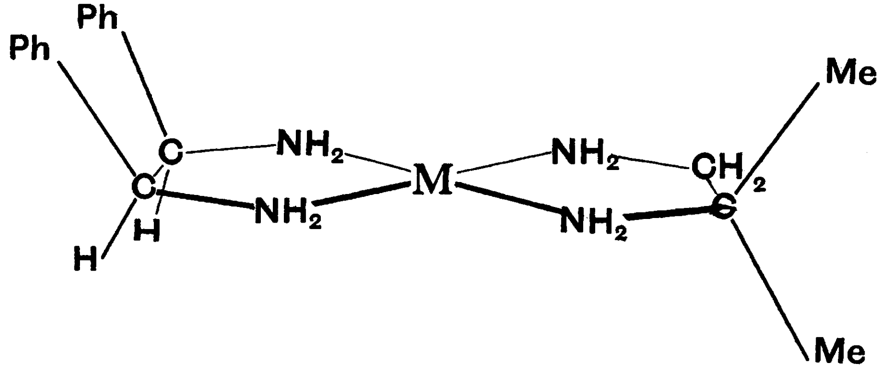
358. *Optical Activity dependent on the Planar Arrangement of the Valencies of the 4-Co-ordinated Palladous Atom.*

By Alan G. Lidstone and William H. Mills.

The method employed by Mills and Quibell (J., 1935, 839) for the examination of the valency configuration of the 4-covalent platinous atom has been applied to palladium. *iso*Butylenediamino*meso*stilbenediaminopalladous salts (III) have been prepared and resolved into optical antimers by means of *d*- and *l*-diacetyltartaric acids. The molecular rotations $[M]^{15^\circ}_{5461}$ observed for the optically active nitrates were 50·5° and − 50·4°. The optical activity of the nitrates was stable at the ordinary temperature, but on heating it diminished more rapidly than that of the analogous platinum derivatives. The molecular dissymmetry of the complex ion thus demonstrated shows that the valencies of the 4-co-ordinated palladous atom cannot have a regular tetrahedral arrangement and accordingly indicates that they lie in one plane (see I).

In a recent communication (*loc. cit.*) one of us and Quibell described an investigation of salts of a substituted bisethylenediaminoplatinous ion (I; M = Pt) in which the substituents were so placed that the salts would be molecularly dissymmetric if the valencies of the 4-covalent platinous atom lay in one plane, but would be symmetrical if these valencies had a regular tetrahedral arrangement. It was shown that the salts could be resolved into stable enantiomorphous optically active forms. The complex cations were accordingly molecularly dissymmetric, and it thus followed (taking the planar and the tetrahedral to be the only arrangements sufficiently probable for consideration) that the platinum covalencies lay in one plane.



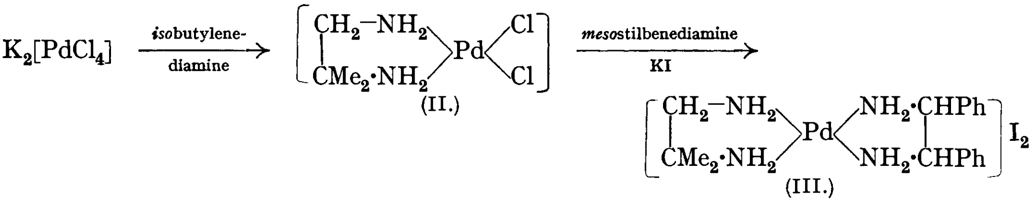
(I.)

In the present communication an account is given of the application of the corresponding method to the investigation of the stereochemistry of the 4-covalent palladous atom.

The planar configuration of the valencies of palladium in this state of combination has been inferred from two kinds of evidence. The first of these is the occurrence of isomerism in various palladium compounds in which a planar arrangement of the valencies would require the existence of geometrical isomerism, *e.g.*, diglycinepalladium (Pinkard, Sharratt, Wardlaw, and Cox, J., 1934, 1012), palladium methylbenzylglyoxime (Dwyer and Mellor, *J. Amer. Chem. Soc.*, 1935, **57**, 605), and amminodinitritropalladium (Mann, Crowfoot, Gattiker, and Wooster, J., 1935, 1643); and the second, the *X*-ray analysis of the crystal structure of various palladium compounds—in particular, potassium chloropalladite (Dickinson, *J. Amer. Chem. Soc.*, 1922, **44**, 2404), palladium salicylaldehyde (Cox, Pinkard, and Wardlaw, J., 1935, 459), and palladium thio-oxalate (Cox, Wardlaw, and Webster, J., 1935, 1475).

To these two lines of evidence is now added a third. We find that *iso*butylenediamino-*meso*stilbenediaminopalladous salts (III) can be resolved into antimeric optically active forms. Since this would not be possible if the palladium valencies were tetrahedrally disposed,* it is to be concluded that they have the alternative planar arrangement.

The preparation of these palladium complex-salts was effected through the successive action of the two bases, *iso*butylenediamine and *meso*stilbenediamine, on potassium palladochloride. The interaction of the former base with the palladochloride gave the non-ionic iso*butylenediaminodichloropalladium* (II). This was then converted by the action of the second base (with subsequent treatment with potassium iodide) into the complex *iodide* (III), a substitution derivative of bisethylenediaminopalladium iodide in which the substituent groups, methyl and phenyl, occupied the special positions necessary for this investigation.



(II.)

(III.)

The resolution of the palladium complex salt into optical antipodes was carried out with the aid of diacetyltartaric acid—the acid which had been found effective for the resolution of the corresponding platinum compound. Fractional crystallisation of *iso*butylenediamino*meso*stilbenediaminopalladium *d*-(—)diacetyltartrate from aqueous alcohol resulted in the isolation of a salt with the molecular rotation (in water) $[M]_{5461}^{15^\circ}$ — 110°. The lævorotation of this salt is about double that which would be produced by the *d*-(—)-diacetyltartrate ion; it was thus the l-*base*–d-*acid* combination. After replacement of the diacetyltartrate radical by the nitrate radical (by precipitation with silver iodide and treatment of the resulting iodide with silver nitrate), the crystalline *iso*butylenediamino-*meso*stilbenediaminopalladous nitrate which was obtained was found to be strongly lævorotatory. The crystals were anhydrous; the palladium was therefore undoubtedly 4-co-ordinated and the optically active compound had the structure (III; with NO_3 instead of I). In aqueous solution ($c = 1{\cdot}61$) it had $[M]_{5461}^{15^\circ}$ — 50·4°.

To prepare the antimeric dextrorotatory nitrate the material in the mother-liquors from which the *d*-(—)diacetyltartrate had crystallised was converted (through the iodide) into the *l*-(+)diacetyltartrate. Fractional crystallisation of this yielded the *d*-base–*l*-acid *salt* with $[M]_{5461}^{15^\circ}$ + 110°, from which the d-iso*butylenediamino*meso*stilbenediaminopalladous nitrate* was obtained with $[M]_{5461}^{15^\circ}$ + 50·5° (in aqueous solution, $c = 1{\cdot}605$).

The optical stability of the *d*- and the *l*-nitrate, though distinctly less than that of the corresponding platinum compounds, is nevertheless considerable. At room temperature no appreciable racemisation was observed in aqueous or aqueous methyl-alcoholic solutions during 24 hours, but at 56° a 2% aqueous solution of the *l*-nitrate lost 30% of its optical activity in 20 hours, and when boiled under reflux it lost 10% of its activity in about 8 minutes.

The optically active iodides are sparingly soluble in water and are obtained as amor-

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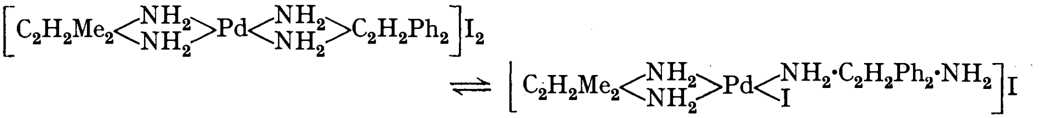
* The relationships correspond exactly with those in the analogous platinum compound discussed by Mills and Quibell (*loc. cit.*, p. 841).

phous precipitates by the addition of potassium iodide to aqueous solutions of the respective diacetyltartrates. The solid precipitates undoubtedly contain the palladium complex cations in their optically active forms, since on interaction with silver nitrate they yield the optically active nitrates, yet when dissolved in methyl alcohol their solutions were found to be inactive. They must therefore lose their activity very rapidly in solution.

This optical instability of the iodide, which stands in marked contrast to the relative stability of the optical activity of the nitrate and the diacetyltartrate, may possibly be due to the establishment of an equilibrium between the *spiro*cyclic complex salt and a small amount of an inactive compound (IV), formed by the opening of the *meso*stilbenediaminopalladium ring through the co-ordination of an iodide ion in place of one of the amino-groups. The tendency to a corresponding co-ordination of a nitrate or diacetyltartrate ion would evidently be much less.

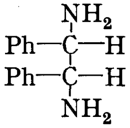


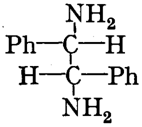
$$\left[\mathrm{C_2H_2Me_2}{<}^{\mathrm{NH_2}}_{\mathrm{NH_2}}{>}\mathrm{Pd}{<}^{\mathrm{NH_2}}_{\mathrm{NH_2}}{>}\mathrm{C_2H_2Ph_2}\right]\mathrm{I_2} \rightleftharpoons \left[\mathrm{C_2H_2Me_2}{<}^{\mathrm{NH_2}}_{\mathrm{NH_2}}{>}\mathrm{Pd}{<}^{\mathrm{NH_2\cdot C_2H_2Ph_2\cdot NH_2}}_{\mathrm{I}}\right]\mathrm{I}$$

(IV.)

The stereochemical evidence for the planar arrangement of the valencies of the 4-co-ordinated palladous atom, which this investigation provides, is dependent on the stilbenediamine retaining its *meso*-configuration (V) when co-ordinating with palladium, since the corresponding derivative of the racemic base (VI) would be resolvable whatever the valency configuration of the palladium.

(V.)





(VI.)

Under the conditions employed for the co-ordination, however, a change of configuration of the base is most improbable, since it is evident from their structure that the stereoisomeric stilbenediamines must be compounds of great configurational stability, especially in acid solution. In view, however, of the importance of this point for the present investigation we have examined it experimentally. We found in the first place that *meso*stilbenediamine (V) exhibited the expected resistance to transformation, for it could be boiled with dilute hydrochloric acid for a considerable time without the formation of any detectable trace of the racemic base. Similarly, the optically active stilbenediamine (VI) could be subjected to prolonged boiling with hydrochloric acid without showing any loss of rotatory power. The two diamines are therefore in fact difficultly transformable in acid solution.

We then found that under very gentle conditions (warming with dilute hydrochloric acid to 50° for 1 hour) the complex iodide could be decomposed quantitatively into its constituents, *viz.*, palladous iodide and the two diamines. The optically active iodide, thus treated, yielded an optically inactive solution from which the stilbenediamine was isolated and found to be the pure *meso*-base (m. p., 119°). We regard this as conclusive evidence that the stilbenediamine in the optically active complex salt is indeed the *meso*-base, since it can hardly be supposed that the *meso*-base suffers a change of configuration into the racemic form on co-ordination and is then changed back quantitatively into the *meso*-form under the gentle conditions of this decomposition. Moreover, we were able to show definitely in the following manner that these changes do not take place.

By the action of the optically active stilbenediamine (VI) on *iso*butylenediaminedichloropalladium (II), we prepared the optically active iso*butylenediamino*-l-*stilbenediaminopalladous nitrate* with the two phenyl groups in the *trans*-configuration. This substance is quite distinct from the analogous optically active nitrate obtained by resolving (III). It is much less soluble in water, it has a much greater molecular rotation, and when decomposed by warming with hydrochloric acid in presence of potassium iodide it gives an optically active solution from which the stilbenediamine is recovered and found to be the pure optically active base with undiminished rotatory power.

There can be no doubt, therefore, that the diphenyldimethylbisethylenediaminopalladous salts which we have resolved are derived from a cation in which the two phenyl groups are in the *cis*-relationship, and the possibility of their resolution shows that in this cation the four valencies of the palladium atom cannot have a regular tetrahedral arrangement and hence presumably lie in one plane, the ion having the configuration indicated diagrammatically in (I; M = Pd).

EXPERIMENTAL.

iso*Butylenediamine.*—This base was prepared by a modification of the method used by Mills and Quibell (*loc. cit.*) whereby a considerably better yield was obtained. Freshly distilled acetonecyanohydrin (75 g.) (Dubsky and Wensink, *Ber.*, 1916, **49**, 1136) was dissolved in absolute alcohol (3 l.) and reduced by the addition of sodium (250 g.) in three lots (75 g.; 75 g.; 100 g.). The dry crude *iso*butylenediamine hydrochloride (50 g.) obtained from the reaction mixture as described by Mills and Quibell was mixed with powdered sodium hydroxide (100 g.). Water (150 c.c.) was then dropped cautiously on the mixture, overheating being prevented by cooling with ice-water. A considerable quantity of ammonia was evolved and the base separated as an oily brown layer. The whole was then distilled under diminished pressure, and the distillate redistilled with ½ its weight of potassium hydroxide to complete the removal of the ammonia. The aqueous solution thus obtained contained 15—18 g. of *iso*butylenediamine and could be employed conveniently for the preparation of the following compound. The concentration of the solution was determined by titration with hydrochloric acid, thymol-blue being used as indicator.

iso*Butylenediaminodichloropalladium* (II).—A 13% aqueous solution of *iso*butylenediamine (210 c.c.; slightly over 2 mols.) was diluted with water (500 c.c.) and heated to 80—90°. Potassium palladochloride in 10% aqueous solution (500 c.c.; 1 mol.) was added during 10 minutes, and the mixture heated till clear. Concentrated hydrochloric acid (50 c.c.) was then added and the solution boiled gently for 10 minutes. On cooling, iso*butylenediaminodichloropalladium* separated in large orange prisms decomposing at about 300° (yield 85—90% of the theoretical) (Found: C, 18·2; H, 4·4; Pd, 40·1. $C_4H_{12}N_2Cl_2Pd$ requires C, 18·1; H, 4·5; Pd, 40·2%).

dl-iso*Butylenediamino*meso*stilbenediaminopalladous Iodide* (III).—*iso*Butylenediaminodichloropalladium (25 g.) was boiled with water (500 c.c.), and a saturated alcoholic solution of *meso*stilbenediamine (20 g.) was run in gradually, care being taken that the liquid never lost its yellow colour until the whole of the palladium derivative had gone into solution. Potassium iodide (32·5 g.) was then added, and the solution cooled to 0°. The anhydrous *iodide* crystallised in nearly colourless prisms, m. p. 242° (decomp.). Yield 90% (Found: C, 32·8; H, 4·2; Pd, 16·0. $C_{18}H_{28}N_4I_2Pd$ requires C, 32·7; H, 4·3; Pd, 16·1%). On crystallisation from dilute aqueous solution the *monohydrate* was obtained (Found: C, 31·7; H, 4·4; Pd, 15·8; H_2O, 2·6. $C_{18}H_{28}N_4I_2Pd,H_2O$ requires C, 31·8; H, 4·5; Pd, 15·7; H_2O, 2·7%).

l-iso*Butylenediamino*meso*stilbenediaminopalladous* d(−)-*Diacetyltartrate.*—The above iodide (III) (25 g.) was shaken for 1 hour with the silver carbonate freshly precipitated from silver nitrate (18 g.). In the filtrate, containing the carbonate of the palladium complex, *d*(−)-diacetyltartaric anhydride (8·15 g.) was dissolved, and the solution was then evaporated to dryness under diminished pressure below 50°. The residue, consisting of the diacetyltartrate of the palladium complex, was dissolved in the minimum quantity of water and precipitated by adding absolute alcohol (400 c.c.). The mixture of the salts of the *d*- and the *l*-base thus obtained consisted of small, colourless, somewhat hygroscopic needles having the composition of a *dihydrate* (Found: Pd, 15·6; H_2O, 5·4. $C_{26}H_{36}O_8N_4Pd,2H_2O$ requires Pd, 15·8; H_2O, 5·3%).

The resolution was carried out by crystallisation from aqueous alcohol. The less soluble *l*-base-*d*-acid salt crystallises in short thick prisms; the stereoisomeric salt separates in a more finely divided form and dissolves more rapidly. The following procedure was therefore adopted. The diacetyltartrate (75 g.) was digested with cold water (60 c.c.), and absolute alcohol (200 c.c.) added. After the undissolved residue (thick prisms) had been collected, absolute alcohol (500 c.c.) was added to the filtrate. The resulting crystals were then again subjected to the process of fractional solution followed by fractional crystallisation, and this procedure was continued till as much as possible of the thick prisms had been accumulated. This material, crystallised once from aqueous alcohol, yielded optically pure l-iso*butylenediamino*meso*stilbenediaminopalladous* d(−)-*diacetyltartrate* (18 g.) as a *dihydrate* (Found: H_2O, 5·4%). As it was somewhat efflorescent, it was dehydrated at 100° in a vacuum for the polarimetric determinations. In aqueous solution it gave $\alpha^{15°}_{5461}$ − 1·35° (*c*, 1·944; *l*, 4), whence $[M]^{15°}_{5461}$ − 111°, and this value was unchanged by repeated recrystallisation. The molecular rotation was found to vary with the concentration as follows :—

c (g./100 c.c.)	9·97	6·33	4·22	1·944	1·25
$[M]^{15°}_{5461}$	$-120{\cdot}5°$	$-117°$	$-113°$	$-111°$	$-110°$

l-iso*Butylenediamino*meso*stilbenediaminopalladous Nitrate*.—This salt was prepared from the corresponding *d*-diacetyltartrate through the iodide. On addition of potassium iodide to the solution of the diacetyltartrate (2·5 g.) in water (25 c.c.) the *iodide* of the palladium complex was precipitated as a resinous mass which solidified on stirring (Found : C, 31·7; H, 4·4; N, 8·2; Pd, 15·7. $C_{18}H_{28}N_4I_2Pd,H_2O$ requires C, 31·8; H, 4·5; N, 8·3; Pd, 15·7%). The solid iodide, after collection and washing with water, was shaken for 1 hour with a solution of silver nitrate (1·25 g.) in water (50 c.c.), and the filtrate from the silver iodide was evaporated to dryness at room temperature over sulphuric acid in a vacuum. The residue, extracted with a little cold water to remove silver nitrate, dissolved in warm water, filtered from a little reduced silver and concentrated, yielded the pure *nitrate* as aggregates of colourless needles (Found : C, 40·6; H, 5·5; N, 15·7; Pd, 20·1. $C_{18}H_{28}O_6N_6Pd$ requires C, 40·7; H, 5·3; N, 15·8; Pd, 20·1%). In aqueous solution the salt showed $[M]^{15°}_{5461} - 50{\cdot}4°$ ($c = 1{\cdot}607$; $l = 4$; $\alpha^{15°}_{5461} - 0{\cdot}61°$). After recrystallisation by partial evaporation of the aqueous solution in a vacuum, the molecular rotation was unchanged (within the observational limit) : $c = 1{\cdot}605$, $l = 4$, $\alpha^{15°}_{5461} - 0{\cdot}61°$, whence $[M]^{15°}_{5461} - 50{\cdot}5°$.

To examine the configurational stability of the salt, a 2% aqueous solution was heated under reflux and kept boiling for 8 minutes. This caused a fall of the *l*-rotation, $\alpha^{15°}_{5461}$ ($l = 2$), from $-0{\cdot}38°$ to $0{\cdot}34°$. Another portion of the same solution after 19¾ hours' keeping at 57° showed a change of rotation, $\alpha^{15°}_{5461}$ ($l = 2$), from $-0{\cdot}38°$ to $-0{\cdot}24°$. Another portion of the solution was mixed with an equal volume of methyl alcohol and kept at 57° for 19¾ hours. The rotation, $\alpha^{15°}_{5461}$ ($l = 2$), changed from $-0{\cdot}22°$ to $-0{\cdot}15°$. Although the iodide, treated with silver nitrate, yielded an optically active nitrate its solution in methyl alcohol was optically inactive, presumably on account of rapid racemisation. Yet when a small quantity of potassium iodide, insufficient to cause a precipitate, was added either to the aqueous or to the aqueous methyl-alcoholic solution of the active nitrate no detectable racemisation occurred during 2 days at 15°.

d-iso*Butylenediamino*meso*stilbenediaminopalladous* l-(+)*Diacetyltartrate*.—The salt remaining in the mother-liquors from which the *d*-acetyltartrate of the *l*-complex had crystallised was recovered by evaporation of the solvent in a vacuum below 35°, and converted through the iodide and carbonate, by means of *l*-(+)diacetyltartaric anhydride, into the *l*-diacetyltartrate. This, fractionated by the same method as had been used for the *d*-diacetyltartrate, yielded the pure d-iso*butylenediamino*meso*stilbenediaminopalladous* l-*diacetyltartrate dihydrate* (Found : H_2O, 5·5. $C_{26}H_{36}O_8N_4Pd,2H_2O$ requires H_2O, 5·3%). In aqueous solution it had $[M]^{15°}_{5461} + 110°$ ($c = 1{\cdot}941$, $l = 4$, $\alpha^{15°}_{5461} + 1{\cdot}34°$).

d-iso*Butylenediamino*meso*stilbenediaminopalladous Nitrate*.—This *salt* was prepared from the above described *l*-diacetyltartrate in the same manner as the *l*-nitrate had been obtained from the *d*-diacetyltartrate (Found : C, 40·4; H, 5·1; N, 15·6; Pd, 20·0. $C_{18}H_{28}O_6N_6Pd$ requires C, 40·7; H, 5·3; N, 15·8; Pd, 20·1%). In aqueous solution the salt had $[M]^{15°}_{5461} + 50{\cdot}5°$ ($\alpha^{15°}_{5461} + 0{\cdot}61°$; c, 1·605; l, 4), and after recrystallisation, $\alpha^{15°}_{5461} + 0{\cdot}61°$ (c, 1·607; l, 4).

Decomposition of iso*Butylenediamino*meso*stilbenediaminopalladous Iodide by Hydrochloric Acid*.—The *dl*-hydrate (0·96 g.) was dissolved in warm water (100 c.c.), concentrated hydrochloric acid (2 c.c.) added, and the mixture kept at 50° for 1 hour. The weight of precipitate formed was 0·524 g. (theoretical weight of palladous iodide : 0·51 g.) The *meso*stilbenediamine which crystallised after addition of excess of ammonia to the concentrated filtrate weighed 0·269 g. (theoretical weight : 0·294 g.). Its m. p. and mixed m. p. with an authentic specimen of *meso*stilbenediamine were 119° (racemic stilbenediamine melts at 91°).

Decomposition of the *l*-iodide in the same way gave a precipitate of palladous iodide and an optically inactive solution. The stilbenediamine recovered from this solution had m. p. 119°, unchanged when mixed with *meso*stilbenediamine.

l-*Stilbenediamine*.—Racemic stilbenediamine was prepared from α-benzildioxime by reduction with sodium and alcohol (Feist, *Ber.*, 1894, **27**, 213; Feist and Arenstein, *Ber.*, 1895, **28**, 3167). The separation as carbamate employed by these authors proved inconvenient, and it was found better to dissolve the crude bases in excess of dilute acetic acid and crystallise the acetates. By this means dl-*stilbenediamine diacetate monohydrate* was obtained in small colourless prisms, m. p. 131—132° (Found : C, 61·8; H, 7·2; N, 8·2. $C_{18}H_{24}O_4N_2,H_2O$ requires C, 61·7; H, 7·4; N, 8·0%). (Feist and Arenstein give 256° as the m. p. of the acetate. This must refer to some other compound.)

The racemic base was resolved through its hydrogen *d*-tartrate (Feist and Arenstein, *loc. cit.*), which was deposited on cooling a solution of the base (20 g.) and *d*-tartaric acid (31·5 g.) in hot water (350 c.c.) (Found: C, 48·2; H, 5·7; H_2O, 6·6. $C_{22}H_{28}O_{12}N_2,2H_2O$ requires C, 48·2; H, 5·9; H_2O, 6·6%. Found in dried substance: N, 5·6. $C_{22}H_{28}O_{12}N_2$ requires N, 5·5%).

This material (50 g.) was fractionally crystallised until three successive crops had the same specific rotation. In this way 15 g., $[\alpha]_{5893}^{15^\circ}$ + 2·70°, were obtained. From this salt the *l*-base was isolated by treatment with 10% sodium hydroxide solution and extraction with ether. The free base was obtained as colourless needles, m. p. 81°. Since it rapidly absorbs carbon dioxide from the air, it was converted into hydrochloride by evaporation with a slight excess of hydrochloric acid. The hydrochloride had $[\alpha]_{5893}^{14^\circ}$ − 19·0° in water ($\alpha_{5893}^{14^\circ}$, − 0·77°; *c*, 2·028; *l*, 2). The picrate of the *l*-base, obtained as a sparingly soluble yellow powder by the addition of sodium picrate solution to the hydrochloride, melts at 202—203°.

Configurational Stability.—A solution of *l*-stilbenediamine (0·984 g.) in dilute hydrochloric acid made up to 100 c.c. with water had $\alpha_{5893}^{14^\circ}$ − 1·10° (*l*, 4). After it had been heated to 100° for 16 hours in a closed vessel, it still had $\alpha_{5893}^{14^\circ}$ − 1·10° (*l*, 4).

To test the configurational stability of *meso*stilbenediamine, a solution of this diamine in excess of dilute hydrochloric acid (350 c.c.) was boiled under reflux for 12 hours. On cooling, a crop of hydrochloride (A) crystallised. The filtrate from this, after concentration to 50 c.c., deposited a second crop (B). The base was then recovered from crops A and B and also from the final mother-liquor (C). The weights and m. p.'s of the successive fractions were: (A) 3·5 g., 119—119·5°; (B) 1·0 g., 119—119·5°; (C) 0·3 g., 118·5—119°.

Both the optically active diamine and the *meso*-base are therefore configurationally stable under conditions considerably more drastic than were employed in the preparation, resolution, and decomposition of the palladium tetramine salts.

iso*Butylenediamino*-l-*stilbenediaminopalladous Iodide.*—This *compound* was prepared by the action of *l*-stilbenediamine on *iso*butylenediaminodichloropalladium, the same conditions being used as had been employed to obtain the corresponding derivative of the *meso*-base. It separated as a monohydrate in the form of very pale yellow needles (Found: Pd, 15·6. $C_{18}H_{28}N_4I_2Pd,H_2O$ requires Pd, 15·7%).

iso*Butylenediamino*-l-*stilbenediaminopalladous Nitrate.*—This *salt* was prepared by the action of silver nitrate on the foregoing iodide in the manner employed for the preparation of the corresponding *meso*stilbendiamino-derivative. Crystallised thrice from hot water, it was obtained as small colourless needles (Found, in the salt dehydrated at 100° in a vacuum: C, 40·3; H, 5·1; N, 15·8; Pd, 19·9. $C_{18}H_{28}O_6N_6Pd$ requires C, 40·7; H, 5·3; N, 15·8; Pd, 20·1%). This derivative of the *l*-base is much less soluble in water than the optically active form of the corresponding derivative of the *meso*-base and solutions of the same concentration as had been employed for the latter could not be prepared for polarimetric observation. The molecular rotation in aqueous solution was found to be $[M]_{5893}^{15^\circ}$ − 497° ($\alpha_{5893}^{15^\circ}$, − 3·75°; *c*, 1·0028; *l*, 4) and $[M]_{5461}^{15^\circ}$ − 624° ($\alpha_{5461}^{15^\circ}$, − 4·56°). The decomposition of the salt was carried out as follows: To a solution of the nitrate (0·5 g.) in water (100 c.c.) were added potassium iodide (0·35 g.) and concentrated hydrochloric acid (2 c.c.). After the mixture had been kept at 50° for 1 hour, the precipitated palladous iodide was removed, and the filtrate concentrated to 5 c.c. Excess of 50% potassium hydroxide solution was added, and the base extracted with ether and then converted into hydrochloride by evaporation with excess of dilute hydrochloric acid. A portion of the hydrochloride treated with sodium picrate gave a picrate which melted at 202—203° and at the same temperature when mixed with *l*-stilbenediamine picrate. Another portion of the hydrochloride (0·0207 g.) in aqueous solution (1 c.c.) gave $\alpha_{5893}^{14^\circ}$ − 0·20 (*l*, 0·5), whence $[\alpha]_{5893}^{14^\circ}$ = − 19·3°.

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