

Contribution from the Department of Chemistry, Faculty of Science, Ehime University, Matsuyama, Ehime 790, Japan

Volume Profiles as Mechanistic Information for Aqueations of *cis*-CoX(NH₃)₄(H₂O)²⁺ (X = Cl⁻, Br⁻, NO₃⁻)

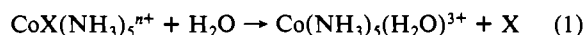
Yoichi Kitamura,* Tetsuroh Itoh, and Masayo Takeuchi

Received February 12, 1986

Acid-dependent aquation velocities ($k_{\text{obsd}} = k_0 + k_1/[H^+]$) of *cis*-CoX(NH₃)₄(H₂O)²⁺ (X = Cl⁻, Br⁻, NO₃⁻) have been studied at an ionic strength (μ) of 0.5 M under high pressures up to 200 MPa (M = mol dm⁻³). Activation volumes for the k_0 and k_1 paths (ΔV_0^\ddagger and ΔV_1^\ddagger), given as X, $\Delta V_0^\ddagger/\text{cm}^3 \text{ mol}^{-1}$, $\Delta V_1^\ddagger/\text{cm}^3 \text{ mol}^{-1}$, $T/^\circ\text{C}$: Cl⁻, -4.3 ± 0.2 , 3.3 ± 0.3 , 55; Br⁻, -3.5 ± 0.6 , 4.9 ± 0.7 , 43.5; NO₃⁻, -2.1 ± 0.1 , 5.4 ± 0.5 , 37.1. Reaction volumes (ΔV) have been dilatometrically obtained at 35 °C. The $\Delta V/\text{cm}^3 \text{ mol}^{-1}$ values at $\mu = \text{ca. } 0.5 \text{ M}$ are -11.2 for X = Cl⁻, -12.4 for X = Br⁻, and -9.7 for X = NO₃⁻. On the basis of these volume profiles, it can be inferred that in the k_0 path aquation of *cis*-CoX(NH₃)₄(H₂O)²⁺ proceeds through an interchange (I) mechanism and that in the k_1 path aquation of *cis*-Co(OH)X(NH₃)₄⁺ proceeds through a mechanism intermediate between the limiting dissociative (D) mechanism and the I mechanism.

Introduction

In a recent report,¹ volume profiles for the aquation reaction of CoX(NH₃)₅ⁿ⁺

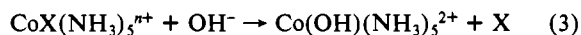


(X = Cl⁻, Br⁻, NO₃⁻, SO₄²⁻, Me₂SO, H₂O, OHCH₃, OHCH₂CH₃, OHCH(CH₃)₂, OC(NH₂)₂, OC(NH₂)(NHCH₃), OC(NHCH₃)₂, OCH(NH₂), OCH(NHCH₃), OCH(N(CH₃)₂)) were examined. It has been pointed out that a five-coordinate intermediate Co(NH₃)₅³⁺ does not exist in the transition state of reaction 1 and that a correlation

$$\Delta V^\ddagger = (0.51 \pm 0.02)\Delta V + (1.2 \pm 0.2) \quad (2)$$

exists between the activation volume (ΔV^\ddagger) and the reaction volume (ΔV) of reaction 1. Then, it has been considered that the entering H₂O and the leaving X almost equally take part in the transition state of reaction 1 and that the transition state should be depicted as H₂O...Co(NH₃)₅³⁺...X, where the dashed line stands for a weak coordination bond. This mechanism of reaction 1 may be called the interchange (I) mechanism.²

In another work,³ volume profiles for the base hydrolysis reaction of CoX(NH₃)₅ⁿ⁺



(X = F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, SO₄²⁻, Me₂SO) were investigated. The results have been consistent with the S_N1 CB mechanism, where reaction 3 proceeds in two steps:



Reaction 4 is a rapid acid-base preequilibrium, and reaction 5 is an aquation of the conjugate base complex Co(NH₂)X(NH₃)₄ⁿ⁻¹. Two features have supported the existence of a five-coordinate intermediate Co(NH₂)X(NH₃)₄²⁺ in the transition state of reaction 5. One is that the differences between the experimental ΔV^\ddagger and ΔV of reaction 3 $\Delta V_{\text{exptl}}^\ddagger(3) - \Delta V_{\text{exptl}}(3)$ are independent of the type of leaving X. The other is that the estimated values of the partial molal volume of Co(NH₂)X(NH₃)₄²⁺ are also independent of the leaving X. Thus, it has been inferred that reaction 5 proceeds through the D mechanism. According to the S_N1 CB mechanism, the experimental ΔV^\ddagger and ΔV of reaction 3 can be written as

$$\Delta V_{\text{exptl}}^\ddagger(3) = \Delta V(4) + \Delta V^\ddagger(5) \quad (6)$$

$$\Delta V_{\text{exptl}}(3) = \Delta V(4) + \Delta V(5) \quad (7)$$

(1) Kitamura, Y. *Inorg. Chem.* 1985, 24, 2.

(2) Langford, C. H.; Gray, H. G. *Ligand Substitution Processes*; Benjamin: New York, 1965. In this report, we do not intend to discriminate between the dissociative-interchange mechanism and the associative-interchange mechanism. The "I mechanism" in this report means "the mechanism of reaction 1".

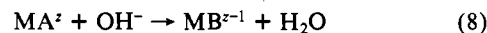
(3) Kitamura, Y.; van Eldik, R.; Kelm, H. *Inorg. Chem.* 1984, 23, 2038.

Table I. Volume Profile (cm³ mol⁻¹) at 25 °C for Aquations of CoX(NH₃)₅²⁺ and Co(NH₂)X(NH₃)₄⁺

a	reactant complex	ΔV^\ddagger	ΔV
1	CoCl(NH ₃) ₅ ²⁺	-7.9	-15.6
1	CoBr(NH ₃) ₅ ²⁺	-6.7	-14.4
1	Co(NO ₃)(NH ₃) ₅ ²⁺	-4.9	-12.3
5	CoCl(NH ₂)(NH ₃) ₄ ⁺	11.0	-12.1
5	CoBr(NH ₂)(NH ₃) ₄ ⁺	10.5	-10.9
5	Co(NH ₂)(NO ₃)(NH ₃) ₄ ⁺	9.0	-8.8

^a Reaction number.

where $\Delta V(4)$, $\Delta V^\ddagger(5)$, and $\Delta V(5)$ are the ΔV of reaction 4, ΔV^\ddagger of reaction 5, and ΔV of reaction 5, respectively. One cannot measure the $\Delta V(4)$ experimentally, since the equilibrium constant of reaction 4 is too small. However, it has been shown that the ΔV at infinite dilution and 25 °C for a series of neutralization reactions



can be summarized as

$$\Delta V (\text{cm}^3 \text{ mol}^{-1}) = (14.5 \pm 0.8) - (2.5 \pm 0.2)\Delta Z^2 \quad (9)$$

where $\Delta Z^2 = (z-1)^2 - z^2$.⁴ In reaction 8, MA^z is an octahedral transition-metal complex with ligand A = H₂O, NH₃, or C₂O₄H⁻ and MB^{z-1} is the corresponding conjugate base complex with ligand B = OH⁻, NH₂⁻, or C₂O₄²⁻. According to eq 9, $\Delta V(4)$ has been estimated as 22.0 cm³ mol⁻¹ for a monovalent leaving X. Then, $\Delta V^\ddagger(5)$ and $\Delta V(5)$ have been calculated from eq 6 and 7, respectively (Table I).

The resulting magnitudes of $\Delta V(5)$ are larger only by 3.5 cm³ mol⁻¹ than the ΔV of reaction 1 with the same leaving ligand X. This difference in reaction volume can be understood by the electrostriction caused by the complex ion. From eq 9 the electrostriction volume for an octahedral complex ion of charge z may be assumed to be $-2.5z^2 \text{ cm}^3 \text{ mol}^{-1}$. Then, $\Delta V(5)$ is expected to be larger by 5 cm³ mol⁻¹ than the ΔV of reaction 1 with the same X.⁵ In contrast, the $\Delta V^\ddagger(5)$ is remarkably (14–19 cm³ mol⁻¹) larger than the ΔV^\ddagger of reaction 1 with the same X. This distinct difference in activation volume can never be ascribed to electrostriction effect due to the complex, but clearly reflects a mechanistic changeover from the I mechanism for reaction 1 to the D mechanism for reaction 5.

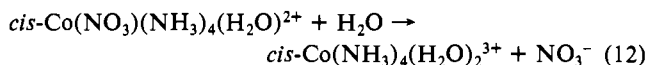
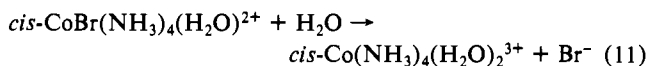
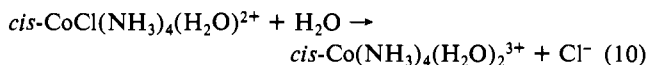
Present work is prompted by an interest regarding whether this correspondence between the magnitude of activation volume and the mechanism can be extended to aquations of *cis*-CoX(NH₃)₄(H₂O)²⁺ (X = Cl⁻, Br⁻, NO₃⁻).

Aquation kinetics of *cis*-CoX(NH₃)₄(H₂O)²⁺ (X = Cl⁻, Br⁻, NO₃⁻) were earlier investigated at normal pressure.⁶⁻⁹ It has been

(4) Kitamura, Y.; van Eldik, R. *Ber. Bunsen-Ges. Phys. Chem.* 1984, 88, 418.

(5) Kitamura, Y. *Bull. Chem. Soc. Jpn.* 1985, 58, 2699.

indicated that reactions proceed as a simple first-order reaction and the final UV-vis spectra coincide with that of *cis*-Co(NH₃)₄(H₂O)₂³⁺.⁷⁻⁹ In the present work, it has been found that isosbestic points are clearly maintained during the reaction: at 337, 356, 430, and 512 nm for X = Cl⁻; at 441 and 523 nm for X = Br⁻; at 221 and 440 nm for X = NO₃⁻. Thus, aquations proceed with retention of configuration.

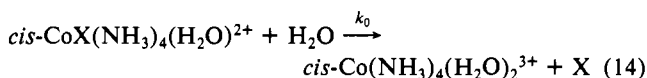


Experimental rate constant k_{obsd} depends on the acidity of the solution:

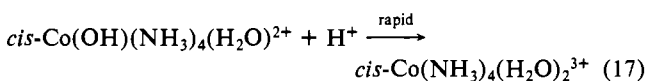
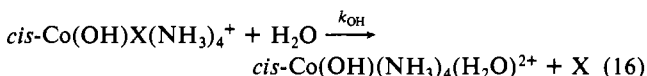
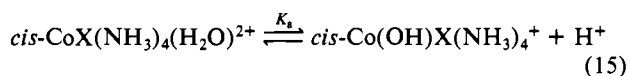
$$k_{\text{obsd}} = k_0 + k_1/[\text{H}^+] \quad (13)$$

Therefore, reaction proceeds through two paths:

k_0 path



k_1 path



$$k_1 = K_a k_{\text{OH}} \quad (18)$$

In this work, k_{obsd} is obtained at several acidities up to 200 MPa. Values of k_0 and k_1 are calculated at each pressure.

$$\Delta V^*_0 = -RT \frac{d \ln k_0}{dP} \quad (19)$$

and

$$\Delta V^*_1 = -RT \frac{d \ln k_1}{dP} \quad (20)$$

are obtained therefrom, and

$$\Delta V^*(16) = -RT \frac{d \ln k_{\text{OH}}}{dP} = \Delta V^*_1 - \Delta V^*(15) \quad (21)$$

is also obtained. $\Delta V^*(15) = -RT(d \ln K_a/dP)$ is estimated as $-0.1 \text{ cm}^3 \text{ mol}^{-1}$, from eq 9 and the value of $\Delta V = -22.1 \text{ cm}^3 \text{ mol}^{-1}$ at 25 °C and at infinite dilution for $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$.⁴ Reaction volumes of reactions 10, 11, and 12 are measured dilatometrically. Reaction volume $\Delta V^*(16)$ for reaction 16 is obtained by

$$\Delta V^*(16) = (\Delta V \text{ of reaction 10, 11, or 12}) - \Delta V^*(15) - (\Delta V \text{ of reaction 17}) \quad (22)$$

where ΔV of reaction 17 is estimated as $-4.9 \text{ cm}^3 \text{ mol}^{-1}$, analogous to $\Delta V^*(15)$.

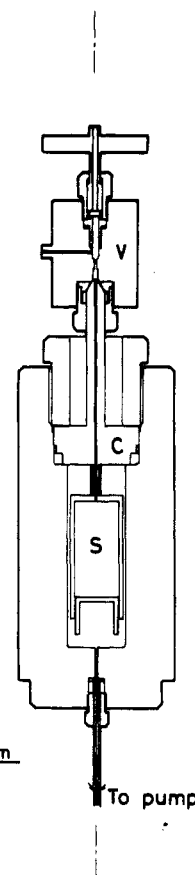


Figure 1. High-pressure reaction apparatus: C, closure; S, syringe; V, valve.

Experimental Section

The following complexes were obtained by the published methods and identified by UV-vis spectra and elemental analysis. λ_{max} , nm (ϵ): *cis*-[CoCl(NH₃)₄(H₂O)]SO₄^{7,10} 530 (56.1), 372 (48.3); *cis*-[CoCl(NH₃)₄(H₂O)]Cl₂¹⁰ 527 (57.4), 373 (48.6); *cis*-[CoBr(NH₃)₄(H₂O)]-Br₂^{8,11} 550 (50.0); *cis*-[Co(NO₃)(NH₃)₄(H₂O)](NO₃)₂^{6,9} 505 (64.2), 355 (51.9); *cis*-[Co(NH₃)₄(H₂O)₂](SO₄)₃·3H₂O^{7,12} 503 (53.8), 354 (43.5).

Reactions 10 and 11 were studied by using a high-pressure apparatus shown in Figure 1. In a glass syringe (S) was contained 60 cm³ of a sample solution. The orifice of this syringe was connected through a thin Teflon tube to a pipe (diameter 0.15 cm) drilled through a closure (C). This syringe was set in a high-pressure vessel filled with pressure-transmitting liquid paraffin and maintained in a thermostat controlled within ± 0.1 °C. Pressure was applied and reaction mixture was taken out from the vent of a valve (V) at appropriate intervals. The initial 1 cm³ was discarded and the following 2 cm³ was analyzed spectrophotometrically. The pressure drop was recovered in a few minutes. The closure was sealed by an O-ring. Thus, a portion of the reacting solution was in contact with the 17-4PH steel constructing the closure or the valve and with the Teflon packing in the valve. Though this portion was always discarded, it was confirmed that contacts with these materials did not cause any effect on the velocity. Reaction 12 was followed in a thermostated Hawley and Chase type cell.¹³ The rate constant was calculated from the time dependence of the optical density (D) at a certain wavelength, where a $\ln(D_t - D_\infty)$ vs. t plot or the Guggenheim method (reaction 12) was used (correlation coefficient ≥ 0.998). Essentially the same rate constant was obtained when the reactions were followed at several wavelengths: reaction 10 at 264–290 nm; reaction 11 at 292–330 nm; reaction 12 at 270–310 nm.

As before, the volume change of a 39.2 cm³ complex solution was followed by the movement of the meniscus height (h_t) in a capillary (diameter 0.0404 cm) up to 2.6 (reaction 12, $\mu = 0.524 \text{ M}$) or 8 half lives.¹³ The value of $h_0 - h_\infty$ was obtained from the intercept of the Guggenheim or $\ln(h_t - h_\infty)$ vs. t plot. It was known spectrophotomet-

(6) Brønsted, J. N. *Z. Phys. Chem., Stoichiom. Verwandtschaftsftsl.* **1926**, *122*, 383.

(7) Kuroda, K. *Nippon Kagaku Zasshi* **1961**, *82*, 181.

(8) Kuroda, K. *Nippon Kagaku Zasshi* **1961**, *82*, 1168.

(9) Kuroda, K. *Nippon Kagaku Zasshi* **1960**, *81*, 1075.

(10) Kauffman, G. B.; Pinnell, R. P. *Inorg. Synth.* **1963**, *6*, 178.

(11) Werner, A.; Wolberg, A. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 2011.

(12) Jörgensen, S. M. *Z. Anorg. Chem.* **1892**, *2*, 296.

(13) Kitamura, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3625.

Table II. Rate Constant and Activation Volume (cm³ mol⁻¹) for the Aquation of *cis*-CoX(NH₃)₄(H₂O)²⁺ at $\mu = 0.5$ M (NaClO₄)

$$X = \text{Cl}^-, {}^a C = 0.7 \text{ mM}, {}^b 55.0 \text{ }^\circ\text{C}, {}^c \lambda = 270 \text{ nm}, {}^d \Delta V^*_0 = -4.3 \pm 0.2, \Delta V^*_1 = 3.3 \pm 0.3$$

P/MPa	$k_{\text{obsd}}/10^{-4} \text{ s}^{-1}$				$k_0/10^{-5} \text{ s}^{-1}$	$k_1/10^{-6} \text{ M}^{-1} \text{ s}^{-1}$
	[HClO ₄] = 495 mM	[HClO ₄] = 41.7 mM	[HClO ₄] = 21.9 mM	[HClO ₄] = 10.4 mM		
5	0.886	1.61	2.40	3.98	8.38	3.28
50	0.950	1.66	2.26	3.90	8.78	3.12
100	1.03	1.67	2.34	3.84	9.62	2.99
150	1.11	1.68	2.35	3.73	10.4	2.81
200	1.17	1.77	2.29	3.59	11.3	2.56

$$X = \text{Br}^-, C = 0.7 \text{ mM}, {}^b 43.5 \text{ }^\circ\text{C}, {}^c \lambda = 300 \text{ nm}, {}^d \Delta V^*_0 = -3.5 \pm 0.6, \Delta V^*_1 = 4.9 \pm 0.7$$

P/MPa	$k_{\text{obsd}}/10^{-4} \text{ s}^{-1}$			$k_0/10^{-5} \text{ s}^{-1}$	$k_1/10^{-6} \text{ M}^{-1} \text{ s}^{-1}$
	[HClO ₄] = 494 mM	[HClO ₄] = 23.88 mM	[HClO ₄] = 12.65 mM		
5	0.91	2.23	3.28	8.88	3.08
50	1.04	2.16	3.03	10.1	2.59
100	1.13	2.16	3.07	10.8	2.53
150	1.17	2.12	2.92	11.3	2.28
200	1.19	2.06	2.78	11.7	2.07

$$X = \text{NO}_3^-, C = 1 \text{ mM}, {}^b 37.1 \text{ }^\circ\text{C}, {}^c \lambda = 280 \text{ nm}, {}^d \Delta V^*_0 = -2.1 \pm 0.1, \Delta V^*_1 = 5.4 \pm 0.5$$

P/MPa	$k_{\text{obsd}}/10^{-4} \text{ s}^{-1}$				$k_0/10^{-4} \text{ s}^{-1}$	$k_1/10^{-6} \text{ M}^{-1} \text{ s}^{-1}$
	[HClO ₄] = 500 mM	[HClO ₄] = 51.4 mM	[HClO ₄] = 23.7 mM	[HClO ₄] = 7.73 mM		
2	2.67	3.82	5.23	11.18	2.50	6.69
40	2.65	3.76	5.25	10.62	2.55	6.25
80	2.76	3.84	5.08	10.22	2.66	5.84
120	2.85	3.80	4.94	9.76	2.73	5.42
160	2.97	3.79	4.77	9.02	2.84	4.76

^aSulfate was used. ^bConcentration of the complex. ^cReaction temperature. ^dReaction was followed at this wavelength. ^eMean of two or more runs.

Table III. Dilatometrically Obtained ΔV at 35 °C for the Aquations of *cis*-CoX(NH₃)₄(H₂O)²⁺

X	C/mM ^b	[HClO ₄]/M	μ /M ^c	$\Delta V/\text{cm}^3 \text{ mol}^{-1}$
Cl ⁻ ^a	8	0.008	0.524	-11.0, -11.3
	8	0.0015	0.026	-12.1
Br ⁻	10	0.003	0.5	-12.6, -12.2
	10	0.006	0.036	-12.1, -11.5
NO ₃ ⁻	8	0.5	0.524	-9.4, -9.9
	8	0.01	0.034	-9.0, -8.9

^aChloride was used. ^bConcentration of the complex. ^cNaClO₄ was added.

rically that under the dilatometric conditions reactions 10, 11, and 12 go to 100%, 97.6%, and 100% completion, respectively.

Results

Kinetic Results. In Table II, values of k_{obsd} at several acidities and pressures are summarized. At high [H⁺], k_{obsd} is small and increases slightly with increase of pressure. At low [H⁺], k_{obsd} is large and decreases slightly with increase of pressure. Good linear correlation exists between the value of k_{obsd} and 1/[H⁺]. The correlation coefficients are higher than 0.996 and are generally 0.999 or 0.998. Values of k_0 and k_1 are calculated at each pressure, and ΔV^*_0 and ΔV^*_1 are obtained by eq 19 and 20.

Dilatometric Results. The dilatometric results are summarized in Table III. It can be noticed that results of duplicate runs under the same conditions coincide well and that the obtained ΔV 's are independent of the ionic strength.

Discussion

As is shown in Table IV, the magnitudes of ΔV for reaction 14 are rather independent of the type of X and have a value around -10 cm³ mol⁻¹. They are only 4–2 cm³ mol⁻¹ larger than those for reaction 1 with the same leaving X (Table I). On the other hand, the magnitudes of ΔV^* for reaction 14 are also negative. They are again slightly larger than the ΔV^* for reaction 1 with the same leaving X. In Table IV, $\Delta V^*_{\text{calcd}}(\text{I})$ is also given for each reaction by inserting its magnitude of ΔV into eq 2. It can be

Table IV. Volume Profile (cm³ mol⁻¹) at $\mu = 0.5$ M for the Aquations of *cis*-CoX(NH₃)₄(H₂O)²⁺ (Reaction 14) and of *cis*-Co(OH)X(NH₃)₄⁺ (Reaction 16)

a	reactant complex	ΔV^*	$\Delta V^*_{\text{calcd}}(\text{I})$	ΔV
14	<i>cis</i> -CoCl(NH ₃) ₄ (H ₂ O) ²⁺	-4.3	-4.5	-11.2
14	<i>cis</i> -CoBr(NH ₃) ₄ (H ₂ O) ²⁺	-3.5	-5.1	-12.4
14	<i>cis</i> -Co(NO ₃)(NH ₃) ₄ (H ₂ O) ²⁺	-2.1	-3.7	-9.7
16	<i>cis</i> -CoCl(OH)(NH ₃) ₄ ⁺	3.4	-2.0	-6.2
16	<i>cis</i> -CoBr(OH)(NH ₃) ₄ ⁺	5.0	-2.6	-7.4
16	<i>cis</i> -Co(OH)(NO ₃)(NH ₃) ₄ ⁺	5.5	-1.2	-4.7

^aReaction number.

noticed that the ΔV^* 's for reaction 14 are close to its value of $\Delta V^*_{\text{calcd}}(\text{I})$. Hence, it seems that the acid-independent aquation of *cis*-CoX(NH₃)₄(H₂O)²⁺ proceeds also through the I mechanism. The slightly larger ΔV^* and ΔV of reaction 14 compared to those of the corresponding reaction 1 might be caused by some difference in specific interaction through the hydrogen bond between the complex and the solvent.

In contrast, the ΔV^* 's for reaction 16 are positive and are rather independent of the type of X. They are considerably larger than their $\Delta V^*_{\text{calcd}}(\text{I})$. If reaction 16 proceeded through the D mechanism, its magnitude of ΔV^* should be similar to those (9–11 cm³ mol⁻¹) for reaction 5, since both *cis*-Co(OH)X(NH₃)₄⁺ and Co(NH₂)X(NH₃)₄⁺ have the same charge. Thus, experimentally obtained values of ΔV^* for reaction 16 lie between limits expected for I and D mechanisms. It seems that the aquation of *cis*-Co(OH)X(NH₃)₄⁺ proceeds through a mechanism intermediate between D and I. These mechanistic insights based on volume profiles are consistent with the mechanistic assignment drawn from the stabilizing power consideration of the nonlabile ligand.

Certain nonlabile ligands in a complex contribute stabilizing power to the leaving ligand.¹⁴ The origin of this power might be partly electrostatic, partly inductive, and partly conjugative. A stabilizing sequence NH₂⁻ > OH⁻ > Cl⁻ has been suggested. Thus, the NH₂⁻ ligand in Co(NH₂)X(NH₃)₄⁺ causes a strong

labilizing effect on the leaving X. Then, X can leave the first coordination sphere without help from the entering H₂O ligand. In the transition state of reaction 5, the entering H₂O is not included in the first coordination sphere (D mechanism). In contrast, CoX(NH₃)₅²⁺ 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 H₂O ligand into the first coordination sphere. In the transition state of reaction 1, the entering H₂O 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(NH₃)₄(H₂O)²⁺ (reaction 14) should proceed through the I mechanism, since neither H₂O nor NH₃ ligand has labilizing power, whereas aquations of *cis*-Co(OH)X(NH₃)₄⁺ might proceed through a mechanism in-

intermediate between I and D, since the OH⁻ ligand has a labilizing power, which may not be so strong as for NH₂⁻.

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 NH₃.

Registry No. *cis*-CoCl(NH₃)₄(H₂O)²⁺, 18460-69-0; *cis*-CoBr(NH₃)₄(H₂O)²⁺, 44433-46-7; *cis*-Co(NO₃)(NH₃)₄(H₂O)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.

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

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

Si-Han Liu and Chung-Sun Chung*

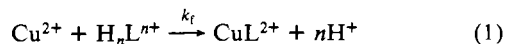
Received April 8, 1985

Equilibrium constants are determined for the protonation and metal complexation of the copper(II) complexes with *N,N'*-bis(β -carbamoyl-ethyl)ethylenediamine (BCEN), *N,N'*-bis(β -carbamoyl-ethyl)trimethylenediamine (BCTN), *N,N'*-bis(β -carbamoyl-ethyl)-1,2-propylenediamine (BCMEN), and *N,N'*-bis(β -carbamoyl-ethyl)-2-hydroxytrimethylenediamine (BCHTN) in 0.10 M NaClO₄ at 25.0 °C. The stability constants in 0.10 M NaClO₄ at 25.0 °C for the complexes Cu(BCEN)²⁺, Cu(BCTN)²⁺, Cu(BCMEN)²⁺, and Cu(BCHTN)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 NaClO₄ 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 × 10⁸, 4.75 × 10⁴, 1.48 × 10⁸, 9.21 × 10⁴, 2.23 × 10⁸, 3.76 × 10⁴, 7.80 × 10⁸, and 4.78 × 10⁵, 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.

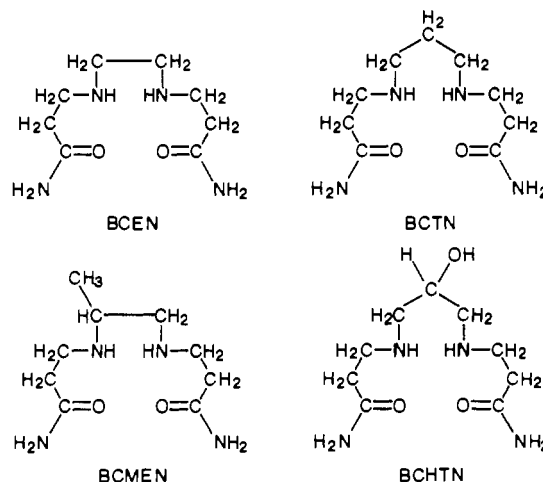


Experimental Section

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.

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

Chart I



ion concentrations in 0.10 M NaClO₄ were calculated from $-\log [\text{H}^+] = \text{pH} - 0.11$ and $k_w = 10^{-13.78}$.⁵⁻⁷ Appropriate aliquots of standard solutions of ligand or ligand and metal were titrated with a standard CO₂-free sodium hydroxide solution. In all titrations the ionic strength

- (1) Liu, S.-H.; Chung, C.-S. *Inorg. Chem.* **1985**, *24*, 2368-2373.
- (2) Lee, T.-J.; Hong, C.-Y.; Liu, S.-H.; Chung, C.-S.; Lee, T.-Y. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 1673-1675.
- (3) Lee, T.-J.; Lu, T.-H.; Liu, S.-H.; Chung, C.-S.; Lee, T.-Y. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 1131-1135.
- (4) Liu, S.-H.; Chung, C.-S. *Inorg. Chem.* **1984**, *23*, 1803-1806.

- (5) Bates, R. G. *Determination of pH*; Wiley: New York, 1964; p 74.
- (6) Pagenkopf, G. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1968**, *90*, 6963-6967.
- (7) Liang, B.-F.; Margerum, D. W.; Chung, C.-S. *Inorg. Chem.* **1979**, *18*, 2001-2007.