L.—*A New Interpretation of the Isomerism amongst Co-ordination Compounds of Platinum.*

By Frederick George Angell, Harry Dugald Keith Drew, and William Wardlaw.

The apparently well-established *cis-* and *trans*-isomerism found among compounds of quadricovalent platinum provides the strongest remaining evidence for the view that the four groups surrounding a central atom may be situated in a plane instead of at the corners of a tetrahedron. We are engaged in a re-examination of the cases in which isomerism of this kind is alleged, and the present paper is concerned with the compounds which platinous chloride forms with diethyl sulphide, these substances being typical of a group in which the evidence for a planar configuration seems most complete. We have now concluded, however, that the isomerism in this instance is of a structural and not of a spatial nature, and hence that, so far as these particular substances are concerned, there is no reason to doubt that the space distribution of four groupings associated with platinum is tetrahedral.

Blomstrand (*J. pr. Chem.*, 1888, **38**, 352) found that diethyl sulphide united with platinous chloride, giving two distinct dichlorides to which he assigned the structures (I) and (II), regarding

$\mathrm{Pt}<\begin{matrix}\mathrm{SEt_2{\cdot}SEt_2Cl}\\ \mathrm{Cl}\end{matrix}$

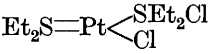
(I.)

α-Dichloride (B).

$\mathrm{Pt}<\begin{matrix}\mathrm{SEt_2Cl}\\ \mathrm{SEt_2Cl}\end{matrix}$

(II.)

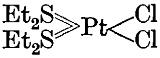
β-Dichloride (B).



$\mathrm{Et_2S{=}Pt}<\begin{matrix}\mathrm{SEt_2Cl}\\ \mathrm{Cl}\end{matrix}$

(III.)

α-Dichloride (K).

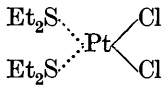


$\begin{matrix}\mathrm{Et_2S}\\ \mathrm{Et_2S}\end{matrix}\gg\mathrm{Pt}<\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}$

(IV.)

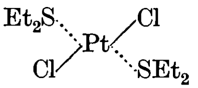
β-Dichloride (K).

both substances as containing bivalent platinum. Klason (*Ber.*, 1895, **28**, 1493) extended these observations, and gave the new formulæ (III) and (IV), where platinum is quadrivalent, or perhaps sexavalent in the β-compound. Neither author contemplated a planar configuration, or gave really satisfactory proof of the structures he alleged, although useful and mainly accurate data were accumulated. Werner (" Lehrbuch der Stereochemie," pp. 338 *et seq.*; see also *Z. anorg. Chem.*, 1893, **3**, 310), ignoring the relevant chemical evidence of his predecessors, attributed the isomerism to the presence of *cis*- and *trans*-planar types, (V) and (VI), in which



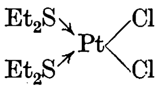
(V.)

α-Dichloride (W).



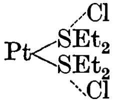
(VI.)

β-Dichloride (W).



(VII.)

α-Dichloride.



(VIII.)

β-Dichloride.

platinum exhibited 4-co-ordination. His view is universally accepted at the present time, although Reihlen has consistently adhered to an hypothesis of the tetrahedral distribution of valencies (*Annalen*, 1927, **447**, 211; **448**, 1312; *Z. anorg. Chem.*, 1926, **151**, 71).

The structures which we propose as a result of the present work are shown in (VII) and (VIII). In the α-dichloride each sulphur atom is united to tetrahedral platinum by a co-ordinate link *

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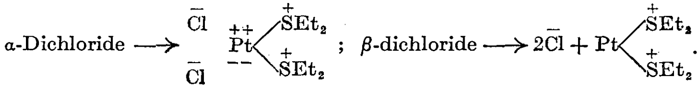
* After this paper had been read, Dr. N. V. Sidgwick pointed out to us that dissociation of the α- and β-dihalides would give rise to the *same* ions in both cases, if the co-ordinate links between the sulphur atoms and the platinum atom in the α-compound were equivalent to semipolar double bonds :



$$\alpha\text{-Dichloride} \longrightarrow \begin{matrix}\overset{-}{\mathrm{Cl}}\\ \\ \overset{-}{\mathrm{Cl}}\end{matrix}\ \overset{++}{\underset{--}{\mathrm{Pt}}}<\begin{matrix}\overset{+}{\mathrm{S}}\mathrm{Et_2}\\ +\\ \overset{+}{\mathrm{S}}\mathrm{Et_2}\end{matrix}\ ;\ \beta\text{-dichloride} \longrightarrow 2\overset{-}{\mathrm{Cl}} + \mathrm{Pt}<\begin{matrix}\overset{+}{\mathrm{S}}\mathrm{Et_2}\\ +\\ \overset{+}{\mathrm{S}}\mathrm{Et_2}\end{matrix}\ .$$

With this proviso, therefore, the α- and β-forms are inter-related in a manner close and unprecedented. The un-ionised forms are nevertheless not identical, because the halogen atoms are situated in different positions in the molecule in the two cases; nor do the two substances represent the ionised and un-ionised forms of the same substance, because the chemical evidence shows, to take one point of several which could be cited, that the β-dichloride is ionised constituted by the sharing with platinum of two electrons derived from each sulphur atom; whilst in the β-dichloride the linkings between the sulphur atoms and platinum are covalencies and the chlorine atoms are potentially ionised as in the sulphonium halides.

Blomstrand and Klason observed that, whilst both the α- and the β-dichloride had the normal molecular weight, the yellow colour of the α-compound was deeper than that of the β-, and in addition the former substance was the more soluble in organic solvents. The β-compound alone showed noticeable solubility in water, and, more significant, it reacted much more rapidly with alcoholic silver nitrate. The conductivity of both dichlorides in aqueous alcohol was very low, but that of the β-isomeride was distinctly the higher. The α- was transformed to the β-dichloride by treatment with hot aqueous diethyl sulphide. The reverse change could be effected by conversion, through silver sulphate and potassium bromide, or through the latter alone, into the dibromide, which with silver chloride gave the α-dichloride. The dibromide and di-iodide existed in one form only, and this form was stated by Blomstrand to be a β-form and by Klason an α-form.

By slight modification of the original procedure, we have been able to prepare at will either the α- or the β-dichloride from diethyl sulphide and potassium chloroplatinite, the latter being best prepared from chloroplatinic acid and potassium oxalate. The α-dichloride is readily purified by taking advantage of its solubility in light petroleum, and the β-dichloride by making use of the fact that it separates from benzene as a sparingly soluble crystalline

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to the extent of about 50% in aqueous solution and yet exists therein free from the α-form, although we should expect rapid recombination of the ions to produce the insoluble α-form, which would be precipitated.

In our opinion, the crux of the matter lies in the assumption that the co-ordinate linkings in the α-compound are equivalent to semipolar double bonds. This assumption cannot be true, because it contradicts the experimental evidence. We are left with only two reasonable alternatives, *viz.*, (1) that the co-ordinate link is an ordinary double bond consisting of two covalencies, which means that the normal shells for the sulphur atoms are expanded in the α-compounds, the sulphur atom being quadricovalent; or (2) that the co-ordinate links in the α-compounds are formed by the sharing with platinum of two electrons from each sulphur atom, the sharing not being such as to provide a free unit charge on the platinum atom for each co-ordinate link. The extent to which such sharing takes place cannot at present be assessed in any particular case; and it will depend in the general case on the nature of the two atoms concerned (compare *J. Soc. Chem. Ind.*, 1928, **47**, 949). At present we refrain from deciding between these two possibilities. It may be that both types of bonding will be found among co-ordinately linked atoms; but we are inclined to prefer the second possibility in the case of the substances under consideration.

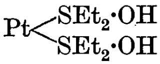
compound with a molecule of the solvent. We have confirmed the molecular weights and analyses of the two substances, and also their physical properties as given by Klason. The most noticeable physical differences between the isomerides, apart from the colours, lie in their solubilities, those of the α-dichloride suggesting a non-polar compound whereas those of the β-dichloride indicate a weakly polar substance. The β-dichloride was sufficiently soluble in water for its conductivity to be measured, and the values obtained showed that the salt is considerably ionised—about 50% at $v = 1000$ if μ_∞ be taken as 100.

We find that the chemical properties of the two dichlorides are so different as to render it highly improbable that they are merely spatial isomerides. The ready transformation, under certain conditions, of the β-compounds to the α- seems to have been the main cause which in the past has prevented a recognition of their true relationship. We have, for example, been able to isolate a second dibromide and to show that this is a β-compound, which, when melted at 95°, passes almost completely into the α-isomeride, m. p. 129°; and we have obtained evidence that a β-di-iodide exists and is still more easily converted into the α-di-iodide.

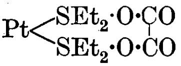
On being kept in the solid state, or in solution or suspension in alcohol or benzene, either dichloride tends to pass into an equilibrium mixture of both. The isomeric dibromides change in a similar manner but much more rapidly; but here the equilibrium mixture consists almost entirely of the α-compound. The di-iodides tend even more strongly to attain the α-state. In carrying out reactions, therefore, it has been found necessary to work with freshly prepared or freshly tested substances and to effect the rapid isolation and examination of the products. In some cases, as will be seen later, the influence of solvents becomes important, and the effect of temperature must also be taken into account.

The most striking chemical difference between the members of the two series of isomeric dihalides, however, is shown by their interaction with silver oxide in presence of water. The β-dichloride, for example, reacts in a few minutes with the production of silver chloride and a markedly basic substance, *platinumbisdiethylsulphonium hydroxide* (IX), which is readily soluble in water. This substance, which may be referred to as the β-base, can be obtained in transparent, yellowish, deliquescent crystals which rapidly absorb carbon dioxide when exposed to the air. After being dried over phosphoric oxide, the base gives correct analytical figures for a dihydroxide. Its aqueous solution is strongly alkaline to litmus, has a moderate conductivity, precipitates metallic hydroxides, and neutralises acids, both mineral and organic, with the production of pure β-salts provided that the temperature is below the point of their transformation to the α-compounds.

(IX.)



$$Pt\begin{matrix}\diagup SEt_2{\cdot}OH \\ \diagdown SEt_2{\cdot}OH\end{matrix}$$



$$Pt\begin{matrix}\diagup SEt_2{\cdot}O{\cdot}CO \\ \diagdown SEt_2{\cdot}O{\cdot}CO\end{matrix}$$

(X.)

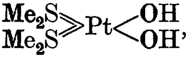
In this manner, besides the β-dichloride, the β-*dibromide* and the β-*oxalate* (X) were prepared, and were shown to belong to the β-series by quantitative reconversion into the β-dichloride, the former by means of silver oxide and hydrochloric acid, and the latter by means of the acid alone. The oxalate, a colourless substance readily soluble in water and in benzene, reacts at once with lime-water, giving a precipitate of calcium oxalate and a solution of the pure β-base, a reaction which suggests ionisation of the oxalate in aqueous solution. Determination of the conductivity confirmed this.

When an aqueous solution of the base was gradually neutralised with 0·5*N*-hydrochloric acid, the β-dichloride initially precipitated rapidly redissolved, but the precipitate became permanent before the half-neutralisation stage was reached. At this stage 0·12 g. of pure β-dichloride had been precipitated from a measured volume of solution which, as shown by another experiment, would have given on full neutralisation a precipitate of 0·54 g. of β-dichloride. Thus, at half-neutralisation the alkaline filtrate from β-dichloride still contains that substance, together with the free base and possibly a proportion of hydroxychloride. On evaporation at the ordinary temperature, this filtrate gave a yellow alkaline oil which partly solidified in a paste. This experiment shows that the β-base is not a complex substance like the base derived from the β-series of Vernon's dimethyltelluronium dihalides.

The α-dichloride, on the other hand, is only very slowly changed by moist silver oxide under precisely similar conditions, the reaction being incomplete after 48 hours. The evolution of diethyl sulphide commences at once, and the formation of silver chloride is attended by the precipitation of platinum as oxide or hydroxide. The filtrate is quite neutral to litmus : $Pt(Et_2S)_2Cl_2 + Ag_2O = 2Et_2S + 2AgCl + PtO$. The same distinction holds good for the isomeric dibromides and di-iodides.

These experimental results cannot be explained adequately on Werner's formulæ. The fundamental difference between the α- and the β-dichloride in their behaviour with silver oxide demonstrates most clearly that the isomerism is structural. On the new formulæ which we propose, the experimental results find a natural interpretation. The α-dichloride should give wholly silver chloride and the unstable co-ordination compound $(Et_2S)_2Pt(OH)_2$, which would be expected to decompose into diethyl sulphide and platinum oxide or hydroxide. The β-dichloride, on the other hand, should furnish silver chloride and the stable base (IX). Both the β-dichloride and the base should be ionised in aqueous solution. Each of these deductions has received confirmation. The reason why the β-dichloride is less polar in character than a true alkylsulphonium halide may well be that the influence of the bivalent platinum atom, which has clearly a tendency to attract electrons, prevents, by restraining to some extent the valency electrons possessed by the sulphur atom, the full development of ionisation of chlorine in the β-dichloride, since this development can occur only if the sulphur atoms are able to yield to the chlorine atoms their fourth valency electrons. The chlorine atoms are therefore partly covalent in the β-dichloride; nevertheless, in aqueous solution it exhibits appreciable conductivity. The α-dichloride is completely non-polar because the chlorine atoms are attached to platinum by covalencies.

The only other example of the production of a basic substance from a platinum compound of this type is described by Blomstrand (*loc. cit.*, p. 362), who noticed that the sulphate derived from a dichloride of the dimethyl sulphide series gave an alkaline filtrate when sulphuric acid was removed by the action of baryta. The liquid left, on spontaneous evaporation, a brownish semi-solid residue, but Blomstrand states that the substance could not be obtained in a condition suitable for analysis. Imagining that the hydroxyl groups were attached to platinum, he gave the formula

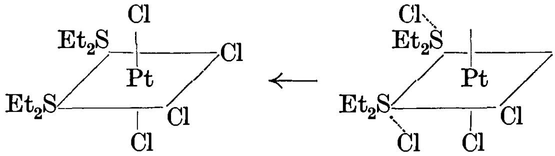


$\begin{matrix}Me_2S\\Me_2S\end{matrix}\!\!>Pt<\!\!\begin{matrix}OH\\OH\end{matrix}$, although he considered that the sulphate belonged to the α-series. Owing, probably, to the gummy nature of his product, Blomstrand failed to follow up his observation by investigating the action of acids upon this substance, contenting himself with the remark that the base absorbed carbon dioxide.

Blomstrand found that either the α- or the β-dichloride, when treated with aqueous silver sulphate and filtered, gave a solution of a sulphate which yielded a dibromide (m. p. 118°) on treatment with potassium bromide. Klason, who gives m. p. 124°, states that this is an α-dibromide and that the same substance is produced by the interaction of alcoholic potassium bromide with either dichloride. We now find that the interaction of the β-dichloride with silver sulphate and potassium bromide in the cold gives the pure β-dibromide (m. p. 95°), identical with that produced by the interaction of the β-dichloride and alcoholic potassium bromide, and also with that prepared by neutralising the β-base, with hydrobromic acid. The α-dichloride does not interact either with alcoholic potassium bromide or with aqueous silver sulphate at the ordinary temperature; if, however, the latter mixture is boiled, some diethyl sulphide is evolved (probably from the unstable α-sulphate), and the aqueous diethyl sulphide then converts the remaining α-dichloride into the β-isomeride, which interacts with the production of β-sulphate. It is evident, therefore, that Blomstrand and Klason must have heated the reaction mixture containing α-dichloride, thereby producing β-dichloride, and also that they must at some stage have heated to at least 95° the β-dibromide prepared from the β-dichloride, thereby converting it into the α-dibromide. These puzzling differences of opinion are therefore to be referred to the occurrence of inter-transformation between members of the α- and the β-series.

Further convincing evidence in favour of our structures for the α- and β-compounds has been obtained by the following methods. When chlorine is added to either of the isomeric dichlorides, conversion into the tetrachloride occurs. Our formulæ indicate that the α-dichloride should give rise to the octahedral form (XI), whereas the β-dichloride should yield the tetrahedral form (XII). We should expect these compounds to differ in properties as profoundly as do the isomeric dihalides. Moreover, (XII) should become transformed to (XI) by means similar to those which effect the change β-dihalide ⟶ α-dihalide.

(XI.)



(XII.)

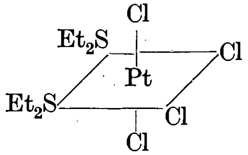
Blomstrand states that no isomerism exists amongst the tetrahalides. He prepared the same yellow tetrachloride (m. p. 175°) by the addition of chlorine to either dichloride, and he obtained similar results with the tetrabromides, tetraiodides, and a series of tetrahalides containing mixed halogens. We find, however, that the α-dichloride gives rise quantitatively to a yellow crystalline *α-tetrachloride* (XI), m. p. 198°, whilst the β-dichloride gives, also quantitatively, a paler yellow crystalline *β-tetrachloride* (XII), which melts at 133° and immediately resolidifies, forming the α-tetrachloride (XI). The β-tetrachloride is transformed to the α-isomeride on being boiled for a few minutes in ethyl or methyl alcohol, although by very rapid crystallisation it may be obtained unchanged from solution in the former solvent. Like the α-tetrachloride, however, it is unaltered by crystallisation from hot benzene, a non-ionising solvent. The transformation of the β- to the α-tetrachloride is therefore an ionic reaction which can be brought about by raising the temperature or by the use of a polarising solvent; and this is precisely what could be predicted from inspection of the formulæ (XII) and (XI).

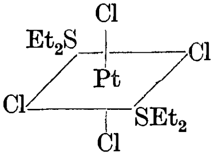
The α- and β-*tetrabromides* were prepared in an analogous manner. They are similarly inter-related, but the transformation of the β- to the α-form is even more readily effected than it is among the tetrachlorides.

When the β-tetrahalides are kept in the solid state their melting points tend to rise, whilst those of the α-tetrahalides appear to fall slightly. It would seem, therefore, that close parallelism exists among the α- and β-dihalides and the corresponding tetrahalides, dynamic equilibria being set up in both cases. The α-tetrahalides may be regarded as bis-dipolar compounds in which each platinum atom bears a double negative charge, whilst the sulphur atoms are each positively charged, this picture giving complete analogy with the accepted formulation of chloroplatinic acid except that the positively charged atoms are in that case free instead of being bound to the platinum atom by covalencies. Alternatively, the α-tetrahalides may be regarded as containing each two co-ordination linkings between platinum and the sulphur atoms, as in the α-dihalides.

It may be urged that the planar formulæ of Werner also account satisfactorily for the existence of two tetrachlorides, which would necessarily have the formulæ (XIII) and (XIV). Although we

(XIII.)



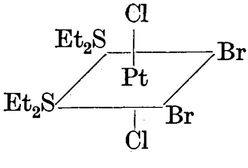


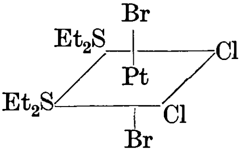
(XIV.)

considered that these formulæ, which might well represent difficultly interchangeable forms, could not account for the experimental results as convincingly as did (XI) and (XII), yet further evidence seemed necessary to prove finally the inadequacy of Werner's supposition. This was obtained from the results of an investigation of the dichlorodibromides.

On the planar hypothesis, if no spontaneous rearrangements of valencies occur, by adding chlorine to the α-dibromide a dichlorodibromide (XV) should be produced which should differ from that

(XV.)



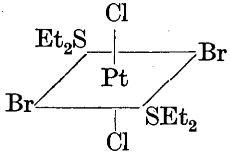


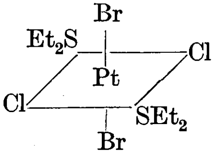
(XVI.)

(XVI) obtained on adding bromine to the α-dichloride. On our hypothesis, however, the two substances should be identical; and we find that this is indeed the case, the sole product being (XX).

As products of the corresponding changes in the β-series, the planar hypothesis demands, respectively, the two substances (XVII)

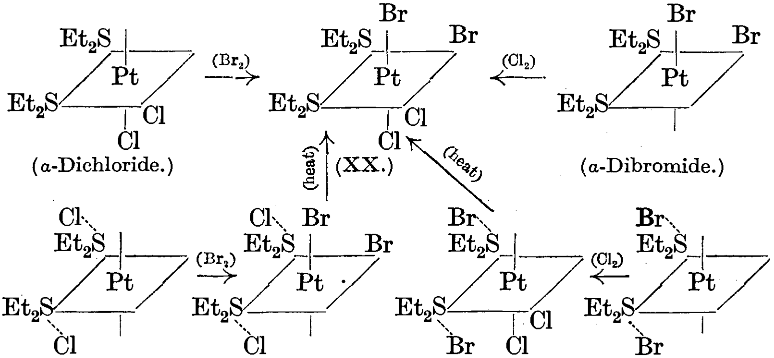
(XVII.)





(XVIII.)

and (XVIII), which should be identical, but different from either (XV) or (XVI). We find that neither of these demands is satisfied.* Labile tetrahedral forms, (XIX) and (XXI), are in both cases initially produced, which may readily be caused to change into the octahedral form (XX), *and this is identical with the dichlorodibromide from the two α-dihalides.* There is thus, finally, only one *dichlorodibromide* from the four sources, and the order in which the two different halogens are added is immaterial. The *labile forms* (XIX) and (XXI) are different, although closely similar, substances, whose properties show that they belong to the β-tetrahalide series; whilst (XX) is, of course, an α-tetrahalide.



(α-Dichloride.) (XX.) (α-Dibromide.)

(β-Dichloride.) (XXI.) (XIX.) (β-Dibromide.)

A curious distinction was noticed between the α- and β-compounds of both the di- and the tetra-halide series: the α-compounds are without exception "electrified" when rubbed upon glass with a bone spatula, the particles scattering strongly when detached from the glass in the attempt to collect them; but the pure β-compounds, dried under the same conditions, do not become "charged." A small proportion of α-compound present as impurity in a β-compound may be detected in this manner. We are not aware that this

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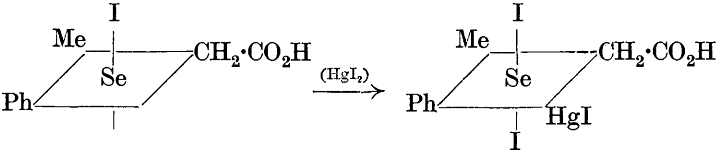
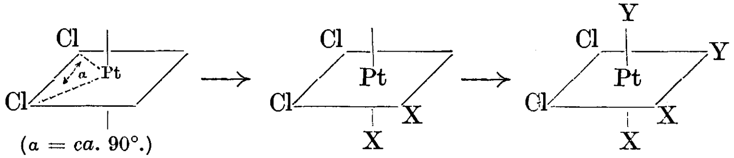
* Even if we suppose that Werner's configurations should be reversed, the α-compounds being *trans-* and the β-compounds *cis*-planar forms, anomaly still persists.

phenomenon has been noticed before in connexion with isomeric series. The triboelectric character of the α-compounds is presumably to be ascribed to asymmetry of crystalline structure.

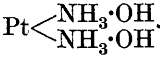
The conclusion emerges from our experiments that virtually quadrivalent platinum in this series is of tetrahedral space structure, and that, when this is converted into the octahedral form, the two entering groups take up exclusively *cis*-positions. In other words, the octahedron is a simple derivative of the tetrahedron, without rearrangement of groupings, the six valency electrons of platinum having directions which are approximately fixed in space. This conclusion is entirely in accord with the results of Pope and Neville (J., 1902, **81**, 1552) in connexion with octahedral sulphur and selenium. They find, for example, that, when mercuric iodide is added to optically active phenylmethylselenitine iodide, complete racemisation is produced, showing that the groups HgI and I must take up *cis*-positions :



The present experiments show, further, that tetrahedral platinum must be regarded as derived from the planar bivalent form by the similar *cis*-addition of groups, whence it follows that the valencies of platinum in platinous chloride are inclined at an angle of some 90°. It is improbable, therefore, that in passing from bivalent to quadrivalent (or quadricovalent) and to octahedral platinum the entering groups take up at either stage other than neighbouring positions of the developed octahedron; and it becomes unnecessary to suppose that the directions in space of the six valencies around the platinum atom are ever modified :



There is thus a possibility that the skew tetrahedron representing, *e.g.*, an α-dihalide may be sufficiently permanent to confer molecular asymmetry. This aspect is under examination.

If it be accepted that in the β-compounds of this series the halogens are united with sulphur and not with platinum, far-reaching questions are at once raised. The case of the platinammines is so similar to that at present being considered as to suggest that the structure must be analogous in both, and it would therefore follow that in the true β-series of platinammines the halogen atoms are united with nitrogen and should be capable of replacement by hydroxyl to give strongly basic substances, *e.g.*,  $\mathrm{Pt}{<}\begin{matrix}\mathrm{NH_3{\cdot}OH}\\ \mathrm{NH_3{\cdot}OH}\end{matrix}$. Evidence that a base of this nature can indeed be produced was put forward by Odling many years ago (*Chem. News*, 1870, **21**, 289), but the significance of his experiments appears to have been overlooked. It seems clear that the structures of many other ammines must be re-examined in the light of these results, and we are now engaged in work upon the foregoing platinammines and other substances. We intend also to examine the possibility of resolving into optically active components (i) the halides of the β-series of the form  $\mathrm{Pt}{<}\begin{matrix}\mathrm{SRR'Hal}\\ \mathrm{SRR'Hal}\end{matrix}$, in which the sulphur atoms should be centres of asymmetry, and (ii) compounds of type (XX), in which the molecule should be asymmetric on our theory but not on that of Werner.

EXPERIMENTAL.

Preparation of the Isomeric Dichlorides.—Potassium chloroplatinite, dissolved in about 5 times its weight of water, was shaken with a slight excess above 2 mols. of diethyl sulphide. (*a*) If the α-dichloride was required, the yellow precipitate, which consisted mainly of this isomeride, was removed after 2 hours, and the α-dichloride was crystallised from light petroleum (b. p. 40—60°), in which the β-isomeride did not dissolve. The aqueous mother-liquor, after concentration at the ordinary temperature, deposited yellowish-white needles of the β-dichloride. As soon as the aqueous liquid commenced to deposit potassium chloride, it was extracted with chloroform, which removed the remaining isomeric dichlorides. In one instance, pure α-dichloride was obtained on evaporation of the chloroform extract. (*b*) If the β-dichloride was required, the yellow precipitate (above) was kept with the mother-liquor in a closed flask for a day, whereupon most of it redissolved. The filtrate from undissolved material (a mixture of the two dichlorides), when evaporated at the ordinary temperature or when freed from ethyl sulphide by passage of air through the liquid, yielded the pure β-dichloride. The residual liquid was finally treated as in (*a*). The total yield of the two isomerides was almost quantitative.

The α-dichloride (VII), m. p. 106—108°, is insoluble in water, but readily soluble in ether, chloroform, benzene, and other organic solvents. It separates from light petroleum in bright yellow platelets, and from benzene in large yellow prisms which are without solvent of crystallisation. It crystallises well from alcohol in prismatic needles (Found : C, 21·55; H, 4·5; Pt, 43·7; *M*, cryoscopic in benzene, 434. Calc. for $C_8H_{20}Cl_2S_2Pt$: C, 21·5; H, 4·5; Pt, 43·7%; *M*, 446·5). It reacts rather slowly with silver nitrate in alcoholic solution; after 2 days, the filtrate from silver chloride gives with potassium chloride a mixture of the α- and the β-dichloride.

The β-dichloride (VIII) melts at 106—107° and is almost white. It is appreciably soluble in water and readily soluble in chloroform. In benzene it first dissolves and then separates in large, light yellow prisms, which often show square faces, containing 1 mol. of benzene of crystallisation which is lost on exposure to the atmosphere or at 60° (Found : C_6H_6, 14·2. Calc.: C_6H_6, 14·9%). The β-dichloride is only sparingly soluble in ether or in light petroleum. When melted, it gives after solidification a mixture of the α- and the β-dichloride (Found, for solvent-free β-dichloride: C, 21·65; H, 4·55; Pt, 43·75; *M*, cryoscopic in benzene, 438).

When the α- and the β-dichloride are mixed, there is very marked depression of the melting point.

Interconversion of the Isomeric Dichlorides.—The α-dichloride is partly converted into the β-isomeride on being heated either alone or in alcoholic solution, or much more completely by Blomstrand's method of treating it with further aqueous diethyl sulphide, preferably in the warm (Klason), which causes it to enter into colourless solution in proportions so high as to suggest the formation of a new soluble complex with diethyl sulphide stable only in presence of an excess of the sulphide. The β-dichloride is partly converted into the α-isomeride on being melted or on being allowed to remain in solution in benzene for some weeks. When kept, each of the crystalline dichlorides slowly reverts to a mixture of both.

Action of Moist Silver Oxide on the Isomeric Dichlorides.—(1) The α-dichloride, ground in a glass mortar with excess of silver oxide and a little water, was only very slowly changed, with production of free diethyl sulphide, silver chloride, and insoluble platinous oxide or hydroxide. After 48 hours, the filtrate showed no alkalinity to litmus and gave no precipitate with dilute hydrochloric acid except a negligible trace of silver chloride. The precipitate, dried at the ordinary temperature and extracted with benzene, gave some unchanged α-dichloride. The insoluble residue was shown to contain both silver chloride and platinum oxide or hydroxide.

(2) The β-dichloride reacted rapidly when treated with silver oxide in the same manner, the change being complete in less than ½ hour. The clear, faintly yellow filtrate from silver oxide and chloride had no odour of diethyl sulphide. It was strongly alkaline to litmus, and when neutralised with dilute hydrochloric acid gave a crystalline precipitate of the pure β-dichloride. The aqueous solution of this

β-base, when evaporated to dryness in a vacuum over phosphoric oxide at the ordinary temperature, gave pale yellow hygroscopic crystals of *platinumbisdiethylsulphonium hydroxide* (IX), which, like the aqueous solution, soon absorbed carbon dioxide if exposed to air (Found, in base exposed to air as little as possible : C, 23·85; H, 5·15; Pt, 47·3, 47·75. $C_8H_{22}O_2S_2Pt$ requires C, 23·45; H, 5·4; Pt, 47·7%). The dried base was easily soluble again in water or in ethyl alcohol. Hydrogen sulphide produced a brown precipitate of a sulphide of platinum, diethyl sulphide being liberated.

By neutralising the aqueous solution of the β-base with aqueous acids, the following salts, shown to be of the β-series by the reactions briefly summarised below, were prepared.

The β-*dibromide*, $Pt(SEt_2Br)_2$, separated from alcohol in pale yellow, domed prisms, m. p. 93—95°; the melt resolidified and then remelted at 128—129°. The substance was identical with a specimen of β-dibromide prepared by a second method, *viz.*, the action of alcoholic potassium bromide in the cold upon the β-dichloride, also dissolved in alcohol; a mixed m. p. of the two specimens showed no depression. A third method, the action (which is rapid) of moist silver sulphate upon the β-dichloride in the cold, followed by filtration and addition of aqueous potassium bromide to the filtrate, gave identically the same substance. The β-dibromide is more soluble in benzene than the corresponding dichloride (Found : Pt, 36·8. $C_8H_{20}Br_2S_2Pt$ requires Pt, 36·45%). It slowly reverts to the α-isomeride when kept, and more rapidly when left in contact with alcohol. The structure was checked by the following reactions :

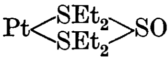
$$\beta\text{-Dibromide} \xrightarrow[Ag_2O]{\text{moist}} \beta\text{-Base} \xrightarrow[HCl]{\text{dilute}} \beta\text{-Dichloride.}$$

The α-*dibromide*, $PtBr_2(SEt_2)_2$, prepared by heating the β-dibromide at 100° for a few minutes, the transformation being nearly quantitative, crystallised from ethyl alcohol in large, golden-yellow, hexagonal spangles, m. p. 129° (Found : Pt, 36·25%). An alcoholic solution of potassium bromide was without action upon the α-dichloride : even when the liquid was warmed for a few minutes, the dichloride was recovered unchanged.

The β-*oxalate* (X) formed colourless transparent crystals when its aqueous solution was allowed to evaporate. It was very soluble in water, the solution being neutral to litmus and giving with limewater a deposit of calcium oxalate and a solution of the β-base, from which, after filtration, the addition of hydrochloric acid precipitated the pure β-dichloride. The latter is also precipitated by direct addition of hydrochloric acid to a solution of the β-oxalate. The β-oxalate melts near 60° if heated slowly, but the melt is not clear and partial resolidification occurs, the solid melting again near 95°.

Probably partial transformation to an α-form takes place at the lower temperature. The substance is in part soluble in benzene, separating as an oil which solidifies on standing to a crystalline mass apparently identical with the initial β-oxalate. For analysis it was crystallised from water and dried over phosphoric oxide (Found : C, 25·7; H, 4·4; Pt, 42·25. $C_{10}H_{20}O_4S_2Pt$ requires C, 25·9; H, 4·35; Pt, 42·1%).

A sulphate crystallising with $7H_2O$ was prepared by Blomstrand (*loc. cit.*) from either dichloride by treating it with aqueous silver sulphate, and hence he prepared what we now know to be the α-dibromide, by treatment with potassium bromide. Klason afterwards showed that Blomstrand's α-dichloride contained 20% of β-dichloride, to which its behaviour (above) is now shown to be due.

Although Blomstrand correctly assigned his sulphate to the β-series, he did so because he prepared from it a dibromide which he thought, incorrectly, to be a β-compound. In reality, he must have obtained the β-dibromide which he unwittingly transformed to the α-isomeride by heating the solution at some stage. We prepared the β-sulphate,  $Pt{<}{\substack{SEt_2\\SEt_2}}{>}SO_4$, from the β-dichloride with silver sulphate and found (p. 354) that its aqueous solution precipitated the pure β-dibromide on treatment in the cold with aqueous potassium bromide. The same result was obtained when the β-base was neutralised with sulphuric acid, and potassium bromide added to the solution. The sulphate is therefore certainly a β-sulphate. We found, also, that the α-dichloride was unaffected in the cold by moist silver sulphate after 16 hours. If, however, the mixture was heated at 100° for some minutes, diethyl sulphide was evolved, and this in the presence of water changed some unaltered α-dichloride to the β-isomeride, which, in turn, reacted with silver sulphate to produce a proportion of β-sulphate. The α-sulphate, therefore, is probably unstable; and, in any case, it cannot be prepared in this manner.

The β-dichromate, prepared from the β-base with potassium dichromate and sulphuric acid, separated from benzene in dark red needles, m. p. 140°. It was decomposed by hot ethyl alcohol.

Attempts to prepare the Isomeric Di-iodides.—Blomstrand prepared a di-iodide (m. p. 136°) from the sulphate with potassium iodide. He considered this to be a β-compound, but Klason assigned it to the α-series. The following experiments indicate that the α-di-iodide melts at 142—144° and that the β-di-iodide changes into it without melting. Attempts to isolate a pure specimen of the β-di-iodide have been fruitless.

(1) Alcoholic potassium iodide reacted in the cold with an alcoholic solution of the α-dichloride (contrast the behaviour of potassium bromide, p. 361). Orange-red crystals of a di-iodide were obtained, which, after extraction by cold benzene, reddened near 115° and melted at 141—143°. By crystallisation from alcohol, square orange prisms in serrated clusters, m. p. 142—144°, were obtained. This substance gave no β-base with moist silver oxide; the mixture slowly evolved diethyl sulphide. The substance was therefore the α-di-iodide. When the above reaction mixture is heated, some diethyl sulphide is evolved.

(2) Alcoholic potassium iodide reacted at once in the cold with an alcoholic solution of the β-dichloride, giving a di-iodide (m. p. 138—140°), which was apparently identical with the former substance. Silver oxide, however, acted upon it to give a very small proportion of β-base.

(3) The action of hydriodic acid (colourless) on a solution of the β-base at the ordinary temperature gave a product (orange-yellow, m. p. 138—140°), which crystallised from alcohol in the same form, and did not depress the m. p. of the former product. It gave no β-base with moist silver oxide.

When the reaction was carried out at 0°, a product was obtained (m. p. 138—140°) which, after crystallisation from alcohol (Found: Pt, 31·2. Calc. for $C_8H_{20}I_2S_2Pt$: Pt, 31·0%), gave a considerable proportion of β-base, together with diethyl sulphide, when treated with moist silver oxide (16 hours). The original material was therefore probably a mixture of the α- and the β-di-iodide.

In another similar experiment, in which the β-base was treated below 0° with aqueous potassium iodide and then with a slight excess of dilute sulphuric acid, a brownish-yellow di-iodide, m. p. 132—135°, was obtained. From methyl alcohol, it separated in minute yellowish-brown crystals, m. p. 141—143°, which partly melted if plunged into a bath at 125°. With moist silver oxide, it gave a small proportion of β-base.

(4) When the β-dichloride was decomposed with aqueous silver sulphate, and to the filtered solution of the β-sulphate an excess of aqueous potassium iodide was added below 0°, a yellow di-iodide was precipitated. After extraction with benzene, however, the orange product was indistinguishable from the α-di-iodide.

It must be concluded from these experiments that the β-di-iodide is easily transformed to the α-isomeride.

Tetrahalides.—The *α-tetrachloride* (XI) was prepared in quantitative yield by passing a slight excess of chlorine at 0° or at the ordinary temperature into a chloroform or benzene solution of the α-dichloride. The crude product had m. p. *ca.* 196° (decomp.); it separated from ethyl alcohol in lemon-yellow needles or in massive rectangular tablets belonging to the cubic system. The pure substance melts and decomposes at 198°, with sintering from 188°. It is readily soluble in benzene, from which it crystallises unchanged in cubic tablets (Found : C, 18·85; H, 4·25; Pt, 37·5. $C_8H_{20}Cl_4S_2Pt$ requires C, 18·55; H, 3·9; Pt, 37·7%).

The β-*tetrachloride* (XII) was similarly obtained from the β-dichloride. The crude product melted between 120° and 130° but contained some α-tetrachloride. Crystallised from benzene, in which it is much less soluble than the α-isomeride, it separates in jagged, light-yellow prisms or (more slowly) in compact prisms capped by pyramids, the crystals being cubic (Found : C, 18·75; H, 4·2; Pt, 37·6, 37·9%). The powdered crystals melt completely when plunged into a bath at 135°; the yellow melt then resolidifies, the solid melting again near 195°. When boiled with methyl or ethyl alcohol for a short time, it is changed to the α-tetrachloride, which separates in the pure state; but it may be crystallised from ethyl alcohol by momentary heating and cooling, whereupon it separates in small, greenish-yellow, glistening platelets, melting first at 133° and then near 198°. The mixed m. p. of the two specimens of α-tetrachloride, prepared (i) directly and (ii) through the β-tetrachloride, was the same as that of either.

The α-*tetrabromide*, $PtBr_4(SEt_2)_2$, obtained quantitatively by the action of bromine on a chloroform solution of the α-dibromide, crystallises from ethyl alcohol in lustrous scarlet needles, sintering from 192° and melting at 198° (decomp.) (Found : C, 14·0; H, 2·95; Pt, 28·0. $C_8H_{20}Br_4S_2Pt$ requires C, 13·8; H, 2·9; Pt, 28·1%); it is much more readily soluble in benzene than the β-form.

The β-*tetrabromide*, $PtBr_2(SEt_2Br)_2$, was obtained by adding at 0° a slight excess of bromine in pure chloroform or, better, in benzene, to a solution of the β-dibromide in the same solvent. The crude product melted completely and resolidified in a few seconds if plunged into a bath at 135°, but if plunged at 115° and then heated it was changed without melting to the α-isomeride. It separated from warm benzene in light red, flat, prismatic needles (Found : C, 13·6; H, 2·95; Pt, 27·8, 28·05%), which melted if plunged at 125° and then resolidified to the α-compound, melting again at about 195°. When crystallised once from ethyl alcohol, it was changed to the α-form, the m. p. and mixed m. p. with that substance being identical. This β-compound is more easily changed to the α-form than is the β-tetrachloride. It should not be heated longer than a few seconds to effect solution even with benzene.

Dichlorodibromides.—In the following reactions addition of halogen to the dihalides was carried out in solution in alcohol-free chloroform, in pure benzene, or in a mixture of chloroform and ligroin. Experiments indicated that benzene was the best solvent and that undue excess of halogen was to be avoided. In all cases the solvent was at once evaporated at the ordinary temperature, the product was quickly dried, and its m. p. observed. The whole product was then crystallised from pure benzene with momentary heating, and the crops were examined as to colour, crystalline form, and m. p. In all cases identities were checked by these means and by mixed m. p.'s and analyses.

(1) *Action of chlorine on the α-dibromide.* The crude *α-dichlorodibromide* (XX) separated as a mass of crystals, m. p. 190—193° (decomp.; after sintering). Crystallised from benzene, in which it was readily soluble, it separated in massive orange-red rhombs showing square and hexagonal faces. The powdered substance, which was strongly triboelectric, showed no signs of melting when plunged into a bath at 140°. It softened somewhat above 185° and melted at 190—193° (decomp.). It separated readily from ethyl alcohol in prismatic crystals, m. p. 192—193° (decomp.); but examination of the mother-liquors showed that the substance is partly reduced by alcohol, the use of which is therefore to be avoided in this connexion (Found: Pt, 31·8, 32·1, 32·3. $C_8H_{20}Cl_2Br_2S_2Pt$ requires Pt, 32·2%). Even from benzene the substance should not be recrystallised more than once.

(2) *Action of bromine on the α-dichloride.* The crude product consisted of crystals of the same α-dichlorodibromide, m. p. 189—192° (decomp.) after sintering. The crystals from alcohol or from benzene were those of (XX). Analyses were carried out after one crystallisation from benzene (Found: C, 16·1; H, 3·65; Pt, 32·15, 32·1%) and then after a recrystallisation from the same solvent (Found: Pt, 31·8. Calc.: C, 15·8; H, 3·3; Pt, 32·2%).

(3) *Action of chlorine on the β-dibromide.* The crude orange-yellow crystalline product, which was thrown out of solution when chlorination was carried out at 0° in benzene, consisted of the *β-dichlorodibromide* (XIX), melting completely when plunged into a bath at 105° and then resolidifying and again melting near 188°. When crystallised from ethyl alcohol, it was completely changed to the α-isomeride (XX); but it could be crystallised by momentary warming with benzene, from which it separated in small, dark yellow, complex prisms or in rhomboidal platelets melting if plunged at 110°, or near 120° (incompletely) if heated in the ordinary way (Found, in different preparations: C, 15·5; H, 3·4; Pt, 31·8, 32·1%). A mixture with the isomeric β-dichlorodibromide (XXI, below), m. p. 125°, melted completely if plunged into a bath at 115°, but if heated in the ordinary way melted only at 190—192°. This

dichlorodibromide was much less permanent than (XXI), changing, even on a few minutes' boiling with benzene, into the α-isomeride, which was shown to be identical with (XX).

(4) *Action of bromine on the β-dichloride.* The crude product consisted of a mass of salmon-yellow prisms of the β-*dichlorodibromide* (XXI), completely melting when plunged at 128°, resolidifying, and again melting near 188°. Crystallised from benzene, in which it was much less soluble than the α-isomeride, it separated in complex prisms, m. p. 125° (with resolidification), of salmon-yellow shade, showing rhomboidal faces (Found : C, 15·8; H, 3·35; Pt, 32·25%). One crystallisation from ethyl alcohol or 10 minutes' heating in solution in benzene changed it completely to the α-form, which was again proved to be identical with (XX). This β-dichlorodibromide, which is of darker shade than (XIX), can be kept in the solid state for several days without suffering more than slight change to the α-form.

All four of the β-tetrahalides prepared were easily wetted and decomposed by concentrated nitric acid, in marked contrast to the α-tetrahalides, which were remarkably stable to the warm reagent.

In solution, the α-tetrahalides are probably in equilibrium with small proportions of the partly ionised β-tetrahalides, for the α-dichlorodibromide tends to pass after many crystallisations from benzene into an α-*chlorotribromide,* large ruby-red prisms from benzene, m. p. 196° (decomp.) (Found : C, 15·05; H, 3·2; Pt, 30·0, 29·9. $C_8H_{20}ClBr_3S_2Pt$ requires C, 14·75; H, 3·1; Pt, 30·0%).

Equimolecular mixture of the α-tetrachloride and α-tetrabromide. The mixed substances, intimately ground together, had the same m. p. as the α-dichlorodibromide (XX), and it was practically unaltered when the latter was added to the mixture. Crystallisation from alcohol (Found : Pt, 31·7%) or benzene gave products very similar to those obtained by crystallising (XX) from the same solvent. It will be seen that the α-tetrachloride does not depress to a normal extent the m. p. of the α-tetrabromide, and this phenomenon is to be expected (compare J., 1928, 512). It is uncertain, therefore, whether an equimolecular mixture of these substances would depress to any noticeable extent the m. p. of a true α-dichlorodibromide (XX). There remains the possibility that (XX) is produced when the mixture crystallises, or that mixed crystals of the two tetrahalides, indistinguishable from (XX) by the means employed, are formed. Again, it is possible that at temperatures near 180° the α-dichlorodibromide (XX) becomes changed into an equimolecular mixture of the two simple α-tetrahalides. The matter will be further examined.

Physico-chemical Measurements.

Molecular Weights.—These determinations were made to show that the isomerism of the α- and β-salts could not be explained by supposing that one was a polymeride of the other, this view of the relationship of certain 4-co-ordinated platinum compounds being maintained by Reihlen and Nestle (*Z. anorg. Chem.*, 1927, **159**, 343; *Annalen*, 1926, **447**, 21, 312, 448).

The benzene used was supplied by the British Drug Houses, Ltd., especially for molecular-weight determinations. Traces of moisture were removed by distillation over phosphoric oxide (compare Sidgwick, J., 1920, **117**, 1340). A determination with naphthalene in this solvent gave *M*, 128·2. The α- and β-salts were analytically pure and their m. p.'s were unchanged by successive recrystallisations from light petroleum (b. p. 40—60°) in the case of the α-, and from hot benzene in the case of the β-form, benzene of crystallisation being afterwards removed [Found: for α-salt, *M*, 434; for β-salt, *M*, 438. $PtCl_2(SEt_2)_2$ requires *M*, 446·5].

Conductivity Measurements.—These determinations, which required special care on account of the small solubility of the substances in water, could not be accurately made by the use of a Kohlrausch slide wire. To overcome these and other disadvantages, a substitution bridge, constructed by Messrs. Tinsley and Son to the specifications of Mr. H. M. Spittle of this Department, was employed.

The arrangement of the apparatus is outlined in Fig. 1.

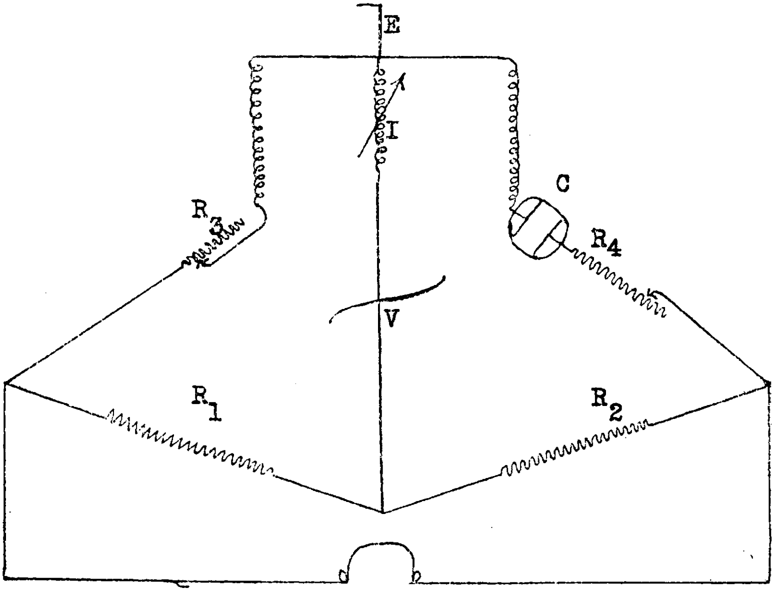
A valve oscillator, V, producing a pure sine wave of 1000 cycles, formed the source of alternating current, all capacity effects being eliminated by the use of two fixed inductances and one variable inductance, I, the effective inductance of which balanced the capacity of the liquid in the conductivity cell, C. Two 2000-ohm non-inductive resistances, R_1 and R_2, formed two arms of the bridge, the third, R_3, consisting of a variable non-inductive resistance of 0—11,000 ohms. The fourth contained another variable non-inductive resistance of 0—10,000 ohms, R_4, which could be coupled with the cell, and, where necessary, R_3 and R_4 were increased by the introduction of additional, standardised non-inductive resistances. Readings were made by altering R_3, so that a balance was obtained with R_4 about 50 ohms, when in series with the cell. By eliminating the cell, the true value of R_3 was determined, the difference between the two readings giving the actual resistance of the cell, although the total resistance of the bridge remained unaltered. In this way successive readings of a resistance of any magnitude never fluctuated by more than 0·1%.

Conductivity water. The water used possessed a conductivity of

$3{\cdot}1 \times 10^{-6}$ mho at 18°, and this did not materially increase during the course of several weeks.

Conductivity vessel. The conductivity vessel was constructed to hold 5 c.c. of liquid and fitted with a ground-glass stopper. After being washed with conductivity water, the vessel was dried in a vacuum desiccator, which was then opened in a slow stream of carbon dioxide-free air. Dilutions (*v*) are given in litres per g.-mol., and the temperature was 18° in each case.

FIG. 1.



Results. Solutions of the β-dichloride were prepared in two ways: (*a*) by warming to 30°, followed by cooling to 18° (the solution was not acid to litmus or Congo-red paper), and (*b*) by shaking the salt (2 mg.) with water (5 c.c.) in the cell over-night.

	v.	*μ*.		*v*.	*μ*.
β-Dichloride (solution *a*)	658·2	43·4	β-Oxalate	355·3	18·6
,, (,, *b*)	1037	50·9	β-Base	276·4	11·4
,, (,, *b*)	1178	50·4		115·0	7·2

Werner and Herty's conductivity data (*Z. physikal. Chem.*, 1901, **38**, 347) for the diammines of platinous chloride are of interest in connexion with our results for the dichloride. Their initial values for μ for the *cis*-form were low (μ 2—4) provided that the solution was prepared at 25°, but if it was first heated to 50° and then cooled to 25° a value of *ca.* 40 was recorded. Owing to the minute solubility of the *trans*-form in water at 25°, they could not obtain suitable solutions for conductivity measurements by operating at this temperature, but they found that if the salt was dissolved in water at 50° and the solution then cooled to 25°, a conductivity of about 40 was registered. Hence they inferred by analogy with the behaviour of the *cis*-form that, if direct solution could have been effected at 25°, the *trans*-form would have been a non-electrolyte. Their statement that the *cis*- and *trans*-diammines are non-electrolytes is based, therefore, on analogy rather than on direct experimental evidence.

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