

**719. Some Five-co-ordinate Complexes of Platinum(II).**

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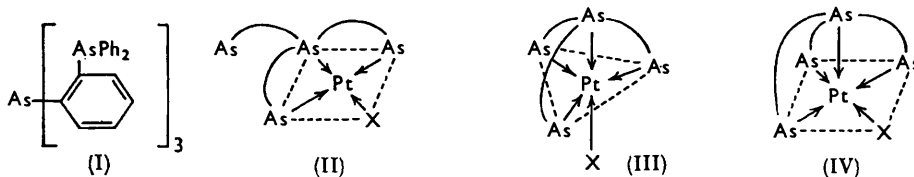
Tris-(*o*-diphenylarsinophenyl)arsine, QAS, forms complexes with platinum(II) of the type  $[\text{PtX}(\text{QAS})]\text{Y}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{and SCN}$ ;  $\text{Y} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}, \text{ClO}_4, \text{and BPh}_4$ ). In these complexes the platinum atom is five-co-ordinate both in solution and in the solid state.

Bis-(*o*-diphenylarsinophenyl)phenylarsine, TAS, on the other hand, forms complexes of the type  $[\text{PtI}(\text{TAS})]\text{X}$  ( $\text{X} = \text{I} \text{ and } \text{ClO}_4$ ), which are four-co-ordinate both in solution and in the solid state.

TRIS-(*o*-DIPHENYLARSINOPHENYL)ARSINE,<sup>1</sup> (QAS) (I), reacts with the halogen-complexes of platinum(II) to form derivatives of the type  $\text{PtX}_2(\text{QAS})$ . These compounds react with sodium perchlorate or sodium tetraphenylborate with replacement of one atom of halogen. The complexes prepared are listed in Table I. All the compounds are 1 : 1 electrolytes in nitrobenzene solution and thus are to be formulated as  $[\text{PtX}(\text{QAS})]\text{X}$  or  $[\text{PtX}(\text{QAS})]\text{Y}$ . Great interest attaches to the structure of these derivatives. The steric requirements

<sup>1</sup> Howell, Pratt, and Venanzi, *J.*, 1961, 3167.

of the tetradentate ligand are such that, if platinum(II) is to maintain its usual co-ordination number 4, only three of the arsenic atoms can be attached to the acceptor atom (see II). Alternatively, the complex could be five-co-ordinate with either a trigonal bipyramidal (III) or a tetragonal pyramidal arrangement (IV) of donor atoms.



The planar structure (II) can be ruled out on the following evidence:

(1) Addition of an excess of methyl iodide to a  $10^{-3}\text{M}$ -solution of  $[\text{PtCl}(\text{QAS})](\text{ClO}_4)$  in nitrobenzene caused no change in the conductance of the solution over a period of 24

TABLE I. Colour, melting point, and molar conductance of complexes of QAS and TAS of platinum(II).

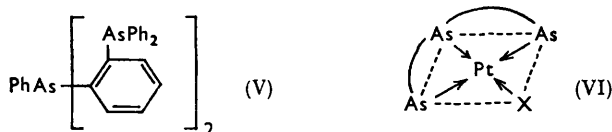
Compound	Colour	M. p.	$\Lambda_{\text{M}}^*$ (mho)
$[\text{PtCl}(\text{QAS})]\text{Cl}$	Yellow orange	338—339°	25.2 (18°)
$[\text{PtBr}(\text{QAS})]\text{Br}$	Orange	356—357	24.9 (19°)
$[\text{PtI}(\text{QAS})]\text{I}$	Maroon	364—365	25.3 (18°)
$[\text{Pt}(\text{SCN})(\text{QAS})](\text{SCN})$	Orange-yellow	332—333	30.5 (20°)
$[\text{PtCl}(\text{QAS})](\text{ClO}_4)$	Orange	363—364	27.0 (18°)
$[\text{PtI}(\text{QAS})](\text{ClO}_4)$	Orange	372—374	29.7 (20°)
$[\text{PtCl}(\text{QAS})][\text{BPh}_4]$	Orange	274—276	17.4 (18°)
$[\text{PtBr}(\text{QAS})][\text{BPh}_4]$	Orange-red	294—295	18.5 (18°)
$[\text{PtI}(\text{QAS})][\text{BPh}_4]$	Red	278—279	20.7 (20°)
$[\text{Pt}(\text{SCN})(\text{QAS})][\text{BPh}_4]$	Orange	257—258	16.0 (18°)
$[\text{PtI}(\text{TAS})]\text{I}$	Yellow	352—353	27.7 (20°)
$[\text{PtI}(\text{TAS})](\text{ClO}_4)$	Yellow	357—358	28.7 (20°)

\* Molar conductance of approx.  $10^{-3}\text{M}$ -solutions of the complexes in nitrobenzene.

hours. A control test with a  $1.102 \times 10^{-3}\text{M}$ -solution of the non-conducting QAS resulted in a steady increase in conductance due to quaternization of the arsenic atoms, the final value of the equivalent conductance being  $1.42 \mu\text{mho}$ . The values of the molar conductance, calculated on the basis of the formation of  $[(\text{QAS})\text{Me}]\text{I}$ ,  $[(\text{QAS})\text{Me}_2]\text{I}_2$ , and  $[(\text{QAS})\text{Me}_3]\text{I}_3$  are 50.8, 57.2, and 63.6 mho respectively, indicating the quaternization of at least three, arsenic atoms.

(2) The spectra of the QAS complexes differ significantly from those of the square-planar complexes of platinum(II). The low-frequency bands (20,000—28,000  $\text{cm}^{-1}$ ) have molar extinction coefficients of the order of  $10^3$ . These bands are about 10,000  $\text{cm}^{-1}$  lower in frequency than the corresponding band <sup>2</sup> in  $[\text{PtCl}(\text{NH}_3)_3]_2\text{SO}_4$  (see Fig. 1).

In order to check that the above frequency shifts are not due to the uncharged ligand, two complexes of bis-(*o*-diphenylarsinophenyl)phenylarsine (V) (TAS) were prepared. These



are listed in Table I. They are 1:1 electrolytes in nitrobenzene solution, and thus are to be formulated as  $[\text{PtX}(\text{TAS})]\text{Y}$  (VI), and their absorption spectra are very similar to that of the  $[\text{PtCl}(\text{NH}_3)_3]^+$  ion (see Fig. 2 and ref. 2).

<sup>2</sup> Chatt, Gamlen, and Orgel, *J.*, 1958, 486.

If the QAS complexes were planar, *i.e.*, of type (II), one would find that their spectra would be similar to those of the TAS complexes. Thus, we have additional evidence in favour of the formation of five-co-ordinate complexes. The band shifts, on going from the TAS to the QAS complexes, are towards longer wave-lengths as would be expected on a crystal-field model.<sup>3</sup>

(3) Comparison of the spectra of the series  $[\text{PtX}(\text{QAS})]\text{Y}$   $\{\text{X} = \text{Cl}$  and  $\text{I}$ ;  $\text{Y} = \text{Cl}$  (or  $\text{I}$ ),  $\text{ClO}_4$ , and  $\text{BPh}_4\}$  shows that the replacement of one donor ion ( $\text{Cl}$  or  $\text{I}$ ) by a non-donor one does not cause a shift in frequency of the absorption bands of the complexes (see Fig. 3). Intensity differences are, however, observed.

FIG. 1. *Absorption spectra of complexes  $[\text{PtX}(\text{QAS})]\text{X}$ .*

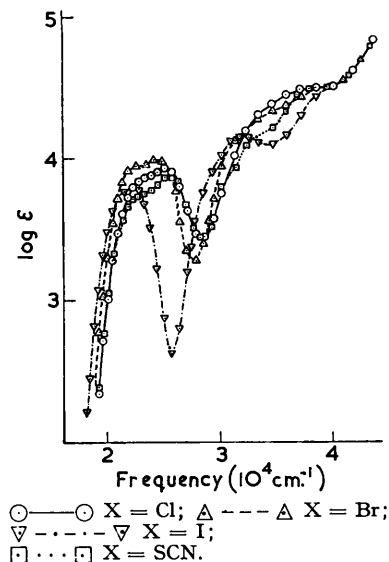
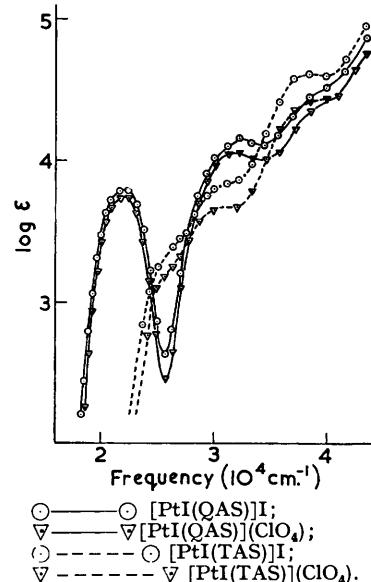


FIG. 2. *Comparison of the absorption spectra of (QAS) and (TAS) complexes.*



While we can postulate five-co-ordination in solutions of complexes of QAS it might be argued that these structures do not persist in the solid state. We have evidence, however, that no structural changes accompany the process of solution:

(a) The reflection spectra of the solid QAS complexes are very similar to those of their methanol solutions (see Figs. 4 and 5).

(b) The infrared spectrum of solid  $[\text{Pt}(\text{SCN})(\text{QAS})](\text{SCN})$  shows clearly two bands attributable to the CN stretching vibration, one at  $2120$  and the other at  $2060 \text{ cm}^{-1}$ . The former corresponds to a co-ordinated thiocyanate and the latter to a free thiocyanate group.<sup>4</sup>

Our experiments do not allow a choice between the trigonal bipyramidal structure (III) and the tetragonal pyramidal one (IV) for the five-co-ordinate complexes, but examination of molecular models indicates the former as the more probable.

Harris *et al.*<sup>5</sup> have described a series of complexes of platinum(II) co-ordinated to four arsenic atoms: these are derivatives of the diarsine  $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$  (DAS) and are of the type  $[\text{PtX}(\text{DAS})_2]\text{Y}$  ( $\text{X} = \text{halide ion}$ ,  $\text{Y} = \text{halide ion}$  or other anion). Harris *et al.*, however, do not report the spectra of their compounds either in solution or in the solid

<sup>3</sup> Basolo and Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, 1958, p. 55.

<sup>4</sup> Pecile, Giacometti, and Turco, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1960, **28**, 189, and previous references quoted therein.

<sup>5</sup> Harris, Nyholm, and Phillips, *J.*, 1960, 4379.

state and thus no direct comparison between the DAS and the QAS complexes is possible.

It is, however, interesting that the DAS complexes of Harris *et al.* have colours which are like those of our TAS complexes but are lighter than those of the QAS complexes. This might be taken as an indication that the characteristic band in the range 20,000—28,000  $\text{cm}^{-1}$  is absent for the complexes of the diarsine (DAS).

An attempt was made to see whether more than one molecule of TAS could be co-ordinated to a platinum atom. Addition of TAS to a nitrobenzene solution of  $[\text{PtI}(\text{TAS})]\text{I}$

FIG. 3. Comparison of the spectra of complexes  $[\text{PtCl}(\text{QAS})]\text{Y}$ .

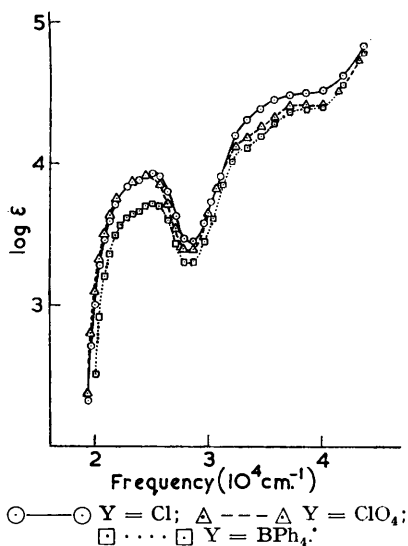


FIG. 4. Reflectance spectra of complexes  $[\text{PtX}(\text{QAS})]\text{X}$ .

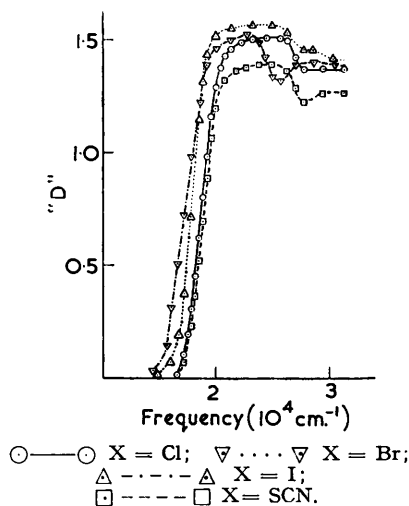
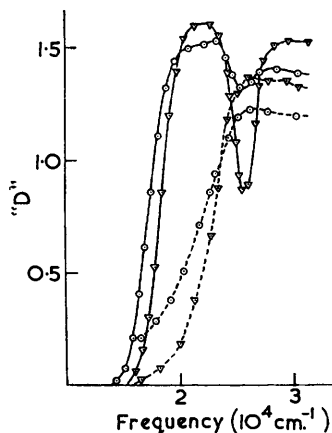
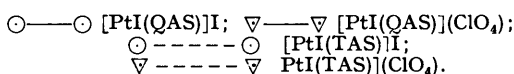


FIG. 5. Reflectance spectra of (QAS) and (TAS) complexes.



showed no increase in conductance and we conclude that the tendency of platinum(II) to form six-co-ordinate complexes with our tridentate arsenic ligands is, at best, very slight.

Powell and his co-workers have carried out *X*-ray structural investigations on the compounds  $\text{MX}_2\text{MeAs}(\text{CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2)_2$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{and Pt}$ ). The nickel derivative is five-co-ordinate in the solid state, with the structure of a distorted tetragonal pyramid, while the palladium and platinum derivatives are four-co-ordinate in the solid state, with near-planar co-ordination around the central metal atom and should, therefore,

be formulated as  $[\text{MX}\{\text{MeAs}(\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{AsMe}_2)_2\}]\text{X}$ .<sup>7</sup> Our TAS complexes are obviously of the same type.

[*Added in proof:* An X-ray structural study of  $[\text{PtI}(\text{QAS})][\text{BPh}_4]$ <sup>8</sup> confirms the trigonal bipyramidal co-ordination at the platinum atom as in (III).]

## EXPERIMENTAL

Preparation of the arsines is described elsewhere.<sup>1</sup>

*Halogeno[tris-(o-diphenylarsinophenylarsine)]platinum(II) Salts.*—The *chloro-chloride*  $[\text{PtCl}(\text{QAS})]\text{Cl}$ . Sodium chloroplatinite tetrahydrate (0.23 g.) in ethanol (25 c.c.) was added gradually to a boiling suspension of the arsine (0.55 g.) in ethanol (50 c.c.). The mixture was refluxed for 2 hr. and the yellow solution filtered from a small amount of brown solid. Evaporation of the filtrate gave the crude *product* (0.57 g.) which was purified by repeated recrystallisation from chlorobenzene (yield 0.23 g.) (Found: Pt, 15.5.  $\text{C}_{54}\text{H}_{42}\text{As}_4\text{Cl}_2\text{Pt}$  requires Pt, 15.5%).

*The bromo-bromide*,  $[\text{PtBr}(\text{QAS})]\text{Br}$ . Sodium chloroplatinite (0.46 g.) and sodium bromide (0.52 g.) in ethanol (80 c.c.) were treated with the arsine (1.10 g.) as above. The *product* (1.04 g.) recrystallised from nitromethane (yield 0.5 g.) (Found: Pt, 14.25.  $\text{C}_{54}\text{H}_{42}\text{As}_4\text{Br}_2\text{Pt}$  requires Pt, 14.5%).

*The iodo-iodide*  $[\text{PtI}(\text{QAS})]\text{I}$ . Sodium iodoplatinite, prepared from the chloro-complex (0.23 g.) and sodium iodide (0.37 g.) in ethanol (35 c.c.), was added to a suspension of the arsine (0.55 g.) in ethanol (30 c.c.), and the mixture was refluxed for 4 hr. The solid *product* recrystallised from nitromethane (yield 70%) (Found: Pt, 13.7; C, 44.6; H, 2.9.  $\text{C}_{54}\text{H}_{42}\text{As}_4\text{I}_2\text{Pt}$  requires Pt, 13.55; C, 45.1; H, 2.8%).

*The thiocyanato-thiocyanate*,  $[\text{Pt}(\text{SCN})(\text{QAS})(\text{SCN})]$ . Prepared as above from  $\text{Na}_2\text{PtCl}_4\cdot 4\text{H}_2\text{O}$  (0.46 g.), potassium thiocyanate (0.46 g.), and the arsine (1.1 g.). The *product* was obtained by evaporation of the solution and purified by recrystallisation from butanol (Found: Pt, 14.9; C, 52.1; H, 3.15; N, 2.3.  $\text{C}_{56}\text{H}_{42}\text{As}_4\text{N}_2\text{PtS}_2$  requires Pt, 15.0; C, 51.7; H, 3.25; N, 2.15%).

*The chloro-perchlorate*,  $[\text{PtCl}(\text{QAS})](\text{ClO}_4)$ . A solution of  $[\text{PtCl}(\text{QAS})]\text{Cl}$  (from 0.69 g. of  $\text{Na}_2\text{PtCl}_4\cdot 4\text{H}_2\text{O}$ ) in ethanol (180 c.c.) and chloroform (70 c.c.) was treated with a solution of sodium perchlorate (0.5 g.) in ethanol (20 c.c.). The *product* (1.85 g.) was precipitated slowly, and after filtration was recrystallised from nitromethane (yield 1.15 g.) (Found: Pt, 14.9; C, 48.8; H, 3.2.  $\text{C}_{54}\text{H}_{42}\text{As}_4\text{Cl}_2\text{O}_4\text{Pt}$  requires Pt, 14.8; C, 49.1; H, 3.2%).

*The iodo-perchlorate*,  $[\text{PtI}(\text{QAS})](\text{ClO}_4)$ . Prepared analogously to the chloro-complex from 0.69 g. of sodium chloroplatinite. Evaporation of the solution was necessary to obtain the *product* (1.6 g.) which recrystallised from nitromethane (yield 0.5 g.) (Found: Pt, 13.8; C, 46.15; H, 2.8; I, 9.3.  $\text{C}_{54}\text{H}_{42}\text{As}_4\text{ClIO}_4\text{Pt}$  requires Pt, 13.8; C, 45.9; H, 3.0; I, 9.0%).

*The chloro-tetraphenylborate*,  $[\text{PtCl}(\text{QAS})][\text{BPh}_4]$ . A solution of  $[\text{PtCl}(\text{QAS})]\text{Cl}$  was treated with the stoichiometric amount of sodium tetraphenylborate in ethanol. The precipitated *salt* was filtered off and recrystallised from anisole (yield 45%) (Found: Pt, 12.4; C, 60.6; H, 4.3.  $\text{C}_{78}\text{H}_{68}\text{As}_4\text{BClPt}$  requires Pt, 12.6; C, 60.6; H, 4.4%).

*The bromo-tetraphenylborate*,  $[\text{PtBr}(\text{QAS})][\text{BPh}_4]$ . This *salt* was prepared analogously to the chloro-complex and recrystallised from nitromethane (Found: Pt, 12.2; C, 58.2; H, 3.75; Br, 4.9.  $\text{C}_{78}\text{H}_{68}\text{As}_4\text{BBrPt}$  requires Pt, 12.3; C, 58.9; H, 4.3; Br, 5.0%).

*The iodo-tetraphenylborate*,  $[\text{PtI}(\text{QAS})][\text{BPh}_4]$ , was prepared and purified analogously to the corresponding perchlorate (Found: Pt, 11.6.  $\text{C}_{78}\text{H}_{68}\text{As}_4\text{BIPt}$  requires Pt, 11.9%).

*The thiocyanato-tetraphenylborate*,  $[\text{Pt}(\text{SCN})(\text{QAS})][\text{BPh}_4]$ , was prepared and purified analogously to the chloro-compound (Found: Pt, 12.4; C, 60.8; H, 3.9; N, 1.0.  $\text{C}_{79}\text{H}_{68}\text{As}_4\text{BNPtS}$  requires Pt, 12.4; C, 60.5; H, 4.4; N, 0.9%).

*Iodo[bis-(o-diphenylarsinophenyl)phenylarsine]platinum(II) Salts.*—The *iodo-iodide*,  $[\text{PtI}(\text{TAS})]\text{I}$ , was prepared and purified analogously to the QAS complex (yield 30%) (Found: Pt, 16.2; C, 41.55; H, 2.7.  $\text{C}_{42}\text{H}_{33}\text{As}_3\text{I}_2\text{Pt}$  requires Pt, 16.1; C, 41.6; H, 2.75%).

*The iodo-perchlorate*,  $[\text{PtI}(\text{TAS})](\text{ClO}_4)$ , was prepared and purified analogously to the QAS complex (yield 30%) (Found: Pt, 11.5.  $\text{C}_{42}\text{H}_{33}\text{As}_3\text{IO}_4\text{Pt}$  requires Pt, 11.05%).

<sup>6</sup> Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publ. Inc., New York 1959, p. 726.

<sup>7</sup> Mair, Powell, and Henn, *Proc. Chem. Soc.*, 1960, 415, and personal communication.

<sup>8</sup> Mair, Powell, and Venanzi, *Proc. Chem. Soc.*, 1961, 170.

*Analyses.*—Platinum analyses were carried out spectrophotometrically by the stannous chloride method.\* “Ashing” of the sample before the determination of platinum was done by using equal amounts of concentrated nitric acid and 72% perchloric acid and refluxing on a sand-bath for several hours. After evaporation of the acids, the residue was treated

TABLE 2. *Frequency of maxima ( $\nu_{\max}$ ), and maximum extinction coefficients ( $\epsilon$ ) in the absorption spectra of platinum(II) complexes of QAS and TAS.*

Compound	Solution		Solid	“D”
	$10^3\nu_{\max}$	$10^3\epsilon$	$10^3\nu_{\max}$	
[PtCl(QAS)]Cl .....	22.99 sh	7.19 *	21.0—26.0	1.50
	25.13	8.60		
	36.77 sh	30.8 *		
	42.74 sh	61.3 *		
[PtBr(QAS)]Br .....	22.32 sh	8.79 *	20.0—26.0	1.56
	24.21	10.0		
	34.48 sh	21.8 *		
	42.55 sh	66.0 *		
	20.83 sh	5.24 *		
[PtI(QAS)]I .....	22.12	6.30	20.0—23.5	1.52
	31.75	12.8 *		
	42.55 sh	62.5 *		
[Pt(SCN)(QAS)](SCN) .....	22.32 sh	5.26 *	21.0—26.0	1.39
	25.25	7.36		
	38.31 sh	32.6 *		
	42.74 sh	60.8 *		
	22.22 sh	6.48 *		
[PtCl(QAS)](ClO <sub>4</sub> ) .....	24.75	8.20	21.0—25.5	1.55
	36.10 sh	23.7 *		
	42.55 sh	54.7 *		
	20.83 sh	4.62 *		
[PtI(QAS)](ClO <sub>4</sub> ) .....	22.22	5.54	21.0—23.0	1.59
	31.75 sh	11.4 *		
	42.55 sh	47.0 *		
	22.94 sh	4.22 *		
	25.32	5.16		
[PtCl(QAS)][BPh <sub>4</sub> ] .....	36.36 sh	22.6 *	21.0—25.2	1.61
	42.55 sh	50.5 *		
	21.98 sh	3.68 *		
	24.39	4.19		
	37.04 sh	25.8 *		
[PtBr(QAS)][BPh <sub>4</sub> ] .....	42.55 sh	49.0 *	Not recorded	
	20.83 sh	3.40 *		
	22.47	3.91		
	31.25 sh	10.2 *		
	42.55 sh	55.0 *		
[PtI(QAS)][BPh <sub>4</sub> ] .....	22.22 sh	3.04 *	Not recorded	
	25.32	4.58		
	37.74 sh	24.7 *		
	42.55 sh	62.0 *		
	29.41 sh	5.8 *		
[PtI(TAS)]I .....	38.46	41.0	26.5 broad	1.36
	45.46 sh	54 *		
	29.41 sh	4.2 *		
[PtI(TAS)](ClO <sub>4</sub> ) .....	36.63 sh	21.7 *	26.7 broad	1.22
	42.55 sh	42 *		
	29.41 sh	4.2 *		
	36.63 sh	21.7 *		

sh = shoulder. \* Extinction coefficients at the point of inflection.

twice with concentrated hydrochloric acid (5 c.c.), and the solution evaporated to dryness. The residue was then used for the determination of platinum.

*Conductance Measurements.*—These were done with  $\sim 10^{-3}$ M-solutions of the complexes in nitrobenzene, a type E 7566 Mullard conductivity bridge being used. A cell with bright platinum electrodes was used, the cell constant being 0.345.

*Measurements of the Absorption Spectra.*—The spectra of solutions (in methanol) were measured at room temperature on a Beckman Ratio Recording Spectrophotometer over the range 10,000—50,000  $\text{cm}^{-1}$ .

The reflectance spectra of the finely powdered solids were measured on a Unicam S.P. 500

spectrophotometer fitted with a Unicam diffuse reflection attachment, S.P. 540, and magnesium carbonate as the reference substance.

The values of  $\nu_{\max}$  and the corresponding extinction coefficients,  $\epsilon$ , are listed in Table 2. The intensity of absorption in the reflection spectra is given on an arbitrary scale, "D," which varies from compound to compound.

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