	137			6.12	40.5
5.07	2.43	3.18	51.5	4.68	2.43	3.18	17.6
		3.92	63.2			3.92	21.1
		4.88	78.4			4.88	26.9
		5.39	86.6			5.39	29.7
		6.12	99.1			6.12	33.5

nitrogen. The involvement of amide nitrogens in this way may happen in basic solution. Under the conditions used in this work, the amide nitrogens are not involved in coordination. Just as protonation of a neutral amide occurs at the amide oxygen, so does complexation of a metal ion.[18] As pointed out by Segal,[19] an interesting characteristic of amides is that the amide nitrogen is no longer nucleophilic or basic. This property can be attributed to the fact that the bonding between nitrogen and carbon is not correclty represented as a single bond. The actual electronic structure is best described as a resonance hybrid of two structures:



Thus, the amide bond has a partial double-bond character, and there is a partial positive charge on the nitrogen atom. The lone pair of electrons on nitrogen in one of the resonance structures is used in bonding in the other resonance structure.

The reactivity sequences BCHTN > BCEN > BCMEN > BCTN and HBCHTN$^+$ > HBCTN$^+$ > HBCEN$^+$ > HBCMEN$^+$ are observed for complexing toward copper(II) and nickel(II). On the basis of proximity and steric effects as well as the basicity of the amino group, if reaction pathway I, initial bonding to an amino nitrogen donor atom, or pathway II, initial bonding to an amide oxygen donor atom, predominated for the rections of copper(II) with BCHTN and HBCHTN$^+$, the rate constants for BCHTN and HBCHTN$^+$ would be smaller than those for the other unprotonated and monoprotonated diamino diamides, respectively. However, the results listed in Table VII clearly indicate that the rate constants for BCHTN and HBCHTN$^+$ are larger than those for the other unprotonated and monoprotonated diamino diamides, respectively. Therefore, the most significant reaction pathway for the complexation reactions of copper(II) and nickel(II) with BCHTN and HBCHTN$^+$ must be pathway III, initial bonding to an alcoholic oxygen donor atom. In this path, outer-sphere association of a coordinated water molecule with the

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Table VI. Rate Constants for Formation (k_f) of $[Cu(BCEN)]^{2+}$, $[Cu(BCTN)]^{2+}$, $[Cu(BCMEN)]^{2+}$, and $[Cu(BCHTN)]^{2+}$ at 25.0 ± 0.1 °C and μ = 0.10 M ($NaClO_4$)

complex	pH	k_f, M^{-1} s^{-1}	complex	pH	k_f, M^{-1} s^{-1}
$[Cu(BCEN)]^{2+}$	5.40	3.40×10^4	$[Cu(BCMEN)]^{2+}$	5.40	3.54×10^4
	5.32	2.62×10^4		5.33	2.91×10^4
	5.22	1.86×10^4		5.24	2.26×10^4
	5.11	1.33×10^4		5.15	1.75×10^4
	5.00	9.32×10^3		5.03	1.26×10^4
	4.92	7.25×10^3		4.94	9.81×10^3
	4.83	5.50×10^3		4.87	8.16×10^3
	4.74	4.26×10^3		4.79	6.58×10^3
	4.68	3.70×10^3		4.72	5.49×10^3
	4.60	2.88×10^3		4.63	4.46×10^3
$[Cu(BCTN)]^{2+}$	5.42	2.15×10^3	$[Cu(BCHTN)]^{2+}$	5.44	5.05×10^4
	5.33	1.72×10^3		5.35	3.77×10^4
	5.24	1.37×10^3		5.25	2.77×10^4
	5.17	1.15×10^3		5.18	2.23×10^4
	5.08	9.22×10^2		5.07	1.61×10^4
	4.96	6.91×10^2		4.99	1.28×10^4
	4.87	5.62×10^2		4.91	1.01×10^4
	4.79	4.64×10^2		4.83	8.07×10^3
	4.70	3.77×10^2		4.75	6.64×10^3
	4.60	3.27×10^2		4.68	5.50×10^3

Table VII. Resolved Rate Constant Values for the Formation and Dissociation at Copper(II) Complexes of Diamino Diamides in Aqueous Solution at 25.0 ± 0.1 °C and μ = 0.10 M ($NaClO_4$)

ligand	$k_{Cu}{}^{L}$, M^{-1} s^{-1}	$k_{Cu}{}^{HL}$, M^{-1} s^{-1}	k^{CuL}, s^{-1}	$k_H{}^{CuL}$, M^{-1} s^{-1}
BCEN	3.35×10^8	4.75×10^4	8.81×10^{-5}	7.56
BCTN	1.48×10^8	9.21×10^4	7.94×10^{-3}	8.21×10^3
BCMEN	2.23×10^8	3.76×10^4	5.35×10^{-5}	6.24
BCHTN	7.80×10^8	4.78×10^5	6.64×10^{-2}	1.38×10^4

amino group increases the value of K_{os} and speeds the replacement of the adjacent axial water by the alcoholic oxygen donor atom. As has been shown in an earlier study,[1] the rate-determining step is the formation of the first metal–amino nitrogen bond. This step presumably involves or follows either (i) the direct loss of an equatorial water or (ii) a Jahn–Teller inversion in which the weakly coordinating alcoholic oxygen donor atom is incorporated into the equatorial plane while a stronger copper–water bond is elongated.[13]

The direct loss of an equatorial water has been predicted to proceed with a rate constant of only about 10^4 s^{-1},[20,21] which is much smaller than the rate constant for the reaction of copper(II) with BCHTN. The other alternative route involves or follows a Jahn–Teller inversion, which is unfavorable from a thermodynamic standpoint.[13] It is interesting to note that the rate constant ratios for the copper(II) and nickel(II) reactions with the unprotonated and monoprotonated diamino diamides, $k_{Cu}{}^{L}/k_{Ni}{}^{L}$, are lower than the normal value of $10^{4.7}$,[14,22] in accord with the unfavorability of the Jahn–Teller inversion.

Protonation has a large effect, causing the $k_{Cu}{}^{L}/k_{Cu}{}^{HL}$ ratio to be (1–7) × 10^3. Several factors can cause a large decrease in the formation rate as a result of protonation. The ligand basicity is an important rate-controlling factor in an internal conjugate base mechanism. The basicity of the monoprotonated diamino diamide is much smaller than that of the unprotonated species. Therefore, the formation rate constant is greatly decreased as a result of protonation because of the ligand basicity, electrostatic repulsion, and a statistical effect.[23]

The pure-solvent dissociation rates of these copper(II) diamino diamide complexes are extraordinarily small. However, acid can accelerate the dissociation of these copper(II) complexes 5 or 6 orders of magnitude. Individual steps in the unwrapping of diamino diamide from copper(II) are expected to be fast, but unless the reaction is assisted by protonating the partially coordinated intermediate and stabilizing it, the successive equilibria leading up to the cleavage of the second copper–nitrogen bond are very unfavorable and a slow dissociation rate results. These results can be explained by a modification of the general accepted mechanism for the dissociation of metal–polyamine chelates proposed by Margerum (Figure 9),[15,24] in which the overall rate constant for the water dissociation pathway represented by the sequence I → II → III → IV is k^{CuL}; the overall rate constant for the proton-assisted pathway represented by I → II → III → V → VI is $k_H{}^{CuL}$. Under the conditions used in this work, $k_{-2} > k_4[H^+]$ and $k_{-2} > k_3$, so that $k^{CuL} = (k_1k_2/k_{-1}k_{-2})k_3$ and $k_H{}^{CuL} = (k_1k_2/k_{-1}k_{-2})k_4$. The rate-determining step for the water dissociation pathway is the breakage of the second copper–nitrogen bond, in accord with the proposed mechanism of the formation reactions of copper(II) with the unprotonated diamino diamides in which the rate-determining step is the formation of the first copper–nitrogen bond. The rate-determining step for the proton-assisted pathway is the protonation of the released amino group, in accord with the proposed mechanism of the formation reactions of copper(II) with the monoprotonated diamino diamides in which proton loss is the rate-limiting step.

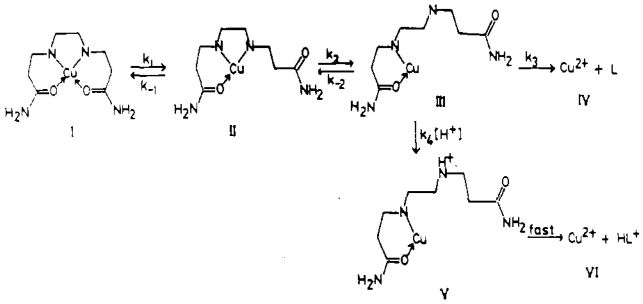

Figure 9. Proposed mechanism for the dissociation reactions of copper(II)–diamino diamide complexes.

There is a substantial difference in the relative rates of these dissociation reactions. The sequence for k^{CuL} or $k_H{}^{CuL}$, $[Cu(BCMEN)]^{2+}$, $[Cu(BCEN)]^{2+}$ < $[Cu(BCTN)]^{2+}$, < $[Cu(BCHTN)]^{2+}$, is related to two factors: (1) the girdle strains among the three linked consecutive chelate rings and (2) the basicity of the ligand. Like the analogous reactions of nickel(II) complexes,[1] the girdle strains among linked consecutive chelate rings strongly favor the dissociation of copper(II) complexes containing three linked six-membered chelate rings,[25,26] and these strains are relieved by the presence of a middle five-membered

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ring in the BCEN or BCMEN complex.[27,28] The very large dissociative rate constant in $[Cu(BCHTN)]^{2+}$ is attributed to both the large steric strains among the three linked chelate rings and the low basicity of the ligand.

It is interesting to note that the rate constants for the dissociation reactions of these copper(II)–diamino diamides are smaller than those for the analogous reactions of the nickel(II) diamino diamides.[1] Of the transition-metal ions copper(II) is one of the most kinetically labile.[29,30] The small values of k^{CuL} and k_H^{CuL} relative to k^{NiL} and k_H^{NiL} reside in low $(k_1k_2/k_{-1}k_{-2})$ values for the reactions of these copper(II) complexes.

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Registry No. BCEN, 3216-87-3; BCTN, 34740-97-1; BCMEN, 89709-74-0; BCHTN, 89709-75-1; Cu, 7440-50-8.

Supplementary Material Available: Figures showing the results of Job's method of isomolar solutions of copper(II)–BCEN, copper(II)–BCTN, copper(II)–BCMEN, and copper(II)–BCHTN at 25.0 ± 0.1 °C (4 pages). Ordering information is given on any current masthead page.

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Leaving-Group Effects on Kinetic Parameters for Solvolysis Reactions of Sterically Hindered Palladium(II) Complexes in Aqueous Solution

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The solvolysis kinetics of a series of sterically hindered square-planar complexes of the type $Pd(R_5dien)X^{n+}$, where dien = diethylenetriamine, was studied as a function of temperature and pressure for differently charged leaving groups X, viz. Cl^-, Br^-, I^-, py, NH_3, and $C_2O_4^{2-}$. The results underline earlier observations that the leaving group has a marked influence on the volume of activation for the process, which varies between −3 and −12 cm^3 mol^{-1}. This trend is discussed in terms of an earlier suggested gradual changeover in substitution mechanism from an associative to an associative interchange mechanism. It is, however, concluded that various factors can account for the observed trend such that solvolysis may proceed according to an associative mechanism in all cases.

Introduction

Our longstanding interest in the intimate nature of substitution reactions of sterically hindered Pd(II) complexes has resulted in a rather complete series of accurately measured activation parameters (ΔH^*, ΔS^*, and ΔV^*) for various degrees of steric hindrance.[1-3] These data clearly demonstrate that ΔS^* and ΔV^* for the solvolysis reactions of a series of $Pd(R_5dien)Cl^+$ complexes (R_5dien = substituted diethylenetriamine) are independent of the degree of steric hindrance.[2,3] The 6 orders of magnitude variation in the solvolysis rate constants can all be accounted for in terms of an increase in ΔH^* with increasing steric hindrance.[3] In addition, the activation parameters clearly demonstrated that an increase in steric hindrance in this system does not lead to a changeover in substitution mechanism from associative to dissociative.[4-6] ΔV^* has an average value of −12 ± 2 cm^3 mol^{-1} for solvolysis of the mentioned chloro comlexes, where R was varied from H to CH_3 and C_2H_5 in all five positions. However, in a few cases, for other leaving groups, significantly less negative ΔV^* values were found, viz. −7.8 ± 0.2 $(Pd(MeEt_4dien)I^+)^2$, −8.2 ± 0.3 $(Pd(Et_5dien)I^+)^2$, and −3 ± 1 cm^3 mol^{-1} $(Pd(Et_4dien)NH_3^{2+})$.[1] It is also rather surprising that similar ΔV^* values were reported[7] for water exchange of $Pd(H_2O)_4^{2+}$ and $Pt(H_2O)_4^{2+}$, viz. −2.2 ± 0.2 and −4.6 ± 0.2 cm^3 mol^{-1}, respectively. The possible changeover from an associative to an associative interchange mechanism was suggested, or at least could not be ruled out completely.

Although the nature of the leaving group is not expected to influence the intimate nature of the substitution process in case of a limiting associative mechanism, these data do indicate significant differences that may be related to other contributions toward ΔV^*. In this respect it is important to realize that leaving-group effects in substitution reactions of square-planar complexes, in general, have received significant attention from kineticists.[1,8,9] Different factors such as steric hindrance, trans effects, nucleophilicity, charge, etc. have been used to account for the observed trends. For systems in which marked leaving-group effects occur, it was suggested[8] that bond breakage of the five-coordinate intermediate produced during an associative substitution process may contribute significantly toward the observed kinetic parameters and may even be the rate-determining step under extreme conditions, for instance for strongly bonded leaving groups. It is, however, difficult to detect the presence of such a second transition state kinetically, especially for solvolysis reactions where it is difficult to measure the concentration dependence of the rate constant (see Results and Discussion). We have, therefore, extended the series of leaving groups studied before to include neutral and doubly charged species such as NH_3, pyridine, and $C_2O_4^{2-}$ and have concentrated on the 4-Me-1,1,7,7-Et_4dien and 1,1,4,7,7-Et_5dien complexes, in an effort to obtain more information on the effect of the leaving group.

Experimental Section

The complexes $[Pd(MeEt_4dien)Cl]ClO_4$, $[Pd(MeEt_4dien)Br]PF_6$, $[Pd(MeEt_4dien)I]ClO_4$, $Pd(MeEt_4dien)py^{2+}$, and $[Pd(Et_5dien)Cl]ClO_4$, where $MeEt_4$dien = 4-Me-1,1,7,7-Et_4diethylenetriamine and Et_5dien = 1,1,4,7,7-Et_5dien, were prepared as described before.[10,11] The [Pd-

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