CCXXVIII.—*The Constitution of Complex Metallic Salts.*

By FREDERICK GEORGE MANN.

ONE of the chief remaining problems in connexion with the constitution of complex metallic salts, *e.g.*, monoaquopentamminocobaltic trichloride, $[H_2O(NH_3)_5Co]Cl_3$, concerns the nature of the linkage between the co-ordinated molecules of water, ammonia, etc., and the central metallic atom. Werner ("Anorganische Chemie," 1905, p. 58 *et seq.*) considered that such molecules were linked to the metallic atom by "auxiliary valencies" ("Nebenvalenzen"), but he used this term, not for any precise physical significance it possessed, but as a convenient method to distinguish this type of valency from the principal valencies ("Hauptvalenzen") present in simple metallic salts, and to base on this distinction an explanation of the stereochemical relationship of the complex salts themselves.

A consideration of the properties of such salts shows that the linkage between the ammonia molecules and the metallic atom must be—in modern nomenclature—a covalency, since it persists without ionisation in solution. Lowry (*Chem. and Ind.*, 1923, **1**, 318) suggested that the linkage between the nitrogen atom in the ammonia molecules and the cobalt atom consisted of two shared electrons, but that both these electrons were contributed by the nitrogen atom itself, *i.e.*, that the linkage was a "mixed double bond," later called a "semipolar double bond." The same theory was put forward simultaneously and in greater detail by Sidgwick (J., 1923, **123**, 725), who later developed it in full ("The Electronic Theory of Valency," 1927, Chapter VII); he considered this type of linkage to be identical with the "co-ordinate link" which joins the oxygen to the chlorine and to the sulphur in the perchlorates and sulphates, respectively, and has been shown to be present also in the tertiary amine oxides and in the sulphoxides.

No experimental evidence for the existence of these co-ordinate links in the metallic ammines has yet been forthcoming. Such evidence could be sought in two directions, however. First, a determination of the parachor of such salts might distinguish decisively between an ordinary covalency and a co-ordinate link, existing between the ammonia molecules and the metallic atom. Such determinations have not yet been made with the metallic ammines, because of the great difficulty of obtaining suitable salts which can be fused without decomposition. Secondly, the stereochemical properties of certain complex salts should provide the required information. Thus, if the linkage between the ammonia molecules and the cobalt atom in hexamminocobaltic chloride, $[Co(NH_3)_6]Cl_3$, is the same as that between the nitrogen and the oxygen atoms in, *e.g.*, methylethylpropylamine oxide, $MeEtPrN \longrightarrow O$, then replacement of one of the ammonia molecules in the cobalt salt by a molecule of the tertiary amine would give a complex salt

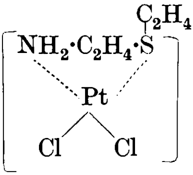
$$[MeEtPrN \longrightarrow Co(NH_3)_5]Cl_3,$$

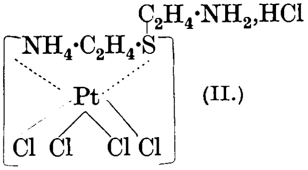
capable of resolution into optically active forms, owing to the presence of the asymmetric nitrogen atom thus linked to the cobalt. Since, however, it is only under exceptional conditions that tertiary amines will co-ordinate with metals (Mann and Pope, *Proc. Roy. Soc.*, 1925, **109**, *A*, 444), the preparation of such compounds would be attended with considerable experimental difficulties. Attention was therefore paid to the complex salts of platinum with the aliphatic sulphides, since usually they are of simple preparation and considerable stability. Attempts were made first to prepare potassium platino(methyl ethyl sulphide)trichloride, $K[MeEtS \longrightarrow PtCl_3]$: here also, if the above views are correct, the linkage between the sulphur and the platinum atoms is the same as that between the sulphur and the oxygen atoms in the sulphoxide, $MeEtS \longrightarrow O$. The platinous salt thus contains an asymmetric sulphur atom, and should therefore be resolvable into optically active forms (compare Harrison, Kenyon, and Phillips, J., 1926, 2079). Experiment showed, however, that in this series of sulphide-platinous complex salts, the neutral non-ionic member, *viz.*, *dichlorobis(methyl ethyl sulphide)platinum*, $[(MeEtS)_2PtCl_2]$, possessed much greater stability than the other members, and was always obtained when potassium chloroplatinite was treated with one molecular proportion of the sulphide. Attempts were therefore made to utilise the great stability of such salts, and to prepare one which, although possessing a non-ionic complex, would have, for resolution purposes, an acidic group as part of the sulphide molecule itself. *p*-Cyanobenzyl chloride was condensed with sodium ethyl sulphide, and the product on hydrolysis furnished p-*carboxybenzyl ethyl sulphide*, $CO_2H\cdot C_6H_4\cdot CH_2\cdot S\cdot C_2H_5$. This compound reacted readily with potassium chloroplatinite to give *dichlorobis-*(p-*carboxybenzyl ethyl sulphide)platinum*, $[(CO_2H\cdot C_6H_4\cdot CH_2\cdot S\cdot C_2H_5)_2PtCl_2]$. The latter, however, like all compounds of this type, was found to exist in two isomeric forms, regarded by Werner as having the *cis* and *trans* planar configuration. The first form, which preponderated markedly in quantity, was orange-yellow and insoluble in all liquids, and thus useless for resolution purposes; the second form, which was almost white, was soluble in alcohol, but occurred in very small yield. Moreover, each of these two isomeric compounds should contain two similar asymmetric sulphur atoms, and could therefore exist as racemic or *meso*-compounds, and in view of these difficulties their further investigation was not undertaken.

Finally, a simpler compound free from these complications was prepared. It had already been shown by the author (J., 1928, 890) that triaminopropane trihydrochloride reacts with potassium chloroplatinite, releasing two molecules of hydrogen chloride and forming dichloro(triaminopropane γ-monohydrochloride)platinum,

$[Cl_2PtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,HCl]$. It was found that a similar reaction occurred when ββ′-diaminodiethyl sulphide dihydrochloride, $(NH_2{\cdot}C_2H_4)_2S,2HCl$, reacted with potassium chloroplatinite in the presence of one equivalent of hydrogen chloride : co-ordination again occurred, with the release of one molecule of the acid, and the formation of *dichloro-*(ββ′*-diaminodiethyl sulphide monohydrochloride*)*platinum*, (I).

(I.)





(II.)

It will be seen that the complex is again of the neutral non-ionic type, since the platinous atom, of co-ordination number four, is linked to two chlorine atoms, to one amino-group, and to the sulphur atom. The second amino-group, not being co-ordinated, is free to form a hydrochloride, and the sulphur atom becomes asymmetric ; if, then, there is a co-ordinate link between the sulphur and the platinum atoms, the disposition of the three valencies of the sulphur atom is similar to that in the asymmetric sulphoxides, and the compound should be resolvable into optically active forms.

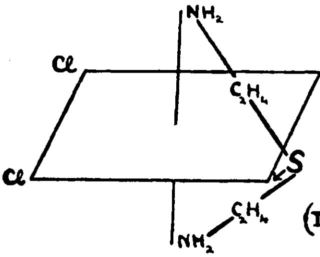
Experiment showed, however, that of the salts of this compound with optically active acids, only the *dichloro-*(ββ′*-diaminodiethyl sulphide mono-*d*-camphor-*β*-sulphonate*)*platinum* could be obtained crystalline, and this salt on repeated recrystallisation gave little sign of resolution. The original monohydrochloride was therefore dissolved in 2 equivs. of *N*-hydrochloric acid and treated with hydrogen peroxide. Oxidation proceeded in the cold, and *tetrachloro-*(ββ′*-diaminodiethyl sulphide monohydrochloride*)*platinum* (II) crystallised. In this salt the platinum atom, now quadrivalent and of co-ordination number six, is still at the centre of a complex of the neutral non-ionic type, and the salt fulfils the same stereochemical requirements as the former dichloro-compound.

When this hydrochloride was treated in solution with ammonium *d*-camphor-β-sulphonate, the d*-tetrachloro-*(ββ′*-diaminodiethyl sulphide* d*-camphorsulphonate*)*platinum* was obtained, having $[M]_{5461} + 1070°$. When this compound, in saturated ice-cold solution, was treated with concentrated calcium chloride solution, a rapid separation of the d*-tetrachloro*(*diaminodiethyl sulphide monohydrochloride*)*platinum*, having $[M]_{5461} + 1110°$, occurred. This activity is therefore decisive evidence that the three valencies of the sulphur atom possess a space direction similar to those of the sulphur atom in the asymmetric sulphoxides. Moreover, this compound is the first complex salt to be prepared in which optical activity is due to the asymmetry of an element directly co-ordinated to the central metallic atom.

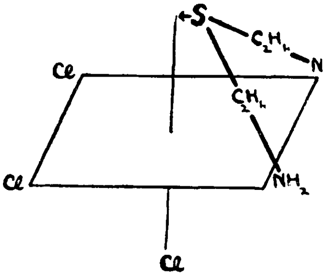
The hydrochloride of this tetrachloro-compound was of interest for another reason. It is not so stable as the dichloro-compound, and when boiled in aqueous solution for several minutes easily loses the hydrogen chloride molecule; the amino-group thus liberated at once co-ordinates with the metal, evicting a chlorine atom from the complex, and giving the highly crystalline *trichloro(diaminodiethyl sulphide)platinic monochloride*, $[Cl_3Pt(NH_2{\cdot}C_2H_4)_2S]Cl$. When the monohydrochloride of the tetrachloro-compound is treated in cold solution with ammonium camphorsulphonate, the corresponding camphorsulphonate of the tetrachloro-compound is obtained, as already described, and is quite stable in cold or even warm solution; if, however, the solution is boiled, hydrogen chloride is again lost, and *trichloro(diaminodiethyl sulphide)platinic* d-*camphorsulphonate*, $[Cl_3Pt(NH_2{\cdot}C_2H_4)_2S]C_{10}H_{15}O{\cdot}SO_3$, results. When, on the other hand, the monohydrochloride of the tetrachloro-compound is treated with ammonium bromocamphorsulphonate, even at room temperature, hydrogen chloride is always lost, and *trichloro(diaminodiethyl sulphide)platinic* d-*bromocamphorsulphonate*,

$$[Cl_3Pt(NH_2{\cdot}C_2H_4)_2S]C_{10}H_{14}BrO{\cdot}SO_3,$$

alone results. Some attention was paid to these compounds, because such salts might exist in two isomeric forms, in one of which the sulphide molecule is arranged about three apices on a square cross-section of the octahedron (III), whilst in the other it occupies three apices on a triangular face (IV). Both these forms possess a plane of symmetry, and cannot be resolved into optically active forms. It should be noted, however, that in the form (III), since the sulphur atom itself can be regarded as lying at one apex of a tetrahedron, it must undergo a lateral displacement away from that apex of the octahedron to which it is co-ordinated, and the only plane of symmetry is that through the three chlorine atoms. All salts of this complex were highly crystalline compounds giving no sign of two



(III)



(IV)

isomeric forms, and it is probable, therefore, that one form is considerably more stable than the other. This result is analogous to that obtained with similar salts of triaminopropane (Mann and Pope, J., 1926, 2675).

It should be added that parachor measurements of the acetylacetone derivatives of aluminium and beryllium have led Sugden (J., 1929, 318) to the conclusion that the organic molecule in these compounds is co-ordinated to the metal by a single electron or "singlet" link. It is possible that in the metallic ammines, a similar link holds the molecules of ammonia, aliphatic sulphides, etc., to the metal, and since a covalent link of this type would probably have a definite space-direction, optical activity might still be shown. It is hoped to prepare certain non-ionic derivatives of platinum with the aliphatic sulphides and disulphides which may be both fusible without decomposition and also soluble in liquids such as chloroform. Parachor measurements could then be made with the complex salt both fused and in solution, and evidence for the actual type of linkage obtained.

Attempts are also being made to prepare and resolve complex salts of platinum with various asymmetric tertiary phosphines and arsines, since the latter compounds, unlike the tertiary amines, co-ordinate readily with the noble metals.

EXPERIMENTAL.

All rotations given in this paper have been measured at 15° in a 4-dcm. polarimeter tube, using (unless otherwise stated) the mercury green line ($\lambda = 5461$).

The Complex Salts of Methyl Ethyl Sulphide.—Dichlorobis(methyl ethyl sulphide)platinum, $[\{(CH_3)(C_2H_5)S\}_2PtCl_2]$. Many experiments were performed in which an aqueous-alcoholic solution of ammonium chloroplatinite was treated with methyl ethyl sulphide in various proportions and at various temperatures. In no case was potassium platino(methyl ethyl sulphide)trichloride isolated, the above non-ionic compound being always the chief product. The latter was best obtained as an individual compound by performing the preparation at 50°: co-ordination was then rapid, and subsequent cooling gave a large yield of yellow crystals. If these were dried and recrystallised from boiling benzene, the *dichlorobis(methyl ethyl sulphide)platinum* was obtained in pale lemon-yellow crystals, m. p. 125—126°, very soluble in chloroform and moderately easily soluble in benzene (Found: S, 15·3; Pt, 46·6. $C_6H_{16}Cl_2S_2Pt$ requires S, 15·3; Pt, 46·7%). When the reaction was performed at room temperature, this compound was obtained mixed with an orange-coloured isomeric form; since, however, these compounds were useless for the purposes of this work, they were not further investigated.

The Complex Salts of p-*Carboxybenzyl Ethyl Sulphide.*—p-*Cyanobenzyl ethyl sulphide*, $CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}S{\cdot}C_2H_5$. *p*-Cyanobenzyl chloride, prepared by the method of Mellinghoff (*Ber.*, 1889, **22**, 3208), was added cautiously to a suspension of 1 equiv. of sodium ethyl sulphide in benzene. After the vigorous reaction had ceased, the product was boiled under reflux for one hour, and filtered from sodium chloride. After distillation of the benzene, the p-*cyanobenzyl ethyl sulphide* was obtained as a colourless oil, b. p. 167—168°/16 mm. (Found : C, 67·4; H, 6·0; S, 18·6. $C_{10}H_{11}NS$ requires C, 67·8; H, 6·2; S, 18·4%). Since the sulphide was an oil, it was further characterised by conversion into a crystalline sulphilimine : it reacted readily with a hot alcoholic solution of chloramine-T, and the solid product which separated on cooling was filtered off, washed with water, and twice recrystallised from hot alcohol. The p-*cyanobenzylethylsulphine*-p-*toluenesulphonylimine*,

$$CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}S(C_2H_5){\colon}N{\cdot}SO_2{\cdot}C_7H_7,$$

was obtained as white crystals, m. p. 158—160° (Found : C, 58·8; H, 5·2; S, 18·3. $C_{17}H_{18}O_2N_2S_2$ requires C, 58·9; H, 5·2; S, 18·5%).

p-*Carboxybenzyl ethyl sulphide*, $CO_2H{\cdot}C_6H_4{\cdot}CH_2{\cdot}S{\cdot}C_2H_5$. The cyano-compound may be hydrolysed with hydrochloric acid or with sodium hydroxide solution, but the latter gives the purer product. A mixture of cyanobenzyl ethyl sulphide (20 c.c.) and 10% sodium hydroxide solution (200 c.c.) was boiled under reflux for 5 hours. The solution when cold was diluted to 600 c.c. and filtered, and the acid was precipitated as a white crystalline solid by the addition of ice-cold dilute hydrochloric acid. The precipitate was dried, and twice recrystallised from benzene, and the p-*carboxybenzyl ethyl sulphide* thus obtained as white crystals, m. p. 124—125° (Found : C, 60·9; H, 6·15; S, 16·7. $C_{10}H_{12}O_2S$ requires C, 61·2; H, 6·1; S, 16·4%).

Dichlorobis-(p-*carboxybenzyl ethyl sulphide*)*platinum*,

$$[(CO_2H{\cdot}C_6H_4{\cdot}CH_2{\cdot}S{\cdot}C_2H_5)_2PtCl_2].$$

A solution of ammonium chloroplatinite (6 g.) in water (30 c.c.) was diluted with hot alcohol (60 c.c.), and the whole added to a warm solution of the above sulphide (6·3 g.) in alcohol (70 c.c.). The clear mixture was heated on the water-bath almost to boiling for 30 minutes, during which period the red colour rapidly faded and orange crystals separated. The solution was allowed to cool slowly and then filtered; the crystals so obtained were washed with hot alcohol, and then with water, and the *dichlorobis*-(p-*carboxybenzyl ethyl sulphide*)*platinum* thus obtained as heavy, deep orange crystals, m. p. 253—255° (decomp.), insoluble in all the usual liquids

(Found : C, 36·2; H, 3·6; Pt, 29·6. $C_{20}H_{24}O_4Cl_2S_2Pt$ requires C, 36·5; H, 3·7; Pt, 29·6%). The second *isomeric form* of this compound was obtained by allowing the original filtrate to stand for 24 hours, during which the separation of the small crop of almost white crystals was helped by occasional scratching. These crystals were freely soluble in hot alcohol, and were best purified by diluting their warm solution in alcohol with hot benzene; cooling gave the pure compound as fine, very pale yellow crystals, m. p. 254—255° (decomp.) (Found : C, 36·6; H, 3·6; Pt, 29·3%).

The Complex Salts of ββ'-Diaminodiethyl Sulphide.—The ββ'-diaminodiethyl sulphide dihydrochloride used in this investigation was prepared by the alkaline hydrolysis of diphthalimidodiethyl sulphide (Gabriel, *Ber.*, 1891, **24**, 1112).

Dichloro-(ββ'-diaminodiethyl sulphide monohydrochloride)platinum semihydrate, $[Cl_2Pt(NH_2\cdot C_2H_4)_2S,HCl],\frac{1}{2}H_2O$. A solution of diaminodiethyl sulphide dihydrochloride (10 g.) in *N*-hydrochloric acid (1 mol.; 52 c.c.) was added to a warm solution of potassium chloroplatinite (21·5 g.) in water (60 c.c.), and the mixture boiled gently under reflux for 5 hours, the colour of the solution changing rapidly from red to yellow. It was then evaporated to half-bulk, filtered, kept over-night, and filtered from a small quantity of a syrup which sometimes separated; on being scratched, it slowly deposited a large crop of the above *monohydrochloride*. This was recrystallised from a little hot water and obtained in fine yellow crystals, m. p. 105—107° (decomp.) (Found : C, 11·0; H, 3·3; N, 6·35; Cl, 24·6; S, 7·2; Pt, 45·1. $C_8H_{28}ON_4Cl_6S_2Pt_2$ requires C, 11·1; H, 3·3; N, 6·5; Cl, 24·6; S, 7·4; Pt, 45·2%).

Unless Gabriel's directions for the hydrolysis of the diphthalimidodiethyl sulphide are carefully followed, the diaminodiethyl sulphide dihydrochloride may be contaminated with some 1 : 4-thiazan monohydrochloride, $NH(C_2H_4)_2S,HCl$ (compare Cashmore and McCombie, J., 1923, **123**, 2884). During the above preparation, any thiazan present co-ordinated with the potassium chloroplatinite to give fine buff-coloured crystals, which, being insoluble in water, separated from the solution during the heating under reflux, and could be filtered off before the final evaporation; these crystals, when purified by washing with boiling water, alcohol, and ether, had m. p. 293—294° (decomp.) (Found : N, 5·5; Cl, 14·5; Pt, 38·35. $C_8H_{22}O_2N_2Cl_2S_2Pt$ requires N, 5·5; Cl, 14·0; Pt, 38·4%). In view of the marked inactivity of the sulphur atom in 1 : 4-thiazan (Davies, J., 1920, **117**, 297), it is probable that the nitrogen atom alone co-ordinates with the platinum, and that the thiazan molecule occupies only one co-ordination position : the compound, therefore, is probably *dichlorobis-(1 : 4-thiazan)platinum dihydrate*,

$[Cl_2Pt(HN{\cdot}C_4H_8S)_2],2H_2O$, and not the isomeric bis(thiazan)-platinous dichloride dihydrate, $[(HN{\cdot}C_4H_8S)_2Pt]Cl_2,2H_2O$.

Dichloro(diaminodiethyl sulphide monohydrogen oxalate)platinum monohydrate, $[Cl_2Pt(NH_2{\cdot}C_2H_4)_2S,(CO_2H)_2],H_2O$. This compound, and the picrate described below, were prepared in order to characterise the complex salt. When a solution of the hydrochloride (1·5 g.) in cold water (40 c.c.) was treated with a saturated solution of oxalic acid (20 c.c.), heavy, pale yellow crystals of the above *monohydrogen oxalate* slowly separated, and when filtered off, washed with cold water, alcohol, and ether, and dried, had m. p. 198—199° (decomp.) (Found: C, 14·7; H, 3·2; Pt, 39·7. $C_6H_{16}O_5N_2Cl_2SPt$ requires C, 14·6; H, 3·2; Pt, 39·5%). The oxalate is only slightly soluble in cold water, but freely so in hot water.

The *picrate*, $[Cl_2Pt(NH_2{\cdot}C_2H_4)_2S,C_6H_2(NO_2)_3(OH)]$, was prepared by adding a dilute aqueous solution of the hydrochloride very slowly, with stirring, to an excess of dilute sodium picrate solution. The picrate separated as a bright yellow powder, which was filtered off, washed with much cold water, and dried. It is moderately easily soluble in hot water, but separates on cooling as an oil, and cannot therefore be recrystallised: it ignites almost explosively on being heated (Found: S, 5·4; Pt, 31·8. $C_{10}H_{15}O_7N_5Cl_2SPt$ requires S, 5·2; Pt, 31·7%).

*Dichloro-(ββ′-diaminodiethyl sulphide mono-*d*-camphor-β-sulphonate) platinum*, $[Cl_2Pt(NH_2{\cdot}C_2H_4)_2S,C_{10}H_{15}O{\cdot}SO_3H]$. Solutions of the monohydrochloride (10 g.) in warm water (20 c.c.) and of ammonium *d*-camphorsulphonate (24 g.) in warm water (40 c.c.) were mixed. On standing, large yellow crystals of the *monocamphorsulphonate* separated. These were filtered off and dried (11·1 g.), and their rotation was determined before recrystallisation, lest racemisation occurred during the latter process. A 1·160% aqueous solution had $\alpha + 0{\cdot}53°$, whence $[\alpha] + 11{\cdot}4°$, $[M] + 71°$. This material was now recrystallised twice from warm water, and then a 1·465% solution had $\alpha + 0{\cdot}55°$, $[\alpha] + 9{\cdot}4°$, $[M] = + 58°$; m. p. 179—181° (decomp.); after six recrystallisations, a 1·660% solution had $\alpha + 0{\cdot}63°$, $[\alpha] + 9{\cdot}5°$, $[M] + 59°$ (Found: S, 10·2; Pt, 31·7. $C_{14}H_{28}O_4N_2Cl_2S_2Pt$ requires S, 10·35; Pt, 31·5%). Since the *d*-camphorsulphonate ion has a rotation of + 65·8° (Graham, J., 1912, **101**, 746), it was obvious that very little resolution was occurring; this was confirmed by converting a portion of each fraction into the corresponding monohydrogen oxalate, which in each case proved to be optically inactive.

All attempts to prepare the corresponding *d*-bromocamphor-π-sulphonate failed. Treatment of the aqueous solution of the hydrochloride with ammonium or potassium bromocamphorsulphonate gave no crystalline product, whilst similar treatment with silver bromocamphorsulphonate, followed by filtration, gave a solution which deposited no crystalline derivative and, when evaporated in a desiccator, gave only a brittle, uncrystallisable, yellow glass.

Action of ammonium nitrocamphor on the monohydrochloride. Many attempts were made to prepare a nitrocamphorate of the complex by double decomposition of the hydrochloride in aqueous solution with ammonium and sodium nitrocamphor. In each case, however, the latter compounds were sufficiently basic in solution (presumably owing to hydrolysis) to split off the hydrogen chloride from the platinous salt, and the free amino-group at once co-ordinated with the platinum, ejecting a chlorine atom from the complex, to give *monochloro(diaminodiethyl sulphide)platinous monochloride*, $[ClPt(NH_2{\cdot}C_2H_4)_2S]Cl$. The precipitate given by the mixed aqueous solutions was separated, and washed with alcohol and ether to remove free nitrocamphor, the above monochloride remaining as a pale yellow powder, without a definite melting point and insoluble in cold water (Found: Pt, 50·6. $C_4H_{12}N_2Cl_2SPt$ requires Pt, 50·55%).

Tetrachloro-(ββ′-diaminodiethyl sulphide monohydrochloride)-platinum monohydrate, $[Cl_4Pt(NH_2{\cdot}C_2H_4)_2S,HCl],H_2O$. The corresponding dichloro-compound (10 g.) was dissolved in *N*-hydrochloric acid (47 c.c.; 2 mols.), and "20-volume" hydrogen peroxide solution (20 c.c.) added in the cold. The large, deep orange crystals (9·7 g.) which separated in the course of a few hours were filtered off, washed with water, and dried, and thus gave the pure *tetrachloro-compound*, m. p. 190—191° (decomp.). The compound may be recrystallised from hot water in small quantities, but this treatment is unnecessary (Found: C, 9·5; H, 2·9; Pt, 38·3. $C_4H_{15}ON_2Cl_5SPt$ requires C, 9·4; H, 2·95; Pt, 38·2%).

d-*Tetrachloro(diaminodiethyl sulphide mono*-d-*camphor*-β-*sulphonate)platinum*, $[Cl_4Pt(NH_2{\cdot}C_2H_4)_2S,C_{10}H_{15}O{\cdot}SO_3H]$. A clear filtered solution of the above monohydrochloride (10 g.) in warm water (70 c.c.) was treated with a solution of a considerable excess of ammonium *d*-camphorsulphonate (15 g.) also in warm water (20 c.c.). The solution was allowed to cool and stand over-night, by which time a small crop of the *d*-camphorsulphonate of the inactive complex had separated in fine yellow crystals. This was filtered off and dried (Found: Pt, 28·5%). A 1·386% solution had $\alpha + 47°$, whence $[\alpha] + 8{\cdot}5°$, $[M] + 58°$.

The filtrate was now kept at room temperature for 3 days, and a large crop of heavy yellow crystals slowly separated, m. p. 198—199° (decomp.); these consisted of the d-*camphorsulphonate* of the dextrorotatory complex, and were apparently optically pure (Found : C, 24·8; H, 4·3; Pt, 28·0. $C_{14}H_{28}O_4N_2Cl_4S_2Pt$ requires C, 24·4; H, 4·1; Pt, 28·3%). A 1·283% solution when freshly prepared had $\alpha + 7·94°$, $[\alpha] + 155°$, $[M] + 1070°$. This solution, when kept at 15°, underwent slow racemisation, since $[M]$ fell to + 1030° after 7 hours, + 320° (24 hrs.), + 74° (50 hrs.), and + 63° (80 hrs.). In spite of this racemisation, the material in small quantities could be recrystallised rapidly from hot water without change in rotatory power. Thus, about 2 g. of the above sample were dissolved in a little hot water, and the solution was rapidly filtered and chilled, the camphorsulphonate crystallising in a few minutes. A 0·8703% solution of this recrystallised material had $\alpha + 5·46°$, $[\alpha] + 157°$, $[M] + 1080°$. The mother-liquor, obtained by the initial filtration of the above crop of *d*-complex *d*-camphorsulphonate, on standing for 10 days produced a further small crop of crystals, which proved to be identical with the first crop, *i.e.*, to be the *d*-camphorsulphonate of the inactive complex.

d-*Tetrachloro(diaminodiethyl sulphide monohydrochloride)platinum monohydrate.* In early experiments the conversion of the camphorsulphonate into the hydrochloride was effected by treating a hot aqueous solution of the former with concentrated calcium chloride solution. The hydrochloride so obtained was, however, always optically inactive, owing to rapid racemisation at the high temperature. To prevent this, a saturated solution of the sulphonate in ice-cold water was prepared, and then filtered and treated with an equal volume of cold saturated calcium chloride solution. The d-*hydrochloride* separated rapidly in yellow crystals, which, when filtered off, drained, and washed with alcohol and ether, had m. p. 187—188° (decomp.) (Found, for different preparations : C, 9·51; H, 3·0; Pt, 38·2, 38·1%). A 0·3693% solution, freshly prepared, had $\alpha_{5780} + 2·68°$, $[\alpha]_{5780} + 181°$, $[M]_{5780} + 926°$; and $\alpha_{5461} + 3·22°$, $[\alpha]_{5461} + 218°$, $[M]_{5461} + 1110°$; when kept at 15°, it had $[M]_{5461}$ + 849° (after 8 hrs.), + 330° (24 hrs.), + 140° (32 hrs.), and after 50 hours the solution was inactive.

Diaminodiethyl sulphide chloroplatinate, $(NH_2{\cdot}C_2H_4)_2S,H_2PtCl_6$. This *compound* was obtained as orange crystals, m. p. 217—218° (decomp.), when solutions of the hydrochloride of the amine, and of platinic chloride were mixed (Found : C, 9·0; H, 2·7; Pt, 37·0. $C_4H_{14}N_2Cl_6SPt$ requires C, 9·05; H, 2·65; Pt, 36·8%). It was prepared in the hope that co-ordination of the amine would occur when the aqueous solution of the chloroplatinate was boiled under reflux, and a quicker method of preparing these complex salts would thus be obtained. Actually, a mixture of compounds was obtained, from which no one individual could easily be isolated.

Trichloro(diaminodiethyl sulphide)platinic monochloride, $[Cl_3Pt(NH_2{\cdot}C_2H_4)_2S]Cl$. This compound was readily obtained by boiling under reflux a moderately concentrated aqueous solution of tetrachloro(diaminodiethyl sulphide monohydrochloride)platinum, whereupon crystals of the above less soluble monochloride separated : the preparation was found (rather unexpectedly) to be facilitated by the presence of dilute hydrochloric acid. The *monochloride* when recrystallised from hot water was obtained in large orange crystals, m. p. 220—222° (decomp.), showing no sign of isomeric forms (Found : C, 10·5; H, 2·7; Cl, 31·4; Pt, 42·65. $C_4H_{12}N_2Cl_4SPt$ requires C, 10·5; H, 2·65; Cl, 31·0; Pt, 42·7%).

Trichloro(diaminodiethyl sulphide)platinic d-*camphorsulphonate monohydrate,* $[Cl_3Pt(NH_2{\cdot}C_2H_4)_2S]C_{10}H_{15}O{\cdot}SO_3,H_2O$. This compound could be obtained either by treating the above monochloride in solution with silver camphorsulphonate, or by boiling under reflux an aqueous solution of the camphorsulphonate of the former tetrachloro-compound, hydrogen chloride being readily lost. The *camphorsulphonate monohydrate* was obtained as yellow crystals, m. p. 216—217° (decomp.), moderately easily soluble in hot water (Found : C, 24·9; H, 4·35; Pt, 29·1. $C_{14}H_{29}O_5N_2Cl_3S_2Pt$ requires C, 25·0; H, 4·35; Pt, 29·1%). A 0·5170% solution had $\alpha + 0{\cdot}24°$, $[\alpha] + 12°$, $[M] + 78°$, this activity being that of the sulphonate ion alone.

Trichloro(diaminodiethyl sulphide)platinic mono-d-*bromocamphor-π-sulphonate,* $[Cl_3Pt(NH_2{\cdot}C_2H_4)_2S]C_{10}H_{14}BrO{\cdot}SO_3$. This compound could also be obtained either by treating the above monochloride with silver bromocamphorsulphonate, or by treating aqueous solutions of the monohydrochloride of the tetrachloro-compound with ammonium or silver bromocamphorsulphonate : the latter experiments, whether carried out in cold or hot solutions, always involved the loss of hydrogen chloride, and the formation of the above *trichloro-sulphonate.* This compound was obtained on recrystallisation from hot water as pale orange crystals, m. p. 224—226° (decomp.) (Found : C, 22·6; H, 3·6; Pt, 26·7. $C_{14}H_{26}O_4N_2Cl_3BrS_2Pt$ requires C, 22·9; H, 3·6; Pt, 26·7%). A 0·284% solution had $\alpha + 0{\cdot}57°$, $[\alpha] + 50°$, $[M] + 367°$, the activity again being due to the sulphonate ion. Neither the above camphorsulphonate nor the bromocamphorsulphonate, although highly crystalline, showed any sign of structural isomerism.

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