*Thermodynamic Studies on Cobalt Complexes. VIII. Some Information about Diaquotetramminecobalt(III) Complexes and Thermal Dissociation of the Corresponding Chloride**

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Although there have been a few reports[1,2] on the visible and ultraviolet absorption spectra of diaquotetramminecobalt(III) complexes, none can be found on the infrared absorption spectra of cobalt(III) diaquo-complexes except in the cases of $[Co(NH_3)_2(OH_2)_2Cl_2]Cl$ and $[Co\,en(OH_2)_2Cl_2]Cl$[3] containing chloride ions as the ligand. The investigation of diaquotetramminecobalt(III) complexes by X-ray diffraction method has never been reported. In the present study the infrared absorption and the X-ray diffraction of diaquotetramminecobalt(III) and aquopentamminecobalt(III) complexes were measured. From these some information about their crystal structures was brought out. Since little has been reported concerning the thermochemical properties of cobalt(III) diaquo-complexes, some of them will be described, with special reference to the thermal dissociation of the diaquotetramminecobalt(III) chloride.

Experimental

Diaquotetramminecobalt(III) chloride, sulfate and perchlorate were prepared[4] by the aquation of carbonatotetramminecobalt(III) nitrate with hydrochloric, sulfuric and perchloric acids respectively. Their visible and ultraviolet absorption spectra were measured with a Hitachi EPU-2 type spectrophotometer. The infrared absorption of diaquotetramminecobalt(III) and aquopentamminecobalt(III) perchlorates were measured by the Nujol mull method with an Ōyō Kōgaku Kenkyūsho DS-201 infrared spectrophotometer, and the X-ray diffraction, with a Rigaku Denki X-ray diffractometer. The results obtained were compared with those of hexamminecobalt(III) perchlorate.

The thermal analysis was carried out for diaquotetramminecobalt(III) chloride, sulfate and perchlorate with a Shimadzu thermobalance. The thermal dissociation pressure of diaquotetramminecobalt(III) chloride was measured in vacuo with a mercury manometer.

Results and Discussion

Thermal Analyses of Diaquotetramminecobalt(III) Chloride, Sulfate and Perchlorate.— In order to verify the fact that the complexes obtained were actually the desired ones, chemical analyses, determinations of coagulation values and thermal analyses were made with them. The weight losses of the complexes upon heating are plotted against the temperature in Fig. 1. It is presumed that the chloride and sulfate decompose according to the following schemes:

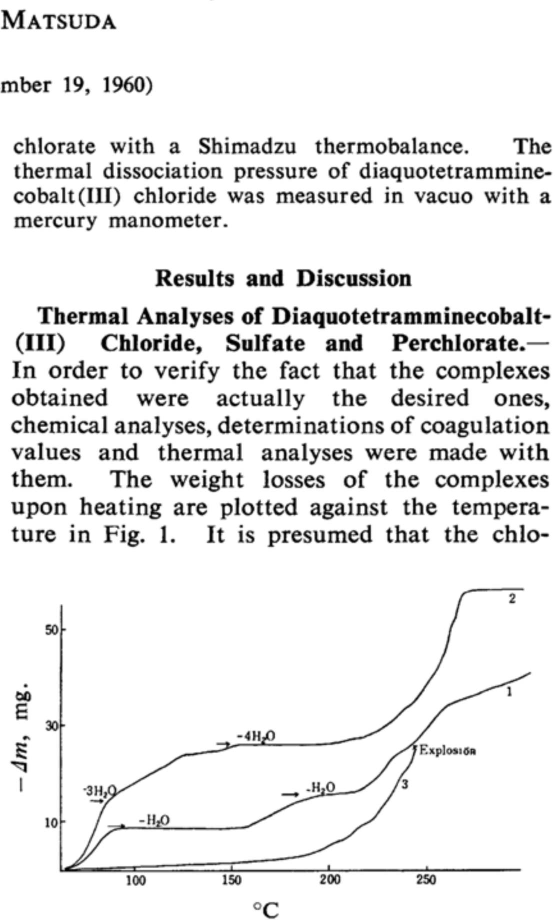

Fig. 1. The relationships between the weight loss and the temperature upon heating diaquotetramminecobalt(III) chloride (1), sulfate hydrate (2) and perchlorate (3). Both the weights of the chloride and of the perchlorate used are 0.2 g. respectively and that of the sulfate hydrate is 0.1 g. The expressions of $-nH_2O$ show the steps of dehydration of n g molecule of water from oneg ram molecule of those complexes.

$$[Co(NH_3)_4(OH_2)_2]Cl_3 \xrightarrow[70\sim90°C]{-H_2O} [Co(NH_3)_4\cdot$$

$$(OH_2)Cl]Cl_2 \xrightarrow[150\sim170°C]{-H_2O} cis\text{-}[Co(NH_3)_4Cl_2]Cl$$

$$\xrightarrow[200\sim234°C]{} CoCl_2$$

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

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

[2] A. Kiss and D. Czeglédy, *Z. anorg. u. allgem. Chem.*, **235**, 407 (1938).

[3] E. Kyuno, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 724 (1959).

[4] S. M. Jörgensen, *Z. anorg. Chem.*, **2**, 296 (1892).

$$[Co(NH_3)_4(OH_2)_2]_2(SO_4)_3\cdot 3H_2O \xrightarrow[80°C]{-3H_2O}$$

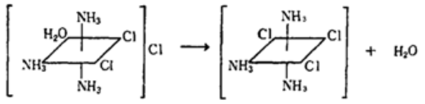
$$[Co(NH_3)_4(OH_2)_2]_2(SO_4)_3 \xrightarrow[90\sim150°C]{-4H_2O} [Co\cdot$$

$$(NH_3)_4SO_4]_2SO_4 \xrightarrow[240\sim260°C]{} 2CoSO_4$$

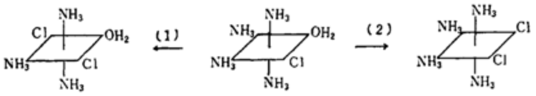
$$+(NH_4)_2SO_4$$

The perchlorate begins to decompose gently at about 190°C and explodes at 243°C. The decomposition of the perchlorate does not take place in a stepwise manner as does the chloride and sulfate.

trans-Aquodichlorotriamminecobalt(III) chloride, $[Co(NH_3)_3(OH_2)Cl_{2(6)}^{(1)}]Cl$, does not decompose at 100°C, whereas even at this temperature the corresponding *cis*-chloride changes to trichlorotriamminecobalt(III) complex releasing water as shown below:



There has been a report⁵⁾ that this phenomenon might be explained by the so-called trans-effect⁶⁾. If the trans-effect is to be applied to the decomposition of aquochlorotetramminecobalt(III) chloride, the product must be *trans*-aquodichlorotriamminecobalt(III) chloride, $[Co(NH_3)_3(OH_2)Cl_{2(6)}^{(1)}]Cl$. But the product actually obtained in our experiment is *cis*-dichlorotetramminecobalt(III) chloride, $[Co(NH_3)_4Cl_{2(2)}^{(1)}]Cl$; i. e. process 1 did not occur, but process 2 did take place:



This shows that the trans-effect can not be applied to this process. A better explanation may be that *cis*-dichlorotetramminecobalt(III) chloride is more stable than the corresponding trans-chloride in the same way as that *cis*-dinitrotetramminecobalt(III) chloride is thermodynamically more stable than the corresponding *trans*-chloride⁷⁾.

Visible and Ultraviolet Absorption Spectra of Diaquotetramminecobalt(III) Complexes.—The visible and ultraviolet absorption spectra of diaquotetramminecobalt(III) complex which have already been reported by Tsuchida and his co-worker¹⁾ and Kiss and his co-worker²⁾ are not in agreement with each other. That is, the maxima of both the first and second absorption bands of the complex reported by the former workers* are remarkably lower than those by the latter. The absorption of the complex measured by us are given in Fig. 2. The maxima of the first and second absorption bands of the complex are found at $\nu_1=59.0\times10^{13}$ sec^{-1} ($\log \varepsilon_1=1.73$) and $\nu_2=84.5\times10^{-13}\cdot$sec^{-1} ($\log \varepsilon_2=1.66$) respectively, where ν is the frequency and ε is the molar extinction coefficient.

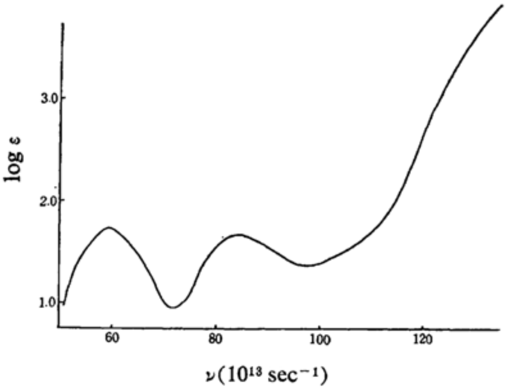


Fig. 2. The absorption spectrum of diaquotetramminecobalt(III) perchlorate.

Dissociation Pressure of Diaquotetramminecobalt(III) Chloride.—It was found above that diaquotetramminecobalt(III) chloride decomposed at 70∼90°C as follows:

$$[Co(NH_3)_4(OH_2)_2]Cl_3(s) = [Co(NH_3)_4\cdot(OH_2)Cl]Cl_2(s) + H_2O(g)$$

The vapor pressure or dissociation pressure of diaquotetramminecobalt(III) chloride was measured at 7∼36.5°C with the apparatus already described⁸⁾. The results are listed in Table I.

The logarithm of the dissociation pressure, p_{mm}, is plotted against the reciprocal of the absolute temperature in Fig. 3. A straight

TABLE I. DISSOCIATION PRESSURE OF DIAQUOTETRAMMINECOBALT(III) CHLORIDE

Temp. C°	$1/T\times10^3$	Dissociation pressure p_{mm}	$\log p_{mm}$
7	3.559	4.15	0.6181
19	3.425	5.40	0.7324
21	3.401	5.89	0.7701
31	3.290	6.99	0.8445
36.5	3.231	7.98	0.9020

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5) M. Mori, M. Shibata, K. Hirota, K. Masuno and Y. Suzuki, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zasshi*), **79**, 1251 (1958).

6) J. V. Quagliano and L. Schubert, *Chem. Revs.*, **50** 201 (1952).

7) M. Mori, R. Tsuchiya and H. Fukuda, This Bulletin, **33**, 1503 (1960).

* By private communication received from R. Tsuchida in Oct., 1959, $\nu_1=59.2$ ($\log \varepsilon_1=1.72$) and $\nu_2=84.6\sim84.7$ ($\log \varepsilon_2=1.64$).

8) M. Mori and R. Tsuchiya, This Bulletin, **32**, 467 (1959).

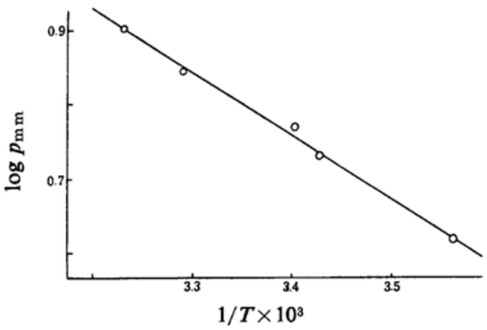

Fig. 3. The relationship between the dissociation pressure of diaquotetramminecobalt(III) chloride and the temperature.

line is obtained. The equation of the straight line is calculated by the method of least squares as,

$$\log p_{\mathrm{mm}}=3.669-856.1/T$$

The free energy change for the dissociation is obtained as,

$$\Delta G^\circ=3916-3.604\ T,\quad \Delta G^\circ_{298}=2842\ \text{cal.} \qquad (1)$$

From the free energy change for the dissociation of hexamminecobalt(III)[8] and aquopentamminecobalt(III) chlorides[9], the free energy change for the reaction in which one gram equivalent of NH_3 is replaced by one gram equivalent of H_2O in the coordination sphere is calculated as below:

$$[Co(NH_3)_6]Cl_3(s)+H_2O(g)=[Co(NH_3)_5\cdot OH_2]Cl_3(s)+NH_3(g)$$

$$\Delta G^\circ=-296+8.32\ T \qquad (2)$$

The entropy change is $\Delta S^\circ=-8.32$ e. u. If it is assumed that the entropy change of the reaction,

$$[Co(NH_3)_5OH_2]Cl_3(s)+H_2O(g) = [Co(NH_3)_4(OH_2)_2]Cl_3(s)+NH_3(g) \qquad (3)$$

in which one gram equivalent of NH_3 in the reactant is replaced by one gram equivalent of H_2O, is equal to the entropy change of the reaction 2, i. e. -8.32 e. u., then the free energy change for reaction 3 is obtained by using the value of the above entropy change and the heats of formation of the substances[10,11] concerning the reaction as:

$$\Delta G^\circ=-1140+8.32\ T \qquad (4)$$

Since the free energies of formation of aquopentamminecobalt(III) chloride, water vapor and ammonia are known, from these values and Eq. 4 the free energy of formation of diaquotetramminecobalt(III) chloride in the solid state is calculated as,

$$\Delta G^\circ_f=-360600+363.2\ T$$

$$\Delta G^\circ_{f298}=-252300\ \text{cal.} \qquad (5)$$

The free energy of formation of aquochlorotetramminecobalt(III) chloride, which is the decomposition product of diaquotetramminecobalt(III) chloride, is obtained from Eqs. 1 and 5 as follows:

$$\Delta G^\circ_f=-298900+349.0\ T$$

$$\Delta G^\circ_{f298}=-194900\ \text{cal.}$$

From the above results the free energies of the reaction in which an ammonia molecule is successively replaced by a water molecule in the coordination sphere of hexamminecobalt(III) chloride are calculated and from these relationships it is concluded that the thermodynamic stabilities of these complexes are in the order:

$$[Co(NH_3)_6]Cl_3>[Co(NH_3)_5OH_2]Cl_3> [Co(NH_3)_4(OH_2)_2]Cl_3>[Co(NH_3)_4(OH_2)\cdot Cl]Cl_2>[Co(NH_3)_5Cl]Cl_2$$

Infrared Absorption Spectra of Cobalt(III) Aquoammine-complexes.—The infrared absorption spectra for diaquotetramminecobalt(III) and aquopentamminecobalt(III) perchlorates are listed in Table II together with those for hexamminecobalt(III) perchlorate already reported[12].

From the table it is seen that the wave numbers of the stretching vibration of N–H, ν_{N-H} for aquo-complexes are lower than those for hexammine-complex, whereas the wave numbers of the degenerate bending vibration, deg. δ_{NH_3}, and the symmetric bending vibration, sym. δ_{NH_3}, of NH_3 for the former are higher than those for the latter. The wave numbers of the rocking vibration of NH_3, ρ_{NH_3}, are remarkably higher for the former. This means that the coordinate bond character of Co—N in the coordination sphere of cobalt(III) ammine-complexes increases when one or two water moleclues coordinate in place of ammonia molecules.

X-Ray Diffraction Data for Cobalt(III) Aquoammine-complexes.—Some reports have been published on the X-ray diffraction for

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[9] M. Mori, R. Tsuchiya and Y. Okano, ibid., **32**, 1029 (1959).

[10] K. B. Yatsimirskii and L. L. Pankowa, *Zhur. Obshcheĭ Khim.*, **19**, 617 (1949); K. B. Yatsimirskii, "Thermochemie von Komplexverbindungen", Akademie-Verlag, Berlin (1956), p. 178.

[11] F. D. Rossini et al., "Selected Values of Chemical Thermodynamic Properties", United States Government Printing Office, Washington (1952), p. 9.

[12] J. Fujita, K. Nakamoto and M. Kobayashi, *J. Am. Chem. Soc.*, **79**, 3295 (1956).

TABLE II. WAVE NUMBER OF VIBRATION FOR O-H AND N-H BONDS IN THE INFRARED ABSORPTION SPECTRA OF HEXAMMINECOBALT(III), AQUOPENTAMMINECOBALT(III) AND DIAQUOTETRAMMINECOBALT(III) PERCHLORATES

Complex	ν_{O-H}	ν_{N-H}		deg. δ_{NH_3}	sym. δ_{NH_3}	ρ_{NH_3}
$[Co(NH_3)_6](ClO_4)_3$		3320	3240	1630	1352	803
$[Co(NH_3)_5OH_2](ClO_4)_3$	3400	3257	3205	1634	1355	826
$[Co(NH_3)_4(OH_2)_2](ClO_4)_3$	3390	3246	3195	1637	1346	839

TABLE III. X-RAY DIFFRACTION DATA FOR AQUOPENTAMMINECOBALT(III) AND DIAQUOTETRAMMINECOBALT(III) PERCHLORATES

$[Co(NH_3)_5OH_2](ClO_4)_3$				$[Co(NH_3)_4(OH_2)_2](ClO_4)_3$			
d(Å)	I/I_0	hkl	a(Å)	d(Å)	I/I_0	hkl	a(Å)
4.019	100	220	11.37	4.001	100	220	11.32
3.276	5	222	11.35				
2.842	18	400	11.37	2.829	20	400	11.32
2.319	4.3	422	11.36	2.307	5.5	422	11.30
2.184	13	333	11.35	2.174	11	333	11.30
2.009	5	440	11.36	2.000	5.5	440	11.31
1.796	6.5	620	11.36	1.789	7	620	11.31
1.518	6	642	11.36	1.511	5.5	642	11.32
1.340	3	822	11.37				
			$a_{mean}=11.36$ Å				$a_{mean}=11.31$ Å
			$D=2.087$				$D=2.119$

hexamminecobalt(III) chloride[13] and perchlorate[14], but none for cobalt(III) aquoammine-complexes except $[Co(NH_3)_5(OH_2)]I_3$[15] and $[Co(NH_3)_4(OH_2)_2][TlCl_6]$[16]. The results of the X-ray diffraction measurement for aquopentamminecobalt(III) and diaquotetramminecobalt(III) perchlorates are shown in Table III. In this table d is interplanar spacing, I/I_0, relative intensity, and hkl, indices of lattice planes.

The crystals of these complexes belong to the cubic system like $(NH_4)_3[FeF_6]$[17] and the number of chemical units in a unit cell is $Z=4$. By comparing the length of the edge of a unit cell, a, and the density, D, for the above two cobalt(III) aquoammine perchlorates with those for hexamminecobalt(III) perchlorate, $a=11.41$ Å and $D=2.048$[14], as already reported, it is found that the dimension of the unit cell becomes smaller when one gram equivalent of NH_3 is replaced by one gram equivalent of H_2O in the coordination sphere of hexamminecobalt(III) or aquopentamminecobalt(III) perchlorate. Such a tendency can be seen also in the cases of $[Co(NH_3)_6][TlCl_6]$ ($a=11.42$ Å)[18] and $[Co(NH_3)_4(OH_2)_2][TlCl_6]$ ($a=11.30$ Å)[16]. It makes us suppose that the change of the bond distance of Co–N is closely related to the increase of the coordination bond character which can be detected from the infrared absorption spectra.

Summary

The visible and ultraviolet absorption spectra of diaquotetramminecobalt(III) perchlorate were measured and its decomposition process was discussed on the basis of the thermal analytical data.

The decomposition pressure of diaquotetramminecobalt(III) chloride was measured and the free energy of formation of aquochlorotetramminecobalt(III) chloride which was the product of the decomposition was calculated.

The infrared absorption and X-ray diffraction were measured for diaquotetramminecobalt(III) and aquopentamminecobalt(III) perchlorates and the relationships between the dimension of the unit cell and the coordinate bond strength, Co–N, were discussed.

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[13] F. M. Jäger, *Z. Kryst.*, **39**, 543 (1904).

[14] R. W. G. Wyckoff, S. B. Hendricks and T. P. McCatcheon, *J. Am. Chem. Soc.*, **13**, 389 (1927).

[15] G. Natta, *Gazz. chim. ital.*, **58**, 624 (1928).

[16] M. Linhard, W. Manthey and K. Plieth, *Z. Elektrochem.*, **57**, 862 (1953).

[17] V. Cagliotti and G. Giacomello, *Naturwissenschaften*, **26**, 317 (1938).

[18] T. Watanabe, M. Atoji and C. Okazaki, *Acta Cryst.*, **3**, 405 (1950).