301. *Some Five-co-ordinate Complexes of Palladium*(II).

By C. A. Savage and L. M. Venanzi.

Palladium(II) with tris-*o*-diphenylarsinophenylarsine (QAS) forms complexes of the type $[PdX(QAS)]^+$ which are analogous to the platinum(II) derivatives and thus have been attributed trigonal bipyramidal co-ordination. Of the complexes with bis-(*o*-diphenylarsinophenyl)phenylarsine (TAS), the complex $[PdI_2(TAS)]$ appears to be four-co-ordinate in methanol solution and five co-ordinate in the solid state and in benzene solution.

The recent isolation and characterisation [1] of some complexes of platinum(II) with tris-*o*-diphenylarsinophenylarsine (QAS) (I) of the type [PtX(QAS)]Y (X = Cl, Br, I, or SCN; Y = Cl, Br, I, SCN, ClO_4, or BPh_4), and the observation that the platinum atom in these complexes has trigonal bipyramidal co-ordination,[2] prompted the preparation and investigation of their palladium(II) analogues.

Complexes of the type [PdX(QAS)]X are obtained on mixing the appropriate palladium salt with the arsine. They are 1 : 1 electrolytes in nitrobenzene solution, their conductivity is not increased by the addition of methyl iodide, and one of the anionic ligands can be replaced by perchlorate or tetraphenylborate. Thus the palladium derivatives are fully analogous to the platinum ones.[1]

For comparison, two complexes of bis-(*o*-diphenylarsinophenyl)phenylarsine (TAS) (II)

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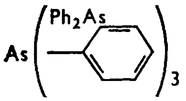
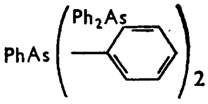
[1] Brewster, Savage, and Venanzi, *J.*, 1961, 3699.

[2] Mair, Powell, and Venanzi, *Proc. Chem. Soc.*, 1961, 170.

were also prepared. All the complexes which were characterised are listed in Table 1. These palladium complexes are formed more easily, and decompose more easily, than the corresponding complexes of platinum, in agreement with the general chemistry of the two elements.

(I) 

 (II)

To check that the complexes had the structure attributed to them, their infrared spectra were examined in the region 4000—650 cm.$^{-1}$. All the bands observed could be attributed either to the arsenic ligand or to the anions present.

The visible and ultraviolet spectra of the palladium complexes with the tetradentate ligand are consistent with trigonal bipyramidal co-ordination at the palladium atom. The long-wavelength band, which is characteristic of complexes of platinum(II) of that structure,[1] occurs between 500 and 600 mμ in the palladium series (see Table 2 and Figs. 1 and 2). The shift towards longer wavelength caused by the replacement of platinum by palladium is consistent with the spectral properties of complexes of the two elements. The complex $[PdI(TAS)](ClO_4)$, which is expected to be four-co-ordinate and planar, does not show the long-wavelength band (see Table 2 and Fig. 2). Further, reflection spectra (see Table 2 and Fig. 3) confirm persistence of the postulated structures in the solid state.

TABLE 1.

Colour, decomposition point, and molar conductance of QAS and TAS complexes of palladium(II).

Compound	Colour	Decomp. pt.	Λ_M (19°) (mho) *
$[PdCl(QAS)]Cl$	Dark red-purple	276—279°	23·1
$[PdBr(QAS)]Br$	Dark purple	281—283	17·6
$[PdI(QAS)]I$	Very dark purple	285—287	15·3
$[Pd(SCN)(QAS)](SCN)$	Red-purple	281—284	20·4
$[PdCl(QAS)](ClO_4)$	Dark red-purple	315—316	25·2
$[Pd(SCN)(QAS)](ClO_4)$	Dark red-purple	289—292	27·1
$[PdCl(QAS)](BPh_4)$	Very dark purple	253—255	16·0
$[PdI(QAS)](BPh_4)$	Purple-brown	247—250	13·1
$[PdI_2(TAS)]$	Orange-red	302—303	9·4
$[PdI(TAS)](ClO_4)$	Orange	327—328	25·1

* In nitrobenzene.

The complex $[PdI_2(TAS)]$, however, differs from the iodo-perchlorate. The reflection spectrum and the solution spectrum in benzene show long-wavelength bands at *ca.* 550 and 463 mμ, respectively, while the solution spectrum in methanol is identical with that of the iodo-perchlorate (see Figs. 2 and 3). These observations can be explained if it is assumed that $[PdI_2(TAS)]$ is five-co-ordinate in the solid state and in benzene solution, and that it is four-co-ordinate in methanol solution. The value of the molar conductance in nitrobenzene solution indicates that an equilibrium of the type $[PdI_2(TAS)] \rightleftharpoons [PdI\{TAS)]^+ + I^-$ is established. This is supported by the conductometric titration of $[PdI(TAS)](ClO_4)$ with $[Ph_3MeAs]I$ (see Fig. 4).

The stereochemistry of $[PdI_2(TAS)]$ could be either trigonal bipyramidal (III) or tetragonal pyramidal (IV). Since molecular models show that the triarsine, TAS, can form complexes of type (III) or (IV) most easily, we believe that $[PdI_2(TAS)]$ has structure (IV), unlike that found in $NiBr_2,MeAs(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}AsMe_2)_2$.[3]

Henn and Powell[4] have established that in the complex $PdI_2,MeAs(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}AsMe_2)_2$ the palladium atom is four-co-ordinate, and it is

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[3] Mair, Powell, and Henn, *Proc. Chem. Soc.*, 1960, 415.

[4] Henn and Powell, personal communication.

TABLE 2.

Wavelength ($\lambda_{\text{max.}}$; mμ), energy ($E_{\text{max.}}$; cm.$^{-1}$) and intensity ($\varepsilon_{\text{max.}}$) in the absorption spectra of complexes of palladium(II) with TAS and QAS.

	Methanol solution			Solid	
	$\lambda_{\text{max.}}$ (mμ)	E (cm.$^{-1}$)	ε	$\lambda_{\text{max.}}$ (mμ)	" *D* "
[PdCl(QAS)]Cl	535(sh)	18,690(sh)	5990 *		
	480	20,830	7540		
	260(sh)	38,460(sh)	28,300 *		
[PdCl(QAS)](ClO$_4$)	535(sh)	18,690(sh)	6700 *		
	480	20,830	8340		
	260(sh)	38,460(sh)	26,600 *		
[PdCl(QAS)][BPh$_4$]	535(sh)	18,690(sh)	4000 *		
	484	20,700	7200		
	296(sh)	33,780(sh)	54,000 *		
[PdBr(QAS)]Br	535(sh)	18,690(sh)	4500 *		
	480	20,830	5820		
	ca. 375(sh)	26,600(sh)	28,300 *		
	ca. 580(sh)	17,200(sh)	3940 *		
[PdI(QAS)]I	535	18,690	6300		
	384	26,040	7530		
	292(sh)	34,250(sh)	19,600 *		
[PdI(QAS)][BPh$_4$]	*ca.* 580(sh)	17,200(sh)	3690 *	500—600	1·59—1·6
	535	18,690	6730	440—370	1·50
	384	26,040	8330		
	295(sh)	33,900(sh)	25,000 *		
[Pd(SCN)(QAS)](SCN)	530	18,870	6440		
	455	21,980	8260		
	372	26,880	7280		
	310(sh)	21,500(sh)	21,500 *		
	264(sh)	37,880(sh)	27,600 *		
[Pd(SCN)(QAS)][BPh$_4$]	532	18,800	6060		
	453	22,080	7880		
	372	26,880	6020		
	310(sh)	32,260(sh)	18,900 *		
	260(sh)	38,460(sh)	26,500 *		
[PdI(TAS)]I	465(sh)	21,510(sh)	1800 *		
	403	24,810	3740		
	306	32,680	24,500		
	272(sh)	36,760(sh)	22,200 *		
	252(sh)	39,680(sh)	29,100 *		
[PdI(TAS)](ClO$_4$)	465(sh)	21,510(sh)	1740 *	*ca.* 640(sh)	1·41 *
	403	24,810	3800	395	1·44
	306	32,680	26,300		
	270(sh)	37,040(sh)	25,700 *		
	252(sh)	39,680(sh)	83,000 *		
	Benzene solution				
[PdI$_2$(TAS)]	463	21,600	5140	*ca.* 550(sh)	1·40 *
	312(sh)	32,050(sh)	25,500 *	460—500	1·42
	387	34,840	32,800	435	1·44

* Extinction coefficient at the point of inflection.

interesting to speculate why palladium(II) complexes with such similar ligands should show different co-ordination numbers. We have evidence that, in complexes of nickel(II), the donor atom of triarylphosphines is a weaker π-electron acceptor than the phosphorus atom in trialkylphosphines,[5] and we believe that this will apply also to tertiary arsines, and that this generalisation can be extended to complexes of palladium(II) and platinum(II). Further, we have evidence that d^8-ions, *e.g.*, Pd(II) and Pt(II), make use of the p_z-orbital, hybridised with a d-orbital, to form π-bonds to suitable ligands.[6] We, therefore, conclude that since the M–AsR$_3$ bonds are expected to have greater π-bond character than M–AsAr$_3$ bonds; the metal p_z-orbital will be more engaged in bonding in the alkyl

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[5] Browning, Mellor, Morgan, Pratt, Sutton, and Venanzi, *J.*, **1962**, 693, and references cited therein.

[6] Chatt and Duncanson, *J.*, **1953**, 2939.

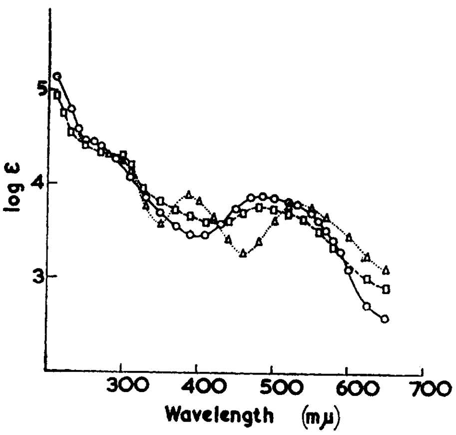


FIG. 1. Visible and ultraviolet spectra of the complexes [PdX(QAS)]X in methanol solution: X = Cl (○), Br (□), I (△).

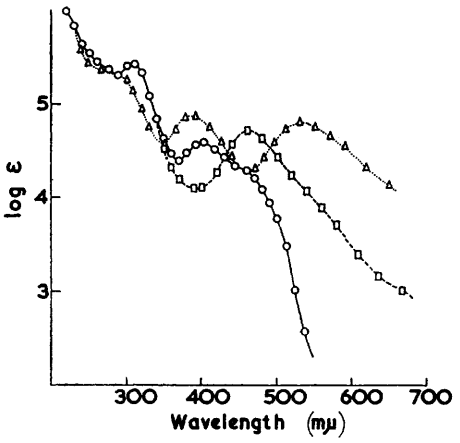


FIG. 2. Visible and ultraviolet spectra of (○) [PdI(TAS)]X (X = I and ClO_4) in methanol solution, (□) $PdI_2(TAS)$ in benzene solution, (△) PdI(QAS) I in methanol solution.

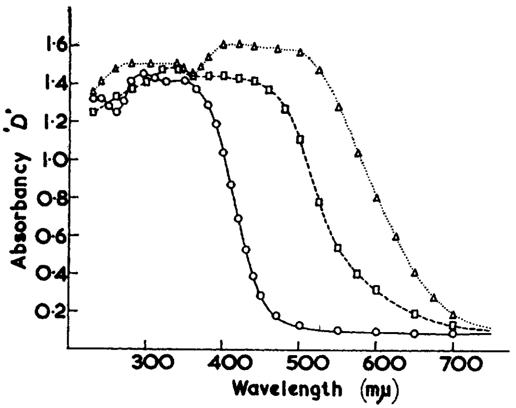


FIG. 3. Reflection spectra of (□) [PdI_2(TAS)], (○) [PdI(TAS)](ClO_4), (△) [PdI(QAS)][BPh_4].

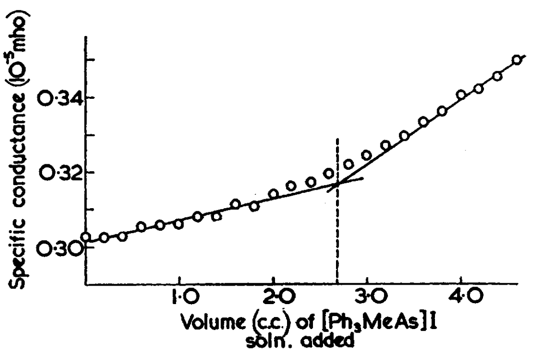
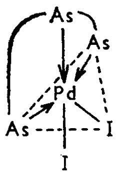
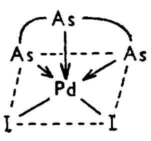


FIG. 4. Conductometric titration of [PdI(TAS)](ClO_4) with [Ph_3MeAs]I in nitrobenzene solution. The broken line is drawn at the equivalence point.

than in the aryl derivatives, and thus less available for the formation of an additional σ-bond. This effect could account for the difference in co-ordination number observed.



(III)



(IV)

The observation that there is a difference in co-ordination number of palladium but not of platinum is in good agreement with the general observation that the amount of metal–ligand π-bonding increases in order Ni < Pd < Pt.[7]

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[7] Ahrland, Chatt, and Davies, *Quart. Rev.*, 1958, **12**, 265.

EXPERIMENTAL

Preparation of the arsines is described elsewhere.[8]

Halogenotris-(o-*diphenylarsinophenylarsine*)*platinum*(II) *Salts.—The chloro-chloride* [PdCl(QAS)]Cl. Sodium chloropalladite tetrahydrate (0·2 g.) in ethanol (15 c.c.) was added to a boiling suspension of the arsine (0·5 g.) in ethanol (100 c.c.)–chloroform (5 c.c.). The mixture was refluxed for 5 hr. and the solvents were removed at the water-pump. The residue was extracted with dichloromethane, and the solution evaporated to dryness. The residual *complex* (0·4 g.) was recrystallised twice from chlorobenzene (Found: Pd, 9·05. $C_{54}H_{42}As_4Cl_2Pd$ requires Pd, 9·1%).

The bromo-bromide, [PdBr(QAS)]Br. Palladous bromide (0·37 g.), the arsine (0·75 g.), and lithium bromide (0·1 g.) were refluxed in ethanol (100 c.c.) for 4 hr. The crude *product* (0·93 g.) was obtained as indicated above and it was purified by recrystallisation from nitromethane (Found: Pd, 8·2. $C_{54}H_{42}As_4Br_2Pd$ requires Pd, 8·5%).

The iodo-iodide, [PdI(QAS)]I, was prepared and purified analogously to the bromo-bromide. Palladous iodide (0·28 g.), the arsine (0·75 g.) and sodium iodide (0·1 g.) gave 0·87 g. of crude product (Found: Pd, 8·1. $C_{54}H_{42}As_4I_2Pd$ requires Pd, 7·9%).

The thiocyanato-thiocyanate, [Pd(SCN)(QAS)](SCN), was prepared and purified analogously to the bromo-bromide. Palladous thiocyanate (0·33 g.), the arsine (0·75 g.) and potassium thiocyanate (0·1 g.) gave 0·83 g. of crude product (Found: Pd, 8·95. $C_{56}H_{42}As_4N_2PdS_2$ requires Pd, 8·8%).

The chloro-perchlorate, [PdCl(QAS)](ClO_4). Sodium perchlorate (0·07 g.) in ethanol (10 c.c.) was added to a solution of the chloro-chloride (0·57 g.) in 1 : 1 ethanol–chloroform (100 c.c.), and the mixture was left overnight. Evaporation left the crude *product* (0·6 g.) which recrystallised from nitromethane (Found: Pd, 8·9. $C_{54}H_{42}As_4Cl_2O_4Pd$ requires Pd, 8·7%).

The thiocyanato-perchlorate, [Pd(SCN)(QAS)](ClO_4), was prepared and purified analogously to the chloro-perchlorate (Found: Pd, 8·5. $C_{55}H_{42}As_4ClNO_4PdS$ requires Pd, 8·5%).

The chloro-tetraphenylborate, [PdCl(QAS)][BPh_4], was prepared and purified analogously to the chloro-perchlorate (sodium tetraphenylborate being used instead of sodium perchlorate) (Found: Pd, 7·2. $C_{78}H_{62}As_4BClPd$ requires 7·35%).

The iodo-tetraphenylborate, [PdI(QAS)][BPh_4]. The iodo-iodide (0·38 g.) and sodium tetraphenylborate (0·1 g.), suspended in 1 : 1 ethanol–chloroform (150 c.c.), were shaken for 3 days. After evaporation of the solvent the *product* was recrystallised twice from nitromethane (Found: Pd, 6·9. $C_{78}H_{62}As_4BIPd$ requires Pd, 6·9%).

Iodobis-(o-*diphenylarsinophenylphenylarsine*)*palladium*(II) *Salts.*—The *di-iodo-complex,* [PdI_2(TAS)], was prepared and purified analogously to the QAS complex (Found: Pd, 9·2. $C_{42}H_{33}As_3I_2Pd$ requires Pd, 9·5%).

The *iodo-perchlorate,* [PdI(TAS)](ClO_4). The crude di-iodo-complex (from 0·5 g. of palladous iodide) in 1 : 1 dichloromethane–alcohol (*ca.* 200 c.c.) was treated with silver perchlorate (0·2 g.) in ethanol (10 c.c.). After filtration from silver iodide, the *product* was obtained by evaporation and recrystallised from nitromethane (Found: Pd, 9·5. $C_{42}H_{33}As_3ClIO_4Pd$ requires Pd, 9·7%).

Analyses.—Palladium was determined spectrophotometrically by the method of Menis and Rains.[9] " Ashing " of the sample was carried out as described elsewhere.[1]

Measurements of Conductance and Absorption Spectra.—These were carried out as described elsewhere.[1]

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[8] Howell, Pratt, and Venanzi, *J.*, 1961, 3167.

[9] Menis and Rains, *Analyt. Chem.*, 1955, **27**, 1932.