

170. *Researches on Ammines. Part V. Dihydroxotetramminocobaltic Hydroxide and its Derivatives.*

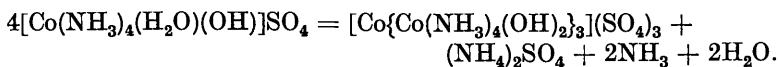
By HERBERT JOSEPH SEYMOUR KING.

JOB (*Compt. rend.*, 1920, **170**, 843; 1922, **174**, 613) added alkali hydroxide gradually to diaquotetramminocobaltic sulphate and chloride, and concluded, from measurements of electrical conductivity and of the *E.M.F.* produced on contact with a platinum wire, that no hydroxyl ions were present until more than 2 equivs. of alkali had been added. Hence, when 2 equivs. of alkali are present, the solutions should contain salts of the dihydroxotetramminocobaltic series, none of which, however, have been prepared :



The purpose of this investigation was to verify the existence of this complex ion, and if possible to isolate its salts.

The filtrate from the interaction of diaquotetramminocobaltic sulphate and 2 equivs. of barium hydroxide was treated with 1 mol. of ammonium picrate, yielding a precipitate of *tris(dihydroxotetramminocobaltic)cobaltic picrate*. Salts of this series are prepared from diaquotetramminocobaltic salts by treatment with alkalis, or from solutions of hydroxo-aquotetramminocobaltic salts by spontaneous decomposition. This result, therefore, suggested that the filtrate originally contained not dihydroxo- but hydroxo-aquotetramminocobaltic sulphate, which decomposed during filtration :



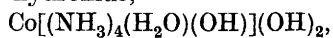
As filtration was tedious, and the solution necessarily somewhat dilute, this reaction was not further examined.

When diaquotetramminocobaltic chloride is triturated with an excess of moist silver oxide, a deep-red alkaline filtrate is obtained, which, if Job's views be correct, should contain dihydroxotetramminocobaltic hydroxide, and should yield a salt of this series when treated with 1 equiv. of an acid. Concentrated solutions of this hydroxide were mixed with 1 equiv. of hydrochloric, nitric, or sulphuric acid, and the ice-cold liquids were treated with excess of alcohol and ether. The first two acids yielded only oils which did not solidify, but sulphuric acid gave a brown precipitate of tris-(dihydroxotetramminocobaltic)cobaltic sulphate. When 2 equivs. of nitric acid were employed, hydroxo-aquotetramminocobaltic nitrate readily separated. Evidently the dihydroxotetramminocobaltic salts of these acids, if they exist at all, are too soluble to be obtained in this way. It was shown in Part I (J., 1924, 125, 1336) that when 2 : 4-dinitro- α -naphthol-7-sulphonic acid solution was added to a solution of hydroxopentamminocobaltic hydroxide, the hydroxopentamminocobaltic salt was precipitated in place of the expected aquopentammine, even when excess of the precipitant was employed. A similar result was obtained on precipitating hydroxopentamminochromic hydroxide with excess of picric acid or ammonium dipicrylamide. It appeared therefore that these acids, whose salts with cobaltamine bases are very sparingly soluble, would be particularly likely to react with the hydroxide derived from diaquotetramminocobaltic chloride, with precipitation of dihydroxotetramminocobaltic salts. It was found that 1 equiv. of 2 : 4-dinitro- α -naphthol-7-sulphonic acid yielded no precipitate with the hydroxide, while 2 equivs. yielded the *hydroxo-aquotetrammino*-salt. One mol. of picric acid yielded the *picrate* of the same base, and 1 mol. of ammonium dipicrylamide gave *tris(dihydroxotetramminocobaltic)-cobaltic dipicrylamide*. In the last case the primary product was probably the *hydroxo-aquotetrammino*-salt, and this was decomposed by the liberated ammonia, for by treating the hydroxide with 1 mol. of nitric acid before adding the ammonium dipicrylamide, *hydroxo-aquotetramminocobaltic dipicrylamide* was obtained. When the hydroxide solution, to which 1 mol. of nitric acid had been added, was treated with sodium dithionate, it yielded tris(dihydroxotetramminocobaltic)cobaltic dithionate on standing. These results suggested that the hydroxide contained, not dihydroxotetrammino-, but hydroxo-aquotetrammino-cobaltic hydroxide, since all the salts obtained from it by treatment with 1 equiv. of acid were hydroxo-aquotetrammines or their decomposition products.

The nature of the hydroxide and its derivatives was then investigated by measurement of electrical conductivities. The hydroxide can be formulated as

(1) dihydroxotetramminocobaltic hydroxide, $[\text{Co}(\text{NH}_3)_4(\text{OH})_2]\text{OH}$,

(2) hydroxo-aquatetramminocobaltic hydroxide,



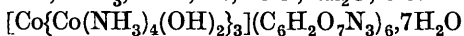
or (2) dihydroxotetramminocobaltic hydroxide, $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{OH}$.

cobaltic hydroxide and its salts. The fact that no solid salts of the series can be isolated is presumably due to their solubility being much higher than that of the corresponding hydroxo-aquo-tetrammines.

EXPERIMENTAL.

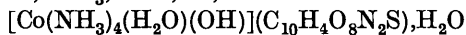
Unless otherwise stated, the compounds were precipitated in the cold and, before analysis, were washed successively with alcohol and ether and kept over-night in a vacuum over soda-lime.

Interaction of Diaquotetramminocobaltic Sulphate and Barium Hydroxide.—Diaquotetramminocobaltic sulphate (5 g.) was shaken with 2 equivs. of cooled barium hydroxide solution, and the filtrate, which smelt of ammonia, was treated with ammonium picrate (1 mol.), yielding an immediate precipitate of *tris(dihydroxotetraamminocobaltic)cobaltic picrate* (3.4 g. of large yellow needles). Found : Co, 11.2; NH₃, 10.0; N, 20.9; H₂O, 6.6.



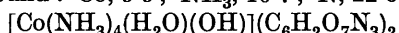
requires Co, 11.6; NH₃, 10.0; N, 20.6; 7H₂O, 6.2%. Water was estimated by finding the loss in weight on heating for 3 hours at 85°, allowance being made for ammonia lost.

Hydroxo-aquo-tetramminocobaltic Salts.—2 : 4-Dinitro- α -naphthoxide-7-sulphonate. Moist silver oxide (from 10 g. of nitrate) was cooled to 0° and triturated for 4 mins. with 2.5 g. of diaquotetramminocobaltic chloride. After filtration, the residue was washed with ice-cold water, and the resulting hydroxide solution was treated with a solution of 3.4 g. (2 equivs.) of trihydrated 2 : 4-dinitro- α -naphthol-7-sulphonic acid. The precipitate (5.2 g. of yellow plates) was washed with water and dried in a vacuum over soda-lime for 3 days {Found : Co, 12.1; NH₃, 13.6; N, 17.2.



requires Co, 12.0; NH₃, 13.8; N, 17.1%. When heated for 3 hours at 85°, the salt lost 2% of its ammonia and 1 mol. of water—probably that in the complex. When the hydroxide was treated with 1 equiv. of the sulphonic acid, no precipitate was obtained.

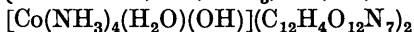
Picrate. 4 G. of diaquotetramminocobaltic chloride were converted into the hydroxide, which was treated with 3.4 g. (1 mol.) of picric acid in 300 c.c. of water, yielding an immediate precipitate (4.2 g. of yellow needles). The filtrate gave a further copious precipitate with picric acid. The original precipitate was collected and analysed {Found : Co, 9.9; NH₃, 10.7; N, 22.6.



requires Co, 9.5; NH₃, 11.0; N, 22.7%. A purer product was obtained by using 2 mols. of picric acid (Found : Co, 9.8; NH₃, 11.1; N, 22.9%).

Dipicrylamide. This salt was obtained as a scarlet precipitate

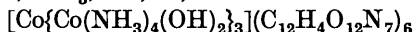
when the hydroxide was treated successively with 1 mol. each of nitric acid and ammonium dipicrylamide. The product was washed with water only, being somewhat soluble in alcohol and readily soluble in ether {Found : Co, 6.1; NH₃, 6.6; N, 24.0.



requires Co, 5.7; NH₃, 6.6; N, 24.3%}.

Tris(dihydroxotetramminocobaltic)cobaltic Salts.—Dipicrylamide.

This compound was obtained, with liberation of ammonia, as a scarlet precipitate when the foregoing hydroxide was treated with 1 mol. of ammonium dipicrylamide. It was washed with water {Found : Co, 7.4; NH₃, 6.5; N, 23.6.



requires Co, 7.4; NH₃, 6.4; N, 23.9%}.

Dithionate. The tetrahydrate, described by Jörgensen (*Z. anorg. Chem.*, 1898, **16**, 193), was obtained when the hydroxide was treated successively with 1 mol. of nitric acid and 1 equiv. of sodium dithionate, large brown needles separating on standing (Found : Co, 21.5; NH₃, 18.4. Calc. : Co, 21.6; NH₃, 18.7%).

Hydroxoquotetramminocobaltic Salts.—The nitrate, which Werner (*Ber.*, 1907, **40**, 4115) prepared by saturating the solution of the bromide of the series with sodium nitrate, was conveniently obtained in quantity by treating ice-cold dihydroxotetramminocobaltic hydroxide (from 5 g. of the diaquo-chloride) with 2*N*-nitric acid (2 mols.). Gradual addition of 400 c.c. of cooled alcohol yielded a precipitate of long reddish-violet needles, and crystallisation was completed by addition of ether (yield 3.8 g.) (Found : Co, 20.6; NH₃, 23.6; N, 29.1. Calc. : Co, 20.6; NH₃, 23.8; N, 29.4%). The compound was readily soluble in concentrated ammonia.

The corresponding bromide was not obtained pure by Werner's method (*loc. cit.*), but was readily prepared in 50% yield by dissolving the nitrate of the series in 2 parts of ammonia (*d* 0.880) and 2 of water, shaking the solution with 2½ parts of solid ammonium bromide, and washing the crystalline precipitate free from ammonium bromide with methyl alcohol (Found : Co, 18.6; NH₃, 21.4; Br, 49.1. Calc. : Co, 18.3; NH₃, 21.2; Br, 49.6%).

Electrical Conductivities.—It was shown in Part II (*loc. cit.*, p. 2105) that salts of bivalent cobaltamine and chromamine kations give, for the dilution range 32—1024 litres, a rectilinear $\lambda-C^{\frac{1}{2}}$ graph, and this rule has been found to apply also to hydroxoquotetramminocobaltic nitrate and bromide. For dihydroxotetramminocobaltic chloride, the same graph was rectilinear up to a dilution of 261.4 litres, but, at greater dilutions, it fell below the actual conductivity values. These values, which are in parentheses in the tables, were doubtless affected by hydrolysis, and were ignored in the calculation

of λ_{∞} . The graph for dihydroxotetramminocobaltic hydroxide was rectilinear up to a dilution of 263.8 litres. Resistances were measured by the Kohlrausch method, the bridge being replaced by a Post Office box. The specific conductivity of the water was 0.59 to 0.67×10^{-6} mho at 0° .

Conductivity Data.—The dilution v is given in litres per mol., and the molecular conductivity λ in mhos. The conductivities at infinite dilution were obtained by means of the $1/\lambda - (c\lambda)^{n-1}$ graph (Noyes and Coolidge, *Carnegie Inst. Pub.*, No. 63, 50).

Hydroxoquatetramminocobaltic salts.

v	32	64	128	256	512	1024	∞
λ_0 for [Co(NH ₃) ₄ (H ₂ O)(OH)](NO ₃) ₂	99.8	109.9	117.5	123.2	128.1	131.8	141.7
λ_0 for [Co(NH ₃) ₄ (H ₂ O)(OH)]Br ₂ ...	—	116.3	123.7	129.6	134.7	137.0	146.9

A fresh solution was prepared for each measurement. The recorded data are the means of two identical or closely concordant results. The aqueous solutions of these salts were quite stable at 0° , but it was not possible to take readings at 25° , owing to rapid decomposition.

Dihydroxotetramminocobaltic hydroxide, [Co(NH₃)₄(OH)₂]OH.

v	31.23	65.96	125.0	263.8	511.0	1002	∞
λ_0	117.9	120.4	121.8	122.8	121.5	113.7	—
λ_0 (corr.) ...	118.0	120.6	122.2	123.6	(123.0)	(116.6)	126.6

The hydroxide solution was prepared as described on p. 1278, conductivity water at 0° being used. A fresh solution (app. $M/32$) was prepared for each measurement, and its concentration was determined by an ammonia estimation. After cooling to 0° and dilution to the required concentration with conductivity water at 0° , the conductivity was determined immediately. A positive water correction was applied (Lamb and Yngve, *loc. cit.*). Lamb and Yngve's results were slightly lower than those now recorded ($\lambda_0 = 116.4$ mhos at $v = 152$).

Dihydroxotetramminocobaltic chloride.

v	33.98	67.96	79.94	159.9	261.4	524.4	1036	∞
λ_0	52.25	55.08	55.71	57.72	59.32	(61.16)	(69.60)	64.10

An approximately $M/32$ -hydroxide solution was prepared at 0° , and its concentration was determined by estimation of ammonia in 10 c.c., after which the remainder was treated with the calculated amount of $N/10$ -hydrochloric acid. After dilution with conductivity water at 0° to the required concentration, the conductivity was determined immediately, for, with the more dilute solutions, it increased on standing.

Ionic Mobilities (at 0°).—*Hydroxoquatetramminocobaltic ion.* The data for the nitrate and bromide gave mobility 60.9 and 60.7 ($n = 1.50$ and 1.52). The mean value 60.8 has been adopted. The

value obtained in Part II (*loc. cit.*) for the mobility of the hydroxopentamminocobaltic ion at 0° was 76.6, so that replacement of an ammonia by a water molecule has reduced the mobility of the bivalent kation by 15.8 mhos.

Dihydroxotetramminocobaltic ion. The data for the hydroxide and chloride give mobility 21.6 and 23.0 mhos ($n = 1.52$ and 1.50). The latter value has been adopted. The values employed for the mobilities of the anions were Cl', 41.1; Br', 43.1; NO₃', 40.4; OH', 105.0.

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