194. *Optical Activity dependent on a Six-covalent Bivalent Osmium Complex.*

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The reaction between potassium osmichloride $K_2[OsCl_6]$ or ammonium osmibromide $(NH_4)_2[OsBr_6]$ and excess of 2 : 2′-dipyridyl at 260—280° yields the complexes [Os $Cl_2$2dipy]Cl,$3H_2O$ and [Os 3dipy]Cl_2,$6H_2O$ and the corresponding bromides after separation and crystallisation from water. The dark-green bivalent osmium complex is stable towards aqueous acids and alkalis and has been converted into the corresponding *iodide, perchlorate,* and *hydroxide.* By use of silver antimonyl tartrate optically active enantiomorphs of the *antimonyl tartrate* and the *iodide* have been obtained.

It was shown some years ago by one of us (Burstall, *J.*, 1936, 173) that 2 : 2′-dipyridyl and ruthenium trichloride gave the well-defined stable salt [Ru 3dipy]Cl_2,$6H_2O$. The cation of this complex salt was sufficiently stable to be resolved into optically active forms by use of ammonium (+)- and (−)-tartrate. It has now been found that reaction of 2 : 2′-dipyridyl and potassium osmichloride and ammonium osmibromide at 260—280° results in reduction of the quadrivalent osmium salts to the tervalent and bivalent states with concurrent formation of the *chlorides* [OsCl_2 2dipy]Cl,$3H_2O$ (I) and [Os 3dipy]Cl_2,$6H_2O$ (II) or the corresponding *bromides.* The reactions of potassium osmichloride and ammonium osmibromide with 2 : 2′-dipyridyl are not, however, identical; the former gives a mixture of (I) and (II), except in presence of metallic osmium or other reducing agents which lead to (II) alone, whereas ammonium osmibromide gives almost entirely the bivalent osmium salt most conveniently isolated as the *iodide* [Os 3dipy]I_2,$3H_2O$ (III).

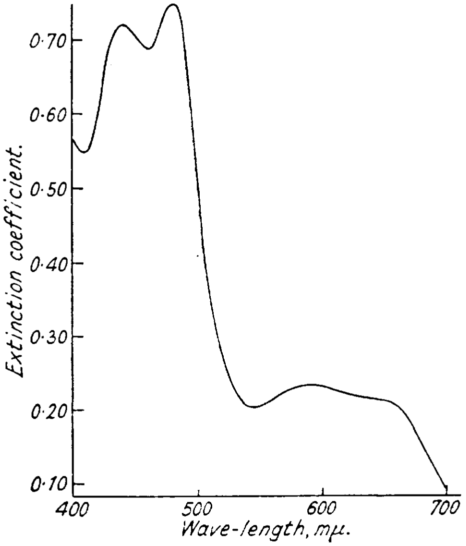
The dark red tervalent chloride (I) has not been closely examined but it can be reduced to (II) by heating it with 2 : 2′-dipyridyl and osmium metal. The chloride (II) and other salts of the complex cation [Os 3dipy]$^{++}$ are very dark green, crystalline substances which give intensely coloured solutions, very dark green by reflected light and dark red by transmitted light, even at concentrations of 10^{-5}M. The complex ion is stable in strongly acid or alkaline solutions, but in nitric acid or concentrated sulphuric acid the colour changes to red, probably by oxidation, with formation of a tervalent osmium complex ion of the type [Os 3dipy]$^{+++}$. Oxidation is accomplished by reagents such as ceric sulphate. The complex ion acts as a reversible redox indicator, the reaction

$$[\text{Os 3dipy}]^{++} \text{ (green)} \longrightarrow [\text{Os 3dipy}]^{+++} \text{ (red)} + e^-$$

having a potential of approximately 1 volt.

The separation of the optically active forms of the iodide [Os 3dipy]I_2,$3H_2O$ was carried out through the corresponding *antimonyl tartrate* but could be achieved, although less effectively, through the (+)-*tartrate* as with the analogous ruthenium derivative. The optically active antimonyl tartrates [Os 3dipy]$(SbOC_4H_4O_6)_2,2H_2O$, the less soluble being the lævorotatory salt, α^{20}_{5461} $-0{\cdot}08°$ in 0·0053% solution, $[\alpha]^{20}_{5461} \sim -1500°$, were converted into the iodides by potassium iodide and crystallised to constant rotation, the active forms separating in the least soluble portions during crystallisation. The observed rotations in 0·004% solutions of [Os 3dipy]I_2,H_2O were +0·085° and −0·09°, hence $[\alpha]^{20}_{5461}$ are about +2100° and −2200° respectively. These figures correspond to molecular rotations of the order of ±21,000°. Although optical activity is manifested in mercury light (λ 5461), the solutions do not show rotation in Na_D light, the wave-length of which is close to an absorption maximum (see Figure) for these solutions. The complex osmium iodide clearly has an abnormal rotatory dispersion, and an investigation of this effect with this salt and the corresponding ruthenium, iron, and nickel complexes is at present being carried out by two of the authors (F. P. D. and E. C. G.). It should also be noted that oxidation of the optically active ion $[Os\ 3dipy]^{++}$ to the tervalent condition $[Os\ 3dipy^{+++}]$ does not destroy the activity; moreover, the original activity is regained on reduction to the bivalent complex.

Absorption spectrum of $Os(dipy)_3I_2,3H_2O$ ($c = 5{\cdot}5 \times 10^{-5}$M.).



The optical resolution of this bivalent osmium salt is the first recorded resolution of an osmium compound in any valency state.

EXPERIMENTAL.

*Dichlorobis-*2 : 2′-*dipyridylosmium*(III) *Chloride Trihydrate* (I).—An intimate mixture of potassium osmichloride (1 g.) and 2 : 2′-dipyridyl (5 g.) was heated and stirred at 260° for 1 hour. The cold dark brown solid was then extracted with benzene to remove excess of 2 : 2′-dipyridyl. The insoluble portion was leached with warm water until no more solid dissolved, and filtered from a brown microcrystalline residue which was not further studied. The aqueous filtrate was evaporated and cooled; red needles of the complex *chloride* then separated. After crystallisation from water this was air-dried (Found : Os, 28·7; Cl, 15·8; H_2O, 8·4. $C_{20}H_{16}N_4Cl_3Os,3H_2O$ requires Os, 28·7; Cl, 16·1; H_2O, 8·1%). A solution of this chloride in water or alcohol was decomposed by aqueous alkalis with separation of a black hydrated osmium oxide but was not altered by being heated with 2N-hydrochloric acid. With a large excess of ammonium (+)-tartrate, the chloride gave an unstable complex tartrate which gave only optically inactive preparations on regeneration of the chloride with ammonium chloride or hydrochloric acid. Aqueous potassium iodide and sodium nitrite gave crystalline sparingly soluble salts with strong solutions of the chloride.

*Tris-*2 : 2′-*dipyridylosmium*(II) *Chloride Hexahydrate* (II).—(*a*) The filtrate after separation of the red chloride (I) was made alkaline with 2N-sodium hydroxide, boiled for a few minutes to decompose tervalent salt, cooled, filtered from a black deposit of hydrated osmium oxide, acidified with hydrochloric acid, and evaporated to dryness. The green chloride was extracted with alcohol, the extract was evaporated, and the residue crystallised from a small quantity of water, to give lustrous dark green leaflets of the chloride (II).

(*b*) Potassium osmichloride or the tervalent salt (I) (0·5 g.), metallic osmium (0·1 g.), and 2 : 2′-dipyridyl were heated at 270° for 1 hour. After removal of excess of 2 : 2′-dipyridyl the residue was extracted with water, and the filtered solution was treated as described in (*a*).

(*c*) A solution of the complex iodide (see below) was triturated with an excess of freshly prepared silver chloride and then filtered, and the resulting dark green solution evaporated to dryness and dried over calcium chloride (Found : N, 10·1, 10·1; Cl, 8·8; Os, 23·0, 22·4; H_2O, 13·1. $C_{30}H_{24}N_6Cl_2Os,6H_2O$ requires N, 10·0; Cl, 8·5; Os, 22·7; H_2O, 13·0%). This *chloride* was easily soluble in water or alcohol but insoluble in ether or benzene.

*Tris-*2 : 2′-*dipyridylosmium*(II) *Bromide Trihydrate.*—This salt was obtained by (*a*) treating the chloride (II) with excess of freshly prepared silver oxide, filtering, and adding hydrobromic acid, (*b*) adding a concentrated solution of potassium bromide to a strong solution of the chloride (II), or (*c*) triturating the corresponding iodide with silver bromide, filtering, and evaporating the solution. This *bromide* which formed dark green hexagonal plates was dried over calcium chloride (Found : N, 9·8, 9·8, 9·9; Br, 18·3; Os, 21·5. $C_{30}H_{24}N_6Br_2Os,3H_2O$ requires N, 9·6; Br, 18·3; Os, 21·8%). It was slightly less soluble in water than was the corresponding chloride, but was otherwise similar.

*Tris-*2 : 2′-*dipyridylosmium*(II) *Iodide Trihydrate.*—Ammonium osmibromide (1·0 g.) and 2 : 2′-dipyridyl (2·0 g.) were mixed intimately and heated carefully in a test-tube until the base in the mixture melted and then became red. The test-tube was loosely stoppered and transferred to an oil-bath at 270—280° for 1 hour; a dark green, almost black product and an almost colourless liquid then remained.

The liquid consisting mainly of unchanged 2 : 2′-dipyridyl was decanted and the solid extracted with hot water (200 ml.). After filtration from traces of a dark insoluble material, the salts in solution were fractionally precipitated with aqueous potassium iodide. The first fraction consisted of a red salt which was not further studied, whereas the more soluble fractions consisted of nearly pure tris-2 : 2′-dipyridylosmium(II) iodide trihydrate which was washed with ice-water and crystallised from hot water with addition of potassium iodide. The complex *iodide*, which has also been made by adding potassium iodide to a solution of the corresponding chloride, formed almost black, lustrous monoclinic prisms and was dried over calcium chloride (Found : N, 8·8; I, 26·9, 26·3; Os, 19·5. $C_{30}H_{24}N_6I_2Os,3H_2O$ requires N, 8·8; I, 26·3; Os, 19·8%).

Tris-2 : 2′-*dipyridylosmium*(II) *Perchlorate Monohydrate.*—This *salt* separated, on addition of sodium perchlorate solution to a hot solution of the corresponding iodide, as a sparingly soluble microcrystalline deposit (Found : N, 9·6; Os, 21·4. $C_{30}H_{24}N_6O_8Cl_2Os,H_2O$ requires N, 9·6; Os, 21·7%).

Tris-2 : 2′-*dipyridylosmium*(II) *Hydroxide Octahydrate.*—This compound was prepared from the corresponding iodide and freshly prepared silver oxide. The mixture was filtered and evaporated to dryness over solid sodium hydroxide. The crystalline *base* was deliquescent and absorbed carbon dioxide from the air (Found: N, 10·0. $C_{30}H_{26}O_2N_6Os,8H_2O$ requires N, 10·1%). Solutions of this hydroxide liberate ammonia from ammonium salts and precipitate ferric and cupric hydroxides from solution.

Optical Activity of Bivalent Osmium Salts.—(1-Dm. tubes were used in all determinations of rotation.) (−)-*Tris*-2 : 2′-*dipyridylosmium*(II) *antimonyl* (+)-*tartrate dihydrate.* The racemic iodide $[Os\ 3dipy]I_2,3H_2O$ (2·0 g.) in hot water (150 ml.) was shaken with silver antimonyl (+)-tartrate (0·8 g.) for 10 minutes and the solution was then filtered. The filtrate was concentrated on a steam-bath until about half the salt in solution could be crystallised by cooling in ice. The crystals of the *tartrate* were separated and washed with small quantities of ice-cold alcohol to remove traces of the more soluble salts (Found : N, 6·6; Os, 15·0. $C_{38}H_{32}O_{14}N_6Sb_2Os,2H_2O$ requires N, 6·65; Os, 15·0%). A 0·0053% solution in water gave α^{20}_{5461} −0·08°.

(−)-*Tris*-2 : 2′-*dipyridylosmium*(II) *iodide trihydrate.* The foregoing antimonyl tartrate was dissolved in warm water and fractionally precipitated with potassium iodide solution. With the exception of the final fraction, which was slightly lævorotatory, all fractions were strongly active. These fractions were crystallised from water to constant rotation, racemate being left in the filtrates. The lævorotatory *iodide* formed flat micaceous plates (Found : N, 8·8; I, 26·4. $C_{30}H_{24}N_6I_2Os,3H_2O$ requires N, 8·7; I, 26·3%) which in 0·004% solution in water gave α^{20}_{5461} (mean) −0·09°.

(+)-*Tris*-2 : 2′-*dipyridylosmium*(II) *iodide trihydrate.* The filtrate from the preparation of the antimonyl tartrate was diluted with water to 120 ml., heated to 60°, and fractionally precipitated with aqueous potassium iodide. The less soluble fractions, which were strongly dextrorotatory, were crystallised several times from water with addition of potassium iodide and formed micaceous crystals of the dextrorotatory *iodide* (Found : N, 8·7; I, 26·0. $C_{30}H_{24}N_6I_2Os,3H_2O$ requires N, 8·7; I, 26·3%). A 0·004% solution in water gave α^{20}_{5461} (mean) +0·085°.

(+)-*Tris*-2 : 2′-*dipyridylosmium*(II) (+)-*tartrate trihydrate.* A solution of 0·3 g. of the chloride $[Os\ 3dipy]Cl_2,6H_2O$ in water (10 ml.) was cooled to 0° and treated with solid ammonium (+)-tartrate (5 g.); the tartrate of the dextrorotatory complex separated in lustrous plates. These were freed from liquid between filter paper and dried by being washed with acetone. The solid was dissolved in alcohol to separate ammonium tartrate, filtered, diluted with a few drops of water, and precipitated by addition of acetone. This *tartrate* was micro-crystalline (Found : N, 9·7; Os, 21·6. $C_{34}H_{28}O_6N_6Os,3H_2O$ requires N, 9·8; Os, 22·1%). A 0·005% solution gave α^{20}_{5461} +0·1°. A dextrorotatory iodide and bromide can be produced from this tartrate by addition of potassium bromide or iodide; lævorotatory salts can also be isolated from the mother-liquors after separation of the dextrorotatory tartrate.

Analyses.—The analyses of the compounds for carbon and hydrogen were unsatisfactory owing to deposition of osmium in the absorption tubes. Halogen was determined by the distillation method (Dwyer and Nyholm, *J. Proc. Roy. Soc., New South Wales*, 1941, **75**, 127), nitrogen by the combustion method (Dumas), and osmium by a colorimetric procedure which will be recorded elsewhere (Dwyer and Gibson).

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