[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ANTIOCH COLLEGE]

# Properties of the Acidocobaltammines. II. Iodopentamminecobalt(III)[1]

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The rates of reaction for the formation and aquation of iodopentamminecobalt(III) and the mechanism of the reduction of iodopentamminecobalt(III) by iodide ion were determined. An explanation is offered for the difference in the relative stability of aquopentamminecobalt(III) and iodopentamminecobalt(III) in the presence of iodide ion.

Fluoro-, chloro- and bromopentamminecobalt(III) salts are readily obtained by the reaction of solutions containing aquopentamminecobalt(III) ion with fluoride, chloride and bromide ions respectively. This reaction is reversible and an equilibrium is established between the aquo, the acido, and the halide ions. The formation of the aquo complex from the acido ion (aquation) may be considered as the characteristic reactions of these pentammines.

Iodopentamminecobalt(III), however, cannot be made directly from solutions containing iodide and aquopentamminecobalt(III) ions.[2,3] Instead, iodine is slowly formed and the Co(III) ion is reduced to Co(II). When iodopentamminecobalt(III) salts are dissolved in water, a similar reaction occurs. It seemed worth while to investigate this anomalous behavior in order to establish whether the characteristic reactions of the other halogenopentammines occur in the case of iodopentamminecobalt(III) and to find the reaction responsible for the formation of iodine.

## Experimental

**Materials. Chloropentamminecobalt(III) Chloride.**—This compound was used as the starting material for the other Co(III) compounds and was prepared according to the method of Willard and Hall.[4]

**Aquopentamminecobalt(III) Iodide.**—Twenty-five grams (0.1 mole) of chloropentamminecobalt(III) chloride was dissolved in 400 ml. of water containing 4 g. (0.1 mole) of sodium hydroxide at room temperature. After filtering, to remove any cobalt hydroxide which may be present, 90 g. (0.6 mole) of sodium iodide was added and the solution was acidified to a *p*H of 5 with acetic acid. After standing overnight at 5°, the acid solution was filtered, washed with ice-cold water, and then alcohol; yield 90%.

**Iodopentamminecobalt(III) Perchlorate.**—The nitrate salt, prepared by the method of Werner[3] from aquopentamminecobalt(III) iodide, was converted to the perchlorate by repeated stirring with 5 molar sodium perchlorate acidified with perchloric acid until the supernatant solution contained only a small amount of nitrate ion. The perchlorate salt was then recrystallized by dissolving it at 45° in water acidified with perchloric acid, filtering, cooling and adding solid sodium perchlorate to make the final perchlorate concentration 1 molar. After standing for several hours below 5, the dark green (nearly black) crystals were filtered, washed with ice-cold water, alcohol and finally dried with ether. In this way, hexammine salts (the main impurity) were removed. The yield, based on aquopentamminecobalt(III) iodide, is 30%. After standing for six months in a desiccator, the perchlorate salt showed no signs of decomposition.

**Aquopentamminecobalt(III) Perchlorate.**—A modification of the method described by Basolo and Steninger[5] for the preparation of hydroxoaquobis-(ethylenediammine)-cobalt(III) bromide using an anion exchange resin was used to prepare the aquo perchlorate. Because of the slight solubility of the chloropentamminecobalt(III) chloride, this compound was dissolved in water containing one equivalent of sodium hydroxide before being passed through the resin bed. The effluent was neutralized with perchloric acid. Decomposition in the column was negligible and the neutralized effluent was used as a stock solution of aquopentamminecobalt(III) perchlorate. One-hundredth molar solutions were easily prepared in this way.

A sodium free salt could be obtained by evaporating slowly on a steam-bath 0.1 molar solutions prepared in the above manner until crystals began to form. After cooling in an ice-chest overnight, the filtered and washed crystals of aquopentamminecobalt(III) perchlorate were recrystallized from dilute perchloric acid.

**Analysis. Total Cobalt.**—Both chloro- and iodopentamminecobalt(III) react rapidly with Hg(II) to form the aquo complex ion whose concentration can be determined from its optical density at 498 mμ. Because of the ease and the high degree of purity with which chloropentamminecobalt(III) chloride can be prepared, it was used as a primary standard for obtaining the absorption spectrum of aquopentamminecobalt(III).

**Reducible Co(III).**—Iodopentamminecobalt(III) reacts rapidly at room temperature with a large excess of iodide ion to form iodine and Co(II). The iodine liberated can be titrated in the usual way.

**Total Iodide Ion.**—Iodide in the complex iodopentamminecobalt(III) reacts with bromine in a buffered acetate solution to form the aquo complex ion (in equilibrium with the bromo complex ion) and iodate ions. The excess bromine is then destroyed with formic acid and the iodate ion can be titrated in the usual manner without interference by Co(III).[6]

The results of these analyses are given in Table I.

TABLE I

ANALYSIS OF $[Co(NH_3)_5I](ClO_4)_2$

| Procedure | Co(III), % Calcd. | Co(III), % Obsd. | I⁻, % Calcd. | I⁻, % Obsd. |
|---|---|---|---|---|
| Total cobalt | 12.64 | 12.75<br>12.65 | 27.01 | |
| Reducible cobalt | | 12.74<br>12.56 | | 27.24<br>27.08 |
| Total iodine | | | | 27.20<br>26.85 |

**Spectral Measurements.**—The optical absorption spectra of iodo- and aquopentamminecobalt(III) perchlorate were determined with a Beckman quartz spectrophotometer using 1 cm. fused silica cells. The cell compartment was mounted between plates containing coils through which water of any desired temperature could be circulated. The solutions of iodopentamminecobalt(III) were prepared in 95% methanol at 1° in order to prevent the aquation or reduction of the iodo complex ion during the time (two hours) required to determine its spectrum. The effects of any reactions which might have taken place during this period were shown to be less than the error involved in making the measurements. All solutions contained thousandth molar perchloric acid which stabilizes the cobaltammines and prevents the hydrolysis of the aquo complex ion.

The absorption spectra of iodopentamminecobalt(III) and aquopentamminecobalt(III) have maxima at 288 and 498 mμ, respectively. The validity of Beer's law was established for each ion at these wave lengths which were then used in the reaction rate studies.

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(1) This paper was made possible through a grant-in-aid from the Research Corporation of America.

(2) J. Sand and G. Bokman, *Ber.*, **40**, 4497 (1907).

(3) A. Werner, *ibid.*, **41**, 3014 (1908).

(4) H. H. Willard and D. Hall, THIS JOURNAL, **44**, 2220 (1922).

(5) F. Basolo and D. H. Steninger, *ibid.*, **72**, 5748 (1950).

(6) L. Spitzer, *Ind. Eng. Chem., Anal. Ed.*, **8**, 465 (1936).

The formation of iodine by air oxidation in solutions containing large amounts of iodide ion interferes with the spectrophotometric determination of iodo- and aquopentamminecobalt(III) ions. The iodine was reduced by adding sodium sulfite to solutions which had been previously chilled in an ice-bath. Previous experiments showed that even at 85° the Co(III) complex was reduced very slowly by sulfurous acid.

**Procedure in Rate Studies.**—Stock solutions of both aquopentamminecobalt(III) and iodopentamminecobalt(III) perchlorate were prepared. The latter solutions were kept in an ice-chest. Aliquots from the stock solutions were then added to desired amounts of perchloric acid, sodium perchlorate and sodium iodide in a volumetric flask and the final volume was adjusted with distilled water. With the exception of the stock solutions of the cobaltammines, all solutions had previously been placed in the constant temperature bath for 30 minutes. The final ionic strength of each solution was 1 molal.

After the volume of the solutions was adjusted, the flasks were placed in a constant temperature bath maintained at 45 ± 0.02°. At desired intervals, 5-ml. samples of the reaction mixtures were rapidly removed from the flask and quickly chilled by delivering them into small flasks placed in an ice-bath. The time at which 50% of the sample was transferred to the cooled flask was recorded. After cooling, one drop of 1 molar sodium sulfite was added to the flask. Portions of this cooled sample were used to rinse the cell after which the optical density of the sample containing the sodium sulfite was determined at 1°.

## Results and Discussion

**The Reactions of Iodopentamminecobalt(III).**—When the initial concentration of iodopentamminecobalt(III) is of the order of $10^{-5}$ molal, then the change in the concentration of iodopentamminecobalt(III) corresponds to a first order reaction. Under these conditions the concentration of iodine formed is undetectable and the concentration of iodopentamminecobalt(III) is directly proportional to the optical density of the solution. A typical reaction curve is shown in Fig. 1 where the logarithm of the optical density is plotted against time. The average slope of several sets of data calculated by the method of least squares was $3.60 \times 10^{-3}$ min.$^{-1}$. The deviation within a single set of measurements was 2%.

As the initial concentration of iodopentamminecobalt(III) is increased, the curve obtained by plotting the logarithms of the optical density against time is no longer a straight line, but it is concave downward and consists of an induction period followed by a steeper straight line portion. This is shown in Fig. 1 where the data for the change in concentration of a solution of iodopentamminecobalt(III) perchlorate having an initial concentration of $2.5 \times 10^{-3}$ molar is plotted. The initial slope agrees with that obtained for the more dilute solutions of the iodo complex ion. The straight line portion of the curve becomes steeper and the induction period decreases with an increase in the initial concentration of iodopentamminecobalt(III) perchlorate.

Analysis of the final products in those experiments containing more concentrated solutions of iodopentamminecobalt(III) perchlorate showed the presence of iodine as well as aquopentamminecobalt(III). The equivalent concentration of iodine formed in every case was equal to the difference in the initial concentration of iodopentamminecobalt(III) and the final concentration of aquopentamminecobalt(III). The final iodide ion concentration is equal to the final concentration of aquopentamminecobalt(III). The results of a number of these experiments are included in Table II.

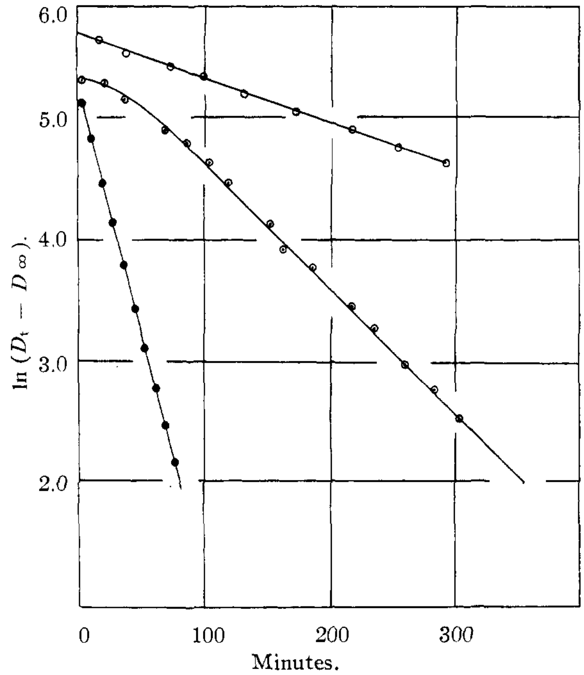

Fig. 1.—Reactions of iodopentamminecobalt(III) in aqueous solutions: O, $1 \times 10^{-5}$ molar Co(III); ⊙, $2.5 \times 10^{-3}$ molar Co(III); ●, $1 \times 10^{-5}$ molar Co(III) in $1 \times 10^{-3}$ molar sodium iodide.

Similar results were obtained in solutions which were saturated with iodine and in solutions which had been deoxygenated by having nitrogen passed through them. On the other hand, when sulfur dioxide was used to deoxygenate the solutions the rate of reduction increased, and the final concentration of aquopentamminecobalt(III) decreased. The results of one of these experiments are included in Table II.

TABLE II

TRANSFORMATION OF IODOPENTAMMINECOBALT(III)

Equiv. concn. in moles × $10^3$, $T = 45°$

| $Co(NH_3)_5I^{++}$ | $Co(NH_3)_5H_2O^{+++}$ | $I_2$ |
|---|---|---|
| 2.50 | 0.60 | 1.90 |
| 4.85 | .82 | 4.00 |
| 5.00 | .91 | 4.08 |
| 5.00[a] | .23 | 0.00 |
| 7.86 | 1.01 | 6.70 |
| 8.30 | 1.17 | 7.18 |
| 10.00 | 1.34 | 8.80 |

[a] $SO_2$ present.

When sodium iodide is present in solutions containing iodopentamminecobalt(III) perchlorate, the rate of disappearance of the iodo complex ion increases and the length of the induction period decreases. At the same time there is a corresponding increase in the amount of iodine and a decrease in the amount of aquopentamminecobalt(III) formed. The results of several of these experiments are given in Table III. When the initial sodium iodide concentration is considerably greater than that of iodopentamminecobalt(III) then a straight line curve is obtained (see Fig. 1). This line corresponds to a first order reaction with respect to the iodo complex ion.

TABLE III

REDUCTION OF IODOPENTAMMINECOBALT(III) BY IODIDE ION

Equiv. concn. in moles × $10^3$, $T = 45°$

| $Co(NH_3)_5I^{++}$ | $I^-$ | $Co(NH_3)_5$-$H_2O^{+++}$ | $I_2$ |
|---|---|---|---|
| 5.00 | 1.00 | 1.20 | 4.00 |
| 5.00 | 2.00 | 0.80 | 4.16 |
| 5.00 | 4.00 | 0.03 | 4.58 |
| 5.00 | 100.00 | | 4.95 |

When the rate constant corresponding to the disappearance of iodopentamminecobalt(III) in the presence of sodium iodide is plotted against the initial iodide ion concentration, the straight line curve shown in Fig. 2 is obtained. The equation of this curve is

$$K_{\text{obsd}} = k_1 + k_2[I^-] \qquad (1)$$

The constants $k_1$ and $k_2$ were determined by the method of least squares and were found to have the values 4 ± 0.2 × $10^{-3}$ min.$^{-1}$ and 11.7 ± 0.1 liters moles$^{-1}$ min.$^{-1}$, respectively.

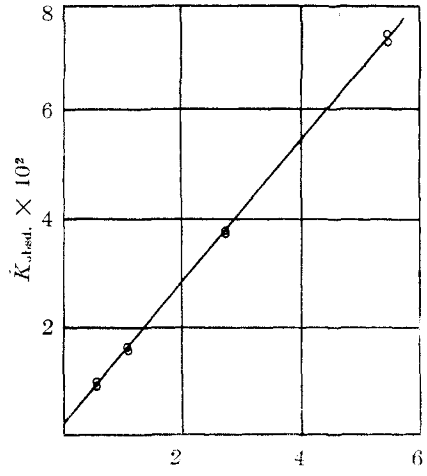

Fig. 2.—Rate of reduction of iodopentamminecobalt(III) in sodium iodide solutions.

**Reactions Involving Aquopentamminecobalt(III).**—Solutions of aquopentamminecobalt(III) in dilute perchloric acid are stable over a period of months at room temperature in diffuse daylight, but they are slowly decomposed in the presence of sodium iodide with the simultaneous formation of iodine. When the sodium iodide concentration is large relative to that of iodopentamminecobalt(III) the reaction rate is of first order with respect to the complex ion.

TABLE IV

THE REDUCTION OF AQUOPENTAMMINECOBALT(III) BY IODIDE ION

$T = 45°$

| Co(III)$^{+++}$ × $10^3$ | $I^-$ × $10^3$ | $H^+$ × $10^3$ | $/I^-$[a] |
|---|---|---|---|
| 4.95 | 0.25 | 0.75 | 7.60 |
| 4.95 | .25 | .05 | 7.62 |
| 4.95 | .50 | .50 | 7.64 |
| 4.95 | .50 | .05 | 7.60 |
| 5.25 | .75 | .25 | 7.38 |
| 5.25 | .75 | .05 | 7.42 |

[a] Average 7.55 ± 0.17 × $10^{-4}$ liter moles$^{-1}$min.$^{-1}$.

From the data in Table IV it can be seen that the rate is also a linear function of the iodide ion concentration and independent of the hydrogen ion concentration.

## Discussion

The data for the reactions involving iodo- and aquopentamminecobalt(III) indicate the occurrence of the following series of reactions

$$Co(NH_3)_5I^{++} + H_2O \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} Co(NH_3)_5H_2O^{+++} + I^- \qquad (2)$$

$$Co(NH_3)_5I^{++} + I^- \xrightarrow{k_2} Co(NH_3)_5I^+ + I \qquad (3)$$

$$Co(NH_3)_5I^{++} + 6H_2O \xrightarrow{k_3} Co(H_2O)_6^{++} + 5NH_3 + I^- \qquad (4)$$

$$I + I \underset{k_{-4}}{\overset{k_4}{\longleftarrow}} I_2 \qquad (5)$$

The rate constant $k_1$, for the aquation of iodopentamminecobalt(III) corresponds to $k_1$ in equation (1). It was found to be 3.60 ± 0.05 × $10^{-3}$ min.$^{-1}$ by carrying out the reaction in very dilute solutions (1 × $10^{-5}$ molal) and 4.0 ± 0.2 × $10^{-3}$ min.$^{-1}$ by observing the rate of reduction of iodopentamminecobalt(III) in the presence of sodium iodide. The rate constant $k_2$, for the reduction of iodopentamminecobalt(III) corresponds to $k_2$ in equation (1) and has a value of 11.7 ± 0.1 liters mole$^{-1}$ min.$^{-1}$. Therefore at a maximum iodide ion concentration of 1.0 × $10^{-5}$ molal obtained by the aquation of 1.0 × $10^{-5}$ molal iodopentamminecobalt(III) the error in the determination of the rate of aquation of iodopentamminecobalt(III) due to its reduction by iodide ion would be less than 3%. The figure 3.60 × $10^{-3}$ molal was calculated from data obtained before the aquation of iodopentamminecobalt(III) was 50% complete and may be too high by about 1%. This error is less than that observed for a single set of measurements.

If the iodopentamminecobalt(III) were not reduced by iodide ion, then an equilibrium would be established between aquo- and iodopentamminecobalt(III). The value of the equilibrium constant for this reaction

$$Co(NH_3)_5I^{++} + H_2O = Co(NH_3)_5H_2O^{+++} + I^-$$

would be

$$K = [Co(NH_3)_5H_2O^{+++}][I^-]/[Co(NH_3)_5I^{++}] = \frac{k_1}{k_{-1}} = 4.8$$

and iodopentamminecobalt(III) would have nearly the same free energy of formation and oxidation reduction potential as aquopentamminecobalt(III).

Bjerrum[7] has pointed out that no particular amminocobalt(III) complex is stable in an ammonia-free solution. The calculation of the oxidation–reduction potential of a complex ion from its constants of formation from the aqueous ion give no indication of the reaction rates of the complex ion. If the rate of transformation of the complex ion to the simple aqueous ion is very slow (as it is for

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(7) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, p. 251.

the cobaltammines), then the complex ions appear to be *stable*.

The presence, then, of the iodide ion within the complex itself in iodopentamminecobalt(III) would be expected to have little or no effect on the stability of this Co(III) ion. When dry, or present in dilute solutions, iodopentamminecobalt(III) behaves similarly to both bromo- and chloropentamminecobalt(III). Its rapid reduction in the presence of additional iodide ions indicates, however, that the reduction of iodopentamminecobalt(III) occurs when there is a collision between an iodide ion in solution and the complexly held iodide ion. An electron is then transferred from the former ion to the cobalt atom after which the Co(III) complex is rapidly converted in successive steps to the normal aqueous cobalt ion.

Because of the loss of iodide ion from the solution in reaction (2) and its reoccurrence due to reaction (3), the reduction of iodopentamminecobalt(III) by iodide ion possesses the characteristics of a catalytic reaction.

I wish to thank Robert Larson for his help in preparing the cobalt compounds and obtaining the rate data.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

# Complex Acids of Cobalt and Chromium. The Green Carbonatocobalt(III) Anion*

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Solutions of free acids containing complex anions of cobalt and chromium have been prepared by the use of ion-exchange resins. These acids reacted with carbonatopentamminecobalt(III) nitrate giving crystalline, insoluble compounds containing the aquopentamminecobalt(III) cation. A method is reported for making the green carbonato anion of cobalt(III), and a stable salt of the anion is described.

The use of cation exchange resins affords a simple and rapid method for preparing pure solutions of heteropoly acids of molybdenum and tungsten.[1] The solutions are free from metallic cations and they give reliable information when used for potentiometric and other measurements.

The same procedure has proved equally successful for obtaining solutions of free acids with complex anions of cobalt and chromium. Acids corresponding to the coördination compounds: ammonium tetranitrodiamminecobaltate(III) (Erdmann's salt), potassium trioxalatocobaltate(III), potassium trioxalatochromate(III) and ammonium tetrathiocyanatodiamminechromate(III), (Reinecke's salt) were prepared by the use of an ion-exchange column, and the effluents were tested for metallic cations, with negative results in each case. The acids in the effluent were about 0.1 *M* and the *p*H of the solutions between one and two. The colors corresponded closely to those of the original salts. These salts were regenerated from the acids by neutralization with the appropriate carbonate or base.

Solutions of the acids in closed containers were stable for a number of days, but the trioxalatochromium(III) acid alone was stable on evaporation, yielding a homogeneous mass of blue needles.

All of the acids were characterized by conversion to the slightly soluble, crystalline compounds formed with the aquopentamminecobalt(III) cation. These salts were made readily by adding a solution of carbonatopentamminecobalt(III) nitrate to solutions of the acids, according to the equation

$$[CoCO_3(NH_3)_5]NO_3 + H_3[Cr(C_2O_4)_3] \longrightarrow [CoH_2O(NH_3)_5][Cr(C_2O_4)_3] + CO_2 + HNO_3$$

Effervescence occurred as soon as the solutions were mixed, followed quickly by an almost quantitative precipitation of the complex salt.

It was anticipated that the intensely green tricarbonatocobalt(III) anion, the product of the well-known Field–Durant reaction, would not withstand contact with the resin in its hydrogen ion phase. As soon as the green solution came in contact with the resin, effervescence occurred throughout the column, and the effluent was colorless. The green anion was made and characterized by a new method described below.

## Experimental

The column and resin (Amberlite IR-100) were the same as used in the preparation of the heteropoly acids. This resin has a capacity of 1.75 millequivalents of exchangeable ion per gram of resin; 200% of the theoretical amount of resin was found sufficient to effect complete exchange. To ensure complete removal of any previously exchanged cations, 300% of the theoretical volume of 10% HCl was used to regenerate the resin.

Ten grams of ammonium tetranitrodiamminecobaltate(III) (Erdmann's salt) was dissolved in 300 ml. of water, giving a solution of *p*H 5.02. The solution was passed slowly through the column and the effluent was tested for ammonium ion by Nessler reagent, with negative results. The liquid leaving the column had a *p*H of 1.30 and showed the brownish-yellow color of the original salt.

A portion of this solution was treated dropwise with dilute ammonia until a *p*H of 7 was reached. On evaporation, typical crystals of Erdmann's salt separated. Potassium, sodium and lithium salts were likewise obtained after neutralizing portions of the acid with the bicarbonates of the metals.

Solutions of potassium trioxalatocobaltate(III), potassium trioxalatochromate(III) and potassium tetrathiocyanatochromate(III) (Reinecke's salt) were passed through the ion-exchange column in the same way, yielding effluents which were dark green, blue and violet-red, respectively. All of the effluents showed a *p*H close to 1.30; the original salts were regenerated in each case by careful neutralization with potassium bicarbonate, and evaporation.

The complex acids were then characterized by conversion to the insoluble derivatives with the aquopentamminecobalt(III) cation, according to the following procedure.

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* Presented at the Miniature Meeting at the Philadelphia Section of the American Chemical Society, January 29, 1953.

(1) L. C. W. Baker, B. Loev and T. P. McCutcheon, THIS JOURNAL, **72**, 2374 (1950).