Stability of Cobalt(III) and Chromium(III) Ammine Complexes in a Strongly Alkaline Solution[*]

By Hayami YONEDA

(Received June 4, 1957)

It is well known that cobalt(III) and chromium(III) ammine complexes are very stable in an acid solution, whereas they decompose more or less rapidly in an alkaline solution to free ammonia and precipitate metal hydroxides. On the other hand, ammine complexes of bivalent transition metal ions, such as zinc, copper(II), nickel and cobalt(II), can remain in solution only in the presence of an excess of ammonia and ammonium salts. The complexes of the latter type are not sensitive to a slight addition of alkali, but decompose instantaneously on addition of acid. Such a marked difference in the chemical behavior may be naturally attributable to the difference in the degree of covalency of the coordination bond. In the ammine complexes of the latter type, the metal-nitrogen bonding is due largely to the ion-dipole attraction, and the ligand can be exchanged constantly with the outer ammonia or water molecule. For cobalt (III) and chromium(III) ammine complexes, the exchange of a ligand with the outer water molecule is presumed to be difficult, since the coordination bonds involved in these complexes are highly covalent. However, any investigation on the decomposition of these cobalt(III) and chromium(III) ammine complexes in an alkaline solution has hardly ever been reported. In the present investigation, the rate of decomposition of cobalt(III) and chromium(III) hexammine and monoaquopentammine complexes was measured in a concentrated solution of sodium hydroxide. At the same time, infrared absorption spectra of these complexes were measured. From these results, the stability of the complexes has been discussed.

Experimental

Determination of the rate of decomposition.—The complexes used in the measurement were hexammine cobalt(III) chloride $[Co(NH_3)_6]Cl_3$ (I), monoaquopentammine cobalt (III) perchlorate $[Co(NH_3)_5H_2O](ClO_4)_3$ (II), hexaammine chromium(III) chloride $[Cr(NH_3)_6]Cl_3$ (III) and monoaquopentammine chromium(III) perchlorate $[Cr(NH_3)_5H_2O](ClO_4)_3$ (IV). The rate of decomposition of these complexes was measured in 1 M sodium hydroxide[**] at various temperatures. The initial concentration of the complex was 0.01 M in all of the measurements. The alkaline solution of the complex for the determination of the rate of decomposition was prepared as follows. Equal volumes of 0.02 M solution of the complexes and 2 M solution of sodium hydroxide, which were separately heated to a given temperature, were mixed together. This was carried out in several brown test-tubes having a stopper, which were dipped in a thermostat. At an appropriate time interval, the content of each test-tube was poured into another tube which was dipped in an ice-bath, and quickly cooled. Then the cooled reaction mixture was filtered to remove the precipitate of the metal hydroxide. To prevent further decomposition, 5 cc of the transparent solution thus obtained was poured into another tube containing 2 cc. of 6 N acid. The opitical densities of solutions thus obtained were measured. By comparing them with the optical densities of the standared solution, the concentrations of the complex were determined. A Beckman DU spectrophotometer was used for measurements of optical densities.

Infrared absorption spectra.—Infrared absorption spectra of I, II, III and IV in Nujol mulls were determined with a Perkin-Elmer Model 21 recording spectrophotometer using a sodium chloride prism.

Results

The measurements of optical densities were carried out at several wavelengths near the maximum of the first absorption band of the complex concerned. In every case, no shift of the absorption maximum was observed. This suggests almost conclusively that series of reacting solutions were composed of the initial complexes. The change in the relative concentration of the complex, which was determined

---

[*] This is Part III of "Stabilities of Metal Ammine Complexes."

[**] With a high concentration of alkali and a low concentration of the ammine complex, the ionic strength of the reacting solution is kept practically constant during the whole process; besides, the decomposition of the complex is approximately of the first order with respect to the complex.

from the observed opitcal densities is shown in Figs. 1∼4. From the analysis of these curves the decomposition of the complex was found to be a practically first-order reaction. Accordingly the activation energy of the decomposition could be obtained from the rate constants at various temperatures, which were calculated from the half-lives (See Fig. 5.).

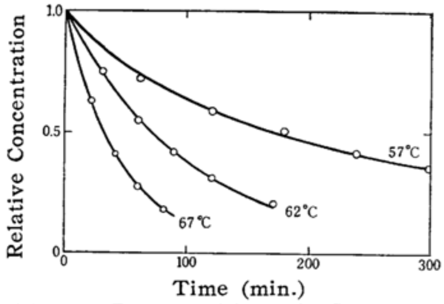

Fig. 1. Decomposition of $[Co(NH_3)_6]Cl_3$ in 1N NaOH.

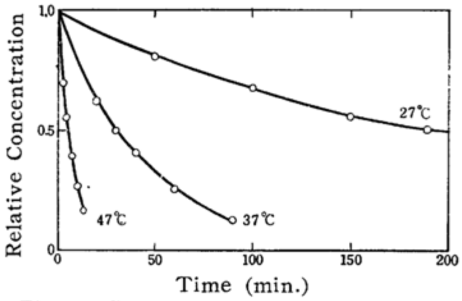

Fig. 2. Decomposition of $[Co(NH_3)_5H_2O](ClO_4)_3$ in 1N NaOH.

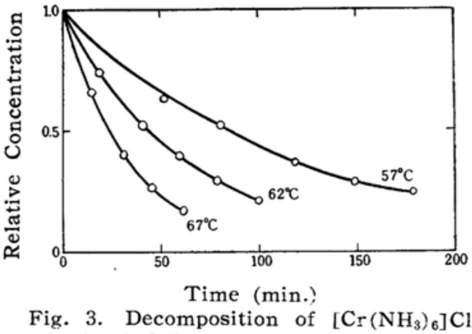

Fig. 3. Decomposition of $[Cr(NH_3)_6]Cl_3$ in 1N NaOH.

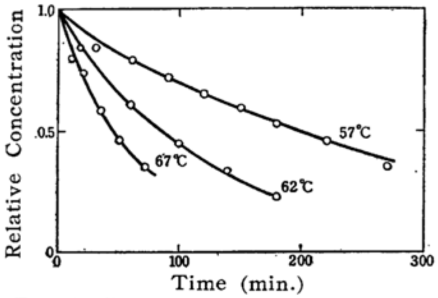

Fig. 4. Decomposition of $[Cr(NH_3)H_2O](ClO_4)_3$ in 1N NaOH.

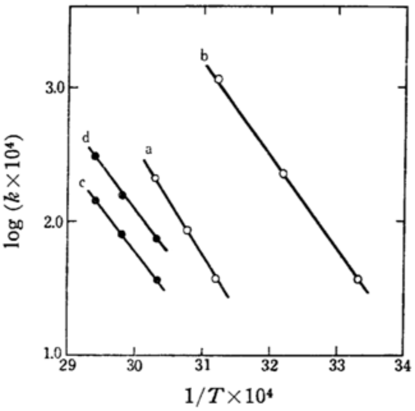

Fig. 5. Determination of the activation energy for the decomposition of cobalt (III) and chromium(III) ammine complexes from plots of $\log k$ against $1/T$.

a) $\log k$ for $[Co(NH_3)_6]Cl_3$
b) $\log k$ for $[Co(NH_3)_5H_2O](ClO_4)_3$
c) $\log k$ for $[Cr(NH_3)_6]Cl_3$
d) $\log k$ for $[Cr(NH_3)_5H_2O](ClO_4)_3$

TABLE I

ACTIVATION ENERGIES OF DECOMPOSITION

$[Co(NH_3)_6]^{3+}$	36 Kcal. mol^{-1}
$[Co(NH_3)_5H_2O]^{3+}$	32 Kcal. mol^{-1}
$[Cr(NH_3)_6]^{3+}$	31 Kcal. mol^{-1}
$[Cr(NH_3)_5H_2O]^{3+}$	31 Kcal. mol^{-1}

Absorption bands, which are regarded as being due to the rocking vibration of ammonia within the complex[1] are shown in Fig. 5. As the hexammine and the monoaquopentammine perchlorates of cobalt (III) and chromium(III) are all isomorphous, we can compare the strengths of the metal-ammonia bonds in these compounds by comparing the frequencies of the rocking vibrations of the coordinated ammonia. As the aquopentammine complex changes into the hydroxopentammine complex in a basic medium, it is more desirable that the strength of the metal-ammonia bond of the hexammine is compared with that of hydroxopentammine. However, as the infrared absorption spectrum is influenced markedly by the change of the symmetry of the crystal structure, the aquopentammine complex was chosen for comparison.

---

[1] S. Mizushima, I. Nakagawa and J. V. Quagliano, *J. Chem. Phys.*, **23**, 1367 (1955).

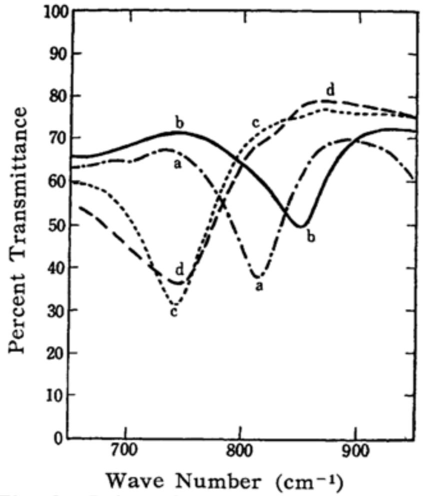

Fig. 6. Infrared absorption spectra of
a) $[Co(NH_3)_6](ClO_4)_3$
b) $[Co(NH_3)_5H_2O](ClO_4)_3$
c) $[Cr(NH_3)_6](ClO_4)_3$
d) $[Cr(NH_3)_5H_2O](ClO_4)_3$

TABLE II
FREQUENCIES OF THE ROCKING VARIATIONS OF THE COORDINATED AMMONIA

$[Co(NH_3)_6](ClO_4)_3$	815 cm^{-1}
$[Co(NH_3)_5H_2O](ClO_4)_3$	853 cm^{-1}
$[Cr(NH_3)_6](ClO_4)_3$	744 cm^{-1}
$[Cr(NH_3)_5H_2O](ClO_4)_3$	747 cm^{-1}

As is easily seen from Table II, the rocking vibration of the coodinated ammonia appears in the shorter wavelength in the cobalt(III) ammine complex than in the chromium(III) ammine complex. This means that the metal-ammonia bond is stronger in the cobalt(III) complex than in the chromium(III) complex. In addition, ammonia in the cobalt(III) pentammine complex combines with the metal ion more firmly than in the hexammine complex. In the chromium(III) complex, a very slight tendency of this kind can be observed. In the chromium(III) complex, the replacement of ammonia with water hardly has any noticeably influence on the other coodination bonds within the complex.

Discussion

From the data of the infrared absorption spectra it was concluded that for the cobalt(III) complexes the metal-ammonia bond is stronger in the pentammine complex than in the hexammine complex. This tendency is observed in the chromium(III) ammine complexes too, although it appears to be much less marked. This tendency can be inferred from the data of the consecutive formation constants of various metal ammine complexes. A part of the data is shown in Table III.

TABLE III
CONSECUTIVE FORMATION CONSTANTS OF THREE HEXAMMINE COMPLEXS[2]

	$\log k_1$	$\log k_2$	$\log k_3$	$\log k_4$	$\log k_5$	$\log k_6$	$\log\left(\frac{k_5}{k_6}\right)$
Ni^{2+}	2.80	2.24	1.78	1.19	0.75	0.03	0.72
Co^{2+}	2.11	1.63	1.05	0.76	0.18	-0.62	0.80
Co^{3+}	7.3	6.7	6.1	5.6	5.5	4.41	0.64

In this table, the values of $\log(k_5/k_6)_{obs.}$ are calculated to be 0.72, 0.80 and 0.64 for nickel(II), cobalt(II) and cobalt(III) ammine complexes respectively. On the other hand, when we take a special case, where the strength of the metal-ammonia bond and the state of aquation of the complex in a solution are almost identical among hexammine, pentammine, tetrammine etc., there is a statistical effect which prevents the successive formation constants from being equal. This was suggested previously by Wegscheider[3] and Adams[4], who gave the following expression;

$$\frac{k_n}{k_{n-1}}=\left(\frac{n-1}{n}\right)\left(\frac{N-n+1}{N-n}\right)$$

where n represents the number of the ligands already attached, except water and N is the coordination number of the complex, and k_n and k_{n+1} are the consecutive formation constants. Thus $\log(k_5/k_6)_{stat.}=0.38$ is obtained. This value is smaller than any value of $\log(k_5/k_6)_{obs.}$ already described. This indicates that in the actual complex the metal-ammonia bond is stronger in the pentammine complex than in the hexammine complex. In fact, Bjerrum compared $\log(k_n/k_{n+1})_{obs.}$ with $\log(k_n/k_{n+1})_{stat.}$ in various complexes and concluded that the ligand of the complex $[M(ligand)_n(H_2O)_{N-n}]$ is linked to the metal ion more firmly than that of the complex $[M(ligand)_{n+1}(H_2O)_{N-n-1}]$.

Thus, both the data of the infrared absorption spectra and those of the consecutive formation constants suggest that the metal-ammonia bond is stronger in the pentammine complex than in the hexammine complex.

---

[2] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen (1941), p. 188, 285.

[3] Wegscheider, *Monatsh.*, **16**, 75 (1895).

[4] Adams, *J. Am. Chem. Soc.*, **33**, 1503 (1916).

In connection with this fact, let us consider the stabilities of I and II in an alkaline solution. The experimental result indicates that II decomposes easily than I. This fact suggests that the decomposition of the cobalt(III) ammine complex in an alkaline solution is not a mere substitution of the coordinated ammonia by hydroxyl ion. As suggested by the fact that ammonia situates ahead of water and hydroxyl ion in the spectrochemical series[5]), it is presumed that ammonia combines more firmly with the central cobalt(III) ion than water or hydroxyl ion does.

Therefore, so long as the coordinated ammonia molecule keeps its original form NH_3, it is difficult to think that the ammonia might be expelled from the coordination sphere. This is borne out by the remarkably great stability of the cobalt (III) ammine complex in an acid solution. However, the situation is quite different in an alkaline solution. Here, let us recall the institability of hexahydroxylamine cobalt(III) complex discussed in the previous paper[6]). In this case, both the first and the second absorption band of the complex lie much farther in the shorter wavelength than those of other hexammine cobalt(III) complexes, and a much stronger metal-amine bond is suggested. Nevertheless, this complex is very unstable in an aqueous solution and decomposes fairly rapidly. We attributed this to the proton dissociation of the ligand. That is, a very strong bonding between the metal and nitrogen atoms induces the relaxation of the N–H bond in the ligand, and facilitates the proton dissociation of the ligand. The amide group thus produced combines with the metal ion very weakly and is easily replaced by a hydroxyl ion in the outside of the complex. In the ammonia complex, the bond between the cobalt(III) ion and the nitrogen atom of the ligand must be weaker than in the hydroxylamine complex. Therefore, the proton dissociation from the coordinated ammonia is expected to take place with much greater difficulty. Thus, as the equilibrium

$$[Co(NH_3)_6]^{3+} + H_2O \rightleftarrows [Co(NH_3)_5NH_2]^{2+} + H_3O^+$$

is shifted almost completely to the left side in an acid or neutral solution, the phenomena which suggest the proton dissociation are hardly detectable. However, in an alkaline solution the reverse reaction does not take place, and the effect of the proton dissociation can be observed. Thus, the proton dissociation from the coordinated ammonia takes place first; then the NH_2^- group thus produced is dissociated. This is our mechanism of the decomposition of the cobalt(III) amine complex. In the above discussion, we regarded the proton dissociation from the coordinated ammonia as the rate-determining step in the decomposition of the ammine complex. On this assumption we can understand that the stability of the pentammine complex is greater than that of the hexammine complex. Here the difference in the activation energy between the two complexes can be interpreted as the difference in the energy required to break off a proton from the coordinated ammonia.

The above discussion is based upon the assumption that the ligand which has dissociated a proton is linked to the central cobalt(III) ion less covalently and less firmly than the ligand which keeps a proton. This assumption seems to be in agreement with the fact that hydroxyl ion is behind water in the spectrochemical series, being linked less firmly to the cobalt(III) ion than water. The chemical behavior of the hexahydroxylammine cobalt(III) complex also supports this assumption. In addition, this assumption finds theoretical support in the concept of hybridization of orbitals of the donor atom. As was pointed out by Coulson[7]), the non-bonding electrons of water and ammonia do not occupy the pure 2s orbital, but the hybrid orbital which has to some extent the character of the p orbital. Consequently, the electronic cloudes of the lone pair have no longer any spherical symmetry, but are pulled out in the direction opposite to the binding hydrogen atoms. The large dipole moments of water and ammonia are mainly due to the so-called atom-dipoles which are produced by such hybridization. However, as a result of hybridization, the bonding electrons also occupy the hybrid orbitals which overlap with the bonding orbitals of the hydrogen atoms to much greater extent than the pure p opbitals. Such an increase of the overlapping of the bonding orbitals results in the gain of energy which compensates for the above mensioned loss of

---

[5]) R. Tsuchida, This Bulletin, **13**, 388, 436 (1938).

[6]) H. Yoneda, This Bulletin, **30**, 924 (1957).

[7]) C. A. Coulson, "Valence" Oxford Press (1953). p. 210.

energy. That is, the tendency to stabilize the bonds by increasing the overlapping of the bonding orbitals and the energy loss due to the pulling out of the non-bonding electrons compete with each other to determine the degree of hybridization. Accordingly, the larger is the number of bonds which are stabilized by hybridization, and the fewer is the number of the non-bonding electrons, the larger would be the degree of hybridization. Thus, the degree of hybridization is greater in water than in hydroxyl ion, and also in ammonia than in amide ion. Therefore, the localization of the lone pair electrons occurs more markedly in water and ammonia than in hydroxyl ion and amide ion. As it is such lone pair electrons that participate in the coordination bond, it is easily understood that the greater degree of hybridization the ligand takes, the more covalent and more stable coordination bond it can form. Previously, Kuroya and Tsuchida[8] found spectrochemically that the affinity of ligands to the metal ion is in the decreasing order of $NH_3>H_2O>OH^->F^-$, and asserted that the larger the num ber of the lone pairs of electrons in the donor atom of the ligand, the less firm the coodination bond becomes. This empirical rule can be understood easily by the above mentioned concept of hybridization.

Thus, we have explained the mechanism of the decomposition of the cobalt(III) ammine complex by assuming the process of proton dissociation of the ligand. In the case of the chromium(III) complex, however, the situation is different. In this case, the frequencies of the rocking vibrations of the coodinated ammonia were found to be almost identical in hexammine and aquopentammine complexes. This suggests that the strength of the metal-ammonia bond is almost identical in hexammine and aquopentammine complexes. Consequently, in the case of the chromium (III) ammine complex, it can not be concluded simply whether the decomposition proceeds through the proton dissociation from the coodinated ammonia or through the mere replacement of ammonia by hydroxyl ion. However, from the data of the infrared spectra, the metal-ammonia bond is concluded to be much weaker in the chromimum(III) complex than in the cobalt(III) complex. Therefore, if we take the proces of proton dissociation of the ligand, the activation energy must be much larger than that of the corresponding cobalt(III) ammine complex. This is not the case, and it may be natural to assume that the decomposition of the chromium(III) complex does not go through the proton dissociation of the ligand, but through the direct dissociation of the coordinated ammonia. That is, since the stability of the metal-ammonia bond in the chromium(III) complex is considerably small, the coordination bond itself is broken with a less amount of energy than that required for the proton dissociation. This tendency becomes much more marked in the case of the ammine complexes of bivalent transition metal ions. In this case, the infrared absorption spectra indicate that the metal-ammonia bond becomes weaker. Accordingly, in the solution of these ammine complexes, the exchange of ligands takes place and the complex can exist only in the equilbrium with an excess of ammonia.

Summary

The rate of decomposition of the cobalt (III) and chromium(III) hexammine and monoaquopentammine complexes in an alkaline solution was measured. The activation energies of the decomposition were found to be 36, 32, 31 and 31 Kcal/mole for $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5H_2O]^{3+}$, $[Cr(NH_3)_6]^{3+}$ and $[Cr(NH_3)_5H_2O]^{3+}$ respectively. At the same time the infrared absorption spectra of these complexes were also measured. The frequencies of the rocking vibration of the coordinated ammonia were found to be 815, 853, 744 and 747cm^{-1} for $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5H_2O]^{3+}$, $[Cr(NH_3)_6]^{3+}$ and $[Cr(NH_3)_5H_2O]^{3+}$ respectively. From these results it was concluded that the decomposition of the cobalt(III) ammine complex was not a mere replacement of the coordinated ammonia by hydroxyl ion, but a reaction through the proton dissociation step as exemplified in the following scheme

$$[Co(NH_3)_6]^{3+}+OH^- \rightarrow [Co(NH_3)_5NH_2]^{2+}+H_2O\,,$$

while, in the chromium(III) ammine complex, the decomposition was inferred to proceed through a substitution of hydroxyl ion for the coordnated ammonia.

We wish to express our sincere thanks to

---

[8] H. Kuroya and R. Tsuchida, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*) **61**, 597 (1940).

[9] For example, D. B. Powell and N. Sheppard, *J. Chem. Soc.*, **1956**, 3108.

Professer R. Tsuchida of Osaka University for his kind advice and encouragement during this work. Our appreciation is also expressed to Professor O. Nagai of Wakayama Medical College who gave us a chance to use a Beckman DU spectrophotometer, and to Mr. S. Kida of Wakayama University for his valuable discussions.

Department of Chemistry, Wakayama University, Masago-cho, Wakayama