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.

YELLOW SPRINGS, OHIO

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

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

BY THOMAS P. MCCUTCHEON AND WILLIAM J. SCHUELE

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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).

One hundred grams of Erdmann's salt in 2,000 ml. of water was converted to the acid, and to this solution there was added a solution of 26.6 g. of carbonatopentamminecobalt(III) nitrate,[2] always keeping the acid in excess. Effervescence was observed almost immediately as the carbonate group of the cation was replaced, and an orange, crystalline precipitate of aquopentamminecobalt(III) tris-(tetranitrodiammine)-cobaltate(III) separated quickly in almost quantitative yield.

Anal. Calcd. for $[Co(H_2O)(NH_3)_5][Co(NO_2)_4(NH_3)_2]_3$: Co, 23.74; N, 32.44. Found: Co, 23.74; N, 32.37.

The solubility was 0.12 g. per 100 g. water at 20°. The derivatives of the other complex acids with the aquopentammine cation were obtained by the same method.

Aquopentamminecobalt(III) trioxalatocobaltate(III), small, dark green crystals, insoluble in water.

Anal. Calcd. for $[Co(H_2O)(NH_3)_5][Co(C_2O_4)_3]$: Co, 24.27; N, 14.43. Found: Co, 24.22; N, 14.33.

Aquopentamminecobalt(III) trioxalatochromate(III), fine brown needles, insoluble in water.

Anal. Calcd. for $[Co(H_2O)(NH_3)_5][Cr(C_2O_4)_3]$: Co, 12.32; Cr, 10.87; N, 14.65. Found: Co, 12.30; Cr, 10.88; N, 14.62.

Aquopentamminecobalt(III) tris-(tetrathiocyanatodiamminechromate)(III), fine red crystals; solubility 0.039 g. in 100 ml. water at 20°. *Anal.* Calcd. for $[Co(H_2O)(NH_3)_5][Cr(SCN)_4(NH_3)_2]_3$: Co, 5.27; Cr, 13.96; N, 28.84. Found: Co, 5.23; Cr, 13.87; N, 28.74.

Cobalt was determined as sulfate in the first two compounds, electrolytically in the others. Chromium was oxidized to the dichromate ion, and determined volumetrically, and nitrogen was determined by the semi-micro Kjeldahl method.

Aquopentamminecobalt(III) trioxalatocobaltate(III) was reported by Sörensen,[3] and the aquopentamminecobalt(III) derivative of Reinecke's salt was used by Brönsted[4] in studies on the solubilities of strong electrolytes.

The Green Carbonatocobalt(III) Anion.—The intensely green solution resulting from the Field–Durant reaction[5] (oxidation of a cobalt(II) salt in the presence of an excess of an alkali bicarbonate) has been the subject of numerous investigations resulting in differing opinions about the composition and structure of the complex. An excellent account of earlier work has been given by Duval.[6] The complex has been used recently in a volumetric method for the determination of cobalt.[7] As stated above, the free acid cannot be obtained by the ion-exchange method.

We have found that the green anion may be prepared readily from a cobalt(III) compound, and it has been converted to a stable derivative with the hexamminecobalt(III) cation,[6] according to the following procedure: a solution containing 2.2 g. of carbonatotetramminecobalt(III) sulfate dissolved in 90 ml. of water at 60° was added to a hot (90°) solution containing 28 g. of potassium bicarbonate and 1.5 g. of potassium persulfate in 80 ml. of water. The mixture was heated on the steam-bath until the red color changed to dark green (about 25 min.), to which was then added 4 g. of hexamminecobalt(III) nitrate dissolved in 100 ml. of water. One-half of the resulting solution was added gradually to another solution of hexamminecobalt(III) nitrate containing 2 g. of the complex in 50 ml. of water, which had been heated just to the boiling point on the hot-plate. The addition was made at such a rate as to maintain the temperature as close to the boiling point as possible without allowing intervals of boiling.

A finely crystalline, grayish-green precipitate of hexamminecobalt(III) tricarbonatocobaltate(III) separated during the process, which was filtered on a sintered glass filter (contact with filter paper caused partial reduction), washed with cold water, and air-dried. The second half of the solution was treated in the same manner. The total yield was 70%. After thorough drying in a dust-free atmosphere, there has been no evidence of decomposition after six months.

Anal. Calcd. for $[Co(NH_3)_6][Co(CO_3)_3]$: Co, 29.46; N, 21.01. Found: Co, 29.44; N, 21.02.

The solubility was 0.038 g. per 100 g. of water at 20°.

Acknowledgment.—We are indebted to Mr. Inman H. Moon, of this Laboratory, for his work on the Field–Durant reaction.

PHILADELPHIA, PENNA.

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[2] Arthur B. Lamb and Karol J. Mysels, *ibid.*, **67**, 468 (1945).

[3] S. P. L. Sörensen, Diss. 87, Copenhagen, 1899.

[4] J. N. Brönsted and A. Petersen, THIS JOURNAL, **43**, 2269 (1921).

[5] F. Field, *Quart. J. Chem. Soc.*, **14**, 51 (1862); R. G. Durant, *ibid.*, **87**, 1782 (1905).

[6] R. Duval, "Traité de Chimie Minérale," Tome X, Masson et Cie, Paris, 1933, p. 968.

[7] H. A. Laitinen and L. W. Burdett, *Anal. Chem.*, **23**, 1268 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

The Dissociation Constants of Acids in Salt Solutions. V. Monohydroxycyclohexanecarboxylic Acids

BY MARTIN KILPATRICK AND JEROME G. MORSE[1]

RECEIVED AUGUST 22, 1952

The *cis*- and *trans*-hydroxy-substituted cyclohexanecarboxylic acids have been synthesized and their dissociation constants measured. An attempt has been made to correlate the structures of these acids with their dissociation constants. The calculated values of the relative acid strengths using electrostatic theory are in poor agreement with the observed values.

The purpose of this work was to study the dissociation constants of the monohydroxycyclohexanecarboxylic acids and if possible to relate the structure to the relative acid strengths in the solvents water, methyl and ethyl alcohol, and ethylene glycol.

The experimental method was the same as given in papers I[2] and II.[3] In all cases the reference acid was cyclohexanecarboxylic acid and the equilibrium measured was

$$A_x + B_0 \rightleftarrows A_0 + B_x \qquad (1)$$

where A_x is the hydroxy substituted acid and B_x the conjugate base. The equilibrium constant of the reaction is the ratio of the dissociation constant of the substituted acid to the parent acid.

A limiting factor in the present investigation which precluded a more extensive comparison with aromatic systems previously examined was the inherent difficulty encountered in the synthesis of these stereoisomeric acids. The hydroxy-substi-

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[1] This paper was abstracted from the dissertation presented by Jerome Gilbert Morse to the Graduate School of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1952.

[2] M. Kilpatrick, THIS JOURNAL, **75**, 584 (1953).

[3] M. Kilpatrick and R. D. Eanes, *ibid.*, **75**, 586 (1953).