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Spectrophotometric Studies on the Ion-pair Formation of Hexamminecobalt(III) and Tris(ethylenediamine)cobalt(III) Complexes with Halide and Sulfate Ions

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The optical density of charge transfer spectra of some tervalent substitution-inert complex cations in an ultraviolet region increases by the addition of halide and sulfate ions. From the change in optical density the association constants were determined at ionic strength 0.07 ($NaClO_4$) and 25°C. The values are 2.2 ± 0.5 for $Co(NH_3)_6{}^{3+}Cl^-$, 2.2 ± 0.6 for $Co(NH_3)_6{}^{3+}Br^-$, $0.7_1\pm0.5$ for $Co(NH_3)_6{}^{3+}I^-$, 114 ± 3 for $Co(NH_3)_6{}^{3+}SO_4{}^{2-}$, 2.9 ± 0.5 for $Co(en)_3{}^{3+}Cl^-$ and 102 ± 8 for $Co(en)_3{}^{3+}SO_4{}^{2-}$ respectively. The difference of these values from the reported values are related to the method for the measurements. Absorption maxima of the third absorption bands are obtained at 196 mμ for $Co(NH_3)_6{}^{3+}$ and at 210 mμ for $Co(en)_3{}^{3+}$.

The ion-pair formation of hexamminecobalt(III) and tris(ethylenediamine)cobalt(III) ions have been studied by many investigators[1-4] and the association constants of these ions with anions have been reported. However these values determined by various methods and/or by various researchers are often different from each other. For instance, Evans and Nancollas[2] determined by the spectrophotometric method the logarithmic constant of $Co(NH_3)_6{}^{3+}Cl^-$ at infinite dilution to be 2.59 at 25°C, whereas King *et al.*[4] obtained the logarithmic constant of <-0.7 for the same ion-pair at $\mu=0.9$ and 35°C. On the other hand, the values obtained by the electrochemical methods are around 1.5 in good agreement with each other.

This investigation was undertaken for the purpose of reexamining these constants and determining the association constants of hexamminecobalt(III) and tris(ethylenediamine)cobalt(III) ions with halide and sulfate ions by the spectrophotometric method.

Experimental

Materials. The compounds $[Co(NH_3)_6](ClO_4)_3$ and $[Co(en)_3](ClO_4)_3$ which were used in this study were converted from the corresponding chlorides; $[Co(NH_3)_6]Cl_3$[5] and $[Co(en)_3]Cl_3\cdot 3H_2O$[6] were prepared with the procedures given in the literatures. Each compound was recrystallized three times from water.

The chemical analysis of cobalt in hexamminecobalt(III) complex was carried out in the following way. The complex was decomposed to cobalt(II) hydroxide by the addition of potassium hydroxide and was converted into cobalt(II) chloride with hydrochloric acid. Cobalt(II) chloride obtained was titrated with the standardized EDTA solution using murexide as an indicator. The halide solutions were standardized by

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[1] M. Linhard, *Z. Elektrochem.*, **50**, 224 (1940).

[2] M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1953).

[3] H. Yoneda, This Bulletin, **28**, 125 (1955).

[4] E. L. King, J. H. Espenson and R. E. Visco, *J. Phys. Chem.*, **63**, 755 (1959).

[5] J. Bjerrum and J. P. MacReynolds, "Inorganic syntheses," Vol. 2, McGraw-Hill, New York (1946), p. 216.

[6] J. B. Work, *ibid.*, p. 221.

the Volhard method. The sulfate solution was prepared by dissolving a known amount of sodium sulfate (Na_2SO_4) of guaranteed reagent grade.

All other chemicals used were of guaranteed reagent grade. Redistilled water was used to prepare the solutions of desired concentrations.

Measurements of Absorption Spectra. The absorption spectra were measured with a Hitachi EPS-3 recording spectrophotometer using 1 mm, 10 mm, 50 mm and 100 mm quartz cells. The measurement was made at 25°C after solution was kept standing for about 30 min to come to thermal equilibrium. Increasing quantities of sodium halide or sulfate were added to each solution containing a small constant concentration of hexammine- or tris(ethylenediamine)-cobalt(III) perchlorate and the corresponding salt solution was used as a reference solution. Special care was taken in the measurement at the constant wavelength because the optical density increases rapidly with decreasing wave lengths. By the addition of appropriate amounts of sodium perchlorate the ionic strength was kept constant at 0.07, a value which was limited by the low solubility of hexamminecobalt(III) perchlorate.

When measured at short wavelengths, the apparatus and all the solutions used were deaerated by bubbling nitrogen gas. Then absorbancy measurements were made down to 185 mμ in wavelength with a considerable accuracy.

Results

From the spectra obtained, the data were treated in the following way.[7] Consider the association reaction

$$M^{3+} + Z^{z-} = M^{3+}Z^{z-} \qquad (1)$$

where M^{3+} represents a complex cation, Z^{z-} a counter anion and $M^{3+}Z^{z-}$ an ion-pair. The observed extinction coefficient, ε_{obs}, is given by

$$\varepsilon_{obs} = \frac{\varepsilon_M + K\varepsilon_{MZ}[Z^{z-}]}{1 + K[Z^{z-}]} \qquad (2)$$

where [ ] means the concentration of the substance indicated, ε_M and ε_{MZ} are the molar extinction coefficients of M^{3+} and $M^{3+}Z^{z-}$, respectively, and K is the association constant of $M^{3+}Z^{z-}$ given by

$$K = \frac{[M^{3+}Z^{z-}]}{[M^{3+}][Z^{z-}]} \qquad (3)$$

Equation (2) is transformed to

$$\frac{[Z^{z-}]}{\varepsilon_{obs} - \varepsilon_M} = \frac{1 + K[Z^{z-}]}{K(\varepsilon_{MZ} - \varepsilon_M)} \qquad (4)$$

Equation (4) indicates that plots of $[Z^{z-}]/(\varepsilon_{obs} - \varepsilon_M)$ *versus* $[Z^{z-}]$ give a straight line and the association constant K is determined from the ratio of its slope to intercept.

The optical densities of $Co(NH_3)_6{}^{3+}$ and $Co(en)_3{}^{3+}$ ions were measured at various concentrations of the given anions and, at each concentration, they were measured at several wavelengths. Examples of the results obtained are shown in Figs. 1 and 2.

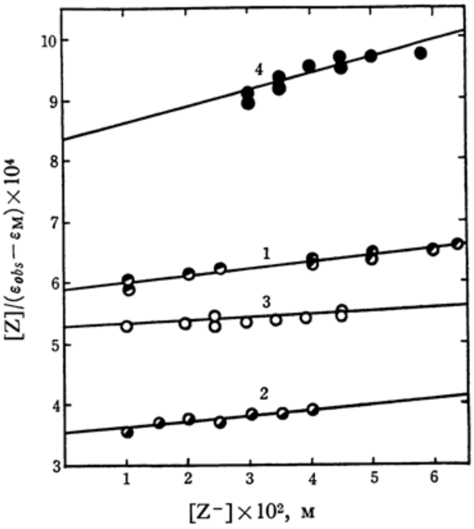

Fig. 1. Plots of the left-hand side of Eq. (4) against the halide ion concentration (1) for $Co(NH_3)_6{}^{3+}Cl^-$ at 247 mμ, (2) for $Co(NH_3)_6{}^{3+}$-Br^- at 265 mμ, (3) for $Co(NH_3)_6{}^{3+}I^-$ at 320 mμ and (4) for $Co(en)_3{}^{3+}Cl^-$ at 264 mμ.

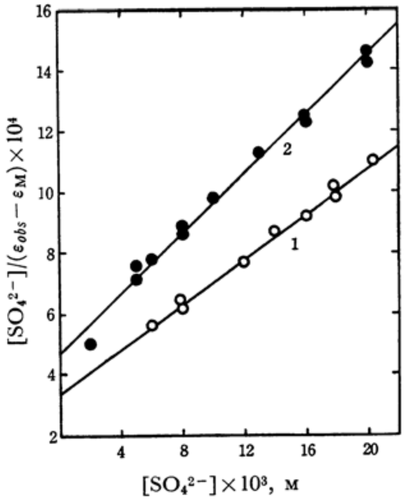

Fig. 2. Plots of the left-hand side of Eq. (4) against the sulfate ion concentration (1) for $Co(NH_3)_6{}^{3+}SO_4{}^{2-}$ at 243 mμ and (2) for $Co(en)_3{}^{3+}SO_4{}^{2-}$ at 262 mμ.

In the case of $Co(NH_3)_6{}^{3+}Z^-$ and $Co(en)_3{}^{3+}Z^-$ (Z=Cl, Br, I), the change in optical density observed by the addition of halide ions was not sufficiently large. Therefore, the measurements were repeated several times to increase the accuracy and the association constant, K, was calculated by the method of least squares. The results are

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

TABLE 1. DETERMINATION OF ASSOCIATION CONSTANT, K, OF $M^{3+}Z^{z-}$

Z^{z-}	Wavelength used for the determination, mμ	K_c at $\mu=0.07$ (average)	$\log K_a$ at $\mu=0$
	$M^{3+}=Co(NH_3)_6^{3+}$		
Cl^-	238, 245, 247	2.2 ± 0.5	0.96 ± 0.1
Br^-	261, 265, 275, 277	2.2 ± 0.6	0.96 ± 0.1
I^-	315, 320	$0.7_1\pm0.5$	$0.4_7\pm0.2$
SO_4^{2-}	238, 243	114 ± 3	3.26 ± 0.01
	$M^{3+}=Co(en)_3^{3+}$		
Cl^-	264, 267	2.9 ± 0.5	0.99 ± 0.07
SO_4^{2-}	262, 264	102 ± 8	3.10 ± 0.03

TABLE 2. ASSOCIATION CONSTANTS AND MOLAR EXTINCTION COEFFICIENTS, ε_{MZ}, FOR THE ION-PAIR OF HEXAMMINECOBALT(III) WITH BROMIDE IONS, OBTAINED AT DIFFERENT WAVELENGTHS

Wavelength, mμ	K_c at $\mu=0.07$	ε_{MZ}
261	2.4 ± 0.03	1515
265	2.4 ± 0.04	1155
275	1.9 ± 0.25	671
277	2.1 ± 0.07	537

given in Table 1. In order to show the accuracy of the association constants which were determined at different wavelengths, the values obtained for the ion-pair of hexamminecobalt(III) with bromide ions are given in Table 2.

The association constants of ion-pairs, $Co(NH_3)_6^{3+}SO_4^{2-}$ and $Co(en)_3^{3+}SO_4^{2-}$, were determined in a similar way, but a successive approximation was applied to obtain the concentration of free sulfate ions. The association constants obtained are also given in Table 1.

The thermodynamic association constants of the ion-pairs of $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$ were calculated with the concentration constants and the activity coefficients, as given in Table 1. The activity coefficients were evaluated with the aid of the equation and the ion-size parameters reported by Kielland.[8] The ion-size parameters used in the calculation were 3 Å for Cl^-, Br^- and I^-, 4 Å for SO_4^{2-} and $Co(NH_3)_6^{3+}$ and 6 Å for $Co(en)_3^{3+}$ ions. As for the ion-size parameters of the ion-pairs which were not reported by Kielland were estimated to be 4.5 Å for $Co(NH_3)_6^{3+}Cl^-$, $Co(NH_3)_6^{3+}Br^-$, $Co(NH_3)_6^{3+}I^-$, $Co(NH_3)_6^{3+}$-SO_4^{2-} and $Co(en)_3^{3+}SO_4^{2-}$ and 5 Å for $Co(en)_3^{3+}Cl^-$ from the consideration of the charge and the structure of the ion-pairs.*2

A tendency to form an ion-pair of $Co(NH_3)_6^{3+}$-HSO_4^- was also investigated. If there exist two ion associations,

$$Co(NH_3)_6^{3+} + SO_4^{2-} \rightleftharpoons Co(NH_3)_6^{3+}SO_4^{2-} \quad (5)$$

$$Co(NH_3)_6^{3+} + HSO_4^- \rightleftharpoons Co(NH_3)_6^{3+}HSO_4^- \quad (6)$$

the observed optical density D_{obs} is given by the equation

$$D_{obs} = \varepsilon_M[M^{3+}] + \varepsilon_{MZ}[M^{3+}Z^{z-}] + \varepsilon_{MHZ}[M^{3+}HZ^{(z-1)-}] \quad (7)$$

If the third term of the right-hand side of Eq. (7) is negligibly small, Eq. (7) is reduced to

$$\varepsilon_{obs} - \varepsilon_M = \frac{\varepsilon_{MZ} - \varepsilon_M}{[M]_t}[M^{3+}Z^{z-}] \quad (8)$$

where $[M]_t$ indicates a total concentration of hexamminecobalt(III). This corresponds to the case when only the equilibrium of Eq. (5) is in existence. A series of measurements were carried out with the solutions containing the same concentration of total sulfate and various concentrations of hydrogen ions. The concentration of free sulfate ions was calculated from the concentrations of total sulfate and hydrogen ions and the second dissociation constant of sulfuric acid. The pK_a of the second dissociation of sulfuric acid at ionic strength 0.07 was taken as 1.52, which was obtained with the value at infinite dilution[9] after correction for the activity coefficients.

Plots of the left-hand side of Eq. (8) against the concentration of ion-pair, $Co(NH_3)_6^{3+}SO_4^{2-}$,

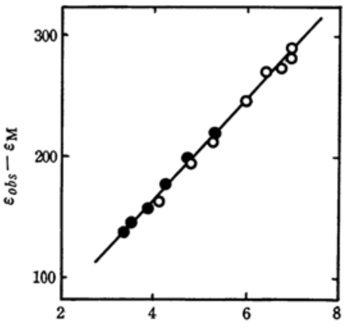

Fig. 3. Plots of the left-hand side of Eq. (8) against the concentration of $Co(NH_3)_6^{3+}SO_4^{2-}$ at 238 mμ in neutral solutions (○) and in solutions containing 3.9×10^{-2}—7.8×10^{-2} M hydrogen ions (●). The total concentration of hexamminecobalt(III) complex is 10^{-3} M and that of sulfate ions, 10^{-2} M.

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*2 The estimation of the ion-size parameters is rather difficult. It is fortunate, however, that the change in ion-size parameter gives only a small effect on the value of $\log K_a$. For example, if the ion-size parameter of $Co(en)_3^{3+}SO_4^{2-}$ is varied from 4.5 Å to 9 Å, the activity coefficient is changed from 0.80 to 0.84 with the result that the $\log K_a$ of $Co(en)_3^{3+}$-SO_4^{2-} is varied from 3.10 to 3.08.

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

[9] For instance, R. Luther, *Z. Elektrochem.*, **13**, 294 (1907).

which was calculated from the concentration of sulfate ions and the association constant of $Co(NH_3)_6^{3+}SO_4^{2-}$ obtained in this study, gave a straight line; two sets of plots lie on a single line as shown in Fig. 3. It may be concluded from these plots that the association with hydrogensulfate ion is negligible compared with that with sulfate ion. The results agree with that obtained with the aid of the polarographic diffusion current.[7]

In order to know the aspects of so-called "end absorption," the absorption spectra in a short wavelength region were recorded with the solutions of various salts of hexamminecobalt(III) and tris(ethylenediamine)cobalt(III) complexes. The solutions of these complexes used in the measurements were prepared as to contain no appreciable amount of the ion-pair with the aid of the stability constants obtained in this study, so that the change of optical density due to the ion-pair formation did not need to be taken into consideration. As the results, all salts of each complex gave an absorption maximum at the same wavelength as shown in Table 3.

Table 3. Wavelengths and molar extinction coefficients of absorption maxima of charge transfer bands of hexamminecobalt(III) and tris(ethylenediamine)cobalt(III) complex ions

Complex	λ_{max}, mμ	log ε_{max}
$[Co(NH_3)_6](ClO_4)_3$	196	4.5_4
$[Co(NH_3)_6]Cl_3$	197	4.5_1
$[Co(NH_3)_6]Br_3$	196	4.4_8
$[Co(NH_3)_6]I_3$	196	4.4_8
$[Co(en)_3](ClO_4)_3$	210	4.3_5
$[Co(en)_3]Cl_3$	210	4.3_5

Discussion

The association constants of hexamminecobalt(III) and tris(ethylenediamine)cobalt(III) with halide and sulfate ions have been reported by several researchers,[2,4,10-21] which are given in Table 4 together with the association constants obtained in this study. The logarithmic constants of $Co(NH_3)_6^{3+}SO_4^{2-}$ and $Co(en)_3^{3+}SO_4^{2-}$ at infinite dilution which were obtained in this study are in reasonable agreement with those in the literature. The values reported by Evans and Nancollas[2] are extremely high as seen from Table 4. They used in their experiments the condition that the concentration of halide ions was much less than that of the complex cations. The calculation showed that, at their experimental conditions, only a small portion of the complex cations was associated with halide ions to form ion-pairs in the solution. This means that the change in optical density due to the formation of the ion-pair might be so small that the association constants determined might not be accurate. In this study, the experiments were also carried out at the same condition reported by Evans and Nancollas, with the results that supported definitely the above discussion.

It seems certain that the association constants of hexamminecobalt(III) and tris(ethylenediamine)-cobalt(III) ions with halide ions which were obtained by the spectrophotometric method in this study are smaller than those obtained by the electrochemical methods, even if the inaccuracy in correction for the activity coefficient is taken into consideration. This is probably because the values obtained by the spectrophotometric method are based on the change in optical density due to the charge transfer of associated ions in short range, whereas the electrochemical methods detect all counter ions which are located in the range shorter than the critical distance defined by the Bjerrum's theory of ion association.[22] Since the distant ion-pairs seem important in the case of highly charged ions, the result in this study that the values obtained by spectrophotometric and electrochemical methods are not so different from each other for 3-2 electrolytes such as $Co(NH_3)_6^{3+}SO_4^{2-}$ is rather unexpected. This was noticed also by Cohen.[22]

The association constants tend to decrease in order of $K_{Cl}\simeq K_{Br}>K_{I}$, the order in which the size of the anion increases. The association with hydrogensulfate ions was found to be negligible compared with that with sulfate ions indicating that the hydrogensulfate ion behaves as a univalent anion, but not as a bivalent anion in spite of similarity in the structure. It may be concluded from these results that the association depends mainly on the coulombic interaction between ions.

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22) S. R. Cohen, *J. Phys. Chem.*, **61**, 1670 (1957).

TABLE 4. LOGARITHMIC ASSOCIATION CONSTANTS FOR $Co(NH_3)_6{}^{3+}+Z^{z-}$ AND $Co(en)_3{}^{3+}+Z^{z-}$ AT INFINITE DILUTION AT 25°C

Z^{z-}	log K_a	Method*	Investigators	Reference
		$Co(NH_3)_6{}^{3+}+Z^{z-}$		
Cl^-	1.49	cond	Jenkins and Monk (1951)	10
	1.5	cond	Tamamushi, Isono and Katayama (1967)	11
	2.59	sp	Evans and Nancollas (1953)	2
	<-0.7**	sp	King and Espenson (1959)	4
	0.96	sp	The present study	
	2.42	sol	Fedorov Minorov and Kul'ba (1962)	12
Br^-	2.38	sp	Evans and Nancollas (1953)	2
	<-0.7**	sp	King and Espenson (1959)	4
	0.96	sp	The present study	
I^-	1.23	sp	Evans and Nancollas (1953)	2
	0.4_7	sp	The present study	
$SO_4{}^{2-}$	3.56	cond	Jenkins and Monk (1951)	10
	3.46	pol	Vlček (1961)	17
	3.21	pol	Tanaka, Ogino and Satô (1966)	7
	3.30	chron	Tanaka and Yamada (1967)	19
	3.32	sp	Posey and Taube (1956)	14
	2.95	sp	Bale, Davies and Monk (1956)	15
	2.89	sp	Davies and Monk (1958)	16
	3.26	sp	The present study	
	3.52	sol	Davies (1930)	13
	3.60	sol	Laurie and Monk (1963)	18
		$Co(en)_3{}^{3+}+Z^{z-}$		
Cl^-	1.72	cond	Jenkins and Monk (1951)	10
	0.99	sp	The present study	
$SO_4{}^{2-}$	3.45	cond	Jenkins and Monk (1951)	10
	2.72	pol	Laitinen and Grieb (1955)	20
	3.22	chron	Tanaka and Yamada (1966)	19
	2.93	sp	Ogino and Saito (1966)	21
	3.10	sp	The present study	

* Method of measurement: cond, conductivity; sol, solubility; sp, spectrophotometry; pol, polarography; chron, chronopotentiometry.

** Concentration constants (log K_c) obtained at $\mu=0.9$ and 35°C.

The absorption maxima found in short wavelengths, that is at 196 mμ for hexamminecobalt(III) complex and at 208 mμ to 213 mμ for tris(ethylenediamine)cobalt(III) complex, are considered to be the absorption bands characteristic of these complex ions, which could be assigned either to the electron transfer between metal cation and ligand or to the electronic transition within a ligand molecule. From the measurement of absorption spectra of ammonia molecule in gas phase in a vacuum ultraviolet region,[23-25] an absorption maximum was found at 1905 Å, which has been assigned to the transition from the highest occupied orbital to the lowest vacant one. The absorption seems to be related with the lone-pair electron of ammonia and consequently it seems to change when the ammonia molecule is coordinated in a hexamminecobalt(III) ion. Taking this fact into consideration, it may be appropriate to state that these bands are due to the electron transfer from a ligand to the central metal ion in the complex.

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