Inorganica Chimica Acta, *72* (1983) 119–126

Alkylaminodithioxodi-λ^5-phosphanes and Related Complexes. Part (IV).* A Novel Series of Copper(I), Palladium(II) and Platinum(II) Complexes: Vibrational Spectra and Molecular Structures

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Received September 27, 1982

Vibrational data are reported and discussed for ten complexes of diethylamino or phenyl-substituted dithioxodi-λ^5-phosphanes (diphosphine disulphides) with copper(I), palladium(II) and platinum(II) salts. The complexes are characterized by the IR activity of the ν(P–P), ν_s(P–S) and ν_{as}(P–S) skeletal stretching vibrations of the coordinated ligands, and by a shift to lower frequency of the ν(P–S) vibration modes upon coordination. The ligands are bonded to the metal atoms through the sulphur atoms, thus forming five-membered chelate rings. The originally centrosymmetric trans *ligand molecules adopt a* cis *or* gauche *conformation when coordinated. From the crystal structure of one of the complexes and of a related compound, the* gauche *conformation is considered the more likely. Electronic and IR spectra are consistent with a square planar environment of the palladium and platinum atoms.*

Introduction

The donor properties of the sulphur atoms in alkyl- or allyl-substituted dithioxodi-λ^5-phosphanes (commonly called diphosphine disulphides) $R_2P(S)$-$P(S)R_2$ have made possible the synthesis of a variety of complexes with metal salts [1–7]. The molecular structures of the diethylamino- or phenyl-substituted dithioxodi-λ^5-phosphanes

$(Et_2N)_2P(S)\text{-}P(S)(NEt_2)_2 = L_I$

$(Et_2N)(C_6H_{11})P(S)\text{-}P(S)(C_6H_{11})(NEt_2) = L_{II}$

$(Et_2N)(C_6H_5)P(S)\text{-}P(S)(C_6H_5)(NEt_2) = L_{III}$

$(C_6H_5)_2P(S)\text{-}P(S)(C_6H_5)_2 = L_{IV}$

have recently been reported [8–10]. These ligands have the usual centrosymmetric *trans* conformation. We have now investigated their donor properties, with particular reference to the following Cu, Pd and Pt complexes:

$(L)_2\cdot CuClO_4$ $(L = L_I, L_{II})$

$(L)\cdot CuCl$ $(L = L_{II})$

$(L)\cdot PdCl_2$ $(L = L_I, L_{II}, L_{III}, L_{IV})$

$(L)\cdot PtCl_2$ $(L = L_I, L_{II}, L_{III})$.

The molecular structures of these complexes are discussed below on the basis of their vibrational spectra and of the previously determined crystal structure of the complex $(L_{II})\cdot PdCl_2$ [11].

Experimental

Copper(I) Perchlorate Complexes

At room temperature, an ethanolic solution of the ligand L was added to a solution of $Cu(ClO_4)_2\cdot 6H_2O$ in the same solvent, the molar ratio being L/Cu = 2/1. The resulting coloured solutions (dark-red with L_I, green with L_{II} and L_{III}) faded progressively to become ultimately colourless, indicating the reduction of copper(II) to copper(I). White solid products spontaneously precipitated from the L_I and L_{II} solutions; they were separated and recrystallized from methanol–ethanol mixtures. From the analytical data (Table I) the solid complexes are formulated as $(L)_2\cdot CuClO_4$ $(L = L_I, L_{II})$. Melting points and ^{31}P NMR shifts are also reported in Table I. The ^{31}P NMR spectra exhibit a single line with a downfield shift as compared with the single line of the related free ligands.

Single crystals of the complex $(L_{II})_2\cdot CuClO_4$ have been obtained but were too small for X-ray structure determinations. Crystal data: monoclinic, space-group Cc or C2/c, $a = 28.14$, $b = 12.73$, $c = 31.68$ Å, $\beta = 98.0°$, $V = 11{,}211$ Å^3, $Z = 8$.

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*Part III: reference 11.

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0020-1693/83/$03.00

TABLE I. Analytical Data.

Complexes	Colour	%	C	H	N	P	S	Metal	Melting point (°C)	$\delta\,^{31}P$ (ppm)
$(L_I)_2CuClO_4$	white	Calc.	38.7	8.1	11.3	12.5	12.9	6.4	98–101[a]	78.9[b]
		Found	38.1	7.9	10.9	12.4	12.6	6.4		
$(L_{II})_2CuClO_4$	white	Calc.	46.4	8.2	5.4	12.0	12.4	6.1	173–5[a]	87.9[c]
		Found	46.3	8.1	5.3	11.8	12.4	6.1		
$(L_I)PdCl_2$	orange	Calc.	32.4	6.8	9.4	10.4	10.8	18.0	172–3	73.0[d]
		Found	31.9	6.8	9.3	10.2	10.5	17.7		
$(L_{II})PdCl_2$	orange	Calc.	39.1	6.9	4.6	10.1	10.4	17.4	210	90.8[d]
		Found	39.1	6.8	4.6	9.7	10.1	16.9		
$(L_{III})PdCl_2$	light brown	Calc.	39.9	5.0	4.6			17.7	125–8	71.0[d]
		Found	39.4	5.2	4.5			17.9		
$(L_{IV})PdCl_2$	dark orange	Calc.	47.1	3.3				17.4	d[e]	–
		Found	46.8	3.2				17.7		
$(L_I)PtCl_2$	light brown	Calc.	28.2	5.9	8.2	9.1	9.4	28.7	175	68.1[d]
		Found	27.7	5.7	8.0	8.8	9.9	27.8		
$(L_{II})PtCl_2$	pale orange	Calc.	34.2	6.0	4.0	8.8	9.1	27.8	175–8	88.6[d]
		Found	33.9	5.8	3.8	8.5	8.9	28.4		
$(L_{III})PtCl_2$	yellow ochre	Calc.	34.8	4.4	4.1	9.0		28.3	130	69.5[d]
		Found	34.6	4.6	4.1	8.5		28.6		

[a] Explosive melting. [b] In $CDCl_3$ solution. [c] In $MeNO_2$ solution. [d] In CH_2Cl_2 solution. [e] Decomposition.

Although the cupric ion was reduced in the presence of L_{III}, no solid product could be isolated. The ^{31}P NMR spectum ($\delta = 71.5$ ppm, free ligand L_{III}, $\delta = 58.5$ ppm) of the ethanolic solution nevertheless suggests the formation of an L_{III}–Cu(I) complex. No visible reaction occurred with the ligand L_{IV}.

Copper(I) Chloride Complexes

These syntheses were carried out in the same way as above, with $CuCl_2 \cdot 2H_2O$. The mixture obtained with L_I had a brown colour which disappeared on boiling, but all attempts to isolate a solid compound failed. The ^{31}P NMR spectrum in benzene–methanol solution showed a resonance at $\delta = 80$ ppm, compared with $\delta = 66$ ppm for the free ligand L_I.

The corresponding reaction with L_{II} yielded a green solution which faded on boiling; a white solid precipitated on cooling. Analytical data and the vibrational spectra of various samples showed the solid to be invariably a mixture of a copper(I) complex and uncoordinated ligand. Electron microprobe analysis of two kinds of differently shaped crystals, sorted under the microscope, confirmed the coexistence of L_{II} with a copper complex. The latter could not be purified but was characterized by a ^{31}P NMR shift of $\delta = 87$ ppm in $CDCl_3$ solution (free ligand: $\delta = 73.0$ ppm). Its most probable stoichiometry is L/Cu = 1/1.

No reaction occurred between L_{III} nor L_{IV} and $CuCl_2 \cdot 2H_2O$.

Note on the Reduction of Copper(II) to Copper(I)

It has previously been observed that the reaction of a copper(II) salt with a dithioxodi-λ^5-phosphane leads to the formation of a copper(I) complex [1] but the reducing agent remains unknown. However in some cases involving similar ligands, the products of the oxidation-reduction reaction have been isolated [12–15]. Their nature implies that the redox process does involve the ligands themselves. It is legitimate to assume that the dithioxodi-λ^5-phosphanes are reducing agents although the oxidized products have not yet been identified.

Palladium(II) Chloride Complexes

A suspension of anhydrous $PdCl_2$ in a solution of the ligand in methylene chloride, molar ratio L/Pd = 2/1, was stirred at room temperature for three days. The solvent was then removed from the orange-red mixture under reduced pressure. The addition of diethylether to the residue yielded an orange precipitate. Bright coloured microcrystals were obtained by recrystallizations in methylene chloride-diethylether or methylene chloride–acetone mixtures. Analytical data (in Table I) are consistent with the general formula $(L) \cdot PdCl_2$ ($L = L_I, L_{II}, L_{III}, L_{IV}$). Melting points and ^{31}P NMR shifts are also given in Table I.

Platinum(II) Chloride Complexes

The complexes $(L){\cdot}PtCl_2$ ($L = L_I, L_{II}, L_{III}$) were prepared in the same way as above (molar ratio L/Pt = 2/1), but the reaction is slower. Analytical data, melting points and ^{31}P NMR shifts are given in Table I. These platinum chloride complexes decompose slowly in air.

The reaction of L_{IV} with $PtCl_2$ yielded an orange solid but the analytical data were unsatisfactory.

The seven solid complexes $(L){\cdot}PdCl_2$ ($L = L_I, L_{II}, L_{III}, L_{IV}$) and $(L){\cdot}PtCl_2$ ($L = L_I, L_{II}, L_{III}$) are the first complexes of dithioxodi-λ^5-phosphanes with palladium(II) or platinum(II) salts reported in the literature*.

Other Synthetic Attempts

Attempts to prepare complexes of the same ligands with some other metal salts such as $Ni(ClO_4)_2{\cdot}6H_2O$, $Co(ClO_4)_2{\cdot}6H_2O$, $ZnCl_2$, $CdCl_2$ or $VOSO_4{\cdot}5H_2O$ were unsuccessful.

Spectra

Infrared spectra were recorded in the 4000–250 cm^{-1} region with Perkin-Elmer 335 and 225 spectrophotometers.

Raman spectra were obtained using a Cary 83 Raman spectrophotometer with 488.0 nm laser excitation, calibrated against appropriate neon lines. Satisfactory spectra were obtained only for the cuprous complexes of L_{II}: other materials degraded rapidly in the laser beam.

^{31}P NMR spectra were recorded with Perkin-Elmer R10 and Bruker WH 90 spectrometers. All shifts refer to external H_3PO_4 (85%) and are in ppm with a positive sign indicating a low field shift.

Electronic spectra were obtained using a Cary 14 spectrophotometer.

Conductivity Measurements

These were carried out with a RC 18 A Beckmann conductimeter, on freshly prepared solutions of nearly 10^{-3} *M* concentration, at room temperature.

Results and Discussion

Copper(I) Complexes

Absorption frequencies below 1000 cm^{-1} are given in Table II for the available IR and Raman spectra. The assignments follow in a straightforward way from those for the uncoordinated ligands [10], the metal–ligand stretching vibrations occurring near 300 cm^{-1}.

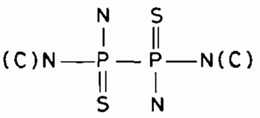
$(L)_2{\cdot}CuClO_4$ ($L = L_I, L_{II}$)

The conductance data are typical of uni–univalent electrolytes:

Complex	Solvent	Λ (Ω^{-1} cm^2 mol^{-1})	Λ for a 1/1 electrolyte [16]
$(L_I)_2{\cdot}CuClO_4$	acetonitrile	172.5	92–199
$(L_{II})_2{\cdot}CuClO_4$	nitromethane	62.0	60–115

Moreover, a strong absorption band at 1090 cm^{-1} in the IR spectra of both complexes must be assigned to the free $(ClO_4)^-$ ion [17]. Thus the complexes should be formulated $[(L)_2{\cdot}Cu]^+[ClO_4]^-$.

Comparisons of the IR and Raman spectra of the complexes with those of the free ligands in the skeletal stretching frequency region (500–650 cm^{-1} approximately) clearly indicate the structural effects of complex formation. Whereas for the free ligand only the ν_{as}(P–S) vibration is IR active, and the ν_s(P–S) and ν(P–P) vibrations are Raman active, three bands readily assignable to the vibrations ν_s(P–S), ν_{as}(P–S) and ν(P–P) occur in the IR as well as in the Raman spectra of the complexes. This implies the loss of the centre of symmetry of the



$$\mathrm{(C)N{-}\underset{\overset{\|}{S}}{\overset{\overset{N}{|}}{P}}{-}\underset{\overset{|}{N}}{\overset{\overset{S}{\|}}{P}}{-}N(C)}$$

skeleton of the free ligand, *i.e.* a transition from a *trans* (C_{2h} or C_i) conformation to a *cis* (C_{2v} or C_s) or *gauche* (C_2 or C_1) conformation.

The ν_s(P–S) and ν_{as}(P–S) vibrations are shifted to lower frequency by 10 to 30 cm^{-1} upon coordination. This effect can be attributed to the weakening of the P–S bond when the sulphur atoms bind to a metal atom [18].

In the IR spectra, the ν(P–P) vibration occurs at 520 cm^{-1} for $(L_I)_2{\cdot}CuClO_4$ and 532 cm^{-1} for $(L_{II})_2{\cdot}CuClO_4$. In the Raman spectrum of the latter complex, the ν(P–P) vibration is observed at 538 cm^{-1}, slightly shifted to the lower frequency when compared with the uncoordinated ligand.

The ν(P–N) and ν(P–C) stretching vibrations are not affected by coordination. As expected from the X-ray structural studies of the free ligands [8, 10], the nitrogen atoms do not take part in the coordination process.

The reduction of the symmetry of the ligand molecule upon coordination does not seriously affect the internal vibrations of the diethylamino or phenyl groups: compared with the free-ligands spectra only the ν(C–N) absorption bands are slightly modified.

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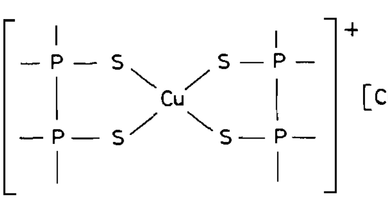
*Pd(II) and Pt(II) complexes of the ligands $R_2P(S)$-$P(S)R_2$ ($R = C_6H_5, CH_3, C_2H_5$) were isolated and characterized by Nicpon (*Ph.D.* Dissertation, The Ohio State University, 1966). However, these complexes have not been described in the scientific literature.

TABLE II. Vibrational Spectra of Copper(I) Complexes (cm^{-1}).

Assignments	$(L_I)_2CuClO_4$	$(L_{II})_2CuClO_4$		$L_{II}\cdot CuCl$	
	IR[a]	IR[a]	R[b]	IR[a]	R[b]
ν(C–C)	1010vs	998ms	993ms	1000vs	998m
ν(C–N)	945s	944s	950vw	946vs	950sh
	935s,br	935s	932s	940vs,br	936w
	925sh	920sh	918vw	920sh	923w
	915m,br				
CH_2 rock (ring)		880w	895vw	881s	890w
		856w	852m	849s	850m
		812w	819m	818s	818ms
CH_2 rock	792s,br	790m,br	790vw	793vs,br	790vw
	775sh	778sh	780vw	780sh	775vw
ν(P–C)		743s	753m	747s	753m
ν(P–N)	705vw				
	692s				
	678s	675m	683w	677s	680w
	635m,sh				
ν_s(P–S)	625s,br	612s	624vs	612vs,br	618s
ν_{as}(P–S)	570m,br	590m	592w	582s	580w
ν(P–P)	520mw	532mw	538m	531ms	535m
δ(PNC_2)	490w	510w	493s	510m	490s
	480w	470sh	465m,sh	465m,br	453m
δ(PCC/CCC)		445w	435m,br	445w	435m
δ(PNC_2)	420ms	420w		425w	
				400sh	
		380s,br		380vs,br	363s
			353m		345sh
ν(Cu–S)			318vs	302s,br	310vvs,br
ν(Cu–Cl)			290s	275m,sh	260s,sh
			248vs		240s,sh
			228vs		224vs
			194vvs		
δ(PPS)			170vvs		155vvs

[a] CsBr pellets. [b] Powdered solids. v, very; s, strong; m, medium; w, weak; br, broad; sh, shoulder.

From the foregoing data it can be inferred that the copper atom is most probably chelated by two ligand molecules giving a structure analogous to that proposed by Corfield [19]



on the basis of X-ray diffraction data for the complex $[S_2P_2Me_4]_2\cdot CuClO_4$. This structure has also been suggested for the complexes $[(S_2P_2Me_4)_2\cdot M]^{2+}$-$[Y^-]_2$ (M = Cd, Co, Y = ClO_4^-, NO_3^-) [4].

The Cu–S stretching vibrations (usually located between 300 and 350 cm^{-1} [17]) are difficult to identify. Indeed no absorption band is observed in this region of the IR spectra of the complexes. The Raman spectra below 400 cm^{-1} are rather complicated but comparison of the spectrum of free L_{II} with that of $(L_{II})_2\cdot CuClO_4$ leads us tentatively to assign a vibration at 318 cm^{-1} to a Cu–S stretching mode.

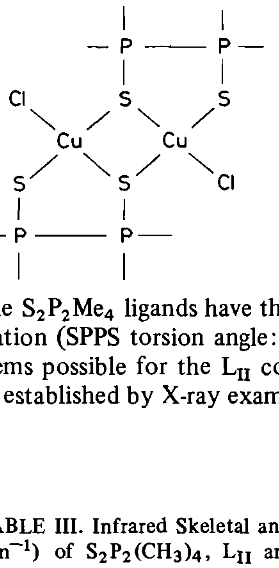
$(L_{II})\cdot CuCl$

This complex was only obtained in a mixture with uncoordinated ligand but the skeletal vibrational bands arising from the coordinated molecule are readily identifiable. Between 500 and 1000 cm^{-1} the vibrational spectrum is similar to that of

$(L_{II})_2 \cdot CuClO_4$, indicating that the ligand is coordinated through the sulphur atoms in the *cis* or *gauche* conformation.

In the low-frequency range, two absorption bands (IR: 275 and 302 cm^{-1}, Raman: 260 and 310 cm^{-1}) can be assigned to the ν(Cu–S) and ν(Cu–Cl) stretching vibrations. On the basis of X-ray structural studies, Ainscough *et al.* [20] located the ν(Cu–S) frequencies between 290 and 315 cm^{-1}, while the ν(Cu–Cl) vibrations are located in the range 220–300 cm^{-1} whether the Cl atom is bridging or terminal. For $(L_{II}) \cdot CuCl$ it is thus logical to assign the lower frequencies (IR: 275 and Raman: 260 cm^{-1}) to ν(Cu–Cl) without being able to infer the position (bridging or terminal) of the Cu–Cl bonds in the molecule.

The skeletal vibrational spectrum of $(L_{II}) \cdot CuCl$ is strikingly similar to that of the complex $[S_2P_2Me_4 \cdot CuCl]_2$ (Table III). The latter is the only copper(I) complex with a dithioxodi-λ^5-phosphane of known crystal structure [21]. In this dimeric centrosymmetric molecule, the copper atoms are tetrahedrally surrounded by three sulphur atoms (two of them are bridging) and one chlorine atom:



The $S_2P_2Me_4$ ligands have the internal *gauche* conformation (SPPS torsion angle: 45°). A similar structure seems possible for the L_{II} complex, but this can only be established by X-ray examination.

TABLE III. Infrared Skeletal and Metal–Halogen Vibrations (cm^{-1}) of $S_2P_2(CH_3)_4$, L_{II} and their Copper(I) Chloride Complexes (Raman frequencies are italicised).

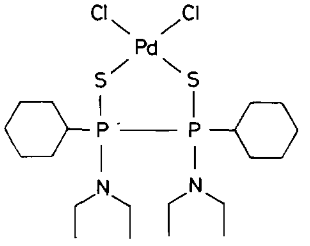
Assignments	$S_2P_2(CH_3)_4$	$[S_2P_2(CH_3)_4 \cdot CuCl]_2$	Ref.	L_{II}	$(L_{II}) \cdot CuCl$
ν(P–C)	747	761	[4]	740	747
	733	730			
ν(P–N)				672	677
ν_s(P–S)	*602*	593		*640*	612
ν_{as}(P–S)	571	554		600	582
ν(P–P)	*431*	430		*547*	531
ν(Cu–Cl)		257	[20]		275 *260*

(L)·PdCl₂ and (L)·PtCl₂ Complexes

These complexes are not electrolytes. Their IR absorption bands are listed in Table IV, together with the proposed assignments following from those for the free ligands [10, 22] and from the knowledge of the crystal structure of $(L_{II}) \cdot PdCl_2$ [11].

(L_II)·PdCl₂

In both the crystallographically independent monomeric molecules



the coordinated ligand has a *gauche* conformation (mean value of the SPPS torsion angle: 46.7°). The metal atom is in a distorted square planar environment [11].

The reduction of symmetry from C_i to C_1 for the skeleton of the L_{II} ligand causes the P–P stretch and all of the symmetric and antisymmetric P–S, P–N and P–C stretching vibrations to become both IR and Raman active. The vibration band at 542 cm^{-1} is readily assigned to ν(P–P) and two bands at 677 and 668 cm^{-1} are ascribable to the ν(P–N) vibrations; only one band at 746 cm^{-1} can be assigned to ν(P–C).

The symmetric P–S stretch is assigned to a strong IR band at 602 cm^{-1}, 38 cm^{-1} below the corresponding free-ligand frequency. Assignment of ν_{as}(P–S) is more problematical, as there is no other strong IR band in the P–S stretching region. A weak band at 565 cm^{-1}, 35 cm^{-1} below the free-ligand frequency, is in the exactly appropriate position and despite its unusually low intensity appears to be the only possible candidate. Exactly similar effects occur in the spectrum of $(L_{II}) \cdot PtCl_2$ and also of $(L_I) \cdot PdCl_2$ and $(L_I) \cdot PtCl_2$. In all of these cases there are appropriately placed (but only very weak) bands in the expected ν_{as}(P–S) frequency regions. In the L_{III} and L_{IV} complexes, in contrast, ν_{as}(P–S) is quite strong and readily identifiable, but there is no reason to believe that the two groups of complexes are structurally dissimilar.

The other absorption bands of the ligand are almost unchanged upon complexation. However three bands, of a possible four in the range 920–955 cm^{-1}, are assigned to the ν(C–N) vibrations while only two are observed in the free ligand spectrum.

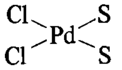
Because of the C_{2v} symmetry of the 

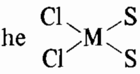
TABLE IV. Infrared Spectra of L•$PdCl_2$ and L•$PtCl_2$ Complexes (cm^{-1})[a].

Assignments skeletal and $N(C_2H_5)_2$	L_I•$PdCl_2$	L_I•$PtCl_2$	$L_{II}PdCl_2$	$L_{II}PtCl_2$	$L_{III}PdCl_2$	$L_{III}PtCl_2$	$L_{IV}PdCl_2$	Assignments C_6H_{11}[b]	C_6H_5[c]
ν(C–C)			1000vs,sh	1000s,sh	1000ms,sh	1000s	1000m		ring (p)
ν(C–N)	960s,br	960s,br	955vs	955ms,br			970w		
	942s	943s	945s,sh	935s	940s,br	945s,br			γ(C–H) (h,i)
	920m,br	920ms,br	920mw	920sh	925sh	925sh	920w		
			895w,sh	890w,sh					
			880m	880m	868s,br	880s,br		CH_2 rock	γ(C–H) (g)
			848m	850m			845vw	γ(CH)	
			813s,sh	810sh			805vw		
$\delta_R(CH_2)$	801s	800vs,br	798vs,br	790s	792ms,br	792s,br			
	785sh		788sh	780sh	770sh				
γ(P–C)			746s	743ms	743ms	748s	747s		γ(C–H) (f)
							740s		
					728ms	725sh	715sh		X-sens. (r)
					708ms	712vs	705s		
ν(P–N)	693m	690sh			690s	692vs	687vs		φ(C–C) (v)
	679ms	678ms,br	677ms	675ms					
	672m	670sh			670m	670sh			
	668sh		668sh	669sh					
					612w	615w	618m		α(C–C–C) (s)
ν_s(P–S)	628s	617ms,br	602s	602s	575m	570s	602ms		
ν_{as}(P–S)	555w	555vw	565vw	562vw	550ms	550s,br	565vs		
ν(P–P)	525m	520m	542s	542m	535ms,br	530sh	515s		
			510w	510w	500s,br	495s,br		δ(PCC/CCC)	X-sens. (y,t)
δ(PNC_2)	478m,br		480w,sh			475sh	480ms		
		470ms,br	470mw,br	470m,br	460sh	460sh			
	440vw	445sh	440w	450m			451m	δ(PCC/CCC)	
δ(PNC_2)	418m	418m					430w		
	405vw	408sh	405w,sh	405vw					
		395sh	387s	380s					
							355m		X-sens. (u)
ν(M–S) and ν(M–Cl)	352w								
	318s,br	320m,sh	315ms,sh	317m	315m,sh	315m,sh	315w		
		310m	310s	300m	305m,sh	310m			
		300m,sh	305ms,sh			300m	298w		
	288mw	288w,sh	280mw,br	290w,sh	288m	290sh	290sh		
	275sh,br	275vw,sh		275w,sh	275m	275w,sh	278vw		

[a] CsBr pellets. [b] See Refs. [10, 23]. [c] Internal phenyl-group vibrations are labelled in conformity with Refs. [24, 25].

group, two vibrations ν(Pd–Cl) and two vibrations ν(Pd–S) are expected. Four bands are indeed observed in the low-frequency region. The ν(Pd–Cl) vibrations with *cis* chlorine atoms are usually observed between 287 and 360 cm^{-1} [26]; this is also the region of the ν(Pd–S) vibrations [17]. They are therefore not individually assigned.

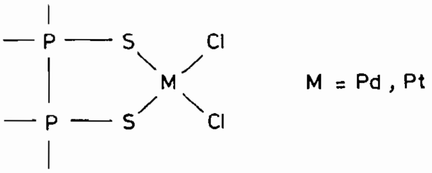
Other (L)•$PdCl_2$ and (L)•$PtCl_2$ Complexes

The IR spectrum of (L_{II})•$PtCl_2$ is almost identical with that of (L_{II})•$PdCl_2$. Assignment of the P–S stretching frequencies in the L_I complexes has been discussed in the preceeding section. The P–N stretching frequencies are close to those of the free ligand, indicating that the nitrogen atoms do not take part in the coordination as expected from the planar distribution of the bonds around the nitrogen atoms of the free ligand. The number of absorption bands observed for the skeletal vibrations is consistent with a *gauche* (C_2) or *cis* (C_{2v}) conformation of the coordinated ligand molecule, the former being strongly suggested by the similarity of the spectra with that of (L_{II})•$PdCl_2$. In the low-frequency region the spectra of (L_I)•$PdCl_2$ and (L_I)•$PtCl_2$ are consistent with a C_{2v} symmetry of the  group. For (L_I)•$PdCl_2$ the two bands at 318 and 352 cm^{-1} are likely to be due to the ν(Pd–S) vibrations, the two others at 275 and 288 cm^{-1} being assigned to the ν(Pd–Cl) [27].

The occurrence in the IR spectra of the complexes $(L_{III})\cdot PdCl_2$, $(L_{III})\cdot PtCl_2$ and $(L_{IV})\cdot PdCl_2$ (Table IV) of the ν(P–P), ν_s(P–S) and ν_{as}(P–S) vibration bands indicates once more the reduction of the symmetry of the ligand molecule. In addition the complexation results in a strong low-frequency shift of the ν_s(P–S) and ν_{as}(P–S) vibration modes (free ligands: ν_s(P–S) = 660 and 649 cm^{-1}, ν_{as}(P–S) = 618 and 639 cm^{-1} for L_{III} and L_{IV} respectively [10, 22]). This is a common feature of the phosphine sulphide ligands when phenyl rings are bonded to the phosphorus atom: compared with their alkyl analogs, the phosphine sulphides with phenyl substituents exhibit high-frequency ν(P–S) vibrations and undergo a strong low-frequency shift upon complexation [28].

The parts of the spectra corresponding to the other molecular vibrations are rather simple, in particular only one ν(P–N) and two ν(C–N) bands are observed for the L_{III} complexes. Assignments for the so-called 'X-sensitive q, r and t' modes (Whiffen notation [24]) corresponding to non-simple P–C stretching vibrations are proposed in the right-hand column of Table IV. Vibrational data below 350 cm^{-1} are comparable with those for the complexes of L_I and L_{II}.

It seems reasonable to propose the same chelate structure for all the seven Pd(II), Pt(II) complexes with a square planar environment of the metal atom and a *gauche* chelate ring:



Electronic Spectra

The complexes obtained with the L_{III} and L_{IV} ligands are only very slightly soluble and have not been studied by electronic spectroscopy. The available electronic spectra of other complexes $(L)\cdot PdCl_2$ and $(L)\cdot PtCl_2$ ($L = L_I$, L_{II}) (Table V) are consistent with square planar geometries around the metal atoms [29, 30]. Characteristic ligand → ligand ($L_\pi \rightarrow L_{\pi^*}$), charge-transfer (L → M and M → L) and spin-allowed (d → d) transitions have been assigned.

The $L_\pi \rightarrow L_{\pi^*}$ bands are slightly shifted from their position in the free ligands. Other very strong bands are logically assigned as typical charge-transfer transitions. The L → M bands follow the accepted energy ordering Pt(II) > Pd(II) [31]. The $M \rightarrow L_{\pi^*}$ band system is observed in the spectra of the platinum complexes and is probably hidden by L → M bands in those of the palladium complexes. As usual for 'd^8 metal' complexes [31, 32], only the first spin-allowed band (of a possible three) is observed. The values of the splitting parameter Δ_1 can be derived from the position of these d → d bands (Table VI) [29, 31, 32]. Δ_1 increases in the expected order Pd < Pt [32]. Comparisons with dithiodiphosphate Pd and Pt complexes data [33] shows the ligand-field strengths to be greater for the dithioxodi-λ^5-phosphane L_I and L_{II} complexes.

Conclusion

It follows from the foregoing discussion that the dithioxodi-λ^5-phosphanes L_I, L_{II}, L_{III} and L_{IV} form five-membered chelate rings with copper(I), palladium(II) and platinum(II). The coordination always takes place through the sulphur atoms and the nitrogen atoms are not involved. The vibrational data indicate that upon coordination the two moieties of the originally centrosymmetric *trans* ligand molecule are rotated with respect to each other about the P–P bond to achieve a *cis* (planar chelate ring) or *gauche* (puckered chelate ring) conformation of the coordinated ligand. The *gauche* conformation is assumed, on the basis of the crystal structures of $[S_2P_2Me_4)\cdot CuCl]_2$ and of $(L_{II})\cdot PdCl_2$.

The ligands exhibit a particular affinity for 'soft' metals (in the Pearson meaning) such as Pd(II) and

TABLE V. Electronic Spectra of Palladium(II) and Platinum(II) Complexes with L_I and L_{II} Ligands.

Transitions	L_IPdCl_2		$L_{II}PdCl_2$		L_IPtCl_2		$L_{II}PtCl_2$	
	$\bar{\nu}$ (cm^{-1})	log ϵ	$\bar{\nu}$ (cm^{-1})	log ϵ	$\bar{\nu}$ (cm^{-1})	log ϵ	$\bar{\nu}$ (cm^{-1})	log ϵ
$L_\pi \rightarrow L_{\pi^*}$[a]	36,200	4.31	38,460	4.17	39,060	3.96	38,460	4.25
$L_\sigma \rightarrow M$	42,550	4.37			43,100	4.10		
$L_\pi \rightarrow M$	31,750	3.75	29,000	3.29			31,250	3.33
$M \rightarrow L_{\pi^*}$					29,300	3.47	29,850	3.23
					27,030	3.36	28,600	3.06
'd → d'	23,530	2.68	23,250	2.64			26,300	2.79

[a] Electronic spectra of free ligands: L_I $\bar{\nu}$ = 37,700 cm^{-1} (log ϵ = 2.93), L_{II} $\bar{\nu}$ = 38,500 cm^{-1} (log ϵ = 3.50).

TABLE VI. Ligand Field Parameter Δ_1 for Palladium(II) and Platinum(II) Complexes.

Complexes	$\bar{\nu}_1$ (cm^{-1})	Δ_1[a] (cm^{-1})
$L_I \cdot PdCl_2$	23.530	25.630
$L_{II} \cdot PdCl_2$	23.250	25.350
$Pd[S_2P(OC_2H_5)_2]_2$ [33]	21.800	23.900
$L_{II} \cdot PtCl_2$	26.300	28.400
$Pt[S_2P(OC_2H_5)_2]_2$ [33]	23.800	25.900

[a]Slater–Condon interelectronic repulsion parameter for both palladium and platinum: $F_2 = 10F_4 = 600\ cm^{-1}$ [29, 31, 32].

Pt(II), and, to a certain extent, Cu(I). Their alkyl analogues, on the contrary, display a more pronounced affinity for 'hard' or 'borderline' metals such as Co(II), Ni(II) and Cd(II). The basicity of the sulphur atoms in the dithioxodi-λ^5-phosphanes is thus dependent on the nature of the substituents on the phosphorus atoms. In the series under consideration the basicity seems greater for L_I and L_{II} than for L_{III} and L_{IV}. Hopefully an appropriate choice of the substituents should make it possible to modify the basicity of the sulphur atoms.

References

1 D. W. Meek and P. Nicpon, *J. Amer. Chem. Soc., 87,* 4951 (1965).

2 M. A. A. Beg and S. H. Khawaja, *Spectrochim. Acta, 24A,* 1031 (1968).

3 W. Levason, F. P. McCullough and C. A. McAuliffe, *Inorg. Nucl. Chem. Lett., 12,* 843 (1976).

4 G. P. McQuillan and I. A. Oxton, *J. Chem. Soc. Dalton,* 895 (1979).

5 G. P. McQuillan and I. A. Oxton, *J. Mol. Struct., 64,* 173 (1980).

6 A. J. Blake, G. P. McQuillan and I. A. Oxton, *Spectrochim. Acta, 36A,* 501 (1980).

7 I. Cuadrado and M. Moran, *Trans. Met. Chem., 6,* 329 (1981).

8 D. Troy, J. Galy and J.-P. Legros, *Acta Cryst., B36,* 398 (1980).

9 A. J. Blake, R. A. Howie and G. P. McQuillan, *Acta Cryst. B37,* 966 (1981).

10 D. Troy, J.-P. Legros and G. P. McQuillan, *Inorg. Chim. Acta, 58,* 217 (1982).

11 J.-P. Legros and D. Troy, *Acta Cryst.,* 1983, in press.

12 W. E. Slinkard and D. W. Meek, *Inorg. Chem., 8,* 1811 (1969).

13 W. E. Slinkard and D. W. Meek, *Chem. Comm.,* 361 (1969).

14 E. W. Ainscough and A. M. Brodie, *Coord. Chem. Rev., 27,* 59 (1978).

15 E. W. Ainscough, A. M. Brodie and K. L. Brown, *J. Chem. Soc. Dalton,* 1042 (1980).

16 W. J. Geary, *Coord. Chem. Rev., 7,* 81 (1971).

17 K. Nakamoto, 'Infra-red Spectra of Inorganic and Coordination Compounds', Wiley, New York (1970).

18 J. A. Tiethof, A. T. Hetey and D. W. Meek, *Inorg. Chem., 13,* 2505 (1974).

19 P. W. Corfield, personal communication in ref. 18 (1973).

20 E. W. Ainscough, H. A. Bergen, A. M. Brodie and K. L. Brown, *J. Chem. Soc. Dalton,* 1649 (1976).

21 F. A. Cotton, B. A. Frenz, D. L. Hunter and Z. C. Mester, *Inorg. Chim. Acta, 11,* 111 (1974).

22 A. J. Blake, G. P. McQuillan, I. A. Oxton and D. Troy, *J. Mol. Struct., 78,* 265 (1982).

23 M. Rey-Lafon, C. Rouffi, M. Camiade and M. T. Forel, *J. Chim. Phys., 67,* 2030 (1970).

24 D. H. Wiffen, *J. Chem. Soc.,* 1350 (1956).

25 G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, 24A,* 845 (1968).

26 J. R. Durig, R. Layton, D. W. Sink and B. R. Mitchell, *Spectrochim. Acta, 21,* 1367 (1965).

27 I. A. Oxton, *Ph.D. Thesis,* Aberdeen University (1974).

28 J. Kincaid, K. Nakamoto, J. A. Tiethof and D. W. Meek, *Spectrochim. Acta, 30A,* 2091 (1974).

29 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier, Amsterdam (1968).

30 R. L. Carlin, 'Transition Metal Chemistry', Vol. 1, M. Dekker, New York (1965), see H. B. Gray, 'Electronic Structures of Square Planar Metal Complexes', 240–286.

31 A. R. Latham, V. C. Hascall and H. B. Gray, *Inorg. Chem., 4,* 788 (1965) and references therein.

32 C. Preti and G. Tosi, *J. Coord. Chem., 8,* 223 (1979).

33 C. K. Jorgensen, *J. Inorg. Nucl. Chem., 24,* 1571 (1962)