510. *Researches on Ammines. Part XII.* Sulphatoaquotetramminocobaltic and Sulphatobisethylenediaminecobaltic Salts.*

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A general method for the preparation of sulphatobisethylenediaminecobaltic salts is given and the presence of the sulphato-ring in the complex is established. Solutions of sulphato-salts undergo more extensive aquation to diaquosulphates than do sulphatoaquo-salts. The method of distinguishing between ionised sulphate and the sulphato-complex is discussed.

IT appeared remarkable that both the sulphito- and the sulphato-radicals occupy one position only in the sulphito- and sulphato-aquotetramminocobaltic complexes, and that no sulphito- or sulphato-tetrammines have been described. On the other hand, no sulphito- or sulphato-aquobisethylenediaminecobaltic salts are known, but sulphito- and sulphato-bisethylenediaminecobaltic salts, in which the sulphito- or sulphato-ring occupies two positions in the complex, have been described. In the present paper, the case of the sulphato-radical has been further investigated.

The sulphatoaquotetrammines were first described by Ephraim and Flugel[1] who based their formulation as aquo-salts on the presence of a water molecule which was not

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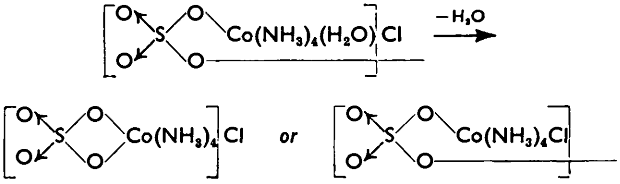
* Part XI, *J.*, 1957, 2402.

[1] Ephraim and Flugel, *Helv. Chim. Acta*, 1924, **7**, 724.

removed at 110°. Job[2] established the presence of the hydroxo–aquo-equilibrium by a conductometric titration with barium hydroxide, and this supported Ephraim and Flugel's formulation. It has now been shown that the sulphatoaquo-chloride $[Co(NH_3)_4(H_2O)(SO_4)]Cl$ yields, with moist silver oxide, a filtrate which is only slightly alkaline, indicating the presence of the non-valent complex $[Co(NH_3)_4(OH)(SO_4)]$. The pH of a 0·02M-solution was 8·56 at 23°, while the expected value for the sulphato-hydroxide $[Co(NH_3)_4(SO_4)]OH$ is about 12·3. This result further supports the formulation of the sulphatoaquotetrammines as aquo-salts. It was similarly shown in Part V[3] that the hydroxide obtained from $[Co(NH_3)_4(H_2O)_2]Cl_3$ is $[Co(NH_3)_4(OH)_2]OH$. Neither aquo- nor diaquo-hydroxides appear to exist.

By prolonged heating at 125°, the water molecule has been completely removed from the sulphatoaquo-chloride, yielding a product which may be the sulphatotetrammine containing the sulphato-ring (formula *A*), or a non-valent complex in which the sulphato-group still occupies one position only (formula *B*).* If (*A*) is correct, this is the only



(*A*) (*B*)

recorded salt of the sulphatotetramminocobaltic series. If the solid has structure (*B*), the complex must undergo immediate aquation with water, since the chlorine is immediately and completely precipitated by silver ion.

A cold solution of the sulphatoaquo-chloride gave a turbidity with barium chloride only after 10 min., whereas the cold solution of the dehydrated salt gave a turbidity forthwith. Thus partial aquation to $\left[Co(NH_3)_4(H_2O)_2\right]^{SO_4}_{Cl}$ takes place more rapidly in the latter case. A quantitative precipitation of the cold sulphatoaquo-chloride solution with barium chloride indicated that only 4% of the total sulphate radical was present as sulphate ions.

The only salt of the sulphatobisethylenediaminecobaltic series hitherto described is $[Co\,en_2(SO_4)]Br,H_2O$, obtained by Duff.[4] Though monohydrated, it became anhydrous on exposure to air, indicating a complex in which the sulphate radical is attached to cobalt by two links. This has been confirmed by preparation of the sulphate, chloride, and nitrate of the series, all of which were anhydrous. Quantitative investigation of the action of barium chloride indicated that in solution the equilibrium :

$$\left[Co\,en_2(SO_4)\right]X + 2H_2O \rightleftharpoons \left[Co\,en_2(H_2O)_2\right]^{SO_4}_{X}$$

lies further to the right than the equilibrium :

$$\left[Co(NH_3)_4(H_2O)(SO_4)\right]X + H_2O \rightleftharpoons \left[Co(NH_3)_4(H_2O)_2\right]^{SO_4}_{X}$$

Considerable difficulty was experienced in preparing the bisethylenediamine salts in pure condition, owing to their high solubility. Duff's method {treatment of $[Co\,en_2(CO_3)]Br$ with the calculated amount of sulphuric acid} proved unsatisfactory for salts other than the bromide. Attempts to prepare $[Co\,en_2(SO_4)]_2SO_4$ by treating $[Co\,en_2Cl_2]Cl$ with three

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* We are indebted to a referee for this suggestion (*B*).

[2] Job, Thesis, Paris, 1921.

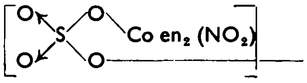
[3] King, *J.*, 1932, 1275.

[4] Duff, *J.*, 1922, 450.

equivalents of silver sulphate were unsuccessful, as the chlorine was not completely eliminated as silver chloride. The method which gave the best results was based on one described in Part VII[5] for introducing bivalent acid radicals into the tetramminocobaltic and tetramminoaquocobaltic complexes. *trans*-Dichlorobisethylenediaminecobaltic chloride was converted into the *cis*-dihydroxo-hydroxide $[\mathrm{Co\,en_2(OH)_2}]\mathrm{OH}$ and the solution of this was treated with two equivalents of sulphuric acid and one equivalent of sulphuric, hydrochloric, or nitric acid.

Unsuccessful attempts to isolate solid dihydroxotetramminocobaltic salts were recorded in Part V.[3] When however *cis*-$[\mathrm{Co\,en_2(OH)_2}]\mathrm{OH}$ was treated with one equivalent of hydrochloric acid, the *cis*-dihydroxo-chloride $[\mathrm{Co\,en_2(OH)_2}]\mathrm{Cl}$ was isolated as a red amorphous solid.

It has been shown in Part XI[6] that sulphatoaquotetramminocobaltic nitrite isomerises to nitroaquotetramminocobaltic sulphate. When sulphatobisethylenediaminecobaltic chloride was treated with one equivalent of silver nitrite, the filtrate yielded a brown amorphous solid which contained no water and from the method of preparation might be expected to be sulphatobisethylenediaminecobaltic nitrite $[\mathrm{Co\,en_2(SO_4)}]\mathrm{O{\cdot}NO}$. However, it gave no oxides of nitrogen even when heated with concentrated hydrochloric acid, and this supports the alternative formulation * as the non-valent complex, nitrosulphatobisethylenediaminecobalt :



If this formula is correct, this is the only recorded sulphatobisethylenediaminecobaltic complex in which the sulphato-group is attached to cobalt by one link only. Quantitative precipitation with barium chloride indicated that only 64% of the sulphate radical remained un-ionised in the aqueous solution, so the equilibrium :

$$[\mathrm{Co\,en_2(SO_4)(NO_2)}] + \mathrm{H_2O} \rightleftharpoons [\mathrm{Co\,en_2(H_2O)(NO_2)}]\mathrm{SO_4}$$

was probably established.

It is usual to ascertain whether a chloride or sulphate radical is present in the ionised condition or as part of a complex ion by precipitation tests with silver or barium salts respectively. If no immediate precipitate is obtained at room temperature, the acid radical is entirely in the complex. For a stable complex ion where no aquation occurs, this method gives a reliable indication. If however an equilibrium such as :

$$\left[\mathrm{Co\,en_2(SO_4)}\right]\mathrm{X} + 2\mathrm{H_2O} \rightleftharpoons \left[\mathrm{Co\,en_2(H_2O)_2}\right]^{\mathrm{SO_4}}_{\mathrm{X}}$$

is established in the solution, addition of barium ion will displace the equilibrium to the right, and a larger proportion of ionised sulphate may be indicated than is actually present in the pure aqueous solution, even if the barium sulphate is collected immediately. Hence the value obtained for the proportion of ionised sulphate may be expected to be somewhat higher than the correct value. This must be borne in mind in interpreting the data in the Table on p. 2634. Job and Urbain[7] suggested that barium chloride is not a suitable reagent for distinguishing ionised from un-ionised sulphate, and recommended benzidine hydrochloride instead. We find that benzidine hydrochloride has no advantages over barium chloride, if precipitation of ionised sulphate in the latter case is carried out in the cold, and the barium chloride is immediately separated by centrifuging.

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* We are indebted to a referee for this suggestion also.

[5] King, *J.*, 1933, 517.
[6] King and Mistry, *J.*, 1957, 2402.
[7] Job and Urbain, *Compt. rend.*, 1920, **170**, 843.

EXPERIMENTAL

Sulphatoaquotetramminocobaltic chloride was prepared from the sulphate as described by Ephraim and Flugel [1] {Found: Co, 21·3; NH_3, 24·7; SO_4, 34·8; Cl, 12·8; H_2O, 6·5. Calc. for $[Co(NH_3)_4(H_2O)(SO_4)]Cl$: Co, 21·3; NH_3, 24·6; SO_4, 34·7; Cl, 12·8; H_2O, 6·5%}. Water was completely removed, without loss of ammonia, in 96 hr. at 125°. The pink sulphatoaquochloride was very soluble to a deep-red acid solution. Barium chloride gave a turbidity only after 10 min. and a quantitative precipitation indicated that in the cold freshly prepared solution 96% of the sulphate radical was un-ionised. The dehydrated salt was less soluble, and the pale-pink acid solution gave a slight turbidity with barium chloride forthwith, and a further precipitate on standing or heating. Chlorine in the dehydrated salt was immediately and completely precipitated by silver ion.

Sulphatohydroxotetramminocobalt $[Co(NH_3)_4(OH)(SO_4)]$ was obtained in solution as a deep-red filtrate, only slightly alkaline to litmus, when sulphatoaquotetramminocobaltic chloride was triturated for 5 min. with freshly prepared moist silver oxide from four parts of silver nitrate. Attempts to isolate the solid product were unsuccessful. The pH of a freshly prepared 0·02M-solution at 23° was found to be 8·56, by using a standardised pH meter with glass electrode and calomel reference electrode.

trans-Dichlorobisethylenediaminecobaltic chloride was prepared by the method given in *Inorg. Synth.*[8] $[Co\ en_2Cl_2]Cl,HCl$ was converted into $[Co\ en_2Cl_2]Cl$ at 95° in 4 hr., as decomposition sometimes occurred at the recommended temperature of 110° (Found: Co, 20·7; N, 19·4; Cl, 37·4. Calc. for $[Co\ en_2Cl_2]Cl$: Co, 20·7; N, 19·6; Cl, 37·3%).

Sulphatobisethylenediaminecobaltic Sulphate.—*trans*-$[Co\ en_2Cl_2]Cl$ (2 g.) was triturated with freshly prepared moist silver oxide (from 8 g. of silver nitrate), for 5 min. Silver chloride and excess of silver oxide were filtered off and washed with the minimum amount of water, till the filtrate was colourless. The deep-red filtrate (30 ml.), containing *cis*-$[Co\ en_2(OH)_2]OH$, was mixed with N-sulphuric acid (21·0 ml., 3 equivs.). The pale-red solution was heated to the b. p., and became dark-red. It was taken to dryness in a vacuum over sulphuric acid, yielding the dark-red amorphous *sulphato-sulphate*, very soluble and very hygroscopic {Found: Co, 18·2; N, 17·3; SO_4, 44·6. $[Co\ en_2(SO_4)]_2SO_4$ requires Co, 18·2; N, 17·3; SO_4, 44·6%}.

Sulphatobisethylenediaminecobaltic Nitrate.—*trans*-$[Co\ en_2Cl_2]Cl$ (2 g.) was converted into *cis*-$[Co\ en_2(OH)_2]OH$ solution (30 ml.) and this was treated successively with one equiv. of 0·5N-nitric acid and two equivs. of N-sulphuric acid. After concentration by boiling, the solution was taken to dryness in a vacuum over sulphuric acid, yielding the red, very hygroscopic and very soluble amorphous *sulphato-nitrate* (1·7 g.). The cold solution gave a turbidity with barium chloride only after several minutes {Found: Co, 17·3; N, 20·7; SO_4, 28·2. $[Co\ en_2(SO_4)]NO_3$ requires Co, 17·5; N, 20·8; SO_4, 28·5%}.

Sulphatobisethylenediaminecobaltic chloride was prepared similarly, with one equiv. of hydrochloric acid and two of sulphuric acid. The red amorphous product (1·9 g.) was hygroscopic and very soluble, and the solution gave a turbidity with barium chloride only after a few minutes {Found: Co, 18·9; Cl, 11·3; SO_4, 30·8. $[Co\ en_2(SO_4)]Cl$ requires Co, 18·9; Cl, 11·4; SO_4, 30·9%}.

Sulphatobisethylenediaminecobaltic bromide was obtained in monohydrated form by Duff,[4] by treating $[Co\ en_2(CO_3)]Br$ with two equivs. of sulphuric acid. It has also been obtained as above by treating $[Co\ en_2(OH)_2]OH$ from $[Co\ en_2Cl_2]Cl$ (2 g.) with hydrobromic acid (1 equiv.) and sulphuric acid (2 equivs.) (yield 2·3 g.) {Found: Co, 16·6; Br, 22·5; SO_4, 27·1. Calc. for $[Co\ en_2(SO_4)]Br$: Co, 16·6; Br, 22·5; SO_4, 27·1%}.

Nitrosulphatobisethylenediaminecobalt.—The salt $[Co\ en_2(SO_4)]Cl$ (2 g.) was shaken for 3 hr. at 0° with silver nitrite (0·991 g.) and water (20 ml.). Silver chloride was separated and washed with the minimum amount of ice-cold water. The filtrate was taken to dryness in a vacuum over sulphuric acid, and yielded dark-brown amorphous *nitrosulphatobisethylenediaminecobalt* (1 g.), very soluble, and giving in solution only a slight turbidity with barium chloride in the cold, increasing considerably on boiling {Found: Co, 18·3; N, 21·8; SO_4, 29·9. $[Co\ en_2(SO_4)(NO_2)]$ requires Co, 18·3; N, 21·8; SO_4, 29·9%}. No oxides of nitrogen were evolved with dilute or concentrated hydrochloric acid, even on boiling.

cis-*Dihydroxobisethylenediaminecobaltic Chloride.*—*trans*-$[Co\ en_2Cl_2]Cl$ (2 g.) was converted into *cis*-$[Co\ en_2(OH)_2]OH$ in water (30 ml.), and one equiv. of 0·1N-hydrochloric acid was added.

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[8] *Inorg. Synth.*, 1946, 2, 223.

The pale-red solution, when concentrated by boiling, became deep-red, and was taken to dryness in a vacuum over sulphuric acid, yielding the red amorphous *dihydroxo-chloride* (0·8 g.), hygroscopic, and very soluble to a strongly alkaline dark-red solution {Found: Co, 23·7; Cl, 14·1. $[\mathrm{Co\ en_2(OH)_2}]\mathrm{Cl}$ requires Co, 23·7; Cl, 14·2%}.

Determination of Ionised and Un-ionised Sulphate Radical in Sulphato- and Sulphatoaquo-salts.—The salt (0·5 g.) in water (30 ml.) was treated in the cold with the calculated amount of barium chloride in water (15 ml.), then immediately centrifuged for 2 min. The barium sulphate was collected and weighed, giving the weight of ionised sulphate. The solution and washings were kept for 24 hr. and finally boiled with excess of barium chloride. From the further weight of barium sulphate thus obtained, the weight of un-ionised sulphate radical was calculated. A similar method was used when benzidine hydrochloride was the precipitant. The results are tabulated.

Salt	Precipitant	Un-ionised sulphate (%)	Ionised sulphate (%)
$[\mathrm{Co(NH_3)_4(H_2O)(SO_4)}]\mathrm{Cl}$	$\mathrm{BaCl_2}$	95·8	4·2
$[\mathrm{Co(NH_3)_4(H_2O)(SO_4)}]_2\mathrm{SO_4}$	$\mathrm{BaCl_2}$	39·0	61·0
,,	$\mathrm{C_{12}H_8(NH_2)_2,2HCl}$	38·4	61·6
$[\mathrm{Co\ en_2(SO_4)}]\mathrm{Cl}$	$\mathrm{C_{12}H_8(NH_2)_2,2HCl}$	50·7	49·3
$[\mathrm{Co\ en_2(SO_4)}]\mathrm{Br}$	$\mathrm{BaCl_2}$	64·4	35·6
$[\mathrm{Co\ en_2(SO_4)}]\mathrm{NO_3}$	$\mathrm{BaCl_2}$	73·7	26·3
$[\mathrm{Co\ en_2(SO_4)}]_2\mathrm{SO_4}$	$\mathrm{BaCl_2}$	44·4	55·6
,,	$\mathrm{C_{12}H_8(NH_2)_2,2HCl}$	44·9	55·1
$[\mathrm{Co\ en_2(SO_4)(NO_2)}]$	$\mathrm{BaCl_2}$	64·1	35·9

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