

460. *Researches on Ammines. Part XI.* cis-Nitroaquo-tetramminocobaltic Salts.*

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Sulphatoaquotetramminocobaltic chloride with one equivalent of silver nitrite gave nitroaquotetramminocobaltic sulphate. The derived chloride, bromide, and nitrate have been obtained. These salts differ considerably from the nitroaquotetramminocobaltic salts described by previous workers. It is concluded that the salts now described have the *cis*-configuration, while those described previously are *trans*-compounds.

NITROAQUOTETRAMMINOCOBALTIC salts were discovered by Jörgensen.¹ By heating *trans*-dinitrotetramminocobaltic sulphate with concentrated hydrochloric acid, he obtained brownish-red chloronitrotetramminocobaltic chloride, which on recrystallisation yielded a red salt regarded as nitroaquotetramminocobaltic chloride, $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NO}_2)]\text{Cl}_2$. From the chloride, a yellow nitrate and sulphate and a red bromide were obtained. Werner² showed that the yellow salts are true nitroaquotetrammines but that the red salts should be formulated $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Hal}]\text{Hal}, \text{H}_2\text{O}$. Werner prepared the true nitroaquotetramminocobaltic chloride and bromide which were yellow but changed rapidly to the red isomers. Chloronitro- and nitroaquo-tetramminocobaltic salts may be expected to exist in *cis*- and *trans*-forms, but in each case only one series has hitherto been recorded. Meyer and Gröhler,³ by treating $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]\text{Cl}$ with concentrated selenic acid, obtained not a selenato-salt $[\text{Co}(\text{NH}_3)_4(\text{SeO}_4)]\text{X}$, but a dihydroselenato-salt, $[\text{Co}(\text{NH}_3)_4(\text{HSeO}_4)_2]\text{X}$, where X is a univalent acid radical: this was considered to indicate a *trans*-structure for the chloronitrotetrammine, since the *cis*-compound would be expected to yield the selenato-salt. The chloronitrotetrammines undergo immediate aquation in

* Part X, *J.*, 1948, 1912.

¹ Jörgensen, *Z. anorg. Chem.*, 1894, **7**, 289.

² Werner, *Ber.*, 1907, **40**, 4124.

³ Meyer and Gröhler, *Z. anorg. Chem.*, 1926, **155**, 91.

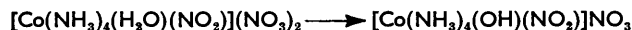
cold water to nitroaquotetrammines, so the latter were also considered to have the *trans*-configuration. Meyer and Rampoldt⁴ prepared both *cis*- and *trans*-nitroaquobisethylenediaminecobaltic salts: the orange *cis*-salts were very soluble and did not crystallise, while the brown *trans*-salts were less soluble and crystallised well. This supported the view that the known series of nitroaquotetramminocobaltic salts, being difficultly soluble and well crystalline, have *trans*-structures.

Ephraim and Flugel⁵ were unable to isolate $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SO}_4)]\text{I}$, owing to its rapid conversion into $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}]\text{SO}_4$, so it appeared likely that the nitrite of the sulphatoaquotetramminocobaltic series would undergo a similar change, in view of the strong tendency of the nitrite ion to enter the complex, at the same time changing to the nitro-group. This was found to be the case, and the sulphate of a new series of nitroaquotetramminocobaltic salts has now been obtained, by treating sulphatoaquotetramminocobaltic chloride with one molecular proportion of silver nitrite. The filtrate yielded a light brown amorphous powder, the solution of which gave an immediate precipitate with barium chloride in the cold and very little further precipitate on boiling. No oxides of nitrogen were evolved, even with concentrated hydrochloric acid. Thus the product had undergone practically complete conversion into nitroaquotetramminocobaltic sulphate:



By treating the sulphate with the calculated amounts of barium chloride, bromide, or nitrate, the chloride, bromide, and nitrate of the new series were obtained, as very soluble brown amorphous powders which gave no oxides of nitrogen on acidification. In addition to their much greater solubility, the properties of these salts differed notably from those of the nitroaquotetrammines described by Jørgensen¹ and Werner.² The chloride and bromide were stable, alone and in presence of water, whereas Werner's salts changed on storage, and more rapidly in water, to the isomeric red compounds, $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Hal}]\text{Hal}\cdot\text{H}_2\text{O}$.

Werner found that nitroaquotetramminocobaltic nitrate dissolved in aqueous ammonia to a red solution which deposited red crystals of the corresponding nitrohydroxo-salt on cooling:



The brown nitroaquotetrammines now described also gave red solutions in aqueous ammonia but it was only possible to isolate the brownish-yellow hydroxonitrotetrammines in very small yield, owing to their high solubility.

If it is accepted that the previous nitroaquotetrammines obtained are *trans*-compounds, the salts now described must be given the *cis*-configuration, and this is supported by the preparation of the new series from sulphatoaquotetramminocobaltic chloride, which is shown to be a *cis*-compound (see below).

The water molecule in the complex of the new series was removed completely at 110°, without loss of ammonia. The substance produced by dehydration of the sulphate was

presumably $\left[\text{Co}(\text{NH}_3)_4(\text{NO}_2) \begin{array}{c} \text{O} \diagup \text{S} \diagdown \text{O} \\ \text{O} \diagdown \text{S} \diagup \text{O} \end{array} \right]^+ \text{O}^-$ in which the sulphate radical may be regarded

as a "bound ion." Dehydration of the chloride and bromide may be expected to yield *cis*- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Hal}]\text{Hal}$, differing from the nitroaquo-salts in having only half the chlorine or bromine in the ionised condition. This was tested experimentally in the case of the nitroaquo-bromide. Before dehydration, the whole of the bromine was precipitated forthwith in the cold by silver nitrate. From a cold solution of the dehydrated salt, three-quarters of the total bromine was precipitated immediately, and the filtrate yielded the remainder on boiling. Evidently the bromonitro-bromide was partially reconverted into the original nitroaquo-bromide in aqueous solution.

* Meyer and Rampoldt, *Z. anorg. Chem.*, 1933, **214**, 1.

The configuration of the sulphatoaquotetramminocobaltic complex was investigated by treating the chloride of the series with one molecular proportion of barium nitrite. The filtrate yielded brown crystals of *cis*-dinitrotetramminocobaltic chloride, indicating that the original sulphatoquo-salt also had the *cis*-configuration.

EXPERIMENTAL

Configuration of the Sulphatoaquotetramminocobaltic Complex.—Sulphatoaquotetramminocobaltic chloride was prepared by Ephraim and Flugel's method.⁵ This salt (2 g.) was shaken mechanically with barium nitrite (1 mol.) and water (20 ml.), and the barium sulphate was removed by centrifuging. The red solution, when treated with ethanol (75 ml.) and ether (20 ml.), yielded very soluble brown microscopic crystals which were dried in a vacuum over magnesium perchlorate {Found: Co, 23.1; NH₃, 26.8; Cl, 13.9. [Co(NH₃)₄(NO₂)₂]Cl requires Co, 23.1; NH₃, 26.8; Cl, 13.9%}. The solution gave a pink precipitate with ammonium oxalate (distinction from *trans*-dinitrotetrammines). The colour and high solubility of the chloride and the insolubility of the oxalate indicate that the salt obtained was the *cis*-compound.

cis-Nitroaquotetramminocobaltic Sulphate.—Sulphatoaquotetramminocobaltic chloride (2 g.), silver nitrite (1 mol.), and water (20 ml.) were shaken for 1 hr., and the deep-red filtrate was taken to dryness in a vacuum over sulphuric acid. The brown amorphous product (1.5 g.) was only moderately soluble (1:30 at 15°). It did not yield oxides of nitrogen when heated with hydrochloric acid. 88% of the sulphate radical was immediately precipitated in the cold by barium chloride, the remainder being precipitated on boiling (the first precipitate was separated by centrifuging) {Found: Co, 20.6; NH₃, 23.7; N, 24.4; SO₄, 33.4; H₂O (lost in 8 hr. at 100°), 6.2. [Co(NH₃)₄(H₂O)(NO₂)]SO₄ requires Co, 20.5; NH₃, 23.7; N, 24.4; SO₄, 33.5; H₂O, 6.5%}. The *nitroaquo-sulphate* (1 g.) was dissolved in the minimum amount (40 ml.) of 3*N*-ammonia at 50°; when the red solution was strongly cooled, the *product* separated as a scanty brownish-yellow amorphous powder (0.1 g.) {Found: Co, 24.8. [Co(NH₃)₄(OH)(NO₂)]₂SO₄ requires Co, 24.7%}.

cis-Nitroaquotetramminocobaltic chloride was obtained when the sulphate (1 g.) was shaken for 1½ hr. with hydrated barium chloride (1 mol.) and water (30 ml.). The solution, after removal of barium sulphate by centrifuging, was taken to dryness in a vacuum over sulphuric acid, and yielded the nitroaquo-chloride (0.7 g.) as a very soluble light-brown amorphous powder. Water in the complex was almost completely removed in 6 hr. at 110°, no ammonia being lost, the colour then being buff {Found: Co, 22.5; NH₃, 25.9; N, 26.7; Cl, 27.0; H₂O, 6.3. [Co(NH₃)₄(H₂O)(NO₂)]Cl₂ requires Co, 22.5; NH₃, 25.9; N, 26.7; Cl, 27.0; H₂O, 6.8%}.

cis-Nitroaquotetramminocobaltic Bromide.—The sulphate (2 g.) was shaken for 1½ hr. with anhydrous barium bromide (2.07 g.) and water (30 ml.). After centrifuging, the brown solution was cooled in ice and treated with ethanol (100 ml.) and ether (100 ml.). The *bromide* separated as a very soluble brown amorphous powder (2 g.) and was kept overnight in a vacuum over magnesium perchlorate. Water in the complex was completely removed, without loss of ammonia, in 9 hr. at 100°, thus yielding a buff powder {Found: Co, 16.8; NH₃, 19.4; N, 20.2; Br, 45.1; H₂O, 5.1. [Co(NH₃)₄(H₂O)(NO₂)]Br₂ requires Co, 16.8; NH₃, 19.4; N, 19.9; Br, 45.5; H₂O, 5.1%}. When treated with silver nitrate, a solution of the dehydrated salt (0.139 g.) gave an immediate precipitate of silver bromide (0.1176 g.) and a further precipitate (0.0391 g.) on boiling.

cis-Nitroaquotetramminocobaltic Nitrate.—The sulphate (1 g.) was shaken for 1½ hr. with barium nitrate (0.91 g.) and water (30 ml.). After centrifuging, the solution was taken to dryness in a vacuum over sulphuric acid, and yielded a brown amorphous very soluble powder (0.9 g.) {Found: Co, 18.7; NH₃, 21.6; N, 31.1. [Co(NH₃)₄(H₂O)(NO₂)](NO₃)₂ requires Co, 18.7; NH₃, 21.6; N, 31.1%}. This *nitrate* (1 g.) dissolved in 3*N*-ammonia (7 ml.) at 50° to a red solution. Cooling and adding methanol gave a scanty brownish-yellow microcrystalline precipitate (0.17 g.), very soluble, to a strongly alkaline solution; this was probably *cis*-[Co(NH₃)₄(OH)(NO₂)]NO₃.