

292. Spectrophotometric Evidence for the Solvation of Halogenopalladate(II) Ions by Various Polar Solvents.

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The visible and ultraviolet spectra of the halogenopalladate(II) ions $[\text{PdX}_4]^{2-}$ ($\text{X} = \text{Cl}$ or Br) and $[\text{Pd}_2\text{X}_6]^{2-}$ ($\text{X} = \text{Cl}$, Br , or I) have been measured in a range of polar solvents and in the solid state. The two ionic species $[\text{PdX}_4]^{2-}$ and $[\text{Pd}_2\text{X}_6]^{2-}$ exhibit absorption maxima at the same wavelengths in the same solvent. Solutions of the bromo-complexes display a progressive shift of the maxima towards shorter wavelengths if the solvents are arranged in the sequence: $\text{Ph}\cdot\text{NO}_2$, Ac_2O , $\text{Me}\cdot\text{NO}_2$, COME_2 , MeOH , MeCN , H_2O . This is attributed to the formation of sexicovalent solvated ions, particularly since the maxima occur at much longer wavelengths in the spectra of the solid compounds. Similar results were obtained for the chloro- and iodo-palladate(II) complexes.

BIVALENT palladium usually forms quadricovalent complexes which are diamagnetic and square-planar. This configuration is associated with $4d5s5p^2$ hybridisation of the palladium atomic orbitals. This square-planar arrangement has been verified by X-ray structure determinations on a number of complexes.¹ Recently, complexes of bivalent palladium with a co-ordination number greater than four have been described. The ligand *o*-phenylenebisdimethylarsine (diarsine) forms sexicovalent complexes of the type $[\text{Pd}(\text{diarsine})_2\text{X}_2]$ ($\text{X} = \text{Cl}$, Br , I , NO_2 , or SCN).² The di-iodo-complex possesses a distorted *trans*-octahedral structure in the solid state.³ In nitrobenzene solution these complexes behave as apparently quinquovalent uni-univalent electrolytes, $[\text{Pd}(\text{diarsine})_2\text{X}]\text{X}$. The sixth co-ordination position is most likely occupied by a molecule of solvent. Dimethyl-*o*-methylthiophenylarsine (thioarsine) forms compounds of the general formula, $\text{Pd}(\text{thioarsine})_2\text{X}_2$ ($\text{X} = \text{Cl}$, Br , or I), which also probably possess a distorted octahedral structure in the solid state.⁴ The higher complexes $[\text{PdCl}_6]^{3-}$ and $[\text{PdCl}_6]^{4-}$ have been postulated to occur in aqueous solution containing the $[\text{PdCl}_4]^{2-}$ ion and excess of chloride ion.⁵ Harris, Livingstone, and Reece,⁶ by a continuous-variation

¹ Wells, "Structural Inorganic Chemistry," Oxford University Press, 1950, p. 645.

² Harris and Nyholm, *J.*, 1956, 4375.

³ Harris, Nyholm, and Stephenson, *Nature*, 1956, 177, 1127.

⁴ Livingstone, *Chem. and Ind.*, 1957, 143; *J.*, 1958, 4222.

⁵ Sundaram and Sandell, *J. Amer. Chem. Soc.*, 1955, 77, 855.

⁶ Harris, Livingstone, and Reece, *Austral. J. Chem.*, 1957, 10, 282.

spectrophotometric study, have demonstrated the formation of the $[\text{PdBr}_6]^{4-}$ ion in nitrobenzene solutions of tetraethylammonium tetrabromopalladate(II) upon the addition of bromide ions. The existence of sixivalent palladium complexes such as $[\text{Pd}(\text{diarsine})_2\text{X}_2]$ has been attributed to the use by the palladium atom of two additional $5p5d$ bonds normal to the plane of the four $4d5s5p^2$ hybrid bonds.^{2,3} Sixivalent structures of this type would be expected to possess a distorted octahedral arrangement due to the repulsion of the filled non-bonding $4d_z^2$ orbital towards the bonding orbitals of the donor atoms of the ligand in the *trans*-octahedral positions.

The $[\text{PdBr}_4]^{2-}$ ion in nitrobenzene solution displays a strong absorption maximum at 427 $m\mu$; the extinction coefficient at this wavelength is appreciably lowered by the addition of excess of bromide ion.⁶ We have investigated further this reaction in methanol and water, so that the spectra could be obtained at shorter wavelengths and high concentrations of bromide ion. In Fig. 1 is shown the absorption spectrum in the visible and the ultraviolet region of the $[\text{PdBr}_4]^{2-}$ ion in *m*-perchloric acid; this acid was used to prevent hydrolysis of the $[\text{PdBr}_4]^{2-}$ ion, since the perchlorate ion does not form complexes with

FIG. 1. Absorption spectra of $\text{K}_2[\text{PdBr}_4]$: (I) in 1M-HClO₄; (II) in water containing Br^- ions in 20,000-fold excess (see Experimental section).

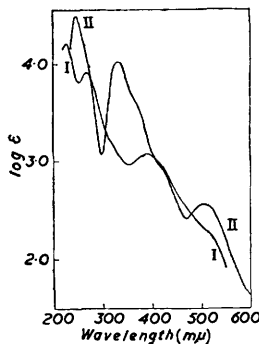
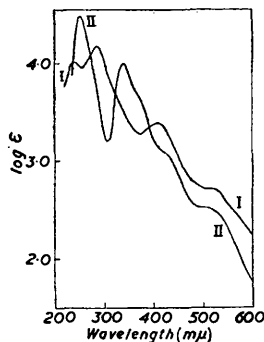


FIG. 2. Absorption spectra of $[\text{NEt}_4]_2[\text{PdBr}_4]$: (I) in MeOH; (II) in MeOH containing NEt_4Br in 1000-fold excess (see Experimental section).



palladium.⁷ This spectrum differs markedly from that of an aqueous solution of $[\text{PdBr}_4]^{2-}$ ions containing a large excess of bromide ions. Similar results are recorded in Fig. 2 for the $[\text{PdBr}_4]^{2-}$ ion in methanol with and without bromide ions. Whilst the spectra of solutions of $[\text{PdBr}_4]^{2-}$ ion in the presence of a large excess of bromide ion in methanol and water are very similar (see Table 1), owing to the formation of one or more higher complexes of bivalent palladium, it can be seen that there is a marked difference between the spectra

TABLE 1. Wavelengths (λ in $m\mu$) and extinction coefficients (ϵ) of maxima in the absorption spectra of tetrabromopalladate(II) ion in water and methanol solutions containing excess of bromide ion.*

Solvent	$\lambda_{\text{max.}}$	ϵ	$\lambda_{\text{max.}}$	ϵ	$\lambda_{\text{max.}}$	ϵ
Water	505	370	332	10,400	247	31,400
Methanol	508	335	341	10,000	252	31,600

* See Experimental section for concentrations used.

of the $[\text{PdBr}_4]^{2-}$ ion in methanol and aqueous *m*-perchloric acid, in that the absorption maxima are shifted to shorter wavelengths in water (see Table 2). This suggested strongly that the donor properties of the solvent affect the wavelengths of the maximum absorptions, owing to the formation of solvated $[\text{PdBr}_4]^{2-}$ ions, and led us to measure the spectra of the $[\text{PdBr}_4]^{2-}$ ion in a variety of solvents. The spectra of the dimeric halogen-bridged species $[\text{Pd}_2\text{Br}_6]^{2-}$ were also investigated for comparison, as we have recently

⁷ Livingstone, J., 1957, 5091.

shown that this ion exists in acetone and nitrobenzene solutions as well as in the solid state.⁸ The wavelengths and extinction coefficients of the absorption maxima are listed in Table 2.

TABLE 2. Wavelengths (λ in $m\mu$) and extinction coefficients (ϵ) of maxima in the absorption spectra of tetrabromopalladate(II) and tetrabromo- $\mu\mu'$ -dibromodipalladate(II) ions in various solvents.

Solvent	Compound	$\lambda_{max.}$	ϵ	$\lambda_{max.}$	ϵ	$\lambda_{max.}$	ϵ	$\lambda_{max.}$	ϵ
Ph·NO ₂	[NEt ₄] ₂ [PdBr ₄]	524	490	427	2600	<i>a</i>	—	<i>a</i>	—
	[NEt ₄] ₂ [Pd ₂ Br ₆]	525 (sh)	850	427	4750	<i>a</i>	—	<i>a</i>	—
Ac ₂ O	[NEt ₄] ₂ [PdBr ₄]	522	450	425	2800	<i>a</i>	—	<i>a</i>	—
	[NEt ₄] ₂ [Pd ₂ Br ₆]	520	900	424	5600	<i>a</i>	—	<i>a</i>	—
Me·NO ₂	[NEt ₄] ₂ [PdBr ₄]	510	400	419	2600	<i>a</i>	—	<i>a</i>	—
	[NEt ₄] ₂ [Pd ₂ Br ₆]	513	800	419	5300	<i>a</i>	—	<i>a</i>	—
COMe ₂	[NEt ₄] ₂ [PdBr ₄]	<i>b</i>	—	412	1320	<i>a</i>	—	<i>a</i>	—
	[NEt ₄] ₂ [Pd ₂ Br ₆]	<i>b</i>	—	412	2750	<i>a</i>	—	<i>a</i>	—
MeOH	[NEt ₄] ₂ [PdBr ₄]	510	520	411	2400	285	15,000	241	10,500
	[NEt ₄] ₂ [Pd ₂ Br ₆]	512 (sh)	600	411	4300	280	22,000	242	20,000
MeCN	[NEt ₄] ₂ [PdBr ₄]	<i>b</i>	—	410	1700	274 ^c	23,000	—	—
	[NEt ₄] ₂ [Pd ₂ Br ₆]	<i>b</i>	—	411	4000	273 ^d	52,000	—	—
H ₂ O (1M-HClO ₄)	K ₂ [PdBr ₄]	500	220	391	1200	268	8000	227	16,000

^a Solvent absorbs in this region. ^b A broad shoulder in the region 520—480 $m\mu$. ^c Also a maximum at 327 $m\mu$ (ϵ 2300). ^d Also a maximum at 327 $m\mu$ (ϵ 5300). sh = shoulder.

In general, these two ionic species [PdBr₄]²⁻ and [Pd₂Br₆]²⁻ exhibit maxima at the same wavelengths in the same solvent. The extinction coefficients of the maxima of the dimeric ion are in most instances approximately double those of the monomeric species. The maxima shift towards shorter wavelengths if the solvents are arranged in the order: Ph·NO₂, Ac₂O, Me·NO₂, COMe₂, MeOH, MeCN, H₂O. It is not unreasonable to assume that this series indicates the order of increasing strength of attachment of solvent molecules to the palladium atom. Water appears in this series as the solvent with the strongest donor property. The compound [Pd(H₂O)₄](ClO₄)₂ is not dehydrated *in vacuo* over phosphoric oxide;⁷ this indicates that the water molecules are firmly attached. The general shift of the absorption maxima of the bromopalladate(II) ions is most marked in the case of the second absorption band in the range 427—391 $m\mu$; the other two bands in the ultraviolet region appear to follow a similar trend in those solvents in which measurements could be made. The same general shift to shorter wavelengths was also observed for the chloropalladate(II) species [PdCl₄]²⁻ and [Pd₂Cl₆]²⁻ (see Table 3). Again

TABLE 3. Absorption maxima ($m\mu$) and extinction coefficients (ϵ) of tetrachloropalladate(II) and tetrachloro- $\mu\mu'$ -dichlorodipalladate(II) ions in various solvents.

Solvent	Compound	$\lambda_{max.}$	ϵ	$\lambda_{max.}$	ϵ
Ph·NO ₂	[AsPh ₃ Me] ₂ [Pd ₂ Cl ₆]	441	650	<i>a</i>	—
Ac ₂ O	[AsPh ₃ Me] ₂ [Pd ₂ Cl ₆]	439	620	345	4000
MeNO ₂	[AsPh ₃ Me] ₂ [PdCl ₄]	437	190	<i>a</i>	—
	[AsPh ₃ Me] ₂ [Pd ₂ Cl ₆]	439	460	<i>a</i>	—
COMe ₂	[AsPh ₃ Me] ₂ [Pd ₂ Cl ₆]	440	600	340 (br)	2800
MeOH	[AsPh ₃ Me] ₂ [Pd ₂ Cl ₆]	431	750	320	2600
MeCN	[AsPh ₃ Me] ₂ [PdCl ₄]	452 (sh), 400	200, 250	332	1200
	[AsPh ₃ Me] ₂ [Pd ₂ Cl ₆]	455 (sh), 400	350, 490	332	2300
H ₂ O (M-HClO ₄)	K ₂ [PdCl ₄]	426	220	305 (sh)	730

^a Solvent absorption in this region. sh = shoulder; br = broad.

the most pronounced shift occurs in the second absorption band (345—305 $m\mu$). In Table 4 are listed the absorption maxima for the [Pd₂I₆]²⁻ ion; in the limited number of solvents in which this species is soluble, the same general tendency is observed. The ion [Pd₂I₆]²⁻ also displays a broad absorption in the region 750—700 $m\mu$ (e.g., see spectrum in

⁸ Harris, Livingstone, and Stephenson, *J.*, 1958, 3697.

acetone, Fig. 3); no definite maximum could be determined. It seems that in this region is located the first absorption band, which corresponds to the bands at 525—500 $m\mu$ and 441—426 $m\mu$ for the bromo- and chloro-species, respectively.

TABLE 4. Absorption maxima ($m\mu$) and extinction coefficients (ϵ) of the tetraiodo- $\mu\mu'$ -di-iodo-dipalladate(II) ion in various solvents.

Solvent	$\lambda_{\max.}$	ϵ	$\lambda_{\max.}$	ϵ	$\lambda_{\max.}$	ϵ
Ph·NO ₂	536	8100	452	11,200	<i>a</i>	—
Me·NO ₂	524	7200	448	9900	<i>a</i>	—
COMe ₂	531	6700	447	9200	342	36,000
MeCN	528	7200	447	9500	339	40,000

^a Solvent absorbs in this region.

Sundaram and Sandell⁵ have postulated the formation of the ions $[\text{PdCl}_6]^{3-}$ and $[\text{PdCl}_6]^{4-}$ in aqueous perchloric acid solutions of $[\text{PdCl}_4]^{2-}$ from shifts of the absorption maximum in the visible region upon the addition of chloride ions. In Fig. 4 are shown the absorption spectra of solutions of potassium chloropalladate(II) in both M-perchloric acid

FIG. 3. Absorption spectrum of $[\text{NEt}_4]_2[\text{Pd}_2\text{I}_6]$ in acetone.

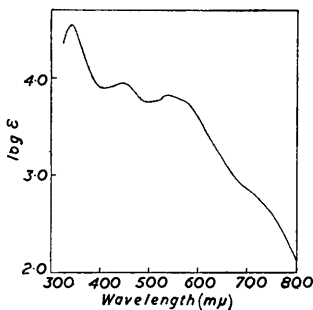


FIG. 4. Absorption spectra of K_2PdCl_4 : (I) in 1M-HClO₄ [$\lambda_{\max.}$ 426, ϵ 220; $\lambda_{\max.}$ 305 (sh), ϵ 730]; (II) in 10M-HCl [$\lambda_{\max.}$ 472, ϵ 170; $\lambda_{\max.}$ 330 (sh), ϵ 650; $\lambda_{\max.}$ 278, ϵ 12,000].

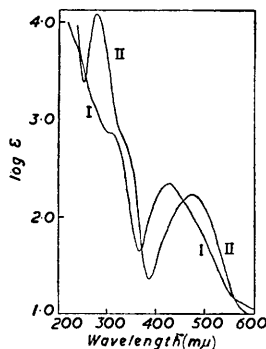
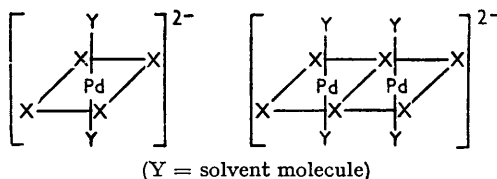


FIG. 5.



and 10M-hydrochloric acid. It can be seen that the spectrum of the hydrochloric acid solution is also markedly altered in the ultraviolet region.

As mentioned above, bivalent palladium in certain instances exhibits a distorted octahedral configuration, and our results suggest that both species $[\text{PdX}_4]^{2-}$ (X = Cl or Br) and $[\text{Pd}_2\text{X}_6]^{2-}$ (X = Cl, Br, or I) in solution form solvated ions, which are no doubt further examples of a distorted octahedral arrangement of bivalent palladium (Fig. 5).

The compound $\text{K}_2[\text{PdCl}_4]$ has been shown to be isomorphous with the square-planar complex $\text{K}_2[\text{PtCl}_4]$ ⁹: X-ray crystal analysis of the compound $[\text{NEt}_4]_2[\text{Pt}_2\text{Br}_6]$ has confirmed the existence of the discrete planar bromo-bridged anion $[\text{Pt}_2\text{Br}_6]^{2-}$. A powder photograph of the analogous palladium compound $[\text{NEt}_4]_2[\text{Pd}_2\text{Br}_6]$ is similar to that of

⁹ Dickinson, *J. Amer. Chem. Soc.*, 1922, **44**, 2404.

the platinum compound, indicating a planar configuration about the palladium atoms.⁸ Consequently, we examined the absorption spectra of the halogenopalladate(II) complexes in the solid state (see Figs. 6—12). The absorption maxima are listed in Table 5.

TABLE 5. *Absorption maxima (mμ) of halogenopalladate(II) complexes in the solid state.*

$K_2[PdCl_4]$	600 (sh)	465 (s)	310 (sh),	$K_2[PdBr_4]$	625 (sh)	500 (s)	—	385 (s)
			275 (s)	$[NEt_4]_2[PdBr_4]$	—	520 (s)	450 (sh)	400 (s),
$[AsPh_3Me]_2[PdCl_4]$	—	485 (s),	300 (s)	$[NEt_4]_2[Pd_2Br_6]$	—	525 (s)	440 (s)	325 (s)
		430 (w, sh)		$[NEt_4]_2[Pd_2I_6]$	700 (sh)	585 (s)	475 (s)	370 (s, br)
$[AsPh_3Me]_2[Pd_2Cl_6]$	—	500 (sh),	325 (s)					
		450 (s)						

(s = strong; sh = shoulder; w = weak; br = broad.)

The first peak was not observed in the spectra of the chloro- and bromo-complexes containing the cations $[AsPh_3Me]^+$ and $[NEt_4]^+$, respectively. It seems reasonable to

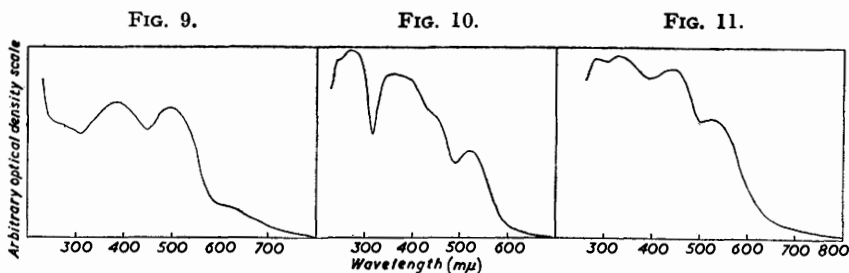
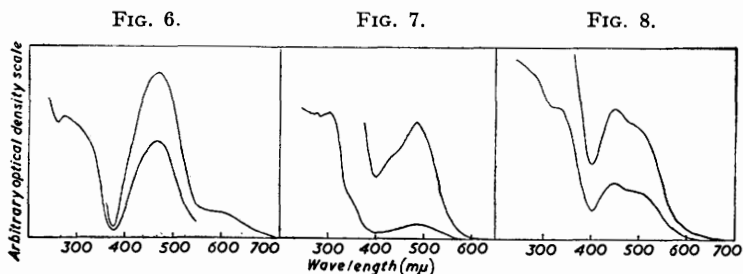
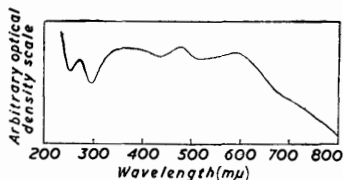


FIG. 6. *Absorption spectrum of $K_2[PdCl_4]$ in the solid state.*
 FIG. 7. *Absorption spectrum of $[AsPh_3Me]_2[PdCl_4]$ in the solid state.*
 FIG. 8. *Absorption spectrum of $[AsPh_3Me]_2[Pd_2Cl_6]$ in the solid state.*
 FIG. 9. *Absorption spectrum of $K_2[PdBr_4]$ in the solid state.*
 FIG. 10. *Absorption spectrum of $[NEt_4]_2[PdBr_4]$ in the solid state.*
 FIG. 11. *Absorption spectrum of $[NEt_4]_2[Pd_2Br_6]$ in the solid state.*

FIG. 12. *Absorption spectrum of $[NEt_4]_2[Pd_2I_6]$ in the solid state.*



correlate the bands obtained for solid $K_2[PdCl_4]$ at 600 and 465 $m\mu$ with those bands obtained for solutions of the chloropalladate(II) complexes at 441—426 and 345—305 $m\mu$, respectively. Similarly, the three bands of solid $K_2[PdBr_4]$ at 625, 500, and 385 $m\mu$ can be correlated with the solution bands at 524—500, 427—391, and 285—268 $m\mu$, respectively. The bands for the solid iodo-complex at 585, 475, and 370 $m\mu$ can be compared with the solution bands at 536—528, 452—447, and 342—339 $m\mu$, respectively, while the

shoulder at 700 $m\mu$ would correspond to the broad absorption occurring at about this wavelength in the solutions. The occurrence of the maxima at much higher wavelengths in the spectra of the solid complexes, which contain quadricovalent palladium, than in to the spectra of the complexes in solution, is in keeping with the postulate of sexicovalent solvated palladium complex ions in polar solvents. A comparison of the spectra of the solid compounds with those of the solution shows that the magnitude of the shift of the maxima to shorter wavelengths is in the order, chloro- > bromo- > iodo-, for these complexes.

Chatt *et al.*,¹⁰ from a study of the visible and ultraviolet spectra of platinum(II) amines, have concluded that bivalent platinum in these compounds shows little, if any, tendency to form sexicovalent complexes. It is noteworthy that the absorption spectra of the $[\text{PtCl}_4]^{2-}$ ion, unlike those of the $[\text{PdCl}_4]^{2-}$ ion, are virtually identical in 1M-perchloric acid and 10M-hydrochloric acid, and that the absorption maxima are not markedly different from those obtained in the solid state (see Table 6).

TABLE 6. Absorption maxima ($m\mu$) and extinction coefficients (ϵ) of potassium tetrachloropalladate(II).

Solvent	$\lambda_{\text{max.}}$	ϵ	$\lambda_{\text{max.}}$	ϵ	$\lambda_{\text{max.}}$	ϵ
1M-HClO ₄	471	16.5	388	51	321	80
1M-HCl	477	15.8	390	59	330	62
2M-HCl (ref. 10)	476	15	392	59	331	64
10M-HCl	475	16.5	388	63	324	76
(Solid) (refs. 10, 11)	500	—	375	—	340	—

Although bivalent platinum in these complexes shows little tendency to increase its covalency beyond four, the compounds $[\text{Pt}(\text{diarsine})_2\text{I}_2]^{3+}$ and $\text{Pt}^{\text{IV}}(\text{NH}_3)_2\text{Br}_4$, $\text{Pt}^{\text{II}}(\text{NH}_3)_2\text{Br}_2$ ¹² contain a distorted octahedral configuration about the bivalent platinum atom in the solid state. In the triad Ni, Pd, Pt it would appear that the tendency to form sexicovalent complexes decreases in the order $\text{Ni}^{\text{II}} > \text{Pd}^{\text{II}} > \text{Pt}^{\text{II}}$.

EXPERIMENTAL

Preparation of Compounds.—*Potassium tetrachloropalladate(II)*. Palladium sponge was dissolved in aqua regia and the solution taken to dryness twice with hydrochloric acid. The residue was dissolved in hot 0.5M-hydrochloric acid, and the calculated quantity of potassium chloride added. The hot solution was filtered to remove traces of potassium hexachloropalladate(IV), and on cooling, deposited crystals of the compound, which was recrystallised from 0.5M-hydrochloric acid (Found: Pd 32.6. Calc. for $\text{Cl}_4\text{K}_2\text{Pd}$: Pd, 32.6%).

Potassium tetrabromopalladate(II). Palladium sponge was dissolved in 48% hydrobromic acid containing a little concentrated nitric acid. The solution was taken almost to dryness several times with hydrobromic acid, the residue dissolved in hot 0.5M-hydrobromic acid, and the calculated quantity of potassium bromide added. Concentration and cooling of the solution gave dark red crystals which were recrystallised from 0.5M-hydrobromic acid, washed with 0.5M-hydrobromic acid, then acetone, and dried at 150° (Found: Br, 63.3. Calc. for $\text{Br}_4\text{K}_2\text{Pd}$: Br, 63.4%).

Potassium tetrachloroplatinatate(II). This compound, prepared as described by Gil'dengershel and Shagisultanova,¹³ was recrystallised from 0.5M-hydrochloric acid and dried (Found: Pt, 46.9. Calc. for $\text{Cl}_4\text{K}_2\text{Pt}$: Pt, 47.0%).

The following compounds were prepared as described in the references:

Tetraethylammonium tetrabromopalladate(II)⁶ (Found: C, 27.8; H, 6.2; N, 3.9; Br, 46.5; Pd, 15.5. Calc. for $\text{C}_{16}\text{H}_{40}\text{N}_2\text{Br}_4\text{Pd}$: C, 28.0; H, 5.9; N, 4.1; Br, 46.5; Pd, 15.5%).

¹⁰ Chatt, Gamlen, and Orgel, *J.*, 1958, 486.

¹¹ Yamada, *J. Amer. Chem. Soc.*, 1951, **73**, 1182.

¹² Brosset, *Arkiv Kemi, Min., Geol.*, 1948, **25**, No. 19.

¹³ Gil'dengershel and Shagisultanova, *Zhur. priklad. Khim.*, 1953, **27**, 222.

Tetraethylammonium tetrabromo- $\mu\mu'$ -dibromodipalladate(II) ⁶ (Found: C, 20.4; H, 4.4; N, 2.8; Br, 49.7; Pd, 22.4. Calc. for $C_{16}H_{40}N_2Br_6Pd_2$: C, 20.2; H, 4.2; N, 2.9; Br, 50.2; Pd, 22.4%).

Triphenylmethylarsonium tetrachloropalladate(II) ⁸ (Found: Cl, 15.9; Pd, 12.0. Calc. for $C_{36}H_{36}Cl_4As_2Pd$: Cl, 15.9; Pd, 12.0%).

Triphenylmethylarsonium tetrachloro- $\mu\mu'$ -dichlorodipalladate(II) ⁸ (Found: Cl, 19.9; Pd, 20.0. Calc. for $C_{36}H_{36}Cl_6As_2Pd_2$: Cl, 19.9; Pd 20.0%).

Tetraethylammonium tetraiodo- $\mu\mu'$ -di-iododipalladate(II) ⁸ (Found: C, 15.6; H, 3.4; N, 2.2; Pd, 17.3. Calc. for $C_{16}H_{40}N_2I_4Pd_2$: C, 15.6; H, 3.3; N, 2.3; Pd, 17.3%).

Solvents.—The acetone and methanol were of "AnalaR" quality and were dry. Nitromethane was distilled, dried ($CaCl_2$), and then twice fractionated (b. p. 100.5°). Nitrobenzene was washed with water, dried ($CaCl_2$), and distilled; the distillate was purified by freezing, followed by fractional distillation at 10 mm. from P_2O_5 . "AnalaR" acetic anhydride was further purified by fractional distillation. Acetonitrile (Hopkin and Williams) was distilled from P_2O_5 (b. p. 81.4—81.8°), then again fractionally distilled (b. p., 81.6—81.7°).

The compounds $[NEt_4]_2[PdBr_4]$ and $[NEt_4]_2[Pd_2Br_6]$ recrystallised unchanged from acetonitrile, indicating that acetonitrile does not replace the bromo-groups.

Measurement of Spectra.—Spectra were recorded on a Cary 11-MS-50 Spectrophotometer. The solids were examined as Nujol mulls in the manner of infrared samples. This necessitated fine grinding to minimise the scattering of radiation and for the potassium salts, in which this effect was most pronounced, a vibration ball mill was used. Samples containing organic residues were easily prepared. The instrument was balanced against two matched scatter-plates of rock-salt, roughened on both sides with emery paper. The mull was then spread on one side of the scatter-plate that had been in the "sample" compartment for balancing and, when required for thinning out the film, a clear rock-salt plate was pressed on to it. In this fashion the amount of scattering produced by the sample was generally only a little more than that which would be produced by one side of the doubly roughened scatter-plate. Roughening the second side of the sample-plate made the process of recording spectra much simpler since this prevented light from passing through clearer spaces in the mull and falling directly on the detector. Thus the position equivalent to 100% absorption was displaced to a reading of higher optical density, since the instrument recorded in optical density rather than in per cent. transmission. The spectra are essentially "as recorded" and are meant to indicate little more than the location of absorption bands. Correction has been made for scattering where this was more than for the reference plate; but where this effect was even as high as 85% more (optical density 0.8), the result was to raise the zero of absorption by the same amount at all wavelengths.

Spectra of Higher Bromo-complexes; see Figs. 1 and 2.—The spectra in water were measured on (a) a solution of $K_2[PdBr_4]$ ($5 \times 10^{-4}M$) in constant-boiling hydrobromic acid (8.6M) for the range 600—375 $m\mu$, and (b) a solution of $K_2[PdBr_4]$ ($5 \times 10^{-5}M$) in *m*-potassium bromide for the range 400—235 $m\mu$. In the range 400—375 $m\mu$ the extinction coefficients of both solutions were almost identical. Hydrobromic acid could not be used below 350 $m\mu$ owing to absorption by traces of bromine.

The spectra in methanol were obtained from (i) a solution of $[NEt_4]_2[PdBr_4]$ ($10^{-3}M$) in methanol containing tetraethylammonium bromide (1M) in the range 600—400 $m\mu$. For the wavelength range 400—235 $m\mu$, a solution of $[NEt_4]_2[PdBr_4]$ ($10^{-4}M$) in methanol, containing tetraethylammonium bromide (0.1M), was used. The value of ϵ at 400 $m\mu$ was the same for both solutions.

Microanalyses.—Microanalyses for carbon, hydrogen, and nitrogen were carried out by Dr. E. Challen, of the Microanalytical Laboratory of this University.

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