Inorganica Chimica Acta, 35 (1979) 265–277
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Systematics of Palladium(II) and Platinum(II) Dithioether Complexes. The Effect of Ligand Structure upon the Structure and Spectra of the Complexes and upon Inversion at Coordinated Sulphur

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Received December 27, 1978

Planar complexes cis-$[MLX_2]$ *(M = Pd, Pt; X = Cl, Br, I) and* $[ML_2](ClO_4)_2$ *have been prepared for the dithioethers (L),* $MeS(CH_2)_nSMe$ *(n = 2, 3),* $PhS(CH_2)_nSPh$ *(n = 2, 3),* cis-*RSCH=CHSR (R = Me, Ph) and* o-$C_6H_4(SR)_2$ *(R = Me, Ph). The ligands* $PhS(CH_2)_nSPh$ *(n = 6, 8) yield polymeric* $[PdLX_2]_n$*, whilst* $PhS(CH_2)_{12}SPh$ *produces the* trans *chelates,* trans-$[PdLX_2]$ *(X = Cl, Br) and* trans-$[PtLCl_2]$*. The infrared, uv–visible (both solid state and solution) and* ^1H *nmr spectra are reported and discussed. The* $[ML_2](ClO_4)_2$ *complexes are 1:2 electrolytes but several show evidence for ion association. The* ^1H *nmr spectra are reported for the complexes of the methyl substituted ligands and the coordination shifts of the methyl and vinyl protons and* $^3J_{Pt-H}$ *coupling are discussed. The variable temperature* ^1H *nmr spectra show that rate of inversion at coordinated sulphur lies in the order Pt < Pd and Cl < Br < I. Variation with backbone gives the order* $-CH_2CH_2- <$ o-$C_6H_4 <$ cis-$CH{=}CH- < -CH_2CH_2CH_2-$.

Introduction

Modification of phosphorus and arsenic donor ligands can dramatically alter the properties of the corresponding transition metal complexes. As a result of the intensive studies of recent years it is now reasonably clear how the various combinations of steric and electronic factors operate – vital information if one wishes to design a specific catalytic system, or stabilise a particular metal geometry or oxidation state. Systematic studies of corresponding effects in neutral VIB donor chemistry are lacking [1] despite current interest in inversion at coordinated sulphur [2], S-dealkylation and S-alkylation and their biological implications [3]. As yet few catalytic systems employ thioether complexes possibly reflecting the lack of work in this area since certain thioether complexes are active catalysts [4]. Here we report a systematic study of dithioether complexes of palladium(II) and platinum(II). S-Dealkylation studies and platinum(IV) complexes will be reported subsequently.

A number of reports of dithioether complexes of these metals have appeared [5–13] and recent studies of tetra [14–16] and monothioethers [17–20] provide valuable comparative data.

Experimental

Infrared spectra were recorded as nujol mulls on Perkin-Elmer 225, 577 and Beckmann IR 11 spectrometers; ^1H nmr spectra in $CDCl_3$, CD_3NO_2 or $(CD_3)_2SO$ solution relative to TMS on a Perkin-Elmer R32 spectrometer. Electronic spectra were recorded in $CHCl_3$, or N,N′-dimethylformamide on a Unicam SP 1700 and in the solid state on a Beckmann MIV Acta. Conductivities were measured as described previously [16]. Molecular weights were measured in 1,2-dichloroethane ($\sim 10^{-3}M$) on a Meckrolab Osmometer.

1,2-Bis(phenylthio)ethane

Sodium (4.6 g; 0.2 g atom) was dissolved in absolute ethanol (500 cm^3) under a dry nitrogen atmosphere, and benzenethiol (22 g; 0.2 mol) added. The solution was stirred for 0.5 hr, heated to reflux and 1,2-dichloroethane (9.9 g; 0.1 mol) added dropwise. The mixture was refluxed for a further 1 hr, the

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ethanol removed on a rotary evaporator and the residue extracted with dichloromethane, filtered and evaporated. The resulting oil was dissolved in ethanol (100 cm^3) and on standing at 0 °C deposited the ligand as white needles. 17 g, 73%. Fnd, C = 68.1%, H = 5.9%, $C_{14}H_{14}S_2$ req. C = 68.3%, H = 5.7%. M.Pt. 61 °C. ^{1}H nmr = 7.25(m)[5H], 3.1(s)[2H] ppm.

The other bis(phenylthio)alkanes were prepared similarly: 1,3-bis(phenylthio)propane, 83%. Fnd, C = 70.2%, H = 6.4%, $C_{15}H_{16}S_2$ req. C = 69.3%, H = 6.2%, (viscous oil). ^{1}H nmr = 7.2(m)[5H], 2.9(t)[2H], 1.9(q)[1H] ppm. 1,6-bis(phenylthio)hexane, 85%. Fnd, C = 71.2%, H = 7.0%, $C_{18}H_{22}S_2$ req. C = 71.6%, H = 7.3%. M.Pt. 74–75 °C, ^{1}H nmr = 7.2(m)[5H], 2.85(t)[2H], 1.5(m)[4H]. 1,8-bis(phenylthio)octane, 85%. Fnd, C = 72.6%, H = 7.6%, $C_{20}H_{26}S_2$ req. C = 72.8%, H = 7.9%, M.Pt. 78–80 °C, ^{1}H nmr = 7.2(m)[5H], 2.8(t)[2H], 1.3(m)[6H]. 1,12-bis(phenylthio)dodecane, 80%, Fnd, C = 76.2%, H = 8.5%, $C_{24}H_{34}S_2$ req. C = 75.5%, H = 8.4%, M.Pt. 85–87 °C, ^{1}H nmr = 7.2(m)[5H], 2.8(t)[2H], 1.25(m)[10H].

cis-*1,2-Bis(phenylthio)ethylene*

A solution of sodium thiophenoxide was prepared from sodium (8.0 g, 0.35 g atom), benzenethiol (22.0 g, 0.2 mol) and ethanol (500 cm^3), heated to reflux and treated with *cis*-1,2-dichloroethylene (10.4 g, 0.1 mol). The solution was refluxed for 6 hrs, the majority of the ethanol distilled off under water-pump vacuum and the residue treated with water (200 cm^3) and diethylether (3 × 100 cm^3). The ether extract was dried over anhydrous sodium sulphate, evaporated and the oil dissolved in ethanol (100 cm^3). On standing at 0 °C yellowish crystals were deposited. 18.2 g, 75%. Fnd, C = 69.0%, H = 5.3%, $C_{14}H_{12}S_2$ req. C = 69.0%, H = 4.9%, M.Pt. 30 °C. ^{1}H nmr = 7.22(m)[5H], 6.48(s)[1H].

1,2-Bis(phenylthio)benzene

Copper phenylsulphide CuSPh [21] (70.0 g, 0.4 mol) suspended in a mixture of quinoline (300 cm^3) and pyridine (20 cm^3) was treated with *o*-dibromobenzene (42.0 g, 0.18 mol) and heated under reflux for 16 hr. The mixture was cooled to 100 °C and poured into a mixture of ice (1500 g) and conc hydrochloric acid (400 cm^3). The aqueous layer was extracted with diethylether (2 × 200 cm^3), the extract added to the residue and stirred vigorously. The combined ether extracts were washed successively with 10% aq HCl, water, 10% aq ammonia, water and dried over potassium carbonate. The ether was distilled off and the residual oil heated to 175 °C/2 mm Hg until all volatiles were distilled (mainly Ph_2S from its mass spectrum and ^{1}H nmr). The residue was dissolved in ethanol (20 cm^3) and on standing deposited white crystals. 24 g, 55%. Fnd C = 73.1%, H = 5.3%, $C_{18}H_{16}S_2$ req. C = 73.4%, H = 5.45%, M.Pt. 42 °C.

1,2-Bis(methylthio)ethane [2,5-dithiahexane]

Ethane-1,2-dithiol (25.0 g, 0.26 mol) was dissolved in ethanol (250 cm^3) under nitrogen, and sodium (12.0 g, 0.52 mol) added. When the sodium had dissolved the mixture was heated to reflux and iodomethane (74.0 g, 0.52 mol) added dropwise. The ethanol was distilled off and the residue fractionated *in vacuo*. B.Pt. 63–64 °C/20 mm Hg. 21 g, 67%. ^{1}H nmr = 2.67(s)[2H], 2.09(s)[3H] ppm.

1,3-bis(methylthio)propane was prepared similarly. 78%. ^{1}H nmr = 2.55(t)[2H], 2.05(s)[3H], 1.80(q)[1H] ppm.

cis-*1,2-Bis(methylthio)ethylene*

Sodium (14.0 g, 0.62 g atom) was dissolved in ethanol (200 cm^3) under nitrogen, the solution cooled to −10 °C, methanethiol (24.0 g, 0.5 mol) added and the mixture stirred at this temperature for 1 hr. It was then treated with *cis*-CHCl=CHCl (24.0 g, 0.25 mol) and heated under reflux for 7 hr. The ethanol was distilled off and the residue fractionated *in vacuo*. B.Pt. 52 °C/6 mm Hg. 17 g, 70%. ^{1}H nmr = 6.10(s)[1H], 2.28(s)[3H] ppm.

1,2-Bis(methylthio)benzene

o-Methylthiobenzenethiol [22] (78.0 g, 0.5 mol) was dissolved in ethanol (250 cm^3) and sodium (12.0 g, 0.52 g atom) added. The mixture was heated to reflux and iodomethane (71.0 g, 0.5 mol) added dropwise. After a further 1 hr under reflux the solvent was distilled off and the residue fractionated. B.Pt. 78 °C/1 mm Hg. 55 g, 65%. ^{1}H nmr = 7.2(m)[2H], 2.45(s)[3H] ppm.

Dichloro{1,2-bis(phenylthio)ethane}palladium(II)

Sodium tetrachloropalladate(II) (0.3 g, 0.001 mol) was dissolved in ethanol (15 cm^3) and the solution filtered. The ligand (0.24 g, 0.001 mol) in dichloromethane (5 cm^3) was added and the mixture refluxed for 3 hr during which any initial precipitate redissolved. Concentration of the deep orange solution yielded an orange solid which was filtered off, washed with ethanol and ether and dried *in vacuo* 78%.

The corresponding $[PdLX_2]$ (X = Br, I) were made similarly, except that the Na_2PdCl_4 solution was stirred with a five-fold excess of LiX for 3 hr before addition of ligand. Yields 70–85%.

Dichloro{1,2-bis(phenylthio)ethane}platinum(II)

Potassium tetrachloroplatinate(II) (0.4 g, 0.001 mol) in water (10 cm^3) and the ligand (0.24 g, 0.001 mol) in dichloromethane (10 cm^3) were mixed and sufficient ethanol added to produce a homogeneous solution. The mixture was heated for 4 hr resulting in an initial pink precipitate which slowly redissolved to give a pale yellow solution. Concentration of the solution gave a yellow solid. 65%.

The $[PtLX_2]$ (X = Br, I) complexes were prepared similarly in the presence of LiX.

The same general method was used to prepare all other halo complexes with the following exceptions.

Dichloro{1,6-bis(phenylthio)hexane}palladium(II)

Sodium tetrachloropalladate(II) (0.3 g, 0.001 mol) was dissolved in ethanol (20 cm^3) and the solution filtered into a vigorously stirred solution of the ligand (0.3 g, 0.001 mol) in ethanol (50 cm^3). After 1 hr the orange precipitate was filtered off, washed with ethanol and diethylether and dried *in vacuo.* 90%.

The other palladium(II) complexes of $PhS(CH_2)_n$-SPh (n = 6, 8) were prepared similarly.

Dichloro{1,12-bis(phenylthio)dodecane}palladium(II)

Sodium tetrachloropalladate(II) (0.3 g, 0.001 mol) was dissolved in ethanol (20 cm^3), filtered and added dropwise to a solution of the ligand (0.38 g, 0.001 mol) in dichloromethane (50 cm^3). The resulting solution was heated to reflux, filtered from the small amount of yellow precipitate and evaporated to dryness. The orange oil was dissolved in dichloromethane, filtered and concentrated to ~10 cm^3. On standing for two days at 0 °C an orange solid precipitated. 80%.

$[Pd(PhS(CH_2)_{12}SPh)Br_2]$ and $[Pt(PhS(CH_2)_{12}SPh)Cl_2]$ were prepared similarly.

$[PdL_2](ClO_4)_2$ Complexes

Dichlorobisacetonitrilepalladium(II) (0.26 g, 0.001 mol) was dissolved in hot acetonitrile (15 cm^3) and silver perchlorate (0.415 g, 0.002 mol) in acetonitrile (10 cm^3) added. A precipitate formed instantly and the mixture was stirred for a further 15 minutes. The solution was filtered and the appropriate ligand (0.002 mol) in dichloromethane (10 cm^3) added and stirred for 1 hr. The solution was evaporated to dryness on a rotary evaporator and extracted with nitromethane (20 cm^3). After filtration the volume of the solution was reduced and the complex allowed to crystallise or acetone added to aid precipitation. Yields 50–70%.

$[PtL_2](ClO_4)_2$ Complexes

These complexes were prepared by a similar method to the palladium analogues. However, the removal of the chloride ligands from dichlorobisacetonitrileplatinum(II) by silver perchlorate required 2 hr under reflux in acetonitrile. Isolation of the complexes usually required precipitation from the nitromethane solution by diethylether. Yields 40–70%.

Results and Discussion

Ligands

The alkane-backboned dithioethers $RS(CH_2)_nSR$ (R = Ph, n = 2, 3, 6, 8, 12) were prepared from NaSPh and the appropriate α, ω-dihaloalkane and recrystallised from ethanol. The ligands (R = Me, n = 2, 3) were prepared from the appropriate dithiol and iodomethane *via* the disodium salt and fractionated *in vacuo.* The *cis*-dithioalkenes *cis*-RSCH=CHSR (R = Me, Ph) were obtained stereospecifically from the reaction of *cis*-CHCl=CHCl with NaSR in the presence of NaOEt [23]. *Trans*-CHCl=CHCl does not react under these conditions [24, 25] and the use of CuSPh in place of NaSPh gave diphenyldisulphide as the major product. Although *trans*-PhSCH=CHSPh has been reported to form on distillation of the *cis* isomer "under reduced pressure" [24, 25], in our hands this method gave a mixture of Ph_2S, PhSSPh and starting material*.

A good yield of 1,2-bis(phenylthio)benzene o-$C_6H_4(SPh)_2$ was obtained from CuSPh and *o*-dibromobenzene in quinoline/pyridine (20:1) solution [21], but *o*-dichlorobenzene gave a much lower yield and mass spectrometry and analysis of the product indicated contamination with substantial amounts of (*o*-chlorophenyl)phenylthioether o-$PhSC_6H_4Cl$. The corresponding methyl ligand o-$C_6H_4(SMe)_2$ was easily obtained from *o*-methylthiobenzenethiol [22], o-$C_6H_4(SMe)(SH)$, sodium ethoxide and iodomethane in ethanol. All the ligands were characterised by analysis, ^1H nmr and mass spectrometry [26].

Halide Complexes

The reaction of $RS(CH_2)_nSR$ (n = 2, 3), *cis* RSCH=CHSR and o-$C_6H_4(SR)_2$ (R = Me, Ph) with K_2PtCl_4 in aqueous ethanol initially produced pink precipitates shown by other workers [10, 27] to be Magnus type salts $[PtL_2][PtCl_4]$ (L = dithioether). This can be rationalised in terms of the greater *trans* effect of sulphur than chloride resulting in the dithioether attacking the first formed $[PtLCl_2]$ faster than $[PtCl_4]^{2-}$ and the resulting complex being an insoluble precipitate. On heating, the solids slowly redissolve to give pale yellow solutions from which the $[PtLCl_2]$ complexes can be obtained by evaporation. The bromo and iodo complexes are similarly formed from $[PtX_4]^{2-}$ (X = Br, I). The reactions of these ligands with $[PdX_4]^{2-}$ (X = Cl, Br, I) also proceed *via* $[PdL_2][PdX_4]$ but these intermediates are much less stable than the platinum analogues and rearrange easily. The isolated complexes are listed in Table I. In general the $[MLX_2]$ complexes were slightly soluble in halocarbons and rather more so in acetonitrile, N,N'-dimethylformamide and dimethylsulphoxide. All the complexes were non-electrolytes in 1,2-dichloroethane or nitromethane and molecular weight measurements on representative complexes in 1,2-dichloroethane confirmed the monomeric formulation.

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*The literature [24, 25] contains conflicting accounts of the properties of '*trans*-PHSCH=CHSPh'.

TABLE I. Analytical and Physical Data of the Halide Complexes.

Complexes	Colour	C%[a]	H%[a]	X%[a]	M.W.[a,b]	ν(M–X) cm^{-1} [c]
$PhSCH_2CH_2SPh$ (L)						
$PdLCl_2$	orange	39.9(39.9)	3.4(3.2)	16.8(16.8)	–	315, 296
$PdLBr_2$	brown	32.8(32.8)	2.8(2.7)	31.3(31.2)	–	258, 245
$PdLI_2$	purple	27.8(27.7)	2.5(2.3)	42.4(41.8)	–	158, 148
$PtLCl_2$	pale yellow	32.9(32.9)	2.8(2.6)	14.0(13.9)	–	315, 302 sh
$PtLBr_2$	yellow	28.5(28.5)	2.4(2.3)	26.0(26.6)	–	245, 226
$PtLI_2$	yellow	24.6(24.2)	2.0(2.0)	36.5(36.5)	695(695)	165, 158 sh
$PhSCH_2CH_2CH_2SPh$						
$PdLCl_2$	yellow	40.2(41.2)	3.8(3.7)	16.5(16.3)	–	324, 308
$PdLBr_2$	orange-yellow	33.8(34.2)	3.0(3.0)	30.3(30.4)	–	254, 240 sh
$PdLI_2$	purple	28.7(29.0)	2.4(2.5)	40.2(40.8)	–	163, 149
$PtLCl_2$	pale yellow	34.1(34.1)	3.0(3.4)	13.9(13.5)	–	328, 312
$PtLBr_2$	fawn	29.4(29.0)	2.7(2.9)	25.5(26.0)	–	242, 228
$PtLI_2$	yellow	25.4(25.4)	2.4(2.5)	35.8(35.8)	692(709)	168, 154
o-$C_6H_4(SPh)_2$						
$PdLCl_2$	orange-brown	46.0(45.8)	3.2(3.0)	15.6(15.1)	–	322, 308
$PdLBr_2$	deep orange	38.5(38.6)	2.4(2.5)	28.4(28.6)	–	260, 248
$PdLI_2$	purple	33.0(33.0)	2.2(2.2)	38.8(38.8)	652(654)	158, 142
$PtLCl_2$	yellow	37.6(38.5)	2.7(2.5)	13.5(12.8)	–	326, 308
$PtLBr_2$	yellow	33.2(33.2)	2.4(2.2)	25.6(24.7)	–	244, 232
$PtLI_2$	yellow	29.5(29.1)	2.0(1.9)	33.2(34.2)	720(739)	165, 150
cis-PhSCH=CHSPh						
$PdLCl_2$	yellow	40.0(39.9)	2.7(2.8)	17.0(16.8)	–	318, 298
$PdLBr_2$	orange	33.4(32.9)	2.6(2.3)	29.8(30.2)	523(510)	246, 228
$PdLI_2$	purple-red	27.6(27.7)	2.0(2.0)	41.8(41.8)	–	164, 162
$PtLCl_2$	yellow	34.0(33.0)	2.1(2.3)	14.4(13.9)	–	316, 300 sh
$PtLBr_2$	yellow	28.4(28.0)	2.3(2.0)	26.9(26.9)	–	248, 232
$PtLI_2$	orange	24.4(24.2)	1.9(1.7)	35.6(36.5)	–	165, 146
$PhS(CH_2)_6SPh$						
$PdLCl_2 \cdot \frac{1}{2}CH_2Cl_2$	yellow	41.7(42.6)	4.5(4.4)	19.7(20.2)	–	343
$PdLBr_2$	orange	39.5(39.0)	4.5(4.0)	28.5(28.3)	–	280
$PdLI_2$	black	32.4(32.0)	3.3(3.1)	37.8(37.6)	–	205
$PhS(CH_2)_8SPh$						
$PdLCl_2 \cdot \frac{1}{2}CH_2Cl_2$	yellow-orange	45.8(44.5)	5.0(5.0)	19.8(19.5)	–	346
$PdLBr_2$	deep orange	40.2(40.3)	4.3(4.3)	27.0(26.8)	–	263
$PdLI_2$	black	34.2(34.7)	3.8(3.7)	37.1(36.8)	–	218
$PhS(CH_2)_{12}SPh$						
$PdLCl_2$	orange	51.7(51.6)	6.1(6.3)	13.0(12.7)	587(564)	352
$PdLBr_2$	orange	44.1(44.2)	5.4(5.3)	24.6(24.8)	665(652)	275
$PtLCl_2$	buff	44.8(44.2)	4.7(5.2)	10.7(10.8)	640(653)	346
$MeSCH_2CH_2SMe$						
$PdLCl_2$	orange-yellow	16.2(16.0)	3.6(3.3)	–	–	314, 298
$PdLBr_2$	orange	12.35(12.4)	2.6(2.6)	–	34(388)	252, 234
$PdLI_2$	red-brown	9.7(9.9)	2.3(2.1)	–	470(482)	162, 141
$PtLCl_2$	pale yellow	12.0(12.4)	2.6(2.6)	–	–	322, 308
$PtLBr_2$	yellow	10.4(10.1)	2.3(2.1)	–	–	248, 222
$PtLI_2$	brown	8.5(8.5)	2.0(1.8)	–	576(571)	168

(Continued overleaf)

TABLE I. *(Continued)*

$MeSCH_2CH_2CH_2SMe$						
$PdLCl_2$	yellow-brown	19.7(19.1)	3.9(3.8)	22.6(22.6)	–	326, 314
$PdLBr_2$	orange	14.4(14.8)	3.1(3.2)	39.7(31.8)	–	240, 232 sh
$PdLI_2$	red	12.3(12.1)	2.4(2.4)	50.7(50.2)	–	160. 155
$PtLCl_2$	pale yellow	14.6(14.8)	2.9(3.0)	19.7(19.5)	–	323, 305
$PtLBr_2$	yellow	12.2(12.2)	2.7(2.4)	32.0(32.5)	–	238, 228
$PtLI_2$	yellow	10.5(10.3)	2.1(2.1)	42.4(42.6)	–	162, 154 sh
o-$C_6H_4(SMe)_2$						
$PdLCl_2$	orange	27.4(27.6)	2.7(2.9)	20.8(20.4)	328(347)	322, 308
$PdLBr_2$	orange	22.3(22.0)	2.4(2.3)	35.8(36.5)	407(446)	260
$PdLI_2$	red	18.1(18.0)	1.9(1.9)	47.9(47.4)	–	164, 140
$PtLCl_2$	yellow	22.6(22.2)	2.7(2.3)	15.9(16.3)	–	322, 310
$PtLBr_2$	yellow	18.0(18.3)	1.9(1.9)	30.0(30.3)	–	258, 244
$PtLI_2$	yellow	15.9(15.4)	1.6(1.6)	40.1(40.0)	607(619)	165, 154
cis-MeSCH=CHSMe						
$PdLCl_2$	orange	17.0(16.3)	2.3(2.7)	23.6(24.0)	367(386)	315, 294
$PdLBr_2$	orange	13.2(12.6)	2.1(2.1)	40.8(41.5)	–	264, 224
$PdLI_2$	red-brown	10.1(10.0)	1.8(1.7)	53.4(53.0)	465(480)	168, 156
$PtLCl_2$	yellow	13.0(12.6)	2.2(2.1)	18.2(18.4)	–	308, 298
$PtLBr_2$	yellow	10.2(9.7)	2.0(1.7)	31.8(32.3)	–	252, 228
$PtLI_2$	deep yellow	8.5(8.2)	1.6(1.4)	42.6(43.1)	–	168, 145

[a]Found (calc), X = halide. [b]$10^{-3}M$ CH_2ClCH_2Cl. [c]Nujol mull.

On the basis of the (necessarily) *cis* structure (C_{2v}), two $\nu(M-X)$ $A_1 + B_1$ and two $\nu(M-S)$ $A_1 + B_1$ infrared active vibrations are expected. The bands principally associated with the M–S linkages appear as moderately intense absorptions in the range 290–350 cm^{-1} and are often broad with ill-defined maxima. The frequencies vary somewhat with L, X and M but in view of the extensive coupling with other vibrational modes, no attempt was made to interpret these variations. Nonetheless the similar values of "Pt–L" and "Pd–L" despite the mass differences is in keeping with the order of bond strength Pt–S > Pd–S as observed elsewhere. The bands principally due to M–X vibrations $\nu(M-X)$ (Table I) were generally easy to assign by inspection and fall in the range established for *cis* MX_2 groups [28–30]. The $\nu(M-Cl)$ for $[Pd(MeSCH_2CH_2SMe)Cl_2]$ are in excellent agreement with the values of Coates and Parkin [29]. Our assignments for the complexes of $PhS(CH_2)_nSPh$ (n = 2, 3) differ considerably from the literature values [8] but are in keeping with the other assignments made in the present study. The variations in $\nu(M-X)$ with changes in L and M are small and irregular and no trends were discernable, a not unexpected result in view of the coupling with other vibrations and the small overall range of values. Comparison with the published data for corresponding complexes of ditertiary phosphines, -arsines and amines [29–32] shows the trend in $\nu(M-X)$ with *trans* donor to be; P < As < S < N consistent with the *trans* influence series [33].

Coordination of the dithioethers to metal ions results in changes in their infrared spectra but in general these did not yield any information about the nature of the coordinated ligand. However, for $MeS(CH_2)_2SMe$ detailed studies [34, 35] show that the gauche conformer of the ligand (and hence chelated L) can be identified. As expected the spectra of the complexes of this ligand prepared in the present study also indicated that the gauche conformer was present.

The electronic spectra recorded in chloroform and/or N,N′-dimethylformamide were characteristic of planar d^8 systems (Table II). Considerable effort has been devoted to the interpretation of the electronic spectra of $[MX_4]^{2-}$ ions [36–38] but relatively little detailed work on lower symmetry complexes has appeared. In the complexes $[MLX_2]$ the lower energy moderately intense band can be assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition (D_{4h}) and the second band at higher energy to $^1A_{1g} \rightarrow {}^1E_g$. The intense absorptions > 30,000 cm^{-1} are predominantly S → M and X → M charge transfer whilst in a few cases weak shoulders on the low energy side of the first 'd–d' band are seen, probably transitions to the spin forbidden triplet states. The solid reflectance spectra are generally similar, the spin forbidden transitions being more commonly observed in the solid state spectra. The expected shifts in band maxima I < Br < Cl and MeS > PhS are observed but the spectrochemical effect of changing the ligand backbone is small. The order with backbone appears to be $-(CH_2)_2- >$

TABLE II. Electronic Spectra of the Halide Complexes.

Complex	$E_{max}(\epsilon_{mol}) \times 10^{-3}$ cm^{-1} [a,b]	$E_{max} \times 10^{-3}$ cm^{-1} [c]
$PhSCH_2CH_2SPh$ [a]		
	24.00(2150), 34.00sh(7370)	23.70, 33.30sh, 37.31
$PdLBr_2$	23.00(2720), 25.20(2440), 2955(6100)	22.50, 31.30sh, 36.60
$PdLI_2$	19.47(3870), 33.77(4500)	17.40sh, 20.40, 36.60
$PtLCl_2$	27.00(1550), 30.60(2255), 36.40sh(3820)	25.64, 31,90, 37.20
$PtLBr_2$	26.72(1880), 29.53(2600), 33.45(1905)	24.71, 29.58, 37.04
$PtLI_2$	25.25(3667), 30.82(2010)	21.74sh, 24.31, 33.00sh, 36.90
$PhSCH_2CH_2CH_2SPh$ [b]		
$PdLCl_2$	23.02(450), 26.32(2770), 30.80(7300)	24.10, 26.30sh, 31.25sh
$PdLBr_2$	21.80sh(570), 24.30(1260), 30.30sh(4430)	23.55, 30.60
$PdLI_2$	19.40(810), 21.65(1080), 29.40(3100), 32.00(3675)	19.61, 22.22, 32.00sh
$PtLCl_2$	27.02sh(3690), 30.25(4030), 33.35(5020)	25.65, 30.32, 37.20
$PtLBr_2$	25.20(1320), 29.20(870), 33.40(1510), 35.50(3100)	24.35, 30.32sh, 33.90
$PtLI_2$	24.80(2100), 33.80sh(5180)	24.70, 33.00sh, 36.00
o-$C_6H_4(SPh)_2$ [a]		
$PdLCl_2$	24.00(4365), 33.00(3912), 35.30(4048)	23.25, 31.25sh, 36.80
$PdLBr_2$	23.50(810), 29.87(3565), 34.30(2440)	22.71, 29.85sh, 34.25
$PdLI_2$	19.27(2975), 23.00(1210), 28.94(9630), 34.67sh	19.60sh, 23.25, 30.30, 37.00
$PtLCl_2$	26.80(1260), 30.95(3480), 34.60(9370)	23.64, 31.06, 35.09
$PtLBr_2$	25.40(1107), 29.33(2076), 34.80(7960)	23.30, 29.41, 36.23
$PtLI_2$	24.20(4880), 33.50(9354), 36.70(19260)	21.28sh, 24.21, 33.44, 35.97
cis-$PhSCH{=}CHSPh$ [b]		
$PdLCl_2$	24.40sh(2010), 29.67(2675), 33.50(6380)	23.25, 33.00sh
$PdLBr_2$	22.80(2375), 25.30(2410), 29.50(3580)	22.62, 26.32, 33.90
$PdLI_2$	19.05(2557), 23.70(1586), 28.80(6990), 33.70(10970)	18.87, 20.83, 33.33
$PtLCl_2$	25.40sh(2068), 31.00(9700)	23.80, 32.00sh, 36.76
$PtLBr_2$	25.30sh(755), 29.00(2075), 33.20sh(3768)	23.11, 31.05, 37.45
$PtLI_2$	23.50(2700), 28.35(13820), 33.75(5280)	21.97sh, 23.36, 33.56
$PhS(CH_2)_6SPh$		
$PdLCl_2$	–	22.23, 29.85, 31.34
$PdLBr_2$	–	21.46, 23.64, 33.00sh, 36.90
$PdLI_2$	–	16.40sh, 19.60, 22.24, 34.48
$PhS(CH_2)_8SPh$		
$PdLCl_2$	–	22.22, 29.41, 35.34
$PdLBr_2$	–	20.83sh, 22.26, 33.78sh, 36.90
$PdLI_2$	–	15.6sh, 17.54sh, 21.37, 28.98, 37.45
$PhS(CH_2)_{12}SPh$ [a]		
$PdLCl_2$	22.80(1080)sh, 29.15(10000)	22.48, 29.90
$PdLBr_2$	21.50(1107)sh, 28.30(9590)	21.62sh, 22.47, 35.54
$PtLCl_2$	28.50sh, 30.80(9030)	28.00, 34.00
$MeSCH_2CH_2SMe$ [b]		
$PdLCl_2$	25.23(1165), 31.75(1710), 35.40sh(8390)	23.54, 29.00sh, 37.45
$PdLBr_2$	24.45(1370), 27.50(1250), 33.30(8100)	22.73, 29.40sh, 37.07

(Continued on facing page)

TABLE II. *(Continued)*

$PdLI_2$	20.75(3055), 24.75(810), 34.10(18240)	20.84, 23.80sh, 35.70
$PtLCl_2$	27.00(910), 31.55(760), 36.00(11900)	21.30sh, 26.74, 31.75, 35.08
$PtLBr_2$	26.80(900), 31.00(510), 35.60(8600)	24.10, 31.45sh, 35.97
$PtLI_2$	26.20(1190), 30.80(315), 34.50(7600)	23.26, 25.97sh, 35.40
$MeSCH_2CH_2CH_2SMe$[b]		
$PdLCl_2$	25.46(2837), 28.90(3270), 33.15(7745)	24.20sh, 32.36sh
$PdLBr_2$	25.18(780), 33.80(8100), 36.70(11250)	23.36, 31.45, 36.42
$PdLI_2$	20.60(1430), 30.20(7450), 35.15(10450)	20.40sh, 21.51, 31.05sh, 36.75
$PtLCl_2$	27.10(385), 32.10(1370)	25.13, 34.84sh
$PtLBr_2$	26.20(900), 30.70(4600), 33.20(4650)	24.27, 31.55, 37.31
$PtLI_2$	25.60(1195), 30.75sh(2440), 35.00(5016)	23.72, 31.85sh, 36.49
$o\text{-}C_6H_4(SMe)_2$[b]		
$PdLCl_2$	25.80(770), 35.07(1740)	23.70, 32.26sh, 35.08
$PdLBr_2$	21.80(645), 26.80(1310), 32.50(5380)	20.83sh, 22.63, 33.00
$PdLI_2$	20.90(3660), 27.00sh(6840), 30.20(2160)	19.25sh, 21.05, 30.4sh, 36.76
$PtLCl_2$	26.40(1430), 32.20sh(2557)	25.00, 32.25sh, 37.20
$PtLBr_2$	25.60(445), 29.75sh(1730), 33.40(3100)	24.51, 31.05sh, 37.04
$PtLI_2$	23.60(3565), 30.67(1740)	21.97sh, 24.50, 36.00
$MeSCH{=}CHSMe$[b]		
$PdLCl_2$	26.00(1135), 30.90sh(2010), 34.33(4685)	23.25, 34.12sh, 37.31
$PdLBr_2$	23.50(890), 26.60(1190), 34.00(5600)	22.73, 30.00sh, 37.04
$PdLI_2$	20.75(1135), 23.30(835), 25.30sh(970), 30.40(4010)	18.50sh, 21.28, 31.25sh, 36.90
$PtLCl_2$	25.90(760), 29.80(1550), 30.65(2076), 31.80 (2080)	23.64, 34.01sh
$PtLBr_2$	25.40(550), 30.60(1675), 35.35(2440)	23.80, 31.05, 37.45
$PtLI_2$	23.90(2366), 30.75(1367)	22.47sh, 23.97, 30.00sh

[a] $10^{-3}M$ solutions in CH_2Cl_2. [b] In N,N-dimethylformamide range 36,000–12,000 cm^{-1}. [c] Diffuse reflectance range 38,000–12,000 cm^{-1}.

$\text{-}(CH_2)_3\text{-} > \text{-}CH{=}CH\text{-} > o\text{-}C_6H_4$, which differs from that observed [39] with group VB donors, $\text{-}CH{=}CH\text{-} > \text{-}(CH_2)_2\text{-} > o\text{-}C_6H_4$.

Dithioethers produce rather weak ligand fields, comparison of the spectra with those of corresponding group VB donors reveals the spectrochemical series P > As > Sb > S > N [31, 32, 39–47]. The order is similar to that deduced by Venanzi *et al.* [42] for monodentate ligands but reverses the positions of antimony and sulphur.

The longer backboned ligands $PhS(CH_2)_nSPh$ (n = 6, 8) reacted with either $Na_2[PdX_4]$ or $[Pd(PhCN)_2X_2]$ (X = Cl, Br, I) to yield $PdLX_2$ complexes which were insoluble in all solvents examined. The electronic spectra of the solids (Table II) contain a number of broad intense bands with shoulders at low energy. The far infrared spectra differ considerably from those of the *cis*-$[PdLX_2]$ complexes discussed above. For the two chlorocomplexes there are broad absorptions at 340–320 cm^{-1} and single sharp strong bands at 343 cm^{-1} (n = 6) and 346 cm^{-1} (n = 8). These can be assigned as 'ν(Pd–L)' and 'ν(Pd–Cl)' respectively and are consistent with a *trans* structure with D_{2h} symmetry at the metal and would produce single 'ν(Pd–Cl)' B_{3u} and 'ν(Pd–L)' B_{2u} infrared active vibrations [20, 43, 44]. Similar assignments can be made for the bromocomplexes and for $Pd(PhS(CH_2)_8SPh)I_2$. However, for $Pd(PhS(CH_2)_6SPh)I_2$ only weak absorptions were present in the range 190–230 cm^{-1}. Duddell *et al.* [40] have shown that the asymmetric M-I vibrations may be weak in *trans*-$[ML_2I_2]$ (L = monodentate ligand) and thus we tentatively assign a weak band at 205 cm^{-1} in the latter complex to this vibration. The *trans*-MX_2 arrangement and insolubility of these complexes indicates a polymeric structure with bridging dithioether. The other possibility of *trans* chelation by the dithioether was ruled out by the relatively short interdonor linkage and by the fact that *trans* chelated complexes are highly soluble (see below). Repeated attempts to prepare platinum(II) analogues were unsuccessful, only intractable yellow oils being formed. These oils were moderately soluble in halocarbon solvents and t.l.c. studies suggested that more than one species was present. Since no pure complexes could be isolated further speculation is probably unprofitable although it may be that cyclic oligomers are present [45].

The reaction of the appropriate sodium tetrahalopalladate(II) $Na_2[PdX_4]$ (X = Cl, Br) with 1,12-bis(phenylthio)dodecane in a 1:1 molar ratio in ethanol/dichloromethane resulted in the rapid precipitation of small amounts of yellow solids (5% by weight) and subsequent filtration and evaporation of the mother liquor gave orange-brown complexes (70–80%) of stoichiometry $[PdLX_2]$ (Table I). Identical products were obtained using $[Pd(PhCN)_2X_2]$ as starting material. Similarly $[PtLCl_2]$ was also obtained but repeated attempts to prepare $[PdLI_2]$ produced black, insoluble powders of low (and variable) C and H content and the majority of the ligand was recovered from the mother liquor. The $[MLX_2]$ complexes were very soluble in halocarbon solvent in which they were non-electrolytes and had molecular weights in excellent agreement with the values expected for monomeric complexes (Table I). The far infrared spectra contained single "ν(M–X)" vibrations in the range expected for *trans* X–M–X groups [43, 44]. In dichloromethane the electronic spectra of the complexes consisted of very broad intense absorptions at 28,000–29,000 cm^{-1} with distinct low energy shoulders. Attempts to grow crystals for X-ray studies have been unsuccessful. The difficulty of isolating solid complexes of this type may well account for the scarcity until recently of such complexes [41], that is *trans*-spanning chelates. These complexes are thus *trans*-$[MLX_2]$ in which the dithioether spans *trans* positions on the metal ion. Unlike $[PtCl_2\{Bu^t_2P(CH_2)_2PBu^t_2\}]$ [46], the dithioether complexes did not sublime in high vacuum. The mass spectra which were recorded in an attempt to provide an independent check of the molecular weights exhibited only fragments of low M/e values, probably the result of S-dealkylation of the ligand.

The small amounts of insoluble by-products from the preparation of the palladium complexes also analysed as $PdLX_2$ and were probably oligomeric with bridging dithioether, although their insolubility precluded conformation of this.

Bis-ligand Complexes $[ML_2](ClO_4)_2$

These complexes could only be satisfactorily prepared in the absence of halide ions and thus the solvento-intermediates $[M(CH_3CN)_4](ClO_4)_2$ (M = Pd, Pt) were reacted with two equivalents of dithioether in acetonitrile. The complexes (Table III) were soluble in polar solvents such as acetonitrile and nitromethane and essentially insoluble in non-polar media. The mull infrared spectra exhibited perchlorate ν_3(~1080 cm^{-1}) and ν_4(~620 cm^{-1}) absorptions which showed no sign of splitting and thus the perchlorate groups were uncoordinated [47]. Absorptions associated with the M–S bond are again observed between 350–290 cm^{-1}.

The solution electronic spectra were characteristic of square- planar d^8 palladium(II) and platinum(II) complexes. The lowest energy absorption in the palladium(II) complexes occurred between 28,000 cm^{-1} and 30,000 cm^{-1} while that of the platinum(II) analogues was higher in energy generally as a shoulder on the more intense charge transfer absorptions. The E_{max} values were, as expected, higher than for the MS_2X_2 system, but lower than for MP_4^{2+} [31]. The solid reflectance spectra, however, exhibited absorptions at very much lower energies, in some cases <23,000 cm^{-1} (Table III, Fig. 1). This effect is not seen for phosphine complexes suggesting that it was not due to spin-forbidden transitions too weak to be seen in the solution spectra. Perchlorate coordination in the solid state was also unlikely since an effect of this magnitude would cause lowering of symmetry of the perchlorate ion and the $\nu_3(ClO_4^-)$ band in the infrared spectrum would show splitting [47] (see above). Intermolecular interaction is a possible explanation, either M....S or M....M. It is interesting that similar effects have not been observed in the diphosphine or diarsine analogues. Coordinated thioether ligands have an extra lone pair and it is conceivable that these would interact with neighbouring metal ions in the solid state producing 'pseudo 5- or 6-coordination' and hence the new spectral absorptions at lower energy. The structure of $[Pt_2Br_4(SEt_2)_2]$ [2, 48] shows that it is possible for both thioether lone pairs to coordinate simultaneously. The ^{129}I Mössbauer spectra of $[M\{o\text{-}C_6H_4(AsMe_2)_2\}_2]I_2$ (M = Pd, Pt) demonstrate significant interaction of the I^- ions with the metal ion in the *trans* axial positions and that the interaction is greater for platinum than palladium [49]. The phenyl substituted thioether complexes appear to show this

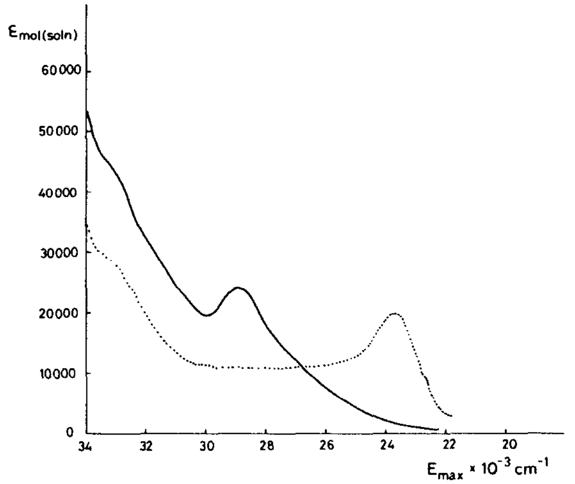

Fig. 1. Electronic spectra (– solution, ... solid state reflectance) of $[Pd(PhSCH_2CH_2SPh)_2](ClO_4)_2$. The solid state reflectance spectrum has an arbitrary absorbance scale.

TABLE III. Analytical and Physical Data of the Bis-ligand Complexes.

	Colour	C%[a]	H%[a]	$E_{max}(\epsilon_{mol})^b \times 10^{-3}$ cm^{-1}	$E_{max} \times 10^{-3}$ cm^{-1}	$\Lambda_M{}^c$ (at $5 \times 10^{-3}M$) ohm^{-1} cm^2 mol^{-1}	$\Lambda_M{}^c$ (at $5 \times 10^{-4}M$) ohm^{-1} cm^2 mol^{-1}
$PhSCH_2CH_2SPh$							
$[PdL_2](ClO_4)_2$	Yellow	42.2(41.6)	3.5(3.6)	28.90(2823), 33.50(4684)	23.70, 33.67	145.3	204.6
$[PtL_2](ClO_4)_2$	White	37.6(37.9)	3.5(3.2)	35.00(sh)	22.50, 35.10sh	147.5	204.8
$PhSCH_2CH_2CH_2SPh$							
$[PdL_2](ClO_4)_2$	Yellow	43.3(43.6)	4.2(3.9)	29.00(sh)(3768), 33.60(7960)	23.40, 37.04	d	173.4
$[PtL_2](ClO_4)_2$	White	38.9(39.4)	3.9(3.4)	[nothing < 36.00]	24.10sh, 33.30sh	115.7	162.4
$PhSCH{=}CHSPh$							
$[PdL_2](ClO_4)_2$	Yellow	42.4(41.9)	3.0(3.3)	29.40sh(2068), 35.00(14250)	22.57, 30.30sh, 35.01	123.0	180.8
$[PtL_2](ClO_4)_2$	Yellow	38.0(38.1)	2.8(2.7)	35.00sh	24.10, 32.25	113.0	150.0
o-$C_6H_4(SPh)_2$							
$[PdL_2](ClO_4)_2$	Brown	47.5(48.4)	3.2(3.2)	28.60sh(4320), 35.00(12400)	22.72, 35.09	137.9	187.1
$[PtL_2](ClO_4)_2$	Off-white	42.5(44.0)	3.0(2.9)	34.50sh	22.50, 30.30	144.5	207.8
$MeSCH_2CH_2SMe$							
$[PdL_2](ClO_4)_2$	Yellow	17.5(17.5)	4.5(3.7)	29.80(1140)	24.20sh, 29.74sh, 35.35	145.8	220.2
$[PtL_2](ClO_4)_2$	White	15.2(15.1)	3.3(3.3)	31.60(10800)	24.40(w), 31.45	130.0	199.6
$MeSCH_2CH_2CH_2SMe$							
$[PdL_2](ClO_4)_2$	Lemon	20.8(20.5)	4.2(4.1)	29.40(2290)	27.00	133.3	208.2
$[PtL_2](ClO_4)_2$	White	18.0(18.1)	3.6(3.8)	31.20(15800)	23.70(w), 31.25, 37.00	138.8	212.0
$MeSCH{=}CHSMe$							
$[PdL_2](ClO_4)_2$	Yellow	17.7(17.6)	2.8(3.0)	28.60(sh)(1760), 35.40sh	24.44sh, 27.74, 30.95sh	136.3	196.1
$[PtL_2](ClO_4)_2$	White	15.2(15.2)	2.6(2.5)	35.7(sh)(5400)	22.70(w), 37.2	149.0	216.8
o-$C_6H_4(SMe)_2$							
$[PdL_2](ClO_4)_2$	Dk brown	29.7(29.7)	3.5(3.1)	29.20(2116), 32.50sh(6490)	22.50, 28.00sh, 37.70	125.5	191.0
$[PtL_2](ClO_4)_2$[e]	Off-white	28.4(27.9)	3.0(3.0)	32.30sh(2780)	23.80(w), 36.8	107.3	164.8

[a] Found (calc). [b] In DMF. [c] In CH_3NO_2. [d] Insufficient solubility. [e] 1:1 acetonitrile adduct. %N 2.0(1.8).

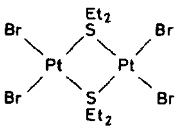

Fig. 2. Structure of $[Pt_2Br_4(SEt_2)_2]$.

effect to a greater extent than the methyl analogues. This again suggests M....S interaction since the phenyl substituted thioethers will be poorer σ-donors and thus the metal ion will be relatively electron poor.

The alternative explanation to M....S interaction involves M....M intermolecular interactions which are well documented for certain planar complexes of these metals, *e.g.* Magnus' Green Salt [33]. It could be postulated that the reduced steric hindrance produced by three-coordinate sulphur compared with four-coordinate phosphorus or arsenic would make the approach of neighbouring metal ions easier. Since the anomalous solid state spectra are observed only in the $[ML_2](ClO_4)_2$ complexes and not with $[MLX_2]$ strongly suggests that this effect, whether M....M or M....S is dependent on electron density factors and lies in a particular range.

Conductivity dilution studies of the complexes were performed in nitromethane solution. Plots of $\Lambda_0 - \Lambda_e/\sqrt{c}$ gave straight lines (correlation coefficients >0.99) over the range 10^{-2} equiv. l^{-1}–2.5×10^{-4} equiv. l^{-1} for most of the complexes. The slope values all lay in the range expected for 2:1 electrolytes [50]. However, a few of the complexes gave curved plots, the more pronounced of these being the complexes of $PhS(CH_2)_3SPh$, *cis*-PhSCH=CHSPh and *o*-$C_6H_4(SMe)_2$. This has been reported previously [8, 51] for the ligand $PhS(CH_2)_3SPh$ and it was suggested that the equilibrium:

$$L_2M^{2+} \rightleftharpoons LM^{2+} + L \qquad (1)$$

occurred allowing association of the perchlorate ion. The occurrence of (1) was supported by increased conductivity on addition of excess ligand, essentially strong electrolyte behaviour for the complex $[Pt(PhSCH_2CH_2SPh)_2](ClO_4)_2$ containing the stable five-membered chelate ring and changes in the electronic spectrum on addition of excess ligand. However, of the three ligands in our series to exhibit the curved plots only the $PhS(CH_2)_3SPh$ complexes gave increased conductivity on addition of excess ligand. The values for Λ_M at $5 \times 10^{-3} M$ and $5 \times 10^{-4} M$ of all the series are given in Table III. Although the values are greater at lower concentration all results are in the recognised range for 2:1 electrolytes [52] except those for the three ligands showing the curved plots and then only at the higher concentration where the values approach those characteristic of 1:1 electrolytes [52]. Our results suggest that ion association may occur without loss of ligand and is concentration dependent.

Attempts to prepare the complexes $[M\{PhS(CH_2)_{12}SPh\}_2](ClO_4)_2$ (M = Pd, Pt) were unsuccessful. Addition of excess halide ion as LiX or NaX to the bis-ligand complexes gave the $[MLX_2]$ species.

Other Complexes

In addition to the planar $[MLX_2]$ and $[ML_2](ClO_4)_2$ attempts were made to prepare other types of complexes. The reaction of $[MLX_2]$ with a large excess of L failed to yield ML_2X_2 in keeping with our previous conclusion from the tetrathioether studies [14–16] that two X^- groups are coordinated in preference to two more thioether donors. The addition of a twenty-fold excess of ligand to solutions of $[MLX_2]$ in 1,2-dichloroethane resulted in negligible increases in conductivity. The highest Λ_M recorded for any of these systems was for $[Pt\{MeS(CH_2)_2SMe\}Cl_2]$ being 0.5 ohm^{-1} cm^2 M^{-1}. The observed ranges in 1,2-dichloroethane are 10–24 ohm^{-1} cm^2 M^{-1} for a 1:1 electrolyte and >28 ohm^{-1} cm^2 M^{-1} for a 2:1 electrolyte [52]. Spectrophotometric studies of $[MLX_2]$ plus added ligand also lead to the same conclusion that the equilibrium:

$$[MLX_2] + L \rightleftharpoons ML_2X_2$$

lies completely to the left. Similarly, the addition of $[NEt_4]X$ to solutions of the bis-ligand diperchlorate complexes resulted in the displacement of one dithioether ligand and $[MLX_2]$ complexes were isolated. There was no evidence for the formation of five-coordinate $[ML_2X](ClO_4)$ complexes which are unknown for dithioethers.

Reaction of the $[MLCl_2]$ species with silver perchlorate (1:1) gave the halide bridged species $[LMCl_2ML](ClO_4)_2$ [53]. Details of thiocyanate complexes are the subject of a further study.

^1H Nmr Spectra

The most detailed previous study of the ^1H nmr spectra of dithioether complexes is that of Cross *et al.* [54] who examined the $[MLX_2]$ complexes (M = Pd, Pt) L = $RS(CH_2)_2SR$ (R = Me, Et, ^{n}Pr, ^{i}Pr and ^{n}Bu). In the present study we have examined the spectra of the methyl substituted dithioethers $MeS\frown SMe$ [$\frown$ = $-(CH_2)_2-$, $-(CH_2)_3-$, *o*-C_6H_4- and *cis*-CH=CH-] to identify any effects due to the chelate backbone. Table IV lists the resonance positions of the CH_3- groups (δ), their shift on coordination (Δ) and for the platinum complexes $^3J_{Pt-H}$. On coordination the CH_3- resonance shifted downfield, the extent of the shift increasing with the *trans* ligand in the order Cl < Br < I; $^3J_{Pt-H}$ was virtually insensitive to the X group or the backbone and lay in the range 45–50 Hz. Interestingly, for the complexes of *cis*-MeSCH=CHSMe, the downfield shift of the vinyl protons was in the order Cl > Br > I (Table V), the reverse of that found for the methyl protons. This can be rationalised in terms of the *trans* influence of

TABLE IV. P.M.R. Data for the Complexes (Methyl Protons)[a].

	Complex	δ (ppm)[b]	Δ (ppm)[c]	$^3J_{Pt-H}$(Hz)	Coalescence Temp. (°C)
MeS(CH$_2$)$_2$SMe	PdLCl$_2$	2.63	0.54	–	+40
2.09 ppm[d]	PdLBr$_2$	2.69	0.60	–	[e]
	PdLI$_2$	2.81	0.72	–	[e]
	[PdL$_2$]$^{2+}$	2.77	0.68	–	[e]
	PtLCl$_2$	2.62	0.53	46.8	+102
	PtLBr$_2$	2.66	0.57	46.8	+92
	PtLI$_2$	2.68	0.59	48.6	+88
	[PtL$_2$]$^{2+}$	2.79	0.70	46.8	[e]
MeS(CH$_2$)$_3$SMe	PdLCl$_2$	2.55	0.50	–	[e]
2.05 ppm[d]	PdLBr$_2$	2.61	0.56	–	[e]
	PdLI$_2$	2.67	0.62	–	[e]
	[PdL$_2$]$^{2+}$	2.55	0.50	–	[e]
	PtLCl$_2$	2.62	0.57	46.8	+30
	PtLBr$_2$	2.70	0.65	48.6	[e]
	PtLI$_2$	2.75	0.70	46.8	[e]
	[PtL$_2$]$^{2+}$	2.70	0.65	45.9	[e]
cis-MeSCH=CHSMe	PdLCl$_2$	2.78	0.50	–	[e]
2.28 ppm[d]	PdLBr$_2$	2.86	0.58	–	[e]
	PdLI$_2$	2.99	0.71	–	[e]
	[PdL$_2$]$^{2+}$	2.86	0.58	–	[e]
	PtLCl$_2$	2.82	0.54	45.0	+35
	PtLBr$_2$	2.89	0.61	45.0	[e]
	PtLI$_2$	2.99	0.71	48.6	[e]
	[PtL$_2$]$^{2+}$	3.17	0.89	44.2	[e]
o-C$_6$H$_4$(SMe)$_2$	PdLCl$_2$	3.00	0.55	–	[e]
2.45 ppm[d]	PdLBr$_2$	3.07	0.62	–	[e]
	PdLI$_2$	3.16	0.71	–	[e]
	[PdL$_2$]$^{2+}$	3.10	0.65	–	[e]
	PtLCl$_2$	3.03	0.58	44.1	+50
	PtLBr$_2$	3.11	0.66	46.8	+39
	PtLI$_2$	3.18	0.73	49.5	[e]
	[PtL$_2$]$^{2+}$				

[a] In (CD$_3$)$_2$SO solution referenced with tms. [b] CH$_3$- signal above coalescence temp referred to tms. [c] Shift of CH$_3$- signal between complex and free ligand. [d] Free ligand in (CD$_3$)$_2$SO. [e] Below m.pt. of (CD$_3$)$_2$SO.

TABLE V. P.M.R. Data for the MeSCH=CHSMe Complexes (Vinyl Protons)[a].

Complex	δ (ppm)[b]	Δ (ppm)[b]	$^3J_{Pt-H}$(Hz)
PdLCl$_2$	6.90	0.80	
PdLBr$_2$	6.84	0.74	
PdLI$_2$	6.75	0.65	
[PdL$_2$]$^{2+}$	7.14	1.04	
PtLCl$_2$	6.98	0.88	77.4
PtLBr$_2$	6.90	0.80	79.2
PtLI$_2$	6.76	0.66	79.2
[PtL$_2$]$^{2+}$	7.37	1.27	67.5

[a] Complexes run in (CD$_3$)$_2$SO with internal tms standard, free ligand 6.10 ppm. [b] See Table IV.

the X group in that as the *trans* influence order increases Cl < Br < I the electron density on the sulphur increases and this is partially delocalised onto the unsaturated backbone, hence the vinyl protons will experience more shielding in the order I > Br > Cl which would give the chloride complex the greatest shift and the iodide the least. The $^3J_{Pt-H}$ coupling to the vinyl protons was much larger than to the methyl protons probably due to the vinyl carbon having more "s character" than the saturated methyl carbon, the values being 77–80 Hz. For the complexes of *cis*-PhSCH=CHSPh the vinyl proton resonances are insensitive to changes in the X group, a reflection of the ability of the phenyl substituent to compensate for electronic effects in the system.

The studies of Cross [54] and Abel [2] have shown that the temperature dependence of the ^{1}H nmr spectra of coordinated thioethers is due to inversion at the sulphur atom and not, in the case of bidentate ligands, to conformational changes in the backbones. At low temperatures the spectra show resonances due to *meso* and *DL* forms of the ligand (Fig. 3) which on warming give way to a complicated second order spectrum, broaden and finally coalesce until only one "form" appears to be present. At this coalescence temperature the inversion process is sufficiently fast compared with the nmr time scale that only the time averaged signal of the isomers is seen (equivalent to a planar intermediate). Thus, observation of the coalescence temperatures indicates the relative rates of inversion at sulphur. The methyl substituted dithioether complexes had very poor solubility in the usual nmr solvents and only $(CD_3)_2$-SO was found to be suitable. Due to the relatively high melting point of the solvent (18.5 °C) we were only able to obtain coalescence temperatures for one of the palladium(II) complexes and seven of the platinum(II) complexes. All the other complexes (Table IV) were already above their coalescence temperatures at the melting point of the solvent. However, sufficient data was available to deduce the following trends: (i) inversion is easier for palladium(II) than platinum(II), (ii) coalescence temperatures fall in the order Cl > Br > I consistent with the *trans* influence [55] of the X group and (iii) the coalescence temperatures decrease with ligand backbone in the order $\text{-(CH}_2)_2\text{-} > o\text{-C}_6\text{H}_4 > cis\text{-CH=CH-} > \text{-(CH}_2)_3\text{-}$. Observations (i) and (ii) are in keeping with previous observations [2, 54, 56]. The dependence on ligand backbone, however, has not been observed previously. The spectra were too complex and of insufficient quality due to solubility problems for a more detailed analysis (*cf.* ref. 2) but the coalescence temperatures, accurate to ±5 °C, demonstrated the trends unequivocally. Inversion is believed to be a function of the strength of the M–S bond [57]. This explains the ease of inversion being palladium > platinum since the bond strengths are in the order Pt–S > Pd–S and also the series reflecting the *trans* influence of halide. It is notable that for the $[ML_2](ClO_4)_2$ complexes where the *trans* ligands are thioethers which have a high *trans* influence [55], all are above the inversion temperature in the measurable range.

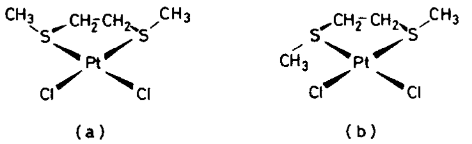

Fig. 3. (a) Meso and (b) DL isomers of $[Pt(MeSCH_2CH_2SMe)Cl_2]$.

The effect of ligand backbone demonstrates the greater stability of five over six membered chelate rings [11] – inversion was easiest with $MeS(CH_2)_3$-SMe complexes. For the three C_2 backboned ligands inversion was easier with the unsaturated systems suggesting that delocalisation of the sulphur lone pair onto the backbone may occur in the transition state.

Acknowledgment

We are grateful to Johnson Matthey Ltd. for the loan of platinum salts and to Dr. P. J. Parsons for helpful discussions.

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