Absorption Spectra and Chemical Behavior of the Hexahydroxylamine Cobalt(III) Complex[1]

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In general, complexes of a transition metal ion having an unsaturated *d*-shell have several absorption bands in the region ranging from the near infrared to the ultraviolet. These bands can be considered, to a good approximation, as arising from the energy transitions between the *d*-levels which are split by the electrical field set up by the ligands[2]. The energy transitions between such split *d*-levels correspond to the frequencies of the absorption maxima of the complex. As the energy intervals of such split *d*-levels increase with the increase of the electrical field by the ligands, the strength of the electrical field produced by various ligands can be estimated by comparing the maximum position of the absorption band of various complexes. Such a comparison must have a special significance in the case of complexes of the same type having a series of ligands which have the same donor atom. Because, by such an investigation, we can look for the main factors governing the stability of the coordination bond. With this purpose, the absorption spectra of a series of hexammine nickel(II) and tetrammine platinum (II) complexes were investigated in the previous study[3]. As a result, it was found that the weaker the basic strength of an amine, the shorter the wavelength at which the characteristic absorption bands of the complex appear. This fact indicates that the interaction between the metal ion and the ligands increases with the decreasing order of the basic strengths of co-ordinating amines. A similar rule must be observed more clearly in the case of cobalt(III) ammine complex which is regarded as having more covalent character. With this in mind, the absorption spectrum of hexahydroxylamine cobalt(III) complex was measured and compared with the hitherto measured data of other hexammine cobalt(III) complexes. The result indicated that both the first and the second absorption band of the hydroxylamine complex lay in a much shorter wavelength than those of other hexammine complexes. As the basic strength of hydroxylamine is much weaker than that of ammonia, methylamine or ethylenediamine, this result indicates that the same rule as found in nickel(II) and platinum(II) ammine complexes holds also in the cobalt(III) complex.

In the course of this study it was found that hexahydroxylamine cobalt(III) complex was very unstable in a solution and decomposed gradually to the cobalt(II) salt. This fact seemed to be apparently inconsistent with the above mentioned spectrochemical result. To clarify the cause of this inconsistency, a detailed study of the decomposition of the complex was carried out by measuring the rate of

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[1] This paper is Part II of "Stabilities of Metal Ammine Complexes".

[2] For examle, L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

[3] Yoneda, This Bulletin, **30**, 132 (1957).

decomposition under various conditions. It was revealed that a very strong binding between the central cobalt(III) ion and the nitrogen atom of the co-ordinating hydroxylamine caused the instability of the complex as a whole. Accordingly, this proved that the instability of hexahydroxylamine cobalt(III) complex supported the validity of the above mentioned rule.

Experimental

Preparation of Hexahydroxylamine cobalt (III) Complex.—Hexahydroxylamine cobalt(III) chloride $[Co(NH_2OH)_6]Cl_3$ was prepared by the following modification of Werner's method[4]. Three g. of *trans*-dichloro-diethylenediamine-cobalt(III) chloride $[Co\ en_2\ Cl_2]Cl$ and 4 g. hydroxylamine hydrochloride $NH_2OH \cdot HCl$ were dissolved in a small amount of water. The solution was cooled below 0°C. To this solution, a concentrated solution containing 2 g. sodium hydroxide was added, and the mixed solution was vigorously stirred. After a while, a light brown precipitate appeared. Then a large excess of concentrated hydrochloric acid was added until the color of the solution became dark green. Within a few minutes, the desired complex began to appear in the form of glittering golden leaflets. After kept standing for an hour, the crystals were filtered and redissolved in slightly acid warm water (near above 50°C in temperature) and reprecipitated by the addition of concentrated hydrochloric acid. The corresponding bromide and perchlorate of the complex* were obtained by the addition of the concentrated corresponding acid to the concentrated solution of the chloride.

Measurement of the Absorption Spectra.—When hexahydroxylamine cobalt(III) complex is dissolved in distilled water, it decomposes fairly rapidly. This decomposition can be stopped by the addition of strong acids. Therfore, the absorption spectrum of the complex was measured in 0.1N perchloric acid solution. In order to know how the absorption spectrum changes with the variation of pH, the absorption spectrum was measured in a buffer solution of pH 4.8. The absorption measurement was carried out using Beckman DU spectrophotometer.

Determination of the Rate of Decomposition.—The rate of decomposition of hexahydroxylamine cobalt(III) complex was measured in the following buffer solutions;

Mixture of 0.5 N acetic acid and 0.5 N sodium acetate pH 4.8

Mixture of 0.05 N acetic acid and 0.5 N sodium acetate pH 5.8

The buffer solution was heated to the desired temperature, and in this solution the complex was dissolved quickly, to let the decomposition start. Five cc. of the reacting solution was taken out with a pipette and pourd into 2 cc. of 2 N perchloric acid, to stop the decomposition. At appropriate time-intervals, this procedure was repeated. Thus, we obtained a series of solutions which contained the complex in various concentrations. Therefore, if we can determine the concentration of the complex in these solutions, we can trace the decomposition of the complex. For this purpose, the optical densities of these solutions were measured at several wavelengths near the maximum position of the first absorption band of the complex. The ratios of the optical densities of these solutions to that of the innitial solution give the relative concentrations of the complex. From these values we can trace the decrease in the concentration of the complex in the decomposition process.

Results

The results of the absorption measurement are shown in Fig. 1 and Table I. In the Table are listed also the maximum positions of the first and the second absorption band of other hexammine cobalt (III) complexes hitherto measured.

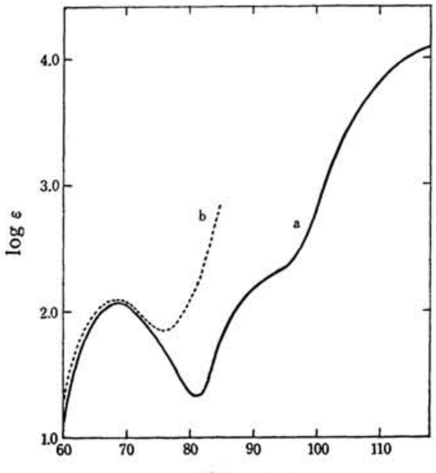

Fig. 1. The absorption spectra of $[Co(NH_2OH)_6](ClO_4)_3$.
a) in 0.1 N $HClO_4$.
b) in the buffer solution of pH 4.8.

The results of the measurement of the rate of decomposition of the complex are represented in Figs. 2 and 3. Each curve in these figures can be transformed into a straight line, when the logarithmic value of the concentration is taken as an ordinate and the time as an abscissa. This indicates that the decomposition of the complex proceeds apparently in the form of the first order reaction. The rate constants of the reaction are as follows: in the solution of pH 4.8 at 50°C 0.0990min.

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[4] A. Werner und E. Berl, Ber., **38**, 893 (1905).

* The crystals of bromide and chloride cannot be preserved for a long time, because they change gradually into the cobaltous salt even in a closed vessel. On the contrary, perchlorate does not change even in summer or in the sunlight, in the absence of moisture.

TABLE I

MAXIMUM POSITIONS OF THE FIRST AND THE SECOND ABSORPTION BAND OF COBALT(III) HEXAMINE COMPLEXES (in 10^{13} sec.$^{-1}$ unit)

Complex	pK of the co-ordinating amine	1st Band	2nd Band
$[Co(NH_2OH)_6]^{3+}$	6.03[5]	68.5 (log ε 2.07)	ca. 94 (log ε ca. 2.3)
$[Co\ en_3]^{3+}$	8.55*[6]	63.9	88.4
$[Co(NH_3)_6]^{3+}$	9.25[7]	62.9	88.3
$[Co(NH_3)_4(CH_3NH_2)_2]^{3+}$	10.63**[7]	61.9	86.3

* mean value of pK_1 7.19 and pK_2 9.92

** pK_a of CH_3NH_2

liter mole., 45°C 0.0462 and 40°C 0.0198; in the solution of pH 5.8 at 35°C 0.0815 min. liter mole., 30°C 0.0347 and 25°C 0.0139.

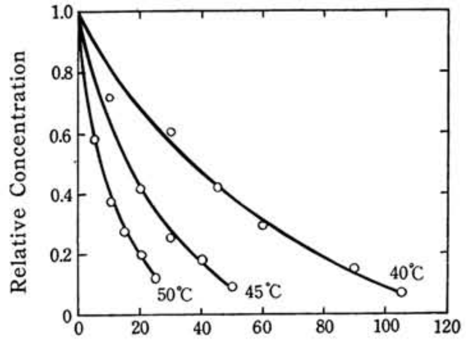

Fig. 2. Decomposition of $[Co(NH_2OH)_6](ClO_4)_3$ in the buffer solution of pH 4.8.

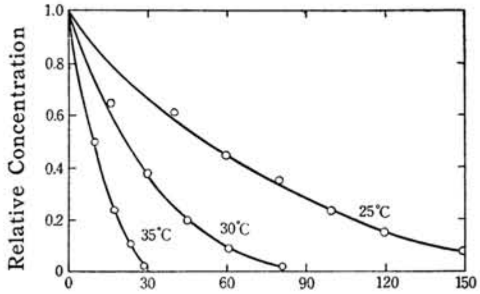

Fig. 3. Decomposition of $[Co(NH_2OH)_6](ClO_4)_3$ in the buffer solution of pH 5.8.

Taking the logarithmic values of these rate constants as an ordinate, and the reciprocals of the absolute temperatures as an abscissa, a straight line is obtained. From its slope, the activation energy is calculated to be 32.5 kcal mole^{-1}. As the two straight lines in Fig. 4 are parallel it is concluded that the activation energy is independent of the variation of pH. Besides, as the ordinate-interval between the two lines is unity, it is concluded that the reaction rate is proportional to the concentration of the hydroxyl ion.

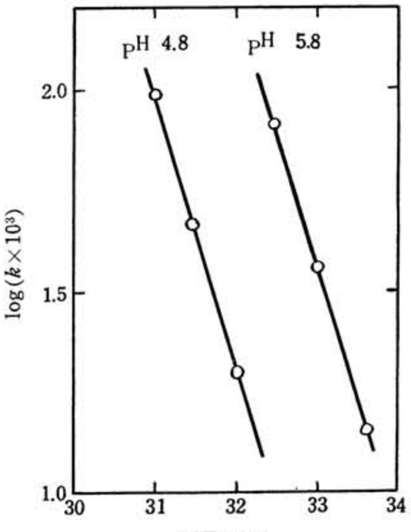

Fig. 4. Determination of the activation energy for the decomposition of $[Co(NH_2OH)_6](ClO_4)_3$ from plots of log *k* against $1/T^{\circ}$.
a) log *k* for pH 4.8.
b) log *k* for pH 5.8.

Discussion

As expected, the first and the second absorption bands of hydroxylamine cobalt(III) complex lie much farther in the shorter wavelength than those of other hexammine cobalt(III) complexes hitherto measured. In addition, as is easily seen in Table I, both the first and the second absorption band of hexammine cobalt(III) complexes show the blue shift with the increase in the acid dissociation constants

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5) H. Hagisawa, Bull. Inst. Phys. Chem. Research, Tokyo, **20**, 251 (1954).

6) G. A. Carlson, J. P. McReynolds and F. H. Verhoek, *J. Am. Chem. Soc.*, **67**, 1334 (1945).

7) H. S. Harned and B. B. Owen, ibid. **52**, 5079 (1930).

8) Y. Shimura and R. Tsuchida, This Bulletin, **29**, 311 (1956).

9) J. Brigando, *Compt. rend.*, **236**, 708 (1953).

of the co-ordinating amine. This fact indicates that the weaker the basic strength the co-ordinating amine has, the more strongly it combines with the central cobalt(III) ion. This tendency can be concluded also from the marked red shift of the charge transfer band of hexahydroxylamine cobalt(III) complex compared with that of hexa-ammonia cobalt(III) complex. In the free state, both hydroxylamine and ammonia have the absorption band in the shorter wavelength region near 2000 Å. This absorption band of hydroxylamine shows a marked red shift when it is co-ordianted to the cobalt(III) ion and this band is superposed partly upon the second absorption band of the complex. In contrast to this, the absorption band of ammonia shows only a slight red shift in the co-ordinated state. Here, it is noteworthy that in the case of the hydroxylamine complex the red shift of such a charge transfer band becomes much more marked as the pH of the solution increases, and conceals completely the second absorption band. This indicates that the interaction between the central cobalt(III) ion and the co-ordinating hydroxylamine increases when the pH of the solution increases. Such a marked change of the charge transfer band was not observed in the case of the ammonia complex, so far as the perchlorate of the complex was concerned. Such a strong interaction between hydroxylamine and the cobalt(III) ion was presumed from the method of preparation of hexahydroxylamine cobalt(III) chloride. As described in the experimental part, hydroxylamine can expel even ethylenediamine from its co-ordination sphere, which is very firmly linked to the central cobalt(III) ion.

When the electronic cloud of the nitrogen atom of hydroxylamine penetrates so deeply into the central cobalt(III) ion, we can expect the relaxation of the N–H bond, which facilitates the proton dissociation in an aqueous solution. Therefore, the following equilibrium may be formed;

$$[Co(NH_2OH)_6]^{3+} + H_2O \rightleftarrows [Co(NH_2OH)_5NHOH]^{2+} + H_3O^+$$

$[Co(NH_2OH)_5NHOH]^{2+}$ thus produced is regarded as the intermediate toward the reduction of the complex. The main reason why hydroxylamine having a strong reducing power does not reduce the cobalt (III) ion and can coexist with the cobalt (III) ion within the hexahydroxylamine cobalt(III) ion, can be attributable to the fact that six co-ordinating hydroxylamine molecules contend with each other and cancel the polarizing power of the cobalt (III) ion. When this balance is lost by the proton dissociation from one co-ordinating hydroxylamine, other hydroxylamine molecules are subjected to the increased polarizing power of the central cobalt(III) ion, so that an electron is easily snatched up by the central cobalt (III) ion, resulting in complete reduction. This is based upon the following empirical rule: the electronic cloud of the ligand, which has lost a proton, must penetrate into the central cobalt(III) ion much more weakly than that of the ligand which keeps a proton. This means that the $NHOH^-$ group is linked to the cobalt(III) ion less covalently and less firmly than the hydroxylamine molecule. As is seen from its position in the spectrochemical series, water is linked to the cobalt(III) ion much more strongly than the hydroxyl ion. A similar relation may be expected in the case of hydroxylamine and $NHOH^-$ too. In fact, the first absorption band of hexahydroxylamine cobalt(III) complex ion makes a slight red shift, when the pH of the solution increases. As the percentage of the complex which has lost a proton must increase more in a weakly acid solution than in a strongly acid solution, and as the red shift means that the field set up by the ligands decreases, the above mentioned red shift suggests that the $NHOH^-$ group is linked to the cobalt (III) ion less firmly than the hydroxylamine molecule. Thus, when one co-ordinating hydroxylamine becomes a less polarizable $NHOH^-$, the degree of the charge neutralization of the central cobalt (III) ion by the co-ordinating electrons of the donor atoms decreases, and consequently, the remaining hydroxylamine molecules in the complex radical is polarized more strongly by the central cobalt (III) ion. Such an increase in polarization induces the reduction. Therfore, if we could depress the proton dissociation by some means, the decomposition of the complex would not take place. Indeed, in a strongly acid solution the decomposition of the complex does not occur. This is the present author's interpretation. With this view, we can understand the cause why penta-, tetra-, and tri-hydroxylamine cobalt(III) complexes such as $[Co(NH_2OH)_5Cl]^{2+}$, $[Co(NH_2OH)_4CO_3]^+$, and

$[Co(NH_2OH)_3(H_2O)_3]^{3+}$ can not be obtained. Even if such complxes could be prepared, the large polarizing power of the central cobalt(III) ion would polarize hydroxylamine over its limit, and the reduction of cobalt(III) to cobalt(II) would take place. Accordingly, if we chose the ligand which decreases the polarizing power of the central cobalt(III) ion very much, we could obtain the cobalt(III) complex containing hydroxylamine. As one of such ligands we know the dimethylglyoximato group*.

The above mentioned view was confirmed further by the investigation of the decomposition of the hexahydroxylamine cobalt (III) complex in an aqueous solution. The result shows that rate of decomposition of the complex is proportional to the concentration of the hydroxyl ion as well as to the concentration of the complex ion. This fact indicates that although the decomposition of the complex is apparently a reaction of the first order in the complex ion, in fact, the rate-determining step of the decomposition is second order in the hydroxyl ion as well as in the complex ion. As such a reaction of the second order in the hydroxyl ion and the complex ion, we can assume the substitution reaction as well as the proton dissociation, such as

substitution

$$[Co(NH_2OH)_6]^{3+}+OH^- \rightarrow [Co(NH_2OH)_5OH]^{2+}+NH_2OH$$

proton dissociation

$$[Co(NH_2OH)_6]^{3+}+OH^- \rightarrow [Co(NH_2OH)_5NHOH]^{2+}+H_2O$$

But as is already stated, the spectrochemical consideration reveals that hydroxylamine is linked to the cobalt(III) ion more firmly than ammonia and that the hydroxyl ion is linked to the cobalt (III) ion less firmly than ammonia. Accordingly, the possibility of substituting the hydroxylamine can be excluded, and the proton dissociation can be regarded as the only possible rate-determining step of the decomposition.

Summary

The absorption spectrum of hexahydroxylamine cobalt(III) complex was measured and compared with the hitherto obtained data of the other hexammine cobalt(III) complexes. The frequencies of the first and second absorption bands of this complex were 68.5×10^{13} and ca. 94×10^{13} sec.$^{-1}$ respectively. These values are much greater than those found in other hexammine cobalt(III) complexes, and this fact may indicate the strong interaction between the central cobalt(III) ion and nitrogen atoms of the co-ordinating hydroxylamine. In addition to the study of absorption spectra, the rate of decomposition of this complex was measured. The rate of decomposition was proportional to the concentration of the hydroxyl ion, and the activation energy was 32.5 kcal. mole^{-1}. In order to explain the above results, the following equilibrium, assuming the proton dissociation, was proposed;

$$[Co(NH_2OH)_6]^{3+}+H_2O \rightleftarrows [Co(NH_2OH)_5NHOH]^{2+}+H^3O^+$$

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* According to Nakahara's report, the dimethylglyoximato group is situated ahead of ethylenediamine in the spectrochemical series, and forms a strongly covalent bond with the central cobalt(III) ion. A. Nakahara, This Bulletin, **27**, 260 (1954).