

Synthesis and Characterization of New Trinuclear Palladium(II) and Platinum(II) Complexes Containing Phosphorus-Sulphur Ligands

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Some new homo and hetero trinuclear Pd(II) and Pt(II) complexes with tridentate hybrid ligands containing phosphorus-sulphur species, of the general formula $[M_nM'_{3-n}L_2Cl_6]$, where $M = M' = Pt$ or Pd , $n = 3$; $M = Pt$, $M' = Pd$, $n = 1$ or 2 and $L = cis$ -1,2-bis(diphenylphosphino) phenylthioethylene (L^1) or cis -1,2-bis(diphenylphosphino)-2-aminophenylthio ethylene (L^2), have been synthesized and characterized physico-chemically and spectroscopically. The structures of the complexes have been elucidated on the basis of their elemental analyses, electronic and infrared spectral measurements.

Key Words: Pd(II), Pt(II), Hybrid P-S ligands, Trinuclear complexes.

INTRODUCTION

The transition metal chemistry of the ligand bis(diphenylphosphino)amine, which is isoelectronic with bis(diphenylphosphino) methane has received widespread attention¹. In contrast, there are limited examples of metal complexes of the neutral ligand bis(chalcogenide), $R_2P(E)NHP(E)R_2$, where $E = O$ or S and $R = Me$ or Ph^{2-4} . The synthesis and multinuclear NMR characterization of new complexes of the hybrid ligands $Ph_2P(CH_2)_2SR$, where $R = Me, Et, Ph$ have been reported; with Rh(I) and Ir(I) metal ions forming complexes of the general formula $[M(Ph_2P(CH_2)_2SR)_2]X_2$, $X = BPh_4$ or BF_4 in which the complexes assigned a square-planar geometry with two phosphorus in *cis*- position⁵. Similarly, a series of Pd(II) and Pt(II) complexes with the hybrid ligand $Ph_2P(CH_2)_2SR$, $R = Me, Et$ have been prepared⁶. In view of the interesting results reported and in connection of our comprehensive studies on palladium and platinum complexes with phosphorus-containing ligands⁷⁻¹¹, we are presenting here the preparation of the ligands, aryl phosphine and sulphur derivatives L^1 and

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L^2 and their $[M_nM'_{3-n}L_2Cl_6]$ complexes, in which $M = M' = Pt$ or Pd , $n = 3$; $M = Pt$, $M' = Pd$, $n = 1$ or 2 and $L = L^1$ or L^2 (Fig. 1).

EXPERIMENTAL

All chemicals were reagent grade, K_2PdCl_4 and K_2PtCl_4 were used as supplied from Fluka A.G. All experiments were carried out under nitrogen using oxygen-free solvents.

The compounds were analyzed for their carbon, hydrogen and nitrogen elements using 1106 Carlo Erba Micro Analyzer. The palladium content was estimated as bis(dimethylglyoximato) Pd(II) complex¹². The platinum content was determined by Shimadzu AA-670 spectrophotometer. Infrared spectra were recorded using Perkin-Elmer 580B spectrophotometer in the range 4000–200 cm^{-1} as CsI pellets. The electronic spectra were recorded on Shimadzu UV-Vis spectrophotometer UV-160 for 10^{-3} M solution of the complexes in CH_2Cl_2 at 25°C. Conductivity measurements were carried out on 10^{-3} M solutions of the complexes in CH_2Cl_2 at ambient temperature. Magnetic measurements were carried out on the solids by the Faraday's method using Bruker BM6 instrument.

Preparation of compounds

Ligands

The ligands L^1 and L^2 were prepared by two stages according to the following general method:

The first stage includes the reaction of potassium thiophenoxide {prepared *in situ* from the reaction of an equivalent amount of KOH (2.24 g, 0.04 mol) and thiophenol (4.40 g, 0.04 mol) in ethanol (50 mL)} with 1,1,2-trichloroethylene (1.75 g, 0.013 mol). The mixture was boiled under reflux for *ca.* 4 h. After cooling to room temperature, KCl was removed by filtration. The solution was reduced in volume to *ca.* 15 mL and on cooling to *ca.* 5°C, a colourless oil of *cis*-1,2-dichlorophenylthio ethylene was separated out. In the second stage, the oily material (above) was added to a hot solution of lithium diphenylphosphide ($LiPPh_2$) {produced by the cleavage of PPh_3 with Li metal¹³} in tetrahydrofuran. The mixture was refluxed for *ca.* 5 h and after cooling to room temperature, LiCl was removed by filtration. The resulting solution was reduced in volume to *ca.* 1/3 and left in the refrigerator overnight. A white solid of L^1 (Fig. 1) was formed; this was filtered off, and dried under vacuum.

A similar procedure was followed for the preparation of the ligand L^2 , except using 2-aminothiophenol instead of thiophenol, to give an off-white solid.

Complexes $[M_nM'_{3-n}L_2Cl_6]$

These were prepared according to the following general procedure:

1. $M = M' = Pt$ or Pd , $n = 3$, $L = L^1$ or L^2

The salt K_2PtCl_4 or K_2PdCl_4 (3 mmol) was dissolved in H_2O (10 mL) and a solution of the corresponding ligand L^1 or L^2 (Fig. 1) (2 mmol) in ethanol (15 mL)

was added under continuous stirring. An immediate precipitation of a solid was observed. The mixture was stirred at room temperature for further *ca.* 6 h to ensure completion of the reaction. The solid thus formed was filtered off, washed with H₂O, ethanol, ether and dried under vacuum for several hours.

2. $M = Pt$, $M' = Pd$, $n = 1$ or 2 , $L = L^1$ or L^2

The salts K₂PtCl₄ (1 or 2 mmol) and K₂PdCl₄ (2 or 1 mmol), respectively, were dissolved in H₂O (10 mL) and a solution of the corresponding ligand L¹ or L² (Fig. 1) (2 mmol) in ethanol (15 mL) was added under continuous stirring. A similar procedure to the above was carried out.

RESULTS AND DISCUSSION

The hybrid ligands were prepared in a high yield by two steps method as described in the experimental section. These ligands react with K₂MCl₄ to afford the complexes [M_nM'_{3-n}L₂Cl₆], where M = M' = Pt or Pd, n = 3 and M = Pt, M' = Pd, n = 1 or 2 and L = L¹ or L² (Fig. 1) by using different molar ratios of ligand to metal ion. The complexes are soluble in CHCl₃, CH₂Cl₂, DMSO, DMF and fairly stable in air.

The analytical data of the complexes (1–8) (Table-1) agree with the proposed formulae of these complexes. The molar conductivities of the complexes measured in CH₂Cl₂ were found to be in the range characteristic of non-electrolyte species¹⁴. Magnetic susceptibility measurements of the complexes showed that all of the complexes are diamagnetic as expected for a d⁸ metal ion in a square-planar field¹⁵.

The most important IR assignment of the ligands as well as their bonding sites (Table-2) have been determined by a careful comparison of the spectra of the ligands with those of their complexes. The IR spectra of the ligands showed a medium band at 1660–1630 cm⁻¹ assigned to ν(C=C) vibration and this remained unchanged in the spectra of all complexes. Another band appearing at 1070–1055 cm⁻¹ in the free ligands which were assigned to ν(C–P) vibration, was found to decrease by *ca.* 25 cm⁻¹ upon complexation. This indicates that this group had been involved in the coordination with the metal ion through phosphorus atom¹⁶. The ν(C–S) absorption band appeared at 670–650 cm⁻¹ in the free ligands was found to appear at lower frequency in the spectra of all the complexes indicating the involvement of sulphur atom of the ligand in the coordination with the metal ion⁶. The IR spectra of the ligand L² exhibited a band in the 3390 cm⁻¹ region attributed to ν(NH₂) and this band remained almost constant upon coordination of this ligand with the metal ions. This indicates that the NH₂ group had not been participated in the coordination.

Moreover, the IR spectra of the complexes showed new bands at 450–430 cm⁻¹ and 370–360 cm⁻¹ which were tentatively assigned to ν(M–P) and ν(M–S), respectively (M = Pt or Pd)¹⁷. Further, the IR spectra of the complexes showed another new band in the region of 340–290 cm⁻¹ which may well be due to ν(M–Cl) frequency¹⁸. This band is split into two bands and this can be taken as evidence for square-planar *cis*-configuration of these complexes.

TABLE-1
PHYSICAL PROPERTIES AND ELEMENTAL ANALYSIS OF THE
FREE LIGANDS AND THEIR METAL-COMPLEXES

Seq.	Compd.	Colour	m.p. (°C)	Analysis(%): Found (Calcd.)				
				C	H	N	Pd	Pt
L ¹	(C ₃₂ H ₂₆ P ₂ S)	White	74–76	76.11 (76.19)	5.13 (5.16)	—	—	—
L ²	(C ₃₂ H ₂₇ NP ₂ S)	Off white	80–82	74.20 (74.00)	5.20 (5.20)	2.69 (2.70)	—	—
1	[Pd ₃ (L ¹) ₂ Cl ₆]	Deep yellow	150–152	49.87 (49.86)	3.22 (3.38)	—	2.60 (20.72)	—
2	[Pt ₃ (L ¹) ₂ Cl ₆]	Beige	138–140	42.40 (42.52)	2.69 (2.88)	—	—	32.31 (32.39)
3	[Pt ₂ Pd(L ¹) ₂ Cl ₆]	Yellow	162–164	44.50 (44.72)	3.00 (3.03)	—	6.11 (6.20)	22.50 (22.71)
4	[PtPd ₂ (L ¹) ₂ Cl ₆]	Brown	158–160	47.12 (47.15)	3.11 (3.19)	—	13.00 (13.06)	11.70 (11.97)
5	[Pd ₃ (L ²) ₂ Cl ₆]	Orange	170–172	48.59 (48.90)	3.40 (3.44)	1.73 (1.78)	20.10 (20.33)	—
6	[Pt ₃ (L ²) ₂ Cl ₆]	Yellow	166–168	41.53 (41.83)	2.90 (2.94)	1.50 (1.53)	—	31.52 (31.86)
7	[Pt ₂ Pd(L ²) ₂ Cl ₆]	Deep yellow	158–160	43.82 (43.95)	3.00 (3.09)	1.54 (1.60)	6.00 (6.09)	11.09 (11.16)
8	[PtPd ₂ (L ²) ₂ Cl ₆]	Pale brown	169–171	46.00 (46.30)	3.20 (3.26)	1.65 (1.69)	12.80 (12.83)	11.71 (11.76)

*Complexes melt with decomposition

TABLE-2
IR SPECTRA (cm⁻¹) AND ELECTRONIC SPECTRA OF THE FREE
LIGANDS AND THEIR METAL-COMPLEXES

Compd.	Selected IR bands (cm ⁻¹)*					λ _{max} (nm)
	ν(C—P)	ν(C—S)	ν(M—P)	ν(M—S)	ν(M—Cl)	
L ¹	1095 m	670 s	—	—	—	254
L ²	1090 m	680 m	—	—	—	280
1	1060 s	630 m	430 m	385 w	385 m, 305 m	291, 358
2	1070 w	635 m	430 m	355 w	330 w, 310 m	290, 345
3	1065 m	625 m	450 m	370 w	310 w, 290 w	340, 360
4	1070 s	640 w	440 m	375 w	330 w, 310 w	350, 365
5	1065 m	650 m	445 m	365 w	315 w, 295 w	285, 370
6	1070 m	660 m	435 m	360 w	320 w, 290 w	300, 360
7	1075 m	655 w	440 m	370 m	320 w, 300 w	295, 355
8	1065 m	640 w	430 m	375 m	315 w, 290 w	290, 350

In order to obtain some more information about the coordination behaviours of the metal ions, the electronic spectra of the complexes have been recorded. The tentative assignments of the absorption bands from the electronic spectra of the ligands and their complexes are listed in Table 2.

The $\pi\text{-}\pi^*$ transitions in the spectra of the ligands L^1 and L^2 were observed at 254 and 280 nm. In the spectra of the complexes, this band was found to appear at 290 and 370 nm. The d-d transitions of the Pt(II) and Pd(II) complex were too low intensive to be observed in the spectra of the complexes and hence calculated according to a literature data¹⁹. These transitions are assumed to be due $A_{1g} \rightarrow {}^1E_g$ and ${}^1A_{1g} \rightarrow {}^1B_{1g}$ or charge transfer transitions suggesting a square-planar geometry around the metal ion⁷.

As a conclusion, the hybrid ligands L^1 and L^2 , used in this study, coordinate to the metal ions in a tridentate fashion from the P and S sites of the ligand forming the trinuclear complexes (1-8) as shown in Fig. 1.

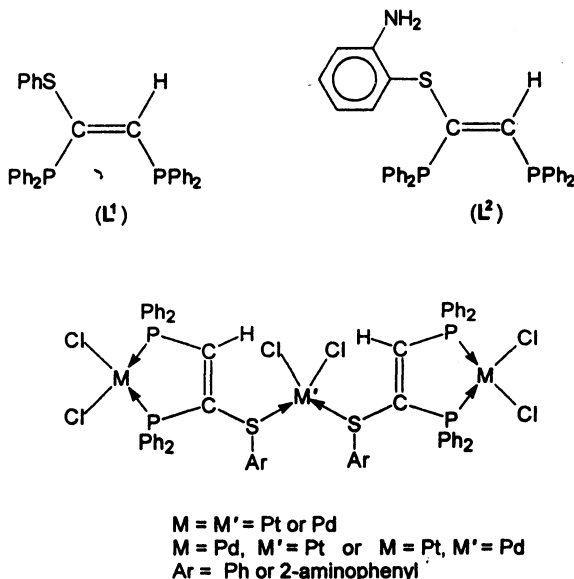


Fig. 1. The hybrid tridentate ligands and the possible structures of their Pt(II) and Pd(II) complexes (1-8)

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