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Polarographic and Spectroscopic Studies on the Ion-pair Formation of Trioxalatocobaltate(III) Ions with Cations in Aqueous Solutions

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The ion association between trioxalatocobaltate(III) anion and uni-, bi- and tervalent cations in aqueous solutions has been studied by polarographic and ultraviolet, visible and infrared spectroscopic methods. The association constants have been obtained by the measurement of the polarographic diffusion current of trioxalatocobaltate(III) ions in the presence of varied concentrations of cations at ionic strength 0.1 (NH_4NO_3) and 25°C. The influence of ammonium ion was taken into consideration in the treatment of polarographic data. The values obtained are 7.9 for $(CH_3)_4N^+[Co(ox)_3]^{3-}$, 3.7 ± 0.4 for $(C_2H_5)_4N^+[Co(ox)_3]^{3-}$, 22 ± 1 for $Na^+[Co(ox)_3]^{3-}$, 56 ± 6 for $Mg^{2+}[Co(ox)_3]^{3-}$, 55 ± 4 for $Ca^{2+}[Co(ox)_3]^{3-}$, 53 ± 3 for $Sr^{2+}[Co(ox)_3]^{3-}$, 55 ± 7 for $Ba^{2+}[Co(ox)_3]^{3-}$ and 118 ± 17 for $Al^{3+}[Co(ox)_3]^{3-}$. The association constant of $NH_4^+[Co(ox)_3]^{3-}$ was determined by the conductivity measurement to be 33.6 ($\log K=1.5_3$) at zero ionic strength. No change was observed in the visible, the ultraviolet and the infrared absorption spectra of trioxalatocobaltate(III) ions upon the addition of various cations even at the concentration at which the ion-pair formation is assumed to occur from the polarographic studies. These facts indicate that, in a sense of equilibrium study, there is no direct interaction between the complex anion and the cation, but one or more water molecules interpose between the two ions.

In recent years a number of investigations have been made of the ion-pair formation in solutions by many kinds of method. However, their results are not necessarily consistent with each other. The so-called " ion-pair " involves many different types, *e.g.*, a contact ion-pair, a solvent shared ion-pair and a solvent separated ion-pair.[1] Different types of ion-pairs are detected according to the characteristics of the methods used in the investigation. This may be a cause of the disagreement.

One of the purposes of this study is to determine the association constants between trioxalatocobaltate (III) anion and univalent, bivalent and tervalent cations using the polarographic method presented in a previous paper.[2] The other is to obtain some informations of the outer-sphere ion association from the comparison of the polarographic data with the visible, the ultraviolet and the infrared absorption spectra.

Experimental

Materials. Potassium trioxalatocobaltate(III) and ammonium trioxalatocobaltate(III) were prepared by the usual method.[3] The preparation of calcium, strontium and barium salts of trioxalatocobaltate(III) was made as follows. Calcium perchlorate which was prepared by the procedure of Smith and Koch[4] was added in excess to the solution of potassium trioxalatocobaltate(III) to precipitate potassium perchlorate. After filtration, calcium trioxalatocobaltate(III) was precipitated by the addition of ethanol. It was purified from aqueous solution by precipitating with ethanol. Strontium and barium trioxalatocobaltates(III) were prepared in the same way. Tetramethylammonium nitrate was prepared from $(CH_3)_4NBr$ and $AgNO_3$, and was recrystallized from water. Tetraethylammonium perchlorate was obtained according to Cokal and Wise.[5] All other chemicals used were of a guaranteed reagent grade.

Measurements. For the measurement of the limiting diffusion current, polarograms were recorded with a Shimadzu RP–2 polarograph in the solution of ionic strength 0.1 (adjusted with NH_4NO_3) containing 0.005% gelatin. The cell temperature was maintained at 25.0°C by means of a water thermostat. To avoid the effect of light, all the measurements were made with a brown-colored cell in a dark room. Since the trioxalatocobaltate(III) ions were reduced gradually to cobalt(II) in the presence of metallic mercury, the polarographic measurements were made as soon as possible after the dissolution of the complex and the removal of the dissolved oxygen in the solution.

The conductivity measurements were made in a glass cell equipped with platinized platinum electrodes using a Yokokawa BV–Z–103 B Wheatstone bridge. The cell constant was obtained to be 0.421 cm^{-1} by measuring

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[1] T. R. Griffiths and C. R. Symons, *Mol. Phys.*, **3**, 90 (1960).

[2] N. Tanaka, K. Ogino and G. Satô, This Bulletin, **39**, 366 (1966).

[3] S. P. L. Sörensen, *Z. Anorg. Chem.*, **11**, 2 (1896).

[4] G. F. Smith and E. G. Koch, *Z. Anorg. Allg. Chem.*, **223**, 18 (1935).

[5] E. J. Cokal and E. N. Wise, *J. Electroanal. Chem.*, **11**, 406 (1966).

the conductivity of 0.1 M KCl solution. The conductivity water of a specific conductivity of 4.2×10^{-7} ohm^{-1} cm^{-1} was prepared by passing the redistilled water through the ion-exchange column. Its specific conductivity, however, raised to 1.36×10^{-6} ohm^{-1}cm^{-1} when it was shaked and kept in a flask for about one hour, and this value was used for the water conductivity correction. All the solutions used were kept at 25.0°C in a water thermostat.

The visible and ultraviolet spectra were obtained with a Hitachi EPS-3 spectrophotometer at room temperature. The ionic strength of the solution was adjusted to be 0.09. The infrared absorption spectra were measured with a Hitachi EPI-2G recording infrared spectrophotometer. Cells with windows of calcium fluoride were used when the measurements were made with solutions. Platinum foil of 0.05 mm thick was used for a spacer. The infrared absorption spectra of solid samples were obtained by the KBr disk method. The wave-length calibration was precisely made with water vapor and carbon dioxide.

Results

The Determination of the Association Constants Using the Polarographic Diffusion Current. In the investigation of the ion association, the addition of a certain salt is often required in order to adjust the ionic strength. In that case, the salt of the ions which seem not to associate with other ions must be chosen. However, in the case that the multivalent ions are involved in the system investigated, the association between the multivalent ions and the ion that is added in order to adjust the ionic strength cannot be sometimes ignored.

A modified equation of the equation which was presented in the previous paper2) was derived for the determination of the association constant using the polarographic diffusion current. The influence of the ion which is added in order to adjust the ionic strength was taken into consideration in the treatment of polarographic data.

In the solution containing two different cations M^{m+} and $M'^{m'+}$ and complex anion X^{x-}, there exist the following equilibria

$$M^{m+} + X^{x-} \rightleftharpoons M^{m+}X^{x-} \tag{1}$$

$$M'^{m'+} + X^{x-} \rightleftharpoons M'^{m'+}X^{x-} \tag{2}$$

where $M^{m+}X^{x-}$ and $M'^{m'+}X^{x-}$ represent an ion-pair of M^{m+} with X^{x-} and that of $M'^{m'+}$ with X^{x-} respectively. Since the dissociation and the association of ion-pairs are very rapid, the apparent diffusion coefficient D is given by

$$D=\frac{D_X + D_{MX}K_{MX}C_M + D_{M'X}K_{M'X}C_{M'}}{1 + C_MK_{MX} + C_{M'}K_{M'X}} \tag{3}$$

where D_X, D_{MX} and $D_{M'X}$ are the diffusion coefficients of X^{x-}, $M^{m+}X^{x-}$ and $M'^{m'+}X^{x-}$, respectively, C_M and $C_{M'}$ are the concentrations of M^{m+} and $M'^{m'+}$ respectively, and K_{MX} and $K_{M'X}$ are the association constants of the corresponding ion-pairs expressed in concentration. When the ionic strength is kept constant, a relation given by the equation,

$$iC_M + jC_{M'} = a \tag{4}$$

holds for C_M and $C_{M'}$ where a is the ionic strength, i and j are the values calculated as follows. Assuming that M salt is of a u-v electrolyte, the value of i is given by $i=(vu^2+uv^2)/2v$. In a similar fashion, M′ salt being u'-v' electrolyte, the value of j is given by $j=(v'u'^2+u'v'^2)/2v'$. Introducing $C_{M'}$ derived from Eq. (4) into Eq. (3), Eq. (5) is obtained, which is rearranged to Eq. (6).

$$D=\frac{D_X+\dfrac{a}{j}D_{M'X}K_{M'X}+\left(K_{MX}D_{MX}-\dfrac{i}{j}K_{M'X}D_{M'X}\right)C_M}{1+\dfrac{a}{j}K_{M'X}+\left(K_{MX}-\dfrac{i}{j}K_{M'X}\right)C_M} \tag{5}$$

$$\frac{C_M}{\dfrac{D_X+\dfrac{a}{j}D_{M'X}K_{M'X}}{1+\dfrac{a}{j}K_{M'X}}-D}=\frac{1+\dfrac{a}{j}K_{M'X}+\left(K_{MX}-\dfrac{i}{j}K_{M'X}\right)C_M}{\dfrac{\left(D_X+\dfrac{a}{j}D_{M'X}K_{M'X}\right)\left(K_{MX}-\dfrac{i}{j}K_{M'X}\right)}{1+\dfrac{a}{j}K_{M'X}}-\left(K_{MX}D_{MX}-\dfrac{i}{j}K_{M'X}D_{M'X}\right)} \tag{6}$$

The first term of the denominator of the left-hand side of Eq. (6) indicates the diffusion coefficient which is obtained in the absence of M^{m+}, that is, the expression which is obtained when C_M equals zero in Eq. (5).

The left-hand side of Eq. (6) can be obtained experimentally. If the left-hand side of Eq. (6) is plotted against C_M, a straight line must be obtained, and the ratio of the slope to the intercept gives

$$\frac{\text{Slope}}{\text{Intercept}}=\frac{K_{MX}-\dfrac{i}{j}K_{M'X}}{1+\dfrac{a}{j}K_{M'X}} \tag{7}$$

When the value of either of K_{MX} and $K_{M'X}$ is known, that of the other can be calculated from Eq. (7). If the association between M′ and X can be neglected, *i.e.*, $K_{M'X}\doteqdot0$, Eq. (6) yields

$$\frac{C_M}{D_M - D} = \frac{1 + K_{MX}C_M}{(D_X - D_{MX})K_{MX}} \tag{8}$$

The association constant K_{MX} can be obtained directly from the ratio of the slope to the intercept. In the present investigation, M′ represents ammonium ion which is added in order to adjust the ionic strength, M represents other cations, and X, trioxalatocobaltate(III) anion.

Since it has been found that the ammonium ion forms ion-pair with trioxalatocobaltate(III) anion from the measurement of the conductivity of ammonium trioxalatocobaltate(III) solution, the results of the measurements of all systems investigated in the present study was treated with Eq. (6). The value of association constant of trioxalatocobaltate(III) ion with ammonium ion which is necessary to solve Eq. (7) was calculated from the conductivity of ammonium trioxalatocobaltate(III) solution. Figure 1 shows the experimental conductivity curve in which observed values of Λ are plotted against $C^{1/2}$. The equivalent conductivity at zero concentration Λ° was obtained from the extrapolation of the curve. The Λ_i° of trioxalatocobaltate(III) ion was obtained to be 91.4 Ω^{-1}cm^2 by subtracting Λ_i° of ammonium ion from Λ°. The association constant corresponding to the reaction,

$$NH_4^+ + [Co(ox)_3]^{3-} \rightleftharpoons NH_4^+[Co(ox)_3]^{3-}$$

was calculated according to the method of Jenkins and Monk.⁶⁾ The thermodynamic association constant was calculated to be 33.6 ($\log K = 1.5_3$) from the concentration association constants K_c obtained, using activity coefficients which were calculated by the Debye-Hückel equation. The concentration association constant $K_{M'X}$ at ionic strength 0.1 was calculated to be 7.9 from the thermodynamic association constant by using the activity coefficient. This value was employed to solve Eq. (7).

The change in current at −0.7 V *vs.* SCE was

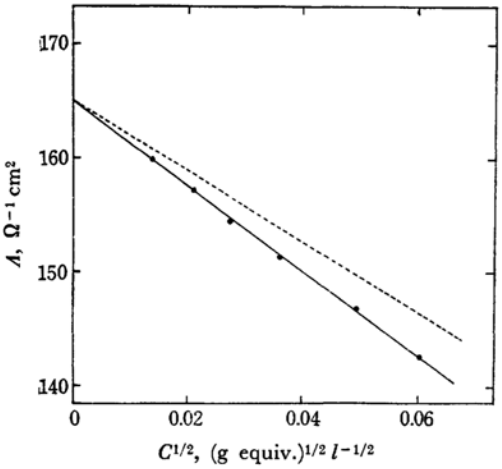

Fig. 1. Equivalent conductivity of $(NH_4)_3[Co(ox)_3]$ solutions as a function of the concentration. A broken line indicates the theoretical values calculated by Onsager's limiting equation.

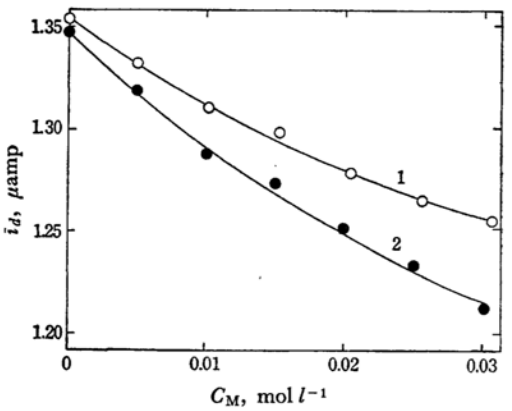

Fig. 2. Variation of the mean diffusion current ($\bar{i}_d$) of the reduction wave of $[Co(ox)_3]^{3-}$ with the change of concentrations of (1) magnesium and (2) barium ions.

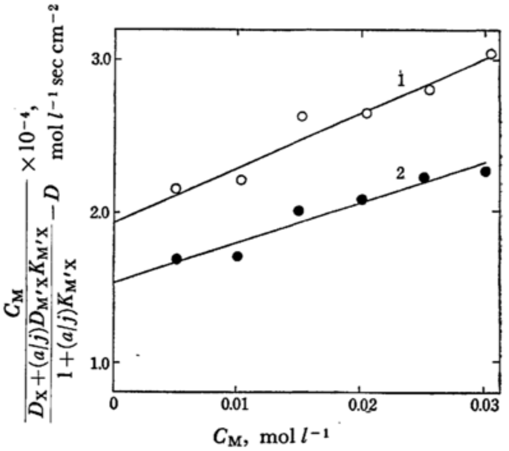

Fig. 3. Left-hand side of Eq. (6) as a function of concentrations of (1) magnesium and (2) barium ions.

TABLE 1. ASSOCIATION CONSTANTS OF TRIOXALATOCOBALTATE(III) ION WITH VARIOUS CATIONS AT 25°C

Cation	Slope / Intercept	K_{MX} (μ=0.1)	$\log K_{MX}$ (μ=0)
Na^+	8±1	22± 1	1.9_4
Mg^{2+}	18±2	56± 6	2.8_9
Ca^{2+}	17±1	55± 4	2.9_2
Sr^{2+}	16±1	53± 3	2.9_4
Ba^{2+}	17±2	55± 7	2.9_5
Al^{3+}	39±3	118±17	3.7_0
$(CH_3)_4N^+$	0	7.9	1.5_2
$(C_2H_5)_4N^+$	−2.4±0.3	3.7±0.4	1.1_8

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6) I. L. Jenkins and C. B. Monk, *J. Chem. Soc.*, **1951**, 68.

measured with the increase of the cation concentration in neutral solution. Typical examples of these plots are given in Fig. 2. The diffusion coefficient was calculated by the Ilkovič equation from the mean diffusion current. The experimental values in Fig. 2 were treated with Eq. (6). The plots thus obtained are given in Fig. 3. The values of the ratio of slope to intercept were determined by a least square method with the plots in Fig. 3. The association constant K_{MX} was obtained by introducing the value of $K_{M'X}$ and that of the ratio of slope to intercept into Eq. (7), which is given in Table 1.[*1] The thermodynamic association constants were calculated from those concentration association constants, using the activity coefficients which were calculated by the Debye-Hückel equation with the following ion-size parameters:[8] 4 Å for Na^+, 8Å for Mg^{2+}, 6Å for Ca^{2+}, 5 Å for Sr^{2+} and Ba^{2+}, 9Å for Al^{3+}, 6 Å for $[Co(ox)_3]^{3-}$ and 6.5 Å for all the ion-pairs $M^{m+}[Co(ox)_3]^{3-}$. The thermodynamic association constants are also given in Table 1.

The treatment with Eq. (6) was successfully extended to the systems containing tetraalkylammonium cations and trioxalatocobaltate(III) anions. The changes in diffusion coefficient with the increase in the concentrations of tetramethylammonium and tetraethylammonium ions are shown in Fig. 4, which are much different from those observed with the other systems. A similar experiment was carried out with the system containing hexamminecobalt(III) and tetraethylammonium cations in which no ion association is likely to take place. Although the addition of tetraethylammonium ion caused a slight decrease in the limiting current of hexamminecobalt(III), the decrease was confirmed to arise from the decrease in the drop time of the mercury electrode due to the surface-active properties of tetraethylammonium ions. These plots are also shown in Fig. 4 (3 in Fig. 4). The great change in current in the system containing $[Co(ox)_3]^{3-}$ anions and tetraalkylammonium cations cannot be accounted for by the decrease in drop time of mercury electrode. This may be attributed to ion-pair formation between $[Co(ox)_3]^{3-}$ anions and tetraalkylammonium cations. Equation (5) indicates that, when $K_{MX}/K_{M'X} \geqq 1 > D_{MX}/D_{M'X}$, plots of the diffusion coefficient D against C_M give curves similar to curves 1 and 2 in Fig. 4. The sign of equality gives a straight line similar to curve 1, while the sign of inequality gives a convex curve similar to curve 2. The experimental values in Fig. 4 corrected for the drop time of mercury electrode were treated with Eq. (6). The plots thus obtained are shown in Fig. 5. The association constants K_{MX} which were obtained with a procedure similar to other cases are given in the last two lines of Table 1.

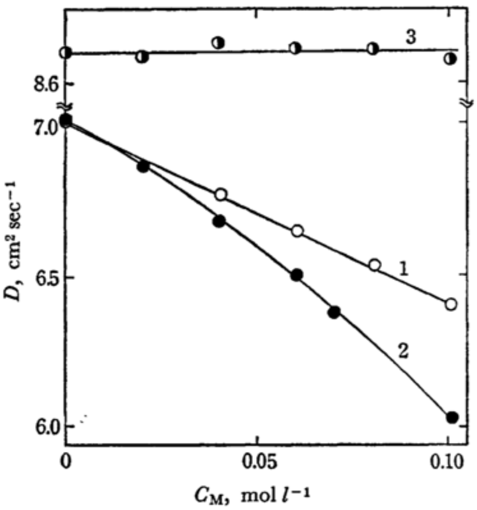

Fig. 4. Apparent diffusion coefficient (D) calculated from the reduction wave of cobalt complexes as a function of the concentration of tetraalkylammonium ions. The systems are: (1) $(CH_3)_4N^+$-$[Co(ox)_3]^{3-}$, (2) $(C_2H_5)_4N^+$-$[Co(ox)_3]^{3-}$ and (3) $(C_2H_5)_4N^+$-$[Co(NH_3)_6]^{3+}$. All the values are corrected for the drop time of DME.

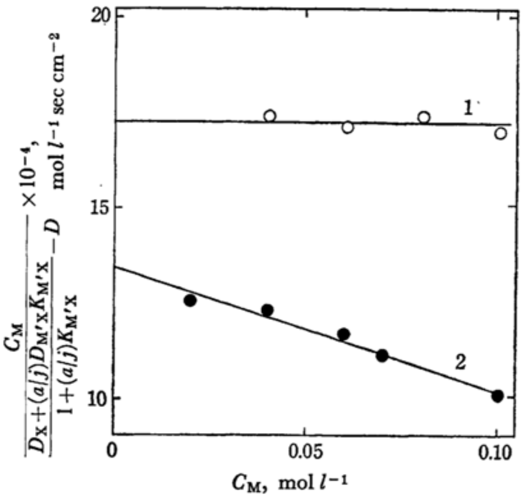

Fig. 5. Left-hand side of Eq. (6) as a function of concentrations of (1) tetramethylammonium and (2) tetraethylammonium ions.

[*1] In the case of aluminum(III) ion, the association between aluminum(III) and nitrate ions seems not to be ignored. In this study, however, the correction for the effect of nitrate ions was not made, because no accurate value has been reported for the association constant of the ion-pair of these two ions. If it is assumed that the association constant of the ion-pair of aluminum with nitrate ions is the same with that of hexamminecobalt(III) with nitrate ions, which is, reported to be 1.6_3 in logarithmic unit at infinite dilution,[7] the association constant of $Al^{3+}[Co(ox)_3]^{3-}$ at ionic strength 0.1 is calculated to be 140 instead of 118 given in Table 1.

7) S. Katayama and R. Tamamushi, presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo (April, 1967).

8) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

Visible and Ultraviolet Spectra. The visible and ultraviolet absorption spectra of trioxalatocobaltate(III) in aqueous solutions were measured in order to know what changes occur on the absorption spectra when an ion-pair $M^{m+}[Co(ox)_3]^{3-}$ is formed, where M^{m+} represents metal ions, such as Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Al^{3+}. The solutions containing potassium trioxalatocobaltate and metal chloride were prepared as about 60—70% of trioxalatocobaltate ions exist in the form of ion-pair. The ion-pair formation gave no effect on the absorption spectra over the range of 210 mμ to 700 mμ.

Infrared Spectra. In order to investigate how the ion association affects the vibration of ligand, the infrared absorption due to ν_s(C-O) + ν(C-C) was measured with the solution of potassium, magnesium, calcium and strontium trioxalatocobaltate(III). The solution of 0.02 M potassium trioxalatocobaltate(III) in which a great part of trioxalatocobaltate(III) ions seemed to exist in the form of free ions gave an absorption maximum due to ν_s(C-O) + ν(C-C) at 1389 cm^{-1}. The solutions which contained 0.02 M potassium trioxalatocobaltate(III) and 0.15 M magnesium, calcium and strontium chloride gave also an absorption due to ν_s(C-O) + ν(C-C) at 1389 cm^{-1}. From the value of the association constants obtained by the polarographic method it was estimated that 80—90% of trioxalatocobaltate(III) ions were present in the form of ion-pair $M^{2+}[Co(ox)_3]^{3-}$ in these solutions. The absorption spectra of potassium, calcium, strontium and barium trioxalatocobaltate(III) in solid state were measured and compared with the spectra of the solutions mentioned above. They are given in Fig. 6.

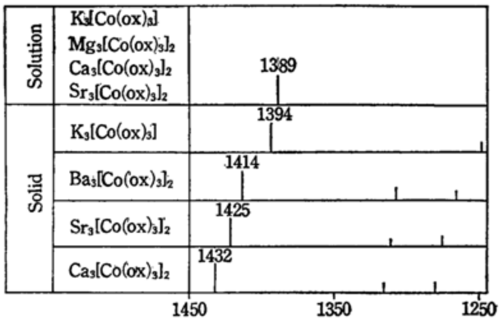

Fig. 6. Wave numbers of the absorption bands of trioxalatocobaltate(III) in aqueous solutions and in solid state.

Table 2. Logarithmic association constants of complex ions with hydrated ions at zero ionic strength at 25°C

$[Co(ox)_3]^{3-}$		$[Fe(CN)_6]^{3-}$		$[Co(NH_3)_6]^{3+}$	
Ion	log *K*	Ion	log *K*	Ion	log *K*
Na^+	1.9_4	K^+	1.40[9]	Cl^-	1.49[6] 1.5[12,13]
NH_4^+	1.5_3			NO_3^-	1.6_3[7]
$(CH_3)_4N^+$	1.5_2			ClO_4^-	1.4_0[7]
$(C_2H_5)_4N^+$	1.1_8				
Mg^{2+}	2.8_9	Mg^{2+}	2.79[10]	SO_4^{2-}	3.56[6]
Ca^{2+}	2.9_2	Ca^{2+}	2.83[10]		
Sr^{2+}	2.9_4	Sr^{2+}	2.85[10]		
Ba^{2+}	2.9_5	Ba^{2+}	2.88[10]		
Al^{3+}	3.7_0	La^{3+}	3.74[11]	$P_3O_9^{3-}$	4.44[14]

Discussion

The association constants of trioxalatocobaltate(III) anion with cations were compared with those of ferricyanide anion with cations and also those of hexamminecobalt(III) cation with anions (see Table 2). The values given for comparison in Table 2 are those of being determined from conductivity measurements, because the conductivity method seems to detect the same type of ion-pair as the polarographic method does. The association constants for the ion-pair $M^{m+}[Fe(CN)_6]^{3-}$ agree well with our results. The radii of $[Co(ox)_3]^{3-}$ and $[Fe(CN)_6]^{3-}$ ions are calculated to be 3.0Å and 2.8Å, respectively, by applying Stokes' law. That both complex anions have similar radii may be a cause of the good agreement. On the other hand, the association constants of hexamminecobalt(III) cation with anions are about five times larger than those of tervalent complex anion with cations except for the case of ion-pairs of 3-1 electrolytes, though the application of Stokes's law gives the radius of $[Co(NH_3)_6]^{3+}$ ion to be 2.8 Å, which is nearly equal to those of the complex anion described above. This great difference on association constant was, therefore, considered to arise from the difference in size between the ions paired with complex ions. The bi- and tervalent metal cations are strongly hydrated than the anions owing to their small sizes, so that the metal cations seem to associate with complex anions in a state of hydrated cations. Hence the apparent size of hydrated cation in a associated state appears to be larger than the size of hydrated anion. This may be a cuase of the great difference. The discussion for the results of spectroscopic study on ion association will lead some support to this consideration.

It would be expected that, if a trioxalatocobaltate(III) anion is associated with a cation, the complex anion is polarized and in consequence the change of absorption band in visible or ultraviolet

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9) C. B. Monk, *J. Chem. Soc.*, **1949**, 423.

10) C. W. Gibby and C. B. Monk, *Trans Faraday Soc.*, **48**, 632 (1952).

11) H. S. Dunsmore and J. G. James, *J. Chem. Soc.*, **1951**, 2925.

12) S. Katayama, *Rikagaku Kenkyusho Hokoku*, **42**, 243 (1966).

13) R. Tamamushi, T. Isono and S. Katayama, This Bulletin, **40**, 334 (1967).

14) C. B. Monk, *J. Chem. Soc.*, **1952**, 1317.

TABLE 3. DIFFUSION COEFFICIENTS OF ION-PAIRS AND COMPLEX IONS

Ion-pair	$D\times10^6$ $cm^2 sec^{-1}$	Ion-pair	$D\times10^6$ $cm^2 sec^{-1}$	Complex ion	$D\times10^6$ $cm^2 sec^{-1}$
$Na^+[Co(ox)_3]^{3-}$	5.8			$[Co(ox)_3]^{3-}$	8.1
$NH_4^+[Co(ox)_3]^{3-}$	5.6			$[Co(NH_3)_6]^{3+}$	8.4[16]
$(CH_3)_4N^+[Co(ox)_3]^{3-}$	4.3			$[Cr(NH_3)_6]^{3+}$	8.5[17]
$(C_2H_5)_4N^+[Co(ox)_3]^{3-}$	2.4			$[Co(en)_3]^{3+}$	6.4[18]
				$[Cr(en)_3]^{3+}$	5.9[19]
$Mg^{2+}[Co(ox)]^{3-}$	4.8	$[Co(NH_3)_6]^{3+}SO_4^{2-}$	5.7[15]		
$Ca^{2+}[Co(ox)_3]^{3-}$	4.4	$[Cr(NH_3)_6]^{3+}SO_4^{2-}$	5.7[15]		
$Sr^{2+}[Co(ox)_3]^{3-}$	4.2	$[Co(en)_3]^{3+}SO_4^{2-}$	5.3[15]		
$Ba^{2+}[Co(ox)_3]^{3-}$	4.2	$[Cr(en)_3]^{3+}SO_4^{2-}$	5.1[15]		
$Al^{3+}[Co(ox)_3]^{3-}$	3.8				

region occurs. However, any change was not observed on the absorption over the range of 210 mμ to 700 mμ. Moreover, if the ion-pair formation occurs, the decrease of the degree of degeneracy and the shift of the absorption band would be expected on the infrared absorption spectra. No changes, however, were observed in all the systems, although in solid state trioxalatocobaltates(III) of potassium and alkali earth metals gave the frequency shift. That is to say, the existence of ion-pairs could not be detected by the measurement of visible, ultraviolet and infrared absorption spectra. On the other hand, the existence of ion-pair was distinctly detected by the polarographic method. The explanation of this apparent discrepancy is that the complex anion has no direct interaction with metal ion, but one or more water molecules interpose between the two ions. The separation of the ions by several water molecules can greatly decrease the polarization effect of the complex anion, so that the absorption spectra show no indication of the ion-pair formation.

The consideration that the metal ion forms the ion-pair in a hydrated state was supported further by the discussion on the diffusion coefficient of ion-pair. The diffusion coefficients of the ion-pairs D_{MX} were obtained by substituting D_X, $D_{M'X}$, K_{MX} and $K_{M'X}$ into the slope of the plots of Eq. (6). D_X was calculated by the application of the Nernst equation to the limiting mobility of complex anion. $D_{M'X}$ was obtained with Eq. (3), when C_M equaled zero. The value of D_{MX} thus obtained are given in the first column of Table 3. The diffusion coefficients of ion-pairs decrease with increasing positive charges on the metal ion. This fact clearly demonstrates the influence of hydration of the cation. The increase in cation charge is accompanied by the increase in size of hydrated cation, and consequently give raise to the decrease in the diffusion coefficient of metal ion. The diffusion coefficients of the ion-pairs of trioxalatocobaltate(III) anion and alkali earth metal cations are further compared with those of the ion-pairs of tervalent complex cations and sulphate anion (see also Table 3). The diffusion coefficients of complex ions are also given in Table 3. It is seen from Table 3 that the diffusion coefficients of ion-pairs of complex anion and cation are smaller than those of complex cation and anion. Since the diffusion coefficient of complex anion is nearly equal to or somewhat larger than those of complex cation, the ions paired with complex ions seem to be responsible for the difference between these two sets of figures in Table 3.

The possibility of the existence of several water molecules between the complex anion and the metal cation was examined also by the estimation of the closest approach of the paired ions. The value of the closest approach was calculated in the same way as presented in the previous paper,[20] and was found to be in good agreement with the sum of Stokes' law radius of trioxalatocobaltate(III) ion and the radius of the hydrated metal ion. From these discussions it may be concluded that in a sense of equilibrium study a trioxalatocobaltate(III) anion and a metal cation has no direct interaction, but one or more water molecules interpose between the two ions.

The closest approach for ion-pair $R_4N^+[Co(ox)_3]^{3-}$ was also calculated. The values are 6.0 Å and 8.0 Å for $(CH_3)_4N^+[Co(ox)_3]^{3-}$ and $(C_2H_5)_4N^+$-$[Co(ox)_3]^{3-}$, respectively. They are in good agreement with the distance which were obtained by adding the crystallographic radius of R_4N^+ ion to the radius of $[Co(ox)_3]^{3-}$ ion.

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