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Metal Complexes of Some Hybrid Bidentate Ligands Containing Tertiary Arsine and Primary Amine Donor Groups. III. Compounds of Pd and Pt

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Palladium(II) and platinum(II) complexes derived from the bidentate hybrid ligands, o*- dimethylarsinoaniline (MAA),* o*-diphenylarsinoaniline (PAA), and 1-amino-2-(diphenylarsino)ethane (APE), containing a* hard *nitrogen and a* soft *arsenic donor atom are described.*

The complexes are of two types:

(i) Pd(ligand)X_2, where ligand = MAA, PAA, or APE, and X = halogen or thiocyanate.

(ii) M(ligand)$_2X_2$, where M = Pd or Pt, ligand = MAA, PAA or APE, X = halogen, SCN or ClO_4.

The interest in this paper in compounds of type (ii), which can exist as square planar compounds with two, one or no ionic X groups, depending upon the action of the two potentially bidentate ligands, as both bidentate, one bi- and one monodentate or both monodentate ligands, respectively. Alternatively, the compounds with one or no ionic X groups can be classified as five or six coordinate species, respectively.

Detailed discussion of likely structures is offered, based upon infrared and conductance measurements on the compounds.

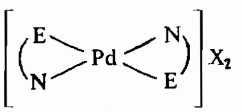
Some neutral compounds of the type [M(ligand-H)$_2$] (where M = Pd or Pt, ligand-H = singly deprotonated MAA or PAA) are also described.

Introduction

It has been established that in divalent square planar complexes of palladium or platinum the tendency of the group *V* donor atoms to confer upon the central atom the ability to engage in pentacoordination increases in the sequence $N < P < As < Sb$. This may be a consequence of decreasing donor and increasing π-acceptor ability along this sequence with the result that increasing positive charge on the central atom enhances its ability to attract additional ligands.[1]

In the case of hybrid donor bidentate ligands containing phosphorus or arsenic as one of the donor atoms, the possible occurrence of structures in which the ligands coordinate only as monodentate groups by utilizing only the phosphorus or arsenic donor atom should be considered. This situation is most likely to occur for ligands in which the second donor atom is «hard» and therefore does not coordinate strongly to palladium(II) or platinum(II), *e.g.*, nitrogen.

Structures of the type described above have been proposed to account for the properties of the palladium(II) complexes formed by the ligands (*o*-dimethylaminophenyl)dimethylarsine[2] (As-N) and (*o*-dimethylaminophenyl)diethylphosphine[3] (P-N). The trans bis-complexes formed by these ligands may be considered to have one of the square planar structures I, II, or III, where E = P or As.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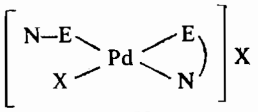
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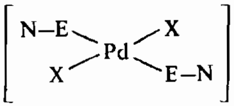
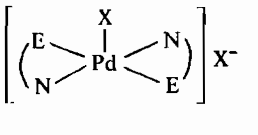

III

Some of these complexes were found to exist in interconvertible isomeric forms corresponding to the structures above, *e.g.*, $Pd(P\text{-}N)_2I_2$ and $Pd(As\text{-}N)Br_2$ were isolated in both structural forms II and III and $Pd(P\text{-}N)_2(NO_2)_2$ was isolated in all three structural forms. In solution, equilibria are established between the three structural isomers depending on the temperature and polarity of the solvent, *e.g.*, $Pd(P\text{-}N)_2X_2$ (where X = Cl or Br) are 2:1 electrolytes in water, but only 1:1 electrolytes in nitrobenzene. Of course, it is also possible to account for the above results by postulating the existence of five and six-coordinate structures IV and V in place of the structures II and III since the authors found no suitable method for detecting the presence of free dimethylamino groups.[3]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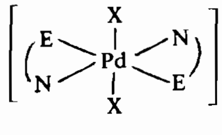
V

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[1] A. D. Westland, *J. Chem. Soc.*, 3060(1965).

[2] F. G. Mann and F. M. C. Stewart, *J. Chem. Soc.*, 1269(1965).

[3] F. G. Mann and H. R. Watson, *J. Chem. Soc.*, 3950 (1967).

8-dimethylarsinoquinoline (8-dmaq), forms bis-complexes with platinum(II) and palladium(II) which are considered to possess four, five, or six-coordinate structures. Four-coordinate structures are obtained using poorly coordinating anions, *e.g.*, $[M(8\text{-dmaq})_2](ClO_4)_2$. These complexes react with neutral or anionic ligands to form five-coordinate complexes of general formula, $[M(8\text{-dmaq}))_2L](ClO_4)_2$ and $[M(8\text{-dmaq})_2X](ClO_4)$ where X = Cl, Br or I and L = pyridine or 4-methylpyridine). The complexes, $Pd(8\text{-dmaq})_2X_2$ (where X = Cl, Br, I or SCN), are only partially dissociated in nitrobenzene and have molar conductance values less than would be expected for 1:1 electrolytes. This may be attributed to an equilibrium between five and six-coordinate species in solution

$$[Pr(8\text{—dmaq})_2X_2] \rightleftharpoons [Pd(8\text{—dmaq})_2X]X$$

(*o*-methylthiophenyl)dimethylarsine (As-S) forms a series of bis-complexes with palladium(II) and platinum(II). The complexes of general formula, $Pd(As\text{-}S)_2X_2$ (where X = Cl, Br or I), tend to disosciate with the formation of the monochelate species, $[Pd(As\text{-}S)X_2]$, in solution. However in the presence of a large excess of the ligand, the complexes appear to exist in solution with the five-coordinate structures $[Pd(As\text{-}S)_2X]^+X^-$.[5] The bis-complexes with platinum(II) show similar properties. Further evidence for the existence of $[Pt(As\text{-}S)_2X]^+$ was provided by the isolation of complexes of general formula, $[Pt(As\text{-}S)_2X]ClO_4$ (where X = Cl, Br or I).[6] The four-coordinate cationic complexes, $[M(As\text{-}S)_2]^{2+}$, are formed in the presence of weakly coordinating anions, *e.g.*, ClO_4^- or $[PtCl_6]^{2-}$.

Some bis-chelate complexes have also been reported for the ligand 2-methyl(dimethylarsino)pyridine.[7]

For all the bidentate ligands discussed above, some examples of monochelate complexes of general formula, $[M(ligand)X_2]$ (where M = Pd or Pt and X = Cl, Br I and SCN), have also been isolated. These are typical square planar complexes and show no tendency to add a fifth ligand.

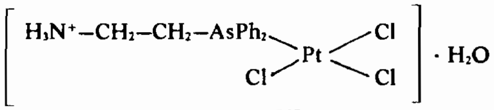
Results and Discussion

1:1 Complexes. When any of the three ligands, 1-amino-2-(diphenylarsino)ethane (APE), *o*-dimethylarsinoaniline (MAA), or *o*-diphenylarsinoaniline (PAA) was reacted with potassium tetrachloropalladate(II) in hot aqueous ethanol in 1:1 proportions, yellow crystalline precipitates of complexes with the general formula, $[Pd(ligand)Cl_2]$ (where ligand = MAA, PAA or APE) were obtained. For the reaction of APE with K_2PdCl_4, the initial product was the light-brown coloured salt $[Pd(APE)_2][PdCl_4]$, but on heating of the solution this was slowly converted to the pale yellow mononuclear complex, $[Pd(APE)Cl_2]$. The complexes, $[Pd(ligand)X_2]$ (where X = I or SCN), were obtained from the reaction of $[Pd(ligand)Cl_2]$ with excess sodium iodide or potassium thiocyanate.

The reaction of MAA or APE with potassium tetrachloroplatinate(II) in aqueous ethanol in 1:1 proportions gave insoluble pink-coloured precipitates of the salts, $[Pt(ligand)_2][PtCl_4]$ (where ligand = MAA or APE). These salts were not readily converted to mononuclear complexes, *e.g.*, when a suspension of $[Pt(APE)_2][PtCl_4]$ in ethanol was boiled, precipitation of platinum metal gradually occurred. However, on stirring a suspension of $[Pt(APE)_2][PtCl_4]$ in ethanol with excess sodium iodide, the yellow complex $[Pt(APE)I_2]$ slowly formed. This complex crystallized from dimethylformamide as $[Pt(APE)I_2]\,.\,\frac{1}{2}(DMF)$, as indicated by the analytical data and the presence of a C=O stretching band at 1660 cm^{-1} in the infrared spectrum.

The complexes of general formula, $[M(ligand)X_2]$ (where M = Pt^{II} or Pd^{II}), appear to have the four-coordinate planar structures which are commonly found for platinum(II) and palladium(II) complexes. Coordination of the amino groups of the ligands is evident from the infrared spectra of the complexes. In the series of complexes, $[Pd(ligand)X_2]$, the N-H stretching frequencies of PAA, APE and MAA are shifted to lower frequencies by about 300, 105-135 and 240-280 cm^{-1} respectively. In the infrared spectrum of each of the complexes, $Pd(APE)(SCN)_2$ and $Pd(PAA)(SCN)_2$, there are two C-N frequencies at 2120, 2115, and 2120, 2100 cm^{-1} respectively, consistent with a cis- arrangement of S-bonded thiocyanate ligands.

Of some interest is the case with which the chelate ring in the APE complexes of platinum(II) and palladium(II) can be opened by protonation of the amino group. Thus $[Pt(APE)_2][PtCl_4]$ dissolves in a hot mixture of ethanol and hydrochloric ecid, and an orange-yellow complex of structure VI separates on cooling.



VI

The complex is an example of zwitterion, and behaves as a non-conductor in nitrobenzene solution (Table Ic). The analogous orange-brown complex $[Pd(APEH)^+Cl_3]\,.\,H_2O$ was obtained from the reaction of $[Pd(APE)Cl_2]$ with hydrochloric acid. In contrast to these complexes, $[Pt(en)Cl_2]$ has been reported to dissolve in 12 *M* hydrochloric acid without reaction.[9]

2:1 Complexes. When two proportions of MAA, PAA, or APE were reacted with one proportion of either potassium tetrachloropalladate(II) or potassium tetrachloroplatinate(II) in aqueous ethanol, solutions were obtained from which complexes of general formula, $M(ligand)_2Cl_2\,.\,nH_2O$ (where M = Pd^{II} or Pt^{II}; ligand = APE, MAA, or PAA; n = 0, 1, or 2), were subsequently isolated. The chloride ion in these complexes was replaced by bromide, iodide, thio-

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[4] G. A. Barclay, M. A. Collard, C. M. Harris and J. V. Kingston, *J. Chem. Soc. (A)*, 830 (1969).
[5] S. E. Livingstone, J. *Chem. Soc.*, 4222 (1958).
[6] B. Chiswell and S. E. Livingstone, *J. Chem. Soc.*, 1071 (1960).
[7] H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, *81*, 311 (1959).
[8] M. J. Hudson, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc. (A)*, 40 (1969).
[9] G. L. Johnson, *Inorg. Syntheses*, *8*, 242 (1966).

Table I. Molar conductances of platinum(II) and palladium(II) complexes.

Complex	Molar Concentration	Λ_M ohm^{-1} cm^2 mole^{-1}
(a) Conductance measured in methanol at 24°C		
$Pd(APE)_2Cl_2 . 2H_2O$	$1.07 \times 10^{-3} M$	116.0
$Pd(MAA)_2Cl_2 . H_2O$	1.02×10^{-3}	97.8
$Pd(PAA)_2Cl_2 . H_2O$	1.00×10^{-3}	119.0
$Pt(APE)_2Cl_2$	1.11×10^{-2}	73.3
„	5.53×10^{-3}	91.3
„	9.73×10^{-4}	139.0
„	3.42×10^{-4}	162.0
$Pt(MAA)_2Cl_2 . 2H_2O$	1.17×10^{-2}	66.9
„	5.84×10^{-3}	79.7
„	1.45×10^{-3}	91.8
„	2.21×10^{-4}	104.0
$Pt(PAA)_2Cl_2 . H_2O$	1.10×10^{-2}	73.5
„	5.51×10^{-3}	92.2
„	1.52×10^{-3}	124.0
„	2.11×10^{-4}	164.0
$Pd(APE)_2I_2$	1.07×10^{-2}	72.7
„	5.69×10^{-3}	31.7
„	1.61×10^{-3}	110.0
„	2.22×10^{-4}	162.0
$Pd(APE)_2(ClO_4)_2 . H_2O$	1.06×10^{-3}	133.0
$Pt(APE)_2(ClO_4)_2 . H_2O$	0.97×10^{-3}	148.0
$Pt(PAA)_2(ClO_4)_2$	0.991×10^{-3}	168.0
(b) Conductances measured in nitromethane		
$Pt(MAA)_2(SCN)_2$	$1.33 \times 10^{-3} M$	32.1
$Pt(APE)_2(ClO_4)_2 . H_2O$	1.00×10^{-3}	144.0
$Pd(MAA)_2(ClO_4)_2$	1.14×10^{-3}	151.0
$Pd(PAA)_2(ClO_4)_2 . H_2O$	1.24×10^{-3}	132.0
$Pt(APE)_2(ClO_4)_2 . H_2O$	9.8×10^{-4}	135.0
$Pt(MAA)_2(ClO_4)_2$	1.12×10^{-3}	154.0
$Pt(PAA)_2(ClO_4)_2$	1.16×10^{-3}	130.0
Known 2:1 electrolyte $(Ph_4As)_2[OsBr_6]$	1.03×10^{-3}	170.0
(c) Conductanccs measurcd in nitrobenzene		
$Pd(PAA)_2Cl_2 . H_2O$	$1.31 \times 10^{-3} M$	0.8
$Pt(PAA)_2Cl_2 . H_2O$	1.54×10^{-3}	2.6
$Pd(APE)_2I_2$	0.97×10^{-3}	9.7
$Pd(MAA)_2I_2$	1.09×10^{-3}	1.5
$Pd(PAA)_2I_2 . C_2H_5OH$	1.60×10^{-3}	0.3
$Pd(APE)_2I_2$	1.04×10^{-3}	14.0
$Pd(MAA)_2I_2$	1.38×10^{-3}	9.9
$Pt(PAA)_2I_2$	1.17×10^{-3}	6.9
$Pd(APE)_2(SCN)_2$	1.19×10^{-3}	13.7
$Pt(APE)_2(SCN)_2$	9.84×10^{-3}	8.1
„	4.91×10^{-3}	10.2
„	1.43×10^{-3}	13.9
„	0.63×10^{-3}	19.0
$Pd(APE)_2(ClO)_2 . H_2O$	1.02×10^{-3}	31.0
$Pt(APE)_2(ClO_4)_2 . H_2O$	9.4×10^{-3}	18.5
„	4.25×10^{-3}	22.7
„	1.22×10^{-3}	31.1
„	0.66×10^{-3}	37.4
Known 2:1 electrolytc $(Ph_4As)_2[OsBr_6]$	1.23×10^{-3}	50.9
$Pd(MAA\text{-}H)_2$	$1.38 \times 10^{-3} M$	0.9
$Pd(PAA\text{-}H)_2 \frac{1}{2} CH_2Cl_2$	1.31×10^{-3}	0.2
$Pt(MAA\text{-}H)_2$	1.15×10^{-3}	0.7
$Pt(PAA\text{-}H)_2$	1.06×10^{-3}	0.7
$Pt(APEH^+)Cl_3 . H_2O$	0.91×10^{-3}	0.0
(d) Conductances measured in water at 22°C		
$Pd(APE)_2Cl_2 . 2H_2O$	$2.36 \times 10^{-3} M$	189.0
$Pd(APE)_2Cl_2 . 2H_2O$	0.89×10^{-3}	198.0
$Pd(MAA)_2Cl_2 . H_2O$	1.28×10^{-3}	190.0
$Pt(APE)_2Cl_2$	1.13×10^{-3}	191.0
$Pt(MAA)_2Cl_2 . 2H_2O$	1.27×10^{-3}	185.0

cyanate, or perchlorate ions, using metathetical reactions.

If both of the As-N groups behave as bidentate ligands, the 2:1 complexes may be considered to possess four-coordinate planar structures as in structure I (where E = As), with the possibility of coordination of one or both anions X.

Alternatively, if one or both As-N groups coordinates only as a unidentate ligand through the arsenic atom, then four coordinate structures of types II and III (where E = As) are possible.

Each of these three structures may exist in cis and trans isomeric forms but in no case was the presence of isomers of this type detected.

The presence of free amino groups in complexes prepared was determined from the infrared spctra of the anhydrous complexes, and information regarding the structures of the complexes in solution was obtained from conductivity measurements.

For the purpose of discussing the infrared spectra of these platinum(II) and palladium(II) complexes, it is convenient to group them according to the anion present. However, the structures of complexes do not depend entirely on the anion, but are also influenced to some extent by the ligand and the metal ion.

(i) *Perchlorates.* The complexes, $Pt(MAA)_2(ClO_4)_2$, $Pt(PAA)_2(ClO_4)_2$, and $Pd(MAA)_2(ClO_4)_2$, show absorption bands near 3200 cm^{-1}, which may be assigned to the N-H stretching vibrations of coordinated amino groups. An additional broad band in the region 3600-3500 cm^{-1} in the infrared spectra of the complexes, $Pt(APE)_2(ClO_4)_2 . H_2O$, $Pd(APE)_2(ClO_4)_2 . H_2O$ and $Pd(PAA)_2(ClO_4)_2 . H_2O$, may be assigned to the O-H stretching vibrations of lattice water. All the perchlorate complexes are considered to have four-coordinate bis-chelate structures (I) with ionic perchlorate groups.

(ii) *Chlorides.* $Pt(APE)_2Cl_2$ was the only chloride complex obtained in an anhydrous state. The highest frequency band in the infrared spectrum of this complex occurs at 2950 cm^{-1}. This broad band arises from the overlapping of the C-H stretching and coordinated NH_2 stretching frequencies. The N-deuterated complex has N-D stretches at 2210 cm^{-1} and 2280 cm^{-1}. The N-H stretching frequencies in $Pt(APE)_2Cl_2$ are at least 200 cm^{-1} lower than those in APE, so the complex is assigned a bis-chelate structure. The four-coordinate structure containing the cation $[Pt(APE)_2]^{2+}$ is most likely, although weak coordination of the chloride ions could produce structures with coordination numbers of five or six.

The hydrated complexes, $Pr(APE)_2Cl_2 . 2H_2O$, $Pd(MAA)_2Cl_2 . H_2O$ and $Pt(MAA)_2Cl_2 . 2H_2O$ display broad bands near 3400 cm^{-1} in the infrared, and these must be assigned to the O-H stretching of water. These bands will mask any absorption that may arise from the presence of free amino groups in these complexes. Other bands are observed in the region 3200-3000 cm^{-1} where the coordinated amino groups are expected to absorb, so at least one of the ligands in these complexes is chelating.

Both $Pd(APE)_2Cl_2 . 2H_2O$ and $Pd(PAA)_2Cl_2 . 2H_2O$

have quite strong yellow colours which indicates the presence of Pd-Cl bonds, but a distinction between a bis-chelate structure with five or six-coordination (IV or V) and a four-coordinate structure, cannot be made. The water can be removed from $Pd(APE)_2Cl_2 \cdot 2H_2O$ by heating. The infrared spectrum of this anhydrous compound is similar to that of $Pt(APE)_2Cl_2$. The anhydrous complex has only a faint cream colour and probably contains the cation, $[Pd(APE)_2]^{2+}$.

(iii) *Iodides.* $Pt(MAA)_2I_2$ has no infrared absorption bands above 3200 cm^{-1} and accordingly may be assigned a bis-chelate structure. On the other hand, $Pd(MAA)_2I_2$ has bands at 3385 and 3315 cm^{-1} which are only slightly lower in frequency than the N-H stretching bands of MAA itself; so this complex evidently possesses the four-coordinate bis-monodentate structure, III. The non-ionic nature of this complex is reflected by its insolubility in water and its solubility in non-polar solvents such as benzene and cyclohexane. The ionic complex, $[Pt(MAA)_2]I_2$ is, on the other hand, soluble in water and insoluble in benzene or cyclohexane.

The bis-complex of PAA with palladium(II) iodide crystallized from ethanol as a solvate, $Pd(PAA)_2I_2 \cdot EtOH$. The presence of ethanol was evident from the analytical results, the presence of O-H stretching bands at 3660 and 3500 cm^{-1}, and aliphatic C-H stretching bands at 2940 and 2900 cm^{-1} in the infrared spectrum. The ethanol was removed by heating the complex to 80°C under vacuum. $Pd(PAA)_2I_2$ exhibits N-H stretching bands at 3440 and 3355 cm^{-1}, which are almost at the same frequencies as the N-H stretching vibrations in «free» PAA. $Pd(PAA)_2I_2$ is therefore considered to possess a bis-monodentate type structure III. In the infrared spectrum of the ethanolate, the O-H stretching vibration appears as a doublet and the splitting of the N-H stretching frequencies is also evident, bands being observed at 3440, 3400 cm^{-1} and 3340, 3240 cm^{-1}. Evidently there is a hydrogen bonding interaction between the hydroxyl and amino groups in this compound. $Pt(PAA)_2I_2$ shows two strong broad bands near 3400 and 3000 cm^{-1} in the infrared spectrum and apparently possesses both free and coordinated amino groups as in the structure II.

The infrared spectrum of $Pt(APE)_2I_2$ and $Pd(APE)_2I_2$ are similar, with a broad band at 3440 cm^{-1} and other bands near 3200 cm^{-1}. These complexes also apear to have the chelate-monodentate structure II.

(iv) *Thiocyanates.* The infrared spectra of $Pd(APE)_2(SCN)_2$ and $Pt(APE)_2(SCN)_2$ are similar. There are no absorption bands at frequencies higher than 3200 cm^{-1} and C-N stretching vibration of the thiocyanate ion appears as a doublet, 2060 and 2030 cm^{-1}, with frequencies in the region expected for ionic thiocyanate groups. The explanation for the appearance of the C-N stretching vibration as a doublet can probably be described to solid state effects. The complexes are considered to have bis-chelate structures as in I.

$Pt(MAA)_2(SCN)_2$ shows N-H stretching bands at 3365 and 3295 cm^{-1} as well as in the region 3200-3000 cm^{-1}, which indicates the presence of both «free» and coordinated amino groups. This complex appears to possess the chelate-monodentate structure II. In support of this postulate, the complex shows C-N stretching vibrations at 2135 and 2060 cm^{-1}; the first band (2135 cm^{-1}) is in the region expected for an S-bonded thiocyanate, and the second band (2060 cm^{-1}) in the region expected for an ionic thiocyanate.

Attempts to prepare $Pd(PAA)_2(SCN)_2$ resulted in the formation of $Pd(PAA)(SCN)_2$, while pure samples of $Pd(MAA)_2(SCN)_2$ and $Pt(PAA)_2(SCN)_2$ could not be obtained, probably because of similar tendency to dissociate to a monochelate complex.

The generalizations that can be drawn from the above results and discussion are:

(a) that platinum(II) has a greater tendency than palladium(II) to form chelate rings with the $R_2As\text{-}NH_2$ ligands.

(b) that APE has a greater ability to chelate to platinum(II) and palladium(II) salts than does either MAA or PAA.

(c) that the anionic ligands with high nucleophilic reactivity towards platinum(II), *e.g.*, iodide ion, are the most effective in displacing the amino group of the ligands from the coordination sphere. The generalizations do not seem to apply in all cases, *e.g.*, $Pt(MAA)_2I_2$. This can be expected since other factors such as the temperature and polarity of the solvent from which the complexes were crystallized will be important in deciding the structure.

Conductance Measurements of 2:1 Complexes. Conductivity data were obtained for solutions of the bis-complexes of general formula, $M(ligand)_2X_2 \cdot nH_2O$ (where ligand = APE, MAA, or PAA; X = Cl, I, SCN, or ClO_4; M = Pd or Pt and n = 0, 1, or 2), at concentrations of about 10^{-3} *M* in water, methanol, nitromethane and nitrobenzene. Molar conductance values, (Λ_M), were calculated by assuming the molecular weight of a complex was equal to its formula weight. Results are listed in Table I.

(a) *Conductivities in Methanol* (See Table Ia). Solutions of the complexes, $M(ligand)_2X_2 \cdot H_2O$ (where ligand = APE, MAA, or PAA; X = Cl, I, or SCN; M = Pd or Pt and n = 0, 1, or 2), at concentrations of about 10^{-3} *M* in methanol gave molar conductance values which were somewhat lower than the values of about 180 ohm^{-1} cm^2 $mole^{-1}$ usually observed for 2:1 electrolytes in methanol.[10] For some of the complexes, the molar conductance values obtained were much closed to the values usually observed for 1:1 electrolytes in methanol, *i.e.*, about 100 ohm^{-1} cm^2 $mole^{-1}$.[11]

It is possible to account for the low molar conductance values of the complexes in at least four ways:

(i) by postulating equilibria between bis-chelate, chelate-monodentate, and bis-monodentate structures in the solutions.

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(10) R. A. Krause and D. H. Busch, *J. Am. Chem. Soc.*, *82*, 4830 (1960).

(11) R. A. Robinson and R. H. Stokes « Electrolyte Solutions », 2nd edition, p. 162, Academic Press Inc., New York (1959).

(ii) by postulating equilibria between bis-chelate structures with coordination numbers of four, five and six in the solutions.

(iii) by postulating equilibria between the bis-chelate, four-coordinate structure and the uncharged monocomplex formed by complete dissociation of one of the chelate ligands.

$$[M(ligand)_3X_2] \rightleftarrows [M(ligand)X_2] + ligand$$

(iv) by postulating ion-pairing which is fortified at the low concentrations by hydrogen bonding of the anions with the amino groups in the cations.

The study of the infrared spectra of the complexes, $M(ligand)_2X_2$ (where X = Cl, I, or SCN), indicated that either a bis-chelate, chelate-monodentate, or bis-monodentate structure occurred in the solid state depending on the particular combination of ligand and anion. It therefore seems most logical to attempt to explain the conductivity results according to postulate (i) rather than postulates (ii) or (iii). Also since some of the complex perchlorates $[M(ligand)_2](ClO_4)_2 . nH_2O$ were found to have lower molar conductances than expected for 2: 1 electrolytes; the effect of ion-pairing as in (iv) may also be significant.

Conductivity data were obtained over a concentration range for solutions of the complexes $Pt(MAA)_2Cl_2 . 2H_2O$, $Pt(APE)_2I_2$, $Pt(APE)_2Cl_2$ and $Pt(PAA)_2Cl_2 . 2H_2O$ in methanol. The results are show in Figure 2 as plots of Λ_M against C_M, and in Figure 1 as plots of Λ_e against C_e where it is assumed that the complexes are 2: 1 electrolytes, *i.e.* $C_e = 2C_M$ and $\Lambda_e = ½\Lambda_M$. Alternatively if the complexes are assumed to be 1: 1 electrolytes the Λ_M against C_M, and Λ_e against C_e plots are equivalent. The variation of Λ_e with concentration for dilute solutions of strong electrolytes in water as well as in non-aqueous solvents is given by the Onsager equation

$$\Lambda_e = \Lambda_o - AC_e$$

Accordingly, plots of Λ_e against C_e are expected to be linear. The slope A, of these linear plots has been shown to be a characteristic of the electrolyte type. Feltham and Hayter give values of about 260 and 510 for 1: 1 and 2: 2 electrolytes respectively in methanol.[12]

The plot of Λ_e against C_e for $Pt(MAA)_2Cl_2 . 2H_2O$ was linear over the concentration range 10^{-2} to 10^{-4} *M*. The Λ_e against C_e plot (Figure 1), which assumes a 2: 1 electrolyte, has a slope of 140; on the other hand the Λ_c against C_e plot (Figure 2), which assumed a 1: 1 electrolyte has a slope of 400. When this latter plot is extrapolated to $C_e = 0$ a value of $\Lambda_0 = 109$ is obtained. A comparison with the data given by Feltham and Hayter shows that the behavior of $Pt(MAA)_2Cl_2 . 2H_2O$ in solution approximately most closely to that of a 1: 1 electrlyte. The species present in solution could have either a chelate-monodentate structure II, or a five-coordinate structure with a cordinated chloride anion.

The plots of Λ_e against C_e for $Pt(APE)_2I_2$ appear to be linear only at concentrations greater than about 5×10^{-3} *M*, and 1: 1 electrolyte type struture similar to those postulated for $Pt(MAA)_2Cl_2 . 2H_2O$ may be present in this concentration range. At lower concentrations the 2: 1 electrolyte type structure $[Pt(APE)_2]I_2$ seems to become increasingly dominant.

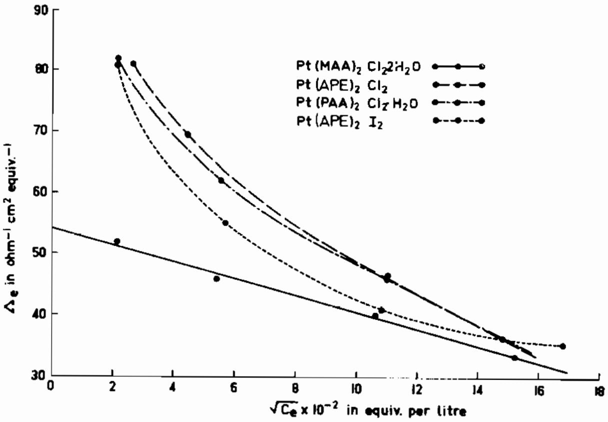

Figure 1. Plots of Λ_e against $\sqrt{C_e}$ for some platinum complexes in methanol solution.

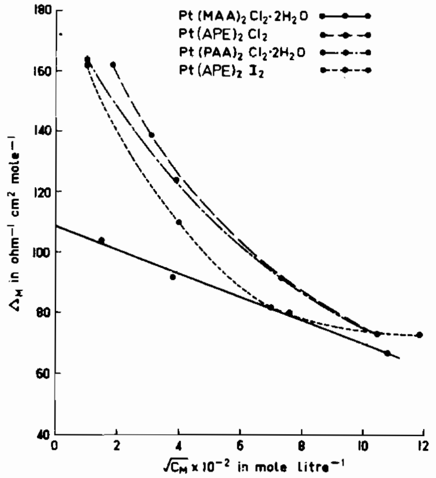

Figure 2. Plots of Λ_M against $\sqrt{C_M}$ for some platinum complexes in methanol solution.

The Λ_c against C_c plots for both the complexes, $Pt(PAA)_2Cl_2 . H_2O$ and $Pt(APE)_2Cl_2$, are non-linear in the concentration range 10^{-2} to 10^{-4} *M*. At low concentrations, the molar conductance approaches values characteristic of 2: 1 electrolytes. The results suggest concentration-dependent equilibria between 2: 1 and 1: 1 type electrolytes having structures of the type discussed above.

10^{-3} *M* solutions of the complex perchlorates have molar conductances closer to, but still slightly less than, values expected for 2: 1 electrolytes. Because of the weak cordinating ability of the perchlorate ion, it is unlikely that it will either displace an amino group from the coordination sphere, or coordinate as a fifth ligand above the MAs_2N_2 plane. The low conductance value in the case of the perchlorates could be a consequence of ion-pair association.

Many of the complexes were not sufficiently solu-

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(12) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

ble in nitromethane for conductivity measurements.

Solutions of the complex perchlorates, $[M(ligand)_2](ClO_4)_2 \cdot nH_2O$ (where M = Pd or Pt; ligand = MAA, APE or PAA; and n = 0 or 1), gave molar conductance values close to the values usually found for 2:1 electrolytes in nitromethane.

$Pt(MAA)_2(SCN)_2$, which has a chelate-monodentate structure in the solid state, has a molar conductance of 32 ohm^{-1} cm^2 $mole^{-1}$ which is somewhat less than the values of about 70 ohm^{-1} cm^2 $mole^{-1}$ usually found for 1:1 electrolytes in nitromethane.[13] Evidently there is a tendency for both amino groups to be displaced from the coordination sphere by the thiocyanate ion in solution.

(c) *Conductivities in Nitrobenzene* (See Table Ic). The complexes $Pd(PAA)_2I_2$ and $Pd(MAA)_2I_2$ behave as non-electrolytes while the other complexes with halide or thiocyanate as anions have molar conductances intermediate between non-electrolytes and 1:1 electrolytes in nitrobenzene. Thus it is concluded that $Pd(MAA)_2I_2$ and $Pd(PAA)_2I_2$ have bis-monodentate structures in solution in nitrobenzene as well as in the solid state. For the other complexes there is probably an equilibrium between chelate-monodentate and bis-monodentate structures, or alternatively an equilibrium between five and six-coordinate complexes with bis-chelate structures.

Molar conductance values were obtained for $Pt(APE)_2(SCN)_2$ at several concentrations. The plot of Λ_M against C_M (Λ_e against C_e for 1:1 electrolyte) appears to be linear at concentrations greater than about 10^{-3} *M* (Figure 3), and the slope of this linear portion, which is about 72, agrees with the slopes reported for 1:1 electrolytes in nitrobenzene, but the molar conductance values are less than those normally found for 1:1 electrolytes in nitrobenzene.[14]

$[Pt(APE)_2](ClO_4)_2 \cdot H_2O$ and $[Pd(APE)_2](ClO_4)_2 \cdot H_2O$ have molar conductances of about 30 ohm^{-1} cm^2 $mole^{-1}$ at 10^{-3} *M* concentrations in nitrobenzene. 2:1 electrolytes in this solvent usually have molar conductances of about 50 ohm^{-1} cm^2 $mole^{-1}$. The plot of Λ_M against C_M for $[Pt(APE)_2](ClO_4)_2 \cdot H_2O$ is not linear over the concentration range 10^{-2} to 10^{-4} *M* (Figure 3).

This behavior is characteristic of a weak electrolyte where the dissociation increases with dilution. Since $[Pt(APE)_2](ClO_4)_2 \cdot H_2O$ is not completely dissociated at concentrations of the order of 10^{-2} to 10^{-4} *M*, it may be postulated that ion-pairing occurs and is enhanced by hydrogen bonding between the perchlorate anion and the amino groups of the cation.

(d) *Conductivities in Water* (See Table Id). The complexes, $M(ligand)_2Cl_2 \cdot nH_2O$ (where M = Pd or Pt); ligand = APE or MAA; and n = 0, 1, or 2) were readily soluble in cold water. The molar conductances of the aqueous solutions at about 10^{-3} *M* are about 190 ohm^{-1} cm^2 $mole^{-1}$, which is almost in the range expected for 2:1 electrolytes in water. The complexes must be mainly present in the solution with bis-chelate, 2:1 electrolyte structures of type I.

Deprotonated Complexes. In aromatic primary amines, the lone pair of electrons on the nitrogen atom participates to some extent in the conjugated system of the aromatic ring. Further reduction of the electron density on the nitrogen by coordinate bond formation with a metal ion may be compensated for by transfer of electron density from the N-H bonds to the nitrogen enabling one of the hydrogens to split off as a proton. Thus in aqueous solution at pH = 10.2 two protons are removed from bis(8-aminoquinoline)palladium(II) chloride with the formation of the neutral non-ionic complexes.[15]

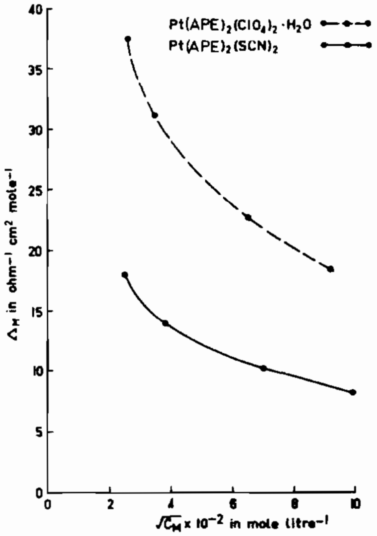

Figure 3. Plots of Λ_M against $\sqrt{C_M}$ for some platinum complexes in nitrobenzene solution.

The bis-complexes of *o*-(dimethylarsino)aniline and *o*-(diphenylarsino)aniline with palladium(II) and platinum(II) chloride were similarly deprotonated by treating with either aqueous ammonia or aqueous potassium hydroxide solutions. The abbreviations (MAA-H) and (PAA-H) are used for the *o*-(dimethylarsino) and *o*-(diphenylarsino)anilinate anions in the following discussion.

The analysis of the deprotonated bis(*o*-diphenylarsinoaniline) complexes recrystallized from dichloromethane revealed the presence of chlorine in the ratio M:Cl = 1:1. However, when dimethylformamide was used in place of dichloromethane as the solvent for recrystallization of the platinum complex, a complex of composition $Pt(PAA\text{-}H)_2$ was obtained. The infrared spectra of this complex and the complex containing chlorine were identical in the N-H stretching region. The chlorine-containing complexes are formulated as solvates, $M(PAA\text{-}H)_2 \cdot \frac{1}{2}CH_2Cl_2$ rather than monodeprotonated derivatives $[M(PAA)(PAA\text{-}H)]Cl$. All of the deprotonated complexes, $M(MAA\text{-}H)_2$ and $M(PAA\text{-}H)_2$, are non-conductors in nitrobenzene solution (Table Ic).

The N-H stretching vibrations in the deprotonated complexes occur in the infrared in the region 3350-3400 cm^{-1} with relatively low intensity. For Pd-

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[13] M. Ciampolini and P Paoletti, *Inorg. Chem.*, 6, 1261 (1967).
[14] E. G. Taylor and C. A. Kraus, *J. Chem. Soc.*, 4587 (1964).
[15] V. K. Gustin and T. R. Sweet, *Analytical Chem.*, 35, 44 (1963).

Table II.

Complex	Colour	Carbon		Hydrogen		Nitrogen		Platinum	
		Calcd %	Found %	Calcd %	Found %	Calcd %	Found %	Calcd %	Found %
(a) Analytical results for palladium complexes									
$Pd(APE)Cl_2$	pale yellow	37.3	37.3	3.6	3.7	3.1	3.1		
$Pd(APE)I_2$	red	26.6	26.9	2.6	2.7	2.2	2.3		
$Pd(APE)(SCN)_2$	orange	38.8	38.8	3.3	3.4	8.5	8.4		
$Pd(APEH^+)Cl_3$	brown	34.5	34.5	3.5	3.6	2.9	2.9		
$Pd(MAA)Cl_2$	yellow	25.7	26.0	3.4	3.4	3.7	3.7		
$Pd(MAA)I_2$	red-brown	17.2	17.3	2.2	2.2	2.5	2.6		
$Pd(MAA)I_2$	yellow	43.4	32.9	3.2	3.6	2.9	2.7		
$Pd(PAA)Cl_2$	orange-yellow	44.2	44.2	3.0	3.1	7.7	7.6		
$Pd(PAA)(SCN)_2$	yellow	44.3	44.2	4.8	4.9	3.7	3.8		
$Pd(APE)_2Cl_2 . 2H_2O$ [a]	cream	40.5	40.7	4.1	4.2	3.4	3.2		
$Pd(APE)_2Br_2 . H_2O$	faint yellow	46.9	46.3	4.2	4.2	7.3	7.7		
$Pd(APE)_2I_2$	faint yellow	38.7	38.6	3.9	3.9	3.2	3.2		
$Pd(APE)_2(ClO_4)_2 . H_2O$	cream	32.6	32.3	4.4	4.6	4.8	4.9		
$Pd(MAA)_2Cl_2 . H_2O$	brownish yellow	28.7	28.7	3.8	4.0	4.2	4.2		
$Pd(MAA)_2Br_2 . \frac{1}{2}H_2O$	orange	25.5	25.5	3.2	3.2	3.7	3.5		
$Pd(MAA)_2I_2$	cream	37.5	27.5	3.5	3.5	4.0	4.1		
$Pd(MAA)_2(ClO_4)_2$ [b]	orange-yellow	51.6	51.0	4.1	4.2	3.3	3.2		
$Pd(PAA)_2I_2 . EtOH$	deep red	43.5	43.7	3.7	3.8	2.7	2.7		
$Pd(PAA)_2I_2$	deep red	43.1	43.3	3.2	3.3	2.8	2.8		
$Pd(PAA)_2(ClO_4)_2 . H_2O$ [c]	faint yellow	44.7	44.9	3.6	3.6	2.9	2.9		
$Pd(MAA\text{-}H)_2$ [d]	brown	38.5	38.4	4.5	4.5	5.6	5.7		
$Pd(PAA\text{-}H)_2 . \frac{1}{2}(CH_2Cl_2)$ [e]	red	55.5	55.3	4.0	3.9	3.6	3.6		
(b) Analytical results for platinum complexes									
$[Pd(APE)_2][PtCl_4]$	pink	31.2	31.2	3.0	3.1	2.6	2.6		
$Pt(APE)_2Cl_2$	orange-yellow	28.3	28.4	3.2	3.3	2.4	2.4	32.9	32.4
$Pt(APE)_2Br_2$	yellow	24.5	24.6	2.6	2.7	2.8	2.8		
$Pt(APE)_2I_2$	pink	20.7	20.7	2.6	2.7	3.0	3.0		
$Pt(APE)_2(SCN)_2$	faint pink	41.4	41.4	4.0	4.0	3.5	3.5	24.0	24.1
$Pt(APE)_2(ClO_4)_2H_2O$	colourless	37.3	37.5	3.6	3.6	3 1	3.1		
$Pt(MAA)_2Cl_2 . 2H_2O$	pale yellow	33.8	33.4	3.2	3.3	2.8	2.8		
$Pt(MAA)_2Br_2 . \frac{1}{2}H_2O$	colourless	42.0	42.0	3.8	3.8	6.5	6.5		
$Pt(MAA)_2I_2$	colourless	35.1	35.1	3.6	3.6	2.9	3.0		
$Pt(MAA)_2(SCN)_2$	pale gold-brown	27.6	27.7	4.1	4.1	4.0	4.2		
$Pt(MAA)_2(ClO_4)_2$		25.4	25.3	3.3	3.4	3.7	3.7		
$Pt(PAA)_2Cl_2 . H_2O$	pale brown	22.8	22.9	2.9	2.9	3.3	3.3		
$Pt(PAA)_2I_2$	pale yellow	30.7	30.7	3.4	3.5	7.9	7.9		
$Pt(PAA)_2(ClO_4)_2$	cream	24.4	24.6	3.1	3.0	3.6	3.6	24.8	25.2
$Pt(MAA\text{-}H)_2$	cream-yellow	46.7	46.6	3 .7	3.8	3.0	3.1		
$Pt(PAA\text{-}H)_2$	yellow	39.6	39.6	3.0	3.5	2.6	2.5		
$Pt(PAA\text{-}H)_2 . \frac{1}{2}(CH_2Cl_2)$ [g]	pale brown yellow	41.7	41.6	3.1	3.1	2.7	2.7	18.8	19.1
$[Pt(APEH^+)Cl_3] . H_2O$	yellow	32.7	32.6	3.8	3.8	4.8	4.9	33.2	32.7
$Pt(APE)I_2 . \frac{1}{2}(DMF)$	yellow	51.8	51.5	3.6	3.8	3.4	3.3		
$[Pt(MAA)_2][PtCl_4]$	yellow	49.9	49.7	3.6	3.7	3 2	3.1	22.2	22.5

[a] Palladium: Clcd. 14.0; Found, 13.8%. [b] Palladium: Calcd. 15.2; Found, 15.8%. [c] Palladium: Calcd. 11.0; Found, 10.6%. [d] Palladium: Calcd. 21.3; Found, 20.9%. [e] Palladium: Calcd. 13.6; Found, 13.8%; Chlorine: Calcd. 4.6; Found, 4.7%. [f] Chlorine: Calcd. 17.9; Found, 17.8%; [g] Chlorine: Calcd. 4.0; Found, 4.0%.

$(MAA\text{-}H)_2$ the adsorption band is weak and broad but some structure is resolved in the band for the other deprotonated complexes.

The deprotonation of the complexes of 1-amino-2-(diphenylarsino)ethane could only be expected to occur under very strongly basic conditions, *e.g.*, potassium amide in liquid ammonia,[16] and was not investigated.

Experimental Section

(Analytical results are shown in Table II).

Potassium tetrachloropalladate(II) and potassium tetrachloroplatinate(II) were prepared from palladium or platinum sponge, respectively, according to methods given in *Inorganic Syntheses*.[17]

(a) *1-amino-2-diphenylarsinoethane(APE) Complexes.*

(i) *Dichloro(1-amino-2-diphenylarsinoethane)palladium(II).* A solution of APE (0.50 g) in ethanol (75 ml) was added to a solution of potassium tetrachloropalladate(II) (0.60 g) in water (25 ml) acidified with 10 *M* hydrochloric acid (0.5 ml). A light-brown

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(16) G. Watt, R. E. Mc Carley and J. W. Dawes, *J. Am. Chem. Soc.*, *79*, 5163 (1957).

(17) G. B. Kauffman and J. Hwa-san Tsai, Inorg. *Syntheses*, *8*, 235 (1966). G. B. Kauffman and D. O. Cowan, Inorg. *Syntheses*, *7*, 240 (1963).

precipitate, probably $[Pd(APE)_2][PdCl_4]$, formed at once. The mixture was heated to boiling point, whereupon the initial precipitate dissolved forming a yellow solution. On cooling the solution, pale yellow crystals of $Pd(APE)Cl_2$ separated. The product was collected and washed with water and ethanol.

(ii) *Diiodo(1-amino-2-diphenylarsinoethane)palladium(II).* Excess sodium iodide (0.50 g) was added to the suspension of $[Pd(APE)_2][PdCl_4]$ prepared from potassium tetrachloropalladate(II) (0.30 g) and 1-amino-2-(diphenylarsino)ethane (0.25 g) in aqueous ethanol, and the mixture was stirred and heated on the steam bath for 1 hour. The red precipitate was collected and recrystallized from hot ethanol.

(iii) *Dithiocyanato(1-amino-2-diphenylarsinoethane)-palladium(II).* This complex was prepared similarly to (ii) above using (0.33 g) potassium tetrachloropalladate(II) (0.40 g) and potassium thiocyanate (0.50 g). $[Pd(APE)(SCN)_2]$ formed as orange crystals.

(iv) *Trichloro(1-ammonium-2-diphenylarsinoethane)-platinum(II) monohydrate.* $[Pt(APE)_2][PtCl_4]$ (0.40 g) was dissolved in 50 ml of 1:1 ethanol and 10 *M* hydrochloric acid by heating. On cooling the solution thus obtained, orange-yellow crystals of $Pt(APE\text{-}H^+)Cl_3 \cdot H_2O$ separated. The product was collected and washed with ethanol.

(vii) *Diiodo(1-amino-2-diphenylarsinoethane)platinum(II).* The suspension of $[Pt(APE)_2][PtCl_4]$, prepared from APE (0.20 g) and potassium tetrachloroplatinate(II) (0.30 g) in aqueous ethanol, was stirred with excess sodium iodide (0.50 g) while heating on the steam bath for about 5 hours. The colour of the suspension gradually changed from pink to yellow. product was collected and recrystallized by dissolving in dimethylformamide and adding ether and hexane. Yellow crystals with the composition of $[Pt(APE)_2I_2]$-½DMF were obtained.

(viii) *Bis(1-amino-2-diphenylarsinoethane)palladium-(II) chloride.* A solution of APE (0.75 g) in ethanol (30 ml) was added to potassium tetrachloropalladate (II) (0.45 g) in water (20 ml). A precipitate of $[Pd(APE)_2][PdCl_4]$ formed initially, but dissolved on heating and a yellow solution was obtained. The solutions was evaporated to dryness on a steam bath and the dry residue was extracted with absolute ethanol (20 ml). The potassium chloride was filtered off and on slowly adding ether to the filtrate, a yellow crystalline precipitate formed. The product was recrystallized by dissolving in ethanol and adding ether. The yield of $Pd(APE)_2Cl_2 \cdot 2H_2O$ was 0.91 g. The complex was readly dehydrated by heating to 110° C. The anhydrous compound was almost colourless but rapidly converted to the bright yellow dihydrate on standing in air. $Pd(APE)_2Cl_2 \cdot 2H_2O$ is readily soluble in water and ethanol.

(ix) *Bis(1-amino-2-diphenylarsinoethane)platinum-(II) chloride.* This complex was prepared similarly to (viii) above from APE (0.53 g) and potassium tetrachloroplatinate(II) (0.40 g). The yield of almost colourless crystals was 0.70 g. $[Pt(APE)_2]Cl_2$ is readily soluble in water and ethanol.

(x) *Complexes of general formula $M(APE)_2X_2 \cdot nH_2O$* where M = Pd or Pt; X = Br, I, SCN, or ClO_4; n = 0 or 1. A slight excess of the appropriate salt, NaX (where X = Br, I, or ClO_4) or KSCN, dissolved in water was added to an aqueous solution of either $[Pt(APE)_2]Cl_2$ or $[Pd(APE)_2]Cl_2 \cdot 2H_2O$. Precipitates of the complexes $M(APE)_2X_2 \cdot nH_2O$ were thus obtained. The complexes were sparingly soluble in cold water but moderately soluble in boiling water enabling water to be used as a solvent for recrystallization. The products thus obtained were:

$Pd(APE)_2Br_2 \cdot H_2O$ (pale yellow)
$Pd(APE)_2I_2$ (orange-red)
$[Pd(APE)_2](SCN)_2$ (pale yellow)
$[Pd(APE)_2](ClO_4)_2 \cdot H_2O$ (faint yellow)
$[Pt(APE)_2]Br_2$ (colourless)
$Pt(APE)_2I_2$ (yellow)
$[Pt(APE)_2](SCN)_2$ (colourless)
$[Pt(APE)_2](ClO_4)_2 \cdot H_2O$ (colourless)

(b) o-*(dimethylarsino)aniline (MAA) complexes.*

(xi) *Dichloro(*o*-dimethylarsinoaniline)palladium(II).* MAA (0.30 g) dissolved in ethanol (50 ml) was added to K_2PdCl_4 (0.50 ml) in water (20 ml). The light brown precipitate that formed initially dissolved on boiling. Yellow crystals of $Pd(MAA)Cl_2$ separated when the solution was cooled. The product was collected and washed with ethanol.

(xii) *Bis(*o*-dimethylarsinoaniline)platinum(II) tetrachloroplatinate(II).* MAA (0.14 g) dissolved in ethanol was added to an aqueous solution of K_2PtCl_4 (0.30 g). A pink precipitate formed at once. The product was collected and washed with water and ethanol.

(xiii) *Diiodo(*o*-dimethylarsinoaniline)palladium(II).* The solution obtained by heating MAA and K_2PdCl_4 in aqueous ethanol as in (xi) above was treated with excess sodium iodide solid. The red-brown precipitate that formed was recrystallized from ethanol.

(xiv) *Bis(*o*-dimethylarsinoaniline)palladium(II) chloride hydrate.* MAA (0.50 g) in ethanol was added to an aqueous solution of K_2PdCl_4 (0.40 g). A light brown precipitate formed initially but dissolved on warming. The solution was evaporated to dryness, and the complex was extracted with absolute ethanol. The complex was precipitated from the ethanol solution by adding low-boiling petroleum ether. The product was dissolved in ethanol and reprecipitated with petroleum ether. The yield of cream coloured product was 0.65 g.

(xv) *Bis(*o*-dimethylarsinoaniline)platinum(II) chloride dihydrate.* This complex was prepared similarly to (xiv) above using K_2PtCl_4 (0.50 g) and MAA (0.48 g). A precipitate of $[Pt(MAA)_2][PtCl_4]$ formed initially but dissolved on heating. The yield of gold-brown product was 0.75 g.

(xvi) *Complexes of general formula $M(MAA)_2X_2$.*

nH_2O (where M = Pd or Pt; X = Br, I, SCN, or ClO_4; and n = ½ or 0.

A solution of $M(MAA)_2Cl_2 \cdot 2H_2O$ (0.1 mole) dissolved in water was treated with a slight excess of an aqueous solution of the appropriate salt, NaX (where X = Br, I, or ClO_4) or KSCN. A crystalline precipitate formed at once or in a few minutes. The products were collected, washed with water, and dried. The products were than recrystallized from a suitable solvent indicated below. The complexes thus obtained were:

Complex	Colour	solvent for recrystallization
$Pd(MAA)_2Br_2 \cdot \frac{1}{2}H_2O$	cream	water
$Pd(MAA)_2I_2$	orange	cyclohexane
$Pd(MAA)_2(ClO_4)_2$	white	not recrystallized
$Pt(MAA)_2Br_2 \cdot \frac{1}{2}H_2O$	pale brownish yellow	water
$Pt(MAA)_2I_2$	pale golden-brown	water
$Pt(MAA)_2(SCN)_2$	pale yellow	water
$Pt(MAA)_2(ClO_4)_2$	faint yellow	not recrystallized

(xvii) *Bis(1-dimethylarsinoanilinato)palladium(II).* An aqueous solution of $Pd(MAA)_2Cl_2 \cdot H_2O$ (0.65 g) was treated with excess 12 *M* ammonia solution. Dichloromethane (50 ml) was added to the suspension of the product which then dissolved in the dichloromethane layer. The red dichloromethane layer was separated and dried ($CaSO_4$). The product was precipitated by adding low-boiling petroleum ether to the dichloromethane solution. $Pd(MAA\text{-}H)_2$ was obtained as a brown microcrystalline precipitate.

(xviii) *Bis(*o*-dimethylarsinoanilinato)platinum(II).* This complex was prepared similarly to (xvii) using $Pt(MAA)_2Cl_2 \cdot 2H_2O$ (0.75 g). $Pt(MAA\text{-}H)_2$ was obtained as bright yellow crystals.

(c) o-*(diphenylarsino)aniline (PAA) complexes.*

(xix) *Dichloro(*o*-diphenylarsinoaniline)palladium-(II).* A solution of PAA (0.50 g) in ethanol (50 ml) was added to a solution of K_2PdCl_4 (0.50 ml) in water (40 ml). A light brown precipitate formed initially, but it slowly became yellow. The precipitate was collected and recrystallized as yellow plates from a 4:1 mixture of ethanol and water.

(xx) *Bis(*o*-diphenylarsinoaniline)palladium(II) chloride monohydrate.* This complex was prepared a procedure analogous to that given for the preparation of $Pd(MAA)_2Cl_2 \cdot H_2O$ (xiv). Using PAA (0.61 g) and K_2PdCl_4 (0.30 g), 0.73 g of the product was obtained as orange-yellow crystals.

(xxi) *Bis(*o*-diphenylarsinoaniline)platinum(II) chloride monohydrate.* This complex was prepared by a procedure similar to that of (xv) for $Pt(MAA)_2Cl_2 \cdot 2H_2O$. From PAA (0.60 g) and K_2PtCl_4 (0.39 g), a yield of 0.82 g of $Pt(PAA)_2Cl_2 \cdot H_2O$ was obtained. The complex separates initially as yellow crystals but changesto a pale brownish-white powder when collected and dried.

(xxii) *Complexes of general formula $M(PAA)_2X_2 \cdot nH_2O$* (where M = Pd or Pt; X = I or ClO_4; and n = 0 or 1).

$M(PAA)_2Cl_2 \cdot H_2O$ was dissolved in ethanol and then diluted with an equal volume of water. To this solution was added a slight excess of either NaI or $NaClO_4$ in water. The products formed as precipitates which were collected and washed with water. They were purified by recrystalling from ethanol (usually twice). The complexes thus obtained were:

$Pd(PAA)_2I_2 \cdot EtOH$	deep red
$Pd(PAA)_2(ClO_4)_2 \cdot H_2O$	pale yellow
$Pd(PAA)_2I_2$	yellow
$Pt(PAA)_2(ClO_4)_2$	pale brownish-yellow

(xxiii) *Dithiocyanato(*o*-diphenylarsinoaniline)palladium(II).* When an attempt was made to prepare $Pd(PAA)_2(SCN)_2$ according to procedure (xxii), $Pd(PAA)SCN_2$ formed instead. The complex was obtained as orange-yellow crystals after three recrystallizations from ethanol.

(xxiv) *Bis(*o*-diphenylarsinoanilinato)palladium(II).* $Pd(PAA)_2Cl_2 \cdot H_2O$ (0.73 g) was suspended in water (20 ml) and 12 *M* ammonia solution (20 ml) was added. The colour of the suspended material changed immediately to orange-red. After stirring for 20 minutes it was collected and washed with dilute ammonia solution and ethanol. On recrystallizing the product from dichloromethane bright red crystals of composition $Pd(PAA\text{-}H)_2 \cdot \frac{1}{2}CH_2Cl_2$ were obtained.

(xxv) *Bis(*o*-diphenylarsinoanilinato)platinum(II).* This complex was prepared by a procedure similar to that given for (xxiv) using $Pt(PAA)_2Cl_2 \cdot H_2O$ (0.80 g) or by an alternative procedure using potassium hydroxide in place of ammonia. A solution of $Pt(PAA)_2Cl_2 \cdot H_2O$ in ethanol was treated slowly with about 1½ times the calculated quantity of potassium hydroxide solution. The yellow precipitate was collected and recrystallized from dichloromethane. Yellow crystals of composition $Pt(PAA\text{-}H)_2 \cdot \frac{1}{2}CH_2Cl_2$ were obtained. If the product was recrystallized from dimethylformamide and washed with water and ethanol, a yellow powder of composition $Pt(PAA\text{-}H)_2$ was obtained.