9. *Researches on Residual Affinity and Co-ordination. Part XXXVI. The Constitution of "Ruthenium Red."*

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In the course of his researches on ruthenium, Joly (*Compt. rend.*, 1892, **114**, 291; **115**, 1299) observed that the metal readily furnished ruthenium trichloride, $RuCl_3$, when heated at 360—440° in chlorine containing a little carbon monoxide. The dark brown chloride was stated to absorb ammonia with the formation of an ammine, $Ru_2Cl_6,7NH_3$. This partly dissolved in water, forming an intense violet-red solution from which a crystalline hydroxy-compound, $Ru_2Cl_4(OH)_2,7NH_3,3H_2O$, was obtained. The hydroxy-compound, also obtained by the action of ruthenium chloride on aqueous ammonia, is known as "ruthenium red" and dyes animal fibres in red shades. Joly (*loc. cit.*) also stated that "ruthenium red" gave the compound $Ru_2Cl_6(OH)_2,7NH_3,HCl,3H_2O$ on treatment with concentrated hydrochloric acid.

These results clearly require revision in the light of modern ideas on molecular constitution. Moreover, analyses were recorded only for the ammine $Ru_2Cl_6,7NH_3$, the corresponding bromide and iodide of which have been reported by Gutbier and Trenker (*Z. anorg. Chem.*, 1905, **45**, 166).

The action of chlorine containing a little carbon monoxide on ruthenium at temperatures between 380° and 420° gives a product consisting mainly of ruthenium trichloride. The preparations always contain traces of unchanged ruthenium and probably ruthenium dichloride (compare Howe, Howe, and Ogburn, *J. Amer. Chem. Soc.*, 1924, **46**, 335). The foregoing specimens of ruthenium trichloride absorb ammonia, but the product is a mixture of amminated chlorides, probably including the hexammine chloride, $[Ru(NH_3)_6]Cl_3$, corresponding with the analogous ferric chloride derivative, $[Fe(NH_3)_6]Cl_3$ (Hüttig, *Z. anorg. Chem.*, 1920, **114**, 169; Ephraim and Millmann, *Ber.*, 1917, **50**, 531; Biltz and Birk, *Z. angew. Chem.*, 1924, **134**, 131). The mixture partly dissolves in water, giving the characteristic purple-red solution of "ruthenium red," which, however, is best prepared by the action of ruthenium trichloride on concentrated aqueous ammonia. It has now been found that "ruthenium red" is *chlorotetramminohydroxoruthenium chloride hydrate* (I), and this structure is supported by the derivatives shown in the following diagram:

$$\begin{tikzcd}
\underset{\text{(II.)}}{[RuCl_2(NH_3)_4]Cl,2H_2O} \arrow[r, shift left] & \underset{\text{(I.) Ruthenium red.}}{[Ru(OH)Cl(NH_3)_4]Cl,H_2O} \arrow[l, shift left] \arrow[r] \arrow[dl] \arrow[d] \arrow[dr] & \underset{\text{(III.)}}{[RuCl(NO_3)(NH_3)_4]NO_3,4H_2O} \\
\underset{\text{(IV.)}}{[Ru(OH)Br(NH_3)_4]Br,H_2O} \arrow[d, shift right, "\text{HBr}"'] & \underset{\text{(VI.)}}{[Ru(OH)Cl(NH_3)_4]I} \arrow[d] & \underset{\text{(IX.)}}{[Ru(OH)Cl(NH_3)_4]_2Ru(NO)Cl_5} \\
\underset{\text{(V.)}}{[RuBr_2(NH_3)_4]Br,H_2O} \arrow[u, shift right, "\text{NH}_3"'] & \underset{\text{(VII.)}}{[Ru(OH)I(NH_3)_4]I} \arrow[r, shift right] & \underset{\text{(VIII.)}}{[RuI_2(NH_3)_4]I} \arrow[l, shift right]
\end{tikzcd}$$

"Ruthenium red" (I) and hydrochloric acid give *dichlorotetramminoruthenium chloride dihydrate* (II), whereas nitric acid furnishes *chloronitratotetramminoruthenium nitrate tetrahydrate* (III), which does not react with silver nitrate except on warming. Aqueous potassium bromide and hydrobromic acid furnish (IV) and (V) respectively with "ruthenium red," and potassium iodide gives successively (VI) and (VII), the latter compound giving (VIII) with hydriodic acid. With potassium nitrosoruthenichloride, "ruthenium red" furnishes the sparingly soluble complex *salt* (IX).

The foregoing results provide strong evidence for the constitutional formula (I) for "ruthenium red," but further confirmatory results have been obtained by the isolation of analogues of this amminated ruthenium halide in which the ammonia molecules are replaced by ethylenediamine, ethylamine, and pyridine respectively.

Ethylenediamine Analogue of Ruthenium Red.—Aqueous ethylenediamine (en) reacts with ruthenium trichloride, forming a deep yellow solution from which alcohol precipitates *chlorobisethylenediaminohydroxoruthenium chloride* (X) in small yield. This compound

$$\underset{\text{(XI.)}}{[RuCl_2en_2]Cl} \longleftarrow \underset{\text{(X.)}}{[Ru(OH)Cl\,en_2]Cl} \longrightarrow \underset{\text{(XII.)}}{[Ru(OH)I\,en_2]I}$$

does not possess the intense colour of the ammonia derivative, and reacts with hydrochloric acid, giving (XI), and with warm concentrated potassium iodide, precipitating (XII).

Pyridine Analogue of Ruthenium Red.—Aqueous pyridine and ruthenium trichloride combine very slowly at 90°, leading to *chlorotetrapyridinohydroxoruthenium chloride* (XIII), a yellow crystalline product which furnishes *dichlorotetrapyridinoruthenium chloride* (XIV) with hydrochloric acid.

$$\underset{\text{(XIII.)}}{[Ru(OH)Cl\,py_4]Cl} \longrightarrow \underset{\text{(XIV.)}}{[RuCl_2\,py_4]Cl}$$

$$\underset{\text{(XV.)}}{[RuCl_2(NH_2Et)_4]Cl} \rightleftarrows \underset{\text{(XVI.)}}{[Ru(OH)Cl(NH_2Et)_4]Cl}$$

Ethylamine Analogue of Ruthenium Red.—Under conditions similar to those used for the production of "ruthenium red," ethylamine and ruthenium chloride react in aqueous media, giving a solution which, after acidification with hydrochloric acid, furnishes *dichlorotetraethylaminoruthenium chloride* (XV). This stable pink salt is converted into the less stable *chlorotetraethylaminohydroxoruthenium chloride* (XVI) by aqueous ammonia.

Ammonia is the only base of the four studied which furnishes an intensely coloured compound such as "ruthenium red." A possible explanation may be based on the view that cations of the foregoing compounds have an octahedral arrangement, consequently hydroxy (OH) and chloro (Cl) groups can occupy *cis*- or *trans*-positions relative to one another. Ammonia may induce one distribution of the hydroxy- and chloro-groups, whereas ethylenediamine, pyridine, and ethylamine favour the other configuration.

EXPERIMENTAL.

Ruthenium Trichloride.—Dry chlorine mixed with approximately 10% of carbon monoxide was passed over finely divided ruthenium at 380—420°, the metal speedily changing to a dark brown or black bulky powder. As soon as the absorption of chlorine had ceased the mixture was cooled in a slow stream of chlorine, this gas being finally displaced by dry nitrogen or carbon dioxide. In two typical experiments, 2·812 g. and 2·142 g. of ruthenium gave 5·460 g. (Found: Ru, 52·6; Cl, 47·1. Calc. for $RuCl_3$: Ru, 48·8; Cl, 51·2%), and 4·065 g. (Found: Ru, 50·1; Cl, 49·2%) respectively of chlorinated product. The preparations dissolved slowly in hot alcohol, forming green solutions and leaving small residues of metallic ruthenium.

The mixture of chlorine and carbon monoxide passed over ruthenium at 600° gave black lustrous dense crystals of ruthenium trichloride. The preparation was purer (Found: Ru, 49·2; Cl, 50·4%) than those obtained at the lower temperature, but was inert and was not used in the following experiments.

Action of Ammonia on Ruthenium Trichloride.—Pure dry ammonia, passed over ruthenium trichloride (1·0 g.) at 0°, was readily absorbed with generation of heat. The product was kept over caustic soda in an ammonia atmosphere in a desiccator (Found: Ru, 37·2, 40·1, 42·7; Cl, 39·9, 41·8, 44·0. $RuCl_3,4NH_3$ requires Ru, 36·8; Cl, 38·6%). The *amminated trihalide* partly dissolved in water to a deep red solution, but was insoluble in alcohol and other organic media.

Chlorotetramminohydroxoruthenium Chloride Hydrate [*Ruthenium Red* (I)].—Powdered ruthenium trichloride (2·0 g.) was added in small quantities to aqueous ammonia (*d* 0·880; 50 c.c.) at 0°. The mixture was left at room temperature for 12 hours, diluted with water, and heated at 90° until no more solid dissolved. The purple-red solution was filtered from ruthenium (0·1 g.), evaporated to 50 c.c., and diluted with alcohol (200 c.c.); the *amminated ruthenium chloride* was then precipitated in small purple crystals, which were further purified by solution in water and precipitation with alcohol. This and the following compounds were dried over sulphuric acid (Found: Ru, 36·8, 37·1, 37·4; Cl, 25·5, 25·2, 25·8; N, 20·35, 20·8; H_2O, 6·3. $H_{15}O_2N_4Cl_2Ru$ requires Ru, 36·9; Cl, 25·7; N, 20·3; H_2O, 6·5%). "Ruthenium red" dissolved in water to an intensely red solution, the colour being perceptible at dilutions of more than 1 in 10^6. Aqueous solutions soon decomposed at room temperature, more rapidly on heating, and gave a precipitate of black hydrated ruthenium oxide. These solutions were more stable in the presence of ammonia and ammonium chloride, very slow crystallisation leading to crystals of (I) having a fine coppery lustre. The well-dried tetrammine was stable under normal conditions, but lost a molecule of water at 150°; it did not decompose further below 200°.

Dichlorotetramminoruthenium Chloride Dihydrate (II).—The compound (I) (0·5 g.) in water (50 c.c.) was treated with concentrated hydrochloric acid (10 c.c.), the red colour of the solution instantly changing to brown. The mixture was warmed for several hours at 40—50°; the brown crystalline powder was then collected and washed with a little 2*N*-hydrochloric acid (Found: Ru, 32·8; Cl, 34·7; N, 17·7. $H_{16}O_2N_4Cl_3Ru$ requires Ru, 32·6; Cl, 34·1; N, 17·9%). This *amminated ruthenium* compound dissolved in water to a yellow solution, which became pink at high dilutions. Aqueous ammonia at once regenerated "ruthenium red" with this dichloro-derivative.

Chloronitratotetramminoruthenium Nitrate Tetrahydrate (III).—A concentrated solution of chlorotetramminohydroxoruthenium chloride (I) in water (20 c.c.) was treated with 2*N*-nitric acid (20 c.c.), and ammonium nitrate stirred into the deep brown solution. After 12 hours the brown leaflets were collected and air-dried (Found: Ru, 25·4; Cl, 9·1. $H_{20}O_{10}N_6ClRu$ requires Ru, 25·4; Cl, 8·8%). The *nitrate* gave the characteristic tint of "ruthenium red" with aqueous ammonia.

Dibromotetramminoruthenium Bromide Hydrate (V).—The compound (I) (1·0 g.) in water (75 c.c.) was treated with a large excess of concentrated aqueous potassium bromide and then, after heating for 1 hour, with constant-boiling hydrobromic acid (10 c.c.). The dark brown, crystalline precipitate was collected and washed with a little hydrobromic acid and alcohol (Found: Ru, 24·1; Br, 55·9. $H_{14}ON_4Br_3Ru$ requires Ru, 23·8; Br, 56·1%). This *tetrammine* was less soluble but possessed similar properties to the corresponding chlorine analogue (II).

Bromotetramminohydroxoruthenium Bromide Hydrate (IV).—The compound (V) was dissolved in concentrated aqueous ammonia, and alcohol was added to the filtered, deep purple solution. The *hydroxo-bromide*, which separated in small, deep purple crystals, was further purified by addition of alcohol to a concentrated aqueous solution (Found: Ru, 27·9; Br, 41·2. $H_{15}O_2N_4Br_2Ru$ requires Ru, 27·9; Br, 40·9%). It was similar in properties to the chlorine analogue.

Chlorotetramminohydroxoruthenium Iodide (VI).—A cold solution of (I) in water was treated with excess of a cold aqueous solution of potassium iodide. When alcohol was added to the well-stirred mixture, the *chloro-iodide* separated in small purple crystals (Found : Ru, 29·1. $H_{13}ON_4ClIRu$ requires Ru, 29·1%).

Iodotetramminohydroxoruthenium Iodide (VII).—An aqueous mixture containing (I) and excess of potassium iodide was heated and evaporated to crystallising point. The almost black crystals of the iodine analogue of " ruthenium red " were washed with aqueous potassium iodide and alcohol (Found : Ru, 24·5; I, 57·9. $H_{13}ON_4I_2Ru$ requires Ru, 23·1; I, 57·6%).

Di-iodotetramminoruthenium Iodide (VIII).—(*a*) The compound (VII) was triturated with hydriodic acid (Found : Ru, 18·8; I, 69·6. $H_{12}N_4I_3Ru$ requires Ru, 18·5; I, 69·1%). (*b*) A mixture of " ruthenium red " (I), potassium iodide, and 2*N*-sulphuric acid was evaporated to crystallisation point. The crystals were washed with a little water and alcohol (Found : Ru, 18·7%). Aqueous ammonia generated the hydroxo-iodide (VII) with this salt.

Chlorotetramminohydroxoruthenium Nitrosoruthenipentachloride (IX).—Aqueous solutions containing equivalent quantities of (I) and potassium nitrosoruthenipentachloride were mixed; the sparingly soluble, purple *salt* then separated and was washed with cold water and alcohol (Found : Ru, 41·2; Cl, 33·1. $H_{26}O_3N_9Cl_7Ru_3$ requires Ru, 40·6; Cl, 32·8).

Chlorotetramminohydroxoruthenium Platinochloride.—Aqueous solutions of (I) and potassium platinochloride were mixed; the reddish-purple microcrystalline deposit was washed with a small quantity of cold water and alcohol (Found : Ru + Pt, 50·7. $H_{26}O_2N_8Cl_6Ru_2Pt$ requires Ru + Pt, 51·0%).

Chlorobisethylenediaminohydroxoruthenium Chloride (X).—Ruthenium trichloride (2·0 g.) was added slowly to ethylenediamine (1·2 g.) in water (50 c.c.). After 12 hours, the mixture was diluted with water (50 c.c.) and heated at 90° for 4 days. The yellow filtrate was evaporated to 50 c.c. and diluted with alcohol; the *hydroxo-chloride* then separated as a microcrystalline powder, which was purified by precipitation from aqueous solution with alcohol (Found : Ru, 33·0; Cl, 23·3. $C_4H_{17}ON_4Cl_2Ru$ requires Ru, 32·8; Cl, 22·9%). The moist, freshly precipitated ruthenium compound was dark grey, but dried to a dark brown, crystalline powder, which dissolved in water to a reddish-yellow solution. The yellow alcoholic filtrate from the preparation of the ethylenediamine compound furnished a dark brown, viscid residue on evaporation, but a crystalline compound has not yet been obtained from this fraction. Analysis indicated a larger proportion of ethylenediamine (Ru, 23·9%) than that in chlorobisethylenediaminohydroxoruthenium chloride.

Dichlorobisethylenediaminoruthenium Chloride (XI).—An aqueous solution of the hydroxo-chloride (X) was treated with excess of 2*N*-hydrochloric acid and evaporated to crystallising point. The dark brown crystals were recrystallised from hydrochloric acid (Found : Ru, 30·8; Cl, 32·1. $C_4H_{16}N_4Cl_3Ru$ requires Ru, 31·0; Cl, 32·4%). This *chloride* dissolved in water to a yellow-brown solution and hydrolysed to the compound (X).

Iodobisethylenediaminohydroxoruthenium Iodide (XII).—An aqueous mixture of the compound (X) and potassium iodide was evaporated to crystallising point; the almost black crystals were collected and washed with a little water and alcohol (Found : Ru, 21·0; I, 51·9. $C_4H_{17}ON_4I_2Ru$ requires Ru, 20·6; I, 51·5%). This *iodide* was sparingly soluble in water and rather unstable.

Chlorotetrapyridinohydroxoruthenium Chloride (XIII).—Ruthenium trichloride (2·0 g.) was added to 30% aqueous pyridine (100 c.c.), and the mixture heated with occasional shaking for several days. The yellow needles were separated as far as possible from admixed ruthenium chloride and crystallised from aqueous pyridine (Found : Ru, 20·6; Cl, 14·5. $C_{20}H_{21}ON_4Ru$ requires Ru, 20·1; Cl, 14·1%).

Dichlorotetrapyridinoruthenium Chloride (XIV).—An aqueous solution of the compound (XIII) was treated with hydrochloric acid and evaporated to crystallising point (Found : Ru, 19·6. $C_{20}H_{20}N_4Cl_3Ru$ requires Ru, 19·4%).

Dichlorotetraethylaminoruthenium Chloride (XV).—Ruthenium trichloride (2·0 g.) was slowly added to 30% aqueous ethylamine (50 c.c.) at 0°. After 12 hours the mixture was diluted with water (50 c.c.) and heated at 90° for 6 hours. The filtered solution was acidified with 2*N*-hydrochloric acid and evaporated to crystallising point. The mixture was triturated with alcohol, and the insoluble pink crystals recrystallised from dilute hydrochloric acid (Found : Ru, 26·1; Cl, 27·0. $C_8H_{28}N_4Cl_3Ru$ requires Ru, 26·2; Cl, 27·4%). This *ethylamine* derivative gave an orange-yellow solution in water, but was practically insoluble in alcohol.

Chlorotetraethylaminohydroxoruthenium Chloride (XVI).—The compound (XV) was dissolved in a small quantity of cold concentrated aqueous ammonia; the *hydroxo*-compound was then precipitated from the red solution by the addition of alcohol. The amorphous product was collected, dissolved in cold water, and again precipitated with alcohol (Found: Ru, 27·2; Cl, 18·8. $C_8H_{29}ON_4Cl_2Ru$ requires Ru, 27·5; Cl, 19·2%). This unstable ruthenium compound dissolved in water to a deep brownish-yellow solution, and hydrochloric acid regenerated the dichloro-compound (XV).

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