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The Association Constants of Hexaamminechromium(III) and Tris(ethylenediamine)chromium(III) Ions with Several Univalent Anions in Aqueous Solutions

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The thermodynamic ion-association constants of hexaamminechromium(III) and tris(ethylenediamine)-chromium(III) with several univalent anions were determined in aqueous solutions at 25.0 °C. The log K_{con} values obtained by the conductometric method are 1.3_7 for $[\mathrm{Cr(NH_3)_6}]^{3+}$-$\mathrm{Cl^-}$, 1.5_8 for $[\mathrm{Cr(en)_3}]^{3+}$-$\mathrm{Cl^-}$, 1.5_7 for $[\mathrm{Cr(NH_3)_6}]^{3+}$-$\mathrm{Br^-}$, 1.5_0 for $[\mathrm{Cr(en)_3}]^{3+}$-$\mathrm{Br^-}$, 1.5_3 for $[\mathrm{Cr(NH_3)_6}]^{3+}$-$\mathrm{NO_3^-}$, and 1.4_9 for $[\mathrm{Cr(en)_3}]^{3+}$-$\mathrm{NO_3^-}$. The log K_{sp} values obtained by the spectrophotometric method are 1.6_5 for $[\mathrm{Cr(en)_3}]^{3+}$-$\mathrm{Cl^-}$, 1.4_6 for $[\mathrm{Cr(en)_3}]^{3+}$-$\mathrm{Br^-}$, and 0.9_0 for $[\mathrm{Cr(en)_3}]^{3+}$-$\mathrm{ClO_4^-}$; the value for $[\mathrm{Cr(en)_3}]^{3+}$-$\mathrm{ClO_4^-}$ could be indirectly calculated from the apparent ion-association constant of $[\mathrm{Cr(en)_3}]^{3+}$-$\mathrm{Br^-}$ determined in the solutions containing both bromide and perchlorate ions. Though the detailed comparison of the ion-association constants obtained in this study was limited, it could be concluded that the K_{con} values were in relatively good agreement with the K_{sp} values obtained on the given ion-pairs and that the ion-association constants of chromium(III) complex cations with several univalent anions are slightly less than those of the corresponding cobalt(III) complex cations with their anions.

In view of the fact that the theories for ion association proposed by Bjerrum,¹⁾ Fuoss,²⁾ and other authors were not fully related to the Debye-Hückel³⁾ theory of electrolyte solutions, Yokoyama and Yamatera⁴⁾ showed that the ion-association constant could be derived in direct relation to the Debye-Hückel theory, reexamined to explain the ion-association. Meanwhile, the determination of the standard enthalpies and entropies for the ion-pair formation,⁵⁾ and the comparison of the ion-association constants obtained by the various types of measurements⁶⁻⁹⁾ were considered to provide some significant information concerning the interaction between the ions.

In this paper, a conductometric investigation of the ion-pairs, $[\mathrm{Cr(NH_3)_6}]^{3+}$-$\mathrm{X^-}$, $[\mathrm{Cr(en)_3}]^{3+}$-$\mathrm{X^-}$ ($\mathrm{X{=}Cl, Br, NO_3}$) and a spectrophotometric investigation of $[\mathrm{Cr(en)_3}]^{3+}$-$\mathrm{Br^-}$, $[\mathrm{Cr(en)_3}]^{3+}$-$\mathrm{Cl^-}$, $[\mathrm{Cr(en)_3}]^{3+}$-$\mathrm{ClO_4^-}$ will be presented. The ion-association constants which were determined in this study and the previous study¹⁰⁾ ($\mathrm{X{=}I, ClO_4}$) will be compared with the values reported for the corresponding cobalt(III) complex cations with several univalent anions, and will be briefly discussed in terms of Bjerrum's theory of ion-association.

Experimental

The compounds, $[\mathrm{Cr(NH_3)_6}]\mathrm{Cl_3}$, $[\mathrm{Cr(NH_3)_6}]\mathrm{Br_3}$, $[\mathrm{Cr(en)_3}]\mathrm{Cl_3\cdot 3.5H_2O}$, $[\mathrm{Cr(NH_3)_6}](\mathrm{NO_3})_3$, $[\mathrm{Cr(en)_3}](\mathrm{NO_3})_3$, and $[\mathrm{Cr(en)_3}]\mathrm{Br_3\cdot 4H_2O}$, were prepared according to the procedures described in the literature. Each compound was carefully recrystallized three times from redistilled water. The purity was examined by the method described in a previous paper;¹⁰⁾ the results were in very good agreement with the theoretical values. All the chemicals used were of an analytical reagent grade and were highly purified by recrystallization from redistilled water.

Solutions of various concentrations were carefully prepared by using conductivity water of a low specific conductance ($<4\times10^{-7}$ $\mho$ cm^{-1}). The electric conductivities were measured with a Yanagimoto conductivity outfit, Model MY-7, in an atmosphere of purified nitrogen over the surface of the solution, after the dissolved carbon dioxide in the solution had been removed by bubbling nitrogen gas through the solution. All the measurements were carried out within 30 min after the preparation of the solution, in a water-thermostat of 25.00±0.02 °C. The absorbancy measurements of solutions were made with a 124-type Hitachi spectrophotometer with a thermostated cell compartment (25.0±0.1 °C), using a 10-mm quartz cell, within 30 min after the preparation of the solution. Increasing quantities of sodium chloride or potassium bromide were added to each solution containing a small, constant concentration of the complex. The reference solutions used for the measurement had exactly the same concentration of $\mathrm{Cl^-}$ or $\mathrm{Br^-}$ as in the corresponding sample solutions.

Results and Discussion

The equivalent conductivities, Λ, of the complexes at various concentrations are summarized in Tables 1 and 2. The relations between the equivalent conductivities obtained and the ionic strength (I) are shown in Figs. 1—3. Table 3 presents the limiting equivalent conductivities, Λ°, of each complex, as determined by Onsager's method of extrapolation,¹¹⁾ and also the limiting ionic equivalent conductivities, λ°, of each complex cation calculated from the Λ° values. Table 4 summarizes the so-called Stokes' radii, r_s, of $[\mathrm{Cr(NH_3)_6}]^{3+}$ and $[\mathrm{Cr(en)_3}]^{3+}$, as determined from the conductivity data in this study and those of the corresponding cobalt(III) complex cations.

Figures 1—3 show the plots of Λ against $I^{1/2}$; the broken lines indicate the theoretical Onsager lines¹¹⁾ calculated. The slight deviation between the experimental conductivity lines and the theoretical lines was assumed to be due to the ion-pair formation between the cations and the anions:

$$\mathrm{M^{3+} + X^- \rightleftharpoons M^{3+}X^-} \qquad (1)$$

$$\mathrm{M{=}Cr(NH_3)_6,\ Cr(en)_3}$$

$$\mathrm{X{=}Cl,\ Br,\ NO_3}$$

The degrees of dissociation, α, of the possible ion pairs were determined according to the successive approximation method described by Jenkins and Monk.¹²⁾ The thermodynamic ion-association constants, K, for Eq. 1 were calculated from both the

Table 1. Conductivities, Λ, degrees of dissociation, α, and thermodynamic association constants, K, of $[Cr(NH_3)_6]^{3+}$-X^- in aqueous solutions at 25.0 °C

Molar concn $\times 10^4$	Λ	α	$\log K$
	(X=Cl)		
2.166	165.6_6	0.989_3	1.3_3
2.647	164.6_8	0.987_4	1.3_3
2.836	164.2_2	0.985_3	1.3_7
2.958	164.1_6	0.987_1	1.3_0
3.851	162.5_7	0.983_2	1.3_2
4.333	161.6_9	0.979_8	1.3_6
4.525	161.5_7	0.981_5	1.3_0
5.262	160.1_4	0.973_9	1.4_1
5.672	159.6_5	0.973_6	1.3_9
6.163	158.9_2	0.970_8	1.4_0
6.835	158.2_1	0.970_7	1.3_7
7.718	157.0_4	0.966_3	1.3_9
8.589	155.9_4	0.961_9	1.4_1
9.898	154.5_7	0.958_4	1.4_1
	(X=Br)		
1.887	168.3_7	0.986_4	1.4_9
1.935	168.2_3	0.985_8	1.5_0
2.748	166.1_5	0.977_1	1.5_8
2.960	165.7_7	0.976_5	1.5_7
3.880	163.9_2	0.969_5	1.5_8
4.828	162.0_9	0.960_9	1.6_2
5.039	162.0_9	0.964_4	1.5_6
5.168	161.8_9	0.963_7	1.5_6
5.280	161.3_7	0.958_2	1.6_2
5.846	160.7_6	0.958_6	1.5_8
6.983	159.5_4	0.958_2	1.5_2
7.813	158.1_0	0.949_0	1.5_8
9.019	156.6_9	0.944_3	1.5_7
9.973	155.3_9	0.937_0	1.5_9
	(X=NO_3)		
1.508	162.6_5	0.989_1	1.4_8
1.861	161.7_0	0.986_1	1.5_1
2.296	160.6_1	0.982_2	1.5_4
2.830	159.5_8	0.980_3	1.5_0
3.462	158.4_2	0.977_4	1.4_9
3.839	157.5_7	0.972_7	1.5_4
4.594	156.3_1	0.968_6	1.5_4
5.283	155.4_1	0.967_5	1.5_0
5.996	154.2_0	0.961_3	1.5_4
6.692	152.9_9	0.954_2	1.5_8
7.483	152.2_4	0.954_6	1.5_4
8.724	150.4_1	0.944_1	1.5_8
9.782	149.2_2	0.939_7	1.5_8

Table 2. Conductivities, Λ, degrees of dissociation, α, and thermodynamic association constants, K, of $[Cr(en)_3]^{3+}$-X^- in aqueous solutions at 25.0 °C

Molar concn $\times 10^4$	Λ	α	$\log K$
	(X=Cl)		
1.751	143.3_8	0.985_1	1.5_6
2.048	142.7_2	0.983_1	1.5_6
2.994	140.8_7	0.976_8	1.5_6
3.821	139.3_3	0.969_4	1.5_9
3.907	139.3_3	0.971_2	1.5_6
4.989	137.5_8	0.962_6	1.5_9
4.990	137.6_7	0.964_3	1.5_7
5.804	136.3_1	0.955_4	1.6_1
6.180	135.9_3	0.955_2	1.6_0
7.170	134.8_5	0.952_4	1.5_7
8.104	133.7_5	0.947_3	1.5_8
8.865	132.7_5	0.940_6	1.6_1
9.340	132.3_7	0.940_5	1.5_9
9.850	131.7_3	0.936_0	1.6_1
	(X=Br)		
1.877	144.8_8	0.986_4	1.4_9
2.121	144.3_0	0.983_9	1.5_2
2.999	142.5_5	0.977_6	1.5_4
3.914	141.3_1	0.977_1	1.4_5
4.255	140.7_8	0.975_1	1.4_6
4.938	139.6_5	0.969_3	1.5_0
5.901	138.0_9	0.959_8	1.5_6
6.052	138.1_7	0.963_7	1.5_1
7.031	137.1_4	0.962_1	1.4_7
7.939	136.0_2	0.956_4	1.5_0
8.954	134.9_6	0.952_6	1.5_0
8.991	134.5_2	0.945_2	1.5_6
9.933	134.4_9	0.958_1	1.4_1
10.040	133.5_6	0.942_6	1.5_5
	(X=NO_3)		
1.526	138.3_1	0.991_3	1.3_8
1.915	137.4_4	0.989_0	1.3_9
2.868	135.5_9	0.983_2	1.4_3
3.327	134.5_3	0.975_8	1.5_4
3.789	133.8_0	0.973_4	1.5_3
4.537	132.6_8	0.969_3	1.5_3
5.378	131.7_8	0.969_5	1.4_7
5.986	130.9_8	0.966_1	1.4_8
6.722	130.0_1	0.961_2	1.5_0
7.487	129.0_4	0.956_0	1.5_2
8.520	127.9_6	0.952_1	1.5_2
9.793	126.6_2	0.945_6	1.5_3

degree of dissociation thus obtained and the activity coefficient, f, of ions as estimated from the Debye-Hückel limiting equation. The results are summarized in Tables 1 and 2. In the present calculation, the λ° values of ion-pairs were assumed to be equal to two-thirds of those of complex cations, and the actual ionic strength, I, is $(1+\alpha)C$, where C is the equivalent concentration of the complex. If the distance of the closest approach of the two ions of an ion-pair is assumed to be equal to the sum of their Stokes' radii, the ion-association constant of the ion-pair can be estimated by Bjerrum's theory.[1] Table 5 presents the $\log K$ values calculated theoretically.

It has generally been observed that, in the ultraviolet region, the ion-association is usually accompanied either by the appearance of a new absorption band or by a shift of an existing band. The present authors also found an increase in the optical densities of the charge-transfer band in the ultraviolet region of $[Cr(en)_3]Cl_3 \cdot 3.5H_2O$ and $[Cr(en)_3]Br_3 \cdot 4H_2O$ upon

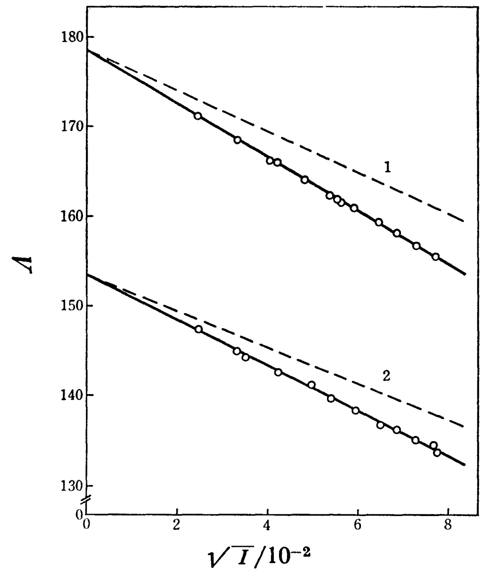

Fig. 1. The Onsager plots of hexaamminechromium(III) bromide (1) and tris(ethylenediamine)chromium(III) bromide (2) in aqueous solutions at 25.0 °C.

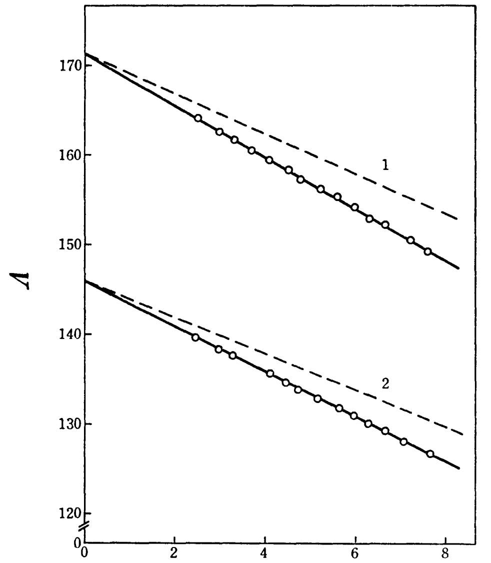

Fig. 2. The Onsager plots of hexaamminechromium(III) nitrate (1) and tris(ethylenediamine)chromium(III) nitrate (2) in aqueous solutions at 25.0 °C.

TABLE 3. THE LIMITING EQUIVALENT CONDUCTIVITY, Λ°, OF CHROMIUM(III) COMPLEXES AND THE LIMITING IONIC EQUIVALENT CONDUCTIVITY, λ°, OF CHROMIUM(III) COMPLEX CATIONS IN AQUEOUS SOLUTIONS AT 25.0 °C

Complex	Λ°	λ°
$[Cr(NH_3)_6](NO_3)_3$	170.1	98.6
$[Cr(NH_3)_6]Br_3$	176.9	98.8
$[Cr(NH_3)_6]Cl_3$	174.5	98.1
$[Cr(en)_3](NO_3)_3$	144.9	73.4
$[Cr(en)_3]Br_3\cdot 4H_2O$	152.6	74.5
$[Cr(en)_3]Cl_3\cdot 3.5H_2O$	150.9	74.5

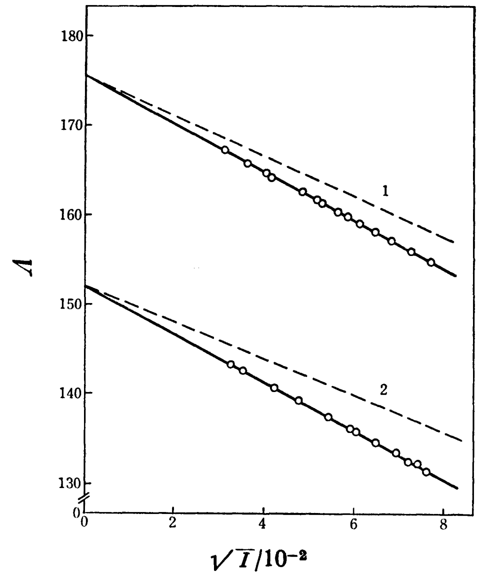

Fig. 3. The Onsager plots of hexaamminechromium(III) chloride (1) and tris(ethylenediamine)chromium(III) chloride (2) in aqueous solutions at 25.0 °C.

TABLE 4. THE LIMITING EQUIVALENT CONDUCTIVITY, λ°, AND THE STOKES' RADIUS, r_s, OF CHROMIUM(III) AND COBALT(III) COMPLEX CATIONS IN AQUEOUS SOLUTIONS AT 25.0 °C

Complex cations	λ°	r_s (Å)
$[Cr(NH_3)_6]^{3+}$	98.5	2.80
	98.5[10]	2.80[10]
$[Cr(en)_3]^{3+}$	74.1	3.72
	73.4[10]	3.75[10]
$[Co(NH_3)_6]^{3+}$	99.2[12]	2.77[12],[a]
	99.0—99.7[7,15]	2.78—2.76[7,15]
$[Co(en)_3]^{3+}$	74.5[12]	3.68[12],[a]

a) These values were calculated by means of this equation: $r_s = 91.6|Z_i|/\lambda_i^\circ$.

TABLE 5. LOGARITHMIC ASSOCIATION CONSTANTS OF THE ION-PAIRS CALCULATED BY BJERRUM'S THEORY IN AQUEOUS SOLUTIONS AT 25.0 °C

Ion-pair	log *K*
$[Cr(NH_3)_6]^{3+}$-NO_3^-	1.7_9
$[Cr(en)_3]^{3+}$-NO_3^-	1.6_5
$[Cr(NH_3)_6]^{3+}$-Br^-	1.8_1
$[Cr(en)_3]^{3+}$-Br^-	1.6_7
$[Cr(NH_3)_6]^{3+}$-Cl^-	1.8_1
$[Cr(en)_3]^{3+}$-Cl^-	1.6_7

the addition of Cl^- or Br^- as a result of the ion-association. When the Reaction 1 of ion-pair formation was in equilibrium, the spectrophotometric data could be approximately treated according to the following equation:

$$\frac{[X^-]_T}{\varepsilon_{obsd}-\varepsilon_M}\cdot\frac{f_M f_X}{f_{MX}} = \frac{1}{K(\varepsilon_{MX}-\varepsilon_M)} + \frac{[X^-]_T}{\varepsilon_{MX}-\varepsilon_M}\cdot\frac{f_M f_X}{f_{MX}} \tag{2}$$

where ε_{obsd} is the observed molar extinction coefficient;

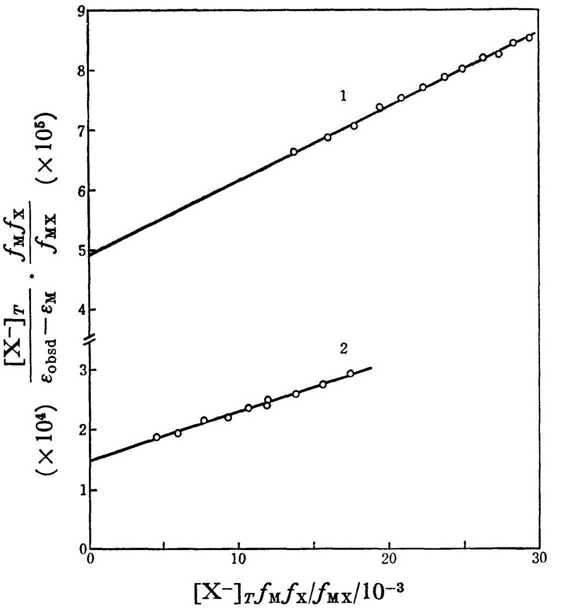

Fig. 4. Plots of the left-hand side of Eq. 2 against the $[X^-]_T f_M f_X/f_{MX}$ at 230 nm
(1): $[Cr(en)_3]^{3+}$-Br^-, (2): $[Cr(en)_3]^{3+}$-Cl^-.

ε_M and ε_{MX}, the molar extinction coefficients of M^{3+} and $M^{3+}X^-$, and f_M, f_X, and f_{MX}, the activity coefficients of M^{3+}, X^- and an ion-pair, $M^{3+}X^-$, respectively. The plot of the left-hand side of Eq. 2 *vs.* $[X^-]_T\cdot f_M f_X/f_{MX}$ gives a straight line, and the thermodynamic ion-association constant, K, can be determined from the ratio of its slope to the intercept. The activity coefficient was calculated from the following equation:

$$\log f_i = \frac{-0.5115\,Z_i^2\sqrt{I}}{1+0.329a\sqrt{I}} \tag{3}$$

The ion-size parameters, a,[13] used in the calculation are 3.0 Å for Cl^- and Br^-, 3.5 Å for ClO_4^-, and 6.0 Å for $[Cr(en)_3]^{3+}$, $[Cr(en)_3]^{3+}$–Cl^-, and $[Cr(en)_3]^{3+}$–Br^-. The results of the experiments are shown in Fig. 4. The linear relationship in Fig. 4 suggests that no appreciable contribution of the ion-pair formations, such as $[Cr(en)_3]^{3+}$–$2Cl^-$, as $[Cr(en)_3]^{3+}$–$2Br^-$, were to be expected in these systems. The $\log K$ values thus obtained were 1.6_5 for $[Cr(en)_3]^{3+}$–Cl^- and 1.4_6 for $[Cr(en)_3]^{3+}$–Br^-. No change was found in the ultraviolet spectra of the $[Cr(en)_3](ClO_4)_3$ solution at higher concentrations of ClO_4^-. These results do not always indicate the lack of the $[Cr(en)_3]^{3+}$–ClO_4^-, ion-pair. On the basis of the conclusion from the conductometric investigation that the $[Cr(en)_3]^{3+}$ did also associate with the ClO_4^- added to adjust the ionic strength, the determination of the ion-association constant of $[Cr(en)_3]^{3+}$–ClO_4^- was carried out by the spectrophotometric method on a system containing both Br^- and ClO_4^-.[14]

Under such experimental conditions, the Eq. 2 is rewritten as:

$$\frac{[Br^-]_T}{\varepsilon_{obsd}-\varepsilon_M} = \frac{1}{K'_{c,MBr}(\varepsilon_{MBr}-\varepsilon_M)} + \frac{[Br^-]_T}{\varepsilon_{MBr}-\varepsilon_M} \tag{4}$$

The apparent ion-association constant of $[Cr(en)_3]^{3+}$–Br^- determined at the given ionic strength, $K'_{c,MBr}$, is given by:

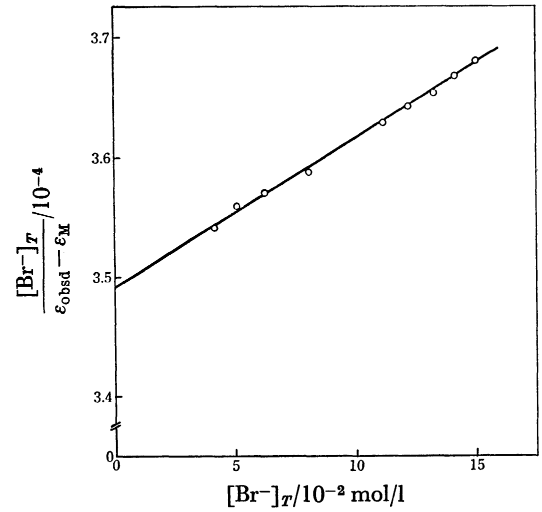

Fig. 5. Plot of the left-hand side of Eq. 4 against the total concentration of bromide ions at I=0.1530 at 230 nm.

$$K'_{c,MBr} = \frac{K_{c,MBr}}{1+K_{c,MClO_4}\cdot A}\left(1-\frac{K_{c,MClO_4}}{K_{c,MBr}}\right) \tag{5}$$

where $K_{c,MBr}$ and $K_{c,MClO_4}$ are the concentration ion-association constants of $[Cr(en)_3]^{3+}$–Br^- and $[Cr(en)_3]^{3+}$–ClO_4^-, and where A indicates the values of $[Br^-]_T$ plus $[ClO_4^-]_T$, which was kept constant in this study. The value of $K'_{c,MBr}$ was found to be $3._6$ from the analysis of the plot of Eq. 4 shown in Fig. 5. In this case, the activity coefficients of these ions are not a unit; therefore, the thermodynamic ion-association constant, K_{MBr}, determined by the spectrophotometric method was reduced to $6._0$ ($K_{c,MBr}$) at the ionic strength of 0.1530. With the $K'_{c,MBr}$, $K_{c,MBr}$ and A values, $K_{c,MClO_4}$ was evaluated to be $1._6$ with the aid of Eq. 5. The ion-association constant of $[Cr(en)_3]^{3+}$–ClO_4^- at an infinite dilution was calculated to be $8._0$ after correction for the activity coefficients of the ions.

The K value for $[Cr(en)_3]^{3+}$–ClO_4^-, estimated indirectly by the spectrophotometric method, was in relatively good agreement with that of the conductometric method, showing that ClO_4^- acts as a counter anion for the ion-association. From these results, it might be considered that the ion-association constants determined by the conductometric method and the spectrophotometric method are not very different from each other. Similar conclusions were drawn in the case of the previous studies of the $[Cr(en)_3]^{3+}$–I^-, $[Cr(en)_3]^{3+}$–ClO_4^-, $[Cr(NH_3)_6]^{3+}$–I^-, and $[Cr(NH_3)_6]^{3+}$–ClO_4^- ion-pairs. On the basis of the assumption that most cations do not associate with ClO_4^- in aqueous solutions, spectrophotometric studies have been made by many investigators of solutions containing large amounts of sodium perchlorate. However, we found that there was a difference between the values obtained previously by the conductometric and spectrophotometric methods. The difference did not occur when a different method was used. However, it might be caused by the fact that the above assumption is in-

TABLE 6. LOGARITHMIC ASSOCIATION CONSTANTS AT AN INFINITE DILUTION AT 25.0 °C

Ion-pair	log K	Method[a]	Investigators	Reference
$[Cr(NH_3)_6]^{3+}$-ClO_4^-	1.1_8	cond	Takahashi, Koiso and Tanaka (1974)	10
	1.0_0[c]	sp	Takahashi, Koiso and Tanaka (1974)	10
$[Co(NH_3)_6]^{3+}$-ClO_4^-	1.4_0	cond	Katayama and Tamamushi (1968)	7
$[Cr(en)_3]^{3+}$-ClO_4^-	1.0_2	cond	Takahashi, Koiso and Tanaka (1974)	10
	1.2_0[c]	sp	Takahashi, Koiso and Tanaka (1974)	10
	0.9_0[c]	sp	The present study	
$[Cr(NH_3)_6]^{3+}$-I^-	1.2_9	cond	Takahashi, Koiso and Tanaka (1974)	10
	1.3_4	sp	Takahashi, Koiso and Tanaka (1974)	10
$[Co(NH_3)_6]^{3+}$-I^-	1.3_8	cond	Katayama and Tamamushi (1968)	7
$[Cr(en)_3]^{3+}$-I^-	1.4_2	cond	Takahashi, Koiso and Tanaka (1974)	10
	1.3_3	sp	Takahashi, Koiso and Tanaka (1974)	10
$[Cr(NH_3)_6]^{3+}$-Cl^-	1.3_7	cond	The present study	
$[Co(NH_3)_6]^{3+}$-Cl^-	1.4_9	cond	Jenkins and Monk (1951)	12
	1.5	cond	Tamamushi, Isono and Katayama (1967)	15
$[Cr(en)_3]^{3+}$-Cl^-	1.5_8	cond	The present study	
	1.6_5	sp	The present study	
$[Co(en)_3]^{3+}$-Cl^-	1.7_2	cond	Jenkins and Monk (1951)	12
$[Cr(NH_3)_6]^{3+}$-Br^-	1.5_7	cond	The present study	
$[Co(NH_3)_6]^{3+}$-Br^-	1.6_5	cond	Katayama and Tamamushi (1968)	7
$[Cr(en)_3]^{3+}$-Br^-	1.5_0	cond	The present study	
	1.4_6	sp	The present study	
$[Cr(NH_3)_6]^{3+}$-NO_3^-	1.5_3	cond	The present study	
$[Co(NH_3)_6]^{3+}$-NO_3^-	1.6_3	cond	Katayama and Tamamushi (1968)	7
$[Cr(en)_3]^{3+}$-NO_3^-	1.4_9	cond	The present study	
$[Cr(NH_3)_6]^{3+}$-SO_4^{2-}	3.1_4[b]	pol	Tanaka, Ogino and Satô (1966)	16
$[Co(NH_3)_6]^{3+}$-SO_4^{2-}	3.2_1[b]	pol	Tanaka, Ogino and Satô (1966)	16
	3.5_6	cond	Jenkins and Monk (1951)	12
	3.3_0	chron	Tanaka and Yamada (1967)	17
	3.2_6	sp	Tanaka, Kobayashi and Kamada (1967)	6
$[Co(en)_3]^{3+}$-SO_4^{2-}	3.1_0	sp	Tanaka, Kobayashi and Kamada (1967)	6

a) Method of measurement. cond: Conductivity, sp: Spectrophotometry, pol: Polarography, chron: Chronopotentiometry. b) The values calculated from concentration constants obtained at an ionic strength of 0.10. c) These values were determined indirectly.

correct, not by the different working principles of the various methods. The thermodynamic ion-association constants for the corresponding cobalt(III) complex cations with some anions have been determined by various methods and/or by various researchers; they are given in Table 6, together with the results obtained in this study and the previous study. It seems certain that the ion-pairs of the chromium(III) complex cations with some anions are slightly less stable than those of the corresponding cobalt(III) complex cations, even if the inaccuracy in the determination of the ion-association constants is taken into consideration. Table 6 also indicates that the ion-pairs formed between $[Cr(NH_3)_6]^{3+}$ and such a Br^-, ClO_4^-, or NO_3^- are much more stable than those of $[Cr(en)_3]^{3+}$ with their anions, whereas the ion-pairs, $[Cr(NH_3)_6]^{3+}$ with I^- or Cl^- are less stable than those of $[Cr(en)_3]^{3+}$ with their anions.

Since the Stokes' radii of $[Cr(en)_3]^{3+}$ are larger than that of $[Cr(NH_3)_6]^{3+}$, the lower tendency of $[Cr(NH_3)_6]^{3+}$ to associate with I^- or Cl^-, shown by the present and previous studies, seems rather unexpected, in so far as the ion-association is assumed to depend on only a pure electrostatic. The ion-association constants of the corresponding cobalt(III) complex cations with Cl^- or SO_4^{2-} were determined by various methods. Similar results were obtained regardless of the method used. That is, the value of $[Co(en)_3]^{3+}$–Cl^- is somewhat greater than that of $[Co(NH_3)_6]^{3+}$–Cl^-, whereas the value of $[Co(NH_3)_6]^{3+}$–SO_4^{2-} is greater than that of $[Co(en)_3]^{3+}$–SO_4^{2-}. Therefore, it seems appropriate to state that the electrostatic interaction between ions exerts a dominant influence, but also the internal conjugate base (ICB) effect[18] proposed in the complex formation mechanism should be considered in the ion-pair formation.

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