34. Optical Activity dependent on Co-ordinated Bivalent Ruthenium.

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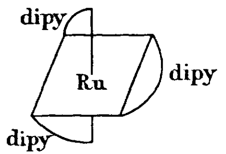
During an investigation on the action of 2 : 2′-dipyridyl (dipy) on ruthenium salts a new series of stable red salts, [Ru dipy$_3$]X$_2$,yH$_2$O, has been discovered. The *chloride* is obtained in good yield by the interaction of 2 : 2′-dipyridyl and ruthenium trichloride at 250° :

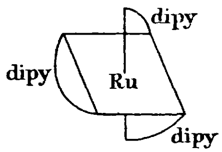
$$2RuCl_3 + 8C_{10}H_8N_2 = 2[Ru(C_{10}H_8N_2)_3]Cl_2 + C_{20}H_{14}N_4 + 2HCl$$

The base $C_{20}H_{14}N_4$ is a new tetrammine which will be the subject of a future communication. The foregoing chloride, which crystallises from water as the hexahydrate, is the starting point for the preparation of a number of salts containing the cation [Ru dipy$_3$]$^{++}$. The corresponding *bromide, iodide,* and *perchlorate* are all obtained by double decomposition with aqueous solutions of the chloride and they also are hexahydrates. Silver oxide, silver nitrate, and silver carbonate furnish respectively the base, *tris-2 : 2′-dipyridylruthenous hydroxide octahydrate,* [Ru dipy$_3$](OH)$_2$,8H$_2$O, the *nitrate,* [Ru dipy$_3$](NO$_3$)$_2$,6H$_2$O, and the *carbonate,* [Ru dipy$_3$]CO$_3$,6 and 10H$_2$O. The r-*tartrate* is conveniently obtained by the action of tartaric acid on the base.

These salts are appreciably more stable than the analogously constituted ferrous, [Fe dipy$_3$]X$_2$, and nickel salts, [Ni dipy$_3$]X$_2$, first prepared by Blau (*Monatsh.*, 1898, **19**, 647). Tris-2 : 2′-dipyridylferrous bromide (6H$_2$O) and iodide (5H$_2$O) were resolved into optically active forms by Werner (*Ber.*, 1912, **45**, 433), and tris-2 : 2′-dipyridylnickelous chloride (6H$_2$O) was resolved by Morgan and Burstall (J., 1931, 2213). The resolution of the tris-2 : 2′-dipyridylruthenous complex into optically active forms (I and II) has now been accomplished. d-*Tris-2 : 2′-dipyridylruthenous* d-*tartrate* separates from an aqueous solution of the chloride and excess of ammonium *d*-tartrate, and after decomposition with aqueous potassium bromide furnishes d-*tris-2 : 2′-dipyridylruthenous bromide hexahydrate,* $[\alpha]_{5791}^{25°}$ + 860°, [*M*] + 7205°. The corresponding lævo-bromide, isolated by using *l*-ammonium tartrate, has a rotation $[\alpha]_{5791}^{25°}$ − 815°, [*M*] − 6828°. Specimens of lower rotation are obtainable from the filtrate after separation of the dextro-salt.



(I)



(II)

In comparison with the analogous iron and nickel salts the rate of racemisation of the ruthenium complexes is extremely slow. The foregoing bromides retain their activity indefinitely at room temperature not only in the solid state but also in 0·1% solution, whereas the rotations of the iron and nickel salts become negligible after about two hours in aqueous media. Moreover, *d*- and *l*-tris-2 : 2′-dipyridylruthenous bromides can be crystallised from hot water or even boiled for a few minutes without loss of optical activity. This resolution of a ruthenium compound is the first in which the metal is contained in a complex cation; activity due to a co-ordinated ruthenium anion has, however, been recorded by Charonnat (*Ann. Chim.*, 1931, **16**, 126), who obtained *d*- and *l*-forms of the complex salts R[Ru(NO)(C$_5$H$_5$N)(C$_2$O$_4$)$_2$] (R = NH$_4$ and C$_5$H$_6$N).

Tris-2 : 2′-dipyridylruthenous salts dye silk and wool in orange-yellow shades.

Experimental.

Tris-2 : 2′-dipyridylruthenous Chloride Hexahydrate.—Ruthenium trichloride (6·0 g.) and 2 : 2′-dipyridyl (50 g.) were stirred and slowly heated; reaction started at 250°, the temperature rose to 260°, and the black ruthenium trichloride became dark brown and crystalline, the change being accompanied by a considerable increase in the quantity of insoluble product. The mixture was stirred at 250—260° for 3 hours; the cooled melt was then extracted with hot benzene until no more solid dissolved. The yellow-brown residue (17 g.) was dissolved in water, filtered from insoluble material, including a little ruthenium, and evaporated to crystallising point. The bright red leaflets were collected, recrystallised from a small quantity of hot water, and dried over sulphuric acid (Found: C, 48·4; H, 4·6; N, 11·35, 11·3; Cl, 10·1, 9·9; Ru, 13·5, 13·4; H_2O, 14·2. $[C_{30}H_{24}N_6Ru]Cl_2,6H_2O$ requires C, 48·1; H, 4·8; N, 11·2; Cl, 9·5; Ru, 13·6; H_2O, 14·4%). The complex chloride was also formed by the action of 2 : 2′-dipyridyl on (a) ruthenium trichloride in an aqueous or alcoholic medium, (b) chlorotetramminohydroxyruthenium chloride hydrate (ruthenium-red) at 250° or in aqueous solution, (c) potassium nitrosoruthenium pentachloride at 250° or on prolonged action in an aqueous medium, (d) neutral salts of the types $R_2[RuCl_6]$ and $R_2[RuCl_5]$ or $R[RuCl_4]$. These preparations did not give such good yields as the method described above. *Tris-2 : 2′-dipyridylruthenous chloride hexahydrate* forms well-defined, bright red leaflets easily soluble in water and alcohol, but insoluble in acetone, chloroform, benzene, and petroleum. Slow crystallisation gave large, deep ruby-red rhombs. The chloride was unchanged by boiling concentrated hydrochloric acid or 50% caustic alkali. Concentrated sulphuric acid gave an orange-yellow solution, which became green on warming, and concentrated nitric acid furnished a deep green solution. Hydrogen peroxide and chlorine were without action at room temperature. Water of crystallisation was eliminated at 200° in a vacuum, but the salt was not decomposed below 300°.

Tris-2 : 2′-dipyridylruthenous Bromide Hexahydrate.—(a) An aqueous solution of the foregoing chloride was treated with excess of a concentrated solution of potassium bromide. (b) A solution of the base (*vide infra*) was treated with hydrobromic acid. The pink leaflets were crystallised from water (Found: Ru, 12·3; Br, 19·6; N, 10·2. $[C_{30}H_{24}N_6Ru]Br_2,6H_2O$ requires Ru, 12·1; Br, 19·1; N, 10·0%).

Tris-2 : 2′-dipyridylruthenous Iodide Hexahydrate.—Concentrated aqueous solutions of the chloride and potassium iodide were mixed. The red crystalline precipitate was recrystallised from hot water (Found: Ru, 11·2; I, 27·6; N, 9·1. $[C_{30}H_{24}N_6Ru]I_2,6H_2O$ requires Ru, 10·9; I, 27·2; N, 9·0%).

Tris-2 : 2′-dipyridylruthenous Perchlorate Hexahydrate.—(a) Concentrated aqueous solutions of sodium perchlorate and the complex chloride were mixed. (b) Perchloric acid was added to a solution of the base (*vide infra*). The sparingly soluble salt was crystallised from water {Found: Ru, 11·5; ClO_4, 22·2. $[C_{30}H_{24}N_6Ru](ClO_4)_2,6H_2O$ requires Ru, 11·6; ClO_4, 22·7%}.

Tris-2 : 2′-dipyridylruthenous Nitrate Hexahydrate.—Aqueous solutions containing equivalent quantities of the complex chloride or bromide (1 mol.) and silver nitrate (2 mols.) were mixed. The heated solution was filtered from silver halide and concentrated to crystallisation point. The red leaflets, which were readily soluble in water and alcohol, showed no signs of tervalent ruthenium {Found: Ru, 12·6; N, 14·2. $[C_{30}H_{24}N_6Ru](NO_3)_2,6H_2O$ requires Ru, 12·7; N, 14·0%}.

Tris-2 : 2′-dipyridylruthenous Hydroxide Octahydrate.—A concentrated aqueous solution of the foregoing chloride or bromide was shaken with an excess of freshly prepared silver oxide until it was free from halogen. The orange-red filtrate from the silver halide was evaporated to dryness over caustic soda. The complex *base* was recrystallised by cooling a solution in a small quantity of hot water to 0°, and dried over caustic potash {Found: Ru, 13·5; N, 11·3. $[C_{30}H_{24}N_6Ru](OH)_2,8H_2O$ requires Ru, 13·6; N, 11·2%}. This stable but rather hygroscopic base displaced ammonia from ammonium salts, precipitated metallic oxides or hydroxides from solutions of heavy-metal salts, and formed a carbonate with carbon dioxide.

Tris-2 : 2′-dipyridylruthenous Carbonate Decahydrate.—(a) An aqueous solution of the complex chloride or bromide was shaken with freshly prepared silver carbonate. (b) Carbon dioxide was passed into a solution of the foregoing base. The complex *carbonate* crystallised from cold concentrated solutions in red leaflets and was air-dried (Found: Ru, 12·5; N, 10·8. $[C_{30}H_{24}N_6Ru]CO_3,10H_2O$ requires Ru, 12·5; N, 10·4%). Four molecules of the water of crystallisation were lost over sulphuric acid in a vacuum (Found: loss, 9·2. Calc. for $4H_2O$, 8·9%).

Tris-2 : 2′-dipyridylruthenous Tartrate Hexahydrate.—Aqueous solutions containing equivalent quantities of the complex base and tartaric acid were mixed and evaporated to crystallising point. The very soluble *tartrate* was dried over sulphuric acid (Found: Ru, 12·6; N, 10·5. $[C_{30}H_{24}N_6Ru]C_4H_4O_6,6H_2O$ requires Ru, 12·3; N, 10·2%). It was also obtained from ammonium tartrate and the complex chloride in aqueous solution.

Optical Resolution of Complex Ruthenium Salts.—d-*Tris-2 : 2′-dipyridylruthenous* d-*tartrate hexahydrate.* Tris-2 : 2′-dipyridylruthenous chloride hexahydrate (2·5 g.) in water (100 c.c.) was cooled to 0°, and ammonium *d*-tartrate (50 g.) added all at once to the mechanically stirred solution. Small red crystals of the complex tartrate soon appeared and after 60 minutes the mixture was decanted from undissolved ammonium *d*-tartrate and filtered, and the complex tartrate dried on a porous plate. A 0·1% solution gave $\alpha + 0{\cdot}73°$; $[\alpha]_{5791}^{25°} + 365°$ ($l = 2$ dm.).

d-*Tris*-2 : 2'-*dipyridylruthenous bromide hexahydrate.* The foregoing active tartrate was dissolved in water and excess of concentrated aqueous potassium bromide added. The active bromide separated in small red plates; it was recrystallised from warm water until no further increase in optical rotation was noted. The final value for a 0·1% solution ($l = 2$) was $\alpha + 1{\cdot}73°$; $[\alpha]_{5791}^{25°} + 860°$, whence $[M] + 7205°$. The active bromide separated as the least soluble fraction in the crystallisations (Found: Ru, 12·6. Calc.: Ru, 12·1%). It remained unchanged in activity at room temperature, but racemised slowly at 90°. The rotation was not altered appreciably after conversion of the bromide into the complex carbonate by silver carbonate.

l-*Tris*-2 : 2'-*dipyridylruthenous bromide hexahydrate* was prepared in a similar manner to the dextrorotatory bromide, ammonium *l*-tartrate being used instead of the *d*-salt. After several crystallisations a 0·1% solution ($l = 2$) gave $\alpha - 1{\cdot}63°$, $[\alpha]_{5791}^{25°} - 815°$; whence $[M] - 6828°$.

Treatment of the filtrate from *d*-tris-2 : 2'-dipyridylruthenous *d*-tartrate with potassium bromide precipitated the lævorotatory bromide, $\alpha - 0{\cdot}45°$, $[\alpha]_{5791}^{25°} - 225°$, but the product was not sufficiently active for repeated crystallisation to lead to a pure specimen.

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