*Thermodynamic Studies on Cobalt Complexes. V. On the Solubility and the Thermal Dissociation of Aquopentamminecobalt(III) Nitrate and Bromide, and on the Thermodynamic Stability of Monoacidopentamminecobalt(III) Complexes**

By Motoshichi MORI and Ryokichi TSUCHIYA

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In the preceding paper[1] the authors determined the standard free energies of formation of aquopentamminecobalt (III) chloride in the solid state and in aqueous solution. In the present study the standard free energies of formation of aquopentamminecobalt(III) nitrate and bromide in the solid state were determind by measuring their solubilities, and those of nitratopentamminecobalt(III) nitrate and bromopentamminecobalt(III) bromide in the solid state were determined by measuring their dissociation pressures.

On the basis of these data the thermodynamic stability of aquopentamminecobalt(III) chloride, nitrate and bromide, that of monoacidopentamminecobalt(III) complexes and that of their ions in aqueous solution were compared and discussed.

Experimental

Aquopentamminecobalt(III) nitrate was precipitated with nitric acid from an aqueous solution of its chloride. The bromide was prepared by the double decomposition of its chloride with ammoium bromide in aqueous solution.

Solubilities of these aquopentamminecobalt(III) complexes were obtained by analyzing the cobalt content in their saturated solutions by iodometry in the same manner as described in the second paper[2] of this series. The dissociation pressures of the complexes were measured with the same apparatus as described in the third paper[3].

Results and Calculation

Solubility of Aquopentamminecobalt(III) Nitrate.—The results obtained for aquopentamminecobalt(III) nitrate are listed in Table I.

As the activity coefficient of the compound was not known, it was assumed that it was approximately equal to that of hexamminecobalt(III) chloride[4] in relatively lower concentrations. When aquopentamminecobalt(III) nitrate is dissolved in water, the change is expressed by

$$[Co(NH_3)_5OH_2](NO_3)_3\ (s) = [Co(NH_3)_5OH_2]^{3+}(aq.\ a) + 3NO_3^-(aq.\ a)$$

If the solubility of the salt in molality and its mean activity coefficient are expressed by m and $\gamma_\pm$ respectively, the equilibrium constant

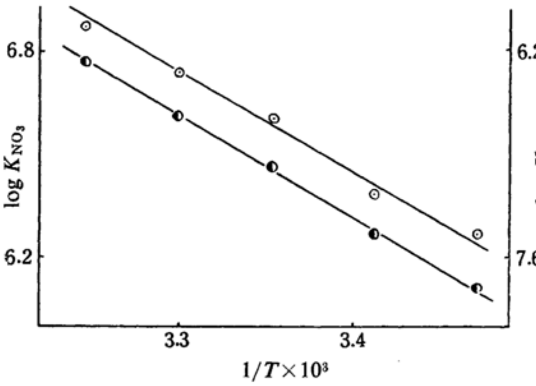

Fig. 1. The relationship between the equilibrium constant of the solution and the temperature.
-⊙-; aquopentamminecobalt(III) nitrate
-◐-; aquopentamminecobalt(III) bromide

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* Read at the Symposium on Coordination Compounds of the Chemical Society of Japan, Fukuoka, Oct., 1959.

[1] M. Mori, R. Tsuchiya and Y. Okano, This Bulletin, 32, 1029 (1959).

[2] M. Mori, R. Tsuchiya and Y. Okano, ibid., 32, 462 (1959).

[3] M. Mori and R. Tsuchiya, ibid., 32, 467 (1959).

[4] M. Mori and R. Tsuchiya, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 79, 1164 (1958).

Table I. Equilibrium of solution for aquopentamminecobalt(III) nitrate

Temp. °C	Solubility in Molality m	$1/T\times10^3$	Mean activity coefficient $\gamma_\pm$	$K_{NO_3}\times10^6$	$\log K_{NO_3}$
15	0.07443	3.471	0.217	1.837	$\bar{6}.2642$
20	0.08516	3.417	0.203	2.412	$\bar{6}.3823$
25	0.1084	3.355	0.181	4.001	$\bar{6}.6022$
30	0.1284	3.299	0.166	5.539	$\bar{6}.7434$
35	0.1472	3.246	0.155	7.317	$\bar{6}.8643$

of the solution, K_{NO_3}, is given by

$$K_{NO_3}=27m^4\gamma_\pm{}^4$$

The plots of its logarithm against the reciprocal of the absolute temperature are shown in Fig. 1, giving an almost straight line. Its equation computed by the method of least squares is

$$\log K_{NO_3}=3.884-2774/T$$

From this equation the heat of solution is obtained as $\Delta H=12.7$ kcal.

The standard free energy change of the solution, ΔG^0, is calculated by the following formula,

$$\Delta G^0=-RT\ln K_{NO_3}=12690-17.76T \quad (1)$$

from which the values of the standard free energy change of the solution at 25°C, $\Delta G^0_{298}=7396$ cal. and its entropy change at 25°C, $\Delta S^0_{298}=17.76$ entropy unit are obtained.

On the other hand, the standard free energy of formation of the aquopentamminecobalt(III) ion in unit activity was calculated in the preceding paper[1] as

$$\Delta G_f{}^0=-192900+296.6T \quad (2)$$

and that of the nitrate ion, $NO_3{}^-$, was obtained in the second paper[2] of this series as

$$\Delta G_f{}^0=-49370+77.03T \quad (3)$$

From formulae 1, 2 and 3, the standard free energy of formation of aquopentamminecobalt(III) nitrate in the solid state is calculated as

$$\Delta G_f{}^0=-353700+545.4T \quad (4)$$

The value at 25°C is $\Delta G^0_{298}=-191100$ cal. and the heat of formation is $\Delta H=353.7$ kcal.

Dissociation Pressure of Aquopentamminecobalt(III) Nitrate.—The weight loss of aquopentamminecobalt(III) nitrate upon heating was followed by a thermobalance. The relationship between the weight loss and the temperature is plotted in Fig. 2, together with those of aquopentamminecobalt(III) bromide, chloride and perchlorate. It is found in this figure

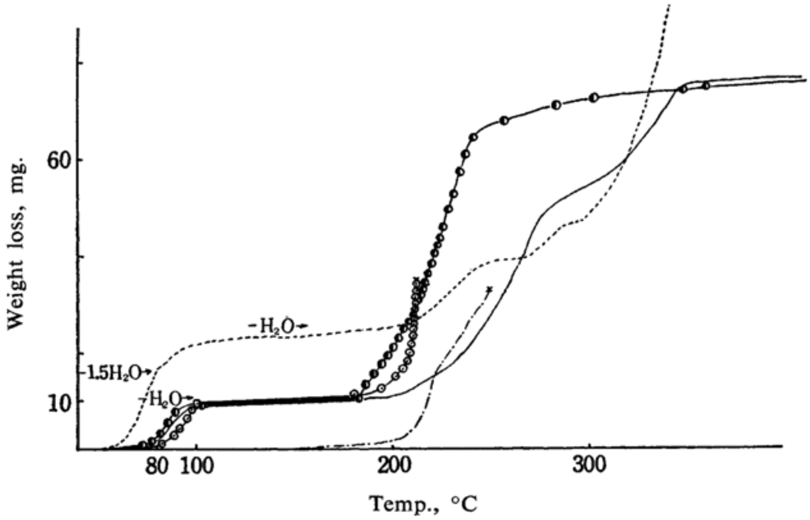

Fig. 2. The relationship between the weight loss and the temperature upon heating for several aquopentamminecobalt(III) complexes by a thermobalance.

-⊙- ; aquopentamminecobalt(III) nitrate

-◐- ; aquopentamminecobalt(III) bromide

—— ; aquopentamminecobalt(III) chloride

------ ; aquopentamminecobalt(III) sulfate hydrate

-·-·- ; aquopentamminecobalt(III) perchlorate that the nitrate decomposes upon heating at 80～100°C to nitratopentamminecobalt(III) nitrate according to the following equation;

$$[Co(NH_3)_5OH_2](NO_3)_3(s) = [Co(NH_3)_5NO_3](NO_3)_2(s) + H_2O(g)$$

The vapor pressure of water produced by this docomposition at 30～68°C, that is, the dissociation pressure of aquopentamminecobalt(III) nitrate measured is shown in Table II.

TABLE II. DISSOCIATION PRESSURE OF AQUOPENTAMMINECOBALT(III) NITRATE

Temp. °C	$1/T \times 10^3$	Dissociation pressure mmHg	$\log p_{mm}$
30	3.299	1.35	0.1303
33	3.267	1.70	0.2305
39	3.204	2.19	0.3404
45	3.144	3.19	0.5038
52	3.076	4.09	0.6117
56	3.039	4.59	0.6618
62	2.984	6.34	0.8021
68	2.932	8.48	0.9284

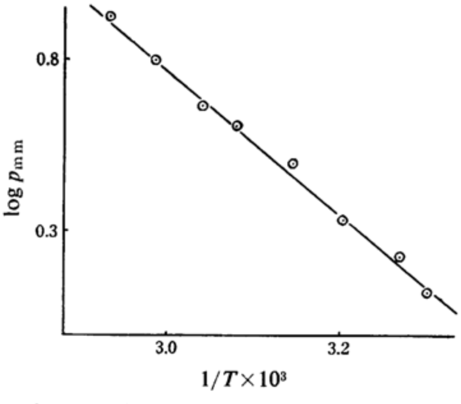

Fig. 3. The relationship between the dissociation pressure and the temperature for aquopentamminecobalt(III) nitrate.

The logarithm of the dissociation pressure, p_{mm}, is plotted against the reciprocal of the absolute temperature in Fig. 3, which shows an almost straight line. By the method of least squares the equation of this line is computed as follows:

$$\log p_{mm} = 7.045 - 2091/T$$

From this equation the heat of dissociation is obtained as $\Delta H = 9562$ cal. The standard free energy change of dissociation, ΔG^0, is given by the following formula,

$$\Delta G^0 = -\boldsymbol{RT} \ln p_{atm} = 9562 - 19.05\,T \qquad (5)$$

from which the values of the free energy change of dissociation at 25°C, $\Delta G^0_{298} = 3885$ cal. and the entropy change of the solution at 25°C, $\Delta S^0_{298} = 19.05$ entropy unit are obtained.

The standard free energy of formation of aquopentamminecobalt(III) nitrate in the solid state was already calculated above as formula 4, and that of $H_2O(g)$ was obtained in the preceding paper¹⁾ as

$$\Delta G_f{}^0 = -57800 + 10.61T \qquad (6)$$

By subtracting formula 6 from the sum of formulae 4 and 5, the standard free energy of formation of nitratopentamminecobalt(III) nitrate in the solid state is calculated as

$$\Delta G_f{}^0 = -286400 + 515.8T$$

The value at 25°C is

$$\Delta G_{f298}^0 = -132600 \text{ cal.} \qquad (7)$$

and the heat of formation is

$$\Delta H_{298} = -286.4 \text{ kcal.}$$

By using the solubility⁵⁾ and the heat of solution⁶⁾ of nitratopentamminecobalt(III) nitrate and by assuming that its activity coefficient is equal to that of bromopentamminecobalt(III) bromide⁷⁾, the free energy change of the solution of the former at 25°C is obtained as

$$G^0_{298} = 7347 \text{ cal.} \qquad (8)$$

Subtracting twice the standard free energy of formation of NO_3^-, −26.41 kcal.⁸⁾, from the sum of the formulae 7 and 8, the free energy of formation of nitratopentamminecobalt(III) ion in unit activity in aqueous solution is obtained as follows:

$$\Delta G_{f298}^0 = 72440 \text{ cal.}$$

If $\Delta H = -168.8$ kcal.⁹⁾ is used as the heat of formation of its ion, the relationship between the free energy of formation and temperature is expressed by

$$\Delta G_f{}^0 = -168800 + 323.3T$$

Solubility of Aquopentamminecobalt(III) Bromide.—The results obtained for aquopentamminecobalt(III) bromide are listed in Table III.

When the aquopentamminecobalt(III) bromide is dissolved in water, the change is expressed by

$$[Co(NH_3)_5OH_2]Br_3(s) = [Co(NH_3)_5OH_2]^{3+}\ (aq.\ a) + 3Br^-(aq.\ a)$$

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5) J. N. Brönsted and A. Petersen, *J. Am. Chem. Soc.*, **43**, 2265 (1921).

6) A. Lamb and J. Simmons, ibid., **43**, 2188 (1921).

7) B. Adell, *Z. anorg. allgem. Chem.*, **246**, 303 (1941).

8) F. D. Rossini et al., "Selected Values of Chemical Thermodynamic Properties", United States Government Printing Office, Washington (1952), p. 53.

9) K. B. Yatsimirskii and L. L. Pankowa, *Zhur. Obshchei Khim.*, **18**, 2051 (1948); K. B. Yatsimirskii, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), p. 179.

TABLE III. EQUILIBRIUM OF SOLUTION FOR AQUOPENTAMMINECOBALT(III) BROMIDE

Temp. °C	Solubility in molality m	$1/T\times10^3$	Mean activity coefficient $\gamma_\pm$	$K_{Br}\times10^7$	$\log K_{Br}$
15	0.03304	3.471	0.317	3.250	$\bar{7}.5119$
20	0.03899	3.412	0.294	4.663	$\bar{7}.6686$
25	0.04771	3.355	0.268	7.218	$\bar{7}.8584$
30	0.05556	3.299	0.251	10.21	$\bar{6}.0091$
35	0.06722	3.246	0.228	14.89	$\bar{6}.1730$

The plots of the logarithm of the equilibrium constant, K_{Br}, against the reciprocal of the absolute temperature are shown in Fig. 1, giving a straight line. Its equation is calculated as follows

$$\log K_{Br}=3.756-2953/T$$

The heat of solution is obtained as $\Delta H=13.5$ kcal.

The free energy change of solution is given by the following formula,

$$\Delta G^0=-\boldsymbol{RT}\ln K_{Br}=13510-17.18T \quad (9)$$

and the value at 25°C is $\Delta G^0_{298}=8385$ cal. and the entropy change at 25°C is $\Delta S^0_{298}=17.18$ entropy unit.

As the standard free energy of formation of bromide ion, Br^-, was obtained in the second paper2) of this series as

$$\Delta G_f{}^0=-28900+14.51T \quad (10)$$

that of aquopentamminecobalt(III) bromide in the solid state is obtained from formulae 2, 9 and 10 as:

$$\Delta G_f{}^0=-293100+357.3T \quad (11)$$

Its value at 25°C is $\Delta G_{f298}^0=-186600$ cal. and the heat of formation is $\Delta H=-293.1$ kcal.

Dissociation Pressure of Aquopentamminecobalt(III) Bromide. — Aquopentamminecobalt(III) bromide changes to bromopentamminecobalt(III) bromide upon heating at 75～95°C as

$$[Co(NH_3)_5OH_2]Br_3(s)$$
$$=[Co(NH_3)_5Br]Br_2(s)+H_2O(g)$$

The vapor pressure of water produced by the above reaction at 18～32°C, that is, the dissociation pressure of aquopentamminecobalt(III) bromide is listed in Table IV.

TABLE IV. DISSOCIATION PRESSURE OF AQUOPENTAMMINECOBALT(III) BROMIDE

Temp. °C	$1/T\times10^3$	Dissociation pressure mmHg	$\log p_{mm}$
18	3.435	3.84	0.5843
20.5	3.406	5.23	0.7185
24	3.366	8.40	0.9243
26	3.343	9.35	0.9708
27	3.332	12.04	1.0806
29	3.310	14.75	1.1688
32	3.278	17.89	1.2526

The logarithm of the dissociation pressure, p_{mm}, is plotted against the reciprocal of the absolute temperature in Fig. 4, which shows an almost straight line. By the method of least squares the equation of this line is computed as:

$$\log p_{mm}=15.65-4382/T$$

From this equation the heat of dissociation is obtained as $\Delta H=9562$ cal.

The standard free energy change of dissociation is given by the formula,

$$\Delta G^0=-\boldsymbol{RT}\ln p_{atm}=20040-58.41T \quad (12)$$

from which the value at 25°C, $\Delta G^0_{298}=2633$ cal. and the entropy change of solution at 25°C, $\Delta S^0_{293}=58.41$ eutropy unit are obtained.

As the standard free energy of formation of aquopentamminecobalt(III) bromide in the solid state was already calculated above according to formula 11, that of bromopentamminecobalt(III) bromide in the solid state is calculated from formulae 6, 11 and 12 as

$$\Delta G_f{}^0=-215300+288.2T$$

The value at 25°C is

$$\Delta G_{f298}^0=-129300\text{ cal.} \quad (13)$$

and the heat of formation is $\Delta H=-215.3$ kcal.

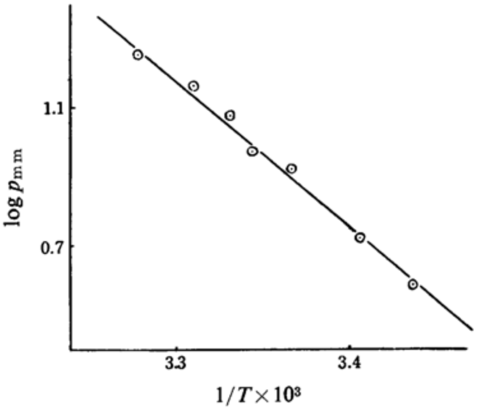

Fig. 4. The relationship between the dissociation pressure and the temperature for aquopentamminecobalt(III) bromide.

By using the solubility[5], the heat of solution[6] and the activity coefficient[7] of bromopentamminecobalt(III) bromide, the free energy change of solution of it at 25°C is obtained as

$$\varDelta G^0_{293} = 8855 \text{ cal.} \qquad (14)$$

Subtracting twice the free energy of formation of Br^-, $\varDelta G^0_{298} = -24.57$ kcal.[10], from the sum of formulae 13 and 14, the free energy of formation of bromopentamminecobalt(III) ion in unit activity in aqueous solution is calculated as:

$$\varDelta G_{f\,298}^0 = -71340 \text{ cal.}$$

If $\varDelta H = -146.8$ kcal.[11] is used as the heat of formation of its ion, the relationship between the free energy of formation and temperature is expressed by

$$\varDelta G_f{}^0 = -146800 + 253.2T$$

Discussion

Thermodynamic Stability of Aquopentamminecobalt(III) Complexes. — The standard free energy of formation of aquopentamminecobalt(III) nitrate and bromide in the solid state, the free energy of the solution and the heat of solution of them calculated above together with those of its chloride obtained in the preceding paper[1] and the radii of each anions are again shown in Table V.

According to these values, it will be seen that the thermodynamic stability of these three aquopentamminecobalt(III) complexes in the solid state and aqueous solution decreases in the following order,

$$[Co(NH_3)_5OH_2]Cl_3 > [Co(NH_3)_5OH_2](NO_3)_3 > [Co(NH_3)_5OH_2]Br_3$$

This order is in good agreement with the decreasing order of the thermodynamic stability of hexamminecobalt(III) complexes,

$$[Co(NH_3)_6]Cl_3 > [Co(NH_3)_6](NO_3)_3 > [Co(NH_3)_6]Br_3$$

reported as in the second paper[2] of this series.

The heat of solution of these aquopentamminecobalt(III) complexes increases in the order, chloride < nitrate < bromide, and increases with the radius of anion as shown in Table V. It is generally known[12] that for simple salts of which the radius of the cation is 2.4 Å, the heat of solution increases with the radius of the anion. It is concluded that this relationship is also valid for these aquopentamminecobalt(III) complexes, the radius of the cation, $[Co(NH_3)_5OH_2]^{3+}$, being 2.4 Å.

The solubility of these complexes decreases in the order, chloride > nitrate > bromide. This may be due to the fact that the radius of anions becomes larger and consequently the ionic character of the bond between the complex cation and anion of the salts diminishes in the order, chloride > nitrate > bromide.

Thermodynamic Stability of Monoacidopentamminecobalt(III) Complexes. — The standard free energy of formation of nitratopentamminecobalt(III) nitrate and bromopentamminecobalt(III) bromide in the solid state obtained above, that of chloropentamminecobalt(III) chloride obtained in the third paper[3] of this series and that of chloropentamminecobalt(III) nitrate and bromide, nitratopentamminecobalt(III) chloride and bromopentamminecobalt(III) chloride and nitrate calculated from the solubility[5] and the heat of solution[9] in the literature are summarized in Table VI.

TABLE V. STANDARD FREE ENERGY OF FORMATION, FREE ENERGY OF SOLUTION AND HEAT OF SOLUTION OF AQUOPENTAMMINECOBALT(III) CHLORIDE, NITRATE AND BROMIDE, AND THE RADII OF EACH ANIONS

Complexes	Free energy of formation kcal.	Free energy of solution cal.	Heat of solution kcal.	Radius of anion, Å
$[Co(NH_3)_5OH_2]Cl_3$	−203.0	4488	8.75	1.81
$[Co(NH_3)_5OH_2](NO_3)_3$	−191.1	7396	12.7	1.89
$[Co(NH_3)_5OH_2]Br_3$	−186.6	8385	13.5	1.96

TABLE VI. STANDARD FREE ENERGY OF FORMATION OF MONOACIDOPENTAMMINECOBALT(III) COMPLEXES

Complexes	$\varDelta G_{f\,298}^0$, kcal.	Complexes	$\varDelta G_{f\,298}^0$, kcal.
$[Co(NH_3)_5Cl]Cl_2$	−144.9	$[Co(NH_3)_5NO_3]Cl_2$	−141.4
$[Co(NH_3)_5Cl](NO_3)_2$	−133.7	$[Co(NH_3)_5NO_3](NO_3)_2$	−132.6
$[Co(NH_3)_5Cl]Br_2$	−131.7		
		$[Co(NH_3)_5Br]Cl_2$	−142.1
		$[Co(NH_3)_5Br](NO_3)_2$	−131.8
		$[Co(NH_3)_5Br]Br_2$	−129.3

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[10] G. Jones and S. Bäckström, *J. Am. Chem. Soc.*, 56, 1524 (1934).

[11] K. B. Yatsimirskii, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), p. 178.

[12] K. B. Yatsimirskii, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), p. 45.

On the basis of these values, it is found that the thermodynamic stability of these complexes in the solid state decreases in the following order:

$$\begin{array}{ccccc}
[Co(NH_3)_5Cl]Cl_2 & > & [Co(NH_3)_5Cl](NO_3)_2 & > & [Co(NH_3)_5Cl]Br_2 \\
\vee & & \vee & & \\
[Co(NH_3)_5NO_3]Cl_2 & > & [Co(NH_3)_5NO_3](NO_3)_2 & & \vee \\
\wedge & & \vee & & \\
[Co(NH_3)_5Br]Cl_2 & > & [Co(NH_3)_5Br](NO_3)_2 & > & [Co(NH_3)_5Br]Br_2
\end{array}$$

The levels of the standard free energy of formation for these complexes are diagrammatized in Fig. 5. From these figures it is found that the decrease of the thermodynamic stability of these monoacidopentamminecobalt(III) complexes is far less for the case when Cl^- in the inner sphere is replaced by NO_3^- or Br^- than for the case when Cl^- in the outer sphere is replaced by NO_3^- or Br^-. This fact might be partly interpreted by the increase of the radius of the anion in the outer sphere in the order, $Cl^- < NO_3^- < Br^-$.

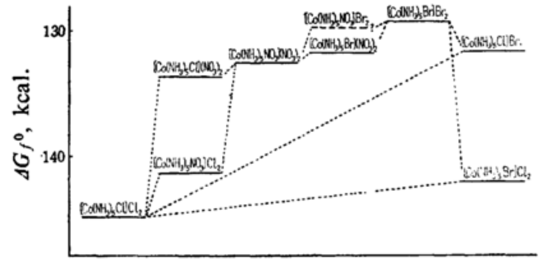

Fig. 5. The levels of the standard free energy of formation for several monoacidopentamminecobalt(III) complexes in the solid state.

Thermodynamic Stability of Monoacidopentamminecobalt(III) Ions. — From the standard free energies of formation of nitratopentamminecobalt(III) and bromopentamminecobalt(III) ions obtained above, and those of chloropentamminecobalt(III) ion[1], nitropentamminecobalt(III) ion[13], sulfatopentamminecobalt(III) ion[6], aquopentamminecobalt(III) ion[1] and hexamminecobalt(III) ion[13], the free energy change for the following substitution reactions are calculated:

$$[Co(NH_3)_5OH_2]^{2+} + NO_2^- = [Co(NH_3)_5NO_2]^{2+} + H_2O(l) \qquad \Delta G^0_{298} = -52590 \text{ cal.}$$

$$[Co(NH_3)_5OH_2]^{3+} + SO_4^{--} = [Co(NH_3)_5SO_4]^+ + H_2O(l) \qquad -6750$$

$$[Co(NH_3)_5OH_2]^{3+} + NH_3\ (aq.) = [Co(NH_3)_5NH_3]^{3+} + H_2O(l) \qquad -320$$

$$[Co(NH_3)_5OH_2]^{3+} + Br^- = [Co(NH_3)_5Br]^{2+} + H_2O(l) \qquad 1040$$

$$[Co(NH_3)_5OH_2]^{3+} + NO_3^- = [Co(NH_3)_5NO_3]^{2+} + H_2O(l) \qquad 1780$$

$$[Co(NH_3)_5OH_2]^{3+} + Cl^- = [Co(NH_3)_5Cl]^{2+} + H_2O(l) \qquad 3825$$

From these values it is concluded that the thermodynamic stability decreases in the order:

$$[Co(NH_3)_5NO_2]^{2+} > [Co(NH_3)_5SO_4]^+ > [Co(NH_3)_6]^{3+} > [Co(NH_3)_5OH_2]^{3+} > [Co(NH_3)_5Br]^{2+} > [Co(NO_3)_5NO_3]^{2+} > [Co(NH_3)_5Cl]^{2+}$$

This order is in good agreement with the spectrochemical series[14] with the exception of $[Co(NH_3)_5SO_4]^+$ and $[Co(NH_3)_5Br]^{2+}$.

Summary

1. By measuring the solubility and the dissociation pressure of aquopentamminecobalt(III) nitrate, the standard free energy of formation of the salt and that of nitratopentamminecobalt(III) nitrate produced by the decomposition of the former in the solid state were determined.

2. In the same way the standard free energy of formation of aquopentamminecobalt(III) bromide and that of bromopentamminecobalt(III) bromide were determined.

3. On the basis of these results, the thermodynamic stabilities of three aquopentamminecobalt(III) complexes, several monoacidopentamminecobalt(III) complexes and their ions were determined.

Department of Chemistry
Faculty of Science
Kanazawa University
Kanazawa

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[13] A. B. Lamb and A. T. Larson, *J. Am. Chem. Soc.*, **42**, 2038 (1920).

[14] Y. Shimura and R. Tsuchida, This Bulletin, **29**, 311 (1956).