394. *The Structure and Configuration of Certain Diamminopalladium Compounds.*

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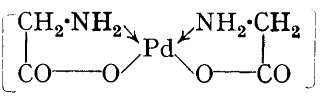
WHEN this investigation was started, two compounds were known corresponding in composition to diamminopalladium dichloride, $[(NH_3)_2PdCl_2]$, one an amorphous or microcrystalline yellow powder, and the other a salmon-pink compound existing usually as minute crystals just detectable by the unaided eye. Both are almost completely insoluble in liquids, and are decomposed by heat, so a direct determination of their molecular weights is extremely difficult. Krauss and Brodkorb (*Z. anorg. Chem.*, 1927, **165**, 73) had produced some evidence, based on molecular-weight determinations in phenol, that both compounds were unimolecular, and represented *cis–trans*-isomerides about the uniplanar complex.

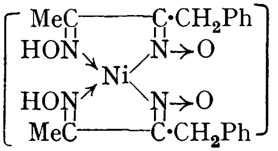
These conclusions were refuted by Krauss and Mählmann (Siebert Festschr., 1931, 215), who deduced that the two forms were monotropic and bimolecular, both having the formula $[(NH_3)_4Pd][PdCl_4]$; *X*-ray photographs, being necessarily limited to the powder method, served solely to show that the two forms differed, but gave no evidence with regard to their chemical identity or configuration. Later, a study of the chemical reactions of the two compounds (Drew, Pinkard, Preston, and Wardlaw, J., 1932, 1895) showed beyond reasonable doubt that the yellow compound [I(a)] was the true diamminopalladium dichloride, $[(NH_3)_2PdCl_2]$, and the pink compound (II) the tetramminopalladium palladochloride, $[(NH_3)_4Pd][PdCl_4]$, and that consequently *cis–trans*-isomerism did not arise.

Considerable interest attached, therefore, to a deep red, highly crystalline form [I(b)] of diamminopalladium dichloride brought to our notice by Mr. R. H. Atkinson, M.A., of the Refinery and Research Laboratory of the Mond Nickel Company, Ltd. During the isolation of the residual metals obtained in the Mond nickel process, the palladium is finally obtained as the ordinary yellow form of diamminopalladium dichloride, which, however, on drying at about 200°, occasionally forms the large, deep red crystals, the precise factor determining this change being then unknown. It appeared probable, therefore, that the drying process might have converted the yellow form into the opposite *cis–trans*-isomeride.

The chemical properties of the yellow and the red form appeared to be identical; *e.g.*, both, when treated with a cold solution of potassium oxalate, gave the corresponding *oxalate*, $[(NH_3)_2PdC_2O_4]$ (III), and similarly with sodium nitrite the dinitrite, $[(NH_3)_2Pd(NO_2)_2]$ (IV), the yield of each compound from both forms being quantitative, moreover. Both forms with potassium cyanide similarly gave the dicyanide. *X*-Ray analysis showed, however, that the oxalate had the *cis*-uniplanar and the dinitrite the *trans*-uniplanar configuration. The interconversion *cis* $\rightleftarrows$ *trans* in the diamminopalladium compounds must therefore usually occur very readily even at room temperature, and the above experiments cannot be cited as proof of chemical identity. Many examples of similar *cis* $\rightleftarrows$ *trans* interconversion are known in the complex compounds of the nickel–palladium–platinum group, but the conversion usually occurs only on heating, as is shown by, *e.g.*, diglycinepalladium (A) (Pinkard, Sharratt, Wardlaw, and Cox, J., 1934, 1012)

(A.)





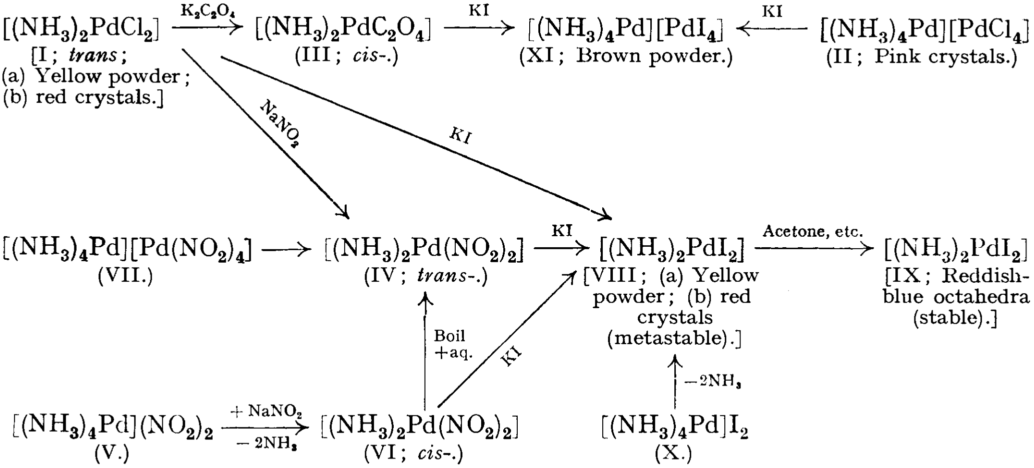
(B.)

and nickel bisbenzylmethylglyoxime (B) (Sugden, J., 1932, 246), in spite of the stabilising action which the chelated groups in each compound should exert. This interconversion is not so readily shown by the true platinous ammines, such as $[(NH_3)_2PtCl_2]$, but is shown, *e.g.*, by the aliphatic sulphide derivatives, such as $[(Et_2S)_2PtCl_2]$, in solution even at room temperature (Angell, Drew, and Wardlaw, J., 1930, 349).

The red crystals of [I(b)] when finely ground gave a yellow powder closely resembling the normal yellow form, but the difference was not due to fineness of division, for *X*-ray powder photographs showed the two forms to be distinct. A detailed *X*-ray investigation of the red crystals was accordingly undertaken. These proved to consist entirely of twinned crystals, showing three distinct habits, each associated with a different twin law. It was not possible to deduce the complete configuration from *X*-ray photographs, partly because of the complexities introduced by the twinning, and partly because of the great disparity in the reflecting powers of the constituent atoms. The former factor recurred more strongly in the similar but not isomorphous di-iodide (IX), where the twinning was found to be of an entirely novel and unexpected type.

Meanwhile, Grünberg and Schulman (*Compt. rend. Acad. Sci., U.R.S.S.*, 1933, 218) have prepared *cis*-diamminopalladium dichloride as a yellow powder by treating potassium palladochloride with ammonium acetate, and it is apparently quite distinct from the above yellow and red forms. Moreover, these authors claim that the action of potassium iodide is a decisive test for configuration in the diamminopalladium compounds studied, since it gives a red coloration with acetone solutions of the *cis*-compounds, but not with those of the *trans*-isomerides. Both the yellow powder [I(a)] and the red crystals [I(b)] in saturated acetone solution give with potassium iodide only a faint yellow coloration, and therefore cannot be identical with the *cis*-dichloride. This test, together with Grünberg and Schulman's isolation of the true *cis*-dichloride, shows that the yellow powder and the red crystals have the *trans*-configuration, and the crystallographic evidence leaves little doubt that their difference is due essentially to different crystal *structures* built up from the same (*trans*) molecules.

Other examples have recently occurred of complex compounds existing in two forms, where geometrical isomerism cannot occur. For instance, both αα′-dipyridylplatinous dicyanide (Rosenblatt and Schleede, *Annalen*, **1933**, **505**, 58) and the corresponding dichloride (Morgan and Burstall, J., **1934**, 965) exist in yellow and red forms: the latter authors suggest that, since the two forms of the dichloride have identical chemical properties, their difference must denote " some modification in the arrangement of the molecules in the crystal rather than a difference in chemical structure." The dimorphism is apparently not limited to non-ionic compounds, for Magnus's green salt, $[(NH_3)_4Pt][PtCl_4]$, also occurs in a red modification (Jörgensen and Sörensen, *Z. anorg. Chem.*, 1906, **48**, 441).



Diamminopalladium dinitrite has also been obtained in two forms, but these are almost certainly geometrical isomerides. The *trans*-dinitrite (IV), originally prepared by Lang (*J. pr. Chem.*, 1861, **83**, 415) by the action of silver nitrite on the dichloride, can be recrystallised from hot water without change, as shown both by *X*-ray powder photographs and by the constancy of its m. p.; it forms pale yellow diamond-shaped crystals which melt at 231—232° with vigorous effervescence. If, however, the dichloride is dissolved in ammonia, and a large excess of sodium nitrite added, the tetramminopalladium dinitrite (V) so formed dissociates if the solution is confined over sulphuric acid, and very pale yellow (almost white) prisms of the *cis*-dinitrite (VI) are deposited. This dissociation is clearly dependent mainly on the excess of sodium nitrite, because if pure potassium palladonitrite, $K_2[Pd(NO_2)_4]$, is dissolved in ammonia solution, similar slow dissociation gives solely the former *trans*-dinitrite (IV). The *cis*- can readily be distinguished from the *trans*-dinitrite because on heating it blackens at 234° without melting or effervescence: it is markedly paler in colour, and at least twice as soluble in cold water. The *cis*-compound is unaffected by very rapid recrystallisation from hot water (showing that the difference is not merely one of crystal habit or structure), but slower recrystallisation causes partial conversion into the *trans*-form; consequently, a consecutive series of such recrystallisations causes the decomposition point first to fall steadily as the proportion of the *trans*-form increases, and finally to rise again to a sharp value (with effervescence) as the conversion becomes complete. Unfortunately, the crystals of the *cis*-form were too imperfect for complete *X*-ray analysis, although their non-identity with the *trans*-form was thus decisively confirmed. The allocation of the *cis*-configuration * is based on two considerations : (*a*) when the *trans*- and the *cis*-form, both in cold saturated aqueous solution, are treated with potassium iodide, both give the same di-iodide (VIII) as a dark yellow powder, but whereas the *trans*-solution rapidly becomes deep red, the *cis*-solution remains colourless; acetone solutions of the *trans*-form, similarly treated, give an immediate deep yellow colour, whereas those of the *cis*-form again remain almost colourless. These results, while not agreeing with Grünberg and Schulman's rule for the dihalides, show clearly that the two forms cannot be chemically identical; (*b*) the *trans*-dinitrite has one molecule per unit cell, whilst the *cis* has eight, it being an almost invariable rule † that *cis*-compounds, by virtue of their more unsymmetrical configuration, have many more molecules per unit cell than the corresponding *trans*-compounds.

Tetramminopalladium palladonitrite (VII) has been prepared as a yellow microcrystalline powder by mixing ice-cold solutions of the dichloride and potassium palladonitrite. Both its appearance and *X*-ray powder photographs showed it to be distinct from either *trans*- or *cis*-dinitrite. It is, however, very readily converted into the former (IV) either by recrystallisation from hot water or by heating; consequently, it appears to have the same m. p. as (IV) because thermal conversion is complete before this temperature is reached.

Diamminopalladium di-iodide is a compound of exceptional interest. Fehling (*Annalen*, 1841, **39**, 116) and Lassaigne (*J. Chim. Méd.*, 1835, **1**, 62) prepared it originally by the evaporation and acidification respectively of aqueous solutions of tetramminopalladium di-iodide (X), from which it separated sometimes as reddish-orange crystals and sometimes as an amorphous yellow-orange powder. The latter form [VIII(a)], now obtained by the action of potassium iodide on the *trans*- and the *cis*-dinitrite, is stable when dry. If, however, it is treated with cold acetone, it changes within a few seconds to reddish-blue octahedra (IX); the yellow powder undoubtedly partly dissolves in the acetone, and therein is so rapidly converted into the sparingly soluble octahedra that separation in the latter form is soon complete. A similar conversion occurs if the yellow powder is warmed with alcohol, in which, however, it is much less soluble than in acetone. The conversion occurs also when an aqueous suspension of the powder is kept at room temperature, requiring either hours or some days for completion, according to the scarcity of nuclei of the reddish-blue form. The colour of the octahedra (IX) depends largely on their physical condition. They are deep brick-red when powdered, but the blue surface reflexion causes well-formed crystals to appear almost steel-blue.

Both forms of the di-iodide dissolved readily in excess of ammonia to give a colourless solution of tetramminopalladium di-iodide (X). If the solution is exposed to the air, dissociation of the tetrammine occurs, and red orthorhombic crystals [VIII(b)] (devoid of blue reflexion) of the di-iodide appear; these are shown by *X*-ray powder photographs to be the crystalline form of the yellow powder [VIII(a)]. After several hours, isolated crystals of the reddish-blue form (IX) appear, and grow at the expense of the red crystals, conversion being ultimately complete.

If a freshly prepared sample of the ordinary yellow form of the dichloride, particularly a sample which has been dried without heating, is shaken mechanically with concentrated potassium iodide solution, the yellow powder form of the di-iodide is at first produced, but

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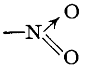
* It is clear that the difference between the *trans*-dinitrite and the apparent *cis*-dinitrite cannot be due to the former having  $-\mathrm{N}\begin{matrix}\nearrow\mathrm{O}\\ \searrow\mathrm{O}\end{matrix}$ groups and the latter $-\mathrm{O}-\mathrm{N}{=}\mathrm{O}$ groups, because, apart from the *X*-ray evidence, Jörgensen (*Z. anorg. Chem.*, 1894, **5**, 168) and Werner (*Ber.*, 1907, **40**, 779) have shown that compounds having the latter group differ markedly in colour and chemical behaviour from those having the former group, into which they change spontaneously and rapidly at room temperature.

† For example, the numbers of molecules per unit cell in the following compounds are : Bis(dimethylsulphide)platinous dichloride, $[(\mathrm{Me_2S})_2\mathrm{PtCl_2}]$, *trans* 2, *cis* 4 (Cox, Saenger, and Wardlaw, J., 1934, 182); diamminoplatinic tetrachloride, $[(\mathrm{NH_3})_2\mathrm{PtCl_4}]$, *trans* 2, *cis* 4 (Cox and Preston, J., 1933, 1089); disalicylaldoximeplatinum, $[(\mathrm{C_7H_6O_2N})_2\mathrm{Pt}]$, *trans* 2, *cis* 32 (Cox, Pinkard, Wardlaw, and Webster, this vol., p. 459); hexahydrochrysene, $\mathrm{C_{18}H_{18}}$, *trans* 2, *cis* 64 (Bernal, *Chem. and Ind.*, 1933, **52**, 288); fumaric acid 6, maleic acid 4 (but a special crystallographic factor enters here; Yardley, J., 1925, **127**, 2207; Reis and Schneider, *Z. Krist.*, 1928, **68**, 543).

passes on standing into the more stable form (IX). An old sample of the dichloride, particularly one which has been dried by heating, reacts more slowly, and the intermediate formation of the yellow powder [VIII(a)] is often not apparent.

X-Ray photographs of the reddish-blue form (IX) of the di-iodide showed a remarkable structure. The lattice due to the palladium atoms is represented as sharply defined spots, indicating a perfectly regular cell structure; the iodine atoms, however, are represented sometimes as sharply defined spots, and sometimes as streaks on which lie moderately definite spots (see Plate). These streaks are caused by irregular positions of the iodine atoms along the *c* axis, and the irregularity is limited to the relative position of the iodine atoms between consecutive molecular layers of the crystal. (The co-ordinated ammonia molecules undoubtedly share this irregularity, since they have a definite position in the molecule relative to the iodine atoms, but as they are not represented on the *X*-ray photographs, there is no *experimental* evidence for their position.) This form of the di-iodide thus shows a highly anomalous type of repeated polysynthetic twinning which corresponds in effect to a two-dimensional crystal as far as the co-ordinated groups and atoms are concerned; it is, moreover, a type of twinning which, although recognised as a theoretical possibility, has not hitherto been realised. The *X*-ray photographs of the red crystal form [I(b)] of the dichloride show similar but very faint streaks for the chlorine atoms, and the same phenomenon clearly occurs in this compound also, and was primarily responsible for the failure to interpret its structure completely. Full crystallographic details of the two forms (VIII and IX) of the di-iodide will be described elsewhere, but there is little doubt that they both represent different crystal forms of the *trans*-di-iodide.

When an aqueous suspension of the mono-oxalate (III) was treated with potassium iodide, a rapid reaction occurred, the crystals of the oxalate being replaced by the chocolate-brown amorphous palladoiodide (XI). Doubt was thrown on the natural assumption that this was the *cis*-diamminopalladium di-iodide by the fact that, unlike the *trans*-di-iodide, it was insoluble in organic liquids, whereas the *cis*- would probably be more soluble than the *trans*-di-iodide. The same brown powder was similarly obtained, however, from an aqueous suspension of the salmon-pink tetramminopalladium palladochloride (II), and also by the interaction of potassium palladoiodide with tetramminopalladium dichloride, and there is no doubt, therefore, that it is actually the tetramminopalladium palladoiodide (XI). This rapid conversion of the mono-oxalate into the palladoiodide, although unexpected, is not entirely without precedent, for Drew, Pinkard, Preston, and Wardlaw (*loc. cit.*, p. 1899) have shown that the dichloride when treated with ethylenediamine gives equivalent quantities of the tetramminopalladium and the bisethylenediaminopalladium ions :

$$2[(NH_3)_2PdCl_2] + 2en = [(NH_3)_4\overset{++}{Pd}] + [en_2\overset{++}{Pd}] + 4\overset{-}{Cl}$$

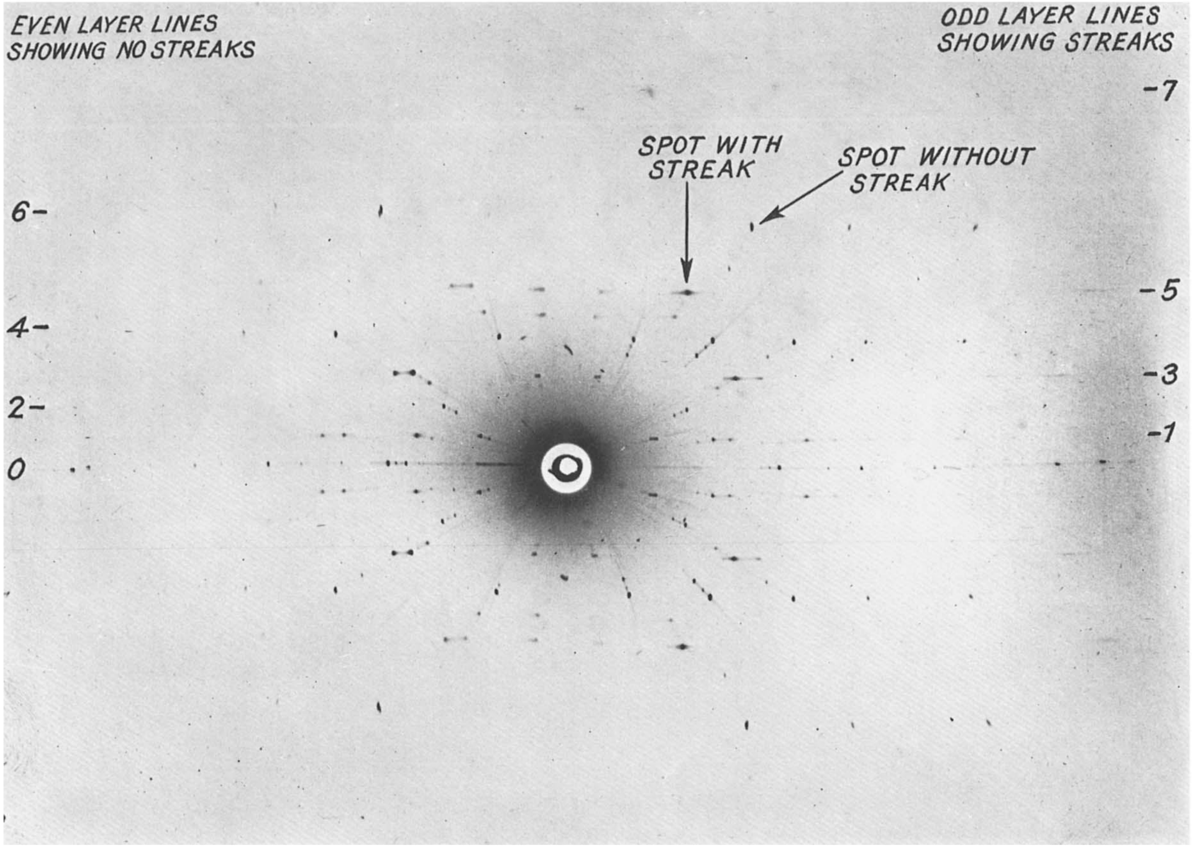
It is clear that a precisely similar rearrangement of the co-ordinated groups occurs when the oxalate is treated with potassium iodide, but in this case it is immediately followed by union of the two oppositely charged complex ions to give the palladoiodide :

$$2[(NH_3)_2PdC_2O_4] + 4KI = [(NH_3)_4\overset{++}{Pd}] + [Pd\overset{--}{I_4}] + 4\overset{+}{K} + 2\overset{--}{C_2O_4}$$

EXPERIMENTAL.

Chemical Data.

Chemical Properties of the Yellow and the Red Dichloride [I, (a) *and* (b)].—(A) A solution of potassium oxalate (17·5 g., 10 mols.) in cold water (80 c.c.) was mechanically shaken with a suspension of the finely ground yellow dichloride (2·00 g.) in water (20 c.c.) for 20 hours; the yellow powder had become entirely replaced by the pale greenish-white *oxalate* (III), which was filtered off, washed with water, alcohol, and ether, and dried (yield, 2·10 g.; 97%) (Found : C, 10·5; H, 2·65; N, 12·1; Pd, 46·4. $C_2H_6O_4N_2Pd$ requires C, 10·5; H, 2·6; N, 12·2; Pd, 46·65%). The powdered red crystals [I(b), Found : N, 13·1; Pd, 50·15. Calc. for $H_6N_2Cl_2Pd$: N, 13·2; Pd, 50·4%], similarly treated (30 hours' shaking), gave 2·05 g. of the oxalate (95%) (Found : C, 10·5; H, 2·8; N, 12·0%). Formation of the oxalate occurs rapidly if similar



A $[(NH_3)_2PdI_2]$ *crystal fragment oscillated about its* a *axis. Alternate layer lines, representing planes of even and odd* h *respectively, show sharp spots and extended streaks. High-order reflexion of even layer lines shows perfectly resolved* K_α *doublets, indicating a perfect structure of the main lattice.*

mixtures are warmed on the water-bath; the above experiments were conducted at room temperature to test the ease with which the *cis* $\rightleftharpoons$ *trans* interconversion occurs.

The oxalate darkens slowly between 175—185°, becoming uniformly black, but without melting or effervescence. This behaviour is unchanged after recrystallisation from much hot water, whereby the oxalate is obtained in pale green (almost white) needles, which on prolonged exposure to light slowly darken as palladium is deposited.

(B) Sodium nitrite (7·5 g., 9 mols.) dissolved in cold water (15 c.c.) was added to the yellow dichloride (2·50 g.), and the mixture shaken for 12 hours, the dichloride being entirely replaced by the finely divided, almost white dinitrite (IV). The latter was collected under suction, washed with ice-cold water, then with alcohol and ether, and dried (yield, 2·70 g.; 98%) (Found: N, 24·1; Pd, 45·5; *M*, ebullioscopic in water with recrystallised material, 236 in 4·394% solution, 225 in 8·083%. Calc. for $H_6O_4N_4Pd$: N, 24·05; Pd, 45·8%; *M*, 233). The crude dinitrite had m. p. 227—228° (efferv.), raised by recrystallisation from hot water to 231—232° (efferv.); *X*-ray powder photographs showed that no change in structure had occurred during recrystallisation, which afforded large pale yellow crystals.

The red dichloride, similarly treated, gave 2·60 g. of the dinitrite (95%), having the same m. p. (efferv.) as that from the yellow dichloride, both before and after recrystallisation.

(C) The yellow dichloride, triturated with a small quantity of cold concentrated aqueous potassium cyanide solution, was rapidly converted into the white dicyanide, which was collected and recrystallised from hot water containing a few drops of ammonia to prevent decomposition (Found: N, 29·1. Calc. for $C_2H_6N_4Pd$: N, 29·1%). Precisely similar results were obtained for the red dichloride.

Acetone (50 c.c.) was shaken with the finely powdered yellow dichloride (0·5 g.) for 2 hours and then filtered; on addition of concentrated aqueous potassium iodide (5 drops) to this saturated but very dilute solution, as Grünberg and Schulman direct, only a very faint yellow coloration appeared. The red dichloride gave an identical result, but a blank control experiment gave no coloration.

cis-*Diamminopalladium Dinitrite* (VI).—A clear solution of tetramminopalladium dichloride, prepared by adding ammonia solution (10 c.c., *d* 0·880) to a suspension of the yellow dichloride (4 g.) in cold water (20 c.c.), was added to a solution of sodium nitrite (10·4 g., 8 mols.) in water (30 c.c.), and the mixture kept in an open basin over sulphuric acid in either a vacuum or an atmospheric desiccator. After about 24 hours, a thick deposit of large, heavy, very pale yellow crystals had settled. These were collected, washed as above, and dried. Pulverisation gave an almost white powder, which on heating darkened slightly at 225°, and then blackened sharply at 234° without melting or effervescence, no other change occurring up to 250° (Found: N, 23·5; Pd, 44·8%. Low values are usually obtained for both elements, due presumably to occlusion of traces of sodium nitrite and chloride). A second and even a third crop of the pure *cis*-dinitrite could be obtained, but further crops were impure.

By rapid recrystallisation of small quantities from hot water, the unchanged *cis*-dinitrite was recovered. Slower recrystallisation caused ultimately complete conversion into the *trans*-dinitrite, as shown by the following m. p.'s for a sample after five consecutive recrystallisations, each crop having been dried and powdered:

(1) Softens 220°, blackens 227°; no melting or effervescence.
(2) ,, 210—211°, darkens, then *melts* 224—225°; no effervescence.
(3)* ,, 210—212°, melts 216°; copious effervescence.
(4) ,, 225°, melts 229°; copious effervescence.
(5) ,, slightly 227—228°, melts 231—232°; copious effervescence.

The m. p. of the final product was unchanged when mixed with an authentic sample of the *trans*-dinitrite.

Ammonia solution (6 c.c., *d* 0·880) was added to a mixture of powdered anhydrous potassium palladonitrite (2 g.) and water (20 c.c.), and the clear solution so obtained was placed over sulphuric acid in a vacuum desiccator for 24 hours. Isolated clusters of well-formed crystals appeared at the bottom and surface of the solution. These, when separated and dried, had m. p. 229° (efferv.), unchanged by admixture with pure *trans*-dinitrite, but lowered to 213—214° by admixture with pure *cis*-dinitrite. The production of the *cis*-dinitrite in the previous experiment must therefore have been due to the presence of either the sodium chloride or the

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* This recrystallisation was intentionally carried out more slowly than the others, and two forms of crystal, feathery needles and prisms, were observed.

sodium nitrite: the latter is probably the active agent, since it is present in so great an excess.

The distinction between the *trans*- and the *cis*-dinitrite is further shown by treating their cold saturated aqueous solutions with thiourea. The latter rapidly gives a copious precipitate of a brown amorphous powder, but the former gives a brown precipitate only sparingly after several days.

Tetramminopalladium Palladonitrite (VII).—Chilled solutions of equimolecular quantities of tetramminopalladium chloride (1·0 g.) and potassium palladonitrite (1·5 g.) in water (10 c.c. and 40 c.c. respectively) were rapidly mixed, a pale canary-yellow powder being immediately precipitated; it was washed with cold water, alcohol, and ether (Found: Pd, 45·6%). Repetition of the preparation at much greater dilution still gave an immediate precipitate, and well-formed crystals could not be obtained. This compound evidently has the structure $[(NH_3)_4Pd][Pd(NO_2)_4]$: it is much darker than the two dinitrites, and the three compounds give distinct X-ray powder photographs. The palladonitrite appears to have m. p. 224—225°, with effervescence and decomposition precisely similar to that of the *trans*-dinitrite; but this is probably due to almost complete conversion into the latter during the heating to the m. p. Recrystallisation from hot water at once gives the pure *trans*-dinitrite, and there is some evidence for a similar conversion on long keeping of the dry material.

Diamminopalladium Di-iodide.—Yellow form [VIII(a)]. A solution of the *trans*-dinitrite (0·6 g.) in cold water (300 c.c.), treated with a cold saturated potassium iodide solution (50 c.c.), became yellow and then red, and the dark yellow powder was rapidly precipitated. After 1 hour, the di-iodide was separated, washed with water, drained, and rapidly dried (Found: N, 7·2; Pd, 27·2. Calc. for $H_6N_2I_2Pd$: N, 7·1; Pd, 27·0%).

When a solution of the *cis*-dinitrite (0·6 g.) in cold water (200 c.c.) was similarly treated, the yellow powder was again rapidly precipitated (Found: N, 7·3; Pd, 26·9%), but the filtrate was colourless, and remained so even after several weeks' standing.

Reddish-blue octahedral form (IX). The above yellow form was kept in contact with cold acetone for 1—2 minutes, although conversion was complete in a few seconds. The dark red crystals, having a steel-blue reflexion, were then filtered off from the pale yellow solution, washed with acetone, and dried (Found: N, 7·1; Pd, 27·2%). The acetone filtrate, on spontaneous evaporation, deposited a further small crop of the reddish-blue needles, apparently contaminated with a trace of the unchanged yellow form.

When the yellow powder was boiled with alcohol, some dissolved, and the remainder was converted into the reddish-blue crystals; these were separated, and the filtrate on cooling and standing deposited similar crystals sufficiently well-grown for X-ray investigation. When the laboratory had once become inoculated with the stable reddish-blue octahedra, further preparations of the yellow powder form from the *cis*- or the *trans*-dinitrite sometimes started spontaneous conversion whilst draining on the filter.

The reddish-blue crystals are soluble in hot acetone and dioxan, less soluble in alcohol; these solutions are brownish-red, and it is possible that an equilibrium is established between the forms (VIII) and (IX) if the dilution is sufficiently great to keep the latter form in solution.

Dissociation of Tetramminopalladium Di-iodide.—(A) Diamminopalladium di-iodide [1 g., either (VIII) or (IX)] was dissolved in ammonia solution (15 c.c.; *d* 0·880) diluted with water (15 c.c.). This clear colourless solution of the tetrammino-compound (X) was kept over-night in an open basin protected from dust. Next day, small, well-formed, red, orthorhombic crystals [VIII(b)], identical with the yellow powder [VIII(a)], had formed on the surface and on the sides of the basin. Isolated clear, deep blue crystals then appeared among the red crystals on the surface of the solution; these were the stable reddish-blue octahedra (IX) but their modified colour was due to surface reflexion. The red crystals in contact with the blue then underwent conversion into the blue crystals, and ultimately only the latter remained.

The dry red crystals [VIII(b)] appear to be stable indefinitely whilst in a desiccator, but on subsequent exposure to the air they pass into the reddish-blue form.

(B) Diamminopalladium di-iodide (1 g.), dissolved in ammonia (15 c.c., *d* 0·880), was left over-night in a shallow basin in a vacuum over sulphuric acid. Next day, clusters of orange-red needles had formed at the bottom of the liquid, and the usual red crystals [VIII(b)] on the surface. The identity of the needles is uncertain, but they are probably a highly complex substance approximating in composition to the tetrammino-compound (X). They are extremely unstable, and usually within a few hours of formation change spontaneously into pseudomorphs consisting of the red crystals [VIII(b)] of the pure di-iodide, which in turn ultimately change into the stable reddish-blue form (IX). Scratching the sides of the basin at any stage of the crystallisation causes separation of the yellow powder [VIII(a)]. If the yellow needles are filtered off and washed with water, they immediately disintegrate to the yellow powder. The conditions of their formation have not been precisely determined, and many repetitions of the above experiments gave solely the usual red crystals.

(C) When a solution of the tetrammino-compound (X) was acidified, preferably with hydriodic acid, the yellow powder form [VIII(a)] of the di-iodide was rapidly precipitated, but if left in contact with the mother-liquor, it slowly passed into the reddish-blue crystals (IX).

Action of Potassium Iodide on the Dichloride.—When the yellow dichloride [I(a)] or the finely powdered red crystals [I(b)] were moistened with water and then shaken mechanically with a considerable excess of saturated potassium iodide solution, the mixture became deep red and the dichloride was slowly converted into the di-iodide, which appeared as an apparently amorphous deep red powder of the stable form (IX); even after 48 hours' shaking, however, the conversion was not complete, as the analyses show [Found: In di-iodide from I(a), Pd, 28·5; from I(b), N, 7·8; Pd, 30·6%]. The filtrate in each case was deep red.

Similar treatment of a freshly prepared sample of the yellow dichloride [I(a)], which had been washed with water, alcohol, and ether, and dried in a vacuum without heating, afforded first a deposit of [VIII(a)], which slowly changed into the reddish-blue octahedra (IX).

Tetramminopalladium Palladoiodide (XI).—When a saturated aqueous potassium iodide solution (50 c.c.) was added to a suspension of the finely divided oxalate (III; 1 g.) in water (100 c.c.), the mixture became deep reddish-purple, and the oxalate appeared momentarily to dissolve before a fine chocolate-brown amorphous powder began to separate. After 1 hour's shaking, the brown powder (XI) was collected, well washed with water, alcohol, and ether, and dried (Found: N, 7·1; Pd, 26·9. $H_{12}N_4I_4Pd_2$ requires N, 7·1; Pd, 27·0%). The clear filtrate had the same deep cherry-red colour as that obtained by similar treatment of the *trans*-dinitrite, but in view of the complete rupture of the oxalate molecule this colour is without configurational significance.

When a suspension of the corresponding palladochloride (II) was similarly treated with potassium iodide, the chocolate-brown powder was again rapidly precipitated (Found: Pd, 27·2%), and the filtrate had the usual deep red colour.

Solutions of ammonium palladochloride (0·5 g., 1 mol.) and potassium iodide (2·3 g., 8 mols.), each in water (100 c.c.), were mixed, and the deep brown solution kept for 20 mins. to ensure complete formation of the palladoiodide. A solution of tetramminopalladium dichloride (0·45 g., 1 mol.) in ice-cold water (20 c.c.) was then stirred in, and a deep chocolate-brown amorphous precipitate rapidly separated, leaving the solution almost colourless. The precipitate was collected, washed as usual, and dried (Found: Pd, 27·3%).

No difference could be detected in the palladoiodide (XI) prepared by these three methods. It is almost insoluble in most organic liquids; if a suspension in acetone is kept for several days, the solution becomes pale brown, indicating partial conversion of the palladoiodide into the di-iodide (VIII or IX).

Crystallographic Data.

Diamminopalladium Dichloride.—The yellow powder form [I(a)] has a higher double refraction than the red crystals [I(b)], and powder photographs showed them to be distinct.

The red crystals showed three distinct habits. (A) The majority were undistorted octahedra about 1 mm. in diameter, only those crystals of diameter about 0·1 mm. being perfect; the birefringence was small, uniaxial, and negative, and the crystals were pleochroic, the fast direction being yellow, and the slow orange. (B) Very small square plates, bounded by octahedral edges, and having the same optical properties as (A), except that a few showed a small optic axial angle. (C) One example of a distorted octahedron, elongated along a (111) axis, was found; *d* (by flotation) 2·85.

Pyroelectric properties (Martin's method): the majority of the crystals were electrically neutral, although a few crystals of type (B), and the one crystal of type (C), were active.

Oscillation photographs showed that all three types had the same tetragonal lattice, $a = 8{\cdot}0$, $c = 7{\cdot}8$ Å., thus giving 4 mols. per cell. The three types were associated with different symmetries as far as the intensities were concerned. Type (A) was tetragonal; (B) showed a curious relationship of intensities, such that while $hk0 = \bar{h}k0 = h\bar{k}0 = \bar{h}\bar{k}0$, $hkl \neq hk\bar{l}$, but $hkl = \bar{h}kl = \bar{h}\bar{k}l = kh\bar{l} = k\bar{h}\bar{l} = \bar{k}h\bar{l}$; (C) showed orthorhombic symmetry, *i.e.*, $hk0 \neq kh0$, but $hkl = hk\bar{l}$.

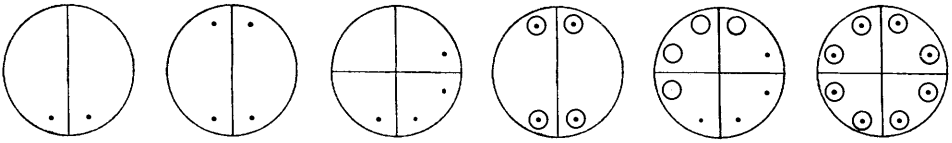
These differences can only be explained by twinning, and none of the crystals examined can be a single crystal. If, however, the single crystal had the symmetry *Pm*, the stereograms (Fig. 1) show how the intensities and the pyroelectric properties may be accounted for: (*a*) is the single crystal; (*b*) this crystal twinned about the vertical axis through 180°; (*c*) is (*a*) similarly twinned through 90°. Since *X*-rays effectively add a centre of symmetry, (*b*) gives rise to (*d*), and (*c*) to (*e*); multiple twinning gives rise to (*f*). (*a*), (*b*), and (*c*) are all pyroelectric. (*b*) has the symmetry shown by the one crystal of habit (C), (*c*) by those of habit (B), and (*f*) by those of habit (A).

All the reflexions fell into two well-defined categories, those corresponding to a face-centred lattice being strong, the remainder only moderately strong or weak. The palladium atoms were clearly contributing only to the former, and can therefore be assigned to a face-centred lattice. The following halvings were observed in the weak spots: (*e* = even, *o* = odd), (*eeo*) and (*ooe*), (*h*0*l*) and (0*kl*). No space group shows such halvings, and no structure has been found which warrants publication.

The fact that the single crystal must be pyroelectric and therefore apparently without a centre of symmetry might be interpreted as indicating that the molecule has the *cis*-configuration, but very little is known about the electrical effects produced by the internal strains due to such complicated twinning; moreover, pyroelectric properties are sometimes found in crystals of high symmetry, *e.g.*, topaz.

It is clear that the formation of the red crystals is not due to the process of drying at *ca.* 200°, because (i) crystals of the red form were found to the extent of about 0·5% in all samples of the yellow powder [I(a)], (ii) a far higher proportion of the red crystals was found in samples of the yellow form which had been prepared by slow controlled precipitation without subsequent drying. Moreover, in oscillation photographs of the red crystals found in the yellow powder, the chlorine atoms were represented only by streaks and not by spots, whilst in the better grown red octahedra they appeared as spots with faint streaks through them. It appears, therefore, that the red crystals represent a stable dimorphous form of the *trans*-dichloride, produced chiefly when conditions of formation are relatively slow.

FIG. 1.



(*a*) (*b*) (*c*) (*d*) (*e*) (*f*)

Occasionally, yellow crystals, *ca.* 0·5 × 0·4 mm. in size, were also found in the yellow powder. Oscillation photographs showed them to belong essentially to the red form, but to have the following peculiarities. The habit is that of a tetragonal prism (100) terminated by small bipyramids (111). Planes (*hkl*), where *h,k,l* are all odd or all even, were distinct and strong, but no trace of other spots was observed: instead, completely uniform streaks elongated along the *c* axis replaced the planes (*hkl*), *h* and *k* odd, precisely as in the smaller, also prismatic, crystals of the di-iodide (IX). The similarity extends to the form of twinning, resulting in a dendritic form. The smeared row lines indicate that successive planes in the *c* direction follow one another in completely irregular order, whereas in the large red octahedra there exists considerable, although never perfect, order.

Diamminopalladium Oxalate (III).—The only form * prepared consisted of small, colourless, transparent, monoclinic needles, flattened on (010) and elongated along [001], with the β angle *ca.* 122°. The plane of symmetry is the plane of the optic axes, with γ along [100], and α accordingly 58° from [001] in the obtuse angle. The birefringence is very high; *d* (flotation) 2·85; no pyroelectric effects.

Oscillation photographs were taken with the crystal rotating about [100] [beam direction 0—15° from //(010), and from //(001)]; [001] [0—15° from //(010)], and [010] [a series of eight, including the range 0—90° from //(001)]. These gave the cell dimensions *a* = 8·1, *b* = 10·47, *c* = 3·67 Å., β = 122° 23′, with 2 mols. per unit cell.

The reflexions (0*k*0) are absent when *k* is odd, and as there is no other halving, the space group is either $P2_1$ or $P2_1/m$, of which $P2_1/m$ is favoured by the apparent absence of pyroelectric effects.

The crystal optics indicate that the greater length of the molecule lies along the *a* direction,

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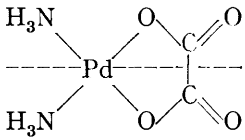
* Grünberg's claim (*Ann. Inst. Platine*, 1933, **11**, 95) to have isolated the oxalate in both *cis*- and *rans*-forms requires considerable experimental confirmation before it can be accepted, as no cases are yet known of 5-membered rings spanning the *trans*-position: nor does it appear probable that the dimensions of the units concerned would allow such a ring.

width in *b*, and thickness in the *a* plane. This thickness is only 3·67 sin β, or 3·10 Å., which indicates a planar configuration of the molecule. The probable molecular length is 8·1 Å. and width 5·2 Å. These dimensions altogether exclude a structure based on a *trans*-configuration, such as could be imagined as built of NH_3–Pd–NH_3 units linked crosswise by oxalate groups. The *cis*-configuration (Fig. 2), on the other hand, agrees perfectly with all the requirements deduced from the *X*-ray data. It has, moreover, the plane of symmetry (along the direction of greater length) required by the space group $P2_1/m$, when (as here) only 2 molecules are present per unit cell. The most probable arrangement of the molecules in the crystals is that shown in Fig. 3, which is drawn in qualitative agreement with the *X*-ray intensities, particularly with the strong intensity of the (00*l*) planes.

FIG. 2.



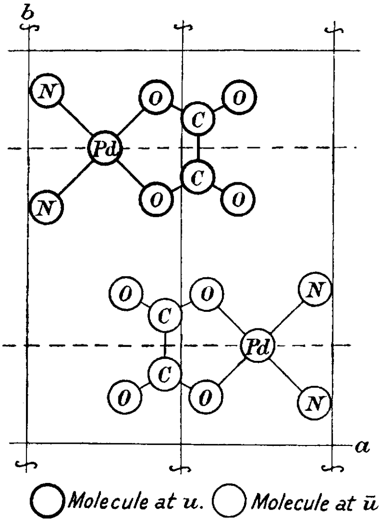
The broken line indicates the plane of symmetry.

trans-*Diamminopalladium Dinitrite* (IV).—Diamond-shaped crystals, 1 × 1·5 mm., having angles of 124° and 56°. Transparent, moderate birefringence. Slow vibration direction making an angle of 16° with the longer axis, and under the polarising microscope an optic eye was just visible on the edge of the field. Probably optically negative. *d* (by flotation), 2·49. No pyroelectric effects.

Oscillation photographs, taken about three crystallographic directions, showed that the crystals belonged to the triclinic system. Cell dimensions : *a* = 6·64, *b* = 4·97, *c* = 6·2 Å., α = 65° 20′, β = 80° 12′, γ = 53° 46′, giving 1 mol. per unit cell.

Since the lattice is triclinic, and the absence of pyroelectric effects indicates a centre of symmetry, the space group must be $P\bar{1}$. Since the cell contains only 1 molecule, this must have a centre of symmetry, and must therefore have the *trans*-configuration. The small values of the translations of the triclinic cell show that co-ordination about the palladium atom must be planar : a tetrahedral configuration would give a minimum distance between the palladium atoms of > 6 Å.

FIG. 3.



Arrangement of $[(NH_3)_2PdC_2O_4]$ *molecules in crystal. Projection on* (100). *Molecules in layers lying in c planes* 3·10 Å. *apart : consecutive layers similar but displaced* 4·3 Å. *in the* a *direction.*

cis-*Diamminopalladium Dinitrite* (VI).—Rather imperfect crystals, consisting of flattened prisms, terminated at one end by two pyramidal faces. Transparent. Optically biaxial, negative : α direction perpendicular to flattened face, β along the length of the crystal, and γ along the breadth. *d* (by flotation), 2·33. No pyroelectric effects.

Oscillation photographs showed that the crystals belonged to the monoclinic system, with a strongly pseudo-hexagonal lattice. Cell dimensions : *a* = 11·0, *b* = 12·4, *c* = 10·8 Å., β = 59° 48′, giving 8 mols. per cell. Halvings were : 0*k*0 halved when *k* is odd. Space group probably $P2_1$.

Hexagonal close packing of the palladium atoms, which would therefore have the co-ordinates 000, $\frac{1}{2}00$, $00\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{6}\frac{1}{2}\frac{1}{6}$, $\frac{1}{6}\frac{1}{2}\frac{2}{3}$, $\frac{2}{3}\frac{1}{2}\frac{1}{6}$, $\frac{2}{3}\frac{1}{2}\frac{2}{3}$, would account for the observed spacings. The compound is distinct from (IV) and has probably the *cis*-configuration, but it has not been possible to determine the position of the amino- and the nitrite-groups.

Tetramminopalladium Palladonitrite (VII).—Oscillation photographs were not possible : powder photographs showed that (VII) was distinct from (IV) and (VI).

Diamminopalladium Di-iodide.—Yellow form [VIII(a)]. The powder under the microscope was found to consist of minute rosettes of yellow crystals showing a feeble pleochroism (which immediately distinguishes them from the reddish-blue form), and a characteristic cross-twinned form of apparently orthorhombic crystals (Fig. 4, in which the arrows indicate the slow vibration direction).

Reddish-blue form (IX). Square plates or truncated bipyramids, which appear to be uniaxial, but actually possess optical anomalies, and divide roughly into quadrants, each quadrant behaving like a biaxial crystal (Fig. 5).

The degree of biaxiality, *i.e.*, the angle between the optic axes, decreases regularly from the edge of the crystal to the centre, which is always apparently uniaxial. *X*-Ray photographs (see Plate) were taken of a fragment of this crystal, showing biaxial character, but even this apparently homogeneous piece was found to be internally highly heterogeneous, and indeed exhibited phenomena never previously recorded for any crystal. If only the stronger spots are considered, the crystal appears isomorphous with the dichloride [I(b)], with a slightly larger cell ($a = 12{\cdot}4 = \sqrt{2} \times 8{\cdot}7$, $c = 8{\cdot}5$ Å.), in comparison with the values 8·0, 7·8 Å. for the dichloride; these spots all have indices *hkl*, of which *h* and *k* are even, corresponding to a face-centred tetragonal cell of sides 8·7 and 8·5, and clearly indicating palladium atoms at the points of such a lattice. The other spots, however, present a most unusual appearance: they are, in fact, not spots, but streaks, elongated in the *c* direction.

There appears to be some evidence that the streaks are more pronounced when the centre portion of a crystal is involved than when the edge is involved, but they occur in both cases. The significance of these streaks can be readily interpreted to indicate a complete absence of regularity in the positions of the iodine atoms along the *c* axis. At the same time, the absence of streaks for palladium reflexions, and more particularly the absence of streaks of the planes (*hk*0), show that the structure itself is a perfectly regular one, and that in every layer in the *c* plane there is perfect regularity.

FIG. 4.

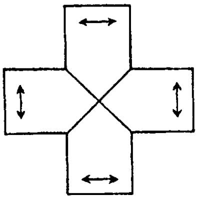
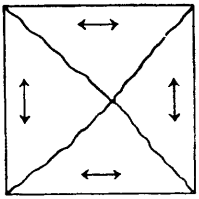


FIG. 5.



Structures of this kind have previously been observed only in crystals such as those of *p*-azoxyanisole, where the long molecules can move in the direction of their length, or in the micas, in which the chemical position changes in different parts of the same crystal. But in both these cases, the streaks indicate an irregularity of the cell itself, whereas in the di-iodide the cell is obviously regular, and irregularity is limited to the position of the iodine atoms between different layers. It is, in fact, a type of repeated polysynthetic twinning which has previously been only a theoretical possibility. Several unsuccessful attempts have been made to prepare crystals free from twinning, and those from alcohol showed greatest separation. The octahedra prepared either by the addition of acetone to the yellow powder or by the dissociation of the tetrammino-compound (X) in solution show the most thorough twinning, as they appear truly tetragonal, and show streaks devoid of spots.

The physical reason for the twin nature of dichloride and di-iodide was also apparent when the transformation from the yellow form to the red * form (IX) of the di-iodide was observed under the microscope. On addition of acetone, or alcohol, to the yellow form, there were observed simultaneously the dissolution of the yellow form and the appearance of small but perfect octahedra of the red form. The actual growth of the latter, however, could not be observed, *i.e.*, it was too rapid to be followed by the eye: what appeared to occur was a multiplication of a number of these octahedra, and not the growth of any one of them. This indicated plainly that they had been produced from a solution highly supersaturated with respect to the reddish-blue form, which is far less soluble than the yellow. Such rapid deposition would enable alternative positions for the iodine atoms, *i.e.*, the orientation of the di-iodide molecules relative to one another, to be adopted in a perfectly haphazard manner, though the equality of the dimensions of the orthorhombic cell led to a perfectly regular crystal shape.

The authors are greatly indebted to Mr. J. D. Bernal for considerable crystallographic assistance, to the Mond Nickel Company, Ltd., for the loan of samples of the two forms of diamminopalladium dichloride, and to the Department of Scientific and Industrial Research for grants.

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[*Received, August* 29*th*, 1935.]

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* The blue surface reflexion being absent when the crystals are viewed under the microscope by transmitted light.