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Formation kinetics of triaza-crown-alkanoic acid complexes of first-row transition metal(II) ions

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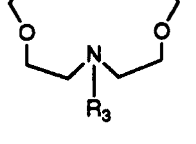
The complex formation reactions of divalent metal ions of Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} with the macrocyclic ligands 1,7-dioxa-4,10,13-triazacyclopentadecane-4,10,13-triacetic acid, 1, and 1,7-dioxa-4,10,13-triazacyclopentadecane-4,10,13-tripropionic acid, 2, have been studied by using stopped-flow and conventional spectrophotometry. The measurements were made at 25.0 ± 0.1°C in an aqueous solution of 0.1M ($NaClO_4$) ionic strength. The formation reaction takes place by rapid formation of an intermediate complex (MH_2L^{+*}) in which the metal ion is incompletely coordinated. This may then proceed to the final product in the rate-determining step. The stability constants ($\log K_{MH2L^{+*}}$) and the second-order rate constants (k_{OH}) for the rearrangement of the intermediate complex have been determined from the kinetic data. In the pH range examined, the monoprotonated (HL^{2-}) form of ligands 1 and 2 is the kinetically active species despite of their low concentration. The structure of the intermediate is proposed in which the metal ions are coordinated to oxygens and one nitrogen of ligands 1 and 2. These observations are also discussed in terms of the ionic radii of the metal ions, the chelate ring size and rigidity of the ligands.

INTRODUCTION

Macrocyclic polyethers, polyoxapolyaza and polyaza-polycarboxylates have the remarkable property of complexing selectivity with alkaline-earth or first-row transition metal(II) ions such that intensive efforts have been made in their application to analytical, biological and other fields of chemistry. Several factors influence the thermodynamic and kinetic stabilities of metal complexes of macrocycle ligands.[1–13] These factors are the size of the metal ion and the ligand topology, such as the charge, cavity size, number of donor atoms, and stereochemical rigidity.

Kasprzyk and Wilkins[4] reported the formation rates of alkaline earth and transition metal complexes of DOTA(1,4,7,10 - tetraazacyclododecane - 1,4,7,10 - tetra-acetic acid) and TETA(1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetraacetic acid). The formation of an intermediate, MH_2L^*, was proposed, followed by rearrangement in the rate-determining step to the final product. But no conclusions regarding the effect of the size of the metal ion on the formation rates were drawn. Additional studies on the formation of Cu^{2+} complexes of the macrocyclic diaza-crown-alkanoic acid ligands were also reported.[5] The effect of pendant arms and ring size of the ligands was demonstrated in this study.

We initiated this project in order to understand how the formation rates and mechanisms of first-row transition metal(II) complexes are affected by the size of metal ions and the number of donor atoms, the chelate ring and cavity size of two macrocyclic triaza-crown-alkanoic acid ligands. We report herein the systematic formation kinetics of first-row transition metal complexes of 1,7-dioxa-4,10,13-triazacyclopentadecane - 4,10,13 - triacetic acid, 1 and 1,7-dioxa-4,10,13-triazacyclopentadecane-4,10,13-tripropionic acid, 2 (Chart 1).



1, $R_1 = R_2 = R_3 = CH_2COOH$

2, $R_1 = R_2 = R_3 = CH_2CH_2COOH$

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EXPERIMENTAL

Reagents

1,7-dioxa-4,10,13-triazacyclopentadecane trihydrobromide was prepared by previously reported procedures.[14] Ligands **1** and **2** were synthesized according to the method of Martell et al.[3] The concentrations of **1** and **2** stock solutions were determined by titration against a standard $Cu(ClO_4)_2$ solution using murexide as an indicator. Stock solutions of Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions were prepared from the metal chloride and perchlorates (Aldrich, 99.9%) and their concentrations determined by EDTA titrations using murexide as an indicator. Analytical grades of all other chemicals were used without further purification. All solutions were prepared in deionized water.

Measurements

The ionic strength of the sample solution was adjusted to 0.1M with $NaClO_4$. A Beckman Model Φ 71 pH meter with combination electrode was used for all pH measurements. The H^+ ion concentration was established from the measured pH value by procedures previously reported.[15] Kinetic measurements were carried out on a Hi-Tech stopped-flow spectrophotometer interfaced with Scientific data acquisition system and a UVIDEC-610 spectrophotometer at 25.0 ± 0.1°C with the use of a Lauda RM 6 circulatory water bath. Most of the formation reactions were studied in weakly buffered solutions (0.10M acetic acid/sodium acetate) by monitoring the pH decreases ($\Delta pH < 0.17$) with bromocresol green (pH range $4.6 < pH < 5.2$, observation wavelength 615nm) as an indicator.[4] The concentration of the indicator was 2.0×10^{-5}M, while the concentration of acetate buffer varied between 5.0×10^{-3}M and 2.0×10^{-2}M, independing upon the rate. The concentration of ligands was 1.0×10^{-4}M, while the Cos^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} concentration varied between 3.0×10^{-4} and 3.0×10^{-3}M. The reactions of Cu^{2+} with **1** and **2** were studied by monitoring the formation of complex directly at 260nm. The data agreed well with some runs using the indicator method.

RESULT AND DISCUSSION

The rate of complex formation in the presence of the excess M^{2+}ion with ligands **1** and **2** may be described by

$$d[ML^+] / dt = k_{obsd}[L]_T \tag{1}$$

where $[L]_T$ is the concentration of the various protonated forms of the ligands and k_{obsd} is a pseudo-first-order rate constant. The formation reactions were studied at different pH values and with varying concentrations of M^{2+} ions. For all systems at each pH, k_{obsd} increased with increasing $[M^{2+}]$, but the curve obtained by plotting the values k_{obsd} against $[M^{2+}]$ is a saturation curve. This behavior can be rationalized in terms of an intermediate complex formation in the equilibrium step, followed by its rearrangement in the rate-determining step. The dependence of k_{obsd} values on the M^{2+}ion concentration can be expressed as

$$k_{obsd} = \frac{k_1 K[M^{2+}]}{1 + K[M^{2+}]} \tag{2}$$

where K is the stability constant for the formation of the intermediate complex and k_1 is the rate constant for rearrangement of the intermediate to product. This equation can be rearranged by the following eq. 3.

$$\frac{1}{k_{obsd}} = \frac{1}{k_1} + \frac{1}{k_1 K[M^{2+}]} \tag{3}$$

Plots of $1/k_{obsd}$ against $1/[M^{2+}]$ lead to straight line as shown in Figure 1. The values of k_1, K and the second-order rate constant $k_2 = k_1K$ were deduced from eq. 3 and summarized in Table 1. The stability constants and the rate constants for the rearrangement of the intermediate were found to be dependent upon pH over the limited range examined as shown in Table 1. The

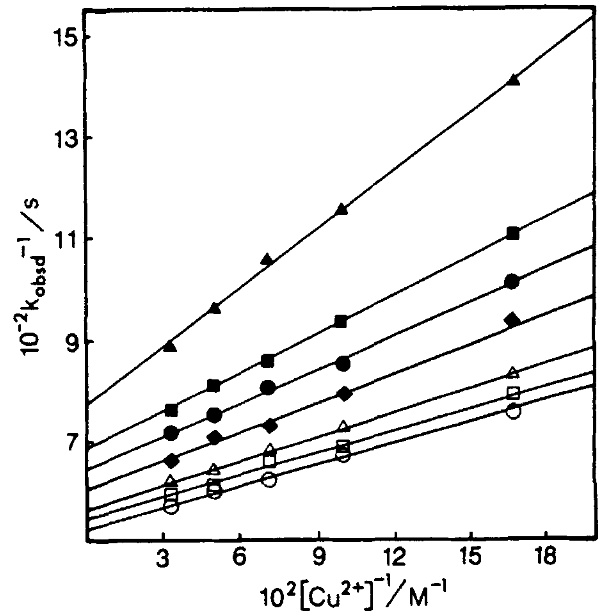

Figure 1 Plots of k_{obsd}^{-1} *vs.* $[Cu^{2+}]^{-1}$ for the formation kinetics of Cu1 at different pH values ($[1]=1.0\times10^{-4}$M, $[OAc^-]=0.01$M, I=0.1M ($NaClO_4$), T=25.0±0.1°C, pH : ○, 4.67; □, 4.90; △, 5.07; ◆, 5.21; ●, 5.32; ■, 5.39; ▲, 5.43).

Table 1 Rate data for reactions of M^{2+} with **1** and **2** at 25.0 ± 0.1°C and I = 0.1M ($NaClO_4$)

M^{2+}	pH	$k_1/\ s^{-1}$	$K/\ M^{-1}$	$k_2/\ M^{-1}s^{-1}$
1				
Co	4.72	$(0.84 \pm 0.02) \times 10^1$	$(3.37 \pm 0.10) \times 10^2$	$(2.82 \pm 0.11) \times 10^3$
	4.89	$(0.97 \pm 0.02) \times 10^1$	$(3.85 \pm 0.07) \times 10^2$	$(3.75 \pm 0.09) \times 10^3$
	5.04	$(1.14 \pm 0.04) \times 10^1$	$(4.24 \pm 0.17) \times 10^2$	$(4.85 \pm 0.27) \times 10^3$
	5.09	$(1.22 \pm 0.05) \times 10^1$	$(4.27 \pm 0.20) \times 10^2$	$(5.23 \pm 0.33) \times 10^3$
	5.14	$(1.30 \pm 0.06) \times 10^1$	$(4.53 \pm 0.23) \times 10^2$	$(5.89 \pm 0.41) \times 10^3$
	5.19	$(1.43 \pm 0.04) \times 10^1$	$(4.58 \pm 0.15) \times 10^2$	$(6.53 \pm 0.30) \times 10^3$
	5.22	$(1.45 \pm 0.07) \times 10^1$	$(4.94 \pm 0.26) \times 10^2$	$(7.14 \pm 0.52) \times 10^3$
Ni	4.71	3.76 ± 0.30	$(0.88 \pm 0.07) \times 10^2$	$(3.30 \pm 0.38) \times 10^2$
	4.88	4.30 ± 0.50	$(0.98 \pm 0.11) \times 10^2$	$(4.21 \pm 0.69) \times 10^2$
	5.03	5.14 ± 0.30	$(1.06 \pm 0.06) \times 10^2$	$(5.43 \pm 0.45) \times 10^2$
	5.08	5.33 ± 0.27	$(1.18 \pm 0.06) \times 10^2$	$(6.28 \pm 0.45) \times 10^2$
	5.13	5.87 ± 0.61	$(1.21 \pm 0.13) \times 10^2$	$(7.08 \pm 1.06) \times 10^2$
	5.18	6.45 ± 0.41	$(1.21 \pm 0.08) \times 10^2$	$(7.79 \pm 0.70) \times 10^2$
	5.21	6.72 ± 0.51	$(1.25 \pm 1.00) \times 10^2$	$(8.41 \pm 0.91) \times 10^2$
Cu	4.67	$(1.30 \pm 0.02) \times 10^{-3}$	$(2.01 \pm 0.05) \times 10^3$	2.61 ± 0.07
	4.90	$(1.48 \pm 0.08) \times 10^{-3}$	$(2.66 \pm 0.15) \times 10^3$	3.93 ± 0.30
	5.07	$(1.56 \pm 0.03) \times 10^{-3}$	$(2.90 \pm 0.06) \times 10^3$	4.52 ± 0.14
	5.21	$(1.66 \pm 0.07) \times 10^{-3}$	$(3.19 \pm 0.14) \times 10^3$	5.31 ± 0.32
	5.32	$(1.79 \pm 0.06) \times 10^{-3}$	$(3.40 \pm 0.12) \times 10^3$	6.08 ± 0.30
	5.39	$(1.84 \pm 0.07) \times 10^{-3}$	$(3.76 \pm 0.16) \times 10^3$	6.90 ± 0.39
	5.43	$(1.93 \pm 0.04) \times 10^{-3}$	$(3.61 \pm 0.08) \times 10^3$	6.96 ± 0.22
Zn	4.58	$(1.91 \pm 0.01) \times 10^1$	$(3.86 \pm 0.03) \times 10^2$	$(0.74 \pm 0.01) \times 10^4$
	4.73	$(2.24 \pm 0.02) \times 10^1$	$(4.53 \pm 0.04) \times 10^2$	$(1.01 \pm 0.01) \times 10^4$
	4.86	$(2.50 \pm 0.04) \times 10^1$	$(5.10 \pm 0.14) \times 10^2$	$(1.27 \pm 0.04) \times 10^4$
	4.91	$(2.72 \pm 0.04) \times 10^1$	$(5.40 \pm 0.09) \times 10^2$	$(1.47 \pm 0.03) \times 10^4$
	4.98	$(3.00 \pm 0.04) \times 10^1$	$(5.51 \pm 0.08) \times 10^2$	$(1.65 \pm 0.03) \times 10^4$
	5.02	$(3.14 \pm 0.05) \times 10^1$	$(5.86 \pm 0.10) \times 10^2$	$(1.84 \pm 0.04) \times 10^4$
	5.05	$(3.27 \pm 0.09) \times 10^1$	$(5.94 \pm 0.19) \times 10^2$	$(1.94 \pm 0.08) \times 10^4$
2				
Cu	4.25	1.00 ± 0.03	$(0.46 \pm 0.02) \times 10^3$	$(0.46 \pm 0.02) \times 10^3$
	4.46	1.08 ± 0.02	$(0.73 \pm 0.02) \times 10^3$	$(0.79 \pm 0.03) \times 10^3$
	4.64	1.18 ± 0.03	$(0.98 \pm 0.02) \times 10^3$	$(1.15 \pm 0.04) \times 10^3$
	4.76	1.24 ± 0.02	$(1.14 \pm 0.02) \times 10^3$	$(1.41 \pm 0.03) \times 10^3$
	4.88	1.36 ± 0.02	$(1.40 \pm 0.03) \times 10^3$	$(1.90 \pm 0.05) \times 10^3$
	5.07	1.60 ± 0.05	$(1.62 \pm 0.06) \times 10^3$	$(2.59 \pm 0.13) \times 10^3$
	5.16	1.77 ± 0.03	$(1.81 \pm 0.03) \times 10^3$	$(3.21 \pm 0.07) \times 10^3$

protonated forms of ligands **1** and **2** could contribute[16,17] to the kinetics of complexation of M^{2+} ions between pH 4.58 and 5.43 : For the species distributions of **1** H_2L^- is the major species in this pH range (from 54 to 89%), H_3L is an important contributor (from 45 to 10%). Whereas, that of HL^{2-} is very low (from 0.003 to 0.03%). On the basis of these results, the formation reactions of M^{2+} ions with **1** can be interpreted in terms of eqs. 4–6.

$$M^{2+} + H_2L^- \overset{K}{\rightleftarrows} (MH_2L^+)^* \tag{4}$$

$$(MH_2L^+)^* \xrightarrow{k_1} ML^- + 2H^+ \tag{5}$$

$$M^{2+} + H_2L^- \xrightarrow{k_2} ML^- + 2H^+ \tag{6}$$

The overall stability constant of the intermediate, $K_{MH_2L^{+*}}$ can be determined by the value of K at a given pH, the ligand protonation constant and with the use of eq. 7.

$$K_{MH_2L^{+*}} = K(1 + K_2[H^+] + K_2K_3[H^+]^2) \tag{7}$$

The calculated values of $\log K_{MH_2L^{+*}}$ for the complexes of **1** and **2** are summarized in Table 2 along with the literature values.[5] The stability constants of the intermediate complexes of **1** and **2** obtained here are larger than those for the corresponding triacetate and tripropionate complexes.[19] Thus, we propose that ligands **1** and **2** are coordinated to one nitrogen in addition to the carboxylate and alcoholic oxygens. A similar result is also observed for the formation of Ce(NOTA)(1,4,7-triazacyclononane-1,4,7-triacetic acid).[6] A comparison of the stability constants of the intermediate of metal complexes of **1** decrease in the order $Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$. This fact may be attributed to the thermodynamic stability[3] ($\log\beta$ = 14.94–17.54) by the Irving-williams order (except for Ni^{2+} complex). The stability constant of the

Table 2 Stability constants(log $K_{MH_2L^{+*}}/M^{-1}s^{-1}$) for reactions of M^{2+} with diprotonated **1**, **2**, and K21DA at 25.0 ± 0.1°C and I = 0.1M($NaClO_4$)

	Ligands		
	$H_2(\mathbf{1})^-$	$H_2(\mathbf{2})^-$	$H_2(K21DA)^b$
Co^{2+}	2.77 ± 0.09	a)	a)
Ni^{2+}	2.19 ± 0.05	a)	a)
Cu^{2+}	3.61 ± 0.13	3.44 ± 0.10	2.05 ± 0.31
Zn^{2+}	2.91 ± 0.07	a)	a)

a) Not observed. b) Ref. 5; this value was resolved by eq. 7.

intermediate of Cu**2** complex is somewhat lower than that of Cu**1**. The reduced stability of intermediate **2** may be due to the decrease of nitrogen donor basicity[16,17] ($pK_{3(1)} = 9.55$ *versus* $pK_{3(2)} = 8.16$) and the enhanced conformational freedom of **2** due to the propionate pendant. While the log $K_{MH_2L^{+*}}$ of Cu**1** is about one order of magnitude larger than that of Cu(K21DA) (1,7-diaza-4,10,13-trioxacyclopentadecane-1,7-diacetic acid), even though K21DA has the same cavity ring size (15cycle) as **1**. This is presumably due to the increase of thermodynamic stability[2,3] ($\log\beta_{Cu1} = 17.54$ *versus* $\log\beta_{CuK21DA} = 16.02$) by the increase in nitrogen donor basicity, the difference in the type of cyclic ring donor atoms (dioxatriaza *versus* trioxadiaza cycle) and the number of acetate pendant arms of ligands.

The second-order rate constant, k_{HnL} also represents $(k_1K)_{HnL}$, since the eqs. 3–4 and 3–5 account equally well for the kinetic data. If one species is markedly more reactive than all the others, the second-order rate constant, k_{HnL} is obtained from the following expression.[5]

$$k_2 = k_{HnL}(1 + K_{H_{(n+1)}L}[H^+])^{-1} \tag{8}$$

where $K_{H_{(n+1)}L}$ is the protonation constant of **1** and **2**. From a plot of k_2 against $(1 + K_{H_{(n+1)}L}[H^+])^{-1}$, the second-order rate constant, $k_{HL^{2-}}$ *and* $k_{H_2L^-}$ for the HL^{2-} and H_2L^- species obtained are collected in Table 3. Despite of their very low concentration in the pH range observed, monoprotonated form, HL^{2-} are 3–4 orders of magnitude more reactive than the diprotonated species, H_2L^- even though the latter is the major component in the solution. The same conclusion was previously reported by Wilkins[5] in a study of the complexation of the Cu^{2+}ion by diaza-crown-alkanoic acids. The low reactivity of the H_2L^- form may be assigned to the formation of dizwitterionic form of **1** and **2**. The two $N\text{-}H^+$ groups in the 15 cycle of H_2L^- probably hinder the rearrangement of the intermediate complex, MH_2L^{+*} into the final chelate product due to the electrostatic repulsion with the incoming metal ion.

The values of rate constant, k_1 were found to be inversely proportional to $[H^+]$ as shown in Figure 2. This relationship indicates that the rearrangement of the intermediate complex into the final chelate product is catalyzed by the OH^-ion. This observation is consistent with the previously reported work.[6] An expression consistent with this functional dependance is given by eq. 9.[9]

$$k_1 = k_{H_2O} + k_{OH}K_w[H^+]^{-1} \tag{9}$$

where k_{H_2O} and k_{OH} are water and hydroxide-catalyzed rate constant of the rearrangement of the intermediate complex. The values of k_{OH} calculated from the slopes of eq. 9 are also summarized in Table 3. For the reaction of the hydroxide-catalyzed arrangement of the intermediates, **1**, MH_2L^{+*} the order of rate constants is $Zn^{2+} > Co^{2+} > Ni^{2+} > Cu^{2+}$. This phenomenon may be rationalized by the lattice energy due to the electron configuration of the transition metal ions. The formation rate constant, k_{OH} of Cu**2** is about three orders of magnitude larger than that of Cu**1**. This is likely a consequence of the conformational difference in the CuH_2L^{+*} intermediate resulted from the different steric requirement of acetate *versus* propionate chelate ring and the destabilizing structural effect by an increase in chelate ring size from 5 to 6. On the other hand, the hydroxide-catalyzed rate of CuK21DA dissociates about 6 orders of magnitude faster than that of Cu**1**. This likely reflects the differing basicity of nitrogen atoms and the rigidities of the trioxadiaza (K21DA) *versus* the dioxatriaza(**1**).

Table 3 Second-order rate constants ($k_{H_nL}/M^{-1}s^{-1}$) and base-catalyzed rate constants ($k_{OH}/M^{-1}s^{-1}$) of the complexes at 25.0 ± 0.1°C and I = 0.1M ($NaClO_4$)

Complexes	$k_{HL^{2-}}/M^{-1}s^{-1}$	$k_{H_2L^-}/M^{-1}s^{-1}$	$k_{OH}/M^{-1}s^{-1}$
Co**1**	$(3.97 \pm 0.12) \times 10^7$	$(1.69 \pm 0.21) \times 10^4$	$(4.29 \pm 0.11) \times 10^9$
Ni**1**	$(4.99 \pm 0.19) \times 10^6$	$(2.05 \pm 0.28) \times 10^3$	$(2.09 \pm 0.09) \times 10^9$
Cu**1**	$(2.02 \pm 0.14) \times 10^4$	$(1.27 \pm 0.13) \times 10^1$	$(2.01 \pm 0.14) \times 10^5$
Zn**1**	$(1.74 \pm 0.04) \times 10^8$	$(4.74 \pm 0.42) \times 10^4$	$(1.42 \pm 0.04) \times 10^{10}$
Cu**2**	$(2.37 \pm 0.08) \times 10^6$	$(5.75 \pm 0.48) \times 10^3$	$(4.66 \pm 0.06) \times 10^8$
CuK21DA[a)]	$(3.58 \pm 0.42) \times 10^8$ [b)]	$(2.29 \pm 0.55) \times 10^5$ [b)]	$(4.26 \pm 0.24) \times 10^{11}$ [b)]

a) Ref. 5 b) These values were estimated from eq. 8 and 9.

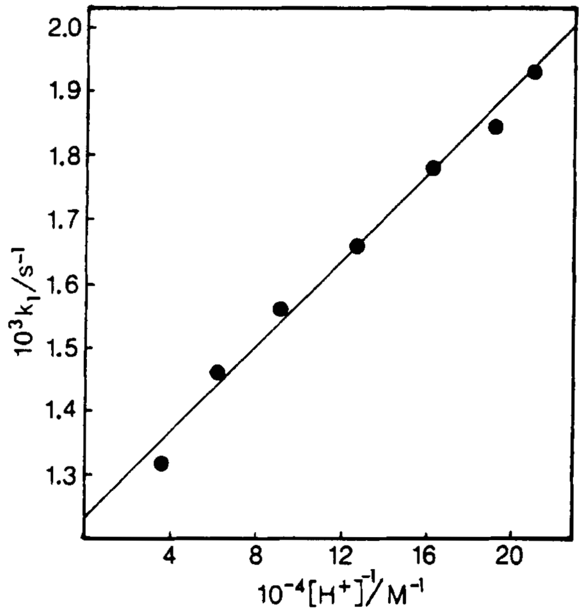

Figure 2 Plots of k_1 *vs.* $[H^+]^{-1}$ for the formation kinetics of Cu**1** at 25.0 ± 0.1°C and I = 0.1M ($NaClO_4$).

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