*Thermodynamic Studies on Cobalt Complexes. VI. Solubility of Nitropentamminecobalt(III), cis- and trans-Dinitrotetramminecobalt(III) and Trinitrotriamminecobalt(III) Complexes**

By Motoshichi MORI, Ryokichi TSUCHIYA and Hiroshi FUKUDA

(Received May 11, 1960)

Thermodynamic discussion of the monoacidopentamminecobalt(III) complexes which have Cl^-, NO_3^- or Br^- as the anionic ligand was carried out in the preceding paper[1]. In the present study the discussion is extended to the cobalt(III) complexes which have one, two or three nitro groups in the coordination sphere. Solubilities of nitropentamminecobalt(III) chloride, nitrate, bromide and perchlorate, *cis*- and *trans*-dinitrotetramminecobalt(III) chlorides and trinitrotriamminecobalt(III) complex were measured, and the standard free energies of their formation were calculated. The thermodynamic stability of the complexes formed by the substitution of ammonia by one, two or three nitro groups was also discussed.

Experimental

Nitropentamminecobalt(III) chloride was prepared by the method of Jörgensen[2]. The nitrate, bromide and perchlorate were precipitated by nitric acid ammonium bromide and perchloric acid respectively from the aqueous solution of the

---

* Read at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo April, 1960.

[1] M. Mori and R. Tsuchiya, This Bulletin, 33, 841 (1960).

[2] S. M. Jörgensen, *Z. anorg. Chem.*, 17, 463 (1898).

chloride. *cis*- and *trans*-Dinitrotetramminecobalt (III) chlorides and trinitrotriamminecobalt(III) were also prepared by the method of Jörgensen[2–4].

The solubility in the saturated aqueous solution was measured colorimetrically by means of a Hitachi EPU-2 spectrophotometer. Since these nitro-complexes are unstable towards light, equilibrium of the solution was attained in a brown flask immersed in the thermostat to prevent the photo-decomposition.

Results and Calculation

Solubility of Nitropentamminecobalt (III) Complexes. — The results obtained for nitropentamminecobalt (III) chloride, nitrate, bromide and perchlorate are listed in Tables I—IV.

The equilibrium of nitropentamminecobalt(III) complex in water is expressed by,

$$[Co(NH_3)_5NO_2]X_2(s)$$
$$= [Co(NH_3)_5NO_2]^{2+}(aq.) + 2X^-(aq.)$$

where X is an anion. If the activities of the cation, the anion and their activity coefficients are expressed by $a_{[Co(NH_3)_5NO_2]^{2+}}$, a_{X^-}, $\gamma_{[(Co(NH_3)_5NO_2]^{2+}}$ and γ_{X^-} respectively, the equilibrium constant, K, is given by

$$K = a_{[Co(NH_3)_5NO_2]^{2+}} \cdot a^2_{X^-}$$
$$= (m\gamma_{[Co(NH_3)_5NO_2]^{2+}})(2m\gamma_{X^-})^2$$
$$= 4m^3\gamma_{[Co(NH_3)_5NO_2]^{2+}} \cdot \gamma^2_{X^-}$$

where m is the solubility in molality. When the mean activity coefficient is expressed by $\gamma_\pm$, the equilibrium constant is given by

$$K = 4\,m^3\gamma^3_\pm \qquad (1)$$

The mean activity coefficient is calculated by the following formula[5] which gives the activity

TABLE I. EQUILIBRIUM OF SOLUTION FOR NITROPENTAMMINECOBALT(III) CHLORIDE

Temp. (°C)	Solubility (Molality m)	$1/T\times10^3$	$\gamma_\pm$	$K\times10^4$	$\log K$
10.8	0.0902	3.521	0.514	3.99	$\bar{4}.601$
15	0.107	3.471	0.497	6.02	$\bar{4}.780$
20	0.117	3.412	0.489	7.49	$\bar{4}.874$
25	0.145	3.355	0.471	12.74	$\bar{3}.105$
30	0.160	3.299	0.461	16.05	$\bar{3}.205$

TABLE II. EQUILIBRIUM OF SOLUTION FOR NITROPENTAMMINECOBALT(III) NITRATE

Temp. (°C)	Solubility (Molality m)	$1/T\times10^3$	$\gamma_\pm$	$K\times10^5$	$\log K$
10.8	0.0301	3.521	0.623	2.64	$\bar{5}.422$
15	0.0345	3.471	0.600	3.55	$\bar{5}.550$
20	0.0419	3.412	0.590	6.04	$\bar{5}.781$
25	0.0531	3.355	0.566	10.86	$\bar{4}.036$
30	0.0591	3.299	0.555	14.12	$\bar{4}.150$

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

Temp. (°C)	Solubility (Molality m)	$1/T\times10^3$	$\gamma_\pm$	$K\times10^4$	$\log K$
10.8	0.0360	3.521	0.605	4.13	$\bar{5}.616$
15	0.0421	3.471	0.589	6.10	$\bar{5}.785$
20	0.0495	3.412	0.573	9.13	$\bar{5}.960$
25	0.0587	3.355	0.556	13.91	$\bar{4}.143$
30	0.0693	3.299	0.540	20.96	$\bar{4}.321$

TABLE IV. EQUILIBRIUM OF SOLUTION FOR NITROPENTAMMINECOBALT(III) PERCHLORATE

Temp. (°C)	Solubility (Molality m)	$1/T\times10^4$	$\gamma_\pm$	$K\times10^4$	$\log K$
10.8	0.0762	3.521	0.537	2.74	$\bar{4}.438$
15	0.101	3.471	0.511	5.50	$\bar{4}.740$
20	0.128	3.412	0.494	10.11	$\bar{3}.005$
25	0.168	3.355	0.469	19.57	$\bar{3}.292$
30	0.202	3.299	0.452	30.45	$\bar{3}.484$

---

[3] S. M. Jörgensen, ibid., **17**, 473 (1898).

[4] S. M. Jörgensen, ibid., **17**, 469 (1898).

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

coefficient of an ion,

$$\log \gamma_{\text{ion}} = \frac{-0.358 z^2 \sqrt{2\omega}}{1 + 0.2325 \times 10^8 a \sqrt{2\omega}} - \log(1 + 0.018\, \nu m)$$

where z is the charge of the ion, ω, the ionic strength of the solution, a, the closest distance between an ion and another one and ν, the number of ions dissociated from one molecule of the salt.

The logarithm of the equilibrium constant of the solution calculated by Eq. 1 is plotted in Fig. 1 against the reciprocal of the absolute temperature. A straight line is obtained. By the method of least squares the equations of these lines are calculated as follows:

$\log K = 6.243 - 2734/T$ for the chloride

$\log K = 7.636 - 3473/T$ for the nitrate

$\log K = 6.732 - 3156/T$ for the bromide

$\log K = 13.080 - 4715/T$ for the perchlorate

The free energy changes of solution are given as

$$\begin{aligned}
&\Delta G^\circ = -RT \ln K = 12510 - 28.56\,T \\
&\quad \Delta G^\circ_{298} = 3991 \text{ cal. for the chloride} \\
&\Delta G^\circ = 15890 - 34.93\,T \\
&\quad \Delta G^\circ_{298} = 5477 \text{ cal. for the nitrate} \\
&\Delta G^\circ = 14440 - 30.79\,T \\
&\quad \Delta G^\circ_{298} = 5262 \text{ cal. for the bromide} \\
&\Delta G^\circ = 21570 - 59.84\,T \\
&\quad \Delta G^\circ_{298} = 3728 \text{ cal. for the perchlorate}
\end{aligned} \tag{2}$$

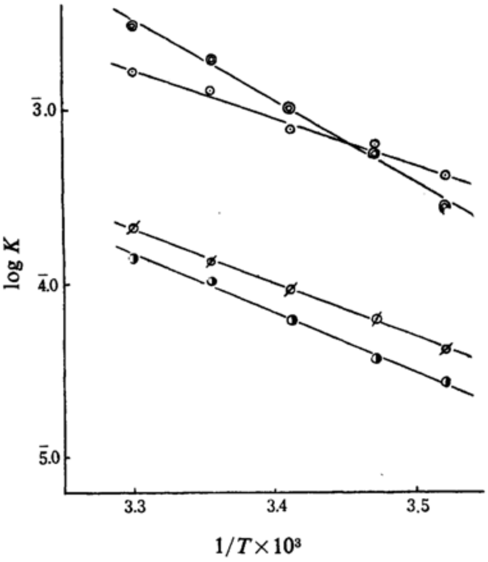

Fig. 1. The relationship between the equilibrium constant of solution and the temperature for nitropentamminecobalt(III) chloride (⊙), nitrate (◑), bromide (∅) and perchlorate(◎).

From these equations the heats of solution of the chloride, nitrate, bromide and perchlorate are obtained as $\Delta H = 12.51$, 15.89, 14.44 and 21.57 kcal. respectively. The entropy changes for each salt are calculated as $\Delta S^\circ =$ 28.6, 34.9, 30.8 and 59.8 e. u., respectively.

Since the standard free energy of formation of nitropentamminecobalt(III) ion in unit activity is known as $\Delta G^\circ_{f\,298} = -108.9$ kcal[6]. and the heat of formation as $\Delta H_f = -153.1$ kcal.[7], the relationship between the former and the absolute temperature is calculated as

$$\Delta G^\circ_f = -153100 + 148.3\,T \tag{3}$$

The free energies of formation Cl^-, NO_3^-, Br^- and ClO_4^- in unit activity were already obtained in the second paper[8] of this series as follows:

$$\begin{aligned}
&\Delta G^\circ_f = -40020 + 29.1\,T \text{ for } Cl^- \\
&\Delta G^\circ_f = -49370 + 77.03\,T \text{ for } NO_3^- \\
&\Delta G^\circ_f = -28900 + 14.51\,T \text{ for } Br^- \\
&\Delta G^\circ_f = -31410 + 96.75\,T \text{ for } ClO_4^-
\end{aligned} \tag{4}$$

Therefore the standard free energy of formation of nitropentamminecobalt(III) chloride in the solid state is calculated by Eqs. 3, 6 and 4 as

$$\begin{aligned}
&\Delta G^\circ_f = -245700 + 235.1\,T \\
&\Delta G^\circ_{f\,298} = -175.6 \text{ kcal.}
\end{aligned}$$

The values for the nitrate, bromide and perchlorate of the same complex were calculated by combining respective equations:

$$\begin{aligned}
&\Delta G^\circ_f = -267700 + 337.3\,T, \\
&\Delta G^\circ_{f\,298} = -167.2 \text{ kcal., for the the nitrate} \\
&\Delta G^\circ_f = -225300 + 208.1\,T, \\
&\Delta G^\circ_{f\,298} = -163.3 \text{ kcal., for the bromide} \\
&\Delta G^\circ_f = -237500 + 401.6\,T, \\
&\Delta G^\circ_{f\,298} = -117.8 \text{ kcal., for the perchlorate}
\end{aligned}$$

Solubility of Dinitrotetramminecobalt(III) Complexes.—The results obtained for *cis*- and *trans*-dinitrotetramminecobalt(III) chlorides are listed in Tables V and VI.

The process of solution of dinitrotetramminecobalt(III) chloride is represented by the following equation,

---

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

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

[8] M. Mori, R. Tsuchiya and Y. Okano, This Bulletin, **32**, 462 (1959).

TABLE V. EQUILIBRIUM OF SOLUTION FOR *cis*-DINTROTETRAMMINECOBALT(III) CHLORIDE

Temp. (°C)	Solubility (Molality m)	$1/T\times10^3$	$\gamma\pm$	$K\times10^2$	$\log K$
10	0.164	3.533	0.737	1.46	$\bar{2}.164$
15	0.189	3.471	0.726	1.88	$\bar{2}.274$
20	0.213	3.412	0.717	2.33	$\bar{2}.367$
25	0.263	3.355	0.701	3.40	$\bar{2}.531$
30	0.321	3.299	0.685	4.83	$\bar{2}.684$

TABLE VI. EQUILIBRIUM OF SOLUTION FOR *trans*-DINITROTETRAMMINECOBALT(III) CHLORIDE

Temp. (°C)	Solubility (Molality m)	$1/T\times10^3$	$\gamma\pm$	$K\times10^4$	$\log K$
10	0.0319	3.533	0.847	7.30	$\bar{4}.863$
15	0.0357	3.471	0.840	8.99	$\bar{4}.954$
20	0.0437	3.412	0.828	13.09	$\bar{3}.117$
25	0.0521	3.355	0.817	18.12	$\bar{3}.258$
30	0.0627	3.299	0.805	25.48	$\bar{3}.407$

$$[Co(NH_3)_4(NO_2)_2]Cl(s)$$
$$=[Co(NH_3)_4(NO_2)_2]^+(aq.)+Cl^-(aq.)$$

When the activities of the cation, the anion and their activity coefficients are expressed by $a_{[Co(NH_3)_4(NO_2)]^+}$, a_{Cl^-}, $\gamma_{[Co(NH_3)_4(NO_2)_2]^+}$ and γ_{Cl^-} respectively, the equilibrium constant of solution, K, is given as

$$K=a_{[Co(NH_3)_4(NO_2)_2]^+}\cdot a_{Cl^-}$$
$$=(m\gamma_{[Co(NH_3)_4(NO_2)_2]^+})(m\gamma_{Cl^-})$$
$$=m^2\gamma_{[Co(NH_3)_4(NO_2)_2]^+}\cdot\gamma_{Cl^-}=m^2\gamma^2_\pm,$$

m and $\gamma_\pm$ being the solubility in molality and the mean activity coefficient.

The plots of the logarithm of the above equilibrium constant against the reciprocal of the absolute temperature are given in Fig. 2 as straight lines for both salts. The straight lines are expressed by the following equations:

$$\log K=5.970-2215/T$$
$$cis\text{-}[Co(NH_3)_4(NO_2)_2]Cl$$
$$\log K=5.234-2376/T$$
$$trans\text{-}[Co(NH_3)_4(NO_2)_2]Cl$$

The free energy changes of solution are given as for the cis salt,

$$\Delta G^\circ=9111-23.87\,T,\quad \Delta G^\circ_{298}=1995\text{ cal.}\quad(5)$$

and for the trans salt,

$$\Delta G^\circ=9556-19.42\,T,\quad \Delta G^\circ_{298}=3767\text{ cal.}\quad(6)$$

From these equations $\Delta H=10.13$ kcal. and $\Delta H=10.87$ kcal. are obtained as the heats of solution of the cis and trans salts respectively and $\Delta S^\circ=27.3$ e. u. and $\Delta S^\circ=23.9$ e. u. are obtained as the entropy changes of the cis and trans salts respectively.

Since the energies of formation of *cis*- and *trans*-dinitrotetramminecobalt(III) ions in unit activity are known as $\Delta G^\circ_{f298}=-164.7$ kcal. and $\Delta G^\circ_{f298}=-161.4$ kcal[6]. and their heat of formation as $\Delta H_f=-159.9$ kcal. and $\Delta H_f=-159.1$ kcal[9]. respectively, the relationships between the free energies of formation and the absolute temperature are calculated for the cis salt as,

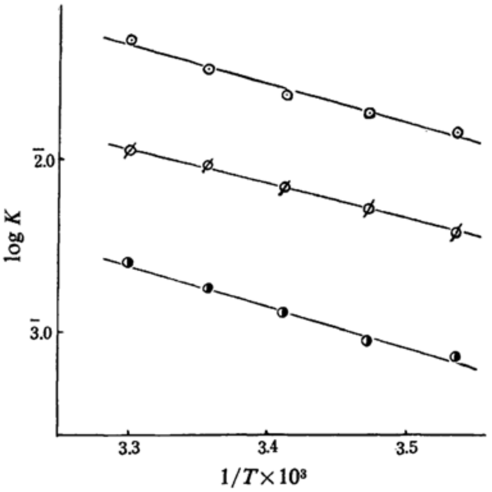

Fig. 2. The relationship between the equilibrium constant of solution and the temperature for *cis*-dinitrotetramminecobalt(III) chloride (⊙), corresponding *trans*-chloride (◑) and trinitrotriamminecobalt(III) complex (∅).

$$\Delta G^\circ_f=-159900-16.10\,T\quad(7)$$

and for the trans salt as,

$$\Delta G^\circ_f=-159100-7.72\,T\quad(8)$$

Then the free energy of formation of *cis*-dinitrotetramminecobalt(III) chloride in the solid state is calculated by Eqs. 4, 5 and 7 as

---

9) K. B. Yatsimirskii and L. L. Pankowa, *Zhur. Obshcheĭ Khim.*, **19**, 623 (1949); K. B. Yatsimirskii, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), pp. 179, 180.

TABLE VII. EQUILIBRIUM OF SOLUTION FOR TRINITROTRIAMMINECOBALT(III) COMPLEX

Temp. (°C)	Solubility (Molality $m\times10^3$)	$1/T\times10^3$	$K\times10^3$	$\log K$
10	3.88	3.533	3.88	$\bar{3}.588$
15	5.18	3.471	5.18	$\bar{3}.714$
20	6.96	3.412	6.96	$\bar{3}.843$
25	9.15	3.355	9.15	$\bar{3}.961$
30	11.19	3.299	11.19	$\bar{2}.049$

$$\Delta G_f^\circ = -210100+40.3\,T,$$
$$\Delta G_{f\,298}^\circ = -198.0\text{ kcal.}$$

and that of *trans*-dinitrotetramminecobalt(III) chloride by Eqs. 4, 6 and 8 as

$$\Delta G_f^\circ = -210000+45.3\,T,$$
$$\Delta G_{f\,298}^\circ = -196.5\text{ kcal.}$$

Solubility of Trinitrotriamminecobalt(III) Complex. — The results obtained for trinitrotriamminecobalt(III) complex is listed in Table VII.

When the solubility in molality of this complex is expressed by m, the equilibrium constant of the solution, K, is given by $K=m$. The relationship between the logarithm of K and temperature is shown in Fig. 2 and it is expressed by the equation as below:

$$\log K=4.696-2008/T.$$

The heat of solution is $\Delta H=9.19$ kcal. The free energy change of solution is given as,

$$\Delta G^\circ=9186-21.44\,T,$$
$$\Delta G_{298}^\circ=2795\text{ cal.} \tag{9}$$

The entropy change at 25°C is $\Delta S^\circ{}_{298}=21.44$ e. u.

The entropy of formation of hexamminecobalt(III) ion, nitropentamminecobalt(III) ion, *trans*- and *cis*-dinitrotetramminecobalt(III) ions were obtained as -306.9[8], -148.3[10], 7.72[10] and 16.10 e. u.[10], respectively. From these values it is found that the entropy of formation increases by 160 e. u., when every one gram equivalent of ammonia is replaced by one gram equivalent of nitro group. Therefore, if it is assumed that the entropy of formation of trinitrotriamminecobalt(III) complex in unit activity in aqueous solution is larger by three times 160 e. u. than that of hexamminecobalt(III) ion in unit activity, the entropy of the former is obtained as $\Delta S^\circ=172$ e. u. As the heat of formation of trinitrotriamminecobalt(III) complex in unit activity in aqueous solution is known as $\Delta H=-160$ kcal.[9], the free energy of formation is obtained as

$$\Delta G_f^\circ=-160000-172\,T,$$
$$\Delta G_{f\,298}^\circ=-211300\text{ cal.} \tag{10}$$

By Eqs. 9 and 10 the free energy of formation of trinitrotriamminecobalt(III) complex in the solid state is obtained as

$$\Delta G_f^\circ=-169200-150.6\,T,$$
$$\Delta G_{f\,298}^\circ=-214.1\text{ kcal.}$$

Discussion

Thermodynamic Stability of Nitropentamminecobalt(III) Complexes. — The solubility, the free energy of solution, the heat of solution and the free energy of formation of nitropentamminecobalt(III) complexes 25°C obtained above are summarized in Table VIII together with the radius of anions[11] forming these complexes. The lattice energy, U_k, required for the dissociation of solid complexes into gaseous ions is calculated by using the heat of solution and the heat of hydration of ions[11] which constitute complexes, and the values are shown in Table VIII.

From this table, the order of decrease of the solubility, the free energy of solution, the heat of solution, the lattice energy, the free energy of formation and the thermochemical and thermodynamic stability are found and shown in Table IX.

The same order was found for the solubility, the free energy of solution and the heat of solution of hexamminecobalt(III) complexes[8]. The order of the thermochemical and thermodynamic stability for the above nitropentamminecobalt(III) chloride, nitrate, bromide and perchlorate is in agreement with the order for the corresponding hexamminecobalt(III)[8], aquopentamminecobalt(III)[1] or acidopentamminecobalt(III) complexes[1]. The above order of the thermodynamic quantities may suggest that the ionic bond character between the complex cation and the anions generally diminishes as the ionic radius of the latter decreases, although several cases of reversal between the nitrate and the bromide are found as shown in Table VIII.

Entropy of Solution of *cis*- and *trans*-Dinitrotetramminecobalt(III) Chlorides. — The solubility, the free energy of solution, the heat of solution and the entropy of solution

---

[10] See Eqs. 6, 11 and 10, in this paper.

[11] K. B. Yatsimirskii, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), pp. 38—40.

TABLE VIII. THERMODYNAMIC FUNCTIONS OF NITROPENTAMMINECOBALT(III) COMPLEXES AT 25°C

Complex	Solubility in Molality m	Free energy of solution ΔG° cal.	Heat of solution ΔH kcal.	Free energy of formation ΔG_f° kcal.	Radius of anion (Å)	Lattice energy U_k kcal.
$[Co(NH_3)_5NO_2]Cl_2$	0.145	3991	12.51	−175.6	1.81	390
$[Co(NH_3)_5NO_2](NO_3)_2$	0.0531	5477	15.89	−167.2	1.89	376
$[Co(NH_3)_5NO_2]Br_2$	0.0587	5262	14.44	−163.3	1.96	374
$[Co(NH_3)_5NO_2](ClO_4)_2$	0.168	3728	21.57	−117.8	2.36	340

TABLE IX. ORDER OF DECREASE OF THE THERMODYNAMIC QUANTITIES

Solubility	Chloride>Bromide>Nitrate
Free energy of solution	Nitrate>Bromide>Chloride
Heat of solution	Nitrate>Bromide>Chloride
Lattice energy	Chloride>Nitrate>Bromide>Perchlorate
Free energy of formation	Perchlorate>Bromide>Nitrate>Chloride
Thermochemical and thermodynamic stability	Chloride>Nitrate>Bromide>Perchlorate

TABLE X. THERMODYNAMIC FUNCTIONS OF *cis*- AND *trans*-DINITROTETRAMMINECOBALT(III) CHLORIDES

Complex	Solubility m	Free energy of solution ΔG° cal.	Heat of solution ΔH kcal.	Entropy of solution ΔS° e. u.
cis-$[Co(NH_3)_4(NO_2)_2]Cl$	0.263	1990	10.13	27.3
trans-$[Co(NH_3)_4(NO_2)_2]Cl$	0.0521	3731	10.87	23.9

of these two isomers at 25°C are summarized in Table X.

As shown in Table X, the cis chloride is more soluble than the trans chloride and the free energy of solution of the former is much lower than that of the latter. The large difference between the free energies of solution is attributed to the fact that the entropy of solution of the cis salt is considerably larger than that of the trans salt, since the heat of solution is approximately the same. In other words, the free energy changes of solution of these two isomers are affected much more by the entropy effect rather than the enthalpy effect.

Relationship between the Free Energy of Formation and the Number of Coordinated Nitro-groups. — The free energies of formation of nitropentamminecobalt(III), dinitrotetramminecobalt(III) and hexamminecobalt(III) complexes are plotted against the number of coordinated nitro-groups in Fig. 3. Straight lines were obtained for the chlorides, nitrates, bromides and perchlorates. These four lines all converge at a point which corresponds to the free energy of formation of trinitrotriamminecobalt(III) complexes. It shows that an additivity rule holds between the free energy of formation and the number of nitrogroups.

When the free energy of formation of these complexes and the number of nitrogroups are expressed by ΔG_f° and n respectively, these straight lines are expressed by

$$\Delta G_f^\circ = an + c, \qquad (11)$$

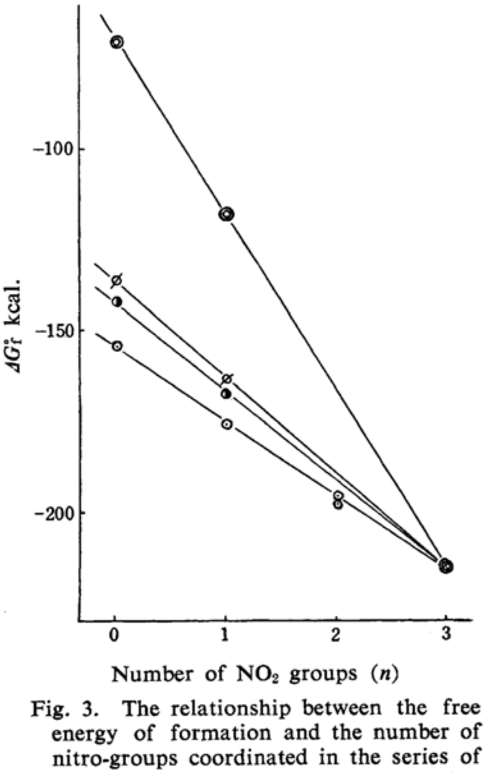

Fig. 3. The relationship between the free energy of formation and the number of nitro-groups coordinated in the series of cobalt(III) nitroammine complexes, that is
$[Co(NH_3)_{6-n}(NO_2)_n]Cl_{3-n}$ (⊙),
$[Co(NH_3)_{6-n}(NO_2)_n](NO_3)_{3-n}$ (◑),
$[Co(NH_3)_{6-n}(NO_2)_n]Br_{3-n}$ (∅)
and $[Co(NH_3)_{6-n}(NO_2)_n](ClO_4)_{3-n}$ (◎).
(⊗) is trinitrotriamminecobalt(III) complex.

where c is the free energy of formation of a hexamminecobalt(III) complex8) and a a constant. The constant a gives the difference between the free energy of formation of $[Co(NH_3)_{6-n}(NO_2)_n]X_{3-n}$ and that of $[Co(NH_3)_{6-n-1}(NO_2)_{n+1}]X_{3-n-1}$, which is obtained from Fig. 3 as:

$a = -19.9$ kcal. for chloride
$a = -24.1$ kcal. for nitrate
$a = -26.0$ kcal. for bromide
$a = -47.6$ kcal. for perchlorate

Free Energy Required for the Dissociation of the Anion from Nitroamminecobalt(III) Complexes. — The value of a in Eq. 11 for the chlorides is assumed as the sum of the changes of the free energy of formation in two processes such as:

(a) $[Co(NH_3)_6]Cl_3(s)$
$\rightarrow [Co(NH_3)_6]Cl_2(s) \quad \Delta(\Delta G_f^\circ)_a$

(b) $[Co(NH_3)_6]Cl_2(s)$
$\rightarrow [Co(NH_3)_5NO_2]Cl_2(s) \quad \Delta(\Delta G_f^\circ)_b$

that is,

$$a = \Delta(\Delta G_f^\circ)_a + \Delta(\Delta G_f^\circ)_b$$

If it is assumed that the change of the free energy of formation in process (b) is approximately equal to that in the following process,

$[Co(NH_3)_6]^{3+}(aq.)$
$\rightarrow [Co(NH_3)_5NO_2]^{2+}(aq.) \quad \Delta(\Delta G_f^\circ)$
$= -54.4$ kcal.6)

that is,

$$\Delta(G_f^\circ)_b \fallingdotseq \Delta(G_f^\circ) = -54.4 \text{ kcal.}$$

then the value in the above process (a) is calculated as $\Delta(\Delta G_f^\circ)_a = 34.5$ kcal. by using the value $a = -19.9$ kcal. for the chloride. The value $\Delta(\Delta G_f^\circ)_a$ is the free energy required for the elimination of one gram equivalent of chloride ion in the outer coordination sphere frome nitroammin cobalt(III) chloride.

In the same way, the free energies required for eliminating one gram equivalent of NO_3^-, Br^- or ClO_4^- in the outer sphere from the respective complexes are calculated as below:

$\Delta(\Delta G_f^\circ)_a = 30.3$ kcal. for nitrate
$\Delta(\Delta G_f^\circ)_a = 28.4$ kcal. for bromide
$\Delta(\Delta G_f^\circ)_a = 6.8$ kcal. for perchlorate

These values show that the dissociation of the anion from cobalt(III) nitroammine complexes becomes more difficult in the order: perchlorate < bromide < nitrate < chloride. This also indicates that the thermodynamic stability of these complexes increases in the same order.

Summary

1. From the solubility of cobalt(III) nitroammine complexes the thermodynamic stability was found to decrease in the order, chloride > nitrate > bromide > perchlorate.

2. The free energy of solution of *cis*-dinitrotetramminecobalt(III) chloride is lower than that of the trans chloride. This fact is attributed to the abnormally large value of the entropy of solution of the former compared with the latter.

3. Between the free energy of formation of cobalt(III) nitroammine complexes and the number of coordinated nitro-groups there exists a linear relationship.

Department of Chemistry
Faculty of Science
Kanazawa University
Kanazawa