

**17. *Structural and Stereochemical Relationships among the Disulphines and Diammines of Platinum and Palladium.***

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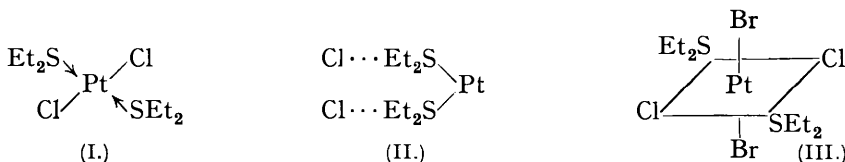
THE complex relationships among the disulphines and diammines of platinum and palladium are at present only imperfectly understood. In this paper an attempt is made to elucidate them (1) by examining the action of ethylene diethyl disulphide (es) and of ethylenediamine (en) on certain of the platinous and palladous diammines and disulphines, using the chelate grouping as a test of whether or not a  $\beta$ - or a *cis*-pair of positions is available in the molecule; (2) by observing whether or not a depression of melting point occurs on mixing apparently analogous platinous and palladous disulphines, and combining the results with the available data on the isomorphism of certain platinous and palladous ammines.

In the first place it is necessary to know with certainty whether or not the  $\alpha$ - and  $\beta$ -forms of the platinous disulphines have their pairs of sulphur atoms in corresponding positions. Previous work (Angell, Drew, and Wardlaw, J., 1930, 349; Drew, Preston, Wardlaw, and Wyatt, J., 1933, 1294) indicated that the two series of isomerides, although structurally different, might correspond stereochemically; but the latter part of this conclusion was dependent upon the assumption that stereochemical changes were absent during the

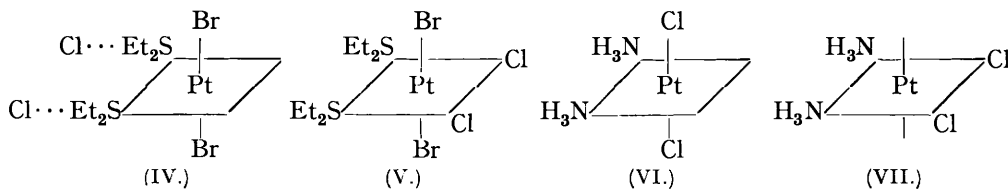
transformations cited in the evidence, a condition which it was impossible to prove. The results now obtained, whilst they do not conflict with any of the previous experimental work, lead us to believe that the  $\alpha$ - and  $\beta$ -disulphines of platinum are not stereochemically similar, and that migrational changes of the sulphur atoms do occur when the  $\beta$ - are transformed into the  $\alpha$ -platinous or -platinic disulphines.

When aqueous ethylenediamine acts upon  $\beta$ -Pt(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub> it gives a solution of the unstable ethylenediamino-disulphine, [Pt(Et<sub>2</sub>S)<sub>2</sub>en]Cl<sub>2</sub>, which can be obtained in the form of its *plato-salt*; the chloride easily loses ethyl sulphide and gives *ethylenediaminomono(diethylsulphine)platinous chloride*, [Pt(Et<sub>2</sub>S) en]Cl, which is also the main product when aqueous ethyl sulphide acts upon ethylenediaminoplatinous chloride; in both of these reactions considerable [Pt en<sub>2</sub>]Cl<sub>2</sub> occurs as a by-product. On the other hand, when aqueous ethylenediamine acts upon  $\alpha$ -Pt(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub>, the sole product is [Pt en<sub>2</sub>]Cl<sub>2</sub>; and even when less than 1 mol. of ethylenediamine is employed no mixed ethylenediamino-sulphine is formed. This difference of behaviour is not occasioned by any difficulty in substituting the halogens of an  $\alpha$ -plato-disulphine, since it is already known that such substitution is effected with great ease by organic sulphides or amines of non-chelate type; the difference must thus be due to a difficulty in accommodating an entering chelate grouping.

It is apparent, therefore, that  $\beta$ - but not  $\alpha$ -Pt(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub> has an available pair of *cis*-positions, and that the formula previously proposed for the latter must be amended to (I), which differs both structurally and stereochemically from that of  $\beta$ -Pt(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub> (II).



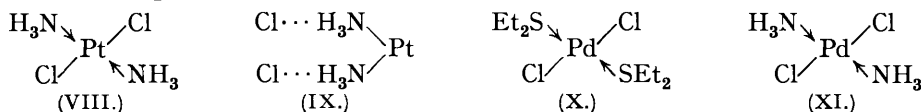
If it be granted that [Pt(Et<sub>2</sub>S)<sub>2</sub>en]Cl<sub>2</sub> is, like [Pt en<sub>2</sub>]Cl<sub>2</sub>, a planar substance, then it follows from considerations parallel to those given later under  $\alpha$ -Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, that formula (I) is *planar*. It is already known (Angell, Drew, and Wardlaw, *loc. cit.*) that the same octahedral platinic tetrahalide, Pt(SEt<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>Br<sub>2</sub>, is given by the addition of bromine to (I) and by the addition of chlorine to the bromide corresponding with (I). It follows that (III) must be the formula of the tetrahalide, which is thus symmetrical, and that the halogens are added to the platinous compounds in *trans*-positions. The two  $\beta$ -platinic tetrahalides, prepared respectively from bromine and  $\beta$ -Pt(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub> and from chlorine and  $\beta$ -Pt(Et<sub>2</sub>S)<sub>2</sub>Br<sub>2</sub>, were apparently not identical, although they are so labile that no very decisive evidence was obtained on this point; but it was shown that each of them gives (III) after transformation into the  $\alpha$ -form by heating to the m. p. or by boiling in certain solvents. The halogens in these labile  $\beta$ -tetrahalides may or not be still associated with sulphur; and so, assuming that *trans*-addition of halogen again occurs, alternative formulæ (IV) and (V) are available for the  $\beta$ -tetrahalide from bromine and  $\beta$ -Pt(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub>, and a similar pair for the other  $\beta$ -tetrahalide.



Either of these formulæ admits of transformation into (III) by the migration of one sulphine group into a neighbouring position, accompanied by the migration of both chlorine atoms in (IV) or of one in (V). Similar migrations must occur in the transformation of the  $\beta$ -platinous disulphine dihalides into their  $\alpha$ -isomerides.

It has already been shown (Drew, J., 1932, 2328; Drew and Tress, J., 1933, 1335)

that  $\beta$ - but not  $\alpha$ -Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> is capable of adding on a chelate diamine to form a mixed tetrammine. Cox (J., 1932, 1015, 1912) showed that [Pt(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub> was planar, and Cox and Preston (J., 1933, 1089) later deduced the planar structure of [Pt en<sub>2</sub>]Cl<sub>2</sub>. In agreement with these X-ray results, the isolation (Drew and Head, *Nature*, 1933, **132**, 210) of *cis*- and *trans*-forms of [Pt ib<sub>2</sub>]Cl<sub>2</sub> and of [Pt am ae ib]Cl<sub>2</sub> (ae = ethylamine; ib = isobutylenediamine) makes it almost certain that all platinous tetrammines not containing constrictor groups are planar. These two sets of data enable the configuration of  $\alpha$ -Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> to be deduced with practical certainty. The addition of ethylenediamine to a platinous diammine dichloride may involve (1) direct replacement of the halogens by the nitrogen atoms of en, or (2) indirect replacement by the completion of the octahedron by addition of en at unoccupied *cis*-positions followed by ionisation of the halogens from platinum. If (1) be the case, it is readily seen that, since en does not become added to  $\alpha$ -Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, the latter must be *trans*-planar in form or else it must possess formula (VI); but formula (VI) cannot be true, since the addition of ammonia would then afford a non-planar tetrammine. If (2) be the case, then again since en is not added to  $\alpha$ -Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, the latter must be *trans*-planar or it must have formula (VII); but formula (VII) cannot be true, for it would again give a non-planar tetrammine with ammonia. Hence,  $\alpha$ -Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> must have the *trans*-planar structure (VIII). It follows immediately



that  $\beta$ -Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (IX) must be stereochemically a *cis*-compound, since with ammonia it gives the same tetrammine as its  $\alpha$ -isomeride.

The  $\alpha$ - and  $\beta$ -platinous disulphines thus come into line, stereochemically, with the  $\alpha$ - and  $\beta$ -platinous diammines; but the  $\alpha$ -disulphines correspond with the  $\alpha$ -diammines, and not, as was supposed by Werner and others, with the  $\beta$ -diammines. The properties of the substances, with the single exception of their colours, amply confirm this relationship. The absence of  $\gamma$ -disulphines corresponding with  $\gamma$ -Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> may perhaps be related to the greater mobility of halogen associated with sulphur as compared with nitrogen. The complete absence of transformation of the  $\beta$ -platinous diammines into their  $\alpha$ -isomerides, and the ease with which this change takes place among the disulphines, has been a puzzling feature of the problem; it can only be referred to the greater repulsion of one sulphur atom for another or to the greater mobility of sulphur atoms as compared with nitrogen atoms in the neighbourhood of platinum.

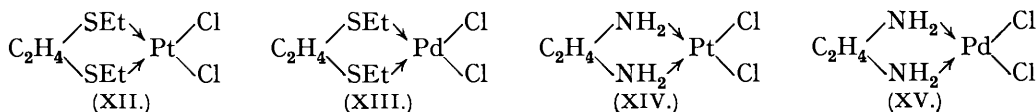
The palladous disulphines and diammines can be linked up with their platinous analogues from the following considerations. It is now found that admixture of Pd es Cl<sub>2</sub> (m. p. 182°) with Pt es Cl<sub>2</sub> (m. p. 188°) produces practically no depression of m. p. These substances are therefore almost certainly structurally and stereochemically similar. The action of aqueous ethylene diethyl sulphide on Pt en Cl<sub>2</sub>, or of aqueous ethylenediamine on Pt es Cl<sub>2</sub>, gives (*ethylenediamino*)*ethylenediethylsulphineplatinous chloride*, [Pt es en]Cl<sub>2</sub>, a colourless soluble substance which forms normal *plato*- and *pallado*-salts. These results confirm the conclusion that Pd es Cl<sub>2</sub>, Pt es Cl<sub>2</sub>, and Pt en Cl<sub>2</sub>, all of which contain their sulphur or nitrogen atoms in the form of chelate groups, correspond stereochemically as regards the disposition of these atoms; but they do not show whether or not Pt en Cl<sub>2</sub> corresponds structurally with Pd es Cl<sub>2</sub> and Pt es Cl<sub>2</sub>. Although Pd en Cl<sub>2</sub> and Pt en Cl<sub>2</sub> have not been shown to be isomorphous, yet they are so closely similar in general properties that they are probably akin both structurally and stereochemically, despite the fact that the tetrammines derived from them, e.g., [Pd en<sub>2</sub>]Cl<sub>2</sub> and [Pt en<sub>2</sub>]Cl<sub>2</sub>, behave quite differently towards hydrochloric acid (Drew, Pinkard, Preston, and Wardlaw, J., 1932, 1895; Drew, *loc. cit.*). These tetrammines are themselves isomorphous (Cox and Preston, *loc. cit.*), and therefore the difference in their behaviour must be connected with the metallic atoms themselves, possibly through their influence upon the manner in which the kationic charges are distributed.

The m. p.'s of  $\alpha$ - and  $\beta$ -Pt(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub> are almost identical (*ca.* 106°), but admixture is

known to produce a large depression; it is now found that the m. p. ( $83^\circ$ ) of the only known form of  $\text{Pd}(\text{Et}_2\text{S})_2\text{Cl}_2$  is greatly depressed by admixture with  $\beta$ - $\text{Pt}(\text{Et}_2\text{S})_2\text{Cl}_2$  but practically not at all by admixture with the  $\alpha$ -isomeride, with which the palladous compound is isomorphous (Ardell, *Z. anorg. Chem.*, 1897, **14**, 143). Hence it must be concluded that  $\text{Pd}(\text{Et}_2\text{S})_2\text{Cl}_2$  corresponds structurally and stereochemically with  $\alpha$ - $\text{Pt}(\text{Et}_2\text{S})_2\text{Cl}_2$  and has thus the *trans*-planar formula (X).

There is no evidence to show that the only known form of  $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$  is isomorphous with  $\alpha$ -,  $\beta$ -, or  $\gamma$ - $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ . The mixed tetrammine,  $[\text{Pd}(\text{NH}_3)_2\text{en}]\text{Cl}_2$ , is not obtained by the action of ethylenediamine on  $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ , but only by that of ammonia on  $\text{Pd en Cl}_2$ ; with hydrochloric acid, this tetrammine gives both  $\text{Pd en Cl}_2$  and  $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ . We consider that  $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$  should be assigned the *trans*-planar formula (XI), which reflects its correspondence with  $\alpha$ - $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  in general physical properties and also its behaviour towards chelate groups. The decomposition of the mixed tetrammine probably yields initially the unknown labile  $\beta$ -form of  $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ , which at once changes into the  $\alpha$ -isomeride. The formation of  $[\text{Pd}(\text{NH}_3)_4]\text{PdCl}_4$  from potassium chloropalladite and ammonia can be accounted for by assuming that the labile  $\beta$ -diammine interacts rapidly with ammonia.

That there is uncertainty as to whether the chlorine atoms in  $\text{Pt en Cl}_2$  are attached to nitrogen or to platinum, owing to the considerable difference in chemical behaviour between this substance and  $\beta$ - $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  (IX), has already been pointed out (Drew and Tress, *loc. cit.*). The absence of the  $\beta$ - and the  $\gamma$ -form of  $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$  points, however, to a direct attachment between chlorine and palladium, and therefore the following provisional formulæ are proposed for the crystalline chelate platinumous and palladous disulphines (XII and XIII) and diammines (XIV and XV):



At the same time, aqueous solutions of (XII) and (XIII) probably contain a proportion of the ionised forms in which the positive charges have become transferred to the sulphur atoms.

It will be seen that the palladous disulphines and diammines always occur in  $\alpha$ -forms except when they are unable to assume this configuration owing to the presence of chelate groups. This accounts for the fact that only one form of a palladous compound is ever found.

It is well known that an excess of aqueous ethyl sulphide leads to the conversion of  $\alpha$ - $\text{Pt}(\text{Et}_2\text{S})_2\text{Cl}_2$  into its  $\beta$ -isomeride, a reaction which appears to be general for plato-disulphines of this type. The change probably occurs through the unstable tetrasulphine,  $[\text{Pt}(\text{Et}_2\text{S})_4]\text{Cl}_2$ , which loses 2 mols. of ethyl sulphide from *cis*-positions; this tetrasulphine is known only in aqueous solution in presence of excess of ethyl sulphide, and its plato-salt is unstable, but the corresponding methyl derivative can be isolated in the form of its moderately stable pink plato-salt. It is now found that when  $[\text{Pt es en}]\text{Cl}_2$  is heated with dilute hydrochloric acid, it loses ethylenediamine and is converted wholly into  $\text{Pt es Cl}_2$ ; *i.e.*, groups are again eliminated from *cis*-positions, and moreover, the residue which might be expected to be the more firmly attached is expelled. The most satisfactory way of accounting for this change seems to be to assume that the positive charges are here located upon the nitrogen atoms. To obtain further evidence, we compared the action of boiling water and of hydrochloric acid upon  $[\text{Pt es en}]\text{Cl}_2$  and upon its plato- and pallado-salts. Although this substance is stable to boiling water, the salts are decomposed respectively into (1)  $\text{Pt en Cl}_2$  and  $\text{Pt es Cl}_2$ , and (2)  $\text{Pt en Cl}_2$  and  $\text{Pd es Cl}_2$ . On keeping, the dry plato-salt soon decomposes in the same manner, but the pallado-salt is much more stable. With hydrochloric acid, the plato-salt gives the same products but the pallado-salt decomposes in the sense of affording  $\text{Pt es Cl}_2$  and  $\text{Pd en Cl}_2$ , the latter being obtained as  $(\text{en H}_2)\text{PdCl}_4$  on account of its known instability to acids. These results can be interpreted if it be assumed that in its plato- and pallado-salts also the  $[\text{Pt es en}]$

kation has the positive charges on the nitrogen atoms, it being therefore the ethylenediamino-radical which is eliminated by hydrochloric acid. With hot water, the decomposition of the salts is thermal, and the more loosely bound disulphine residue is removed and then reacts with the anion in the normal manner.

Cox and Preston (*loc. cit.*) have criticised our view that the elimination of groups from the tetrammines by hydrochloric acid is controlled by the manner of location of the positive charges which produces an apparent pairing of valencies, on the ground that no such phenomenon has been noted among the cobaltammines. Further examination, however, may disclose the phenomenon now the possibility is indicated. These authors also state that a pairing of *trans*-valencies occurs in  $\alpha$ - and  $\beta$ -Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>, where ions are presumed to be absent. It is difficult to imagine a pairing of bonds of different kinds (to NH<sub>3</sub> and to Cl respectively) on the lines laid down by Cox and Preston, such as must occur if their deduction regarding  $\beta$ -Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub> is correct. Their theory appears inadequate to explain the *cis*-elimination which occurs in the pallado-tetrammines, in [Pt es en]Cl<sub>2</sub>, and to some extent even in [Pt en<sub>2</sub>]Cl<sub>2</sub> and the like.

The plato-salt [Pt(Et<sub>2</sub>S)<sub>2</sub>en]PtCl<sub>4</sub> decomposes when boiled with water, giving [Pt(Et<sub>2</sub>S)enCl]Cl, Pt en Cl<sub>2</sub>, Pt(Et<sub>2</sub>S)Cl<sub>2</sub>, and Pt(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub>. The plato-salt of the first of these products is a somewhat soluble pink substance, obtained as the monohydrate; when kept or when boiled with water, it changes into a mixture of [Pt(Et<sub>2</sub>S)enCl]Cl, Pt en Cl<sub>2</sub>, Pt(Et<sub>2</sub>S)Cl<sub>2</sub>, and some Pt(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub>. In the cases of both of the above plato-salts it is clear that the ethyl sulphide residues are loosely held and that they interact with the anions of the salts.

We attempted to examine the action of sulphides on palladous diammines and disulphines, and of amines on palladous disulphines, but the ease with which groups co-ordinated to palladium are exchanged or eliminated makes it difficult to interpret the results. We have not been able to isolate any mixed diammino-disulphines or tetrasulphines of palladium, these compounds being less stable than the palladous tetrammines. The most interesting result was obtained in the action of ethyl sulphide on Pd en Cl<sub>2</sub>, which ultimately gave Pd(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub> and [Pd en<sub>2</sub>]Cl<sub>2</sub>. Here it is probable that the first product is the unstable [Pd(Et<sub>2</sub>S)<sub>2</sub>en]Cl<sub>2</sub>, which is rearranged to a mixture of [Pd en<sub>2</sub>]Cl<sub>2</sub> and the unstable [Pd(Et<sub>2</sub>S)<sub>4</sub>]Cl<sub>2</sub>, the latter at once losing 2 mols. of ethyl sulphide to give Pd(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub>; the pallado-disulphine proved to be the ordinary substance and not the unknown  $\beta$ -disulphine. This  $\beta$ -form would be expected from a tetrasulphine particularly in the case of palladium, since that element favours *cis*-elimination. It seems, therefore, that the non-chelated  $\beta$ -pallado-disulphines are labile, as we have supposed to be the case with the non-chelated  $\beta$ -pallado-diammines.

#### EXPERIMENTAL.

(es = SEt·CH<sub>2</sub>·CH<sub>2</sub>·SEt; en = NH<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>·NH<sub>2</sub>.)

(Ethylenediamino)ethylenediethylsulphineplatinous Chloride, [Pt es en]Cl<sub>2</sub>.—(a) Pt es Cl<sub>2</sub> is dissolved in a slight excess of aqueous ethylenediamine at room temperature (1 day) or on the water-bath (in both cases there is some displacement of the disulphide, especially at the higher temperature); the colourless solution is evaporated in a current of air at room temperature, and the residue recrystallised from ethyl alcohol (99%), in which the by-product, [Pt en<sub>2</sub>]Cl<sub>2</sub> (Found: Pt, 50.8. Calc.: Pt, 50.5%), is insoluble. (b) Pt en Cl<sub>2</sub> is dissolved in aqueous ethylene diethyl disulphide on the water-bath (2 hrs.) and the above procedure is followed. The substance was usually obtained as the *monohydrate*, in the form of colourless plates, very soluble in water, insoluble in chloroform, and soluble in cold alcohol (96%) (Found: Pt, 39.5; C, 19.6; H, 4.8. C<sub>8</sub>H<sub>24</sub>ON<sub>2</sub>Cl<sub>2</sub>S<sub>2</sub>Pt requires Pt, 39.5; C, 19.5; H, 4.9%). On one occasion the *anhydrous* substance was obtained (Found: Pt, 41.2. C<sub>8</sub>H<sub>22</sub>N<sub>2</sub>Cl<sub>2</sub>S<sub>2</sub>Pt requires Pt, 40.95%). The dry solid became yellow at 130°; the aqueous solution is unchanged by boiling ( $\frac{1}{4}$  hr.). Warm dilute hydrochloric acid dissolves it, giving ethylenediamine hydrochloride and Pt es Cl<sub>2</sub> (Found: Pt, 46.75, 46.5. Calc.: Pt, 46.95%); no ethylene diethyl disulphide is set free in this reaction. With aqueous potassium chloroplatinite it forms a *plato-salt*, [Pt es en]PtCl<sub>4</sub>, consisting of minute salmon-pink needles (Found: Pt, 52.75. C<sub>8</sub>H<sub>22</sub>N<sub>2</sub>Cl<sub>4</sub>S<sub>2</sub>Pt<sub>2</sub> requires Pt, 52.55%). The plato-salt is decomposed on being warmed with

aqueous solvents, or in the dry state at about 130°; it is insoluble in organic solvents. With aqueous tetramminoplatinous chloride it gives Magnus's green salt on warming. It gives a red-brown coloration with phenoxtellurine dibisulphate. When boiled with water it gives a mixture of Pt es Cl<sub>2</sub> and Pt en Cl<sub>2</sub> in approximately equimolecular proportion. A similar reaction occurs with boiling dilute hydrochloric acid.

With aqueous potassium chloropalladite, [Pt es en]Cl<sub>2</sub> gives a *pallado-salt*, [Pt es en]PdCl<sub>4</sub>, in minute orange-brown crystals (Found : C, 14.65; H, 3.6; Pt + Pd, 46.4. C<sub>8</sub>H<sub>22</sub>N<sub>2</sub>Cl<sub>4</sub>S<sub>2</sub>PtPd requires C, 14.7; H, 3.4; Pt + Pd, 46.2%). This resembles the plato-salt in general properties. It dissolves in hot water, the yellow solution giving Pd es Cl<sub>2</sub>, m. p. 183° (Found : Pd, 32.8, 32.3. Calc. : Pd, 32.55%) (which was extracted by chloroform), and Pt en Cl<sub>2</sub> (Found : Pt, 59.7. Calc. : Pt, 59.8%) in approximately equimolecular proportion. When the pallado-salt was boiled with aqueous hydrochloric acid (16%), however, it gave Pt es Cl<sub>2</sub> (Found : Pt, 47.2. Calc. : Pt, 46.95%), which separated on cooling; the red mother-liquor on evaporation gave (en H<sub>2</sub>)PdCl<sub>4</sub> in deep-red square prisms with blue reflex (Found : Pd, 33.8. Calc. : Pd, 34.35%), which could be recrystallised from concentrated hydrochloric acid but gave Pd en Cl<sub>2</sub> on being warmed with water (cf. Kurnakow and Gwosdarew, *Z. anorg. Chem.*, 1900, 22, 385). A portion of the above red mother-liquor was shown to be free from chloroplatinite ions by addition of aqueous [Pt(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub>, which gave no Magnus's green salt but produced only the pallado-salt, [Pt(NH<sub>3</sub>)<sub>4</sub>]PdCl<sub>4</sub>·½H<sub>2</sub>O, in the characteristic glistening lilac-grey plates (Found : Pd + Pt, 57.95. Calc. : Pd + Pt, 57.95%).

*Ethylenediaminomono(diethylsulphine)platinous Chloride*, [Pt(Et<sub>2</sub>S)enCl]Cl.—(a) β-Pt(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub> was dissolved in aqueous ethylenediamine at room temperature (2 hrs.); the colourless solution contains the unstable [Pt(Et<sub>2</sub>S)<sub>2</sub>en]Cl<sub>2</sub>, since if treated with aqueous potassium chloroplatinite it gives the plato-salt of that substance (see later); the solution is evaporated at room temperature over phosphoric oxide, whereupon ethyl sulphide is liberated, and the white residue, consisting of [Pt(Et<sub>2</sub>S)enCl]Cl and some [Pt en<sub>2</sub>]Cl<sub>2</sub>, is crystallised from alcohol (99%), in which the latter is insoluble. (b) Pt en Cl<sub>2</sub> is dissolved in aqueous ethyl sulphide on the water-bath (½ hr.); the yellow solution, which contains both [Pt(Et<sub>2</sub>S)enCl]Cl and [Pt en<sub>2</sub>]Cl<sub>2</sub>, as well as a little Pt en Cl<sub>2</sub>, but not [Pt(Et<sub>2</sub>S)<sub>2</sub>en]Cl<sub>2</sub>, is treated as above. The *chloride* forms colourless pearly hexagonal plates from alcohol (Found : C, 17.5; H, 4.5; Pt, 46.8, 47.0, 46.7. C<sub>6</sub>H<sub>18</sub>N<sub>2</sub>Cl<sub>2</sub>SPt requires C, 17.3; H, 4.35; Pt, 46.9%); it is readily soluble in cold water, the solution giving an immediate precipitate with silver nitrate. Cold concentrated solutions give with potassium chloroplatinite a pale pink precipitate of the *plato-salt*, [Pt(Et<sub>2</sub>S)enCl]<sub>2</sub>PtCl<sub>4</sub> as glistening square plates of the *monohydrate* (Found : Pt, 52.5, 52.6. C<sub>12</sub>H<sub>36</sub>N<sub>4</sub>Cl<sub>6</sub>OS<sub>2</sub>Pt<sub>3</sub> requires Pt, 52.4%). It decomposes on keeping, or more rapidly on boiling with water. It then gives a red solution, which rapidly turns yellow, and a yellow solid separates. The mother-liquor on evaporation gave [Pt(Et<sub>2</sub>S)enCl]Cl, crystallised from alcohol (99%) and identified by crystal form and behaviour towards chloroplatinite. The yellow solid was a mixture of Pt(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub>, Pt(Et<sub>2</sub>S)Cl<sub>2</sub>, and Pt en Cl<sub>2</sub>. Chloroform dissolved the first (Found : Pt, 44.4. Calc. : Pt, 43.7%), evaporation giving the solid, m. p. 76—78°, *i.e.*, mixed α- and β-forms. Hot very dilute hydrochloric acid dissolved the Pt en Cl<sub>2</sub>, which was deposited on cooling (Found : Pt, 59.9. Calc. : Pt, 59.8%). The remaining insoluble substance was amorphous Pt(Et<sub>2</sub>S)Cl<sub>2</sub> (Found : Pt, 54.3. Calc. : Pt, 54.8%). [Pt(Et<sub>2</sub>S)enCl]Cl gave no precipitate with potassium chloroplatinite at room temperature but on warming there was produced a yellow precipitate. This was separated as above into Pt(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub>, Pt(Et<sub>2</sub>S)Cl<sub>2</sub>, and Pt en Cl<sub>2</sub>.

Ethylenediaminobis(diethylsulphine)platinous chloroplatinite, [Pt(Et<sub>2</sub>S)<sub>2</sub>en]PtCl<sub>4</sub>, was prepared as above. It forms brick-red square prisms. It was dried over phosphoric oxide (the crystals fell to powder) and extracted with chloroform to remove any admixed Pt(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub>; it cannot be recrystallised. With aqueous [Pt(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub> its suspension in water at once gives Magnus's green salt. Phenoxtellurine dibisulphate gives with it an intense violet coloration. It is soluble in hot water but the solution rapidly becomes yellow, depositing yellow material on cooling; this product was seen to consist of pale yellow granules and deep yellow prisms, and these were separated by flotation of the former in chloroform (or, in another experiment, by extracting the prisms with boiling very dilute hydrochloric acid); the prisms were recrystallised from much water and were then found to consist of Pt en Cl<sub>2</sub> (Found : Pt, 59.3, 59.8. Calc. : Pt, 59.8%); the lighter material was insoluble in water and consisted of Pt(Et<sub>2</sub>S)Cl<sub>2</sub> (Found : Pt, 54.7, 54.7. Calc. : Pt, 54.8%); the chloroform on evaporation yielded Pt(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub>, m. p. 68—70°, *i.e.*, mixed α- and β-forms (Found : Pt, 44.5. Calc. : Pt, 43.7%); the first mother-liquor (above) was evaporated and found to contain [Pt(Et<sub>2</sub>S)enCl]Cl, which was isolated as hexagonal plates (Found : Pt, 46.2. Calc. : Pt, 46.9%).

*Action of Ethyl Sulphide, Ethylene Diethyl Disulphide, or Ethylenediamine on Palladous Diammines and Disulphines.*—The following is a summary of preliminary results. The diammine or disulphine was usually shaken at room temperature in aqueous suspension with a slight excess over the calculated quantity of sulphide or amine; the filtered solution was then evaporated in a desiccator, and the residue examined. The products were identified by m. p. and mixed m. p., where possible; by analysis; and by examination of properties.

Et<sub>2</sub>S and Pd en Cl<sub>2</sub> gave [Pd en<sub>2</sub>]Cl<sub>2</sub> and Pd(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub>;  
 es and Pd en Cl<sub>2</sub> gave Pd es Cl<sub>2</sub> and unchanged Pd en Cl<sub>2</sub>;  
 es and Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> gave Pd es Cl<sub>2</sub> and [Pd(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub>;  
 es and Pd(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub> gave Pd es Cl<sub>2</sub> and Pd(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub>;  
 en and Pd es Cl<sub>2</sub> gave [Pd en<sub>2</sub>]Cl<sub>2</sub> and unchanged Pd es Cl<sub>2</sub>.

The results afford no definite indication of the mechanism of reaction, but they illustrate the survival of the more stable palladous tetrammines under conditions in which the mixed disulphinediammines and tetrasulphines are spontaneously broken down.

#### SUMMARY.

(1) The previous view of Angell, Drew, and Wardlaw on the relationship between the  $\alpha$ - and  $\beta$ -disulphines of platinum is revised, it being now evident that migratory change occurs in the transformation  $\beta \longrightarrow \alpha$ -disulphine.

(2) The  $\alpha$ -disulphines of platinum are shown to be *trans*-planar forms and to correspond stereochemically and structurally with the  $\alpha$ -diammines, and not with the  $\beta$ -diammines as was supposed by Werner.

(3) The  $\beta$ -disulphines of platinum are *cis*-compounds corresponding stereochemically and structurally with the  $\beta$ -diammines of platinum; two structural types appear to be possible.

(4) The disulphines and diammines of palladium, which occur in only one form, correspond with the  $\alpha$ -forms of their platinum analogues unless a chelate group is present, in which case they correspond with the  $\beta$ -forms of the platinum analogues.

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