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STUDIES  
IN MAGNETOCHEMISTRY

PART II.

COMPLEX PLATINUM COMPOUNDS

BY

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The complex platinum compounds which we have investigated in this paper contain divalent platinum as a central ion and four coordinated groups. The substances comprise the following types: — Compounds analogous to the first salt of REISET, the second salt of REISET, PEYRONES compounds, the CLEVE and the COSSA salt and the MAGNUS salts. Furthermore we have investigated the compound  $\left[ \text{Pt} \begin{matrix} (\text{NH}_3)_4 \\ (\text{NC} \cdot \text{CH}_3)_2 \end{matrix} \right] \text{Cl}_2$ , which as far as we know is the only complex compound of divalent platinum which contains 6 coordinated groups. The number of classification<sup>1)</sup> of these substances is 84 and for the last-mentioned compound 88. The difference between the atomic number of Radon and the number of classification is respectively 2 and — 2. According to the rule of BOSE these substances therefore might be expected to be paramagnetic; they are, however without exception all diamagnetic. The magnetic moment of the  $\text{Pt}^{++}$  ( $\mu$  eff. = 2.8 for spin only) has perfectly disappeared. This fact is of principal interest in connection with the wave-mechanical considerations of PAULING<sup>2)</sup>, who deduced that 4-covalent compounds of Ni, Pd, and Pt should have a planary configuration. A consequence of PAULING's theory is that this configuration involves a diamagnetic susceptibility while the tetrahedral distribution of

<sup>1)</sup> J. A. CHRISTIANSEN and R. W. ASMUSSEN: Studies in Magnetochemistry I, Det kgl. danske Vidsk. Selsk. Math.-fys. Medd. XII. 10. 1934.

<sup>2)</sup> L. PAULING: J. Am. Ch. Soc. **53** 1391. 1931.

the coordinated groups would give a paramagnetic moment. If we had certain chemical evidence for the planary configuration of the 4-covalent platinum complexes, the present work would favour the theory of PAULING. However, the proofs are as a rule not quite decisive, although in some cases the planary arrangement of the valencies seems to be rather definitely proved. In his classical paper on the constitution of inorganic compounds WERNER<sup>1)</sup> showed that 4-covalent platinum compounds of the type  $\left[ \text{Pt} \begin{array}{c} \text{X}_2 \\ \text{Y}_2 \end{array} \right]$  occur in two forms, which are chemically different and which he assumed to be cis and trans isomers. S. M. JØRGENSEN<sup>2)</sup> had prepared 2 different compounds of the composition  $\left[ \text{Pt} \begin{array}{c} \text{PY}_2 \\ \text{Cl}_2 \end{array} \right]$  which according to WERNER are cis and trans isomers having a planary configuration. The measurements of the magnetic susceptibility gives as a result for the cis and trans compounds respectively  $-0,417 \cdot 10^{-6}$  and  $-0,421 \cdot 10^{-6}$ , i. e. practically the identical values. HANTZSCH<sup>3)</sup> has determined the molecular weight of both substances in phenol in which solvent they give the normal molecular weight. This result supports the view of WERNER. In other cases, e. g. the (assumed) cis and trans  $\left[ \text{Pt} \begin{array}{c} (\text{NH}_3)_2 \\ \text{Cl}_2 \end{array} \right]$ , the molecular weight has been shown to be normal for the cis form whilst the "trans" form is bimolecular<sup>4)</sup>. This of course is no decisive proof against the planary configuration but it lessens the value of the arguments for this configuration. The compounds of GRÜNBERG<sup>5)</sup> cis and trans  $\left[ \text{Pt} \begin{array}{c} (\text{NH}_3)_2 \\ (\text{CNS})_2 \end{array} \right]$

<sup>1)</sup> A. WERNER: Zeit. f. anorg. u. allg. Ch. **3**, 310. 1893.

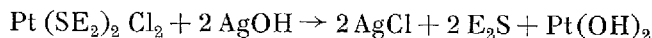
<sup>2)</sup> S. M. JØRGENSEN: J. pr. Ch. [2] **33**, 510, 1886.

<sup>3)</sup> HANTZSCH, Ber. **59**, 2761 1926; Zeit. f. anorg. u. allg. Ch. **159**, 273. 1927.

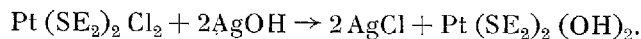
<sup>4)</sup> REIHLEN and NESTLE: Ann. d. Chem. **447**, 211. 1926.

<sup>5)</sup> GRÜNBERG, A.: Zeit. f. anorg. u. allg. Ch. **157**, 299. 1926.

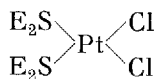
are unimolecular when dissolved in acetone. However, REIHLEN and NESTLE<sup>1)</sup> called attention to the point that these compounds are not necessarily cis-trans isomers but may be "salt isomers" (normal and iso-thiocyanates), which of course is possible. Furthermore, we mention the very interesting compounds of ANGELL, DREW and WARDLAW<sup>2)</sup> namely the two substances both of which have the composition  $\left[ \text{Pt} \begin{matrix} (\text{S}(\text{C}_2\text{H}_5)_2)_2 \\ \text{Cl}_2 \end{matrix} \right]$ . Both isomers are soluble in benzene and both give the simple molecular weight. We might then interpret these compounds as cis and trans forms. However, it turns out that the properties of the two forms ( $\alpha$  and  $\beta$ ) are so different that it seems difficult to assume merely a cis-trans isomerism. The  $\alpha$ -compound is insoluble in water, the  $\beta$ -compound is rather soluble in water. The  $\alpha$ -form reacts slowly with  $\text{Ag}_2\text{O} + \text{H}_2\text{O}$  according to:



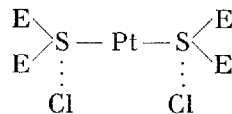
whilst the  $\beta$ -form gives a rapid reaction according to:



ANGELL, DREW and WARDLAW assume that the  $\alpha$ -compound has a constitution corresponding to the WERNER formula (I) and that the  $\beta$ -form is a sulphonium compound (II).



I.



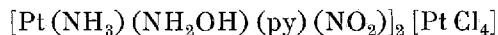
II.

<sup>1)</sup> REIHLEN and NESTLE: Zeit. f. anorg. u. allg. Ch. **159**, 343, 1927.

<sup>2)</sup> F. G. ANGELL, H. D. K. DREW and W. WARDLAW: J. Chem. Soc. **1930**, 349.

However, there are obvious objections to formula II and the problem of the constitution of these compounds cannot be considered as settled.

As further chemical evidence of the planary configuration we mention that TSCHERNIAEFF<sup>1)</sup> has succeeded in the isolation of 3 different compounds:



and it was not possible to resolve the compounds in optical antimers. This supports WERNER'S view. Some physical evidence for the plane structure has been obtained during the last few years from the x-ray examination of some complex platinous compounds. In the following table is given the material available and the results of our magnetic measurements on the same compounds.

Table 1.

Substance	X-ray evidence	$\chi \cdot 10^6$
$[\text{PtCl}_4] \text{K}_2$	planary <sup>2)</sup>	-0.383
$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$	planary <sup>3)</sup>	-0.412
$[\text{Pt}(\text{en})_2]\text{Cl}_2$	planary <sup>4)</sup>	-0.365
$[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$	planary <sup>5)</sup>	-0.306

The results of the X-ray examinations and the magnetic measurements are in conformity to the theory of PAULING.

<sup>1)</sup> E. TSCHERNIAEFF: Abstracts Ch. Soc. **1928**. 974.

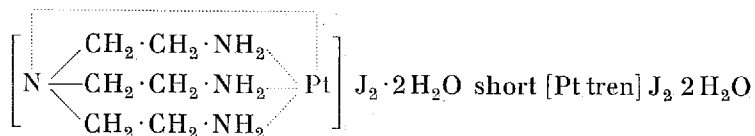
<sup>2)</sup> R. G. DICKINSON: J. Am. Ch. Soc. **44**. 774, 2404. 1922.

<sup>3)</sup> E. G. COX: J. Ch. Soc. **1932**. 1912.

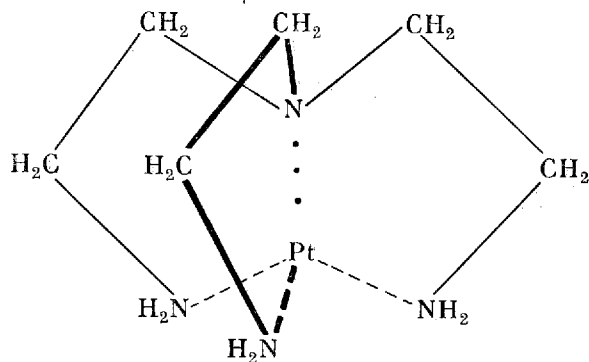
<sup>4)</sup> E. G. COX, F. W. PINKARD, W. WARDLAW and G. H. PRESTON: J. Ch. Soc. **1932**. 2527.

<sup>5)</sup> E. G. COX and G. H. PRESTON: J. Ch. Soc. **1933**. 1089.

In the year 1925 MANN and POPE<sup>1)</sup> prepared a compound which had the composition:



The 2 water molecules are given off in a vacuum and do not belong to the complex part of the molecule. MANN and POPE assumed that this substance had a planary configuration. This is however difficult to imagine. REIHLEN<sup>2)</sup> has proposed the more obvious constitution according to which the four nitrogen atoms are tetrahedrally distributed around the platinum atom:



The molecular weight of the compound has not been determined because no solvent has been found in which the substance is soluble. The 2 iodine ions atoms do not belong to the complex part, because the tetrachloroplatinite  $[\text{Pt tren}] [\text{PtCl}_4]$  has been prepared. This compound does not contain water. If the theory of PAULING is correct, and REIHLEN'S view is correct, this compound should be paramag-

<sup>1)</sup> MANN and POPE: Proc. Roy. Soc. A. 109 444, 1925.

<sup>2)</sup> REIHLEN: Liebigs Ann. 448 312, 1926.

netic. Our measurements show, however, that it is diamagnetic as well as the chloroplatinite.

It is obvious that more chemical investigation is necessary to give convincing evidence for the planary configuration of complex platinum compounds (the same is true in the case of  $\text{Ni}^{\text{II}}$  and  $\text{Pd}^{\text{II}}$  compounds) before this can be considered as an experimental proof of the theory of PAULING. On the other hand PAULING's theory, as far as magnetism is concerned, seems to be too approximate to be applied in the decision of constitution problems without other supporting evidence.

Two compounds in the table of magnetic susceptibility given at the end of this paper are of particular interest, namely: MAGNUS' green salt and the red salt of JØRGENSEN and SØRENSEN, both of which have the composition  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$  but are different in colour. Both the substances are diamagnetic with practically the same susceptibility ( $\chi_{\text{red}} < \chi_{\text{green}}$ ). An x-ray examination by HERTEL and SCHNEIDER<sup>1)</sup> has shown that both salts contain ions of planary structure. The position of the complex ion  $[\text{Pt}(\text{NH}_3)_4]^{++}$  in the two different forms relative to the  $[\text{PtCl}_4]^{--}$  is different, and this fact is supposed to be the reason for the existence of these two MAGNUS salts. A different distribution of the coordinated groups (planary or tetrahedral) is consequently not responsible for the different colour.

### Chemical Part.

In a series of papers entitled "Zur Konstitution der Platinbasen"<sup>2)</sup> S. M. JØRGENSEN has studied the preparation

<sup>1)</sup> E. HERTEL and K. SCHNEIDER, Z. anorg. u. allg. Ch. **202** 77, 1931.

<sup>2)</sup> Zur Konstitution d. Platinbasen I J. pr. Ch. **33** 489, 1886. — Ibid. II Zeit. f. anorg. u. allg. Ch. **24** 153, 1900. — Ibid. III Zeit. f. anorg. u. allg. Ch. **25** 353, 1900. — Ibid. IV Zeit. f. anorg. u. allg. Ch. **48** 374, 1906.



and structure of important complex platinum compounds. Of the collection of complex platinum compounds left by S. M. JØRGENSEN at this laboratory was selected a group of salts, the crystals of which judging by appearances might be expected to have preserved their composition. However, several of them were omitted because the analysis showed that their composition had changed. Others were omitted because the amount of the substances after having been pulverized turned out to be too small for filling the glass tube used in the magnetic measurements. The compounds which we have measured have preserved their composition. However, we notice that a few compounds were re-prepared. With regard to the magnetic purity of the substances we point out that the substance which has been used as a mother substance in most cases is potassium tetrachloroplatinite. This compound it is very easy to obtain in a high degree of purity.

The quantitative analysis of the substances comprises estimations of platinum and in some compounds chlorine and ammonia. These compounds, when heated in a current of hydrogen, give a mirror of platinum on the wall of the tube. For this reason is it impossible to use the method which we have described in the paper on complex rhodium compounds<sup>1)</sup>. We have then adopted the method of determination which is of common use in determining platinum in complex compounds, namely: The compound is melted together with sodium carbonate. Free platinum is formed. The salts are eliminated and the platinum weighed after having been heated in a current of pure hydrogen.

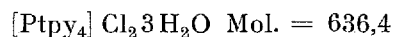
The platinum obtained in these analysis was used in

<sup>1)</sup> J. A. CHRISTIANSEN and R. W. ASMUSSEN: Kgl. Danske Videnskab. Selsk. XII, 10, pag. 8, 1934.

the preparation of some other complex platinum compounds. We give the results of the analysis in the following general view.

### The Results of Analysis.

#### Tetrammineplatinous compounds.

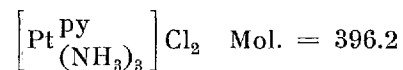


Dried in air.

When this substance is heated in air at  $100^\circ$  two molecules of pyridine and three molecules of water are given off.

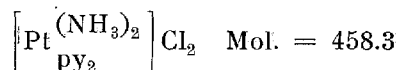
Substance: 0.3621	2py + 3H <sub>2</sub> O, S.M.J.: 33.39 %
Total loss of weight: 0.1209	- - - R.W.A.: 33.34 —
	- - - Calc.: 33.33 —

Substance: 0.2974	S.M.J.: 30.50 % Pt
Platinum: 0.0912	R.W.A.: 30.66 — Pt
	Calc.: 30.67 — Pt



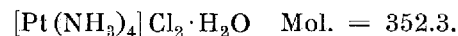
Dried in air.

Substance: 0.1793	Calculated: 49.27 % Pt
Platinum: 0.0882	Found: 49.18 — —



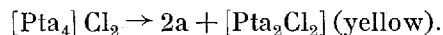
Dried at  $100^\circ$

	S.M.J.: 42.45 % Pt
Substance: 0.1727	R.W.A.: 42.54 — —
Platinum: 0.0735	Calc.: 42.59 — —



The label of this specimen had been lost. However, the crystals were very nice. As it turned out that the compound

when heated gave off ammonia and became yellow, it was concluded that this compound was a tetrammine, which gives the general reaction:



The analysis shows that this substance had the composition mentioned above. The analysis was carried out after drying in the air.

Substance: 0.7598      Platinum found: 55.34 %; Calc.: 55.38 %  
Platinum: 0.4205

A sample was heated at 250°; 2NH<sub>3</sub> + H<sub>2</sub>O given off.  
Substance: 0.4356      2NH<sub>3</sub> + H<sub>2</sub>O Calc.: 14.79 %  
Total loss of weight: 0.0642      —      —      Found: 14.73 %

Ammonia was determined by titration (after distillation with sodium hydroxide)

Substance: 0.2642      Calc.: 19.33 % NH<sub>3</sub>.  
30.20 cc 0.0990 n HCl      Found: 19.27 — —

[Pt<sub>en</sub>]<sub>2</sub>Cl<sub>2</sub> Mol. = 386.3

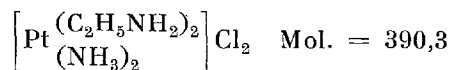
Dried at 100°

Substance: 0.2157      S.M.J.: 50.55, 50.37 % Pt  
Platinum: 0.1087      R.W.A.: 50.41 —  
Calc.: 50.54

$\left[ \text{Pt}^{\text{en}} \right] \text{Cl}_2$  Mol. = 360.06  
(NH<sub>3</sub>)<sub>2</sub>

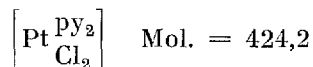
Dried in air

Substance: 0.2044      S.M.J. 54.12 % Pt  
Platinum: 0.1110      R.W.A.: 54.31 —  
Calc.: 54.19 —



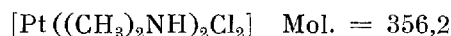
Dried at 100°

	S.M.J.: 50.01 % Pt
Substance: 0.2008	R.W.A.: 49.62 —
Platinum: 0.0996	Calc.: 49.98 —

**Non-electrolytes**

Dried at 100°

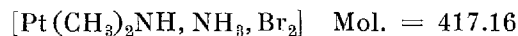
	S.M.J.: 45.86; 45.82 % Pt
Substance: 0.4520	R.W.A.: 45.82 %
Platinum: 0.2072	Calc.: 46.02 —



Dried in air

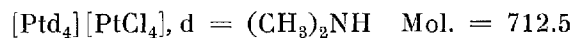
	S.M.J.: 54.56 % Pt
Substance: 0.4663	R.W.A.: 54.83 —
Platinum: 0.2557	Calc.: 54.81 —

According to the label the compound should be  $[\text{Pt}(\text{CH}_3)_2\text{NH}]\text{Cl}_2$ . The analysis shows that the composition is the one given above, see also S.M.J. Z. an. Ch. 48. 379, 1906.



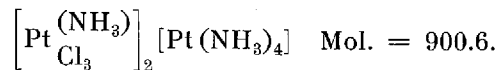
Dried in air

	S.M.J.: 46,47 % Pt
Substance: 0.2962	R.W.A.: 46.31 —
Platinum: 0.1372	Calc.: 46.78 —

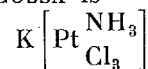
**Compounds of the type:  $[\text{Pt}_4] [\text{PtCl}_4]$ .**

Dried in the air.

	S.M.J.: 54.82 % Pt
Substance: 0.2173	R.W.A.: 54.90 —
Platinum: 0.1193	Calc.: 54.80 —



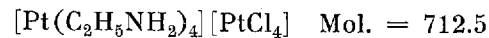
Cossa's salt Ber. **23**. 2504. 1890. First salt of COSSA is



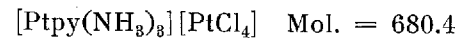
Substance: 0.2092	Calc.: 65.03 %
Platinum: 0.1360	Found: 65.01 —



Substance: 0.2228	S.M.J.: 59.52, 59.65 % Pt
Platinum: 0.1327	R.W.A.: 59.56 —
	Calc.: 59.84 —

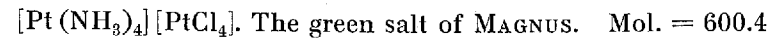


Substance: 0.2603	S.M.J.: 54.68
Platinum: 0.1430	R.W.A.: 54.94
	Calc.: 54.80



Dried in vacuum over  $\text{H}_2\text{SO}_4$

Substance: 0.2126	S.M.J. 57.42
Platinum: 0.1223	R.W.A.: 57.53
	Calc.: 57.37



Dried in air.

Substance: 0.2876	Calc.: 65.03 % Pt.
Platinum: 0.1874	Found: 65.15

$[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ . The red salt of S. M. JØRGENSEN and  
S. P. L. SØRENSEN<sup>1)</sup>

Dried at 96°

Substance: 0.2667	Calc.: 65.03 % Pt
Platinum: 0.1736	Found: 65.09 —

$\left[ \text{Pt} \begin{array}{c} \text{PY}_2 \\ (\text{NH}_3)_2 \end{array} \right] [\text{PtCl}_4]$ . Mol. = 724.4.

Dried at 100°	S.M.J.: 53.71, 53.68 % Pt
Substance: 0.2734	R.W.A.: 53.91 —
Platinum: 0.1474	Calc.: 53.76 —

$[\text{Pt}(\text{NH}_2\text{C}_2\text{H}_4)_3\text{N}]\text{J}_2$ <sup>2)</sup>

Molecular weight by platinum estimation 605. Calc. 595.

$\left[ \text{Pt} \begin{array}{c} (\text{NH}_3)_4 \\ (\text{CH}_3\text{CN})_2 \end{array} \right] \text{Cl}_2$ <sup>3)</sup>

Molecular weight by platinum estimation 419. Calc. 416.4.

### The Results of the Magnetic Measurements.

The measurements were performed with the same apparatus and using the same mode of procedure as we have described in our paper on complex rhodium compounds<sup>4)</sup>. In the following table we give the mass susceptibilities calculated from our measurements.

		Temperature	$-\chi \cdot 10^6$	$-\chi \cdot 10^6$ mean
$[\text{Ptpy}_4]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$	I	18° 0	0.470	
			0.464	
				0.472
—	—	18° 5	0.475	
	II		0.479	

<sup>1)</sup> Z. anorg. und allgem. Ch. 48 441, 1906.

<sup>2)</sup> MANN and POPE: Proc. Roy. Soc. A. 109, 444, 1925; 482, 1926.

<sup>3)</sup> TSCHUGAEFF: C. r. 161, 563, 1928. We thank Magister K. A. JENSEN who kindly prepared and analysed the compounds <sup>2)</sup> and <sup>3)</sup>.

<sup>4)</sup> J. A. CHRISTIANSEN and R. W. ASMUSSEN: Studies in Magnetochemistry Part I. Det. kgl. danske Vidsk. Selsk. Math.-fys. Medd. XII. 10, 1934.

	Temperature	$-\chi \cdot 10^6$	$-\chi \cdot 10^6$ mean
$\left[ \text{Pt} \begin{array}{c} \text{py} \\ (\text{NH}_3)_3 \end{array} \right] \text{Cl}_2$	20°.5	0.430	0.436
		0.442	
$\left[ \text{Pt} \begin{array}{c} \text{PY}_2 \\ (\text{NH}_3)_2 \end{array} \right] \text{Cl}_2$	19°.0	0.391	0.397
		0.404	
$[\text{Pt}(\text{NH}_3)_4] \text{Cl}_2 \cdot \text{H}_2\text{O}$	I 18°.2	0.410	0.412
		0.404	
— — —	II 18°.5	0.413	
		0.419	
$[\text{Pten}_2] \text{Cl}_2$	19°.2	0.370	0.365
		0.359	
$\left[ \text{Pt} \begin{array}{c} \text{en} \\ (\text{NH}_3)_2 \end{array} \right] \text{Cl}_2$	20°.0	0.312	0.306
		0.301	
$\left[ \text{Pt} \begin{array}{c} (\text{NH}_3)_2 \\ (\text{C}_2\text{H}_5\text{NH}_2)_2 \end{array} \right] \text{Cl}_2$	19°.8	0.403	0.411
		0.418	
$\left[ \text{Pt} \begin{array}{c} \text{PY}_2 \\ \text{Cl}_2 \end{array} \right] \text{cis.}$	19°.5	0.409	0.417
		0.424	
$\left[ \text{Pt} \begin{array}{c} \text{PY}_2 \\ \text{Cl}_2 \end{array} \right] \text{trans}$	20°.5	0.415	0.421
		0.426	
$[\text{Pt}((\text{CH}_3)_2\text{NH})_3\text{Cl}_2]$	19°.0	0.386	0.379
		0.372	
$\left[ \begin{array}{c} (\text{CH}_3)_2\text{NH} \\ \text{Pt NH}_3 \\ \text{Br}_2 \end{array} \right]$	19°.2	0.313	0.321
		0.328	
$[\text{Pt}((\text{CH}_3)_2\text{NH})_4][\text{PtCl}_4]$	21°.0	0.394	0.387
		0.380	
$\left[ \text{Pt} \begin{array}{c} \text{NH}_3 \\ \text{Cl}_3 \end{array} \right]_2 [\text{Pt}(\text{NH}_3)_4]$	21°.0	0.332	0.327
		0.321	
$[\text{Pten}_2][\text{PtCl}_4]$	21°.0	0.301	0.306
		0.310	
$[\text{Pt}(\text{C}_2\text{H}_5\text{NH}_2)_4][\text{PtCl}_4]$	21°.5	0.336	0.344
		0.350	

	Temperature	$-\chi \cdot 10^6$	$-\chi \cdot 10^6$ mean
$\left[ \text{Pt} \begin{matrix} (\text{NH}_3)_2 \\ ((\text{CH}_3)_2\text{NH})_2 \end{matrix} \right] [\text{PtCl}_4] \text{H}_2\text{O}$	20°.0	0.309	0.316
		0.322	
$\left[ \text{Pt} \begin{matrix} \text{PY} \\ (\text{NH}_3)_3 \end{matrix} \right] [\text{PtCl}_4]$	20°.5	0.294	0.292
		0.290	
$[\text{Pt} (\text{NH}_3)_4] [\text{PtCl}_4]$ green	21°.5	0.299	0.306
		0.310	
$[\text{Pt} (\text{NH}_3)_4] [\text{PtCl}_4]$ red	21°.5	0.290	0.293
		0.295	
$\left[ \text{Pt} \begin{matrix} \text{PY}_2 \\ (\text{NH}_3)_2 \end{matrix} \right] [\text{PtCl}_4]$	21°.5	0.300	0.307
		0.314	
$[\text{PtCl}_4] \text{K}_2$	20°.0	0.388	0.383
		0.377	
$[\text{Pt} (\text{NH}_2\text{C}_2\text{H}_4)_3\text{N}] \text{J}_2$	21°.5	0.432	0.440
		0.448	
$\left[ \text{Pt} \begin{matrix} (\text{NH}_3)_4 \\ (\text{CH}_3\text{CN})_2 \end{matrix} \right] \text{Cl}_2$	21°.5	0.391	0.398
		0.405	

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