Diphosphane Derivatives. Part 3.[1] The Donor Characteristics of Tetramethyl-1,2-dithioxodi-λ^5-phosphane (Tetramethyldiphosphine Disulphide) and the Vibrational Spectra and Structures of Some of its Complexes

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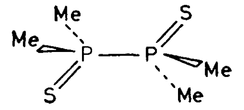
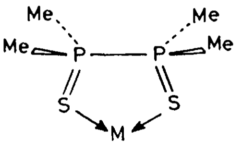
The i.r. spectra of tetrahedral [M(P$_2$Me$_4$S$_2$)$_2$]$^{2+}$, pseudo-tetrahedral MX$_2$·P$_2$Me$_4$S$_2$, and *cis*-octahedral MX$_4$·P$_2$Me$_4$S complexes of tetramethyl-1,2-dithioxodi-λ^5-phosphane (tetramethyldiphosphine disulphide), P$_2$Me$_4$S$_2$ (X = halide), are all consistent, in the region of the ligand skeletal stretching frequencies, with D_{2d} or C_{2v} symmetry for the complex species and with a planar *cis*-chelate configuration for the co-ordinated P$_2$Me$_4$S$_2$ ligand. Comparisons with the spectra of (CuCl·P$_2$Me$_4$S$_2$)$_2$, which contains *gauche*-chelate P$_2$Me$_4$S$_2$, and with (CuCl$_2$·P$_2$Me$_4$S$_2$)$_n$, in which the ligands retain the internal *trans* conformation, indicate that the *trans* ligand may be identified by the absence or relative weakness of the P–P and symmetric P–S stretching absorptions, but the vibrational data alone cannot distinguish reliably between the *cis*- and *gauche*-chelate structures. The ligand-field parameters 10*Dq* and β measured for P$_2$Me$_4$S$_2$ in the [Co(P$_2$Me$_4$S$_2$)$_2$]$^{2+}$ ion both appear to be significantly higher than the corresponding values for unidentate PMe$_3$S in [Co(PMe$_3$S)$_4$]$^{2+}$.

In the solid state, tetramethyl-1,2-dithioxodi-λ^5-phosphane (tetramethyldiphosphine disulphide), P$_2$Me$_4$S$_2$, has the centrosymmetric *trans* structure (1).[2-5] This structure is preserved in solution, at least to the limit detectable by vibrational spectroscopy.[5,6] As a ligand, P$_2$Me$_4$S$_2$ forms numerous complexes with transition-metal and main-group acceptors:[7-14] the i.r. spectra indicate a significantly lower ligand symmetry than that in free P$_2$Me$_4$S$_2$ and it is usually assumed that the co-ordinated molecule adopts a *cis*-chelate conformation (2).



(1)



(2)

Cotton *et al.*[10,11] have determined the crystal structures of the copper complexes (CuCl$_2$·P$_2$Me$_4$S$_2$)$_n$ and (CuCl·P$_2$Me$_4$S$_2$)$_2$. In the unstable polymeric copper(II) complex (CuCl$_2$·P$_2$Me$_4$S$_2$)$_n$ the ligands retain the *trans* structure to form –CuSPPSCu– chains,[11] whereas in the binuclear copper(I) complex (CuCl·P$_2$Me$_4$S$_2$)$_2$ the ligands are chelate but have the *gauche* rather than the *cis* conformation.[10] The ligands in the latter complex are asymmetrically bound, with one sulphur atom terminally attached to a copper atom while the other is in a bridging position between two copper atoms. The Cu–S(terminal) and Cu–S(bridging) bond lengths are significantly different.[10] The *gauche* conformation of the P$_2$Me$_4$S$_2$ ligand may thus be dictated by its environment in the complex and need not necessarily be reproduced in other P$_2$Me$_4$S$_2$ complexes. Copper is by no means a typical acceptor atom and it seems more likely that in mononuclear complexes with the sulphur atoms in equivalent co-ordination sites the ligand will adopt the *cis* conformation, forming a planar chelate ring, rather than the puckered *gauche* conformation.

We have prepared a representative series of P$_2$Me$_4$S$_2$ complexes in order to assess the extent to which the vibrational spectrum may be used as a guide to the structure of the co-ordinated ligand. Ainscough *et al.*[12] have reported the spectra of a few copper–P$_2$Me$_4$S$_2$ complexes but the only discussion of an extended series of P$_2$Me$_4$S$_2$ complexes to have appeared in the literature is restricted to i.r. data only, over a limited frequency range, and is based on an incorrect assignment of the P–S and P–C stretching vibrations in the unco-ordinated ligand.[9]

RESULTS AND DISCUSSION

Details of the i.r. and Raman spectra of P$_2$Me$_4$S$_2$ and the representative complex ZnCl$_2$·P$_2$Me$_4$S$_2$ are given in Table 1 and the i.r.-active skeletal stretching vibrations for a variety of P$_2$Me$_4$S$_2$ complexes are listed in Table 2. The assignments follow in a straightforward way from those for the unco-ordinated ligand and the metal–ligand stretching vibrations in most cases give rise to prominent i.r. bands near 300 cm^{-1}. Weaker bands in this region (*e.g.* at 280 cm^{-1} for ZnCl$_2$·P$_2$Me$_4$S$_2$) are assigned to internal vibrations of the ligand.

MX$_2$·P$_2$Me$_4$S$_2$ *and* MX$_4$·P$_2$Me$_4$S$_2$ *Complexes*.—The *cis*-chelate P$_2$Me$_4$S$_2$ ligand will have local C_{2v} symmetry, and tetrahedral or square-planar MX$_2$·P$_2$Me$_4$S$_2$, or *cis*-octahedral MX$_4$·P$_2$Me$_4$S$_2$ complexes (X = halide) containing *cis*-P$_2$Me$_4$S$_2$, will also belong to the C_{2v} point group. In the solid complexes the spectra may be modified by the effects of site- or factor-group symmetry, or both, but initially it is legitimate to treat the vibrations of the co-ordinated ligand in terms of the C_{2v} selection rules.

In point group C_{2v} the 18 normal vibrations of the C$_2$(S)PP(S)C$_2$ skeleton consist of $6A_1 + 4A_2 + 5B_1 + 3B_2$. All of these vibrations are Raman-active but only the A_1, B_1, and B_2 vibrations are i.r.-active. The seven skeletal stretching vibrations[5,6] fall between 760 and 400 cm^{-1} (*i.e.* below the methyl rocking frequencies): six of them [ν(PC), A_1, B_1, B_2; ν(PS), A_1, B_1; ν(PP), A_1] are i.r.-active but the seventh [ν(PC), A_2] is not. For comparison, in strict C_{2h} (*trans*) symmetry only three stretching vibrations [ν(PC), A_u, B_u; ν(PS), B_u] are i.r.-

active, whereas in C_2 (*gauche*) or lower symmetry all seven stretching vibrations are i.r.-active.

The tin complex $SnCl_4 \cdot P_2Me_4S_2$ and all of the $MX_2 \cdot P_2Me_4S_2$ complexes listed in Table 2 exhibit the pattern of six i.r.-active skeletal stretching vibrations predicted for a *cis*-chelate $P_2Me_4S_2$ ligand in a C_{2v} complex. The P–C stretching absorptions consist of a sharp well defined band near 760 cm^{-1} and a stronger composite band between 720 and 730 cm^{-1}. In most cases the latter band is partially resolved into two distinct absorption maxima, separated by *ca.* 5 cm^{-1}, and in the others it displays an identifiable shoulder on the side of the principal absorption. Although all the skeletal vibrations are formally Raman-active, in practice only about half of them have sufficient intensity to be detectable in the experimental spectra. (Raman spectra were obtained in only a few cases since most of the complexes degraded rapidly in the laser beam.) Between 700 and 800 cm^{-1} we observe (*e.g.* in $ZnCl_2 \cdot P_2Me_4S_2$) two Raman lines which are coincident, within the experimental limits (*ca.* ± 3 cm^{-1}), with the i.r. absorptions at 760 and 730 cm^{-1}. The i.r.-inactive P–C stretch (A_2) cannot thus be identified from the available Raman data.

The two P–S stretching vibrations give rise to one strong and one very weak Raman line, which we assign to the symmetric (A_1) and antisymmetric (B_1) modes, respectively. Both vibrations appear at lower frequencies than in the unco-ordinated ligand, the shift in the antisymmetric mode (15—25 cm^{-1}) being consistently greater than that in the symmetric mode (10—15 cm^{-1}). The symmetric (A_1) frequency is probably affected by interaction with the P–P stretch (A_1) but the B_1 vibration is not subject to any comparable effect. The P–P stretching frequencies in the complexes are only slightly altered from that in the free ligand.

For $P_2Me_4S_2$ in C_{2v} symmetry we expect six i.r.-active methyl-rocking vibrations between 1 000 and 800 cm^{-1}. The spectrum is complicated by a number of possible overtones or combinations [6] and most of the complexes display seven i.r. bands in this region (Table 1).

No assignments are proposed for the low-frequency Raman-active vibrations in the co-ordinated ligand, but it is noteworthy that the very strong line which is observed at $\Delta\nu = 170$ cm^{-1} in unco-ordinated $P_2Me_4S_2$ has no obvious counterpart in the spectra of the complexes. We have assigned this line in the free ligand to a symmetric PPS bending mode: on co-ordination it will be drastically modified, to become, in effect, a vibration of the chelate ring. Its non-appearance in the spectrum of the co-ordinated ligand thus tends to support the original assignment.

TABLE 1

Infrared (250—1 000 cm^{-1}) and Raman (100—1 000 cm^{-1}) spectra of $P_2Me_4S_2$ and $ZnCl_2 \cdot P_2Me_4S_2$

	$P_2Me_4S_2$ [a]		$ZnCl_2 \cdot P_2Me_4S_2$	
	I.r. [b]	Raman [c]	I.r. [b]	Raman [b]
CH_3 rock		950w	961ms	961vvw
	941vs		950ms	
		923w	933ms	931w
	889vs		905s,br	
	884vs (sh)			
		864w	869m	872vw
	861m		860mw	861mw
		848w	841mw	
	824w [d]			
P–C str.	747s		760m	761mw
		739mw		
	733vs		729s (sh)	729m
		727mw	724s	
P–S sym str.		602s	590s	587s
P–S asym str.	571vs		554s	551vvw
P–P str.		431s	433ms	430m
(ZnCl; ZnS) str.	*(300 vvw)* [e]		315s (sh)	
			305vs	
			290s (sh)	297s [f]
PC_2 twist, B_g [g]		287s		
	277m		280m	
PC_2 wag, A_g [g]	*(265 vvw)* [e]	274mw		273m
	254w		256mw	251s
	240m		245w	
PC_2 def., A_g [g]		228m		219s
	224w			209s
PC_2 rock, B_g [g]		201m		188 (sh)
PPS bend, A_g [g]		170vvs		150mw
				139m

[a] Refs. 5 and 6. [b] Nujol mulls, ± 2 cm^{-1}. [c] Powdered solids, ± 2 cm^{-1}. [d] Possible non-fundamental vibration (ref. 6). [e] Very weak bands not assigned as fundamentals. [f] This line may be associated with an internal ligand vibration. [g] Tentative assignments for Raman-active vibrations in unco-ordinated ligand. Assignments do not apply to co-ordinated $P_2Me_4S_2$.

TABLE 2

Infrared-active $P_2Me_4S_2$ skeletal stretching and metal–ligand vibrations (cm^{-1})[a] in $P_2Me_4S_2$ complexes (L = $P_2Me_4S_2$)

	L[b]	$CoCl_2L$[c]	$CoBr_2L$	CoI_2L	$[CoL_2][ClO_4]_2$[d]
P–C str.	747s *739* 733vs *727*	758m 725s 720s	758m 727s 721s	754m 725s 718s	760m 728s 721s
P–S sym str.	*602*	585s	586s	582s	588s
P–S asym str.	571s	545s	547ms	541s	548s
P–P str.	*431*	430m	432m	429m	433m
M–S, M–Cl str.		333s 317s 308s	309ms 297ms	306s 299s	335vs 321vs 310vs
M–Br str.			254s		

	$[CoL_2][NO_3]_2$[e]	$[NiLn][ClO_4]_2$[d,g]	$FeCl_2L$	$FeBr_2L$	$ZnCl_2L$[c]
P–C str.	760m 729s 722s	758m 731s 721 (sh)	757m 726s 721s	757m 727s 721 (sh)	760m 729s (sh) 724s
P–S sym str.	590s	591s	588s	588s	590s
P–S asym str.	548s	551m	547s	548s	554s
P–P str.	435m	437m	431m	434m	433ms
M–S, M–Cl str.	336vs 321vs 312vs	300m,br	340s 314s 300s	299 (sh) 292	315 (sh) 305s 290 (sh)
M–Br str.				269vs	

	$ZnBr_2L$[c]	$CdCl_2L$	$CdBr_2L$[c]	CdI_2L	$[CdL_2][NO_3]_2$[c,e]
P–C str.	758m 727s 720s	757m 727s 719 (sh)	754m 727s 720 (sh)	752m 725s 719 (sh)	760m 732s 725 (sh)?
P–S sym str.	589s	594s	588s	587s	590s
P–S asym str.	552s	554s	552s	550s	554s
P–P str.	431m	432m	422m	423m	430m
M–S, M–Cl str.	305s 297s	300m,br	300s 291vs	298 (sh) 288vs	300 (sh) 295s,br

	$[CdL_2][ClO_4]_2$[d]	$HgCl_2L$[e]	$HgBr_2L$[c]	$SnCl_4L$	$(CuClL)_2$[c,f]	$(CuCl_2L)_n$
P–C str.	757m 728s 720 (sh)?	759m 725s 722 (sh)	757m 726s 721 (sh)	761m 735s 722s	761ms 730s,br	
P–S sym str	594s	585s	585s	582s	593s	578w
P–S asym str.	554s	549s	549s	545s	554s	580ms
P–P str.	428m	425ms	420ms	439m	430m	
M–S, M–Cl str.	292ms,br	328m 300s 260vs, br	295s 288s	330 (sh) 310vs,br 281m 273m?		

[a] Nujol mulls. [b] From refs. 5 and 6. Raman frequencies are italicised. [c] Yields a Raman spectrum in the 400—1 000 cm^{-1} region similar to that of $ZnCl_2L$ (Table 1). [d] I.r. spectrum indicates ionic perchlorate. [e] I.r. spectrum indicates ionic nitrate. [f] See also ref. 12. [g] Stoicheiometry not established (complex is explosive).

$[M(P_2Me_4S_2)_2]Y_2$ *Complexes* ($Y = [ClO_4]^-$ *or* $[NO_3]$).—The undistorted tetrahedral complexes $[M(P_2Me_4S_2)_2]^{2+}$ belong to the point group D_{2d} and should give rise to two i.r.-active M–S stretching vibrations ($B_2 + E$). The perchlorate and nitrate salts of the $[Co(P_2Me_4S_2)_2]^{2+}$ ion display three strong i.r. bands between 335 and 310 cm^{-1}. Reduction of the symmetry from D_{2d} to C_{2v} would cause all four Co–S stretching modes to become i.r.-active ($2A_1 + B_1 + B_2$), but the totally symmetric A_1 mode (which is derived from the corresponding i.r.-inactive modes in D_{2d} or T_d symmetry) is likely to be very weak in the i.r. spectrum. The appearance of three strong i.r. bands in the Co–S stretching region is thus consistent with a site symmetry no higher than C_{2v} for the $[Co(P_2Me_4S_2)_2]^{2+}$ ion. The Cd–S stretching absorptions in the $[Cd(P_2Me_4S_2)_2]^{2+}$ ion are much less structured and are more closely consistent with the D_{2d} selection rules.

The spectra of the cobalt and cadmium complexes between 1 000 and 400 cm^{-1} are indistinguishable from those of the metal halide complexes and the discussion of the internal ligand vibrations in the preceding section applies equally well to the $[M(P_2Me_4S_2)_2]^{2+}$ ions.

$(CuCl{\cdot}P_2Me_4S_2)_2$.—The $P_2Me_4S_2$ ligands in this complex have the internal *gauche*-chelate conformation.[10] The $(CuCl{\cdot}P_2Me_4S_2)_2$ dimer is centrosymmetric and, with $Z = 2$, must occupy a C_i site in the $P2_1/n(P2_1/c)$ unit cell. The vibrational species are thus divided between the A_g and A_u irreducible representations of the site group. However, the two rather widely separated $P_2Me_4S_2$ ligands are likely, at best, to be very weakly coupled and we would expect the observed spectrum to be dictated by the C_2 symmetry of the ' isolated ' P_2MeS_2 molecule. Apart from the P–P and P–S stretching bands, the i.r. spectrum should therefore contain four P–C stretching and eight methyl-rocking absorptions. In fact, we observe only two P–C stretching bands (761, 730br cm^{-1}; Ainscough *et al.*[12] mention a shoulder at 722 cm^{-1}) and only six bands, some of which are rather broad compared with the other complexes, in the methyl-rocking region (800—1 000 cm^{-1}). The unexpectedly simple spectrum presumably is the result of accidental degeneracies or near-degeneracies in the i.r.-active modes, but it is clear that vibrational data alone will not distinguish reliably between the *cis* and *gauche* ligand conformations. Thus, although the spectra of most of the complexes listed in Table 2 are entirely consistent with the proposed *cis*-$P_2Me_4S_2$ conformation, this structure is still presumptive and requires confirmation by *X*-ray analysis.

Complexes with trans-$P_2Me_4S_2$ *Ligands*.—The unstable polymeric complex $(CuCl_2{\cdot}P_2Me_4S_2)_n$, with *trans*-$P_2Me_4S_2$ ligands, is obtained as a minor product of the reaction of copper(II) chloride with $P_2Me_4S_2$.[11] The i.r. spectrum of the freshly precipitated material is essentially that of $(CuCl{\cdot}P_2Me_4S_2)_2$ with the addition of a weak band at 578 cm^{-1} and a rather stronger band at 530 cm^{-1}. These bands disappear over 4—5 h with accompanying minor changes in the profiles of the P–C stretching and higher-frequency absorptions. Ultimately, the spectrum is identical with that of the copper(I) complex. We therefore assign the bands at 578 and 530 cm^{-1} to the symmetric and antisymmetric P–S stretching vibrations, respectively, in the *trans*-$(CuCl_2{\cdot}P_2Me_4S_2)_n$ complex. The profile of the P–P stretching absorption does not noticeably change during the decomposition process: at the most, the P–P stretch can only be very weak in the i.r. spectrum of the *trans* complex. [From their i.r. and analytical data, Beg and his co-workers [8,9] appear to have successfully isolated this *trans* complex but do not mention its reduction to the copper(I) complex. Our observations are similar to those of Meek and Nicpon,[7] Cotton *et al.*,[10,11] and Ainscough *et al.*[12] Crystals of *trans*-$(CuCl_2{\cdot}P_2Me_4S_2)_n$ for *X*-ray analysis were obtained by Cotton *et al.*[11] only by using a rather elaborate preparative technique.]

TABLE 3

Visible spectra of cobalt–$P_2Me_4S_2$ complexes

	Bands (cm^{-1}) in ν_3 $[^4T_1(P) \leftarrow {}^4A_2]$ envelope	Bands (cm^{-1}) in ν_2 $[^4T_1(F) \leftarrow {}^4A_2]$ envelope	Centre of gravity of envelope (cm^{-1})		10 *Dq* [a]/cm^{-1}	*B* [b]/cm^{-1}	β [c]	Λ [d] / S cm^2 mol^{-1}
			ν_3	ν_2				
$[Co(P_2Me_4S_2)_2][ClO_4]_2$ [d]	17 300 16 240 15 680	8 900 6 740	16 050	7 200	4 260	699	0.72	145.0
$[Co(P_2Me_4S_2)_2][NO_3]_2$ [d]	17 260 16 290 15 760	9 000 (sh)	16 020	7 300	4 200	696	0.72	137.0
$CoCl_2{\cdot}P_2Me_4S_2$ [e]	16 000 14 800 12 800	7 000	15 050	7 000	3 920	646	0.67	1.9
$CoBr_2{\cdot}P_2Me_4S_2$ [e]	15 800 14 200 12 500	6 800	14 400	6 600	3 750	626	0.65	9.0
$CoI_2{\cdot}P_2Me_4S_2$ [e]	14 950 13 400 12 200	7 000 6 000 (sh)	13 300	6 300	3 510	577	0.60	9.5

[a] Estimated uncertainty ±130 cm^{-1} for $[CoL_2]^{2+}$, ±180 cm^{-1} for CoX_2L. [b] Estimated uncertainty ±15 cm^{-1} for $[CoL_2]^{2+}$, ±25 cm^{-1} for CoX_2L. [c] Assuming $\beta = 967$ cm^{-1} for gaseous Co^{2+}. [d] In nitromethane solution. [e] In Nujol.

The simple *trans*-$P_2Me_4S_2$ spectrum is retained in the iodine addition compounds $P_2Me_4S_2{\cdot}I_2$ and $P_2Me_4S_2{\cdot}2I_2$, with a downward shift of *ca.* 20 cm^{-1} in the antisymmetric P–S stretching frequency.[13] Structures containing both chelate and bridging $P_2Me_4S_2$ have been proposed for the complexes $[(MOCl_3)_2(P_2Me_4S_2)_3]$ (M = Mo or W) which display three distinct P–S stretching absorptions between 520 and 590 cm^{-1}.[14]

The experimental data indicate that *trans*-$P_2Me_4S_2$ ligands can be identified with reasonable confidence by the absence or relative weakness in the i.r. spectrum of the P–P and symmetric P–S stretching absorptions. For the chelate ligand the P–S stretches appear near 590 and 550 cm^{-1} and vary only slightly from one complex to another. The assignments for the individual P–S stretching absorptions in the ' mixed ' molybdenum and tungsten complexes are not altogether obvious, but taken together with the frequency data for $(CuCl_2{\cdot}P_2Me_4S_2)_n$ suggest that P–S stretching vibrations may appear at frequencies down to 520 cm^{-1} in the *trans*-coordinated ligand.

The reaction of an excess of $CdCl_2$ with $P_2Me_4S_2$ is reported to yield the 2 : 1 complex $2CdCl_2{\cdot}P_2Me_4S_2$, presumably containing a bridging *trans*-$P_2Me_4S_2$ ligand.[9] We have been unable to repeat this preparation and our results suggest that the unstable chelate complex $CdCl_2{\cdot}P_2Me_4S_2$ is the only product of the $CdCl_2$–$P_2Me_4S_2$ system (see Experimental section).

Visible Spectra of Cobalt(II) *Complexes*.—Details of the visible spectra of the cobalt–$P_2Me_4S_2$ complexes are given in Table 3. The complexes $[Co(P_2Me_4S_2)_2][NO_3]_2$ and $[Co(P_2Me_4S_2)_2][ClO_4]_2$ are typical 1 : 2 electrolytes in dry nitromethane and have very similar spectra in the solid (Nujol mull) and in nitromethane solution. The ligand-field parameters 10*Dq* and β are both unusually high for $[CoS_4]^{2+}$ species;[15-20] even allowing for the uncertainties involved in the determination of these parameters, it is clear that the values for $P_2Me_4S_2$ are significantly higher than those for unidentate PMe_3S in the corresponding $[Co(PMe_3S)_4]^{2+}$ complexes ($10Dq$ = 3 890 cm^{-1}, $\beta = 0.65$).[17] With only two electron-releasing methyl groups attached to each phosphorus atom, the net negative charge associated with the sulphur atoms will tend to be less in $P_2Me_4S_2$ than in PMe_3S. The sulphur atoms will thus be less polarisable in $P_2Me_4S_2$ than in PMe_3S and a lower nephelauxetic parameter β is reasonable for the latter ligand. The reduced charge on the donor atoms in $P_2Me_4S_2$ will also tend to favour metal-to-ligand rather than ligand-to-metal π interactions and at a rather superficial level is consistent with a greater value of $10Dq$ for $P_2Me_4S_2$ than for PMe_3S. There is no reason at this stage to suppose that the SPPS backbone has any significant π character which could noticeably modify the donor–acceptor characteristics of the $P_2Me_4S_2$ ligand.

The halogeno-complexes $CoX_2{\cdot}P_2Me_4S_2$(X = Cl, Br, or I) are essentially non-conducting in dry nitromethane but the conductivities of such solutions increase rapidly on exposure to the atmosphere and the band profiles in the solution spectra are difficult to reproduce. The data in Table 4 therefore refer to the solid complexes. In view of the problems associated with the identification of the ν_2 band centres in the rather indistinct mull spectra, undue significance should not be attached to the precise numerical values obtained. Furthermore, the ν_3 bands are very highly structured and introduce additional uncertainties into calculations based on an assumption of cubic symmetry. Nevertheless the trends in $10Dq$ and β are in the expected sequence from chloride to iodide and the numerical values of $10Dq$ are correlated reasonably well with the high value found for the $[Co(P_2Me_4S_2)_2]^{2+}$ ion.

TABLE 4

Analytical data (%) for new complexes

	Found				Calc.			
Complex	C	H	S	X	C	H	S	X
$CoCl_2{\cdot}P_2Me_4S_2$	15.3	4.0	20.1	22.1	15.2	3.8	20.2	22.0
$CoBr_2{\cdot}P_2Me_4S_2$	12.4	3.2	16.1	39.1	12.0	3.0	15.8	39.5
$CoI_2{\cdot}P_2Me_4S_2$	9.9	2.8	12.4	49.9	9.7	2.5	12.8	50.9
$[Co(P_2Me_4S_2)_2][ClO_4]_2$	15.6	4.0	19.6		15.2	3.8	20.3	
$[Co(P_2Me_4S_2)_2][NO_3]_2$	17.4	4.4	23.1		17.3	4.3	23.3	
$FeCl_2{\cdot}P_2Me_4S_2$*				23.1				22.7
$FeBr_2{\cdot}P_2Me_4S_2$	11.9	3.1		39.8	11.9	3.0		39.8
$ZnBr_2{\cdot}P_2Me_4S_2$	11.6	2.8	15.3	38.4	11.7	2.9	15.6	38.9
$CdBr_2{\cdot}P_2Me_4S_2$*			13.0	33.5			14.0	34.9
$CdI_2{\cdot}P_2Me_4S_2$	9.5	2.1		45.2	8.9	2.2		46.0

* Unstable.

EXPERIMENTAL

Preparation of Complexes.—Metal halide complexes. These were obtained from the reaction of the metal halides with equimolar quantities of the ligand in acetone solution.[9,10] The tin complex was prepared by direct addition of $SnCl_4$ to the ligand solution.

Perchlorates and nitrates. The hydrated metal perchlorates or nitrates were dissolved in acetone and dehydrated by boiling with ethyl orthoformate. A solution containing 2 equivalents of the ligand in acetone was added and the reaction mixture boiled to reduce the volume. The complexes precipitated on cooling and (if necessary) addition of light petroleum. Analytical data for new complexes are given in Table 4.

Stability. **CAUTION:** Most of the complexes decompose slowly (*i.e.* over weeks or months) to the metal sulphide and tetramethyldiphosphane (which tends to inflame when old sample bottles are opened). The cobalt complexes do not decompose in this way but are readily hydrated by atmospheric water. The cadmium and nickel perchlorate complexes are shock-sensitive and violently explosive. The 1 : 2 metal : ligand stoicheiometry proposed for the cadmium complex is based on the metal : ligand ratio used in the preparative reaction, the presence of 'ionic perchlorate' absorptions in the i.r. spectrum, and the close similarity of the spectrum to that of $[Co(P_2Me_4S_2)_2][ClO_4]_2$. The nickel perchlorate complex is an unusual yellow-orange colour, but apart from the i.r. spectrum we have been unable to make any physical measurements to establish the nature of the nickel co-ordination.

Cadmium chloride complexes. The reaction of $CdCl_2$ in methanol with $P_2Me_4S_2$ in chloroform, in a 2 : 1 mol ratio, is reported to yield the 2 : 1 complex $2CdCl_2{\cdot}P_2Me_4S_2$.[9] We have made many attempts to repeat this reaction but our products appear to consist of unchanged $CdCl_2$ and $P_2Me_4S_2$ or to contain the chelate complex $CdCl_2{\cdot}P_2Me_4S_2$. The i.r. spectrum of dried $CdCl_2$ contains bands at 550s,br and 724m,br cm^{-1} which are close to frequencies assigned in ref. 9 to the co-ordinated $P_2Me_4S_2$ ligand. When the preparative reaction was carried out in ethanol or acetone the initial product displayed three strong P–S stretching bands at 594, 571, and 554 cm^{-1}. The band at 571 cm^{-1} could arise from unco-ordinated $P_2Me_4S_2$ and repeated recrystallisation caused it to diminish and eventually almost to disappear. The bands at 594 and 554 cm^{-1} remained unaffected and the final spectrum is to all intents and purposes identical with those of the other chelate complexes. The recrystallisation process induces a measure of decomposition (smell of H_2S, appearance of slight yellow CdS colour) but the results strongly suggest that the initial reaction product is a mixture of the chelate complex $CdCl_2{\cdot}P_2Me_4S_2$ and unco-ordinated or very loosely bound $P_2Me_4S_2$.

Palladium and platinum complexes. No square-planar $MX_2{\cdot}P_2Me_4S_2$ complexes (M = Pd or Pt) are included in Table 1. Reactions of $P_2Me_4S_2$ with palladium(II) or platinum(II) halides yielded products having i.r. spectra generally similar to those quoted in the Table but partial decomposition also occurred and the analytical data were unsatisfactory.

Spectra.—Infrared spectra were obtained using a Perkin-Elmer 457 spectrophotometer and Raman spectra using a Cary 83 Raman spectrophotometer with argon-ion laser excitation (488.0 nm). Visible spectra were recorded with a Unicam SP 700 spectrophotometer.

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REFERENCES

[1] Part 2, G. P. McQuillan and I. A. Oxton, *Spectrochim. Acta*, 1978, **A34**, 33.

[2] C. Pedone and A. Sirigu, *J. Chem. Phys.*, 1967, **47**, 339.

[3] J. D. Lee and J. W. Goodacre, *Acta Cryst.*, 1971, **B27**, 302.

[4] A. H. Cowley and H. Steinfink, *Inorg. Chem.*, 1965, **4**, 1827.

[5] A. H. Cowley and W. D. White, *Spectrochim. Acta*, 1966, **22**, 1431.

[6] G. P. McQuillan and I. A. Oxton, *Spectrochim. Acta.*, 1977, **A33**, 233.

[7] D. W. Meek and P. Nicpon, *J. Amer. Chem. Soc.*, 1965, **87**, 4951.

[8] M. A. A. Beg and K. S. Hussain, *Chem. and Ind.*, 1966, 1181.

[9] M. A. A. Beg and S. H. Khawaja, *Spectrochim. Acta*, 1968, **A24**, 1031.

[10] F. A. Cotton, B. Frenz, D. L. Hunter, and Z. C. Mester, *Inorg. Chim. Acta*, 1974, **11**, 119.

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

[12] E. W. Ainscough, H. A. Bergen, A. M. Brodie, and K. A. Brown, *J.C.S. Dalton*, 1976, 1649.

[13] E. W. Ainscough and A. M. Brodie, *J.C.S. Dalton*, 1977, 565.

[14] W. Levason, F. P. McCullough, and C. A. McAuliffe, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 843.

[15] H. R. Weakliem, *J. Chem. Phys.*, 1962, **36**, 2177.

[16] F. A. Cotton, O. D. Faut, and J. T. Mague, *Inorg. Chem.*, 1964, **3**, 17.

[17] A. M. Brodie, S. H. Hunter, G. A. Rodley, and C. J. Wilkins, *J. Chem. Soc.* (*A*), 1968, 2039.

[18] A. M. Brodie, S. H. Hunter, G. A. Rodley, and C. J. Wilkins, *J. Chem. Soc.* (*A*), 1968, 987.

[19] A. Davidson and E. S. Switkes, *Inorg. Chem.*, 1971, **10**, 837.

[20] W. E. Slinkard and D. W. Meek, *J.C.S. Dalton*, 1973, 1024.