

**132. Researches on Ammines. Part VII. The Action of Acids on Dihydroxotetramminocobaltic Hydroxide.**

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It was shown in Part V (J., 1932, 1275) that diaquotetramminocobaltic chloride, when triturated with moist silver oxide, gave a solution of dihydroxotetramminocobaltic hydroxide,  $[\text{Co}(\text{NH}_3)_4(\text{OH})_2]\text{OH}$ , which yielded, with one equivalent of an acid, a solution of a dihydroxotetramminocobaltic salt, while with two equivalents, solid hydroxoquo-tetramminocobaltic salts were obtained.

As it appeared likely that the hydroxide would prove a suitable reagent for the introduction of acid radicals into the tetramminocobaltic complex, the action upon it of three equivalents of acid has now been investigated. To introduce dibasic radicals into the complex, a concentrated solution of the hydroxide was treated successively with one equivalent of nitric acid and two of the dibasic acid. With sulphuric acid, sulphatoquo-tetramminocobaltic nitrate,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SO}_4)]\text{NO}_3$ , was obtained. It was distinguished from the isomeric  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NO}_3)]\text{SO}_4$  by measurement of its electrical conductivity at  $0^\circ$ , which was of the order required for a salt of a univalent kation.

Replacement of sulphuric by oxalic acid yielded *oxalatotetramminocobaltic nitrate*. Similarly malonic acid gave *malonatotetramminocobaltic nitrate*, and the formulæ were checked in both cases by measurement of the electrical conductivity. Succinic and phthalic acids gave syrups which did not solidify, though the intense red colour which developed on warming indicated that the radicals had entered the complex.

Salicylatotetramminocobaltic nitrate, obtained by Morgan and Main Smith (J., 1922, 121, 1965), could not be prepared by this method, the precipitate consisting of the *hexahydrate* of tris(dihydroxotetramminocobaltic)cobaltic nitrate:  $4[\text{Co}(\text{NH}_3)_4(\text{OH})_2]\text{OH} + 4\text{C}_6\text{H}_4(\text{OH})\text{CO}_2\text{H} + 6\text{HNO}_3 = [\text{Co}\{\text{Co}(\text{NH}_3)_4(\text{OH})_2\}_3](\text{NO}_3)_6 + 4\text{C}_6\text{H}_4(\text{OH})(\text{CO}_2\text{NH}_4) + 6\text{H}_2\text{O}$ .

The sulphatoquo- differs from the oxalato- and the malonato-salt in that the bivalent acid radical is attached to the cobalt atom by one link instead of two, and the electrical conductivity measurements recorded for the two types of salt differ markedly. For sulphatoquotetramminocobaltic nitrate, the  $\lambda-C^{1/3}$  graph, with  $\lambda$  as ordinate, curves steeply upwards with diminishing concentration, indicating that progressive hydrolysis to the diaquotetramminocobaltic salt occurs. No increase of conductivity on standing was detected, so equilibrium was evidently attained rapidly. At a dilution of 512 litres, the molecular conductivity of the sulphatoquo-nitrate was 61% higher than that of the oxalato- and 51% higher than that of the malonato-nitrate. The conductivities of the

oxalato- and the malonato-salt show little if any indication of hydrolysis, giving rectilinear  $\lambda-C^{13}$  graphs (see Part II, J., 1925, 127, 2105).

When the hydroxide was treated with three equivalents of hydrochloric, hydrobromic, nitric, or picric acid, the acidoaquotetramminocobaltic salt,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{X}]\text{X}_2$ , was obtained in each case. With  $\text{X} = \text{Cl}$  or  $\text{Br}$ , the anhydrous salts were obtained, and the identity of the former was confirmed by converting it into *chloroaquatetramminocobaltic picrate*. With  $\text{X} = \text{NO}_3$ , however, the hemi-hydrate was obtained; this became anhydrous when kept over sulphuric acid. Its electrical conductivity at  $0^\circ$  increased on standing. Even when measured as rapidly as possible, the values obtained were, at all concentrations, much higher than those required for a salt of a bivalent cation, indicating very extensive hydrolysis to diaquatetramminocobaltic nitrate.

*Picratoquatetramminocobaltic picrate* was obtained as the tetrahydrate, and was shown not to be the diaquo-salt by measurement of its molecular conductivity, which at  $25^\circ$  and  $v = 4096$  litres, was 296.2 mhos, *i.e.*, of the order required for a salt of a bivalent cation, and much lower than the expected value for diaquatetramminocobaltic picrate. Werner and Miolati (*Z. physikal. Chem.*, 1893, 12, 42) recorded 417.4 mhos for the molecular conductivity of diaquatetramminocobaltic bromide at  $25^\circ$  and  $v = 2,000$  litres.

With three equivalents of hydriodic acid, the hydroxide yielded *iris(dihydroxotetramminocobaltic)cobaltic iodide*,  $[\text{Co}\{\text{Co}(\text{NH}_3)_4(\text{OH})_2\}_3]\text{I}_6$ , instead of the expected iodoaquotetramminocobaltic salt.

Ephraim (*Ber.*, 1923, 56, 1538) stated that he obtained iodoaquotetramminocobaltic iodide by mixing solutions of diaquatetramminocobaltic chloride and potassium iodide. He recorded no analyses, however, and repetition of his experiment yielded the tris(dihydroxotetramminocobaltic)cobaltic salt, so that neither diaquo- nor iodoaquotetramminocobaltic iodide has yet been obtained.

These results show that, in cases where the free acid is available, acidification of dihydroxotetramminocobaltic hydroxide provides a new method, of fairly general applicability, for introducing acid radicals into the tetramminocobaltic complex, and the method has the advantage that the salts are obtained in analytically pure condition.

#### EXPERIMENTAL.

$[\text{Co}(\text{NH}_3)_4(\text{OH})_2]\text{OH}$  was obtained in solution by triturating 4 g. of  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_2$  for 4 min. with freshly pptd. moist  $\text{Ag}_2\text{O}$  (from 16 g. of  $\text{AgNO}_3$ ) at  $0^\circ$ . After filtration, the residue was washed with a little ice-cold  $\text{H}_2\text{O}$ , so that the vol. of the hydroxide solution did not exceed 40 c.c. This was particularly necessary in preparing the more easily sol. salts, for, although they are insol. in  $\text{EtOH}$  and  $\text{Et}_2\text{O}$ , excess of these reagents does not necessarily ppt. them completely (or even at all) if the solution is too dil. For analysis, the salts were washed successively with  $\text{EtOH}$  and  $\text{Et}_2\text{O}$ , and left in vac. over soda-lime over-night (picrates were washed first with  $\text{H}_2\text{O}$ ).

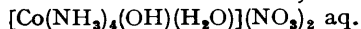
*Introduction of Dibasic Radicals.*—The above amount of hydroxide solution was treated successively with 1 equiv. of 2N- $\text{HNO}_3$  and 2 equiv. of the dibasic acid, the latter if solid being shaken with the solution till dissolved. On heating to  $60-70^\circ$ , the red colour was intensified considerably. The filtered solution was cooled to  $0^\circ$ , and ice-cold  $\text{EtOH}$  was added, if necessary, till pptn. was complete. Very sol. salts required addition of  $\text{Et}_2\text{O}$  also.

1. With  $\text{H}_2\text{SO}_4$ , anhyd. sulphatoaquotetramminocobaltic nitrate was obtained, pptn. with 20 c.c. of  $\text{EtOH}$  yielding 2.5 g. of hexagonal pink plates (Found: Co, 19.5;  $\text{NH}_3$ , 22.6;  $\text{SO}_4$ , 31.3. Calc.: Co, 19.4;  $\text{NH}_3$ , 22.5;  $\text{SO}_4$ , 31.7%). Ephraim and Flügel (*Helv. Chim. Acta*, 1924, 7, 736) prepared the salt indirectly from the sulphate.

2. From  $\text{H}_2\text{C}_2\text{O}_4$ , *monohydrated oxalatotetramminocobaltic nitrate* crystallised on cooling (2.2 g.) (Found: Co, 19.8;  $\text{NH}_3$ , 22.8.  $[\text{Co}(\text{NH}_3)_4(\text{C}_2\text{O}_4)]\text{NO}_3 \cdot \text{H}_2\text{O}$  requires Co, 20.0;  $\text{NH}_3$ , 23.1%). Jörgensen (*Z. anorg. Chem.*, 1896, 11, 431) prepared the salt by double decomp. from the chloride, but gave no analyses.

3. Crystn. of *malonatotetramminocobaltic nitrate*, from malonic acid, was completed by addition of 150 c.c. of  $\text{EtOH}$ , yielding 1.5 g. of reddish-violet needles, readily soluble in  $\text{H}_2\text{O}$  (Found: Co, 18.6;  $\text{NH}_3$ , 21.5; N, 22.0.  $[\text{Co}(\text{NH}_3)_4(\text{C}_3\text{H}_2\text{O}_4)]\text{NO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$  requires Co, 18.5;  $\text{NH}_3$ , 21.4; N, 22.0%). The monohydrate was described by Schramm (*Z. anorg. Chem.*, 1929, 180, 178) as being sparingly sol.

4. When salicylic acid was used, the red solution could not be warmed without decomp. On standing for a few mins., it became brown, and *hexahydrated tris(dihydroxotetramminocobaltic)cobaltic nitrate* (1.3 g. of grey crystals) was pptd. by 900 c.c. of EtOH and Et<sub>2</sub>O (Found: Co, 23.2; NH<sub>3</sub>, 19.9; N, 25.0. [Co{Co(NH<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>}<sub>3</sub>](NO<sub>3</sub>)<sub>6</sub>·6H<sub>2</sub>O requires Co, 23.1; NH<sub>3</sub>, 20.0; N, 24.7%). This salt was also obtained as the *trihydrate* when conc.



was kept for a few hr. (Found: Co, 24.2; NH<sub>3</sub>, 21.2; N, 25.8. Trihydrate requires Co, 24.4; NH<sub>3</sub>, 21.1; N, 26.0%). Jörgensen prepared the anhyd. nitrate by double decomp. from the chloride, drying it over H<sub>2</sub>SO<sub>4</sub> (*Z. anorg. Chem.*, 1898, 16, 193).

*Introduction of Monobasic Radicals.*—The same amount of hydroxide as before was treated with 3 equiv. of the monobasic acid. The subsequent procedure was the same as for the derivatives of dibasic acids.

1. Anhyd. [Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Cl]Cl<sub>2</sub> (1 g. of violet crystals) was pptd. by 200 c.c. of EtOH (Found: Co, 23.4; NH<sub>3</sub>, 27.4; Cl, 41.9. Calc.: Co, 23.4; NH<sub>3</sub>, 27.1; Cl, 42.3%). The compound was previously prepared by Jörgensen by a more complicated process (*J. pr. Chem.*, 1890, 42, 212).

*Chloroaquotetramminocobaltic picrate* was pptd. when 0.5 g. of the chloride was shaken with a cold solution of 0.91 g. (2 mols.) of picric acid, converted into the NH<sub>4</sub> salt in 85 c.c. of H<sub>2</sub>O (1 g. of large brown needles, sparingly sol. in H<sub>2</sub>O) {Found: Co, 8.7; NH<sub>3</sub>, 10.3; N, 20.9; Cl, 5.0. [Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Cl](C<sub>6</sub>H<sub>2</sub>O<sub>7</sub>N<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O requires Co, 8.8; NH<sub>3</sub>, 10.1; N, 20.8; Cl, 5.3%}.

2. From colourless 6*N*-HBr, anhyd. [Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Br]Br<sub>2</sub> was obtained as a finely divided violet ppt. (2.1 g.) on addition of 400 c.c. of EtOH and 150 c.c. of Et<sub>2</sub>O (Found: Co, 15.2; NH<sub>3</sub>, 17.5; Br, 61.8. Calc.: Co, 15.3; NH<sub>3</sub>, 17.7; Br, 62.3%) (see Werner and Miolati, *Z. physikal. Chem.*, 1893, 12, 44).

3. *Nitratoaquotetramminocobaltic nitrate hemihydrate* was pptd. by 400 c.c. of EtOH and 50 c.c. of Et<sub>2</sub>O (2.6 g. of small pink plates, readily sol. in H<sub>2</sub>O) {Found: Co, 17.3; NH<sub>3</sub>, 19.8; N, 28.9. [Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)(NO<sub>3</sub>)](NO<sub>3</sub>)<sub>2</sub>·½H<sub>2</sub>O requires Co, 17.3; NH<sub>3</sub>, 20.0; N, 28.8%}; when kept in vac. over H<sub>2</sub>SO<sub>4</sub> for 4 days, it yielded the anhyd. salt (Found: Co, 17.9; NH<sub>3</sub>, 20.8. Calc.: Co, 17.8; NH<sub>3</sub>, 20.6%). Brønsted (*Z. physikal. Chem.*, 1926, 122, 383) investigated the reaction of this salt with H<sub>2</sub>O, but recorded no analyses. Only the nitrate of the series has been prepared.

4. *Picratoaquotetramminocobaltic picrate* was obtained as a microcryst. orange ppt. (2 g.) when the hydroxide was treated with an aq. solution containing 3 equiv. of picric acid at 60° {Found: Co, 6.6; NH<sub>3</sub>, 7.7; N, 20.0. [Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)(C<sub>6</sub>H<sub>2</sub>O<sub>7</sub>N<sub>3</sub>)](C<sub>6</sub>H<sub>2</sub>O<sub>7</sub>N<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O requires Co, 6.5; NH<sub>3</sub>, 7.6; N, 20.2%}.

5. The red solution obtained from colourless 5*N*-HI could not be warmed without decomp. After addition of the acid, fairly rapid separation of *tris(dihydroxotetramminocobaltic)cobaltic iodide trihydrate* took place, the compound being collected after 10 min. (1.8 g. of dark brown, hexagonal plates, fairly sol. in H<sub>2</sub>O to a reddish-brown solution). To prepare the analytically pure product, the theo. amount of HI was used (2½ equiv.) (Found: Co, 17.4; NH<sub>3</sub>, 15.0; I, 55.7. [Co{Co(NH<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>}<sub>3</sub>]I<sub>6</sub>·3H<sub>2</sub>O requires Co, 17.4; NH<sub>3</sub>, 15.1; I, 56.0%).

When a conc. aq. solution of [Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>3</sub> was treated with KI at room temp., NH<sub>3</sub> was liberated, with separation of brown crystals. The ppt., though very similar to the above, was somewhat darker, and the I content was variable. When 3 mols. of KI were used, the ratio Co: NH<sub>3</sub> was 1.16, agreeing with a tris(dihydroxotetramminocobaltic)cobaltic salt, which requires 1.15, but the number of mols. of I associated with the 4 Co atoms was approx. 7 instead of 6.

#### Electrical Conductivities (See Part V, *loc. cit.*).

*v* is the dilution in mols. per l., and  $\lambda$  the mol. conductivity in mhos. The conductivities at infinite dilution were obtained by means of the  $1/\lambda - (c\lambda)^{n-1}$  graph. The sp. conductivity of the H<sub>2</sub>O was 0.60—0.65 × 10<sup>-6</sup> mho at 0°.

<i>v</i> .....	32	64	128	256	512	1024	∞	
$\lambda_0$ for [Co(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O)(SO <sub>4</sub> )]NO <sub>3</sub> ...	56.83	63.10	70.42	78.04	89.25	—	—	
$\lambda_0$ for [Co(NH <sub>3</sub> ) <sub>4</sub> (C <sub>2</sub> O <sub>4</sub> )]NO <sub>3</sub> .....	47.12	49.98	52.34	54.15	55.36	56.79	59.53	( <i>n</i> = 1.50)
$\lambda_0$ for [Co(NH <sub>3</sub> ) <sub>4</sub> (C <sub>2</sub> H <sub>3</sub> O <sub>4</sub> )]NO <sub>3</sub> .....	45.32	49.93	53.74	56.61	59.13	(62.58)	66.44	( <i>n</i> = 1.52)
$\lambda_0$ for [Co(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O)(NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>	140.2	157.1	170.4	183.8	196.1	210.8	—	
<i>v</i> .....			256	512	1024	2048	4096	
$\lambda_0$ for [Co{Co(NH <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub> } <sub>3</sub> ](NO <sub>3</sub> ) <sub>6</sub> .....			280.7	317.4	354.2	392.8	430.6	
$\lambda_{25}$ for picratoaquotetramminocobaltic picrate .....		—	—	—	—	—	296.2	

Measurements with the picrato-picrate at higher concns. were not practicable, owing to its low solubility.

*Ionic Mobilities (at 0°).*—The value 40·4 being used for the mobility of  $\text{NO}_3'$ , the above data give mobilities of 19·1 and 26·0 for the oxalato- and the malonato-tetramminocobaltic ion. Although the latter figure is unexpectedly high, yet the former agrees well with the values 18·1 and 17·9 calc. for the 1 : 2- and the 1 : 6-dinitrotetramminocobaltic ion at 0° (Lamb and Yngve, *J. Amer. Chem. Soc.*, 1921, **43**, 2362).

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