Thermodynamic Studies on Cobalt Complexes. X. Chemical Equilibrium between Aquopentamminecobalt(III) Complex and Oxalate Ion[*]

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(Received August 7, 1961)

It was found in the preceding paper(1) of this series that, when the oxalate ion in the mixed solution of oxalic acid and potassium oxalate reacted with the diaquotetramminecobalt(III) ion, the oxalate ion coordinated as a bidentate ligand, producing an oxalatotetrammine cobalt(III) ion. On the other hand, when ammonium oxalate reacted with the diaquotetramminecobalt(III) ion, an oxalatopentamminecobalt(III) ion containing an oxalate inon as a unidentate ligand was produced. As is thus shown, the oxalate ion coordinates as a bidentate ligand in some cases and as a unidentate ligand in others.

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[*] Read at the Symposium on Coordination Compounds of the Chemical Society of Japan, Sendai, September, 1960.

1) M. Mori, R. Tsuchiya and E. Matsuda, This Bulletin, 34, 1761 (1961).

An oxalatopentamminecobalt(III) ion was also produced when the oxalate ion in the mixed solution of oxalic acid and potassium oxalate reacted with the aquopentamminecobalt(III) ion.

In the present study, the chemical equilibrium between aquopentamminecobalt(III) and oxalate ions is examined spectrophotometrically, just as in the preceding paper[1], to find the thermodynamic properties of the oxalatopentamminecobalt(III) complex. By combining this result of the equilibrium with that between the diaquotetramminecobalt(III) and oxalate ions, the difference in the thermodynamic properties between the oxalatotetramminecobalt(III) and oxalatopentamminecobalt(III) ions, the former containing an oxalate ion as bidentate ligand and the latter as a unidentate ligand, is discussed.

Experimental

Aquopentamminecobalt(III) perchlorate was prepared by the method of Jörgensen[2]. When the buffer solution, consisting of oxalic acid and potassium oxalate, was added to the aqueous solution of aquopentamminecobalt(III) perchlorate at room temperature, the reaction did not take place, but it proceeded when the solution was heated to 65°C. It was found, as is shown below, by spectral and electric conductivity measurements that the reaction product was an oxalatopentamminecobalt(III) complex, in which the hydrogenoxalate ion was contained as a unidentate ligand.

The electric conductivity of the oxalatopentamminecobalt(III) complex in an aqueous solution was measured by a Yanagimoto Conductivity Outfit Model MY-7. The measurement of the equilibrium was made spectrophotometrically by using a Hitachi EPU 2-type spectrophotometer in the same way as in the case of the reaction between a diaquo-complex and an oxalate. The maximum of the first absorption band of aquopentamminecobalt(III) ion is at $\nu=61.6$ ($\log \varepsilon=1.62$)[3], while that of the oxalatopentamminecobalt(III) ion produced is at $\nu=59.2$ ($\log \varepsilon=1.87$)[4]. Since the equilibrium was shifted toward the aquo-complex, the measurement of the absorbancy was made at 490 mμ. A brown flask was used as the reaction vessel to prevent photodecomposition. The measurement of the pH of the solution at equilibrium was carried out with a Horiba HRL Model M pH meter.

Results

Figure 1 shows the absorption spectra of the solution at the equilibria of the reaction of aquopentamminecobalt(III) perchlorate at different concentrations with the buffer solution consisting of oxalic acid and potassium oxalate at different concentrations. The absorption spectra of aquopentamminecobalt(III) and oxalatopentamminecobalt(III) ions are also shown in this figure. It is presumed from this figure that the reaction product between aquopentamminecobalt(III) and oxalate ions is an oxalatopentamminecobalt(III) ion.

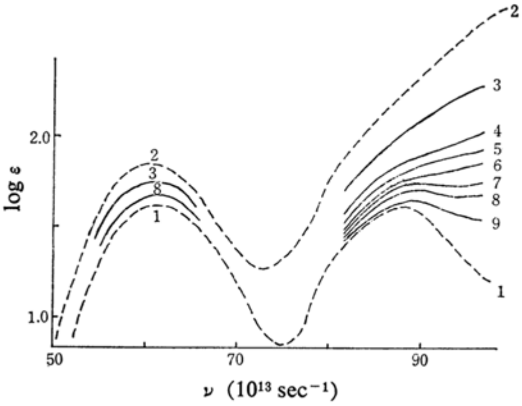

Fig. 1. The absorption spectra of the solution containing aquopentamminecobalt(III) perchlorate reacted with oxalate ion.

1. Aquopentamminecobalt(III) perchlorate only.
2. Oxalatopentamminecobalt(III) ion produced from the above reaction.

Initial concentration of cobalt(III) aquo-complex and that of oxalate ion are as follows respectively:

3.	1/500 F/*l*,	1/5 F/*l*
4.	1/200 F/*l*,	1/10 E/*l*
5.	1/300 F/*l*,	1/20 F/*l*
6.	1/300 F/*l*,	1/40 F/*l*
7.	1/300 F/*l*,	1/80 F/*l*
8.	1/300 F/*l*,	1/160 F/*l*
9.	1/600 F/*l*,	1/320 F/*l*

TABLE I. MOLECULAR CONDUCTANCES OF OXALATOPENTAMMINECOBALT(III) OXALATE AT DIFFERENT CONCENTRATIONS IN AN AQUEOUS SOLUTION AT 25°C

Values calcd. as $[\mathrm{Co(NH_3)_5HC_2O_4}]\mathrm{C_2O_4}$	Values calcd. as $[\mathrm{Co(NH_3)_5C_2O_4}]_2\mathrm{C_2O_4}$
$\Lambda_{200}=236.12$	$\Lambda'_{200}=472.24$
$\Lambda_{250}=247.84$	$\Lambda'_{250}=495.68$
$\Lambda_{500}=261.77$	$\Lambda'_{500}=523.54$
$\Lambda_{1000}=259.21$	$\Lambda'_{1000}=518.42$
$\Lambda_{2000}=274.28$	$\Lambda'_{2000}=548.56$

The number of the suffix in Λ and Λ' is the dilution, i.e., the volume of solution containing one gram molecule of solute.

In order to obtain information about the oxalatopentamminecobalt(III) complex, the electric conductivity of the complex oxalate solution was measured. The molecular conductances obtained are listed in Table I.

In this table, the values Λ and Λ' were

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[2] S. M. Jörgensen, *Z. anorg. Chem.*, **17**, 461 (1898).

[3] Y. Shimura and R. Tsuchida, This Bulletin, **29**, 312 (1956).

[4] R. Tsuchida, ibid., **13**, 388, 436 (1938).

calculated on the assumption that the oxalatopentamminecobalt(III) oxalate was formulated by $[Co(NH_3)_5HC_2O_4]C_2O_4$ and $[Co(NH_3)_5 \cdot C_2O_4]_2C_2O_4$ respectively. The former formula is reasonable for oxalatopentamminecobalt(III) oxalate, but the latter should be excluded, since Λ' is too large to be applied to the formula $[Co(NH_3)_5C_2O_4]_2C_2O_4$. Therefore, the reaction between the aquopentamminecobalt(III) complex and the oxalate buffer is expressed by

$$\begin{aligned}&[Co(NH_3)_5OH_2]^{3+}(aq.) + HC_2O_4^-\\&\quad = [CO(NH_3)_5HC_2O_4]^{2+}(aq.) + H_2O\ (l) \qquad (1)\end{aligned}$$

There also exist the following ionization equilibria in the solution:

$$H_2C_2O_2 \rightleftarrows H^+ + HC_2O_4^- \qquad (2)$$

$$HC_2O_4^- \rightleftarrows H^+ + C_2O_4^{2-} \qquad (3)$$

$$K_2C_2O_4 \rightleftarrows 2K^+ + C_2O_4^{2-} \qquad (4)$$

The first and second dissociation constants of oxalic acid, K_1 and K_2, are given a follows:

$$K_1 = \frac{C_{H^+} \cdot C_{HC_2O_4^-}}{C_{H_2C_2O_4}} \qquad (5)$$

$$K_2 = \frac{C_{H^+} \cdot C_{C_2O_4^{2-}}}{C_{HC_2O_4^-}} \qquad (6)$$

where $C_{H_2C_2O_4}$, $C_{HC_2O_4^-}$, $C_{C_2O_4^{2-}}$ and C_{H^+} are respectively the concentrations of oxalic acid, the hydrogenoxalate ion, the oxalate ion and the hydrogen ion at equilibrium.

When the initial concentrations of oxalic acid and potassium oxalate are expressed by $C^\circ_{H_2C_2O_4}$ anc $C^\circ_{K_2C_2O_4}$, they are given by the sum of the concentration of the oxalatopentamminecobalt(III) ion, C_2, which is equal to the concentration of the hydrogenoxalate ion consumed by the aquo-complex and the concentrations of unionized oxalic acid, the hydrogenoxalate ion and the oxalate ion at equilibrium of reactions 1, 2, 3 and 4:

$$\begin{aligned}&C^\circ_{H_2C_2O_4} + C^\circ_{K_2C_2O_4}\\&\quad = C_2 + C_{H_2C_2O_4} + C_{HC_2O_4^-} + C_{C_2O_4^{2-}} \qquad (7)\end{aligned}$$

By removing $C_{H_2C_2O_4}$ and $C_{C_2O_4^-}$ from Eqs. 5 and 6 respectively as below,

$$C_{H_2C_2O_4} = \frac{C_{H^+} \cdot C_{HC_2O_4^-}}{K_1}$$

and $$C_{C_2O_4^{2-}} = \frac{K_2 \cdot C_{HC_2O_4^-}}{C_{H^+}}$$

by inserting them into Eq. 7, and by rearranging it, the following equation is obtained for the concentration of the hydrogenoxalate ion at equilibrium:

$$C_{HC_2O_4^-} = \frac{K_1 C_{H^+}(C^\circ_{H_2C_2O_4} + C^\circ_{K_2C_2O_4} - C_2)}{K_1 C_{H^+} + K_1 K_2 + C^2_{H^+}} \qquad (8)$$

If the concentrations of aquopentamminecobalt(III) and water at equilibrium are expressed by C_1 and C_{H_2O} respectively, the equilibrium constant of reaction 1 is given as:

$$K_C = \frac{C_2 \cdot C_{H_2O}}{C_1 \cdot C_{HC_2O_4}} \qquad (9)$$

The concentrations of the aquo-complex and the oxalato-complex, C_1 and C_2, at equilibrium are obtained by the observed absorbancy of the solution and the known molar extinction coefficients of the above two complexes[3,4] in the same way as in the preceding paper[1]. The dissociation constants are reported as $K_1 = 5.9 \times 10^{-2}$ [5] and $K_2 = 6.4 \times 10^{-5}$ [5]. By using these values in Eqs. 8 and 9, the apparent equilibrium constant, K_C, is calculated. The concentrations and the ionic strengths of each ion at equilibrium are given as follows:

	Concentration	Ionic strength
$[Co(NH_3)_5OH_2]^{3+}$	C_1	$9\,C_1/2$
$[Co(NH_3)_5HC_2O_4]^{2+}$	C_2	$4\,C_2/2$
$3\,ClO_4^-$	$3(C_1+C_2)$	$3(C_1+C_2)/2$
$HC_2O_4^-$	$C_{HC_2O_4^-}$	$C_{HC_2O_4^-}/2$
$C_2O_4^{2-}$	$K_2 C_{HC_2O_4^-}/C_{H^+}$	$K_2 \cdot C_{HC_2O_4^-}/2\,C_{H^+}$
K^+	$2C^\circ_{K_2C_2O_4}$	$C^\circ_{K_2C_2O_4}$
H^+	C_{H^+}	$C_{H^+}/2$

The total ionic strength, μ, in the solution is calculated by

$$\begin{aligned}\mu = {}&6\,C_1 + 7\,C_2/2 + C_{HC_2O_4^-}/2\\&+ K_2 \cdot C_{HC_2O_4^-}/2\,C_{H^+} + C^\circ_{K_2C_2O_4} + C_{H^+}/2 \qquad (10)\end{aligned}$$

The value obtained by pH measurement is not that of the hydrogen ion concentration, C_{H^+}, but that of the activity of hydrogen ion. Therefore, the calculations of Eqs. 8 and 10 were at first made by using this activity in place of the hydrogen ion concentration. The hydrogen ion concentration can be obtained by finding the activity coefficient[6] of the hydrogen ion in each ionic strength in the solution calculated by Eq. 10. The recalculations of Eqs. 8 and 10 were carried out by using the hydrogen ion concentration obtained above, and the apparent equilibrium constant, K_C, was calculated.

The results of the measurements and calculations are summarized in Table II.

The logarithm of the apparent equilibrium constant, K_C, is plotted against the aquare root of the ionic strength, μ, in Fig. 2. If it is assumed that this plotting gives a quadratic curve, the equation is calculated as:

$$\log K_C = 3.790\,\mu - 3.954\sqrt{\mu} + 3.428$$

The value of $\log K_C$ obtained by extrapolating this curve up to $\sqrt{\mu} = 0$ is given as:

$$\log K = 3.4$$

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[5] R. Gane and C. K. Ingold, *J. Chem. Soc.*, **1931**, 2153.

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

TABLE II. EQUILIBRIUM OF $[Co(NH_3)_5OH_2]^{3+} + HC_2O_4^- = [Co(NH_3)_5HC_2O_4]^{2+} + H_2O$, AT 25°C
MEASUREMENT OF EXTINCTION COEFFICIENT WAS MADE AT 490 mμ

Initial concn. of $[Co(NH_3)_5 \cdot OH_2](C_2O_4)_3$ $C \times 10^3$ F/l	Initial concn. of $H_2C_2O_4$ $C^\circ_{H_2C_2O_4}$ $\times 10^2$ F/l	Initial concn. of $K_2C_2O_4$ $C^\circ_{K_2C_2O_4}$ $\times 10^2$ F/l	ε*	$C_1 \times 10^3$ F/l	$C_2 \times 10^3$ F/l	pH	$K_C \times 10^{-2}$	log K_C	$\mu \times 10^2$	$\sqrt{\mu}$
1.667	0.250	0.250	43.8	1.532	0.135	3.32	11.350	3.055	1.484	0.1218
1.667	0.313	0.313	43.8	1.532	0.135	3.27	8.918	2.950	1.612	0.1270
1.667	0.417	0.417	44.6	1.480	0.187	3.20	9.482	2.977	1.809	0.1345
1.667	0.417	0.417	44.4	1.493	0.174	3.20	8.732	2.941	1.813	0.1347
1.667	0.500	0.500	45.0	1.454	0.212	3.18	9.083	2.958	1.968	0.1403
1.667	1.250	1.250	46.8	1.338	0.328	2.89	5.891	2.770	3.447	0.1857
3.333	1.250	1.250	47.4	2.600	0.734	2.68	6.893	2.838	4.355	0.2087
3.333	1.250	1.250	46.5	2.716	0.618	2.68	5.530	2.743	4.390	0.2095
1.667	2.500	2.500	49.2	1.184	0.483	2.79	4.874	2.688	5.876	0.2424
3.333	2.500	2.500	48.6	2.445	0.888	2.54	4.419	2.645	6.772	0.2602
1.667	5.00	5.00	51.0	1.068	0.598	2.66	3.343	2.524	10.744	0.3278
5.00	5.00	5.00	51.0	3.204	1.796	2.52	3.421	2.534	12.362	0.3516
5.00	10.00	10.00	53.0	2.819	2.181	2.44	2.366	2.374	21.883	0.4678
5.00	10.00	10.00	53.6	2.703	2.298	2.44	2.601	2.415	21.849	0.4728

* ε is the value corresponding to the molar extinction coefficient of the solution observed at equilibrium.

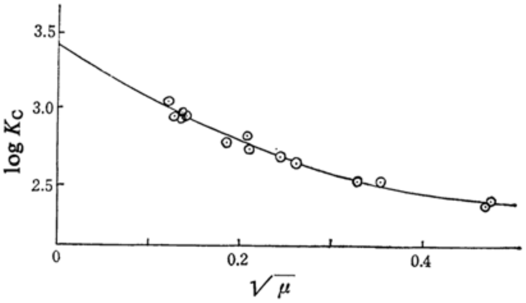


Fig. 2. The relationship between the logarithm of the equilibrium constant of the reaction of aquopentamminecobalt(III) complex with hydrogenoxalate ion, log K_C and the square root of the ionic strength of the solution, $\sqrt{\mu}$.

This is the thermodynamic equilibrium constant of the reaction between the aquopentamminecobalt(III) and hydrogenoxalate ions. The free energy change of the reaction is obtained as:

$$\Delta G^\circ_{298} = -4640 \text{ cal.}$$

Since the free energies of the formation of the aquopentamminecobalt(III) ion, the hydrogenoxalate ion and water in unit activity are known as -104.5 kcal.[7], -167.1 kcal.[8], and -56.69 kcal.[9] respectively, the free energy of the formation of the hydrogenoxalatopentamminecobalt(III) ion in unit activity is calculated as $\Delta G^\circ_{f298} = -219.6$ kcal.

Discussion

By using the free energies of the formation of the hydrogenoxalatopentamminecobalt(III) ion obtained above, and the oxalatotetramminecobalt(III) ion[1] and hexamminecobalt(III) ion[5] obtained in previous papers, the free energies of the following two reactions are calculated as:

$$[Co(NH_3)_6]^{3+} + HC_2O_4^- = [Co(NH_3)_5HC_2O_4]^{2+} + NH_3(aq.)$$

$$\Delta G^\circ_{298} = -4.37 \text{ kcal.}$$

$$[Co(NH_3)_5HC_2O_4]^{2+} = [Co(NH_3)_4C_2O_4]^+ + NH_3(aq.) + H^+$$

$$\Delta G^\circ_{298} = -0.77 \text{ kcal.}$$

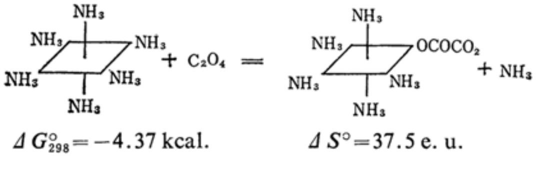
If it is assumed that the free energy required to drive off the hydrogen ion from the hydrogenoxalatopentamminecobalt(III) ion,

$$[Co(NH_3)_5HC_2O_4]^{2+} = [Co(NH_3)_5C_2O_4]^+ + H^+$$

is approximately equal to the free energy change of the second dissociation constant of oxalic acid,

$$HC_2O_4^- = H^+ + C_2O_4^{2-} \qquad \Delta G^\circ_{298} = 5.8 \text{ kcal.}$$

then the free energy and entropy changes of the following two reactions are obtained as below:



$\Delta G^\circ_{298} = -4.37$ kcal. $\Delta S^\circ = 37.5$ e. u.

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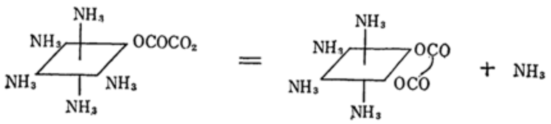
[7] A. B. Lamb and A. T. Larson, ibid., **42**, 2038 (1920).

[8] F. D. Rossini et al., "Selected Values of Chemical Thermodynamic Properties", United States Government Printing Office, Washington (1952), p. 120.

[9] F. D. Rossini et al., ibid., p. 9.



$\Delta G^\circ_{298} = -6.57$ kcal. $\Delta S^\circ = 44.9$ e. u.

The difference in the free energy changes between the two reactions, $\Delta = -2.2$ kcal., corresponds to the difference in those between the change when an oxalate ion coordinates as a unidentate ligand and that when the unidentate oxalate ion undergoes change to a bidentate. It gives a depression of the free energy owing to the formation of a chelate ring. In the same way, the difference in the entropy changes between the two reactions, $\Delta = 7.5$ e. u., gives the entropy effect in the formation of a chelate ring. It is concluded that the chelate effect, having hitherto been interpreted by the entropy effect, can also be applied to the formation of the chelate ring by an oxalate ion.

Summary

It was confirmed by absorption spectral and electric conductivity measurements that the product of the reaction of the aquopentamminecobalt(III) complex with an oxalate ion was a hydrogenoxalatopentamminecobalt(III) complex in which the oxalate ion was coordinated as a unidentate ligand. The equilibrium of the reaction,

$$[\mathrm{Co(NH_3)_5OH_2}]^{3+} + \mathrm{HC_2O_4}^- = [\mathrm{Co(NH_3)_5HC_2O_4}]^{2+} + \mathrm{H_2O}$$

was measured spectrophotometrically, by which method the free energy of formation of the hydrogenoxalatopentamminecobalt(III) ion was calculated.

On the basis of this value and the free energy of the formation of the oxalatotetramminecobalt(III) ion obtained in the preceding paper, the differences in free energy and entropy changes between the bidentate and unidentate oxalate ions were calculated. It was verified that the chelate effect of the oxalate ion was due to the entropy effect.

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