*Thermodynamic Studies on Cobalt Complexes. VII. Solubility of Erdmann's Salt and Related Complexes**

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Although there have been several investigations[1] on the structure of Erdmann's salt, ammonium tetranitrodiamminecobaltate(III), no thermodynamic study has ever been made on it. In the preceding paper[2] we determined the solubility of nitropentamminecobalt(III), *cis*- and *trans*-dinitrotetramminecobalt(III) and trinitrotriamminecobalt(III) complexes and calculated the standard free energy of formation of solid cobalt(III) ammine complexes containing one, two or three nitrogroups. In the present paper the solubility of the cobalt(III) ammine complexes containing four nitrogroups, i. e., tetranitrodiamminecobaltate(III) complexes was measured. The solubilities of some of these salts have already been reported[3,4]. In the present study the measurement was extended to several other salts and to different temperatures.

Experimental

The complexes studied were the following: [I] the so called Erdmann's salt, namely ammonium tetranitrodiamminecobaltate(III) $NH_4[Co(NH_3)_2\cdot(NO_2)_4]$, [II] the corresponding potassium salt $K[Co(NH_3)_2(NO_2)_4]$, [III] *cis*-dinitrotetramminecobalt(III) - tetranitrodiamminecobaltate(III) *cis*-$[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$, and [IV] the corresponding trans isomer among 1-1 valency type salts, [V] nitropentammincobalt(III)-tetranitrodiamminecobaltate(III) $[Co(NH_3)_5NO_2][Co(NH_3)_2\cdot(NO_2)_4]_2$ and [VI] chloropentamminecobalt(III)-tetranitrodiamminecobaltate(III) $[Co(NH_3)_5Cl][Co\cdot(NH_3)_2(NO_2)_4]_2$ among 1-2 valency type salts and [VII] hexamminecobalt(III) - tetranitrodiamminecobaltate(III) $[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$ among 1-3 valency type salts.

Erdmann's salt [I] was prepared by the method of Jörgensen[5] and the potassium salt [II] was precipitated from the aqueous solution of I with potassium nitrate. III and IV were prepared by the double decomposition of I and *cis*-dinitrotetramminecobalt(III) nitrate[6] and the trans form chloride[7] respectively. V, VI and VII were prepared by the double decomposition of I and nitropentamminecobalt(III) chloride[8], chloropentamminecobalt(III) chloride[9] and hexamminecobalt(III) chloride[10], respectively.

The measurement of the solubility was made by measuring the cobalt content or the absorbancy of the saturated aqueous solution. The former was carried out by iodometry and the latter with a Hitachi EPU-2 spectrophotometer.

Results and Calculation

The results of measurement are listed in Tables I—VII. The solubilities are expressed in molality, m. The mean activity coefficients $\gamma_\pm$ given for I and II are the values obtained in the first paper of this series[11] and those for the other salts are the values calculated by Debye-Hückel's limiting formula,

$$\log \gamma_\pm = -0.505\ z_+ z_- \sqrt{\mu}$$

where z_+ and z_- are the charges of each cation and anion and μ is the ionic strength of each solution.

Equilibrium Constant of Solution and Standard Free Energy of Formation of Erdmann's Salt.— When Erdmann's salt is dissolved in water, the change is expressed by

$$NH_4[Co(NH_3)_2(NO_2)_4]\,(s) = NH_4{}^+\,(aq.) + [Co(NH_3)_2(NO_2)_4]^-\,(aq.)$$

The equilibrium constant of the solution, K, is given as in the preceding paper[2] by $K=m^2\gamma^2{}_\pm$.

A plot of the logarithm of K against the reciprocal of the absolute temperature is given in Fig. 1 as a straight line, the equation being calculated by the method of least squares as

$$\log K = 0.8981 - 771.8/T$$

The free energy change of solution is given by

$$\Delta G^\circ = 3530 - 4.108\ T,\quad \Delta G^\circ_{298} = 2305\ \text{cal.} \qquad (1)$$

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[1] Y. Komiyama, This Bulletin, 30, 13 (1957). Other references in the past were cited in this paper.

[2] M. Mori, R. Tsuchiya and H. Fukuda, This Bulletin, 33, 1503 (1960).

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

[4] E. Kyuno, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 78, 1494 (1957).

[5] S. M. Jörgensen, *Z. anorg. Chem.*, 17, 477 (1898).

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

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

[8] S. M. Jörgensen, ibid., 17, 463 (1898).

[9] W. A. Hynes, L. K. Yanowsky and M. Schiller, *J. Am. Chem. Soc.*, 60, 3053 (1938).

[10] W. C. Fernelius, "Inorganic Syntheses", Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y. (1946), p. 216.

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

TABLE I. SOLUBILITY OF ERDMANN'S SALT

Temp. (°C)	Solubility (Molality m)	$1/T\times10^3$	$\gamma_\pm$	K	$\log K$
15	0.186	3.471	0.690	0.0164	$\bar{2}.215$
20	0.199	3.412	0.686	0.0186	$\bar{2}.270$
25	0.209	3.355	0.681	0.0203	$\bar{2}.308$
30	0.224	3.299	0.675	0.0228	$\bar{2}.358$
35	0.233	3.246	0.671	0.0244	$\bar{2}.387$

TABLE II. SOLUBILITY OF $K[Co(NH_3)_2(NO_2)_4]$

Temp. (°C)	Solubility (Molality m)	$1/T\times10^3$	$\gamma_\pm$	$K\times10^4$	$\log K$
0	0.0107	3.662	0.914	1.23	$\bar{4}.869$
15	0.0364	3.471	0.847	3.08	$\bar{4}.736$
20	0.0516	3.412	0.821	4.23	$\bar{4}.627$
25	0.0684	3.355	0.796	5.45	$\bar{4}.488$
30	0.0969	3.299	0.763	7.39	$\bar{4}.090$

TABLE III. SOLUBILITY OF *cis*-$[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$

Temp. (°C)	Solubility (Molality $m\times10^3$)	$1/T\times10^3$	$\gamma_\pm$	$K\times10^5$	$\log K$
15	4.49	3.471	0.925	1.73	$\bar{5}.237$
20	6.49	3.412	0.911	3.49	$\bar{5}.543$
25	8.99	3.355	0.896	6.49	$\bar{5}.812$
30	11.39	3.299	0.883	10.12	$\bar{4}.005$

TABLE IV. SOLUBILITY OF *trans*-$[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$

Temp. (°C)	Solubility (Molality $m\times10^4$)	$1/T\times10^3$	$\gamma_\pm$	$K\times10^7$	$\log K$
15	4.56	3.471	0.975	1.97	$\bar{7}.295$
20	6.05	3.412	0.972	3.46	$\bar{7}.539$
25	8.38	3.355	0.967	6.56	$\bar{7}.817$
30	11.09	3.299	0.962	11.38	$\bar{6}.056$

TABLE V. SOLUBILITY OF $[Co(NH_3)_5NO_2][Co(NH_3)_2(NO_2)_4]_2$

Temp. (°C)	Solubility (Molality $m\times10^3$)	$1/T\times10^3$	$\gamma_\pm$	$K\times10^9$	$\log K$
10	0.670	3.532	0.906	0.892	$\overline{10}.950$
15	0.928	3.471	0.887	2.24	$\bar{9}.349$
20	1.12	3.412	0.879	3.81	$\bar{9}.581$
25	1.46	3.355	0.865	8.07	$\bar{8}.907$
30	1.62	3.299	0.857	10.71	$\bar{8}.030$

TABLE VI. SOLUBILITY OF $[Co(NH_3)_5Cl][Co(NH_3)_2(NO_2)_4]_2$

Temp. (°C)	Solubility (Molality $m\times10^3$)	$1/T\times10^3$	$\gamma_\pm$	$K\times10^9$	$\log K$
15	0.501	3.471	0.914	0.383	$\overline{10}.584$
20	0.731	3.412	0.896	1.16	$\bar{9}.066$
25	1.00	3.355	0.880	2.73	$\bar{9}.436$
30	1.32	3.299	0.864	5.97	$\bar{9}.776$
35	1.76	3.246	0.845	13.03	$\bar{8}.115$

TABLE VII. SOLUBILITY OF $[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$

Temp. (°C)	Solubility (Molality $m\times10^4$)	$1/T\times10^3$	$\gamma_\pm$	$K\times10^{14}$	$\log K$
15	1.55	3.471	0.899	1.02	$\overline{14}.010$
20	2.25	3.412	0.880	4.17	$\overline{14}.620$
25	2.84	3.355	0.866	9.88	$\overline{14}.995$
30	4.09	3.299	0.841	37.94	$\overline{13}.579$

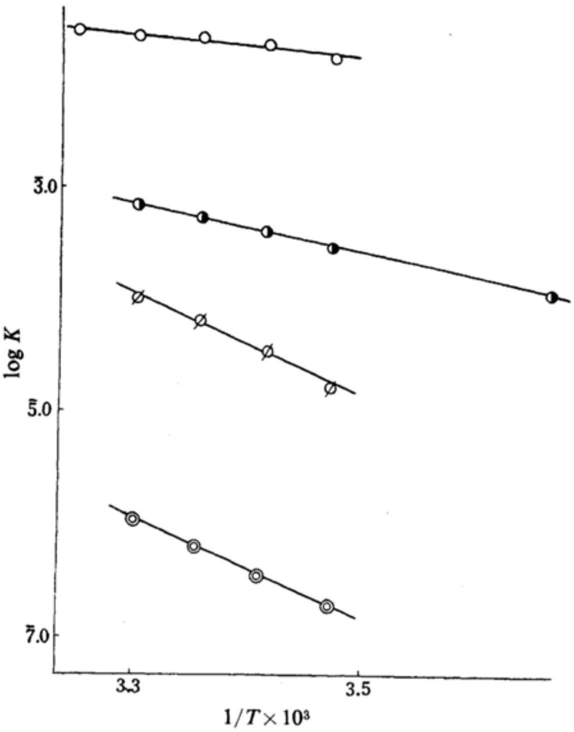

Fig. 1. The relationship between the equilibrium constant of solution and the temperature for Erdmann's salt, $NH_4[Co(NH_3)_2(NO_2)_4]$ (○), $K[Co(NH_3)_2(NO_2)_4]$ (◐), *cis*-$[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$ (∅), and *trans*-$[Co(NH_3)_4(NO_2)_2]\cdot[Co(NH_3)_2(NO_2)_4]$ (◎).

The heat of solution and the entropy change of solution at 25°C are obtained as $\Delta H=3530$ cal. and $\Delta S^\circ=4.108$ e. u., respectively.

As described in the preceding paper[2)], it is found that the entropy of formation of cobalt (III) nitroammine complexes increases by 160 e. u. for each replacement of one gram equivalent of ammonia by one gram equivalent of nitrogroup. Therefore the sum of this value and the entropy of formation of trinitrotriamminecobalt(III) complex in unit activity in aqueous solution, $\Delta S^\circ=172$ e. u., may be regarded as that of tetranitrodiamminecobaltate (III) anion in unit activity in aqueous solution, i. e. $\Delta S^\circ=332$ e. u. Since the heat of formation of the latter is $\Delta H=-164.9$ kcal.[12)], the free energy of formation is given by the equation:

$$\Delta G_f^\circ=-164900-332\,T,\quad \Delta G_{f\,298}^\circ=-263.9\text{ kcal.}\tag{2}$$

The free energy of formation of NH_4^+ in unit activity is given as[13)]

$$\Delta G_f^\circ=-31740-42.74\,T\tag{3}$$

From Eqs. 1, 2 and 3, the free energy of formation of Erdmann's salt in the solid state is calculated as

$$\Delta G_f^\circ=-200200-288.9\,T,$$

$$\Delta G_{f\,298}^\circ=-286.3\text{ kcal.}$$

Free Energy of Formation of Potassium Tetranitrodiamminecobaltate(III).—The equilibrium constant of the solution of potassium tetranitrodiamminecobaltate(III) is given by $K=m^2\gamma^2_\pm$ in the same way as that of Erdmann's salt described above. The relationship between $\log K$ and $1/T$ is given by a straight line in Fig. 1, which is expressed by the equation,

$$\log K=3.917-2138/T$$

The free energy change of solution is given as

$$\Delta G^\circ=9777-17.92\,T,\quad \Delta G^\circ_{298}=4436\text{ cal.}\tag{4}$$

and the heat of the solution is $\Delta H=9777$ cal., and the entropy change of the solution at 25°C is $\Delta S^\circ=17.92$ e. u. The free energy of formation of K^+ in unit activity in aqueous solution is given as

$$\Delta G_f^\circ=-60040-24.91\,T\tag{5}$$

From Eqs. 2, 4 and 5, the free energy of formation of potassium tetranitrodiamminecobaltate(III) in the solid state is calculated as below:

$$\Delta G_f^\circ=-234700-339\,T,\quad \Delta G_{f\,298}^\circ=-335.8\text{ kcal.}$$

Free Energy of Formation of *cis*- and *trans*-Dinitrotetramminecobalt(III)-Tetranitrodiamminecobaltates(III).—The equilibrium constants of solution of these salts are given by $K=m^2\gamma_\pm^2$ as above and the relationships between $\log K$ and $1/T$ are given by two straight lines for both salts in Fig. 1, which are expressed for the cis salt by

$$\log K=10.71-4450/T$$

and for the trans salt by

$$\log K=9.014-4532/T$$

The free energy change of solution of the cis salt is obtained as

$$\Delta G^\circ=20350-48.98\,T,\quad \Delta G^\circ_{298}=5751\text{ cal.}\tag{6}$$

and that of the trans salt is obtained as

$$\Delta G^\circ=20730-41.23\,T,\quad \Delta G^\circ_{298}=8438\text{ cal.}\tag{7}$$

The heat of solution and the entropy change of solution of the above cis salt are $\Delta H=20350$ cal. and $\Delta S^\circ=48.98$ e. u. and those of the above trans salt are $\Delta H=20730$ cal. and $\Delta S^\circ=41.23$ e. u., respectively.

[12)] K. B. Yatsimirskii and L. L. Pankowa, *Zhur. Obshchei Khim.*, **19**, 623 (1949); K. B. Yatsimirskii, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), p. 180.

[13)] C. C. Stephenson, *J. Am. Chem. Soc.*, **66**, 1436 (1944).

[14)] A. E. Hill and J. E. Ricci, *J. Am. Chem. Soc.*, **53**, 4305 (1931).

In the preceding paper[2] the free energy of formation of *cis*- and *trans*-dinitrotetramminecobaltate(III) ions was obtained respectively as

$$\Delta G_f^\circ = -159900 - 16.10\,T \qquad (8)$$

$$\Delta G_f^\circ = -159100 - 7.72\,T \qquad (9)$$

From Eqs. 2, 6 and 8, the free energy of formation of the cis salt in the solid sate is obtained as

$$\Delta G_f^\circ = -345200 - 299.1\,T,$$

$$\Delta G_{f\,298}^\circ = -434.4\ \text{kcal.}$$

and from Eqs. 2, 7 and 9, that of the trans salt in the solid state is obtained as

$$\Delta G_f^\circ = -344700 - 298.5\,T,$$

$$\Delta G_{f\,298}^\circ = -433.7\ \text{kcal.}$$

Free Energy of Formation of Nitropentamminecobalt(III)-Tetranitrodiamminecobaltate(III).—The equilibrium constant of solution of this complex is given by $K = 4\,m^3\gamma^3{}_\pm$ and a plot of $\log K$ against $1/T$ gives a straight line in Fig. 2, which is expressed by the equation:

$$\log K = 7.530 - 4667/T$$

The free energy change of solution is given by

$$\Delta G^\circ = 21390 - 34.44\,T,$$

$$\Delta G_{298}^\circ = 11130\ \text{cal.} \qquad (10)$$

The heat of solution and the entropy change of solution are obtained as $\Delta H = 21.39$ kcal. and $\Delta S^\circ = 34.44$ e. u.. respectively.

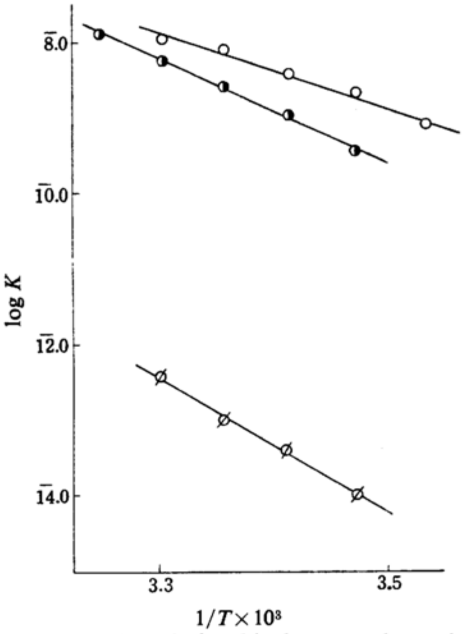

Fig. 2. The relationship between the equilibrium constant of solution and the temperature for $[Co(NH_3)_5NO_2][Co\cdot(NH_3)_2(NO_2)_4]_2$ (○), $[Co(NH_3)_5Cl][Co\cdot(NH_3)_2(NO_2)_4]_2$ (◑) and $[Co(NH_3)_6]\cdot[Co(NH_3)_2(NO_2)_4]_3$ (∅).

The free energy of formation of nitropentamminecobalt(III) ion was obtained in the preceding paper[2] as

$$\Delta G_f^\circ = -153100 + 148.3\,T \qquad (11)$$

From Eqs. 2, 10 and 11, that of nitropentamminecobalt(III)-tetranitrodiamminecobaltate(III) is obtained as below:

$$\Delta G_f^\circ = -504300 - 481.3\,T,$$

$$\Delta G_{f\,298}^\circ = -647.8\ \text{kcal.}$$

Free Energy of Formation of Chloropentamminecobalt(III)-Tetranitrodiamminecobaltate(III).—The equilibrium constant of solution of this complex is also given by $K = 4\,m^3\gamma^3{}_\pm$ in the same way as the above. A plot of $\log K$ against $1/T$ gives a straight line in Fig. 2 and its equation is calculated as

$$\log K = 13.93 - 6714/T$$

The free energy change of solution is given by

$$\Delta G^\circ = 30710 - 63.72\,T,$$

$$\Delta G_{f\,298}^\circ = 11710\ \text{cal.} \qquad (12)$$

The heat of solution is $\Delta H = 30710$ cal. and the entropy change of solution, $\Delta S^\circ = 63.72$ e. u.

The free energy of formation of chloropentamminecobalt(III) ion is obtained from the solubility data[3] and given by the equation,

$$\Delta G_f^\circ = -156100 + 270.9\,T \qquad (13)$$

From Eqs. 2, 12 and 13, the free energy of formation of chloropentamminecobalt(III)-tetranitrodiamminecobaltate(III) in the solid state is calculated as

$$\Delta G_f^\circ = -516600 - 329.4\,T,$$

$$\Delta G_{f\,298}^\circ = -614.8\ \text{kcal.}$$

Free Energy of Formation of Hexamminecobalt(III)-Tetranitrodiamminecobaltate(III).—The equilibrium constant of solution of this complex is given by $K = 27\ m^4\gamma^4{}_\pm$ in the same way as that of the hexamminecobalt(III) salts already reported[15]. The logarithm of K is plotted against $1/T$ in Fig. 1 as a straight line, the equation being

$$\log K = 16.83 - 8873/T$$

The free energy change of solution is given by

$$\Delta G^\circ = 40590 - 76.98\,T,$$

$$\Delta G_{298}^\circ = 17640\ \text{cal.} \qquad (14)$$

The heat of solution is obtained as $\Delta H =$ 40590 cal. and the entropy change of solution as $\Delta S^\circ = 76.98$ e. u.

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

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

Complex	Solubility	Heat of solution	Equivalent free energy of solution	Entropy change of solution	Lattice energy	Standard free energy of formation
	m	ΔH cal.	ΔG° cal.	ΔS° e.u.	U kcal.	ΔG_f° kcal.
$NH_4[Co(NH_3)_2(NO_2)_4]$	0.209	3530	2305			−286.3
$K[Co(NH_3)_2(NO_2)_4]$	0.0684	9777	4436			−335.8
cis-$[Co(NH_3)_4(NO_2)_2]\cdot[Co(NH_3)_2(NO_2)_4]$	8.99×10^{-3}	20350	5751	48.98	101.4	−434.4
trans-$[Co(NH_3)_4(NO_2)_2]\cdot[Co(NH_3)_2(NO_2)_4]$	8.38×10^{-4}	20730	8438	41.23	101.7	−433.7
$[Co(NH_3)_5NO_2][Co(NH_3)_2(NO_2)_4]_2$	1.46×10^{-3}	21390	5565		321.4	−647.8
$[Co(NH_3)_5Cl]\cdot[Co(NH_3)_2(NO_2)_4]_2$	1.00×10^{-3}	30710	5857		323.7	−614.8
$[Co(NH_3)_6][Co(NH_3)_2\cdot(NO_2)_4]_3$	2.84×10^{-4}	40590	5880		664.6	−863.7

In the second paper[15] of this series the free energy of formation of hexamminecobalt(III) ion was already obtained as

$$\Delta G_f^\circ = -146000 + 307\,T \qquad (15)$$

Therefore, from Eqs. 2, 14 and 15, the free energy of formation of hexamminecobalt(III)-tetranitrodiämminecobaltate(III) in the solid state is given by

$$\Delta G_f^\circ = -681300 - 612\,T,$$

$$\Delta G_{f\,298}^\circ = -863.7\ \text{kcal.}$$

Discussion

The thermodynamic functions of the nitroamminecobalt(III) complexes at 25°C calculated above are summarized in Table VIII. In this table the free energy of solution is the value for one gram equivalent of each complex, i. e., equivalent free energy of solution.

As shown in this table, the solubilities of these complexes decrease in the order of 1-1, 1-2 and 1-3 valency type salts. In these respects *trans*-$[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2\cdot(NO_2)_4]$ presents a single exception. The equivalent free energies of solution lie within the region between 5500 and 5900 cal. except for *trans*-$[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$, $K[Co(NH_3)_2(NO_2)_4]$ and Erdmann's salt. This corresponds to the free energy required for breaking a bond between the cation and the anion and hydrating each of the ions when the salt is dissolved.

The free energy of solution of *cis*-dinitrotetramminecobalt(III)-tetranitrodiamminecobaltate(III) is remarkably less than that of the corresponding trans salt. This is due to the fact that the entropy change of solution of the former is much greater than that of the latter. In other words, the entropy effect plays an important role when the cis and trans salts are dissolved in water just as in the case of the *cis*- and *trans*-dinitrotetramminecobalt(III) chloride reported in the preceding paper[2].

The heats of hydration of the complex ions concerned are listed in Table IX[16].

TABLE IX. HEAT OF HYDRATION OF COMPLEX IONS

Complex ion	Heat of hydration (kcal.)
$[Co(NH_3)_4(NO_2)_2]^+$	−40
$[Co(NH_3)_5NO_2]^{2+}$	−218
$[Co(NH_3)_5Cl]^{2+}$	−211
$[Co(NH_3)_6]^{3+}$	−501
$[Co(NH_3)_2(NO_2)_4]^-$	−41

By using these values and the heats of solution of the cobalt(III) nitroammine complexes described above, their lattice energies are computed. These are also shown in Table VIII.

The standard free energies of formation of four cobalt(III) nitroammine complexes in the solid state are given by:

$$2Co(s) + 6N_2 + 9H_2 + 6O_2 = cis\text{-}[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2\cdot(NO_2)_4] \quad \Delta G_f^\circ = -434.4\ \text{kcal.} \qquad (a)$$

$$2Co(s) + 6N_2 + 9H_2 + 6O_2 = trans\text{-}[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2\cdot(NO_2)_4] \quad \Delta G_f^\circ = -433.7\ \text{kcal.} \qquad (b)$$

$$3Co(s) + 9N_2 + 27/2H_2 + 9O_2 = [Co(NH_3)_5NO_2][Co(NH_3)_2(NO_2)_4]_2 \quad \Delta G_f^\circ = -647.8\ \text{kcal.} \qquad (c)$$

$$4Co(s) + 12N_2 + 18H_2 + 12O_2 = [Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3 \quad \Delta G_f^\circ = -863.7\ \text{kcal.} \qquad (d)$$

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[16] K. B. Yatsimirskii, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), p, 38.

By dividing a and b by two, c by three and d by four the following values are obtained:

$$\mathrm{Co(s)+2N_2+9/2H_2+3O_2}$$
$$=1/2\ cis\text{-}\mathrm{[Co(NH_3)(NO_2)_2]\cdot[Co(NH_3)_2(NO_2)_4]}$$
$$\Delta G_f^\circ=-217.2\ \mathrm{kcal.}$$

$$\mathrm{Co(s)+3N_2+9/2H_2+3O_2}$$
$$=1/2\ trans\text{-}\mathrm{[Co(NH_3)_4(NO_2)_2]\cdot[Co(NH_3)_2(NO_2)_4]}$$
$$\Delta G_f^\circ=-216.9\ \mathrm{kcal.}$$

$$\mathrm{Co(s)+3N_2+9/2H_2+3O_2}$$
$$=1/3\ \mathrm{[Co(NH_3)_5NO_2][Co(NH_3)_2\cdot(NO_2)_4]_2}\quad \Delta G_f^\circ=-215.9\ \mathrm{kcal.}$$

$$\mathrm{Co(s)+3N_2+9/2H_2+3O_2}$$
$$=1/4\ \mathrm{[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3}$$
$$\Delta G_f^\circ=-215.9\ \mathrm{kcal.}$$

From these values it is found that the free energy of formation of the above-mentioned cobalt(III) nitroammine complexes is proportional to the number of cobalt atoms contained in one molecule of these complexes.

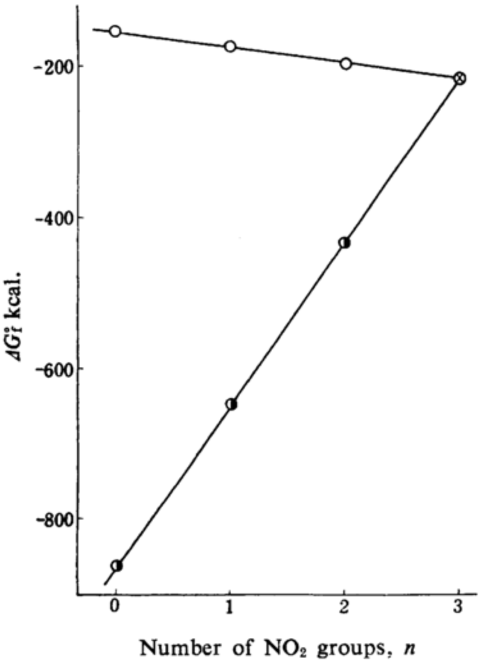

Fig. 3. The relationship between the free energy of formation and the number of nitrogroups co-ordinated in the series of several tetranitrodiamminecobaltates-(III), that is $\mathrm{[Co(NH_3)_{6-n}(NO_2)_n][Co\cdot(NH_3)_2(NO_2)_4]_{3-n}}$ (◑) and $\mathrm{[Co(NH_3)_{6-n}\cdot(NO_2)_n]Cl_{3-n}}$ (○).
(⊗) is trinitrotriamminecobalt(III) complex.

When the free energies of formation of the series consisting of $\mathrm{[Co(NH_3)_6][Co(NH_3)_2\cdot(NO_2)_4]_3}$—$\mathrm{[Co(NH_3)_5NO_2][Co(NH_3)_2(NO_2)_4]_2}$—$\mathrm{[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]}$ are plotted against the number of NO_2 contained in their cations in Fig. 3, a straight line is obtained. This line passes through a point giving the free energy of formation of $\mathrm{[Co(NH_3)_3(NO_2)_3]}$. The line for the free energy of formation of the series, $\mathrm{[Co(NH_3)_6]Cl_3}$—$\mathrm{[Co(NH_3)_5NO_2]Cl_2}$—$\mathrm{[Co(NH_3)_4(NO_2)_2]Cl}$, against the number of NO_2 also converges to the same point as shown in Fig. 3.

It can be expected that the free energies of formation of $\mathrm{[Co(NH_3)_6][Co(NO_2)_6]}$, $\mathrm{[Co\cdot(NH_3)_5NO_2][Co(NH_3)(NO_2)_5]}$, $\mathrm{[Co(NH_3)_4\cdot(NO_2)_2][Co(NH_3)_2(NO_2)_4]}$ and $\mathrm{2[Co(NH_3)_3\cdot(NO_2)_3]}$, are almost equal. The latter three are produced by the successive replacement of NH_3 in cation and NO_2 in anion of $\mathrm{[Co\cdot(NH_3)_6][Co(NO_2)_6]}$ with NO_2 and NH_3 respectively, thus forming a set of coordination isomers. Thus the free energy of formation of $\mathrm{2[Co(NH_3)_3(NO_2)_3]}$ is $\Delta G_f^\circ=-428.2$ kcal., that of *cis*-$\mathrm{[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]}$ $\Delta G_f^\circ=-434.4$ kcal. and that of the trans salt $\Delta G_f^\circ=-433.7$ kcal., although those of $\mathrm{[Co\cdot(NH_3)_6][Co(NO_2)_6]}$ and $\mathrm{[Co(NH_3)_5NO_2][Co\cdot(NH_3)(NO_2)_5]}$ have not been found. These facts mean that the free energy of formation cobalt(III) nitroammine complexes is additive with respect to the NO_2 group.

Furthermore, it is also found that the thermodynamic stability of $\mathrm{[Co(NH_3)_5NO_2][Co\cdot(NH_3)_2(NO_2)_4]_2}$ is greater than that of $\mathrm{[Co\cdot(NH_3)_5Cl][Co(NH_3)_2(NO_2)_4]_2}$, since the free energy of formation of the former is less than that of the latter.

Summary

The solubilities of Erdmann's salt, $\mathrm{NH_4[Co\cdot(NH_3)_2(NO_2)_4]}$, and the following complexes which have the same complex anion, $\mathrm{K[Co\cdot(NH_3)_2(NO_2)_4]}$, *cis*- and *trans*-$\mathrm{[Co(NH_3)_4\cdot(NO_2)_2][Co(NH_3)_2(NO_2)_4]}$, $\mathrm{[Co(NH_3)_5NO_2][Co(NH_3)_2(NO_2)_4]_2}$, $\mathrm{[Co(NH_3)_5Cl][Co(NH_3)_2\cdot(NO_2)_4]_2}$ and $\mathrm{[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3}$ were measured. Based upon the thermodynamic functions calculated from the above measurement, the free energy of solution, the lattice energy and the free energy of formation of these complexes were calculated and discussed.

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