Complexes of Palladium(II) and Platinum(II) with Phenoxathiin and Thianthrene

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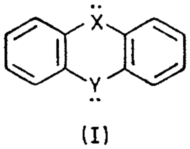
Phenoxathiin interacts not only with Pd^{II} but also with Pt^{II}. Thianthrene undergoes closely parallel interactions with these metal ions. For each metal–ligand pair, 1:1 and 1:2 complexes, $[MCl_2L]$ and $[ML_2]Cl_2$ have been identified by the method of continuous variation. The 1:2 complexes have, in addition, been characterized by microanalysis, i.r. and electronic spectra, and conductivity measurements. These complexes are believed to have approximate square-planar structures in which the heterocyclic compounds act as bidentate ligands. In nitrobenzene solutions, it appears that, in the 1:2 complexes, one or both of the chloride ions may be weakly bonded to Pd^{II} or Pt^{II}.

PHENOXATHIIN (Ia; X = S, Y = O) has been used as a reagent for colorimetric detection and determination of palladium(II) ion by Konig and Crowell [1] and by Ziegler and Schroeder.[2] A solid complex of empirical formula $[Pd(C_{12}H_8OS)_2Cl_2]$ was also isolated. Platinum(II) was one of the metal ions that were reported to be unreactive towards this reagent.

Phenoxathiin is a member of a series of heterocyclic compounds of general formula (I), where X and Y are heteroatoms or groups such as O, S, Se, Te, NH, AsH, PH, *etc.* Although Konig and Crowell proposed structure (II) for the palladium(II) complex, and Ziegler and Schroeder also suggested that the metal ion is bonded only through the S atom of the ligand, compounds (I) are potential bidentate ligands with the possibility of both heteroatoms bonding to the metal ion. To facilitate this, they should preferably assume a molecular structure which is folded along the *XY* axis so that the heteroatoms have approximate tetrahedral configurations and the lone pairs are in more favourable positions for bond-



(I)

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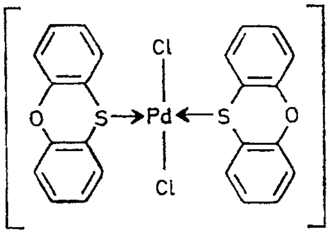
[1] O. Konig and W. R. Crowell, *Mikrochem. Mikrochim. Acta*, 1943, **33**, 298.

[2] M. Ziegler and H. Schroeder, *Z. Naturforsch.*, 1967, **B22**, 557.

ing with the metal ions. At least one member of the series, phenothiazine (Ic; X = S, Y = NH), has been shown by *X*-ray structure studies to possess such a folded configuration.[3]



(II)

We have now reinvestigated the interactions of phenoxathiin (Ia) with Pd^{II} and Pt^{II} and found that, contrary to earlier findings, both metal ions react to form not only the 1 : 2 complexes but also 1 : 1 complexes. Moreover, a parallel study has been made of the interactions of these metal ions with thianthrene (Ib; X = Y = S), the chelating properties of which have until now not been investigated. If only the sulphur atom in phenoxathiin is bonded to the metal ion, then thianthrene with two such atoms should be capable of bonding with these metal ions at both ends and, consequently, the complexes formed by these two ligands would be expected to have divergent characters. On the contrary, the closely similar properties of the two series of complexes, as reported below, suggest a similar mode of bonding between these ligands and the two metal ions.

TABLE 1

Electronic absorptions (cm^{-1}) and molar absorption coefficients[a] for the 1 : 1 and the 1 : 2 complexes, $[MCl_2L]$ and $[ML_2]Cl_2$

Ligand	1 : 1 Complex					
	In aqueous ethanol or ethanol		In chloroform		1 : 2 Complex in chloroform	
Phenoxathiin	M = Pd	Pt	Pd	Pt	Pd	Pt
	22 700[b]	21 900[b]	23 000[b]	22 200[b]	21 980 (3 350)	20 000 (1 940)
33 900 (3 630)					34 980 (17 500)	34 500 (4 630)
40 800 (13 500)					40 440 (37 960)	40 700 (20 600)
Thianthrene	M = Pd	Pt	Pd	Pt	Pd	Pt
	23 800[b]	22 800[b]	24 000[b]	23 000[b]	23 000 (1 340)	22 000 (1 000)
34 500 (5 720)					34 130 (5 000)	34 500 (12 000)
38 820 (57 200)					38 800 (60 600)	38 800 (60 500)
40 820 (38 140)					41 000 (33 700)	40 600 (46 400)

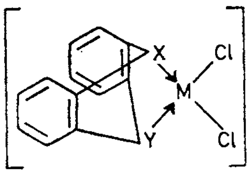
[a] In parentheses. [b] Absorption coefficients of these species could not be evaluated as their corresponding concentrations were not accurately known.

RESULTS AND DISCUSSION

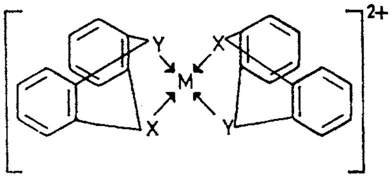
Stoicheiometry and Proposed Structures.—When ethanolic solutions of phenoxathiin or thianthrene were mixed with solutions of palladium(II) chloride in dilute hydrochloric acid, or of hexachloroplatinic(IV) acid in ethanol, intense colourations developed instantaneously, indicating complex formation. The complexes were readily extractable with chloroform. For each metal–ligand pair, the visible spectra of the aqueous ethanolic or ethanolic solution and of the chloroform extract were similar. However, when the reaction mixtures, without extraction with chloroform, were allowed to stand for periods of time, which varied with the concentrations of the reactants, solid complexes gradually precipitated. The solid complexes were only sparingly soluble in ethanol, but were more readily soluble in chloroform. In each case, the visible spectrum of the solid complex in chloroform was different from that of the corresponding chloroform extract of the reaction mixture before precipitation, indicating that each metal–ligand pair probably formed two different complexes. This was verified by the results of stoicheiometry determinations.

The stoicheiometries of the complexes were determined by a modified Job's method[4] of continuous variation. In each case, the ethanol-soluble complex had a metal : ligand ratio of 1 : 1 both in ethanol solution and in the chloroform extract, whereas this ratio for the solid complex was 1 : 2. The 1 : 1 complexes could not be isolated since evaporation of the chloroform extracts produced essentially the 1 : 2 solid complexes. This could be due to further interaction of the 1 : 1 complex, in each case, with ligand that had also been extracted into the chloroform solution. The stoicheiometry of the solid complexes was further confirmed by microanalysis.

Probable structures for the 1 : 1 and 1 : 2 complexes respectively are (III) and (IV), in which the metal ions assume approximate square-planar configurations.



(III)



(IV)

Electronic Spectra.—The electronic spectra of the 1 : 1 complexes were recorded only in the visible region as their solutions, either in ethanol or in chloroform, also contained excesses of ligands which absorbed strongly in the u.v. regions. The electronic spectra of the 1 : 2 complexes, however, were recorded in both the visible and the u.v. regions. While the absorptions in the latter region

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[3] J. D. Bell, J. F. Blount, O. V. Briscue, and H. C. Freeman, *Chem. Comm.*, 1968, 1656.

[4] S. Chaberak and A. E. Martell, 'Organic Sequestering Agents,' John Wiley, 1959, p. 78.

are largely those due to the ligands $L(\pi)\rightarrow L(\pi^*)$, the bands in the former region were of much too high intensity for assignment to *d–d* transitions. These visible bands could conceivably be due to $M\rightarrow L(\pi^*)$ transitions, and probably mask the *d–d* bands. It is interesting to note that these bands for the complexes of Pd^{II} are of higher energy than those for the corresponding platinum(II) complexes. A similar trend was observed for the maleonitriledithiol[5] and quinoxaline-2,3-dithiol complexes[6] of these two metal ions. Moreover, the increase in frequencies in going from phenoxathiin to thianthrene was observed for both metal ions. Such an increase would not be expected if only unidentate co-ordination through sulphur occurs in these complexes. Thus the observed trend appears to support our postulation that in these complexes both phenoxathiin and thianthrene function as bidentate ligands.

Infrared Spectra of the 1 : 2 *Complexes*.—The i.r. spectra of the palladium(II) and platinum(II) complexes of each ligand are strikingly similar. When these spectra in the region 400—4000 cm^{-1} are compared with those of the ligands (Table 2), it is evident that both the C–O–C and C–S–C bands have changed in vibration frequencies and/or intensities. Moreover, in the far-i.r. region 200—600 cm^{-1}, new bands due to M–O and M–S vibrations were clearly detectable in the spectra of all four complexes. These findings further support the postulation that the metal ion is bonded to both heteroatoms in each case.

TABLE 2

Infrared absorptions (cm^{-1}) of the 1 : 2 complexes, $[ML_2]Cl_2$

L = Phenoxathiin	M = Pd	M = Pt	Assignments
1 290w	1 310s	1 310s	C–O–C
1 205—1 225m,b	1 225vs	1 225vs	
1 085m	1 065m	1 065m	
875m,b	880s	885s	C–S–C
	865m	865m	
720w	705m	705m	
685m	688w	688w	
	472s	476s	M–O *
	445s	454m	M–O
	420w	420w	M–S
	400w	400w	M–S
	328m	350m	M–S
	310, 300m	328m	M–O, M–S
L = Thianthrene			
877w	870m,b	868m,b	C–S–C
872w			
715w	705m	705m	
660w	660m	660m	
	405w	406w	M–S *
	325m	348m	
	315m	336m	
	290w	320m,b	
		290w	

s = strong, m = medium, w = weak, v = very, and b = broad.

* D. M. Adams, 'Metal–Ligand and Related Vibrations,' Edward Arnold, London, 1967.

Magnetic-susceptibility and Conductivity Measurements on the 1 : 2 *Complexes*.—Using the Gouy method, all four solid complexes were found to be diamagnetic. Conductivities were measured in nitrobenzene solutions; whereas the palladium(II) complexes conduct weakly, the complexes of Pt^{II} are practically non-conducting. The molar conductivities of the complexes of Pd^{II} (Table 3) are comparable to that of the 1 : 1 electrolyte $[Pd(pdma)_2Cl]Cl$,[7] but not to that of the 1 : 2 electrolyte $[Pd(pdma)_2][ClO_4]_2$ [pdma = *o*-phenylenebis(dimethylarsine)].[7] Thus, it appears that, in nitrobenzene, the palladium(II) complexes of phenoxathiin and thianthrene behave like five-co-ordinate species in which a chloride ion bonds weakly to the metal ion along the axial direction. That the platinum(II) analogues behave as non-electrolytes probably results from the greater tendency for axial bonding of Pt^{II} than of Pd^{II}. This difference could be due to the larger spatial extension of the 5*d* orbitals of Pt^{II} than the 4*d* orbitals of Pd^{II}, which more readily facilitates d_π–d_π interactions of the former than of the latter metal ion.

TABLE 3

Molar conductivities in nitrobenzene at 25 °C

Complex	Λ/S cm^2 mol^{-1}
$[Pd(Ia)_2]Cl_2$	23
$[Pd(Ib)_2]Cl_2$	22
$[Pd(pdma)_2Cl]Cl$	25
$[Pd(pdma)_2][ClO_4]_2$	46

However, it should be noted that such Pd–Cl or Pt–Cl bonds, if they exist in the complexes in the solid state, must be weak so that the metal ions remain essentially square planar as demonstrated by the magnetic measurements. It is also likely that changes in geometry of the metal ions may occur in going from the solid state to solution as in equations (1) and (2). The observed low

$$[PdL_2]Cl_2 \xrightarrow{\text{nitrobenzene}} [PdClL_2]Cl \qquad (1)$$

$$[PtL_2]Cl_2 \xrightarrow{\text{nitrobenzene}} [PtCl_2L_2] \qquad (2)$$

values for the molar conductivities of these complexes are in accord with other literature data.[8]

EXPERIMENTAL

Physical Measurements.—Infrared spectra were recorded on a Perkin-Elmer model 337 spectrophotometer which was calibrated with polystyrene film. The KBr pellet technique was employed throughout. Electronic spectra were recorded for *ca*. 10^{-3} mol dm^{-3} solutions in distilled chloroform using a Hitachi 124 spectrometer. Conductivities were determined at a constant temperature of 25 °C, using a Mullard conductivity bridge. Magnetic susceptibilities were measured on a Gouy balance calibrated with $Hg[Co(NCS)_4]$.

Determination of Stoicheiometry by Job's Method of Continuous Variation.—(a) *Ethanol-soluble complexes*. A series of ten solutions were prepared by mixing calculated volumes of a 0.0025 mol dm^{-3} solution of palladium(II) chloride in 0.1 mol dm^{-3} HCl or H_2PtCl_6 in ethanol and of the solvent, such that the volume of each of these mixtures was 10 cm^3

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[5] S. H. H. Chaston and S. E. Livingston, *Austral. J. Chem.*, 1967, **20**, 1079.

[6] C. K. Jørgensen, *Inorg. Chim. Acta Rev.*, 1968, **2**, 65.

[7] C. M. Harris and R. S. Nyholm, *J. Chem. Soc.*, 1956, 4375.

[8] A. D. Westland, *J. Chem. Soc.*, 1965, 3060.

and that they contained different mole fractions of the reactants while their total concentrations remained constant. No precipitation occurred for at least the first hour. Fifteen minutes after mixing, the absorbances of each mixture were measured at its $\nu_{max.}$ and at two other frequencies. Plots of each series of absorbances against mole fraction were approximately symmetrical and showed maxima at the mole ratio of 1 : 1. A typical plot is shown in Figure 1. The experiment was repeated, but in this case each mixture was extracted with chloroform (10 cm^3) 15 min after mixing. The absorbances of these chloroform extracts were recorded and plotted against mole fractions as before. Maximum absorbance again occurred at a mole ratio of 1 : 1.

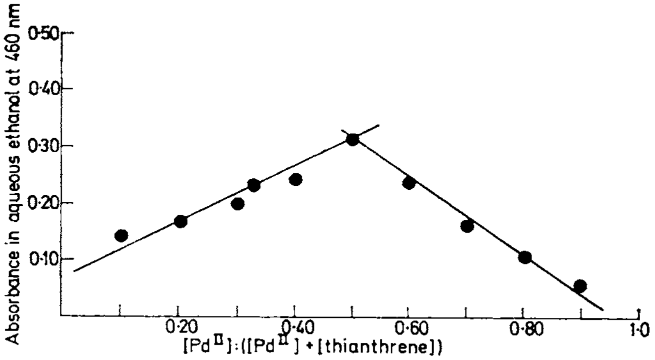

FIGURE 1 Continuous-variation study of the reaction between $PdCl_2$ and thianthrene to give the 1.1 complex. The absorbance was corrected for any excess of $PdCl_2$

(b) *The solid complexes.* Following a similar procedure to (a), a series of ten mixtures were prepared using 0.01 mol dm^{-3} solutions of the ligand and of the metal ion. After standing for 1 h, precipitation was practically complete in all the mixtures The mixtures were then extracted with portions (10 cm^3) of chloroform, in which the precipitate dissolved completely. The absorbances at $\nu_{max.}$ were recorded and plots of absorbance against mole fraction showed a maximum at a metal to ligand mole ratio of 1 : 2. A typical plot is shown in Figure 2.

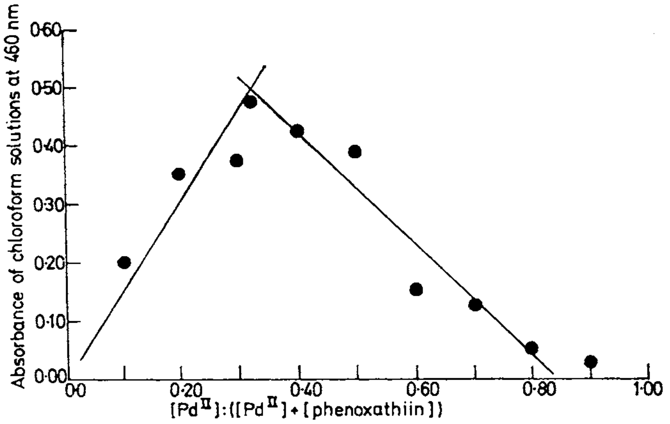

FIGURE 2 Continuous-variation study of the reaction between $PdCl_2$ and phenoxathiin to give the 1 : 2 complex

Synthesis of Complexes.—(a) *Dichlorobis(phenoxathiin)-palladium*(II). An aqueous solution of $PdCl_2$ (0.10 g) in 0.1 mol dm^{-3} HCl was treated with a solution of phenoxathiin (0.24 g) in ethanol. A red precipitate formed immediately. The resulting solution was stirred for *ca.* 15 min, after which the precipitate (yield 100%) was filtered off, washed successively with 0.1 mol dm^{-3} HCl and ethanol, and then dried *in vacuo*, m.p. 255—258 °C (decomp.) (Found: C, 49.9; H, 2.9; Cl, 12.4; S, 11.4. $C_{24}H_{16}Cl_2O_2PdS_2$ requires C, 50.0; H, 2.8; Cl, 12.3; S, 11.0%).

(b) *Dichlorobis(thianthrene)palladium*(II). This was prepared in a similar manner to (a), using $PdCl_2$ (0.10 g) and thianthrene (0.25 g). The yellow precipitate (yield 96%) which formed was carefully washed with 0.1 mol dm^{-3} HCl and ethanol and then dried *in vacuo*, m.p. 310—312 °C (decomp.) (Found: C, 46.9; H, 2.8; Cl, 11.5; S, 21.3. $C_{24}H_{16}Cl_2PdS_4$ requires C, 47.3; H, 2.6; Cl, 11.6; S, 21.0%).

(c) *Dichlorobis(phenoxathiin)platinum*(II). On mixing ethanolic solutions of H_2PtCl_6 (0.22 g) and of phenoxathiin (0.24 g), a reddish orange colour developed immediately. After stirring the mixture magnetically for 2 h, the reddish orange precipitate (yield 60%), which formed gradually, was filtered off, washed repeatedly with absolute alcohol, and then dried *in vacuo*, m.p. 270—271 °C (decomp.). The filtrate, on standing overnight, yielded more of the same complex (Found: C, 43.5; H, 2.4; Cl, 10.3; S, 9.9. $C_{24}H_{16}Cl_2O_2PtS_2$ requires C, 43.3; H, 2.9; Cl, 10.5; S, 9.6%).

(d) *Dichlorobis(thianthrene)platinum*(II). A mixture of ethanolic solutions of H_2PtCl_6 (0.23 g) and thianthrene (0.25 g) was heated gently under reflux for 6 h. The yellow precipitate (yield 80%), which formed gradually, was filtered off, washed with absolute alcohol, and dried *in vacuo*, m.p. 322—326 °C (decomp.) (Found: C, 41.3; H, 2.6; Cl, 10.0; S, 18.4. $C_{24}H_{16}Cl_2PtS_4$ requires C, 41.4; H, 2.8; Cl, 10.1; S, 18.4%).

In the process of reacting with the ligands, platinum is evidently reduced from the IV to a II state, as shown by the stoicheiometry of the two platinum complexes.

(e) *Effect of hydrochloric acid.* Whereas the use of dilute HCl was necessary to dissolve the $PdCl_2$, excess of it retarded the complex formation. This was shown by the progressively slower development of the red colouration with increasing acid concentration. Moreover, although the solid 1 : 2 complex was formed in practically quantitative yields from solutions containing 0.05—0.5 mol dm^{-3} HCl, it could not be prepared if the acid concentration exceeded 1 mol dm^{-3}.

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