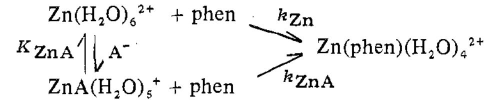
Contribution from the Laboratory of Analytical Chemistry,
Faculty of Science, Nagoya University, Nagoya, 464 Japan

The Bound Ligand Effect in the Complexation Kinetics of Some Monoanionozinc(II) Complexes with 1,10-Phenanthroline

SHINKICHI YAMADA, KIYOMI OHSUMI, and MOTOHARU TANAKA*

Received March 23, 1978

Kinetics and mechanism of the complex formation reaction of monohydroxo-, monoacetato-, monothiocyanato-, monoazido-, and monofluorozinc(II) complexes with 1,10-phenanthroline have been studied spectrophotometrically by means of a highly sensitive stopped-flow apparatus. The reaction scheme can be described as



where phen refers to unprotonated 1,10-phenanthroline and A^- a monodentate ligand such as hydroxide, acetate (OAc^-), thiocyanate, azide, or fluoride. The formation constants K_{ZnA} of the monoanionozinc(II) complexes and rate constants k_{Zn} and k_{ZnA} are kinetically determined: $K_{ZnOAc} = 10^{1.4 \pm 0.1}$ dm^3 mol^{-1}, $K_{ZnNCS} = 10^{1.7 \pm 0.1}$ dm^3 mol^{-1}, $K_{ZnN_3} = 10^{1.7 \pm 0.1}$ dm^3 mol^{-1}, $k_{Zn} = (1.5 \pm 0.1) \times 10^7$ dm^3 mol^{-1} s^{-1}, $k_{ZnOH} = (6 \pm 1) \times 10^7$ dm^3 mol^{-1} s^{-1}, $k_{ZnOAc} = (3.3 \pm 0.3) \times 10^7$ dm^3 mol^{-1} s^{-1}, $k_{ZnNCS} = (3.9 \pm 0.4) \times 10^7$ dm^3 mol^{-1} s^{-1}, $k_{ZnN_3} = (3.9 \pm 0.4) \times 10^7$ dm^3 mol^{-1} s^{-1}, $k_{ZnF} = (1.6 \pm 0.7) \times 10^7$ dm^3 mol^{-1} s^{-1}, all at 25 °C and $I = 1.0$ ($NaClO_4$). The zinc(II) complexation proceeds by the I_d mechanism. The bound ligand effect on the rate of loss of water molecules of these zinc(II) complexes is discussed in terms of electron donation from the ligands. In accordance with the earlier consideration, the value of log k_{ZnA} is linearly related to the electron-donating ability of the ligand A, and the proportionality constant γ, characteristic of zinc(II), is correlated with the softness parameter σ: $\gamma = -5.8\sigma + 5.7$.

Introduction

From the mechanistic consideration on the formation constants of metal complexes,[1,2] it has been shown that the rate of dissociation of the ligand L from the complex MAL is expressed as

$$\log (k_{MAL}^{-L}/k_M^{-H_2O}) = \gamma E(A) - \alpha E(L) - \beta H(L) \quad (1)$$

where $(k_{MAL}^{-L}/k_M^{-H_2O})$ is a relative (to water) rate of removal of L from the complex MAL, E and H refer to the electron donor constant and the basicity constant of the specified ligand, respectively, and α, β, and γ are constants characteristic of the metal ion M. Using values of E and H as given by Edwards,[3] normalized to zero for L or A = H_2O, we have for A = H_2O

$$\log (k_M^{-H_2O}/k_{ML}^{-L}) = \alpha E(L) + \beta H(L) \quad (2)$$

and for L = H_2O

$$\log (k_{MA}^{-H_2O}/k_M^{-H_2O}) = \gamma E(A) \quad (3)$$

By means of eq 2, we have estimated α and β for 26 metal ions and proposed the σ parameter ($\sigma \equiv \alpha/(\alpha + \beta)$) which is considered as a quantitative measure of the softness of metal ions.[4] We have also estimated the γ parameter for chromium(III), cobalt(II), iron(III), nickel(II), and oxovanadium(IV) by eq 3 and found that this γ parameter is linearly correlated with the softness parameter σ.[5]

To confirm this relationship between the values of γ and σ experimentally, we have been studying the bound ligand effect on the complexation kinetics. The present paper describes the kinetic results on the complexation reaction involving some monoanionozinc(II) complexes (A^- and phen refer to monodentate ligand and unprotonated 1,10-phenanthroline, respectively):

$$ZnA^+ + \text{phen} \xrightarrow{k_{ZnA}} Zn(\text{phen})^{2+}$$

1,10-Phenanthroline is particularly suitable for studying the complexation kinetics of metal ions: the formation constants with metal ions are high and the molar extinction coefficients in the ultraviolet region are large, so that by lowering the concentrations of both reactants, the complexation kinetics can be directly followed by a stopped-flow method. On the other hand, a highly sensitive stopped-flow method with a computer of average transients developed in our laboratory[6] enabled us to measure absorbance changes as small as 0.001 at about several milliseconds; thus lowering the reactant concentration we can directly follow the rapid complexation reaction involving labile metal ions such as zinc(II). 1,10-Phenanthroline is not protonated in neutral and weakly acidic solution and thus the studies in this pH region are free from "proton ambiguity" on the assignment of the proton dependence. Finally for unprotonated 1,10-phenanthroline having a rigid framework, anomalous kinetic behavior is not anticipated, at least in aqueous solution.[7]

Experimental Section

Reagents. Zinc perchlorate: Zinc metal (99.999%) was dissolved in perchloric acid to prepare zinc perchlorate solution.

1,10-Phenanthroline: Reagent grade 1,10-phenanthroline was purified by recrystallization from distilled water. The amount of water of crystallization was determined by the Karl Fischer method with coulometric generation of iodine.

Sodium perchlorate: Sodium perchlorate was prepared by dissolution of sodium carbonate in perchloric acid. Heavy-metal impurities in the sodium perchlorate were precipitated as hydroxides at pH 8.5. Sodium perchlorate was then recrystallized twice from distilled water. The purity of sodium perchlorate was checked by an ultraviolet absorption spectrum and the color reaction with PAR (4-(2-pyridylazo)resorcinol). The concentration of sodium ion in the sodium perchlorate solution was determined gravimetrically as sodium sulfate.

Monodentate ligands: Commercial G. R. reagents were purified by recrystallization twice from distilled water. The concentration of sodium thiocyanate was determined by argentometry, and the solutions of the other ligands (sodium acetate, sodium azide, sodium fluoride) were prepared by weighing the well-dried reagent.

Sodium borate: Reagent grade sodium borate was recrystallized from distilled water and dried in an air bath at 100 °C.

Measurements. All experiments were carried out in a room thermostated at 25 ± 0.5 °C. The ionic strength was maintained at 1.0 mol dm^{-3} with sodium perchlorate.

The kinetics of complexation was studied spectrophotometrically by means of a stopped-flow analyzer, RA 401 (Union, Ltd., Hirakata, Japan), equipped with a data processor (Union RA 450). The monoanionozinc(II) and 1,10-phenanthroline solutions were transferred to the thermostated mixing syringes (each 15 cm^3) and brought to temperature equilibrium at 25 ± 0.1 °C. The changes in absorbance

0020-1669/78/1317-2790$01.00/0

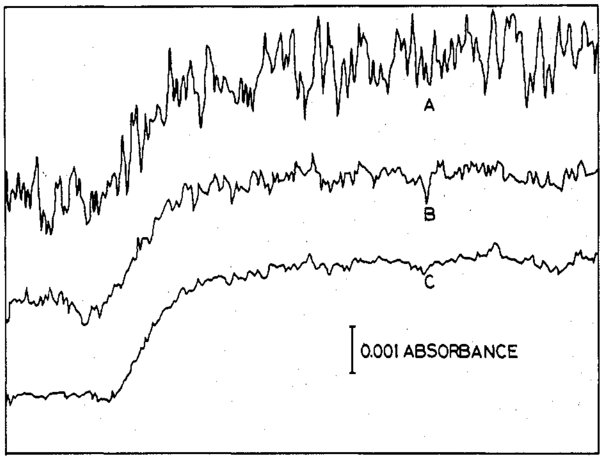


Figure 1. Smoothing of the trace for the reaction of monoazidozinc(II) complex with 1,10-phenanthroline: A, single flow; B, average of 15 flows; C, average of 50 flows. Conditions: $C_{Zn} = 3.09 \times 10^{-5}$ mol dm^{-3}, $C_{N_3} = 9.97 \times 10^{-5}$ mol dm^{-3}, $C_{phen} = 2.17 \times 10^{-6}$ mol dm^{-3}, $-\log [H^+] = 7.42$, 25 °C, $I = 1.0$; coordinate: 20 ms per full scale.

at 271 nm were accumulated to obtain high S/N curves (Figure 1) and recorded as a function of a reaction time. Borate buffer solution (the concentration of borate is 4×10^{-4} mol dm^{-3}; borate up to 4×10^{-3} mol dm^{-3} kinetically gives no effect) was added to adjust the hydrogen ion concentration.

Equilibrium measurements were made spectrophotometrically with a Union High-Sens spectrophotometer, SM 401, and a Hitachi Perkin-Elmer 139 UV–Vis spectrophotometer with a thermostated cell compartment.

Hydrogen ion concentration was determined by a Radiometer pH meter (PHM 22 Type) with a calomel electrode filled with saturated sodium chloride as an internal solution instead of saturated potassium chloride. A 1.000×10^{-2} mol dm^{-3} perchloric acid solution containing 0.99 mol dm^{-3} of sodium perchlorate was employed as a standard of hydrogen ion concentration ($-\log [H^+] = 2.000$), and the liquid junction potential was taken into consideration.[8]

Results

Protonation Equilibrium of 1,10-Phenanthroline. In acidic solution ($-\log [H^+] = 3$–7), the absorption spectra of 1,10-phenanthroline at various concentrations of hydrogen ion change with the isosbestic points at 269, 286, and 294 nm. From the plot of the absorbance change at 275 nm vs. $-\log [H^+]$, the protonation constant for 1,10-phenanthroline was determined by means of the curve-fitting method. The combination of the constant and the molar extinction coefficients which gives the best-fit curve was $K_{Hphen} = [Hphen^+][H^+]^{-1}[phen]^{-1} = 10^{5.31 \pm 0.02}$ dm^3 mol^{-1}, $\epsilon_{phen} = 1.78 \times 10^4$, and $\epsilon_{Hphen} = 2.96 \times 10^4$ at 25 °C and $I = 1.0$.

Complexation Equilibrium of Zinc(II) Complex. With the knowledge concerning the protonation of 1,10-phenanthroline in hand, we have studied the complexation equilibrium with zinc(II) ion. Zinc(II) ion forms a 1:1 complex with 1,10-phenanthroline in acidic solution ($-\log [H^+] = 1$–3) where the concentration of zinc(II) ion is in excess over that of the ligand. Spectral change, having the isosbestic points at 274, 287, and 298 nm, is attributable to the equilibrium

$$Zn^{2+} + Hphen^+ \rightleftharpoons Zn(phen)^{2+} + H^+$$

The equilibrium constant for this reaction was determined from the plot of the absorbance change at 280 nm vs. $-\log [H^+]$ by means of the curve-fitting method. The combination of the constant and the molar extinction coefficients which gives the best-fit curve was $K_{Zn(phen)}{}^{Hphen} = [Zn(phen)^{2+}][H^+] \cdot [Zn^{2+}]^{-1}[Hphen^+]^{-1} = 10^{1.21 \pm 0.02}$ dm^3 mol^{-1}, $\epsilon_{Zn(phen)} = 1.31 \times 10^4$, and $\epsilon_{Hphen} = 2.46 \times 10^4$ at 25 °C and $I = 1.0$. Using the molar extinction coefficients thus obtained, we confirmed this equilibrium constant from the logarithmic plot. The plot of $\log ([Zn(phen)^{2+}]/[Hphen^+])$ vs. $-\log [H^+]$ yielded a straight line with a slope of unity and the value of $K_{Zn(phen)}{}^{Hphen}$ was $10^{1.20 \pm 0.02}$ dm^3 mol^{-1} at 25 °C and $I = 1.0$. Thus we have

$$K_{Zn(phen)}{}^{phen} = [Zn(phen)^{2+}][Zn^{2+}]^{-1}[phen]^{-1} = K_{Zn(phen)}{}^{Hphen}K_{Hphen} = 10^{6.52 \pm 0.04} \text{ dm}^3 \text{ mol}^{-1}$$

Taking the difference in experimental conditions into account, these protonation and formation constants compare favorably with the results previously reported.[9]

Scheme I

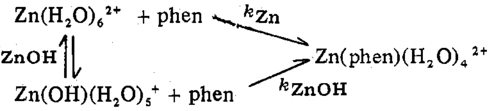


Table I. Conditional Rate Constants $k_{0(H)}$ at 25 °C[a]

$-\log [H^+]$	$k_{0(H)}/10^7$ dm^3 mol^{-1} s^{-1}	$-\log [H^+]$	$k_{0(H)}/10^7$ dm^3 mol^{-1} s^{-1}
6.97	1.57	8.07	1.91
7.39	1.62	8.19	1.96
7.66	1.71	8.24	2.02
7.84	1.73	8.31	2.12
7.94	1.78		

[a] $C_{Zn} = 3.09 \times 10^{-5}$ mol dm^{-3}, $C_{phen} = 2.17 \times 10^{-6}$ mol dm^{-3}, $I = 1.0$.

The Reaction of Zinc(II) Ion with 1,10-Phenanthroline. All reactions were first order in zinc(II) ion, which was always held in sufficient excess to ensure pseudo-first-order kinetics and complete formation of the mono complex. The unprotonated form of the ligand predominates in the range of the studies. Therefore the reaction scheme is as described in Scheme I and the kinetic equation for this reaction scheme is described in eq 4, where $[Zn']$ denotes the total concentration

$$d[Zn(phen)^{2+}]/dt = k_{0(H)}[Zn'][phen] \qquad (4)$$

of zinc(II) not combined with phen and $k_{0(H)}$ is the conditional rate constant involving the concentration of hydrogen ion.

The rate plot of $\ln[(A_\infty - A_0)/(A_\infty - A_t)]$ vs. t was linear for over 90% of the reaction (A_0, A_t, and A_∞ are the absorbances of the reaction systems at reaction time 0, t, and ∞, respectively). The conditional rate constants $k_{0(H)}$ were determined from the slope of this plot. Values of the conditional rate constants at various concentrations of hydrogen ion are given in Table I (each value is the average of at least three determinations). The results show that the conditional rate constant $k_{0(H)}$ increases with decreasing concentration of hydrogen ion. Under the present experimental conditions of 1,10-phenanthroline not being protonated at all, the increase of $k_{0(H)}$ is attributable to the monohydroxozinc(II) ion.

The kinetic equation is expressed by

$$d[Zn(phen)^{2+}]/dt = k_{Zn}[Zn^{2+}][phen] + k_{ZnOH}[ZnOH^+][phen]$$

Then the conditional rate constant can be written as

$$k_{0(H)} = \frac{k_{Zn} + k_{ZnOH}K_{ZnOH}[H^+]^{-1}}{1 + K_{ZnOH}[H^+]^{-1}} \qquad (5)$$

where K_{ZnOH} ($=[ZnOH^+][H^+][Zn^{2+}]^{-1}$) is the hydrolysis constant of zinc(II) ion. Employing the K_{ZnOH} value reported by Perrin,[10] the rate constants were determined from the linear plot of $k_{0(H)}(1 + K_{ZnOH}[H^+]^{-1})$ vs. $[H^+]^{-1}$ to be $k_{Zn} = 1.54 \times 10^7$ dm^3 mol^{-1} s^{-1} and $k_{ZnOH} = 6.08 \times 10^7$ dm^3 mol^{-1} s^{-1}.

The Reaction of Monoanionozinc(II) Complexes with 1,10-Phenanthroline. For a complexation reaction of zinc(II) ion with the monodentate ligands studied, one can reasonably

Table II. Conditional Rate Constants $k_{0(\mathrm{H,A})}$ at 25 °C[a]

C_A/mol dm^{-3}	$k_{0(\mathrm{H,A})}/10^7$ dm^3 mol^{-1} s^{-1}	$-\log\,[\mathrm{H}^+]$
	(i) Acetate	
1.15×10^{-4}	1.87	7.89
2.30×10^{-4}	1.82	7.96
6.90×10^{-4}	1.94	7.97
1.15×10^{-3}	1.98	7.97
2.30×10^{-3}	2.03	7.97
3.45×10^{-3}	1.98	7.96
6.90×10^{-3}	2.01	7.94
1.15×10^{-2}	2.14	7.91
2.30×10^{-2}	2.37	7.93
3.45×10^{-2}	2.59	7.92
6.90×10^{-2}	2.72	7.94
	(ii) Thiocyanate	
5.65×10^{-5}	1.71	7.62
1.12×10^{-4}	1.75	7.78
2.25×10^{-4}	1.73	7.84
5.62×10^{-4}	1.77	7.70
8.42×10^{-4}	1.80	7.70
1.40×10^{-3}	1.86	7.65
1.97×10^{-3}	1.97	7.60
2.81×10^{-3}	2.13	7.59
4.21×10^{-3}	2.16	7.83
5.62×10^{-3}	2.24	7.70
5.62×10^{-3}	2.25	7.70
8.14×10^{-3}	2.34	7.79
1.41×10^{-2}	2.45	7.78
2.81×10^{-2}	2.85	7.76
5.62×10^{-2}	3.34	7.77
	(iii) Azide	
9.97×10^{-5}	1.75	7.42
1.99×10^{-4}	1.93	7.27
2.99×10^{-4}	1.85	7.41
5.98×10^{-4}	2.00	7.53
9.97×10^{-4}	2.15	7.33
1.99×10^{-3}	2.00	7.16
2.99×10^{-3}	2.16	7.44
5.98×10^{-3}	2.31	7.25
9.97×10^{-3}	2.54	7.58
1.99×10^{-2}	2.87	7.60
	(iv) Fluoride	
1.01×10^{-4}	1.69	7.72
6.05×10^{-4}	1.92	7.72
1.01×10^{-3}	1.63	7.69
2.02×10^{-3}	1.56	7.70
3.02×10^{-3}	1.61	7.70
6.05×10^{-3}	1.82	7.72
1.01×10^{-2}	1.83	7.68
2.02×10^{-2}	1.60	7.69
3.02×10^{-2}	1.77	7.66
6.05×10^{-2}	1.56	7.56
1.01×10^{-1}	1.79	7.55

[a] $C_\mathrm{Zn} = 3.09 \times 10^{-5}$ mol dm^{-3}, $C_\mathrm{phen} = 2.17 \times 10^{-6}$ mol dm^{-3}, $I = 1.0$.

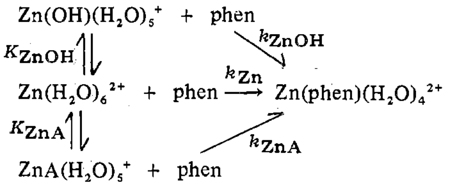
expect a rate similar to that of the zinc(II) ion with phen. The concentration of these monodentate ligands being much higher than that of phen (see Table II), these monoanionozinc(II) complexes are certainly in equilibrium with the aquazinc(II) ion during the reaction. Under the present experimental conditions only the monoaniono species $\mathrm{ZnA(H_2O)_5}^+$ can be expected from the reported values[9] of formation constants for these complexes. This is confirmed by the present study. Thus the reaction can be considered to proceed as in Scheme II.[11]

The kinetic equation for this reaction scheme is described as

$$d[\mathrm{Zn(phen)}^{2+}]/dt = k_{0(\mathrm{H,A})}[\mathrm{Zn'}][\mathrm{phen}] \qquad (6)$$

where $k_{0(\mathrm{H,A})}$ is the conditional rate constant involving concentrations of hydrogen ion and monodentate ligand A. The rate plot was also linear for over 90% of the reaction and the conditional rate constants $k_{0(\mathrm{H,A})}$ were determined from the slope of this rate plot. Values of $k_{0(\mathrm{H,A})}$ at various concentrations of monodentate ligands are given in Table II (each value is the average of at least three determinations).

Scheme II



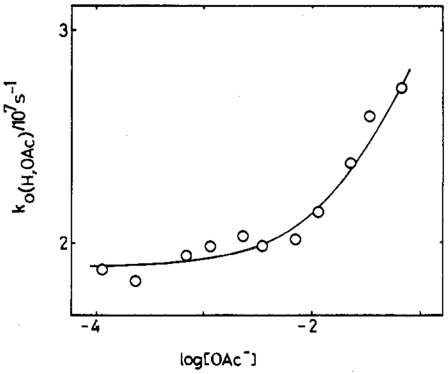


Figure 2. Plot of $k_{0(\mathrm{H,OAc})}$ vs. log [OAc$^-$]. The line is the theoretical curve calculated with the values obtained by the curve fitting. The points are experimental.

For the systems involving acetate, thiocyanate, and azide, the results show that the conditional rate constant $k_{0(\mathrm{H,A})}$ increases with increasing concentration of A$^-$, and this increase of the rate is attributable to $\mathrm{ZnA(H_2O)_5}^+$ which is reasonably expected to be more reactive than the aquazinc(II) ion. Considering Scheme II, the rate of this system is described as

$$d[\mathrm{Zn(phen)}^{2+}]/dt = k_\mathrm{Zn}[\mathrm{Zn}^{2+}][\mathrm{phen}] + k_\mathrm{ZnOH}[\mathrm{ZnOH}^+][\mathrm{phen}] + k_\mathrm{ZnA}[\mathrm{ZnA}^+][\mathrm{phen}]$$

Then the conditional rate constant $k_{0(\mathrm{H,A})}$ can be written as

$$k_{0(\mathrm{H,A})} = k_\mathrm{ZnA} + \frac{(k_\mathrm{ZnOH} - k_\mathrm{ZnA})K_\mathrm{ZnOH}[\mathrm{H}^+]^{-1} + k_\mathrm{Zn} - k_\mathrm{ZnA}}{1 + K_\mathrm{ZnOH}[\mathrm{H}^+]^{-1} + K_\mathrm{ZnA}[\mathrm{A}^-]} \qquad (7)$$

At constant pHs the result may be compared with a normalized function:

$$y = p/(a + x) = \mathrm{f}(\log x)$$

Variation of the value of a due to the variation of pH is within ±1% in a series of runs for a given ligand A. The experimental plot of $k_{0(\mathrm{H,A})}$ vs. log [A$^-$] fits well with one of a family of the normalized curves. Fitting the plot with curves of y vs. log x at various values of p, we obtained log K_ZnA from the reading of the abscissa and k_ZnA from the ordinate of the best-fit curve. For the acetate system the formation constant K_ZnOAc and the rate constant k_ZnOAc are $10^{1.4}$ dm^3 mol^{-1} and 3.26×10^7 dm^3 mol^{-1} s^{-1}, respectively (Figure 2). We also confirmed these constants from the linear plot of $k_{0(\mathrm{H,A})}(1 + K_\mathrm{ZnOH}[\mathrm{H}^+]^{-1} + K_\mathrm{ZnA}[\mathrm{A}^-])$ vs. [A$^-$]. For the thiocyanate and azide systems, the formation and rate constants are determined also by the curve-fitting method and the results are summarized in Table III. The uncertainty of the constants in Table III indicates the range. For the fluoride system, according to a potentiometric study by Ahrland and Rosengren,[12] several tens percent of the monofluorozinc(II) complex being present at 0.1 mol dm^{-3} of fluoride ion, the conditional rate constant $k_{0(\mathrm{H,F})}$ did not change with increasing total concentration of

Table III. Formation and Rate Constants at 25 °C and $I = 1.0$

A	E(A)	$k_{\mathrm{ZnA}}/10^7$ dm^3 mol^{-1} s^{-1}	log K_{ZnA}
H_2O	0.00	1.5 ± 0.1	
OH^-	1.65	6 ± 1	
OAc^-	0.96	3.3 ± 0.3	1.4 ± 0.1
SCN^-	1.83	3.9 ± 0.4	1.7 ± 0.1
N_3^-	1.58	3.9 ± 0.4	1.7 ± 0.1
F^-	−0.27	1.6 ± 0.7	

fluoride ion up to 0.1 mol dm^{-3}. Employing $10^{0.77}$ [12] for K_{ZnF}, k_{ZnF} was determined to be $(1.6 \pm 0.7) \times 10^7$ dm^3 mol^{-1} s^{-1} (contribution of the outer-sphere complex Zn^{2+},F^- to the denominator in eq 7 was taken into consideration).

Discussion

Solvent Exchange Rate at Zn^{2+}. It is now generally accepted that complex formation occurs by the two-step mechanism

$$M(H_2O)_6{}^{n+} + L^{m-} \underset{}{\overset{K_{os}}{\rightleftharpoons}} M(H_2O)_6{}^{n+},L^{m-} \xrightarrow{k_M{}^{-H_2O}} ML(H_2O)_5{}^{n-m} + H_2O$$

in which the diffusion-controlled formation of the outer-sphere complex $M(H_2O)_6{}^{n+},L^{m-}$ between the aquametal ion $M(H_2O)_6{}^{n+}$ and the monodentate ligand L^{m-} precedes the loss of a coordinated water molecule as the rate-determining step and the overall rate constant $k_M{}^L$ is given by $K_{os}k_M{}^{-H_2O}$ where K_{os} is the formation constant of the outer-sphere complex. For the complexation reactions involving multidentate ligands, it should be noted that some feature of the chemical system alters the rate-determining step. For example, anomalously low values of rate constants for $Hnta^{2-}$ (H_3nta = nitrilotriacetic acid)[13] and H_2edta^{2-} (H_4edta = ethylenediamine-*N,N,N′,N′*-tetraacetic acid)[14] with Zn^{2+} are interpreted to be due to the rate-determining proton transfer occurring prior to chelate ring closure. Sometimes chelate ring size may affect the kinetic behavior in certain complexation reactions.[15,16] However, this two-step mechanism seems to be also applicable to almost all complexation reactions involving the multidentate ligands which have no extra stabilization of an outer-sphere complex[17] and no steric inhibition due to their bulkiness.[18,19]

A complexation reaction which involves a change in coordination number and geometry about the metal ion may exhibit anomalous kinetic behavior if the configurational change is the rate-determining step. The aquazinc(II) ion is known to be six-coordinated,[20,21] while the possibility of the transformation between $Zn(H_2O)_6{}^{2+}$ and $Zn(H_2O)_4{}^{2+}$ is suggested.[22] For monoanionozinc(II) complexes, it is suggested from equilibrium and enthalpy measurements on the complex formation that coordination changes from an octahedral to a tetrahedral structure at the second step of the successive reaction (dicomplex formation) for halide[23] and thiocyanate[24] systems and at the third step (tricomplex formation) for the azide system.[25] For the zinc(II)–phenanthroline complex, any unusual changes of the formation constants, $\Delta H°$, and $\Delta S°$ attributable to a configurational change not being observed for each consecutive step,[26,27] it seems reasonable that the monophenanthroline–zinc(II) complex is octahedral. An octahedral configuration is also consistent with the coordination of three bidentate ligands at the zinc(II) ion. It is therefore pertinent to consider that the complexation reactions of aquazinc(II) and monoanionozinc(II) ions involve $Zn(H_2O)_6{}^{2+}$ and $ZnA(H_2O)_5{}^+$, respectively, and that these processes are "normal".

The value of $10^{-0.5}$ dm^3 mol^{-1} being taken for K_{os},[2] the rate constant of the water exchange at Zn^{2+} is estimated to be $10^{7.7}$ s^{-1} from the overall complexation rate constant of Zn^{2+} with phen, k_{Zn}. Since the value of $\Delta H°_{os}$ does not significantly contribute to the overall activation enthalpy, the activation enthalpy of water exchange at Zn^{2+} is estimated to be 50 kJ mol^{-1} [28] from a study of the same system but at $I = 0.1$ ($NaClO_4$).

Complexation kinetics of Zn^{2+} with $SO_4{}^{2-}$,[29,30] NH_3,[31] 1,10-phenanthroline,[32] bipyridine,[32] serine,[33] glycine,[34] pyridine-2-azo-*p*-dimethylaniline,[35,36] terpyridine,[32] murexide,[30,37,38] ethylenediamine-*N,N,N′,N′*-tetraacetic acid,[14] 2-*N′*-hydroxyethylethylenediamine-*N,N,N′*-triacetic acid,[14] 1,3-propylenediamine-*N,N,N′,N′*-tetraacetic acid,[39] and ethylenediamine-*N,N′*-diacetic-*N,N′*-dipropionic acid[39] have been studied and yielded the overall rate constants ranging from 10^6 to 10^9 dm^3 mol^{-1} s^{-1}. But for almost all of the systems the rate constant of the inner-coordinated water exchange at Zn^{2+} can be estimated to be $10^{7.3}$–$10^{7.9}$ s^{-1} at 25 °C. For the system involving $SO_4{}^{2-}$ the value of $k_{Zn}{}^{-H_2O}$ has been directly determined to be $10^{7.5}$ s^{-1} at 25 °C by the sound absorption method.[29] Comparison of this value with that of the present system ($10^{7.7}$ s^{-1}) indicates that they are almost the same within probable error due to uncertainty in estimating K_{os} and difference in ionic strength. This result also indicates that the rate constant for chelate ring closure in 1,10-phenanthroline is rapid compared with that for the formation of the half-bonded intermediate. Thus we conclude that the complexation of zinc(II) with 1,10-phenanthroline is accommodated within the framework of an I_d mechanism.

The Effect of Bound Ligands. The reaction sequence involving ZnA^+ may be described as follows:

$$\underset{\mathrm{I}}{ZnA(H_2O)_5{}^+} + phen \rightleftharpoons \underset{\mathrm{II}}{[ZnA(H_2O)_5{}^+,phen]} \xrightarrow[\mathrm{rds}]{} \underset{\mathrm{III}}{ZnA(phen)(H_2O)_3{}^+} + 2H_2O$$

$$\mathrm{III} + H_2O \rightleftharpoons \underset{\mathrm{IV}}{Zn(phen)(H_2O)_4{}^{2+}} + A^- \qquad (8)$$

Monoanionozinc ion (I) forms at first an outer-sphere complex with phen (II). Then phen enters into the inner sphere of ZnA^+ as one of the water molecules coordinated at ZnA^+ dissociates. The next step of the chelate ring closure should be fast as compared to the preceding step. The product $ZnA(phen)^+$ may be in equilibrium with $Zn(phen)^{2+}$.[11]

As seen from Table III, in the reaction of monoanionozinc(II) complexes with 1,10-phenanthroline the order of reactivity increases for monodentate ligand as $F^- \simeq H_2O < OAc^- < N_3^- \simeq SCN^- < OH^-$ with a fourfold effect over the whole range. The same effect has been found in the reaction of nickel(II) complexes with 4-(2-pyridylazo)resorcinol[40] and the effect of bound ligands on the ease of replacement of the remaining water molecule has been interpreted by their ability to donate electrons to the central metal.

For such reactions as given in the sequence 8, the bound ligand effect has been quantitatively predicted by eq 3.[1] It

$$\log k_{MA}{}^{-H_2O} = \log k_M{}^{-H_2O} + \gamma E(A)$$

is reasonable to assume that the values of outer-sphere association constants for the reactions of zinc(II) complexes with phen are similar because one of the reactants, phen, is noncharged. Then the plot of $\log k_{ZnA} - \log k_{Zn}$ vs. E(A) should yield a straight line with an intercept of zero. The plot is given in Figure 3. The value of γ for zinc(II) was estimated from the slope of this plot to be 0.30. We have already proposed that this γ parameter is approximately linearly correlated with the softness parameter σ.[5] The plot of γ vs. σ involving the result obtained for zinc(II) is given in Figure 4. By means of the method of least squares we have

$$\gamma = -5.8\sigma + 5.7 \qquad (9)$$

Equation 9 implies that the harder the metal ion, the more sensitive is the water exchange rate to the electron-donating ability of the ligand already attached. This seems reasonable

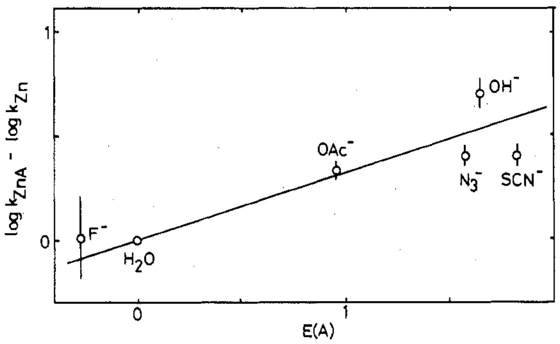


Figure 3. Plot of log k_{ZnA} − log k_{Zn} vs. E(A).

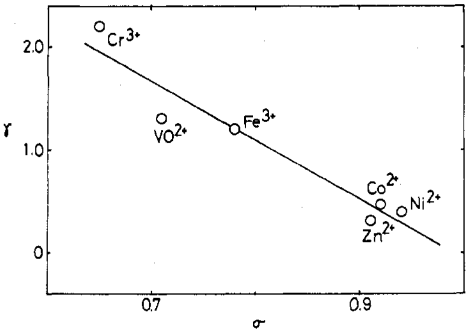


Figure 4. Plot of γ vs. σ.

because soft metal ions form bonds with more covalent character via extensive back-donation than hard metal ions.

The value of σ being known for 26 metal ions, the values of γ may be predicted using eq 9 for these metal ions. The value of γ thus estimated enables us to predict quantitatively the effect of bound ligand(s) on the water exchange rate at metal complexes. In particular, the knowledge for the reactivity of monohydroxometal ion (log $k_{MOH}{}^{-H_2O}$ = log $k_M{}^{-H_2O}$ + 1.65γ) gives an empirical approach to "proton ambiguity": the comparison of the calculated $k_{MOH}{}^{-H_2O}$ with the experimentally obtained $k_{MOH}{}^{-H_2O}$ will allow one to check the *soundness* of the constant and the postulated mechanism.

Acknowledgment. The financial support from the Mitsubishi Foundation (1975) is gratefully acknowledged.

Registry No. $Zn(H_2O)_6{}^{2+}$, 15906-01-1; $Zn(OH)(H_2O)_5{}^+$, 38530-89-1; $Zn(OAc)(H_2O)_5{}^+$, 67316-55-6; $(ZnSCN)(H_2O)_5{}^+$, 67316-69-2; $Zn(N_3)(H_2O)_5{}^+$, 67316-68-1; $Zn(F)(H_2O)_5{}^+$, 67316-67-0; phen, 66-71-7.

References and Notes

(1) Tanaka, M. *J. Inorg. Nucl. Chem.* **1973**, 35, 965.
(2) Tanaka, M. *J. Inorg. Nucl. Chem.* **1974**, 36, 151.
(3) Edwards, J. O. *J. Am. Chem. Soc.* **1954**, 76, 1540.
(4) Yamada, S.; Tanaka, M. *J. Inorg. Nucl. Chem.* **1975**, 37, 587.
(5) Tanaka, M.; Yamada, S. *J. Chem. Soc., Chem. Commun.* **1976**, 178.
(6) Tanaka, M.; Funahashi, S.; Nagamura, T. The 1977 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy: Cleveland, Ohio; Abstr. 63.
(7) Coetzee, J. F., in *Solute Solvent Interactions*; J. F. Coetzee and C. D. Ritchi, Ed.; Marcel Dekker, New York, N.Y., 1976; Vol. 2, Chapter 14.
(8) Yamada, S.; Nagase, J.; Funahashi, S.; Tanaka, M. *J. Inorg. Nucl. Chem.* **1976**, 38, 617.
(9) Sillên, L. G.; Martell, A. E. *Stability Constants of Metal Ion Complexes*; the Chemical Society, London, 1964; Supplement No. 1, the Chemical Society, London, 1971.
(10) The hydrolysis constant written in terms of concentrations of the reactants, calculated from the mixed constant given by Perrin (Perrin, D. D. *J. Chem. Soc.* **1962**, 4500) is $K_{ZnOH} = 10^{-9.16 \pm 0.05}$ mol dm^{-3} at 25 °C and $I = 1.0$.
(11) The formation of a small amount of a mixed-ligand complex $Zn(phen)A^+$ may be anticipated. However, the coordination of one phen being quantitative under the present experimental conditions, the following treatment is valid even in the presence of such a mixed-ligand complex.
(12) Ahrland, S.; Rosengren, K. *Acta Chem. Scand.* **1956**, 10, 727.
(13) Rabenstein, D. L.; Kula, R. J. *J. Am. Chem. Soc.* **1969**, 91, 2492.
(14) Reed, G. H.; Kula, R. J. *Inorg. Chem.* **1971**, 10, 2050.
(15) Kustin, K.; Pasternack, R. F.; Weinstock, E. M. *J. Am. Chem. Soc.* **1966**, 88, 4610.
(16) Kowalak, A.; Kustin, K.; Pasternack, R. F.; Petrucci, S. *J. Am. Chem. Soc.* **1967**, 89, 3126.
(17) Taylor, R. W.; Stepien, H. K.; Rorabacher, D. B. *Inorg. Chem.* **1974**, 13, 1282.
(18) Turan, T. S. *Inorg. Chem.* **1974**, 13, 1584.
(19) Lin, C. T.; Rorabacher, D. B.; Cayley, G. R.; Margerum, D. W. *Inorg. Chem.* **1975**, 14, 919.
(20) Irish, D. E.; McCroll, B.; Young, T. F. *J. Chem. Phys.* **1963**, 39, 3436.
(21) Ohtaki. H.; Yamaguchi, T.; Maeda, M. *Bull. Chem. Soc. Jpn.* **1976**, 49, 701.
(22) Swift, T. J. *Inorg. Chem.* **1964**, 3, 526.
(23) Gerding, P. *Acta Chem. Scand.* **1969**, 23, 1695.
(24) Ahrland, S.; Kullberg, L. *Acta Chem. Scand.* **1971**, 25, 3692.
(25) Ahrland, S.; Avsar, E. *Acta Chem. Scand.* **1975**, A29, 890.
(26) Anderegg, G. *Helv. Chim. Acta* **1963**, 46, 2813.
(27) Eatough, D. J. *Anal. Chem.* **1970**, 42, 635.
(28) Yamada, S.; Kimata, T.; Tanaka, M. unpublished result.
(29) Fittipaldi, F.; Petrucci, S. *J. Phys. Chem.* **1967**, 71, 3414.
(30) Maass, G. *Z. Phys. Chem.* (*Frankfurt am Main*) **1968**, 60, 138.
(31) Rorabacher, D. B. *Inorg. Chem.* **1966**, 5 1891.
(32) Holyer, R. H.; Hubbard, C. D.; Kettle, S. F. A.; Wilkins, R. G. *Inorg. Chem.* **1966**, 5, 622.
(33) Karpel, R. L.; Kustin, K.; Pasternack, R. F. *Biochim. Biophys. Acta* **1969**, 177, 434.
(34) Miceli, J. A.; Stuehr, J. E. *Inorg. Chem.* **1972**, 11, 2763.
(35) Wilkins, R. G. *Inorg. Chem.* **1964**, 3, 520.
(36) Cayley, G. R.; Hague, D. N. *Trans. Faraday Soc.* **1971**, 67, 786.
(37) Bewick, A.; Robertson, P. M. *Trans. Faraday Soc.* **1967**, 63, 678.
(38) Geier, G. *Helv. Chim. Acta* **1968**, 51, 94.
(39) Fuhr, B. J.; Rabenstein, D. L. *Inorg. Chem.* **1973**, 12, 1868.
(40) Funahashi, S.; Tanaka, M. *Inorg. Chem.* **1969**, 8, 2159.