#### 877. Metal-Metal Interactions in Square-planar Complexes.

## By J. R. MILLER.

Ten double complex salts of copper, palladium, and platinum are isomorphous with Magnus's green salt,  $[Pt(NH_a)_4][PtCl_4]$ . Abnormal colours, associated with metal-metal interaction, are restricted to compounds containing platinum in both anion and cation. It is therefore concluded that adoption of the structure is not dependent on metal-metal interaction, and it is shown on simple electrostatic grounds that the structure would be expected to be very stable.

Some of the theories concerning interactions in these compounds and in the comparable vic-dioxime complexes of nickel, palladium, and platinum are discussed, and it is suggested that the interaction could be of an antibonding nature.

THE deep green colour of tetrammineplatinum(II) chloroplatinate(II), Magnus's green salt, has attracted attention for many years; the anion is usually red in salts and solutions, the cation colourless, so the green colour of the combined salt points to some abnormality. In 1932, Cox et al.<sup>1</sup> showed that the tetragonal crystal contains chains of alternate squareplanar anions and cations stacked flat on top of each other with a separation of 3.21 Å; the ionic planes are perpendicular to the *c*-axis. These authors did not make any suggestions about the source of the unusual colour.

In 1951, Yamada<sup>2</sup> found that the crystal spectrum is very unusual. The absorption maxima of " normal " chloroplatinate(II) and tetrammineplatinum(II) are shifted to lower frequencies and the dichroism is "abnormal," i.e., absorption of light with its electric vector perpendicular to the ionic planes is at a lower frequency and more intense than that of light with electric vector parallel to these planes. One normally finds the reverse situation in the spectra of flat molecules. Yamada concluded that there is some sort of direct interaction between neighbouring platinum atoms.

The first theoretical approach was made by Godycki and Rundle,<sup>3</sup> in a study of bis(dimethylglyoximato)nickel(II). This compound has a structure analogous to Magnus's green salt in that planar molecules are stacked in chains, alternate ones being twisted through 90° to allow a close approach of nickel atoms (3·245 Å). These workers sought an explanation of the specificity of dimethylglyoxime as a gravimetric reagent for nickel and for palladium, and, citing the slight pleochroism of the compound, suggested that there is a bonding interaction between the nickel atoms. This would be of sufficient strength to stabilise the simple packing and to cause the low solubility, in contrast to the very soluble copper compound. They suggested that the bonding could arise from partial excitation of 3d-electrons to empty 4p-orbitals, with pairing of electrons on neighbouring atoms. Thus the hybridisation would be effectively changed from  $dsp^2$  to  $d^2sp^3$ . This theory was supported by the discovery that the dichroism is, in fact, abnormal in a way similar to that of Magnus's green salt.<sup>4</sup> Å gold compound,  $[Au(DH)_2][AuCl_2]$  (DH<sub>2</sub> = dimethylglyoxime), was found to have a structure <sup>5</sup> analogous to that of bis(dimethylglyoximato)nickel, but was later shown to exhibit normal dichroism.<sup>6</sup>

In 1957, Rundle extended his theory of the interaction by using molecular-orbital theory.<sup>7</sup> The only essential difference was that a copper(II) compound of this structure would have its odd electron in a  $b_{1g}^*$  orbital (anti-bonding orbital derived from  $3d_{x^2-y^2}$ ), instead of in a 4p-orbital. Thus the odd electron of copper(II) would play no part in the

- <sup>8</sup> Godycki and Rundle, Acta Cryst., 1953, **6**, 487. <sup>4</sup> Yamada and Tsuchida, J. Amer. Chem. Soc., 1953, **75**, 6351.
- <sup>5</sup> Rundle, J. Amer. Chem. Soc., 1954, **76**, 3101. <sup>6</sup> Yamada and Tsuchida, Bull. Chem. Soc. Japan, 1957, **30**, 715.
- <sup>7</sup> Rundle, J. Phys. Chem., 1957, 61, 45.

<sup>&</sup>lt;sup>1</sup> Cox, Pinkard, Wardlaw, and Preston, J., 1932, 2527. <sup>2</sup> Yamada, J. Amer. Chem. Soc., 1951, **73**, 1579.

interaction, and the earlier notion that copper(II) compounds could not adopt this structure was modified.

At about the same time the crystal structure of Magnus's green salt was re-examined,<sup>8</sup> and a more satisfactory sideways packing of the chains was found. The platinumplatinum distance was corrected to 3.245 Å, exactly the same as the nickel-nickel distance in bis(dimethylglyoximato)nickel.

Sharpe and Wakefield,<sup>9</sup> in a study of a series of vic-dioxime complexes, concluded that the solubility does depend on the nickel-nickel distance; their ligands were all similar and may be presumed to have had little effect on solubility differences. Banks and Barnum,<sup>10</sup> in a similar study, used a very much larger range of ligands and found that these differences had a greater effect on the solubility than did variations in the intermetallic distance.

In a second publication,<sup>11</sup> the latter authors described the solution and solid-state spectra of their complexes. They found bands at the long-wavelength ends of the solidstate spectra which were not present in the solution spectra, and they justifiably concluded that these bands were associated with the metal-metal interactions. For an isomorphous series of nickel(II) and palladium(II) complexes, the frequency decreases with decreasing intermetallic distance.

In an attempt to study the effect of increasing intermetallic distance, Yamada and Tsuchida<sup>12</sup> measured the dichroism of alkyl homologues of Magnus's green salt. Only the green compound, [Pt(Me·NH<sub>2</sub>)<sub>4</sub>][PtCl<sub>4</sub>], shows abnormal dichroism; higher amines give rise to pink compounds with normal dichoism. The result that compounds of this nature with more or less expected colours show normal dichroism is used extensively in the present study to indicate those cases where interaction does not occur.

Finally, two copper compounds must be mentioned which show direct stacking in their structures; in neither case has the dichroism been examined. First, tetramminecopper(II) chloroplatinate(II) is isomorphous with Magnus's green salt and has a slightly shorter c-axis; <sup>13,14</sup> secondly, bis-(N-methylsalicylaldiminato)copper(II) has a structure <sup>15</sup> rather similar to that of bis(dimethylglyoximato)nickel,<sup>3</sup> with an interplanar distance of 3.33 Å. It is therefore clear that this type of structure is not confined to ions and molecules of  $d^{3}$ -configuration, and, under the right conditions, it may be much more general.

The object of this study is to examine some of the factors affecting the occurrence of the Magnus's green salt structure and of metal-metal interaction. Some of the results have already been published,<sup>14</sup> but are repeated for completeness.

### **RESULTS AND DISCUSSION**

The Table lists the important properties of the compounds examined. All substances are tetragonal except (XII). It is clear that all these compounds, except (XII), have unit cells very similar to that of Magnus's green salt. Close examination of absent reflections and of intensities in the powder photographs indicates that the compounds have the same space-group P4/mnc, and therefore, by analogy, the anions and cations are stacked in chains with metal-metal distances of c/2.

The green compounds (V, VI, and VIII) are known to be abnormally dichroic;  $^{2,12}$  it is assumed that (IX) also has this property, but that the remainder are either normal or show very slight interaction. Thus, in the compounds examined, only four of the five containing platinum in both ions show strong interaction; introduction of another metal

- <sup>11</sup> Banks and Barnum, J. Amer. Chem. Soc., 1958, 80, 4767.
   <sup>12</sup> Yamada and Tsuchida, Bull. Chem. Soc. Japan, 1958, 31, 813.
- <sup>13</sup> Bukovska and Porai-Koshits, Kristallografiya, 1960, 5, 137.
- <sup>14</sup> Miller, Proc. Chem. Soc., 1960, 318.
- <sup>15</sup> Lingafelter, Morosin, and Simmons, Acta Cryst., 1960, 13, 1025.

<sup>&</sup>lt;sup>8</sup> Atoji, Richardson, and Rundle, J. Amer. Chem. Soc., 1957, 79, 3017.
<sup>9</sup> Sharpe and Wakefield, J., 1957, 281.
<sup>10</sup> Banks and Barnum, J. Amer. Chem. Soc., 1958, 80, 3579.
<sup>10</sup> Banks and Barnum, J. Amer. Chem. Soc., 1958, 80, 3579.

removes it, without appreciably changing the lattice constants. Close similarity of bond lengths is of common occurrence in corresponding palladium and platinum compounds, and interaction in the all-platinum salts is not sufficient to disturb this.

Substitution of methylamine for ammonia in the salts has no effect on the length of the c-axis, indicating that the methyl groups are held in the platinum-nitrogen plane, and that the structure is strong enough to prevent rotation about the platinum-nitrogen bonds. Models show that ethylamine is too large to fit into the plane, and the ethylamine complex has a totally different structure from Magnus's green salt; this fits in well with the pink colour and the "normal" dichroism.<sup>12</sup> (It should be pointed out that the choice of axis in the dichroism measurements on this compound may have been in error, but this would not affect the issue as in any case no large shift was observed.)

Compound (XI) occupies a special place in the scheme. The metal-metal distance is  $3\cdot35$  Å, only very slightly greater than the longest to be found among the abnormal compounds [ $3\cdot31$  Å in (VIII)], and so, when the small spectroscopic difference between red and green is borne in mind, it may well be that this compound shows a weakly abnormal dichroism. Attempts were made to correlate the interplanar distances with the known dichroism <sup>2,12</sup> of compounds (V, VI, and VIII), but this was not very informative as the spectra seem to have been measured in slightly different regions. Remarkably, the shift of the perpendicular absorption is greater for the bromide (VIII) than for Magnus's green salt; the former has a longer *c*-axis, and so it seems that the ligand, as well as the metal-metal distance, must have an effect on the interaction. A complete investigation of the crystal spectra of compounds (IX and XI) is required.

The magnetic susceptibility of compound (III) was measured down to liquid-nitrogen temperatures; it obeyed the Curie-Weiss law with a Weiss constant of only 13°, giving  $\mu_{\text{eff.}} = 1.90$  B.M. Thus copper-platinum interaction is ruled out in this temperature

		Expected					
Compound		Colour	colour	a (Å)	c (Å)		
[Pd(NH <sub>3</sub> ) <sub>4</sub> ][PdCl <sub>4</sub> ]	Ι	Pink	Pink	8.96	6.49		
$[Pt(NH_3)_4][PdCl_4]$	II	Pink	Pink	8.98	6.45		
$[Cu(NH_3)_4][PtCl_4]$	III	Purple	Purple $\left\{ \right.$	9·07 9·06 13	6·46 6·43 13		
[Pd(NH <sub>3</sub> ) <sub>4</sub> ][PtCl <sub>4</sub> ]	IV	Pink	Pink	9.00	6.50		
[Pt(NH <sub>3</sub> ) <sub>4</sub> ][PtCl <sub>4</sub> ]	v	Green	Pink {	8·96 9·03 8	6·46 6·50 <sup>8</sup>		
$[Pt(Me \cdot NH_2)_4][PtCl_4]$	VI	Green	Pink	10.35	6.49		
[Pd(NH <sub>3</sub> ) <sub>4</sub> ][PdBr <sub>4</sub> ]	VII	$\mathbf{Red}$	Red	9.32	6.66		
$[Pt(NH_3)_4][PtBr_4]$	VIII	Green	Red	9.32	6.62		
$[Pt(Me \cdot NH_2)_4][PtBr_4]$	$\mathbf{IX}$	Green	$\mathbf{Red}$	10.55	6.61		
$[Pd(NH_3)_4][Pd(SCN)_4]$	X	Pink	Pink	10.60	6.69		
$[Pt(NH_3)_4][Pt(SCN)_4]  \dots  \dots  \dots  \dots  \dots  \dots  \dots  \dots  \dots  $	XI	$\mathbf{Red}$	Orange	10.62	6.70		
$[Pt(Et\cdot NH_2)_4][PtCl_4]$	XII	Pink	Pink	Not tetra	agonal		

range; it must, however, be remembered that the odd electron is in the  $b_{1g}$ \*-orbital, which is not suitable for interaction, being localised in the copper-ammonia plane. If a complex ion of cobalt(II), for example, were found in a similar environment, there would be a good chance of finding anomalous magnetic behaviour, as the odd electron would lie in the allimportant  $a_{1g}$ \*-orbital ( $3d_{z^2}$  with some intermixing of 4s).

It has been suggested that the metal-metal interaction is responsible for the adoption of this structure, and for the low solubility of Magnus's green salt.<sup>3,8</sup> Whilst no quantitative solubility measurements have been carried out, it is worth noting that the pink compounds (I--IV) are insoluble, whilst the green compounds (VI and IX) are moderately soluble in water (giving red solutions). Solubility depends on the difference between lattice energy and heats of solvation. By applying the relationship,<sup>16</sup>  $U_c =$ 

 $2Nz^2e^2 \ln 2/d$ , for the Coulombic lattice energy of a chain of positive and negative charges,

<sup>16</sup> Moelwyn-Hughes, "Physical Chemistry," Pergamon Press, London, 1957.

values of  $U_c$  from -575 to -550 kcal./mole are obtained as d varies from 3.20 to 3.35 Å. These are in all probability lower than the true lattice energies, as sideways attractions between charges have been neglected. They are much higher than those of the alkalimetal halides, and somewhat smaller than those of the insoluble oxides and sulphides of bivalent metals.<sup>17</sup> Since the flat complex ions are considerably larger than alkalineearth, oxide, or sulphide ions, they would be expected to have smaller heats of solvation. It follows that low solubility is to be expected, and that the Magnus's green salt structure is particularly stable, regardless of the existence of any metal-metal interactions.

Theory of Interaction .- There are three types of compound which form "directstacking" structures. First, there are the well-established organic addition complexes such as quinhydrone, which consists of chains of alternate quinone and quinol molecules stacked in parallel,<sup>18</sup> with an interplanar spacing of 3.16 Å. The dichroism is strongly abnormal,<sup>19</sup> and the properties can be readily interpreted as due to co-ordination of the quinol  $\pi$ -electrons to the empty  $\pi$ -orbitals of the quinone. The fact that hexamethylbenzene,<sup>20</sup> for example, does not form quite such a simple structure may be put down to repulsion of the  $\pi$ -electrons.

The second type of compound consists of the *vic*-dioximates of nickel, palladium, and platinum, and bis-(N-methylsalicylaldiminato)copper(II). Abnormal dichroism is apparent in the nickel and platinum dimethylglyoxime complexes.<sup>4</sup> This cannot be ascribed to a charge-transfer mechanism as in quinhydrone, because neighbouring molecules are identical. In Rundle's theory 7 interaction between only two molecules is considered, but this theory may be readily extended to cover a chain of *n* molecules. The  $a_{1g}^*$ - and the  $a_{2u}(4\phi_z)$ -orbitals each form a bonding and an anti-bonding band; those from the  $a_{1a}^*$ -orbitals are fully occupied, and without further treatment it can be seen that the net result would be anti-bonding. Rundle suggested that configurational interaction between the anti-bonding  $a_{1g}^{*}$ - and the bonding  $a_{2u}$ -bands would give the modification required to lower the energy. Such interaction would presumably give a function which allowed the highest-energy electrons considerable freedom of movement along the chain.

An alternative presentation is to allow the  $a_{1q}^{*}$ - and the  $a_{2u}$ -orbitals on one molecule to form two equivalent hybrids; each would have a large lobe along the axis. When a chain of n molecules is formed, the hybrids give rise to two non-bonding orbitals, n-1 equivalent bonding and n-1 equivalent anti-bonding orbitals. If n is large, the non-bonding orbitals, which are at each end of the chain, may be neglected. The electrons fill the bonding orbitals and half-occupy the non-bonding orbitals, and so the overall effect would be bonding.

There is the further possibility that the anti-bonding band from  $a_{1g}^*$  can reach above the  $b_{1g}^*$  level, which is intermediate between  $a_{1g}^*$  and  $a_{2u}$  in an isolated molecule. In this case, half of the axial electrons would be forced into the  $b_{1g}$ -orbitals in the planes of the molecules, while the other half would be stabilised along the axis.

Banks and Barnum<sup>11</sup> attributed the band in the solid-state spectra of their dioxime complexes to a transition from  $a_{1q}^*$  to  $b_{1q}^*$ . In order to account for the *drop* in frequency with decreasing metal-metal distance, one must assume that the gap between  $a_{1g}^*$  and  $b_{1a}$ \* becomes smaller as the metal-metal distance decreases. This could come about very simply by interaction of the  $a_{1q}$ -orbitals alone, the  $a_{2u}$ -orbitals being neglected; these orbitals would interact to form an energy band, which would have an overall anti-bonding effect, since all levels are occupied. In such a case, the structure would be formed in spite of the interaction, rather than on account of it.

By combining the two extremes, of interaction between the  $a_{1a}$ \*-orbitals alone and of

<sup>&</sup>lt;sup>17</sup> Waddington, "Advances in Inorganic Chemistry and Radiochemistry," Academic Press, 1959, Vol. I.

<sup>&</sup>lt;sup>18</sup> Matsuda, Bull. Chem. Soc. Japan, 1958, **31**, 611.

 <sup>&</sup>lt;sup>19</sup> Nakamoto, J. Amer. Chem. Soc., 1952, 74, 1739.
 <sup>20</sup> Robertson, "Organic Crystals and Molecules," Cornell Univ. Press, 1953.

hybridisation of  $a_{1g}^*$  and  $a_{2u}$ , it is seen that the amount of bonding or anti-bonding would depend on the exact amount of mixing of the  $a_{2u}$ - into the  $a_{1g}^*$ -orbitals.

Compounds with the composition of Magnus's green salt form the third class. In this case the co-ordination theory applicable to quinhydrone is equivalent to the molecular-orbital theory, as neighbouring species are not identical. Co-ordination could be considered to occur from the  $a_{1g}^*$  of the anion to the  $a_{2u}$  of the cation. The exact reason why palladium compounds do not seem to have this interaction must lie in the relative sizes of the orbitals concerned, or it may be that platinum can use its 4f-orbitals to advantage.

The conclusion to be drawn from this work is that metal-metal interaction cannot be held responsible for the adoption of the Magnus's green salt structure, but rather that such interaction can occur in certain compounds which crystallise in this way. The Magnus's green salt structure is an electrostatically favourable one for doubly-charged square-planar ions to adopt, without the influence of these interactions which at present seem to be limited to platinum-platinum salts with intermetallic distances less than  $3\cdot35$  Å. Present indications are that several other materials crystallise in slightly deformed versions of the Magnus's green salt lattice, and this can be explained by repulsion of  $\pi$ - and  $a_{1g}$ \*-electrons. It is suggested that the analogous structures of *vic*-dioxime complexes may be explained in terms of favourable packing, and that when metal-metal interaction occurs, the possibility of its being anti-bonding should not be excluded.

#### EXPERIMENTAL

Compounds were obtained as crystalline precipitates by mixing stoicheiometric amounts of the appropriate ions in aqueous solution. The solutions were cooled to  $0^{\circ}$  before mixing to avoid formation of monomers such as dichlorodiamminepalladium and to discourage exchanges of ligand between different metal atoms. Acid was added, where it did not react with the cation, as this is reputed to encourage the formation of green compounds.<sup>1</sup> The analyses are listed.

Tetramminepalladium chloropalladate(II). Found: Pd, 49.8; Cl, 32.9. Calc. for  $H_{12}Cl_4N_4Pd_2$ : Pd, 50.3; Cl, 33.6%.

Tetrammineplatinum chloropalladate(II). Found: Pd, 20.4; Cl, 27.4. Calc. for  $H_{12}Cl_4N_4PdPt$ : Pd, 20.8; Cl, 27.7%.

Tetramminepalladium chloroplatinate(II). Found: Pd, 20.6; Cl, 27.6%.

Tetramminecopper chloroplatinate(II). Found: N, 12·3; Cl, 30·4. Calc. for  $H_{12}Cl_4CuN_4Pt$ : N, 11·95; Cl, 30·25%.

Tetrammineplatinum chloroplatinate(II). Found: Cl, 23.5. Calc. for  $H_{12}Cl_4N_4Pt_2$ : Cl, 23.6%.

Tetramminepalladium bromopalladate(II). Found: Pd, 34.8; Br, 53.4. Calc. for  $H_{12}Br_4N_4Pd_2$ : Pd, 35.5; Br, 53.2%.

Tetrammineplatinum bromoplatinate(II). Found: Br, 40.8. Calc. for  $H_{12}Br_4N_4Pt_2$ : Br, 41.1%.

Tetramminepalladium thiocyanatopalladate(II). Found: Pd, 40.8; SCN, 45.0. Calc. for  $C_4H_{12}N_8Pd_2S_4$ : Pd, 41.5; SCN, 45.2%.

Tetra (methylamine) platinum chloroplatinate(11). Found: C, 6.7; H, 3.1; N, 9.05; Cl, 21.6. Calc. for  $C_4H_{20}N_4Cl_4Pt_2$ : C, 7.3; H, 3.1; N, 8.5; Cl, 21.6%.

Tetra(methylamine)platinum bromoplatinate(II). Found: C, 5·1; H, 2·4; N, 6·1; Br, 38·4.  $C_4H_{20}Br_4N_4Pt_2$  requires C, 5·8; H, 2·4; N, 6·7; Br, 38·3%.

Tetra (ethylamine) platinum chloroplatinate(II). Found: C, 13.0; H, 3.3; N, 8.1; Cl, 19.9. Calc. for  $C_8H_{28}Cl_4N_4Pt_2$ : C, 13.5; H, 4.0; N, 7.9; Cl, 19.9%.

X-Ray Powder Photographs.—These were taken in Unicam 19 cm. cameras, with Cu-K $\alpha$  radiation. The finely powdered samples were packed into thin-walled Pyrex glass capillaries, which were sealed with picein wax. The sin<sup>2</sup>  $\theta$  values and the indexing are tabulated. The unit cell dimensions are listed in the discussion section.

Magnetic Susceptibility.—The susceptibility of  $[Cu(NH_3)_4][PtCl_4]$  was measured by the Gouy method in the temperature range 83—293° K. It obeyed the equation  $\chi_M = \mu_{eff.}^2/2\cdot 84^2(T + 13)$ , where  $\mu_{eff.} = 1\cdot90$  B.M.

# Square-planar Complexes.

	si	n²θ	$\sin^2 \theta$			$\sin^2 \theta = \sin^2$	$\theta \sin^2 \theta$			sin² θ	$\sin^2 \theta$	
Int.	(0	bs.)	(calc.)	hkl	Int.	(obs.) (calc	.) (B)	hkl	Int.	(obs.)	(calc.)	hkl
	[Pc	I(NH <sub>8</sub> )	[PdCl <sub>4</sub> ]			[Cu(NH <sub>3</sub> ),	][PtCl <sub>4</sub> ]			[Pd(NH <sub>a</sub> ) <sub>4</sub> ][P	d(SCN),].	
vs	0.0	)144	0.0148	110	s	0.0290 0.028	39 0.0290	200		0.0000	0.0952	330
s	0.0	293	0.0295	200	w	0.0500 0.050	04 0.0506	211	m	0.0923 {	0.0954	222
w	0.	050 <b>1</b>	0.0510	211	s	0.0568 0.057	70 0.0575	002	e	0.1069	0.1058	420
s	0.0	)559	0.0564	002	vs	$0.0719 \begin{cases} 0.071 \\ 0.0719 \end{cases}$	15 0.0720	112	3	· · · · · · · · · · · · · · · · · · ·	0.1060	312
S	0.0	0706	0.0712	112		0.072	23 0.0724	310	ms	0.1377 {	0.1375	510
S	0.0	1130	0.0250	310	mw	0.0795 0.075	13 U·U/96	301		0.1492	0.1492	402
me	0.0	874	0.0879	202	5	0.1083 0.108	19 0.1085	202	me	0.1403	0.1580	002 499
ms	0.1	176	0.1180	400	m	0.1157 0.115	52 0·1035	400	m	0.1689	0.1693	440
ms	0.1	296	0.1302	312		0 1007 ( 0.129	3 0.1299	312		0 1000	. 1000	
w	0.1	325	0.1328	330	nis	0.1297 { 0.130	4 0.1301	330		{Pt(NH_),]{P	t(SCN),]	
ms	0.1	469	0.1475	420	mw	0.1369 0.137	2 0.1375	411	vs	0.0105	0.0106	110
ms	0.1	738	0.1744	402	$\mathbf{m}$	0.1451 0.144	l6 0·1448	<b>42</b> 0	vw	0.0188	0.0185	101
mw	0.1	.889	0.1892	332	m	0.1729 0.172	27 0.1734	402	S	0.0211	0.0211	200
$\mathbf{m}\mathbf{w}$	0.1	.918	0.1918	510	m	$0.1881 \begin{cases} 0.187\\ 0.187 \end{cases}$	1 0.1879	332	w	0.0423	0.0422	220
	[Pd.	(NH.).10	P+C1.1			0.1040	SO 0-1883	510	VC	0.0520 5	0.0528	310
110	0.0	144	0.0147	110	w	0.1949 0.195	C 0.9094	431	*3	0 0025 <b>\</b>	0.0529	002
v5 mu	, 0.0	0144 0911	0.0914	101	$\mathbf{ms}$	$0.2022 \begin{cases} 0.201 \\ 0.209 \end{cases}$	0 0.2024	422	mw	0.0634	0.0635	112
m	0.0	290	0.0293	200		(0·202	2 0.2021	. 1 6	vw	0.0822	0.0818	321
m	0.0	561	0.0562	002	the un	it coll in rof 1	are calcula	ted from	w	0.0844	0.0050	220
m	0.0	708	0.0708	112	the un	at cen in rei, i	э.		mw	0.0951	0.0950	220
m	0.0	729	0.0734	310		$\sin^2 \theta$	$\sin^2 \theta$				0.1055	420
vw	0.0	798	0.0801	301	Int.	(obs.)	(calc.)	hkl	s	0.1059	0.1057	312
m	0.0	860	0.0856	202		[Pd(NH_)]	[PdBr]			0 1070	0.1372	510
w	0.1	169	0.1174	400	s	0.0135	0.0137	110	m	0.1319 {	0.1373	402
mw	0.1	296	0.1296	312	w	0.0201	0.0202	101	w	0.1591	0.1584	422
mw	0.1	468	0.1468	420	ms	0.0272	0.0274	200	w	0.1200	0.1688	440
mw	0.1	736	0.1738	402	w	0.0345	0.0343	210	mw	0.1793	0.1793	530
w	0.1	894 {	0.1008	332 510	$\mathbf{m}$	0.0476	0.0477	211	mw	0.1903 {	0.1899	600
m	0.2	036	0.2030	422	S	0.0534	0.0536	002		Ş	0.1901	512
w	0.2	491	0.2496	530	$\mathbf{ms}$	0.0673	0.0673	112	mw	0.2115	0.2110	620
			0 - 100	000	$\mathbf{ms}$	0.0687	0.0685	310		C	0.2110	004
	[Pt(	$NH_{3}_{4}[$	PdCl₄]		ms	0.0817 {	0.0810	202		[Pt(MeNH_)]	1(P+CL)	
vs	0.0	143	0.0148	110	m	0.1006	0.1006	311	110	0.0109	0.0111	110
s	0.0	286	0.0296	200	m	0.1991	0.1991	210	v 5 6	0.0220	0.0222	200
vw	0.0	366	0.0370	210	m	0.1371	0.1370	420	m	0.0444	0.0444	220
w	0.0	517	0.0513	211	m	0-1633	0.1632	402		0.0770	0.0555	310
5	0.0	969 710	0.0720	002	vw	0.1702	0-1700	412	S	0.0228	0.0564	002
5	0.0	715	0.0740	210		0 1700	0.1769	332	ms	0.0675	0.0675	112
m	0.0	869	0.0868	202	vw	0.1100 {	0.1781	510	vw	0.0691	0.0696	311
w	0.1	182	0.1184	400	$\mathbf{m}\mathbf{w}$	0.1908	0.1906	422	m	0.0783	0.0786	202
ms	0.1	312	0.1312	312	$\mathbf{m}\mathbf{w}$	0.2467	0.2466	600	mw	0.0886	0.0888	400
$\mathbf{m}$	0.1	481	0.1480	420		(Pt/NH.) 1	(P+Br ]		s	0.1003	0.0999	330
mw	0.1	759	0.1756	402		0.0120	0.0197	110		Ş	0.1110	222
w	0.1	926	0.1924	510	VS VW	0.0152	0.0204	101	vs	0.1114 {	0.1110	319
m	0.2	054	0.2052	422	5	0.0272	0.0274	200			0.1442	510
w	0.5	498	0.2516	530	vw	0.0337	0.0342	210	ms	0.1447 {	0.1452	402
	$\sin^2 \theta$	sin² θ	sin² θ		mw	0.0475	0.0478	211	m	0.1564	0.1563	332
Int.	(obs.)	(calc.)	(R)	hkl	s	0.0539	0.0542	002	s	0.1676	0.1674	422
	[Pt(	NH.).II	PtCL		vs	0.0681	0.0685	310	w	0.1779	0.1775	440
m	0.0140	0.0142	0.0141	601	s	0.0812	0.0816	202	mw	0.1889	0.1886	530
s	0.0150	0.0148	0.0146	110	m	0.1094	0.1096	400	m	0.2008 {	0.1997	600
m	0.0298	0.0296	0.0292	200	S	0.1227	0.1227	312		0.0792	0.2006	012
mw	0.0572	0.0570	0.0564	002	vw m	0.1297	0.1270	411	ms	0.2100	0.2103	022
mw	0.0592	0.0592	0.0583	220	m	0.1638	0.1638	420		[Pt/MeNH_].]	PtBr.1	
mw	0.0722	0.0718	0.0710	112	ш	0.1033	0.1706	402	110	0.0105	0.0107	110
s	0.0743	0.0740	0.0729	310	vw	0.1712	0.1712	430	v 5 VW	0.0189	0.0189	101
mw	0.1107	0.1104	0.0856	202		0 1701	0.1775	332	m	0.0212	0.0214	200
m	0.1300	0.1310	0.1902	400	m	0.1/81 {	0.1781	510	w	0.0425	0.0427	220
m	0.1339	0.1339	0.1319	330	vw	0.1848	0.1848	431	s	0.0541	0.0544	002
s	0.1481	0.1480	0.1458	420	$\mathbf{ms}$	0.1916	0.1915	422	vw	0.0614	0.0617	301
m	0.1753	0.1754	0.1731	402		DAINH VID	d(SCN) 1		s	0.0647	0.0651	112
m	0.1922	0.1924	0.1895	510				110	m	0.0756	0.0758	202
ms	0.2043	0.2050	0.2022	422	vs	0.0108	0.0196	110	w	0.082	0.0854	400
sin	<sup>2</sup> θ (R) v	alues a	re calculate	ed from	w e	0.0210	0.0219	200	m	0.0963 {	0.0961	330
the un	it cell of	Atoji et	al.8		vw	0.0399	0.0398	211			0.1068	422
	ain? a				vw	0.0423	0.0423	220	s	0·1070 {	0.1078	319
Int	(obs)	sin* Ø	SID* U	661		0.0521	0.0529	310	m	0.1383	0.1388	510
1110.	(008.)	(carc.)		IKU	vs	0.0221 {	0.0531	002	m	0.1207	0.1505	332
	[Cu(	NH <sub>3</sub> ) <sub>4</sub> ][H			s	0.0636	0.0637	112	s	0.1611	0.1612	422
vs	0.0142	0.0145	0.0145	110	ms	0-0743	0.0743	202	w	0.1814	0.1816	530
8	0.0213	0.0219	0.0216	101	m	0.0820	0.0821	321	m	0.1934	0.1932	512

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