191. *The Configuration of the Valencies of 4-Covalent Platinum: The Optical Resolution of* meso-*Stilbenediamino*iso*butylenediaminoplatinous Salts.*

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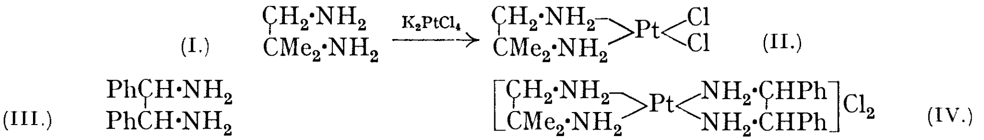
Although the weight of evidence yielded by the many investigations carried out in recent years on the stereochemistry of the compounds of 4-covalent nickel, palladium, and platinum would seem to favour the view (first advanced by Werner for platinous compounds of the type $[\mathrm{Pt\ a_2b_2}]$; *Z. anorg. Chem.*, 1893, **3**, 267) that the valencies of these elements in their 4-covalent state, instead of having the tetrahedral configuration usual in the compounds of 4-covalent elements, have a uniplanar arrangement, yet the question can scarcely be regarded as settled. We have therefore endeavoured to obtain evidence which would give a definite decision between the planar and the tetrahedral configuration of the valencies of platinum in one of the most stable types of the 4-co-ordination compounds of this element.

The compounds investigated were substitution derivatives of bisethylenediaminoplatinous salts, $[\mathrm{en_2Pt}]\mathrm{X_2}$. Although the frequency with which isomerism occurs in compounds containing a complex of the type $[\mathrm{a_2Pt\ b_2}]$ gives great weight to Werner's interpretation, yet it is always difficult, in dealing with geometrical isomerism, to make certain that the isomerism is actually of the nature supposed. There is no such difficulty with mirror-image isomerism. We have accordingly studied the salts of a substituted bisethylenediaminoplatinum in which the substituents are so placed that the salts will possess molecular dissymmetry if the platinum covalencies lie in one plane, but must have symmetrical ions if these valencies have a regular tetrahedral arrangement (*i.e.*, if they have the relative directions of the four three-fold axes of the regular tetrahedron).

These substances were the diphenyldimethyl derivatives of bisethylenediaminoplatinous salts in which the substituents had the positions indicated in formula (IV), the two phenyl groups being in the *cis*-relationship.



$$\text{(I.)}\quad \begin{array}{l}\mathrm{CH_2{\cdot}NH_2}\\ \mathrm{CMe_2{\cdot}NH_2}\end{array} \xrightarrow{\mathrm{K_2PtCl_4}} \begin{array}{l}\mathrm{CH_2{\cdot}NH_2}\\ \mathrm{CMe_2{\cdot}NH_2}\end{array}\!>\mathrm{Pt}<\!\begin{array}{l}\mathrm{Cl}\\ \mathrm{Cl}\end{array}\quad \text{(II.)}$$

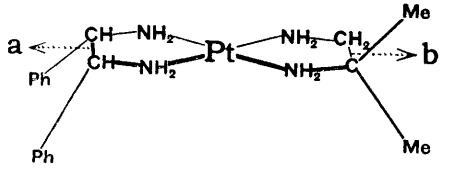
$$\text{(III.)}\quad \begin{array}{l}\mathrm{PhCH{\cdot}NH_2}\\ \mathrm{PhCH{\cdot}NH_2}\end{array} \qquad \left[\begin{array}{l}\mathrm{CH_2{\cdot}NH_2}\\ \mathrm{CMe_2{\cdot}NH_2}\end{array}\!>\mathrm{Pt}<\!\begin{array}{l}\mathrm{NH_2{\cdot}CHPh}\\ \mathrm{NH_2{\cdot}CHPh}\end{array}\right]\mathrm{Cl_2}\quad \text{(IV.)}$$

To obtain these salts iso*butylenediamine* (I) was treated with potassium chloroplatinite, and the resulting dimethylethylenediaminoplatinous chloride (II) (Drew and Head, J., 1934, 226) was made to interact with the *meso*-form of diphenylethylenediamine (stilbenediamine) (III).

The chelate base displaces (as chloride ions) the two chlorine atoms directly linked to the platinum, and occupies the co-ordination positions thus vacated, forming a salt (IV) of the required type.

It is evident that a cation of this structure will be dissymmetric if the platinum valencies lie in one plane, as shown in Fig. 1, but will possess a plane of symmetry if they have a tetrahedral arrangement, since the plane of symmetry of the diphenylated ring will then coincide with the plane of the dimethyl ring and become a plane of symmetry of the whole ion.

FIG. 1.



On investigation, these salts proved to be resolvable into antimeric optically active forms showing a high degree of optical stability.

The resolution was effected by means of diacetyltartaric acid. By fractional crystallisation of the *d*-diacetyltartrate the d-*diacetyltartrate* of the lævorotatory form of the platinum complex was isolated as the less soluble of the two diastereoisomeric salts. It showed $[M]_{5461}$ − 101° in water, the rotation due to the *d*-diacetyltartrate ion being − 52°. On conversion into iodide, a lævorotatory *iodide* [bn Pt sn]I_2 * with $[M]_{5461}$ − 68° in alcohol was obtained, and this, treated with silver chloride, gave the *chloride* [bn Pt sn]Cl_2, with $[M]_{5461}$ − 48·5° in water.

The platinum complex contained in the more soluble fractions of the *d*-diacetyltartrate was separated as *iodide* and converted into l-*diacetyltartrate*. By crystallisation of this, the *l*-diacetyltartrate of the *dextrorotatory* platinum complex was isolated ($[M]_{5461}$ + 103° in water) and from it the *dextrorotatory stilbenediamino*iso*butylenediaminoplatinous iodide* ($[M]_{5461}$ + 70·5° in alcohol) and the corresponding *dextrorotatory chloride* ($[M]_{5461}$ + 48·5° in water) were obtained.

The iodide and chloride crystallise with water of crystallisation, but there is no reason to doubt that the central platinum atom of the complex cation is truly 4-covalent; for, although the iodide is difficult to dehydrate completely, the chloride is readily obtained anhydrous, and the active chlorides retain their full optical activity after dehydration.

Also, a cryoscopic comparison of the chloride with barium chloride in aqueous solution showed that the two salts correspond closely in their cryoscopic behaviour, indicating that the platinum complex salt, like barium chloride, is unimolecular and at corresponding dilutions similarly dissociated into three ions.

The active salts have very considerable optical stability. In the cold no racemisation could be detected. Heated with dilute hydrochloric acid at 100°, a very slow loss of optical

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* bn = *iso*butylenediamine; sn = *meso*-stilbenediamine.

activity takes place, but this may be due in part to interaction with the acid, since heating with concentrated hydrochloric acid was found to bring about the change

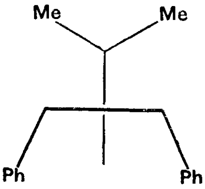
$$[\text{bn Pt sn}]\text{Cl}_2 + 2\text{HCl} = [\text{sn PtCl}_2] + \text{bn,2HCl}.$$

The complex salts are decomposed by reducing agents, such as magnesium or hydrazine, with the precipitation of metallic platinum and liberation of the co-ordinated bases.

The optically active chloride was treated in this manner, and after removal of the platinum, the resulting mixture of bases was found to be completely inactive. The diphenylethylenediamine thus liberated was extracted and found to be the pure inactive *meso*-form of the base (m. p. 119·5°). This observation removes any doubt there might be as to the actual optical inactivity of the bases co-ordinated with the platinum in the active salts. It proves that the dissymmetry of the molecule of the complex salt must arise from the relative positions in which the molecules of the two co-ordinated bases, themselves not dissymmetric, are held by the four co-valencies of the platinum atom.

With regard to the conclusions that may be drawn from the optical activity of these complex platinum salts, it is to be noted that, of the various possible arrangements of the four platinum covalencies, those which would give a *symmetrical* configuration for the cation of these salts (and are therefore excluded by the existence of the salts in antimeric optically active forms) are (1) the regular tetrahedral arrangement, and (2) all other arrangements in which the plane containing the two valencies linking the *iso*butylenediamine contains the line bisecting the angle between the two valencies linking the stilbenediamine and is at right angles to the plane of the latter valencies.

FIG. 2.



Dissymmetric configurations of the complex ion, on the other hand, would result from either (1) a planar arrangement, or (2) pyramidal, or (3) completely irregular tetrahedral arrangements, and any of these would accordingly be compatible with our observations.

That the four platinum covalencies could have such an irregular tetrahedral arrangement as their normal configuration is, however, so improbable that it can safely be disregarded. It is also clearly impossible that the bisethylenediaminoplatinous ion, if regularly tetrahedral in its unsubstituted state, should undergo such distortion in consequence of the particular type of substitution we have employed as to produce a degree of molecular dissymmetry that would give rise to stable optical activity. This is apparent from the symmetrical disposition of the substituent groups in Fig. 2, which represents a projection of the tetrahedral ion on the plane perpendicular to the axis *ab* (Fig. 1).*

There are also no reasons for inferring a pyramidal rather than the more symmetrical planar configuration. A pyramidal configuration would lead to molecular dissymmetry in comparatively simple compounds, as, for example, in diammino*iso*butylenediaminoplatinous salts $[\text{bn Pt(NH}_3)_2]\text{X}_2$. The actual alternative configurations between which a decision is required are therefore the regular tetrahedral and the planar; and the stable optical activity of these diphenyldimethylbisethylenediaminoplatinous salts shows that, if these are the two alternatives, then the latter—the planar configuration—is that which the 4-covalent platinum atom must in fact possess.

In conclusion, it may be pointed out that cyclic systems in which, as in these platinum salts, one atom of the ring has a much greater diameter than the others present somewhat special stereochemical features.

If the valencies of 4-covalent platinum were tetrahedrally arranged, and consequently

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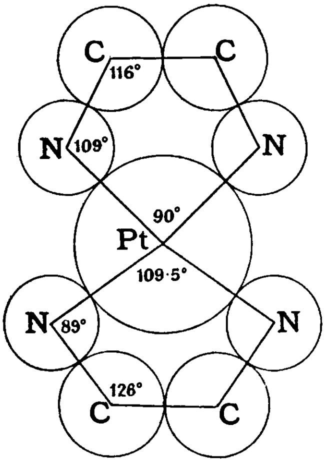
* In a ring of symmetrical structure containing two *cis*-phenyl groups as vicinal substituents, the interaction between the phenyl groups will doubtless produce some distortion of the molecule in one direction or the other, in consequence of which it would exist, when at rest, in one of two antimeric equilibrium configurations. But the forces causing a distortion of this kind must be quite inadequate to prevent rapid inter-transformation from one configuration to the other through thermal agitation, so that optical activity stable at ordinary temperatures could not possibly arise from such a cause.

A parallel case exists in *cis*-hexahydrophthalic acid, which is well recognised to be incapable of existing in optically active forms (Werner and Conrad, *Ber.*, 1899, **32**, 3046).

had an intervalency angle of 109·5°, there would be very considerable interannular strain in a five-ring system composed of carbon and nitrogen atoms and one (4-covalent) platinum atom. On the other hand, the planar arrangement of the platinum valencies with the corresponding intervalency angle of 90° gives a practically strainless ring.

FIG. 3.



This is apparent from Fig. 3, which represents the ring atoms of the ethylenediaminoplatinum ring in the positions they assume (*a*) when the platinum intervalency angle is fixed at 90° (upper ring) and (*b*) at 109·5° (lower ring). For the atomic radii, the following values are taken: 4-covalent platinum 1·32 Å. (Pauling and Huggins, *Z. Krist.*, 1934, **87**, 205); carbon 0·77 Å.; nitrogen 0·70 Å.; and the resulting intervalency angles are indicated on the figure. Actually, of course, the strains would be distributed between the different atoms.

If the normal intervalency angles of carbon and ammonium nitrogen are taken as 109·5°, the average valency deflexion per atom amounts to 15° in the lower ring, but is only 3° in the upper ring.

These favourable stereochemical relationships of the five-membered ring with the planar platinum atom doubtless constitute one of the factors contributing to the stability of the ethylenediaminoplatinous compounds.

EXPERIMENTAL.

iso*Butylenediamine.*—The preparation of this base was first attempted by Ssidorenko (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 955), and subsequently it has been obtained, but incompletely described, by Reihlen, von Hessling, Hühn, and Weinbrenner (*Annalen*, 1932, **493**, 20), by Strack and Schwaneberg (*Ber.*, 1932, **653**, 710), and by Drew and Head (J., 1934, 49). Catalytic reduction of α-acetamido*iso*butyronitrile was used by Reihlen, and of α-amino*iso*butyronitrile itself by Strack; Drew's method involved the reduction of α-amino*iso*butaldoxime. It has been found practicable to prepare *iso*butylenediamine by reduction of α-amino*iso*butyronitrile with sodium and alcohol, a method partially described by Strack and Fanselow (*Z. physiol. Chem.*, 1929, **180**, 159).

Dry ammonia is passed into crude acetone cyanohydrin (80 g.) in presence of anhydrous sodium sulphate (50 g.), the mixture being cooled at first in water. When the theoretical weight of ammonia is absorbed (about 4 hours), the liquid is decanted into 3 l. of fresh absolute alcohol and reduced by the rapid addition of 250 g. of sodium in 50-g. portions. The resulting mass is treated with water (600 c.c.) and distilled up to 100° in a vacuum, and the residue distilled in superheated steam at 140°. The distillates are collected in just sufficient dilute hydrochloric acid to keep the mixture acid, the alcohol removed and recovered, and the aqueous liquors evaporated to dryness on the water-bath. The yield of crude salt, which contains a little ammonium chloride, when dried in a vacuum over sulphuric acid, is usually 15—20 g. The dry salt is washed with alcohol, and boiled in concentrated aqueous solution with the gradual addition of 10% caustic soda until ammonia is removed. The hot, almost saturated solution is cautiously treated with an excess of 50% potash solution, and the upper layer of base separated and warmed with solid potash. The base is again separated from the aqueous potash layer and distilled from solid potash. The product is a colourless fuming oil, b. p. 112—115°/754 mm., 50°/21 mm., is hygroscopic, and approximates to the *monohydrate* in composition (Found: N, 25·0. $C_4H_{12}N_2,H_2O$ requires N, 26·3%).

The *anhydrous base*, prepared by the action of sodium on the hydrate and twice distilled from sodium in a vacuum, is an oil, b. p. 59°/20 mm., 62°/25 mm. (Found: C, 55·0; H, 13·7. $C_4H_{12}N_2$ requires C, 54·5; H, 13·7%).

The dihydrochloride was prepared from the base and dry hydrogen chloride in methyl-alcoholic solution, and dried in a vacuum. It forms small hygroscopic plates, which decompose at about 260° if heated slowly, and on rapid heating melt at 298—300° (decomp.). Strack (*loc. cit.*) gave m. p. 295° (Found: C, 29·9; H, 8·9; N, 17·2; Cl, 43·65. Calc.: C, 29·8; H, 8·8; N, 17·4; Cl, 44·0%).

The *dibenzoyl* derivative, after two crystallisations from aqueous alcohol, had m. p. 182° (Found : C, 72·9; H, 6·9; N, 9·4. $C_{18}H_{20}O_2N_2$ requires C, 72·9; H, 6·8; N, 9·5%).

meso-*Stilbenediamine*.—This base is prepared from amarin, either by Grossmann's method (*Ber.*, 1889, **22**, 2298) or, much more conveniently, by acetylation and hydrolysis of acetylamarin first to *N*-benzoyl-*N'*-acetylstilbenediamine, and then to *meso*-stilbenediamine itself.

Hydrobenzamide (100 g.) is heated in an oil-bath at 120—130° for 5 hours, and to the warm yellow product are added acetic anhydride (175 c.c.) and fused sodium acetate (3 g.), and the mixture boiled gently for 3 hours. The product is then treated with water (300 c.c.) and concentrated hydrochloric acid (25 c.c.) and heated for 2 hours on the water-bath. The precipitate is filtered off, well dried by means of the pump, and boiled out twice with 250 c.c. of spirit. The colourless solid is then dried at 100—120°. Yield, 54 g. (46%); m. p. 314—315°. On account of its marked insolubility in most solvents, benzoylacetylstilbenediamine is conveniently separated by boiling out soluble substances with alcohol. The pure substance is obtained by crystallisation from nitrobenzene, from which it separates in fine colourless needles; m. p. 316° (Japp and Moir, J., 1900, **77**, 611, gave 316°) (Found : C, 75·9; H, 6·2; N, 7·8. Calc. : C, 77·1; H, 6·2; N, 7·8%). The carbon determination was always low as stated by Japp and Moir.

54 G. of the crude benzoylacetylstilbenediamine are heated with water (550 c.c.) and concentrated sulphuric acid (550 c.c.) to boiling, and a current of steam passed to remove benzoic acid and prevent concentration of the sulphuric acid, which otherwise causes the production of yellow or brown colouring matter. After 2—3 hours, when hydrolysis is complete, the mixture is well cooled, and cautiously treated with ammonia and ice, the total volume being kept as small as possible. After the addition of 600 c.c. of ammonia (*d* 0·880), the mixture is left over-night, filtered through glass-wool to remove a sticky product, and made alkaline in the cold with excess (about 150 c.c.) of ammonia (*d* 0·880). The stilbenediamine separates in good yield and is almost colourless. It is crystallised several times from water, and forms colourless leaflets of m. p. 119·5° (uncorr.) (Japp and Moir gave m. p. 120°) (Found : C, 79·2; H, 7·55; N, 13·4. Calc. : C, 79·2; H, 7·6; N, 13·2%). The base is fairly soluble in hot water, only moderately in cold. On heating in air at 100°, it slowly develops a yellow colour.

*Dichloro*iso*butylenediaminoplatinum* (cf. Drew and Head, J., 1934, 226).—This was prepared by the action of *iso*butylenediamine on a slight excess of aqueous potassium platinochloride at the room temperature, and filtered off at intervals to avoid further action. It was thus almost free from the Magnus salt and formed yellow prisms in 64% yield. It decomposed without melting from about 263° upwards (Found : C, 13·5; H, 3·4; Cl, 20·0; Pt, 55·5. Calc. : C, 13·55; H, 3·4; Cl, 20·0; Pt, 55·1%).

dl-meso-*Stilbenediamino*iso*butylenediaminoplatinous Iodide*.—19·5 G. of dichloro*iso*butylenediaminoplatinum are heated with *meso*-stilbenediamine (12 g.) in water (130 c.c.) to 100° for 5 hours, the mixture is then cooled and filtered, and warmed to about 30° whilst to it are added slowly with stirring 22 g. of sodium iodide dissolved in the least quantity of water. After some hours, the chilled mixture is filtered, and the precipitate washed with cold sodium iodide solution and a little water. The almost colourless complex *iodide* is obtained and dried at 100°. After recrystallisation from spirit, it forms colourless needles of the pure *monohydrate*; yield 19·4 g. The water is lost with difficulty even at 140°. The iodide has m. p. 269—270° (decomp.), and is sparingly soluble in cold water (Found : C, 28·1; H, 3·7; I, 33·05; Pt, 25·3. $C_{18}H_{28}N_4I_2Pt,H_2O$ requires C, 28·15; H, 3·9; I, 33·1; Pt, 25·4%).

dl-meso-*Stilbenediamino*iso*butylenediaminoplatinous Chloride*.—The chloride is prepared by shaking the iodide (2·02 g.) in suspension in hot water (75 c.c.) with excess of freshly precipitated silver chloride. The liquid is decanted through an ordinary filter, and the residue extracted with a little boiling water. The filtrates are evaporated almost to dryness, the residue taken up in a little hot alcohol, and ether added to promote crystallisation. The yield of crystalline *chloride* is 1·37 g. (91%). Dried at 110°, it is anhydrous and has m. p. 291·5—292° (decomp.) (Found : C, 38·2; H, 5·0; Cl, 12·7; Pt, 33·9. $C_{18}H_{28}N_4Cl_2Pt$ requires C, 38·1; H, 5·0; Cl, 12·5; Pt, 34·5%). It is very soluble in water.

The d-*α-bromocamphor-π-sulphonate* was prepared from the iodide (3 g.) in boiling water (70 c.c.) and silver bromocamphorsulphonate (3·35 g.) in hot water (25 c.c.). After being heated for ½ hour at 100°, the mixture was filtered, and the precipitate extracted with boiling water (50 c.c.). On concentration, the combined filtrates gave successive crops of fine colourless needles, apparently identical, and sparingly soluble in water, but rather more soluble in alcohol (Found : C, 39·8; H, 5·15; Pt, 17·3; loss at 145°, 2·2. $C_{38}H_{56}O_8N_4Br_2S_2Pt,1\frac{1}{2}H_2O$ requires C, 39·9; H, 5·2; Pt, 17·1; $1\frac{1}{2}H_2O$, 2·4%).

The two extreme fractions from the aqueous liquor gave $[M]_{5461} = +\ 690°$ in 20% alcohol, and + 691° in 25% alcohol respectively, and no change of rotation was observed after 24 hours. Each fraction was precipitated from the aqueous alcohol as the insoluble picrate by means of aqueous sodium picrate, and the picrate filtered, washed and decomposed by dilute hydrochloric acid. After removal of the picric acid an inactive solution was obtained.

On crystallisation from alcohol the bromocamphorsulphonate afforded a homogeneous material giving $[M]_{5461} = +\ 700°$ in water, indicating no resolution.

The *picrate* is a yellow powder insoluble in water or alcohol, and when dried at 100° gave Pt, 20·5 ($C_{30}H_{32}O_{14}N_{10}Pt$ requires Pt, 20·5%).

The d-*camphor*-10-*sulphonate* was prepared from the iodide and an equivalent quantity of silver camphorsulphonate in aqueous solution. It is colourless and very soluble in water. The salt was crystallised six times from alcohol–ether, and dried at 100°. It crystallised easily and was apparently homogeneous (Found : C, 45·7; H, 6·1; Pt, 19·6. $C_{38}H_{58}O_8N_4S_2Pt,2H_2O$ requires C, 45·9; H, 6·3; Pt, 19·6%). 0·1444 G. in 20 c.c. of aqueous solution showed $\alpha = +\ 0{\cdot}19°$, $l = 2$, $\lambda = 5461$, or $[M]^{15°}_{5461} = +\ 135°$, accounted for by the camphorsulphonate ions.

0·92 G. of this camphorsulphonate was precipitated in the cold by concentrated sodium iodide solution, but the iodide obtained was inactive in spirit.

The d-*tartrate* is best prepared from the soluble carbonate (obtained from the iodide and silver carbonate) by treatment in cold aqueous solution with the correct amount of tartaric acid. The solution is evaporated under reduced pressure at the ordinary temperature. The salt is very soluble in water and hot alcohol, and its solutions decompose gradually on heating or keeping. The salt obtained by evaporation at room temperature is the tetrahydrate (Found : Pt, 27·2. $C_{22}H_{32}O_6N_4Pt,4H_2O$ requires Pt, 27·3%). The salt dissolved in hot methyl alcohol but separated after a minute as the *monohydrate* in a fine powder, which was dried at the ordinary temperature (Found : C, 39·6; H, 5·6; N, 8·4; Pt, 29·4. $C_{22}H_{32}O_6N_4Pt,H_2O$ requires C, 39·9; H, 5·2; N, 8·5; Pt, 29·5%). This crystallised slowly in very small crystals from aqueous methyl alcohol on the addition of acetone. The product was converted into the iodide, which proved to be inactive in alcohol.

The diacetyl-d-*tartrate.* 25 G. of iodide (m. p. 269—270°), suspended in 250 c.c. of warm water, were well shaken for an hour with freshly precipitated silver carbonate from 15 g. of silver nitrate, and the mixture filtered first at the pump, then through an ordinary filter to remove finely divided silver salts. To the filtrate were added 7·25 g. of diacetyltartaric anhydride (Chattaway and Parkes, J., 1923, **123**, 663), and the whole was evaporated in a vacuum below 60° as rapidly as possible to avoid hydrolysis. The products from four such preparations were mixed and crystallised. The only satisfactory procedure was to dissolve the salt (10 g.) in a very little warm water (6 c.c.) and to add a large excess (200 c.c.) of absolute (99%) alcohol. The salt separates slowly and is filtered after 24 hours, and dried in a vacuum over sulphuric acid after each crystallisation. It is hygroscopic, exceedingly soluble in water, and hydrated. Dried at 100°, it approximates to the dihydrate.

After seven crystallisations thus from aqueous alcohol, a less soluble fraction consisting of well-formed colourless plates was obtained, which after drying in a vacuum at 85° gave $[\alpha]_{5461} = -\ 13{\cdot}9°$ in water. After two further crystallisations $[\alpha]_{5461}$ was − 13·6°.

By systematic fractionation, 16·4 g. of l-meso-*stilbenediamino*iso*butylenediaminoplatinous diacetyltartrate* (Found : C, 41·9; H, 5·2; Pt, 26·1. $C_{26}H_{36}O_8N_4Pt,H_2O$ requires C, 41·8; H, 5·1; Pt, 26·2%) were obtained from the initial 100 g. of racemic iodide. The substance when vacuum-dried at 85° discolours from about 245° and melts with rapid decomposition at 275°. 0·2535 G. in 30 c.c. of aqueous solution at 16° gave $\alpha = -\ 0{\cdot}46°$ ($l = 4$), $\lambda = 5461$, whence $[\alpha]^{16°}_{5461} = -\ 13{\cdot}6°$, $[M]^{16°}_{5461} = -\ 101°$. Attempts to dry the salt at temperatures above 100° led to gradual decomposition.

For comparison, the rotation of the *d*-diacetyltartrate ion was found by observations on disodium diacetyltartrate in similar conditions to be $[M]_{5461} = -\ 52°$ approximately, indicating therefore a rotation for the complex platinum ion of about − 49°.

2·2743 G. of diacetyltartaric anhydride and 1·7683 g. of sodium bicarbonate were each dissolved in cold water, mixed, well shaken until evolution of carbon dioxide ceased, and made up to 100 c.c., the total concentration being equal to 2·928 g. of disodium salt in 100 c.c. The solution, with $l = 4$, $\lambda = 5461$, at 20°, gave $\alpha = -\ 2{\cdot}11°$; diluted to half strength, $\alpha = -\ 1{\cdot}08°$, and diluted to $\frac{1}{6}$ strength, $\alpha = -\ 0{\cdot}38°$. The corresponding values of $[\alpha]$ are − 18·0°, − 18·4°, − 19·4°; and of $[M]$ − 50°, − 51°, − 54°.

l-meso-*Stilbenediamino*iso*butylenediaminoplatinous Iodide.*—To 8·47 g. of the *l*-complex diacetyltartrate dissolved in water (20 c.c.) was slowly added a solution of sodium iodide (5 g.) in water (9 c.c.). The complex iodide crystallised, and was filtered off, washed with 20% sodium iodide solution followed by acetone, and dried at 100°.

The l-*iodide* is sparingly soluble in water but more soluble in alcohol; 0·2995 g. in 30 c.c. of alcoholic solution, at 17°, $\lambda = 5461$, gave $\alpha = -0{\cdot}355°$, $l = 4$, or $[M]^{17°}_{5461} = -68°$. After one crystallisation from spirit, 7·14 g. of colourless, long, thin prisms were obtained. These, when dried at 100°, had m. p. 271—272° (decomp.) (Found: C, 28·6; H, 3·9; N, 7·3; I, 33·1; Pt, 25·25; loss at 85° in a vacuum, 1·7. $C_{18}H_{28}N_4I_2Pt,H_2O$ requires C, 28·2; H, 3·9; N, 7·3; I, 33·1; Pt, 25·4; H_2O, 2·3%). 0·358 G. in 30 c.c. of alcoholic solution gave $\alpha = -0{\cdot}42°$, $l = 4$, at 19°, $\lambda = 5461$, whence $[M]^{19°}_{5461} = -68°$. The rotation remained constant.

l-meso-*Stilbenediamino*iso*butylenediaminoplatinous Chloride*.—4 G. of the iodide suspended in water (75 c.c.) at 40° were shaken with an excess of freshly precipitated silver chloride for 2 hours. The silver halides were filtered off and washed with 20 c.c. of hot water, and the solution evaporated rapidly on the water-bath until crystallisation set in. The mass was taken up in hot spirit (30 c.c.), filtered from traces of silver halide, and caused to crystallise by the addition of ether. The l-*chloride* crystallises as the *dihydrate* in clusters of colourless fine silky needles; yield 3·13 g. (almost theoretical) (Found: Cl, 11·8; Pt, 32·3. $C_{18}H_{28}N_4Cl_2Pt,2H_2O$ requires Cl, 11·8; Pt, 32·4%).

The water is lost at 100° or in a vacuum at 90°. For polarisation and analysis, the salt was dried for 3 hours at 90° in a vacuum. It discolours at 290—291°, and melts at 295° (decomp.) (Found: C, 37·9; H, 5·1; N, 9·8; Cl, 12·5; Pt, 34·2. $C_{18}H_{28}N_4Cl_2Pt$ requires C, 38·1; H, 5·0; N, 9·9; Cl, 12·5; Pt, 34·5%).

1·0038 G. in 30 c.c. of aqueous solution ($l = 4$) at 18° gave: $\alpha = -1{\cdot}03°$, $\lambda = 5780$, $[M]_{5780} = -43{\cdot}5°$; $\alpha = -1{\cdot}15°$, $\lambda = 5461$, $[M]_{5461} = -48{\cdot}5°$; $\alpha = -1{\cdot}88°$, $\lambda = 4359$, $[M]_{4359} = -79{\cdot}7°$.

0·5 G. of the chloride ($[M]_{5461} = -48{\cdot}5°$) in water (25 c.c.) was heated on the water-bath for 2 hours with 50% hydrazine hydrate (4 c.c.) and sodium hydroxide (0·3 g.). After acidification with acetic acid and removal of the precipitated platinum, the solution, made up to 30 c.c., was found to be optically inactive. On making it alkaline, *meso*-stilbenediamine (0·144 g.; 77% of theory) crystallised with m. p. 119—119·5°; mixed m. p. with authentic *meso*-stilbenediamine, 119—119·5° (Found: C, 79·4; H, 7·8. Calc.: C, 79·2; H, 7·6%).

In a comparison by the freezing-point method with barium chloride, the results in the same conditions were:

Barium chloride.			l-*Complex chloride.*		
G.-mols./1000 g. H_2O.	Measured depression.	Molecular depression.	G.-mols./1000 g. H_2O.	Measured depression.	Molecular depression.
0·01617	0·088°	5·44°	0·0327	0·192°	5·88°
0·03678	0·192	5·22	0·0389	0·200	5·27
0·09677	0·495	5·12	0·0692	0·343	4·95
0·1439	0·727	5·05			
	Mean	5·2		Mean	5·4

Hall and Harkins (*J. Amer. Chem. Soc.*, 1916, **38**, 2674) found 5·08° and 4·70° for concentrations of 0·01 and 0·1 g.-mol. of barium chloride per 1000 g. of water respectively.

The chloride values thus correspond with those for barium chloride, indicating that the complex chloride is a monomeric ternary electrolyte.

d-meso-*Stilbenediamino*iso*butylenediaminoplatinous Diacetyl*-l-*tartrate*.—The more soluble fractions of the diacetyl-*d*-tartrate which were found polarimetrically to contain an appreciable excess of the *d*-complex *d*-acetyltartrate were reconverted into the iodide, and the iodide converted by way of the carbonate and diacetyl-*l*-tartaric anhydride into the diacetyl-*l*-tartrate.

20·5 G. of this iodide furnished diacetyltartrate, from which, after four crystallisations as described, were isolated 10·2 g. of pure *d*-complex *diacetyltartrate*. This was dried in a vacuum at 90°, and showed m. p. 275° (decomp.), after previous discoloration. The salt forms colourless hygroscopic plates and is the monohydrate (Found: C, 41·6; H, 5·4; Pt, 26·0. $C_{26}H_{36}O_8N_4Pt,H_2O$ requires C, 41·8; H, 5·1; Pt, 26·2%). 0·2014 G. in 30 c.c. of aqueous solution gave $\alpha_{5461} = +0{\cdot}37°$ ($l = 4$), at 20°, or $[\alpha]^{20°}_{5461} = +13{\cdot}9°$, $[M]^{20°}_{5461} = 103°$.

The d-*iodide*. 8·1 G. of the above diacetyltartrate were converted into the iodide by the method used for the *l*-series, and the *d*-iodide was crystallised from spirit and dried at 100°. Yield, 7·15 g. of colourless long flat prisms, which discolour at about 255° and melt at 270—272° (rapid decomp.). The *monohydrate* is thus obtained (Found: C, 28·3; H, 3·8; N, 7·3;

I, 33·2; Pt, 25·4; loss in vacuum at 115°, 2·2. $C_{18}H_{28}N_4I_2Pt,H_2O$ requires C, 28·2; H, 3·9; N, 7·3; I, 33·1; Pt, 25·4; H_2O, 2·3%). The *anhydrous* salt gave I, 34·1 ($C_{18}H_{28}N_4I_2Pt$ requires I, 33·9%).

An alcoholic solution of 0·3630 g. of the monohydrate in 30 c.c. gave $\alpha_{5461} = + 0{\cdot}445°$ at 19° ($l = 4$), whence $[M]_{5461}^{19°} = + 70{\cdot}5°$. The rotation was constant.

The d-*chloride.* 4 G. of the *d*-iodide monohydrate were converted by means of silver chloride into the chloride, and this crystallised from alcohol with the addition of ether. Yield, 3·03 g. (97%) of the *dihydrate* in clusters of colourless, fine, silky needles (Found : Cl, 11·7; loss in a vacuum at 90°, 6·1. $C_{18}H_{28}N_4Cl_2Pt,2H_2O$ requires Cl, 11·8; $2H_2O$, 6·0%).

The *anhydrous* salt was prepared from the hydrate by drying for 3 hours at 90° in a vacuum (Found : C, 38·1; H, 5·0; Cl, 12·4; Pt, 34·6. $C_{18}H_{28}N_4Cl_2Pt$ requires C, 38·1; H, 5·0; Cl, 12·5; Pt, 34·5%). It discolours at 290—291° and melts at 295° (decomp.).

1·0006 G. of this anhydrous chloride were made up to 30 c.c. in water at 19° and gave ($l = 4$) : $\alpha = + 1{\cdot}01°$, $\lambda = 5780$, $[M]_{5780} = + 42{\cdot}7°$; $\alpha = + 1{\cdot}14°$, $\lambda = 5461$, $[M]_{5461} = + 48{\cdot}5°$; $\alpha = + 1{\cdot}90°$, $\lambda = 4359$, $[M]_{4359} = + 81{\cdot}2°$.

The rotation was stable in aqueous solution. The solution (total volume 32 c.c.) was then heated with 3·5 c.c. of 10*N*-hydrochloric acid for 1½ hours at 100°, being allowed to concentrate to just less than 30 c.c. After being made up to 30 c.c. again, it had $\alpha_{5461} + 1{\cdot}12°$, a reduction of only 2%. After 4 hours' heating, the solution being allowed to concentrate to about 7 c.c., 0·025 g. of yellow crystals separated. The filtrate, made up to 30 c.c., gave $\alpha_{5461} = + 0{\cdot}92°$; hence 82% of the activity persists. The yellow substance, washed with hot alcohol and ether, proved to be *dichlorostilbenediaminoplatinum* (Found : Pt, 40·8. $C_{14}H_{16}N_2Cl_2Pt$ requires Pt, 40·8%).

Melting-point determinations indicate the formation of a racemic compound between the *d*- and the *l*-complex chloride. Parallel determinations of m. p.'s gave the following results : *d*-chloride, 295°; 71·5% *d* + 28·5% *l*, 287·5—288·5°; racemic chloride, 291·5—292°; 31% *d* + 69% *l*, 284—285°; *l*-chloride, 295°.

l-*Diacetyltartaric Anhydride.*—*l*-Tartaric acid, from ammonium *l*-tartrate (Kellett, *J. Soc. Chem. Ind.*, 1932, **51**, 204), was acetylated by heating with acetic anhydride and two drops of concentrated sulphuric acid at 80° for a few minutes, and on scratching, the acetyltartaric anhydride separated. It was filtered off, washed with acetic anhydride, and dried in a vacuum over potash. It was recrystallised from dry benzene containing a little acetic anhydride, washed with dry ether, and dried in a vacuum. It forms long needles, m. p. 133·5—135°, and is very deliquescent, absorbing moisture from the air even at 100° (Found : C, 44·5; H, 4.2. $C_8H_8O_7$ requires C, 44·4; H, 3·7%).

One of the authors (T. H. H. Q.) thanks the Department of Scientific and Industrial Research for a maintenance grant.

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