Complexes of Metal Ions with Phosphorus or Arsenic containing Ligands, Part XX. Chelates of o-Phenylenebis(diarylarsines) with Palladium(II) and Platinum(II) Halides, Pseudohalides and Perchlorates

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Summary
Two ditertiaryarsines, o-phenylenebis(diphenylarsine), (pdpa) and o-phenylenebis(di-p-tolylarsine), (pdta) yield some new complexes of palladium(II) and platinum(II). These are: square planar M(pdta)X2·nCH2Cl2, [M = Pd, X = Cl, Br or NCS; M = Pt, X = Cl]; [Pt(A-A)2]·nCH2Cl2, [(A-A) = pdta, X = Cl, NCS or ClO4; (A-A) = pdpa, X = ClO4]; [M2(A-A)2(NCS)2]·nCH2Cl2, [M = Pd, (A-A) = pdta; M = Pt, (A-A) = pdpa]; distorted octahedral M(pdta)X2 ·nCH2Cl2, [M = Pd, X = I; M = Pt, X = Br or I] and [Pd(pdta)(H2O)2](ClO4)2, and five coordinate [M(A-A)2X](ClO4)n·nCH2Cl2 complexes are novel in the sense that they contain bridging thiocyanate together with ionic perchlorate. The stereochemical assignments have been made on the basis of i.r. and u.v. spectra as well as conductance data.

Introduction
In continuation of earlier studies(1, 2) on the complexes of o-phenylenebis(diphenylarsine), (pdpa) and o-phenylenebis(di-p-tolylarsine), (pdta) with cobalt(II), nickel(II), copper(I) and mercury(II), the present paper deals with the complexes of palladium(II) and platinum(II).

Experimental
PdCl2 and H2PtCl6·nH2O were obtained from Johnson Matthey, England. All solvents used were purified and dried by standard methods. The syntheses of the ligands and associated physical measurements have been described earlier(1).

References

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Concentration of the filtrate from the above reaction yielded a slightly impure sample of Pt(pdta)$_2$Cl$_2$. A similar reaction designed to obtain Pt(pdta)$_2$X$_2$ (X = NCS, Br or I) failed, but gave impure Pt(pdta)$_2$X$_2$.

\[ M(pdta)_2X_2 \cdot nCH_2Cl_2, \quad (M = Pd, X = I, n = 0.5; M = Pt, X = Cl or Br, n = 1; X = NCS or I, n = 0) \]

Ligand pdta (0.59 g, 1.0 mmol) dissolved in CH$_2$Cl$_2$ (15 cm$^3$) was added to a solution of Na$_2$MCl$_4$ (M = Pd or Pt, 0.5 mmol) in EtOH (12 cm$^3$) in the presence of an excess of NaX (X = Br, NCS or I). The reaction mixture was filtered, the filtrate was evaporated almost to dryness and the residue extracted with a minimum amount of CH$_2$Cl$_2$. Addition of a small amount of EtOH gave pure crystals (Yield 0.5 g).

An attempt to prepare the Pd(pdta)$_2$X$_2$ complexes (X = Cl, Br or NCS) by this method failed and resulted in the formation of Pd(pdta)$_2$X$_2$ · nCH$_2$Cl$_2$ solvated adducts, where X = Cl, n = 1.5. (Yield, 0.2 g), for X = Br or NCS, n = 1 (Yield, 0.3 g).

\[ [Pt(pdpa)_2Br]ClO_4 \]

Reaction of pdta with Na$_2$PdCl$_4$ following the above method in the presence of an excess of HClO$_4$ (60%) yielded a pink precipitate of Pd(pdta)$_2$(ClO$_4$)$_2$ · 2 H$_2$O which was filtered and washed successively with H$_2$O, EtOH and CH$_2$Cl$_2$ (Yield 0.5 g).

\[ [M(A-A)_2X_2]ClO_4 \cdot nCH_2Cl_2, \quad (M = Pd, (A-A) = pdpa, X = I, n = 0. M = Pt, (A-A) = pdpa, X = Br, n = 0; X = I, n = 2; (A-A) = pdta, X = I, n = 1) \]

The M(A-A)$_2$X$_2$ · nCH$_2$Cl$_2$ complex (0.5 mmol) dissolved in a minimum amount of warm CH$_2$Cl$_2$ (30 cm$^3$) was treated with a solution of LiClO$_4$ (5 mg, 0.5 mmol) in EtOH (15 cm$^3$). Concentration of the reaction mixture to a small vol yielded a solid which was filtered and recrystallised from 4:1 v:v CH$_2$Cl$_2$ : EtOH (Yield, 0.5 g).

A similar reaction of Pt(pdpa)$_2$(NC$l_2$)$_2$ and Pt(pdta)$_2$X$_2$, (X = Br or NCS) yielded only [Pt(A-A)$_2$(ClO$_4$)$_2$, ([A-A] = pdpa or pdta) while that of Pt(pdta)$_2$Br$_2$ yielded a white precipitate of Pt(pdta)$_2$(ClO$_4$)$_2$ · 2CH$_2$Cl$_2$ which was filtered (Yield 0.4 g). The yellow filtrate on concentration gave [Pt(pdta)$_2$Br]ClO$_4$ which was recrystallised from 1:4 v:v EtOH : CH$_2$Cl$_2$ (Yield, 0.15 g).

\[ Pd(pdta)(H_2O)$_2$ClO_4 \]

A solution of the Pd(pdta)(H$_2$O)$_2$ClO$_4$ complex (0.8 g, 1.0 mmol) in Me$_2$CO (50 cm$^3$) on treatment with an excess of HC$l_4$O$_4$ (60%) yielded a pink precipitate of Pd(pdta)$_2$(ClO$_4$)$_2$ · 2H$_2$O which was filtered and washed successively with H$_2$O, EtOH and CH$_2$Cl$_2$. A similar reaction of Pt(pdta)$_2$(NCS)$_2$ and Pt(A-A)$_2$X$_2$, (X = Cl, Br or NCS) directly, whereas under similar conditions pdta and Na$_2$PtCl$_4$ yield a highly insoluble complex, which gives Pt(pdta)$_2$Cl$_2$ only on prolonged heating with DMF. The complexes lose solvent molecules in boiling DMF or on long standing (6-8 h) in vacuo at 100$^\circ$. All these complexes are nonelectrolytes in CH$_2$Cl$_2$ and CH$_3$HgCl$_2$. They appear to be square planar as suggested by their u.v. spectra which show a charge transfer band ($\lambda_{ct}$ = 440 nm) at 31 000-36 000 cm$^{-1}$ and a band or shoulder ($\lambda_{b}$ or $\lambda_{sh}$ = 6 400 nm) at 23 000-27 000 cm$^{-1}$ with extinction coefficients well within the expected range.(4, 5). The resistance of these complexes to treatment with boiling DMF is an indication of their thermal stability.(3, 6, 7)

Like its phenyl analogue(4) the Pd(pdta)(NC$l_2$)(SC$l_2$O)$_2$ complex shows Ni, S-bonding in both the physical states [v(CN) 2070 br, 2100 cm$^{-1}$ in solid and 2090 br, 2130 cm$^{-1}$ in CH$_2$Cl$_2$]. However, the other bands diagnostic of the thiocyanate group are obscured by the ligand absorptions.(8, 9). Although electronically, pdpa and pdta are somewhat different, they possess the same steric requirements with respect to the metal ion. The same bonding mode in both the complexes indicates the importance of steric effects in determining the bonding mode, in accord with the views of Palenik et al.(10).

\[ [Pt(pdta)N(CH_3)CO]ClO_4 \]

The reflectance spectra of Pd(pdta)$_2$X$_2$ show the stereochemical order: Cl = ca. NCS > Br as expected for N, S-bonding, but in solution the change to: Cl > Br > SCN is not understood.

The shifting of the lowest energy band, observed at 21 000, 21 730 and 22 000 cm$^{-1}$ in the reflectance spectra of the Pd(pdta)$_2$I$_2$ · 0.5 CH$_2$Cl$_2$ and Pt(pdta)$_2$X$_2$ · nCH$_2$Cl$_2$ complexes (X = Br, n = 1; X = I, n = 0) respectively to higher energy on dissolution, indicate a distorted octahedral structure in the solid state. The Pd(pdta)$_2$I$_2$ · 0.5CH$_2$Cl$_2$ complex is a non-electrolyte in C$_2$H$_5$Cl$_2$ which also shows the same stereochemistry in solution. However, CH$_2$Cl$_2$ solutions of the Pt(pdta)$_2$X$_2$ · nCH$_2$Cl$_2$ complexes [X = Br, n = 1; X = I, n = 0] behave as univalent electrolytes and show absorption bands in the 22 000-27 000 cm$^{-1}$ range in CH$_2$Cl$_2$ as expected for five coordination.

\[ Pt(pdta)(H_2O)_2ClO_4 \]

Pt(pdta)(H$_2$O)$_2$ClO$_4$ and the univalent behaviour together with the presence of one band at 35 000 cm$^{-1}$ in the CH$_2$Cl$_2$ solution spectrum of the Pd(pdta)$_2$(ClO$_4$)$_2$ complex, supports the above assignment. However, the conductance values of Pt(A-A)$_2$X$_2$ · nCH$_2$Cl$_2$ (X = Cl or NCS) are slightly lower than the range expected for univalent electrolytes, which may be attributed to the tendency of the ion to associate. The appearance of a shoulder at 23 000 cm$^{-1}$ (X = Cl) and 22 720 cm$^{-1}$ (X = NCS) in the solution spectra of these complexes is also consistent with the presence of small amounts of five coordinate species in solution.(11)

\[ Pt(pdta)(H_2O)_2ClO_4 \]

The dropwise addition of a solution of LiClO$_4$ (5 mg, 0.5 mmol) in EtOH (5 cm$^3$) to a solution of Pt(pdta)$_2$(SC$l_2$O)$_2$ (0.75 g, 1.0 mmol) in CH$_2$Cl$_2$ (20 cm$^3$) and subsequent concentration yielded a yellow precipitate which was purified by recrystallisation from 4:1 v:v CH$_2$Cl$_2$ : EtOH (Yield, 0.7 g).

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