The Bound Ligand Effect in the Complexation Kinetics of Some Anionogallium(III) Complexes

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The formation rate of some anionogallium(III) complexes (GaA) with 4,5-dihydroxy-1,3-benzenedisulfonate (H_2L^{2-}) in the presence of thiocyanate ion has been studied spectrophotometrically by a stopped-flow technique. The rate law is expressed as $d[GaL^-]/dt=k_{Ga}[Ga^{3+}][H_2L^{2-}]+k_{GaOH}[GaOH^{2+}][H_2L^{2-}]+k_{Ga(OH)_2}[Ga(OH)_2{}^+]$-$[H_2L^{2-}]+k_{GaNCS}[GaNCS^{2+}][H_2L^{2-}]$, with $k_{Ga}=10^{1.23}$ $M^{-1}\,s^{-1}$ (M=mol dm^{-3}), $k_{GaOH}=10^{3.36}$ $M^{-1}\,s^{-1}$, $k_{Ga(OH)_2}=10^{4.37}$ $M^{-1}\,s^{-1}$, and $k_{GaNCS}=10^{3.90}$ $M^{-1}\,s^{-1}$ at 25 °C and I=0.50M. The enhanced reactivity of GaA as compared to that of Ga^{3+} is attributable to the labilizing effect of the bound ligand A on the rate of loss of coordinated water molecules at GaA. Together with the additional formation rate constants of monoisothiocyanato- and monooxalatogallium(III) with 2-hydroxy-2,4,6-cycloheptatrien-1-one, this labilizing effect is quantitatively discussed in terms of the electron-donating ability of the ligand.

From the mechanistic consideration on the formation constants of metal complexes,[1,2] it has been shown that, taking into account the statistical factor arising from the number of water molecules available for exchange, the water exchange rate constant at MA ($k_{MA}{}^{-H_2O}$) is expressed as

$$\log (k_{MA}{}^{-H_2O}/\text{number of } H_2O \text{ in MA}) = \log (k_M{}^{-H_2O}/\text{number of } H_2O \text{ in M}) + \gamma E(A) \quad (1)$$

where $E(A)$ refers to the electron donor constant[3] of the ligand A and γ is a constant characteristic of the metal ion M.

In the preceding paper,[4] we have studied the kinetics and mechanism of the complex formation of monohydroxo-, monoacetato-, monothiocyanato-, monoazido-, and monofluorozinc(II) complexes with 1,10-phenanthroline and found that the labilizing effect of the bound ligand on the rate of loss of coordinated water molecules is quantitatively described by Eq. 1. Recently, we have shown[5] that Eq. 1 can predict the bound ligand effect of the multidentate-ligand complexes of nickel(II). In the system, the value of the effective $E(A)$ for a multidentate ligand is given by the summation of $E(X)$ of each donor atom X involved in A which is corrected for the effect of vicinal functions. This effective $E(A)$ value is particularly useful in the estimation of the γ parameter for a hard metal ion such as gallium(III): The number of bound ligands suitable for kinetic measurements is limited due to their small formation constants with gallium(III) ion in acidic medium.

To understand how the rate of loss of coordinated water molecules at GaA is labilized by the presence of the coordinated ligand A, we have studied the complexation kinetics described as

$$GaA + H_2L^{2-} \xrightarrow{k_{GaA}} GaAL(\text{and/or } GaL^- + A) + 2H^+, \quad (2)$$

$$GaA + HL \xrightarrow{k_{GaA}} GaAL(\text{and/or } GaL^{2+} + A) + H^+, \quad (3)$$

where A is a bound ligand such as hydroxide, thiocyanate or oxalate. H_2L^{2-} and HL refer to tiron (4,5-dihydroxy-1,3-benzenedisulfonate) and tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one), respectively. With these two entering ligands, we have already described the thermodynamic and kinetic results on the complexation reaction of the gallium(III) ion and provided definite mechanistic information on the reaction of this cation, on the basis of values of activation volume obtained by a high-pressure stopped-flow technique.[6]

Experimental

The solutions of gallium(III) perchlorate, tropolone, tiron, and sodium thiocyanate were prepared as described elsewhere.[4,6] Sodium oxalate of primary standard quality (Wako-junyaku) was used without further purification. All experiments were carried out in a room thermostated at 25.0±0.5 °C. Temperature of the reaction solution was controlled to within ±0.1 °C. Ionic strength was maintained at 0.50 M with sodium perchlorate. Reaction rates were followed by a stopped-flow spectrophotometer equipped with a data processor. The changes in absorbance at 305 nm and 313 nm, wavelength of the maximum absorption of the 1:1 Ga(III)-tiron and Ga(III)-tropolone complexes respectively, were accumulated to obtain high S/N curves. Other experimental details are described elsewhere.[4,6]

Results

Reaction of Gallium(III) Ion with Tiron. Gallium(III) ion forms a 1:1 complex with tiron in acidic solution where the concentration of gallium(III) is in large excess over that of the ligand:[6]

$$Ga' + H_2L^{2-} \underset{k_{r(H)}}{\overset{k_{f(H)}}{\rightleftarrows}} GaL^- + 2H^+ \quad (4)$$

where $k_{f(H)}$ is a second-order conditional rate constant involving the concentration of hydrogen ion for the formation of the complex and $k_{r(H)}$ is a pseudo-first-order conditional rate constant involving the concentration of hydrogen ion for the dissociation of the complex. Then the kinetic equation for this reaction is described by

$$\begin{aligned} \mathrm{d}[\mathrm{GaL}^-]/\mathrm{d}t &= k_{\mathrm{f(H)}}[\mathrm{Ga}'][\mathrm{H_2L}^{2-}] - k_{\mathrm{r(H)}}[\mathrm{GaL}^-] \\ &= k_{\mathrm{f(H)}}C_{\mathrm{L}}[\mathrm{Ga}'] - k_{\mathrm{o(H)}}[\mathrm{GaL}^-] \end{aligned} \tag{5}$$

where [Ga′] denotes the total concentration of gallium(III) not combined with the ligand L^{4-} (aqua and hydroxo gallium ions), and $C_L=[H_2L^{2-}]+[GaL^-]$ and $k_{o(H)}=k_{f(H)}\,[Ga']+k_{r(H)}$.

Integration of Eq. 5 gives

$$\ln\frac{k_{\mathrm{f(H)}}C_{\mathrm{L}}[\mathrm{Ga}']}{k_{\mathrm{f(H)}}C_{\mathrm{L}}[\mathrm{Ga}'] - k_{\mathrm{o(H)}}[\mathrm{GaL}^-]} = \ln\frac{A_\infty - A_0}{A_\infty - A_t} = k_{\mathrm{o(H)}}t,$$

where A_0, A_t, and A_∞ are the absorbances at 305 nm for reaction systems at reaction time 0, t, and ∞, respectively. The rate plot of $\ln\{(A_\infty-A_0)/(A_\infty-A_t)\}$ *vs.* t was linear for over 90% of the reaction. The conditional rate constant involving the concentration of hydrogen ion $k_{o(H)}$ determined from the slope of this plot is correlated with $k_{f(H)}$ and $k_{r(H)}$ by the following relations:

$$k_{\mathrm{o(H)}} = k_{\mathrm{f(H)}}[\mathrm{Ga}'] + k_{\mathrm{r(H)}}$$

$$k_{\mathrm{f(H)}}/k_{\mathrm{r(H)}} = K_{\mathrm{GaL}}{}^{\mathrm{H_2L}}/(\alpha_{\mathrm{Ga(OH)}}[\mathrm{H}^+]^2)$$

where $K_{GaL}{}^{H_2L}=[GaL^-][H^+]^2[Ga^{3+}]^{-1}[H_2L^{2-}]^{-1}$ and $\alpha_{Ga(OH)}=1+K_{GaOH}[H^+]^{-1}+K_{GaOH}K_{Ga(OH)_2}[H^+]^{-2}$. Employing the values of $K_{GaL}{}^{H_2L}$ and $K_{GaOH}=[GaOH^{2+}][H^+][Ga^{3+}]^{-1}$ previously determined[6] and $K_{Ga(OH)_2}=[Ga(OH)_2{}^+][H^+][GaOH^{2+}]^{-1}$ reported,[7] the values of $k_{f(H)}$ and $k_{r(H)}$ were calculated as in Table 1.

The increase of the conditional rate constant $k_{f(H)}$ with decreasing concentration of hydrogen ion is attributable to the hydrolyzed species of gallium(III).[8] Thus

$$\begin{aligned} \mathrm{d}[\mathrm{GaL}^-]/\mathrm{d}t = \{&k_{\mathrm{Ga}}[\mathrm{Ga}^{3+}] + k_{\mathrm{GaOH}}[\mathrm{GaOH}^{2+}] \\ &+ k_{\mathrm{Ga(OH)_2}}[\mathrm{Ga(OH)_2}^+]\} \\ &\times [\mathrm{H_2L}^{2-}] - k_{\mathrm{r(H)}}[\mathrm{GaL}^-] \end{aligned} \tag{6}$$

and

$$\begin{aligned} k_{\mathrm{f(H)}}\alpha_{\mathrm{Ga(OH)}} = k_{\mathrm{Ga}} &+ k_{\mathrm{GaOH}}K_{\mathrm{GaOH}}[\mathrm{H}^+]^{-1} \\ &+ k_{\mathrm{Ga(OH)_2}}K_{\mathrm{GaOH}}K_{\mathrm{Ga(OH)_2}}[\mathrm{H}^+]^{-2}. \end{aligned}$$

The values of the rate constants for these three reaction paths were determined from the plot of $k_{f(H)}\alpha_{Ga(OH)}$ *vs.* $[H^+]^{-1}$ as shown in Fig. 1 and they are given in Table 2.

The conditional rate constant for the dissociation of the complex, $k_{r(H)}$, is found to be correlated with the concentration of hydrogen ion as

$$k_{\mathrm{r(H)}} = 10^{-1.29} + 10^{1.75}[\mathrm{H}^+].$$

Reaction of Isothiocyanatogallium(III) with Tiron. Under the conditions where only $GaNCS^{2+}$ is responsible for the reaction of the gallium(III)-thiocyanate complex, the complexation reaction of gallium(III) complexes with tiron is considered to proceed as in Scheme 1.

With the total concentration of thiocyanate ion much

Table 1. Conditional rate constants for the complexation of gallium(III) with tiron[a)]

$-\log([H^+]/M)$	$k_{o(H)}$ / s^{-1}	$k_{f(H)}$ / $10^2 M^{-1} s^{-1}$	$k_{r(H)}$ / s^{-1}
1.530	3.07	1.23	1.70
1.566	3.16	1.38	1.62
1.606	2.98	1.42	1.39
1.642	2.98	1.52	1.27
1.691	3.12	1.74	1.17
1.733	3.29	1.96	1.09
1.797	3.38	2.19	0.92
1.860	3.54	2.46	0.78
1.931	3.85	2.84	0.66
2.022	4.50	3.52	0.55
2.150	5.74	4.74	0.43
2.152	5.47	4.52	0.41
2.215	6.29	5.29	0.36
2.255	6.93	5.88	0.34
2.282	7.01	5.98	0.31
2.362	8.92	7.70	0.29
2.433	10.23	8.90	0.25
2.458	10.42	9.09	0.23
2.566	14.68	12.90	0.22
2.649	18.14	16.00	0.20
2.675	18.97	16.75	0.19
2.757	24.05	21.29	0.18
2.769	23.05	20.41	0.17
2.779	23.06	20.42	0.16
2.790	24.05	21.31	0.16

a) $C_{Ga}=1.12\times10^{-2}$ M, $C_{H_2L}=1.08\times10^{-4}$ M, $I=0.50$ M, 25 °C.

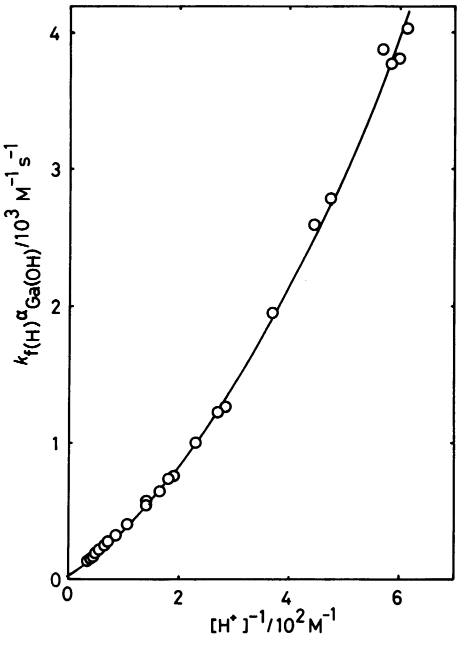

Fig. 1. Plot of $k_{f(H)}\alpha_{Ga(OH)}$ *vs.* $[H^+]^{-1}$.
The solid line is the curve calculated with the values obtained by a least-squares procedure.

TABLE 2. VALUES OF RATE CONSTANTS FOR THE COMPLEXATION REACTION OF GALLIUM(III) WITH VARIOUS ENTERING LIGANDS AT 25 °C

Entering ligand(L^{n-})$^{a)}$	I	$\log(k_{Ga}/M^{-1}s^{-1})$	$\log\{(k_{Ga}^{-H_2O}/s^{-1})/6\}$	Ref.
Tiron(H_2L^{2-})	0.5	1.23	0.95	This work
Tropolone(HL)	0.5	1.58	1.30	6
NSAL(HL^-)	0.1	2.61	1.06	18
PCV(H_3L^-)	0.2	1.84	1.56	19
SAL(HL^-)	0.1	2.83	1.28	20
SXO(H_2L^{2-})	0.1	2.84	1.29	21
		$\log(k_{GaOH}/M^{-1}s^{-1})$	$\log\{(k_{GaOH}^{-H_2O}/s^{-1})/5\}$	
Tiron(H_2L^{2-})	0.5	3.36	3.16	This work
Tropolone(HL)	0.5	3.91	3.71	6
NSAL(HL^-)	0.1	3.81	2.76	18
PCV(H_3L^-)	0.2	3.94	3.74	19
SAL(HL^-)	0.1	4.53	3.48	20
SXO(H_2L^{2-})	0.1	4.08	3.03	21
		$\log(k_{Ga(OH)_2}/M^{-1}s^{-1})$	$\log\{(k_{Ga(OH)_2}^{-H_2O}/s^{-1})/4\}$	
Tiron(H_2L^{2-})	0.5	4.37	4.26	This work
NSAL(HL^-)	0.1	4.56	4.06	18
SAL(HL^-)	0.1	5.30	4.80	20
		$\log(k_{GaNCS}/M^{-1}s^{-1})$	$\log\{(k_{GaNCS}^{-H_2O}/s^{-1})/5\}$	
Tiron(H_2L^{2-})	0.5	3.90	3.70	This work
Tropolone(HL)	0.5	3.12	2.92	This work
		$\log(k_{Ga(ox)}/M^{-1}s^{-1})$	$\log\{(k_{Ga(ox)}^{-H_2O}/s^{-1})/4\}$	
Tropolone(HL)	0.5	3.27	3.16	This work

a) Ligand abbreviation: NSAL for 5-nitrosalicylic acid, PCV for Pyrocatechol Violet, SAL for salicylic acid, and SXO for Semixylenol Orange.

$$\begin{array}{l}
Ga(OH)_2^{+} + H_2L^{2-} \xrightarrow{k_{Ga(OH)_2}} GaL^{-} \\
\downarrow\uparrow K_{Ga(OH)_2} \\
GaOH^{2+} + H_2L^{2-} \xrightarrow{k_{GaOH}} GaL^{-} + H^{+} \\
\downarrow\uparrow K_{GaOH} \\
Ga^{3+} + H_2L^{2-} \xrightarrow{k_{Ga}} GaL^{-} + 2H^{+} \\
\downarrow\uparrow K_{GaNCS} \\
GaNCS^{2+} + H_2L^{2-} \xrightarrow{k_{GaNCS}} \\
\qquad [Ga(NCS)L]^{2-}(\text{and/or } GaL^{-} + SCN^{-}) + 2H^{+}
\end{array}$$

Scheme 1.

higher than that of tiron (see Fig. 2), $GaNCS^{2+}$ would be certainly in equilibrium with aquagallium(III) during the reaction. The formation of a small amount of a mixed-ligand complex such as $[Ga(NCS)L]^{2-}$ may be anticipated. However, the coordination of tiron being quantitative at $-\log[H^+]=2.3$ (see Table 1), the kinetic equation for this reaction scheme is described as

$$\begin{aligned}
d[GaL^-]/dt &= k_{f(H,SCN)}[Ga'][H_2L^{2-}] \\
&= \{k_{Ga}[Ga^{3+}] + k_{GaOH}[GaOH^{2+}] \\
&\quad + k_{Ga(OH)_2}[Ga(OH)_2^{+}] \\
&\quad + k_{GaNCS}[GaNCS^{2+}]\}[H_2L^{2-}] \qquad (7)
\end{aligned}$$

where,

$$k_{f(H,SCN)} = \frac{k_{f(H)}\alpha_{Ga(OH)} + k_{GaNCS}K_{GaNCS}[SCN^-]}{\alpha_{Ga(OH)} + K_{GaNCS}[SCN^-]}$$

and $K_{GaNCS}=[GaNCS^{2+}][Ga^{3+}]^{-1}[SCN^-]^{-1}$ is the formation constant of the inner-sphere complex of isothiocyanatogallium(III).

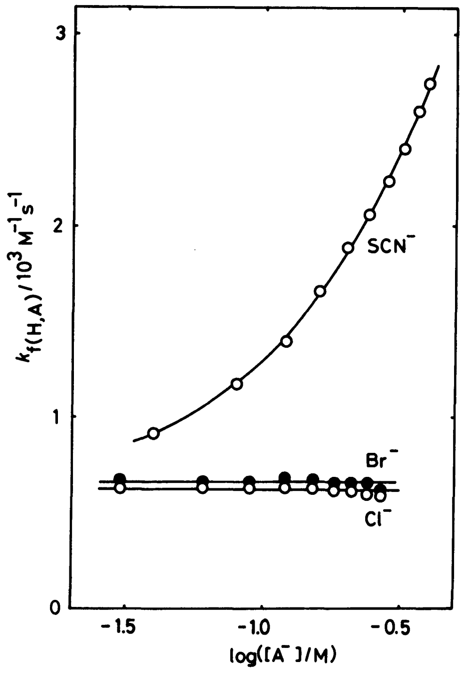

Fig. 2. Plot of $k_{f(H,A)}$ *vs.* $\log[A^-]$.
Conditions: $C_{Ga}=1.12\times10^{-2}$ M, $C_L=1.08\times10^{-4}$ M, and $-\log[H^+]=2.32\pm0.02$ for $A^-=SCN^-$; $C_{Ga}=1.12\times10^{-2}$ M, $C_L=1.01\times10^{-4}$ M, and $-\log[H^+]=2.28\pm0.01$ for $A^-=Cl^-$; $C_{Ga}=1.12\times10^{-2}$ M, $C_L=1.11\times10^{-2}$ M, and $-\log[H^+]=2.28\pm0.01$ for $A^-=Br^-$; all at 25 °C and $I=0.50$ M.

The increase of $k_{f(H,SCN)}$ at constant pH with increasing concentration of SCN^- is attributable to the enhanced reactivity of $GaNCS^{2+}$. From the plot of $k_{f(H,SCN)}$ *vs.* log[SCN^-] (Fig. 2), the k_{GaNCS} value was determined by a least-squares procedure to be $k_{GaNCS}=10^{3.90}$ $M^{-1}s^{-1}$ with $K_{GaNCS}=10^{0.11}$ M^{-1} at 25 °C and I=0.50 M.

In the presence of chloride and bromide, the conditional formation rate constants $k_{f(H,Cl)}$ and $k_{f(H,Br)}$ did not change with increasing total concentration of A up to 0.27 M as shown in Fig. 2. This is most probably due to the small formation constant K_{GaA} for these complexes.9,10)

Reaction of Isothiocyanatogallium(III) with Tropolone. Gallium(III) ion quantitatively forms the 1:1 complex with tropolone (HL) in acidic solution ($-\log[H^+]=$ 0.6—1.3) where the concentration of gallium(III) ion is in large excess over that of the ligand. Under such conditions, the complexation reaction and the kinetic equation for the formation of the (tropolonato)gallium(III) (GaL^{2+}) is expressed as6)

$$Ga' + HL' \xrightarrow{k_{f(H)}} GaL^{2+} + H^+ \tag{8}$$

$$\begin{aligned} d[GaL^{2+}]/dt &= k_{f(H)}[Ga'][HL'] \\ &= k_{f(H)}\alpha_{Ga(OH)}\alpha_{HL(H)}[Ga^{3+}][HL] \\ &= \{k_{Ga}[Ga^{3+}] + k_{GaOH}[GaOH^{2+}]\}[HL]. \end{aligned} \tag{9}$$

where $[Ga']=[Ga^{3+}]+[GaOH^{2+}]$ and $[HL']=[HL]+[H_2L^+]=(1+K_{H_2L}[H^+])[HL]=\alpha_{HL(H)}[HL]$.

As in the reaction with tiron, the conditional rate constant $k_{f(H,SCN)}$ increased with increasing concentration of thiocyanate ion. At $-\log[H^+]=1.25$, the values of $k_{f(H,SCN)}$ obtained at various thiocyanate concentrations (C_{SCN}=0.04—0.40 M) were analyzed with the following equation

$$k_{f(H,SCN)}\alpha_{HL(H)} = \frac{k_{f(H)}\alpha_{HL(H)}\alpha_{Ga(OH)} + k_{GaNCS}K_{GaNCS}[SCN^-]}{\alpha_{Ga(OH)} + K_{GaNCS}[SCN^-]}$$

and the k_{GaNCS} value was determined to be $10^{3.12}$ $M^{-1}s^{-1}$ with $K_{GaNCS}=10^{0.47}$ M^{-1} at 25 °C and I=0.50 M. The k_{GaNCS} value obtained with tiron as an entering ligand is higher than this value. This may be due to the partial formation of $[Ga(NCS)(OH)]^+$ at higher pH where kinetics with tiron was carried out.

Reaction of Oxalatogallium(III) with Tropolone. Under the conditions where only $Ga(ox)^+$ is present as the gallium(III)-oxalate complex, the reaction of the gallium(III) complex with tropolone can be expressed as6)

$$\begin{aligned} &Ga' + HL' \xrightarrow{k_{f(H,ox)}} \\ &\qquad Ga(ox)L(\text{and/or } GaL^{2+} + ox^{2-}) + H^+ \end{aligned} \tag{10}$$

and the kinetic equation is described as

$$d[Ga(ox)L]/dt = k_{f(H,ox)}[Ga'][HL'] \tag{11}$$

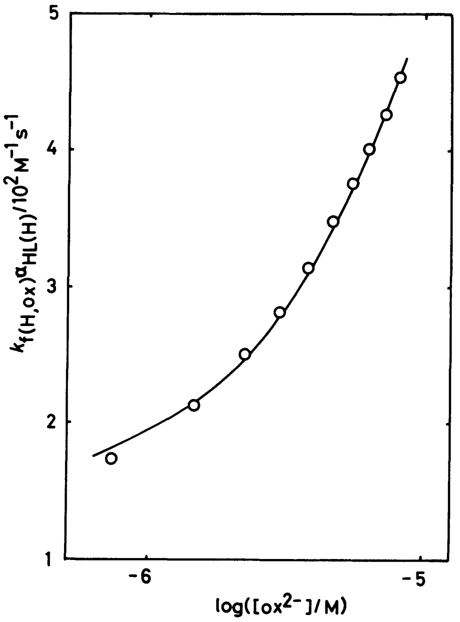

Fig. 3. Plot of $k_{f(H,ox)}$ *vs.* log[ox^{2-}].
Conditions: $C_{Ga}=2.81\times10^{-2}$ M, $C_L=1.03\times10^{-4}$ M, $C_{ox}=1.00\times10^{-3}$—1.00×10^{-2} M, $-\log[H^+]=1.056\pm$ 0.002, at 25 °C and I=0.50 M.

where $[Ga']=[Ga^{3+}]+[GaOH^{2+}]+[Ga(ox)^+]$. Then we obtain

$$k_{f(H,ox)}\alpha_{HL(H)} = \frac{k_{f(H)}\alpha_{HL(H)}\alpha_{Ga(OH)} + k_{Ga(ox)}K_{Ga(ox)}[ox^{2-}]}{\alpha_{Ga(OH)} + K_{Ga(ox)}[ox^{2-}]}$$

where $K_{Ga(ox)}=[Ga(ox)^+][Ga^{3+}]^{-1}[ox^{2-}]^{-1}$ is the formation constant for the inner-sphere complex of monooxalatogallium(III).

At constant pH, the values of $k_{f(H,ox)}$ obtained at various oxalate concentrations were analyzed as a function of [ox^{2-}] by a least-squares procedure.11) The solid line in Fig. 3 was calculated with $K_{Ga(ox)}=10^{4.44}$ M^{-1} and $k_{Ga(ox)}=10^{3.27}$ $M^{-1}s^{-1}$ at 25 °C and I=0.50 M. The value of $k_{f(H)}\alpha_{HL(H)}\alpha_{Ga(OH)}$ obtained (1.50×10^2 $M^{-1}s^{-1}$) compares favorably with the value calculated (1.59×10^2 $M^{-1}s^{-1}$) from the relation of $k_{f(H)}\alpha_{HL(H)}\alpha_{Ga(OH)}=k_{Ga}+k_{GaOH}K_{GaOH}[H^+]^{-1}$ and the values of k_{Ga}, k_{GaOH}, and k_{GaOH} previously determined.6)

Discussion

On the basis of the values of activation volume, we have shown6) that the complexation of gallium(III) is accommodated within the framework of a dissociative-interchange mechanism.12) For the complexation reactions dissociatively activated, the values of k_M/K_{os} and k_{MA}/K_{os} (apart from a statistical factor which is not far from unity,13) where K_{os} is the formation constant of an outer-sphere complex) are not very different from the values of $k_M{}^{-H_2O}$ and $k_{MA}{}^{-H_2O}$, respectively.14,15) We calculated rate constants, $k_{Ga}{}^{-H_2O}$ and $k_{GaA}{}^{-H_2O}$, for our system and others. The results are summarized in Table 2 in which are also given the second-order rate

TABLE 3. BOUND LIGAND EFFECTS OF GaA COMPLEXES

A	E(A)	R(A)[a]
H_2O	0.00	0.00
OH^-	1.65	2.07±0.26
$(OH)_2^{2-}$	3.30	3.28±0.21
SCN^-	1.83	2.19±0.57
ox^{2-}	1.70	1.86

a) $R(A)=\log(k_{GaA}{}^{-H_2O}/\text{number of } H_2O \text{ in GaA})-\log(k_{Ga}{}^{-H_2O}/6)$.

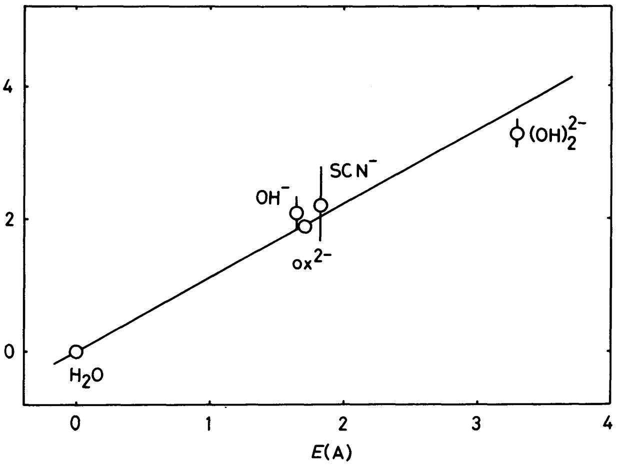

Fig. 4. Plot of R(A) *vs.* E(A).
$R(A)=\log(k_{GaA}{}^{-H_2O}/\text{number of } H_2O \text{ in GaA})-\log(k_{Ga}{}^{-H_2O}/6)$.

constants for complexation reactions. K_{os} were calculated from the Fuoss equation[16] with the distance of closest approach=5 Å, assuming that a negatively charged group removed from the eventual coordination site is unimportant in the calculation of K_{os} values.[17]

With the water exchange rate constant calculated, the bound ligand effect of GaA on the water exchange rate can be estimated by the difference between $\log(k_{GaA}{}^{-H_2O}/\text{number of } H_2O \text{ in GaA})$ and $\log(k_{Ga}{}^{-H_2O}/6)$, which is shown in Table 3 under the heading of R (A). In this Table, the values of E (A) for the monodentate ligands are taken from Ref. 3 and the value for oxalate is the effective E(A) which is given by $E\ (ox^{2-})=2E(OAc^-)-2\Delta E_{OO}$.[5] Since the donor-donor interaction between hydroxo ligands coordinated to gallium(III) may be anticipated to be small, the value of $E\ (2OH^-)$ is assumed to be $2E\ (OH^-)$.

The positive values of R(A) indicate that the coordinated ligands do have the expected libilizing effect on the water exchange rate at GaA. If this labilizing effect is attributable to the electron donation from the ligand to the gallium(III) ion, the bound ligand effect could be quantitatively predicted by Eq. 1. Then the plot of R(A) *vs.* E(A) should yield a straight line with an intercept of zero. The value of γ for gallium(III) was estimated from the slope of Fig. 4 to be 1.1. As stated previously,[4,22] a hard metal ion[23] such as Ga(III) has higher γ value than less hard metal ions such as Co(II) (γ=0.47), Ni(II) (γ=0.40), and Zn(II) (γ=0.30). This 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.

References

1) M. Tanaka, *J. Inorg. Nucl. Chem.*, **35**, 965 (1973).

2) M. Tanaka, *J. Inorg. Nucl. Chem.*, **36**, 151 (1974).

3) J. O. Edwards, *J. Am. Chem. Soc.*, **76**, 1540 (1954).

4) S. Yamada, K. Ohsumi, and M. Tanaka, *Inorg. Chem.*, **17**, 2790 (1978).

5) S. Yamada, T. Kido, and M. Tanaka, *Inorg. Chem.*, **23**, 2990 (1984).

6) S. Yamada, A. Iwanaga, S. Funahashi, and M. Tanaka, *Inorg. Chem.*, **23**, 3528 (1984).

7) V. A. Nazarenko, V. P. Antonovich, and E. M. Nevskaya, *Zhur. Neorg. Khim.*, **13**, 1574 (1968).

8) Distinction between reaction paths with proton ambiguity is made by checking the reasonableness of the rate constants calculated (see Ref. 6).

9) L. G. Sillēn and A. E. Martell, "Stability Constants of Metal-Ion Complexes," the Chemical Society, London (1964); Supplement No. 1, the Chemical Society, London (1971).

10) E. Högfeldt, "Stability Constants of Metal-Ion Complexes," IUPAC Chemical Data Series, No. 21, Pergamon Press, Oxford (1982).

11) pK_a values for oxalic acid are taken from "Critical Stability Constants," ed by A. E. Martell and R. M. Smith, Plenum Press, New York (1977), Vol. 3. The value of $\alpha_{HL(H)}$ was calculated with the protonation constant K_{H_2L} previously determined.[6]

12) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York (1965).

13) J. Neely and R. Connick, *J. Am. Chem. Soc.*, **92**, 3476 (1970).

14) D. W. Margerum, G. R. Cayley, D. C. Weatherburn, and G. K. Pagenkopf in "Coordination Chemistry," ed by A. E. Martell, American Chemical Society, Washington DC (1978), ACS Monogr. No. 174, Chap. 1.

15) M. Tanaka, *Inorg. Chim. Acta*, **76**, L243 (1983).

16) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

17) J. C. Cassatt and R. G. Wilkins, *J. Am. Chem. Soc.*, **90**, 6045 (1968).

18) B. Perlmutter-Hayman, F. Secco, E. Tapuhi, and M. Venturini, *J. Chem. Soc., Dalton Trans.*, **1980**, 1124.

19) R. Corigli, F. Secco, and M. Venturini, *Inorg. Chem.*, **18**, 3184 (1979).

20) B. Perlmutter-Hayman, F. Secco, E. Tapuhi, and M. Venturini, *J. Chem. Soc., Dalton Trans.*, **1977**, 2220.

21) Y. Kawai, T. Takahashi, K. Hayashi, T. Imamura, H. Nakayama, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, **45**, 1417 (1972).

22) M. Tanaka and S. Yamada, *J. Chem. Soc., Chem. Commun.*, **1976**, 178.

23) S. Yamada and M. Tanaka, *J. Inorg. Nucl. Chem.*, **37**, 587 (1975).