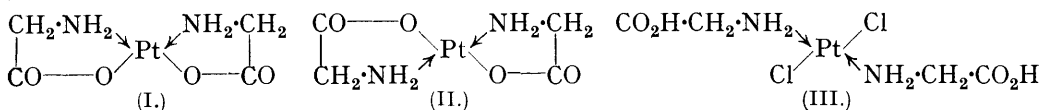


211. Isomerides of Quadricovalent Palladium and Platinum.

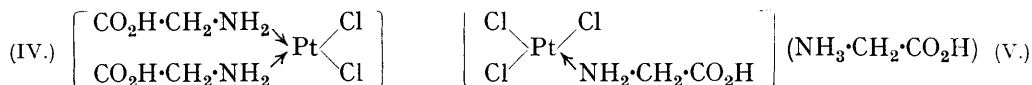
By F. W. PINKARD, E. SHARRATT, W. WARDLAW, and (in part) E. G. COX.

WHEN Ley and Ficken (*Ber.*, 1912, **45**, 377) examined the reaction of glycine and potassium chloroplatinite, they obtained one compound of the empirical formula $\text{Pt}(\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2)_2$ whose properties showed it to be covalent. However, if the valencies in 4-covalent platinum are coplanar, two isomerides (I) and (II) should exist.



Recently, Grünberg and Ptizyn (*J. pr. Chem.*, 1933, **136**, 143) re-investigated this reaction and reported the isolation of two compounds which they considered to be the required isomerides. Both substances were colourless and sparingly soluble in water, producing non-conducting solutions. The more soluble was described as crystallising in needles, and the other in plates. We have confirmed these experimental facts, but would describe the needles rather as prisms. Moreover, we find that these compounds are characterised by remarkable stability in aqueous solutions; hydrogen sulphide does not precipitate the platinum. This great stability is fully in accordance with the formulæ proposed. Nevertheless, the chemical proof put forward by Grünberg and Ptizyn to establish the *cis-trans*-isomerism does not appear to us to be convincing. Briefly, configuration (II) for the plates is based on the fact that, when warmed with hydrochloric acid, they yield a dichloride, which those authors contend must have the structure (III), since with ethylenediamine, $[\text{Pt en}_2]\text{Cl}_2$ is formed. This was isolated as the plato-salt, $[\text{Pt en}_2][\text{PtCl}_4]$, by reaction with potassium chloroplatinite.

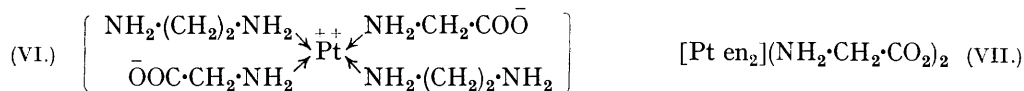
We find that a dichloride of the composition $\text{PtCl}_2(\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ is actually produced, but it is always accompanied by other substances. Nevertheless, these reactions do indicate that formula (II) is probable for the plates. Grünberg and Ptizyn's evidence in favour of formula (I) for the so-called needles is, however, definitely inadequate: their needles were never isolated pure, being always contaminated with plates. Moreover, on treating these needles with hydrochloric acid, some *trans*-dichloride (III) was always obtained, but no other dichloride. However, Grünberg and Ptizyn assume that the dichloride (IV) must be in solution, for on addition of ethylenediamine a compound is produced capable of isolation as the plato-salt $[\text{Pt en}(\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2][\text{PtCl}_4]$. This



interpretation of the experimental results is not a necessary one. A plato-salt of this type may equally well be obtained from the analogue of the well-known Cossa's salt (V)

with ethylenediamine. Moreover, (V) is obviously obtained from either (III) or (IV) by reaction with hydrochloric acid, and therefore from (I) and (II). Incidentally, we have obtained indirect experimental evidence that (V) exists in the yellow solution obtained from the reaction of the plates and hydrochloric acid. It will be seen, therefore, that the case for *cis-trans*-isomerism is not established beyond question.

We have now, however, obtained the two isomerides of diglycineplatinum in a pure state and demonstrated that they will react directly with ethylenediamine. Without any assumptions, such as Grünberg and Ptizyn make, as to the constitution of intermediate substances, we have proved that the plates have the structure (II) and the prisms (I). That the plates are represented by (II), is confirmed by their reaction with ethylenediamine, which disrupts the principal valencies producing first (VI) and then (VII), and by the fact that addition of hydrochloric acid to (VII) gives $[\text{Pt en}_2]\text{Cl}_2$, readily isolated as



the plato-salt $[\text{Pt en}_2][\text{PtCl}_4]$. Similarly structure (I) is confirmed for the prisms, for (VIII) is formed instead of (VI), and thence, by analogous reactions, the *plato*-salt (IX); no other structure explains these reactions.



The establishment of *cis*- and *trans*-isomerism in the glycine derivatives of 4-covalent platinum adds a very interesting new type of compound to the series of planar structures. The association of a platinum atom with (a) four chlorine atoms, (b) four nitrogen atoms, (c) four sulphur atoms, (d) two sulphur atoms and two chlorine atoms has been shown to result in planar structures. Now, the association of two atoms of oxygen and two atoms of nitrogen has been proved to give a similar result.

Palladium, like platinum, has been shown by X-ray methods to give planar configurations in certain of its 4-covalent compounds. In no case, however, has the *cis*- and *trans*-isomerism demanded by theory been established. This is due presumably to the instability of the *cis*-configuration when the associating units are not chelate groups. It appeared to us, therefore, that the establishment of *cis*- and *trans*-isomerism would most probably be accomplished by use of an unsymmetrical chelate group such as glycine. This has proved to be the case, for we have succeeded in isolating two *substances*, $\text{Pd}(\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2)_2$, which are the required isomerides.

When an aqueous solution of potassium chloropalladite reacts with glycine at room temperature a mixture of substances separates, *viz.*, yellow prisms $\text{Pd}[\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2]_2 \cdot 3\text{H}_2\text{O}$ and glistening, light-yellow, anhydrous plates. The *trihydrate* readily loses its water of crystallisation in air; after an hour there is appreciable loss, and the crystals are totally dehydrated after a few days. The slight possibility that the prisms might be a metastable form of the plates was easily disposed of by chemical and physical tests. Since the two substances crystallised together at room temperature and at 30° , and on keeping in water for ten days gave no indication of interconversion, the hypothesis of a metastable form is disposed of. A crucial chemical test was obtained by the reaction with thiourea; its addition to a suspension of the plates in water gave immediately a yellow *precipitate* of the composition, $\text{Pd}[\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2]_2 \cdot 2\text{CS}(\text{NH}_2)_2$, whereas the prisms, under identical conditions, gave at once a red solution from which a black precipitate separated consisting of various decomposition products. This test is a striking one and makes it certain that the substances are structurally different. Moreover, the prisms on dehydration give the same reaction as the hydrated product, showing that they have not changed to the structure of the plates. An important fact about the plates and the prisms is that they are practically non-conducting in aqueous solution. This indicates that they have a co-

ordinated structure like their platinum analogues. Neither of the palladium isomerides is very soluble in cold water but they are more soluble than the corresponding platinum compounds. The solubility of the palladium derivatives increases rapidly with rise in temperature, but in boiling water decomposition takes place. There is evidence that the palladium isomerides are interconvertible by heating with water, unlike the diglycine compounds of platinum. Another point of interest is that hydrogen sulphide will precipitate palladium from aqueous solutions of either compound. Hence the palladium derivatives have not the great stability of their platinum analogues. In addition, both palladium compounds react so readily with ammonia and with ethylenediamine that the simple tetramines are formed immediately, and thus the convenient method which we used for establishing *cis*- and *trans*-isomerism in the platinum series is not available here. Fortunately, crystallographic and X-ray results bearing on these matters are available. Since the compounds are covalent, one cannot be the dimeric form of the other, because the required ring system would be very unstable. It is reasonable to conclude, therefore, that they are monomeric. The instability of the compounds in boiling water does not admit of molecular-weight determinations, and no organic solvent is available.

The X-ray diagrams of the anhydrous plates and the anhydrous prisms prove definitely that these compounds are structurally different, thereby confirming the findings from the chemical test with thiourea. The plates of the palladium compound are isomorphous with those of the platinum derivative, and as this has a *trans*-planar structure the palladium compound must be similarly constituted. The only possible structure for the prisms is one where the two nitrogen atoms and the two oxygen atoms are in *cis*-positions. It is not fully established that this is a planar structure. The possibility that it is a tetrahedral structure is so remote, however, that it seems unnecessary to consider it as a serious alternative to the *cis*-planar structure.

EXPERIMENTAL.

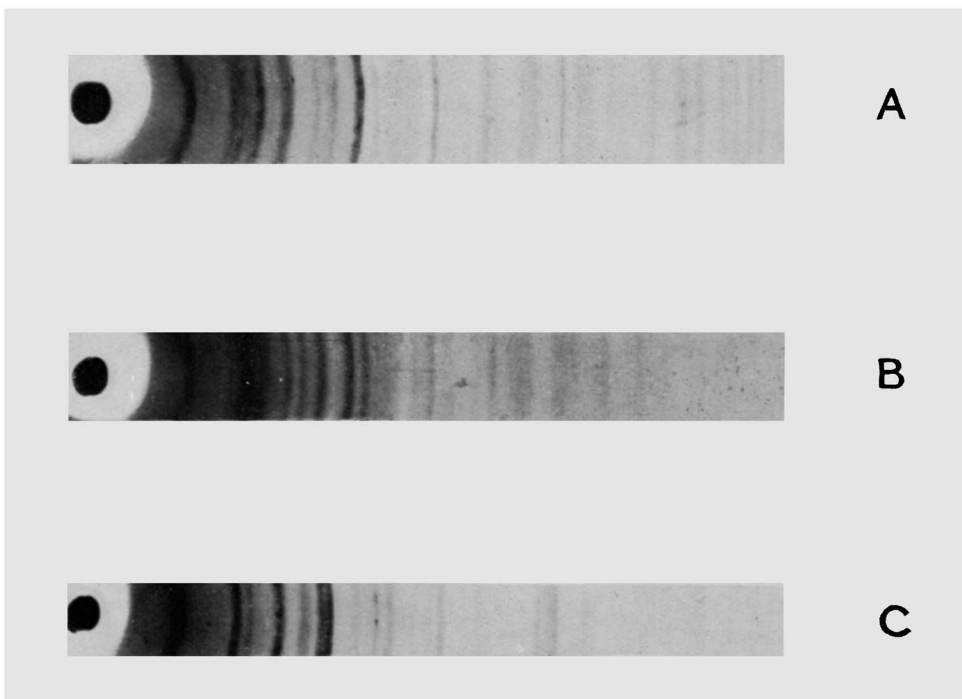
trans-Diglycineplatinum.—An aqueous solution of glycine (4 g. in 40 ml.) was warmed with potassium chloroplatinite (4 g.) on a water-bath for about an hour. Colourless crystals separated from the hot solution, and on cooling a further crop was obtained; they were recrystallised from hot water (Found : Pt, 56.86. Calc. for $\text{PtC}_4\text{H}_8\text{O}_4\text{N}_2$: Pt, 56.85%). The crystals are elongated, six-sided plates, the angles between the long edges and those at the end being 60° and 45° ($\pm 3^\circ$). They are frequently four-sided, showing an angle of 60° . The extinction direction is nearly parallel to the edge inclined at 45° , while an optic axis emerges at about 45° to the normal, in a plane perpendicular to the direction of elongation. The optic axial angle appears to be large. The crystals are triclinic, or possibly monoclinic. An aqueous solution ($v = 9266$) gave $\mu = 3.15$ at 25° , showing that the substance is a non-electrolyte.

cis-Diglycineplatinum.—The yellow filtrate from the foregoing preparation was concentrated. The crystals which separated were a mixture of various proportions of plates and prisms. This product was extracted with hot water (30 ml.), and the extract cooled. A crystalline product, mainly prisms, separated, but the mother-liquor on concentration yielded only prisms (Found : Pt, 56.77%). The crystals are elongated prisms, showing straight or slightly inclined extinction. An X-ray photograph is reproduced (A). In aqueous solution ($v = 1075$) $\mu = 2.63$, showing that the substance is not ionised in solution.

Reactions of the Isomerides with Ethylenediamine.—(a) *cis*-Diglycineplatinum was warmed for 4 minutes with aqueous ethylenediamine, the solution cooled, filtered, and just acidified with hydrochloric acid. The addition of potassium chloroplatinite produced a pink precipitate of *ethylenediaminodiglycineplatinum chloroplatinite monohydrate* (IX) (Found : Pt, 51.52, 51.12; N, 7.46. $\text{C}_8\text{H}_{20}\text{O}_5\text{N}_4\text{Cl}_4\text{Pt}_2$ requires Pt, 51.32; N, 7.37%). Prolonged heating of the *cis*-diglycineplatinum with aqueous ethylenediamine led to the complete replacement of the glycine; on acidification, $[\text{Pt en}_2]\text{Cl}_2$ was formed, and identified as its violet plato-salt (Found : Pt, 59.35. Calc. for $[\text{Pt en}_2][\text{PtCl}_4]$: Pt, 59.82%).

(b) *trans*-Diglycineplatinum was warmed for 4 minutes with aqueous ethylenediamine, the solution cooled and filtered, then just acidified with hydrochloric acid. Addition of potassium chloroplatinite gave the violet plato-salt $[\text{Pt en}_2][\text{PtCl}_4]$ (Found : Pt, 59.0; N, 8.50. Calc. : Pt, 59.8; N, 8.58%).

Reactions of Isomerides with Ammonia.—(a) *cis*-Diglycineplatinum was warmed with



X-Ray powder photographs.

A. *cis-Diglycineplatinum*. B. *cis-Diglycinepalladium (anhydrous)*. C. *trans-Diglycinepalladium*.

[To face p. 1014.

aqueous ammonia, and the solution treated as in the preceding preparation. *Diamminodiglycineplatinum chloroplatinite* was obtained as a pink salt, which on drying over phosphoric oxide in a vacuum turned pale mauve, owing to loss of water. It rapidly rehydrated in the air (Found : Pt, 54.21. $[\text{Pt}(\text{NH}_3)_2(\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2][\text{PtCl}_4]$ requires Pt, 54.47%).

(b) *trans*-Diglycineplatinum was treated in the same manner. The *plato*-salt is a deeper pink than the preceding one, and on drying over phosphoric oxide in a vacuum it becomes deep mauve. Like the corresponding *cis*-compound, it is hygroscopic and rapidly becomes pink in the air (Found : Pt, 53.96%).

Reactions of the Isomerides with Pyridine.—*cis*-Diglycineplatinum similarly gave with pyridine a chamois-coloured *plato*-salt (Found : Pt, 44.93. $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_2(\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2][\text{PtCl}_4]\cdot\text{H}_2\text{O}$ requires Pt, 45.45%). No *plato*-salt is precipitated when *trans*-diglycineplatinum is similarly treated.

Reactions of the Isomerides with Hydrochloric Acid.—(a) On heating *trans*-diglycineplatinum for 15 minutes with hydrochloric acid (5*N*) and then cooling, a yellow solid and a light yellow solution (S) were obtained. The former proved to be *trans*-dichlorodiglycineplatinum, as stated by Grünberg and Ptizyn (*loc. cit.*) (Found : Pt, 46.92. Calc. for $[\text{PtCl}_2(\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2]$: Pt, 46.89%); it had the properties ascribed to it by those authors. This product could not be recrystallised from water, as it was partially transformed thereby into *trans*-diglycineplatinum. The solution (S) yielded, in a vacuum over phosphoric oxide, an orange, hygroscopic mass, which on analysis gave results suggesting a mixture. This opinion was confirmed by the isolation of two derivatives, *viz.*,

(i) $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ and (ii) $[\text{Pt}(\text{NH}_3)_3(\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H})][\text{PtCl}_4]$;

(i) was obtained by adding tetramminoplatinous chloride to a portion of solution (S) (Found : Pt, 64.4. Calc. : Pt, 65.00%); (ii) resulted when ammonia was warmed with solution (S), the liquid neutralised with hydrochloric acid, and potassium chloroplatinite added (Found : Pt, 59.4. $\text{C}_2\text{H}_{14}\text{O}_2\text{N}_4\text{Cl}_4\text{Pt}_2$ requires Pt, 59.33%). This *plato*-salt is green-grey.

(b) Treatment of *cis*-diglycineplatinum with hydrochloric acid under the same conditions did not afford dichlorodiglycineplatinum, and evaporation of the solution gave a hygroscopic glass which analysis indicated was a mixture.

cis-Diglycinepalladium.—An aqueous solution of glycine (4 g.; 40 ml.) was mixed with potassium chloropalladite (4 g.) and kept for 2–3 days at room temperature. Yellow crystals separated from the red-brown solution (X), and were dried by pressing between filter-papers for 15 minutes [Found : Pd, 34.57; 34.54; N, 9.0; H_2O , 16.9. $\text{Pd}(\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2)_2\cdot 3\text{H}_2\text{O}$ requires Pd, 34.56; N, 9.1; H_2O , 17.5%]. On dehydration in air (see p. 1013) they became anhydrous [Found : Pd, 41.92; 41.85. $\text{Pd}(\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2)_2$ requires Pd, 41.88%]. Dehydration was also effected by alcohol or acetone or by warming with water above 40°. The hydrated crystals are elongated prisms and appear to be orthorhombic. The loss of water disrupts the structure almost completely, since, although the crystals retain their original form, X-ray photographs show that no appreciable orientation remains. The anhydrous substance is too finely divided to yield information by microscopic examination, but the X-ray powder photograph (B) shows that it is quite different in crystalline structure from the other palladium isomeride (C). The photographs also show that there is a similarity between this substance and the *cis*-diglycineplatinum (A), but the similarity is not close enough to prove definite isomorphism. The substance in aqueous solution gave $\mu = 6.13$ ($v = 608$).

trans-Diglycinepalladium.—The red-brown solution (X) (see above) was kept for one week at room temperature, and afforded glistening yellow plates; these were dried by pressing between filter-papers for 15 minutes [Found : Pd, 41.76; 41.78; N, 10.84. $\text{Pd}(\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2)_2$ requires Pd, 41.88; N, 10.99%]. The crystals are elongated six-sided or four-sided plates with the same form and optical properties as the *trans*-diglycineplatinum with which they are undoubtedly isomorphous. Presumably owing to different conditions of growth, the six-sided plates usually show an angle of 60° instead of 45°, and the tendency to elongation is not so marked as with the platinum compound. An X-ray photograph is reproduced (C). The plates are not ionised in aqueous solution : $v = 861$, $\mu = 4.45$.

When ammonium chloropalladite is substituted for the potassium salt in the preparation of the isomerides, the reaction is quite different. No prisms are obtained, but after some months a small yield of plates is produced. This is due to the solubility of the isomerides in ammonium chloride.

Reaction of the Isomerides with Thiourea.—(a) *cis*-Diglycinepalladium, when shaken with a cold saturated aqueous solution of thiourea, gave immediately an intense red solution. After some minutes, a very finely divided black precipitate was formed, which analysis showed to

be a mixture (Found : Pd, 45.16, 43.50, 41.85, 39.44%). The result was independent of the proportion of thiourea used.

(b) *trans*-Diglycinepalladium, treated in the preceding manner, gave immediately a yellow solution and a bright yellow precipitate of $\{Pd[(NH_2)_2CS]_2(NH_2 \cdot CH_2 \cdot CO_2)_3\}$ (Found : Pd, 26.68. $C_6H_{16}O_4N_6S_2Pd$ requires Pd, 26.23%). The *substance* always contained a little of the original diglycinepalladium. Attempts to recrystallise it resulted in complete decomposition. If Kurnakow's rule (*J. Russ. Phys. Chem. Soc.*, 1893, 25, 585) applies to palladium compounds, then the results obtained with thiourea confirm the *trans*-structure: he found that two mols. of thiourea became associated with the metal atom in *trans*-isomerides of platinum, and four mols. in *cis*-isomerides. Possibly the instability of the product from *cis*-diglycinepalladium is due to the instability of the system $[Pd, 4CS(NH_2)_2](NH_2 \cdot CH_2 \cdot CO_2)_2$.

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[Received, April 28th, 1934.]
