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STEREOCHEMICAL ASPECTS OF PHOSPHOR-1,1-DITHIOLATO METAL COMPLEXES (DITHIOPHOSPHATES, DITHIOPHOSPHINATES): COORDINATION PATTERNS, MOLECULAR STRUCTURES AND SUPRAMOLECULAR ASSOCIATIONS—I

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CONTENTS

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ABBREVIATIONS

Me	methyl
Et	ethyl
Pr	propyl
Bu	butyl
Cy	cyclohexyl
Ph	phenyl
Bz	benzyl
Ar	aryl
Mes	mesityl, 2,4,6-$Me_3C_6H_2$-
phen	1,10-phenathroline
bipy	2,2′-bipyridyl
Ln	lanthanide
THF	tetrahydrofuran
Py	pyridine
Ac	acetyl
DMSO	dimethylsulphoxide, Me_2SO
DMF	dimethylformamide, $HC(O)NMe_2$
DMA	dimethylacetamide, $MeC(O)NMe_2$
quin	quinoline

DABCO	diazabicyclooctane, $N(CH_2CH_2)_3N$
TMED	tetramethylethylenediamine, $Me_2NCH_2CH_2NMe_2$
DPED	diphenylethylenediamine, $PhHNCH_2CH_2NHPh$
en	ethylenediamine, $H_2NCH_2CH_2NH_2$
ApesS	$Ph_2AsCH_2CH_2P(=S)Ph_2$
terpy	terpyridyl
datau	1,11-diamino-3,6,9-triazaundecane, $HN(CH_2CH_2NHCH_2CH_2NH_2)_2$
urotr	urotropine, hexamethylenetetramine, $(CH_2)_6N_4$
ment	menthyl
biph	biphenylyl
binaph	binaphthyl

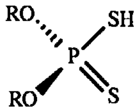
A. INTRODUCTION

Organodithio-derivatives of phosphorus have important industrial and agricultural applications, e.g. additives to lubricant oils, solvent extraction reagents for metals, flotation agents for mineral ores, insecticides and pesticides, to name only the major ones. The understanding of the chemistry of their metal derivatives is important in relation with these uses. Pure academic interest is also great, since the broad diversity of compositions and structures of metal compounds of dithiophosphorus ligands illustrates the richness of metal–sulphur bonding interaction modalities and also may serve as models for biological metal–sulphur interactions.

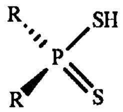
An up-to-date review of the subject is highly desirable, since the last comprehensive surveys covering phosphorodithioates[1] and phosphinodithioates[2] were published many years ago, and more recent ones cover only particular aspects of the field : main group derivatives,[3] tin derivatives.[4,5] The diversity of coordination patterns was reviewed[6] in 1981 ; since then many new structures have been determined and even new coordination modes have been discovered.

The continuous interest towards dithiophosphorus ligand metal compounds produced a large volume of literature and a comprehensive coverage, including synthesis, spectroscopic characterization and uses, would require a whole book. Therefore, we will limit ourselves to a discussion of only structural aspects, as an expansion of the earlier review.[6] Much of the preparative chemistry and spectroscopic information is covered in the references cited here and the reader will have thus a door open to the aspects not discussed in this review. The emphasis will be on the dithiophosphorus ligands, rather than the metal coordination centres, but these will not be completely ignored.

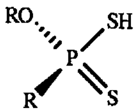
The ligands to be dealt with in this review are mostly mononegative anions of monoprotic acids of the following general types, known under the names shown :



phosphorodithioic acid*
dithiophosphoric acid
(*O*,*O*′diesters)

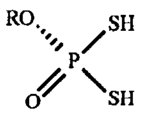


phosphinodithioic acid*
dithiophosphinic acid

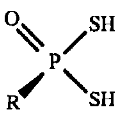


phosphonodithioic acid
dithiophosphonic acid
(*O*-esters)

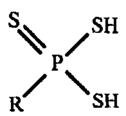
Di- and trithiophosphorus ligands derived from diprotic acids as dinegative anions are also possible but few examples of metal complexes or organometallic derivatives are known.



phosphorodithioic acid*
dithiophosphoric acid
(*O*-diesters)



phosphonodithioic acid*
dithiophosphonic acid



phosphonotrithioic acid
trithiophosphonic acid

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* *Chemical Abstracts* nomenclature.

Still less important, so far, are the related ligands derived from fluorophosphonodithioic acids (fluorodithiophosphonic acids) R(F)P(S)SH, dihalogenodithiophosphoric acids $X_2P(S)SH$ (X = F, Cl, Br), or amidophosphonodithioic acids R(R′R″N)P(S)SH, and other similar compounds.

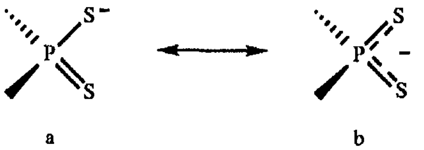
This review covers the literature available up to September 1994. The first part will deal with phosphorodithioates (dithiophosphates), and phosphinodithioates, phosphonodithioates and other related complexes (much less investigated) will be treated in Part II. This will also contain the concluding remarks for the whole review. The chapters and subchapters, tables, formulae and literature references will be numbered consecutively, the second part continuing the numbering from Part I.

Our aim was to provide a comprehensive review of the molecular and crystal structure of phosphor-1,1-dithiolato and related complexes, to stress the broad structural diversity and to reveal gaps where new research is possible or needed. We hope that the readers will find new ideas for the synthesis and/or structural investigations of this type of compound. Although it cannot be said that phosphor-1,1-dithiolato ligands were neglected, their versatility has not been fully exploited and can offer a field of fruitful future investigations.

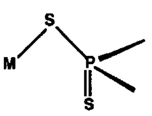
All compounds are numbered in the text and can be found under the same numbers in Tables. Not all structures are graphically illustrated, and this explains the apparent discontinuity in illustrations, but the numbers corresponding to missing structure diagrams can be located in the Tables. The Tables contain much unpublished or difficultly available material from Chinese journals, not listed even in the Cambridge Crystallographic Centre Data Base, and is made available here for the first time. These data were collected from the original publications or were calculated for this review by the Chinese colleagues.

B. COORDINATION PATTERNS

The deprotonation of the acids listed above produces anions which can be described by two resonance structures:



Either one of them can predominate in certain cases. Thus, soft metals tend to interact with hybrid **a** to form primary, covalent metal–sulphur bonds. In these cases the second phosphorus–sulphur bond does not participate in any interaction with the metal (monodentate coordination, pattern **1**) and retains double bond character, or may participate in a dative bond (pattern **2**) or secondary interaction (pattern **3**) with the metal (anisobidentate coordination). This second metal–sulphur connection may affect to a certain extent the double bond character of the P═S bond. In the anisobidentate coordination pattern **2** the dative S—M bond length is of the same order of magnitude, but somewhat larger than the covalent M—S bond. The distinction between the two-electron covalent bond and two-electron dative bond is useful and its rationale has been recently discussed.[7]



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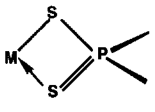

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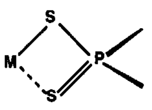

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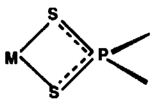
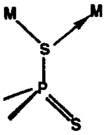


4

In the anisobidentate coordination pattern **3** there is an M ... S "secondary interaction", reflected in an interatomic distance intermediate between the sum of covalent radii of M and S, and the sum of van der Waals radii of the same metal atoms.[8] It can also be described as "semibonding interaction". These interactions can cover a broad range of M ... S interatomic distances in this range and sometimes are difficult to recognize, because the van der Waals radii are not very exactly defined.[9]

Hard metals seem to prefer the hybrid **b** and display metal–ligand interactions with a more pronounced ionic character, leading to isobidentate coordination (pattern **4**), in which the metal–sulphur bonds are roughly equal in strength (reflected in equal or nearly equal bond lengths). In this case the phosphorus–sulphur bonds are also equalized (or nearly so), corresponding to a delocalization of the negative charge over the S—P—S fragment. However, it should be mentioned that even in alkali metal or other salts the discrete anionic dithiophosphorus ligand is not always totally symmetric, as shown by significantly different P—S bond lengths, measured by X-ray diffraction in the solid state. This may be due to crystal packing effects, especially when the two sulphur atoms do not occupy equivalent positions due to the cation.

In all cases cited the ligand is attached to only one metal atom and these coordination patterns are called *monometallic monoconnective* or *biconnective*, according to the number of metal–ligand interactions. Quite often this does not exhaust the donor ability of the ligand, and a second metal atom can become involved. Thus, dithiophosphorus ligands may bridge two metal atoms in various ways. The simplest, but rare (see Section F.15) is bridging through one sulphur connecting two metal atoms. In this type of coordination one sulphur atom forms a primary bond to a metal atom, a dative (pattern **5**) or a secondary (pattern **6**) bond to another metal atom and leaves the second sulphur independent (non-involved), doubly-bonded to phosphorus.



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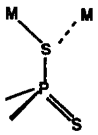
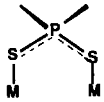


6

Much more frequent is *biconnective bridging* through both sulphur atoms. Again, several variations can be distinguished. Thus, the bridging ligand may be symmetric, with equal (or nearly equal) P—S and M—S bonds (pattern **7**) or asymmetric, with one of the phosphorus–sulphur bonds retaining a high degree of double bond character and further coordinating through either dative (pattern **8**) or secondary bonding (pattern **9**). This coordination of the ligand can be described as *bimetallic biconnective*.



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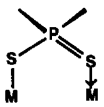

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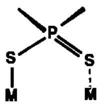

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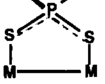
When the ligand is attached to a metal–metal bond coordination centre, five-membered rings **10, 11** and **12** result.



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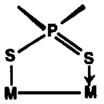

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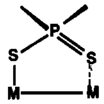
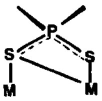


12

This distinction is not always so clear-cut and sometimes structures intermediate between those depicted may occur, making a rigid classification rather difficult.

Bimetallic triconnective bridging (patterns **13** and **14**) and bimetallic tetraconnective bridging (patterns **15** and **16**) are also possible. While the coordination patterns **13** and **14** are well illustrated by several known structures (to be discussed below) we have yet to find examples for patterns **15** and **16**.



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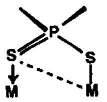

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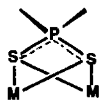

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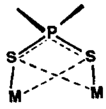
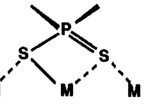


16

Trimetallic triconnective coordination of dithiophosphorus ligands are rare, but some examples are known. In pattern **17** a four-membered chelate ring is involved in further secondary interactions with two neighbouring metal atoms. Pattern **18** seems to be confined to coordination of the ligand to a triangular face of a polymetallic cluster. Both types are seldom observed. Thus, the coordination pattern **17** was found in organothallium compounds (see Sections E.13 and F.12), while pattern **18** was observed in a tetrahedral Cu^{I}_{4} cluster derivatives (see Section E.11.a).



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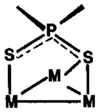
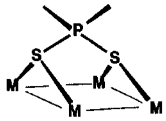


18

A *tetrametallic tetraconnective* coordination pattern **19** was only imaginary a dozen years ago[6] but in the meantime it has been discovered in a cubic Cu_8 cluster derivative (see Section E.11.a).

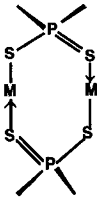


19

C. SUPRAMOLECULAR ASSOCIATIONS

The metal complexes containing dithiophosphorus ligands coordinated as monometallic monoconnective (unidentate, **1**) or biconnective (bidentate, **2–4**) are molecular compounds, i.e. consist of discrete molecules both in solution and in solid state. Other coordination patterns, in which the ligand connects two or more metal atoms, lead to *supramolecular associations*. According to Lehn, supramolecular chemistry is defined as "*the chemistry of molecular assemblies and of the intermolecular bond*" and deals with "*organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces*".[10–12] Such associations are mostly observed in Main Group metal complex compounds, when the coordination centre is an organometallic moiety of low functionality and the metal requires a high coordination number. In such cases the ligand participates in *primary bonds* which satisfy the "normal" valence state of the metal, and is also involved in additional *secondary interactions* leading to dimeric, trimeric, tetrameric, hexameric or polymeric supramolecular associations.[13,14] Numerous dithiophosphorus ligand metal complexes which seem to be discrete molecular compounds in solution, are associated in the solid state in a mode which falls under the definition cited above.

The simplest example is offered by the dimerization of four-membered ring chelates formed with either monodentate or iso- and anisobidentate ligands (coordination patterns **1–4**). Dimerizaton may occur through either dative bonds or weak secondary ("semibonding") interactions. Thus, dimerization of monodentate ligand complexes (coordination pattern **1**) leads to eight-membered cyclic dimers **20** (with dative bond bridging of type **8**) and **21** (with secondary bond bridging of type **9**).



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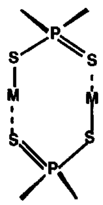
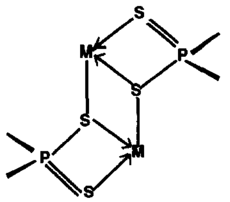


21

The structural motif **20** is illustrated by a dinuclear copper compound (see Section E.11.a) and structure **21** by organomercury compounds (see Sections E.12.c and F.11.c), and an organoantimony phosphinodithioate (See Section F.14.b). By forming such dimers the dithiophosphorus ligand changes the coordination pattern to **8** and **9**, respectively.

The four-membered chelate rings formed by aniso or isobidentate coordination (patterns **2–4**) dimerize to form (quasi)tricyclic systems **22, 23,** and **24**, based on eight-membered rings with strong (dative) or weak (secondary or "semibonding") *transannular interactions*. This process makes the ligand trimetallic triconnective, as shown in **13** and **14**. Usually, the eight-membered ring displays a chair conformation.



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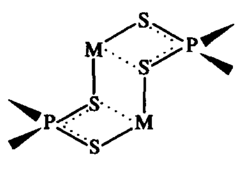

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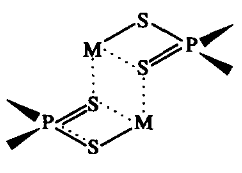
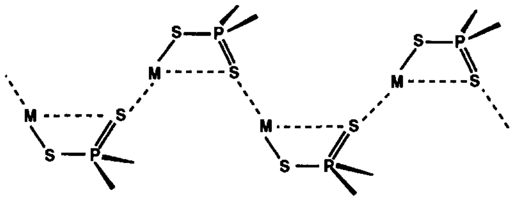


24

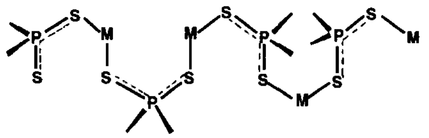
The two-step ladder structures of type **22**–**24** are rather common and are illustrated by dithiophosphorus ligand complexes of manganese and rhenium (see Sections F.7), platinum (see Section F.10.c), silver (see Section E.11.b), zinc, cadmium (see Section E.12.a,b and F.11.a,b), tin^{II} (see Section E.14.c), lead (see Section E.14.b), arsenic (see Section F.14.a) and antimony (see Section F.14.b). Still more complex supramolecular structures are formed when these dimers interact further and associate in polymeric ribbons, through secondary M . . . S bonds, as in $Pb(S_2PMe_2)_2$ (see Section F.13.d).

Four-membered chelate rings, e.g. **3**, can form polymeric chains by association through secondary bonds, as in **25**. Examples are offered by $[Ph_2SbS_2P(OPr^i)_2]_n$ (see Section E.15.b) and $[Me_2SbS_2PMe_2]_n$ (see Section F.14.b). In the polymer the ligand becomes bimetallic triconnective (pattern **14**). Other types of supramolecular associations involving trimetallic triconnective bridges are known, e.g. for lead (see Sections E.14.d and F.13.d).



25

The symmetric and asymmetric bridges **7**–**9** give rise to polymeric structures **26** and **27**. These polymers are illustrated by zinc bis(diethylphosphorodithioate) (see Section E.12.a) and mercury bis(diisopropylphosphorodithioate) (see Section E.12.c).



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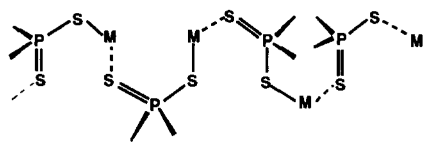


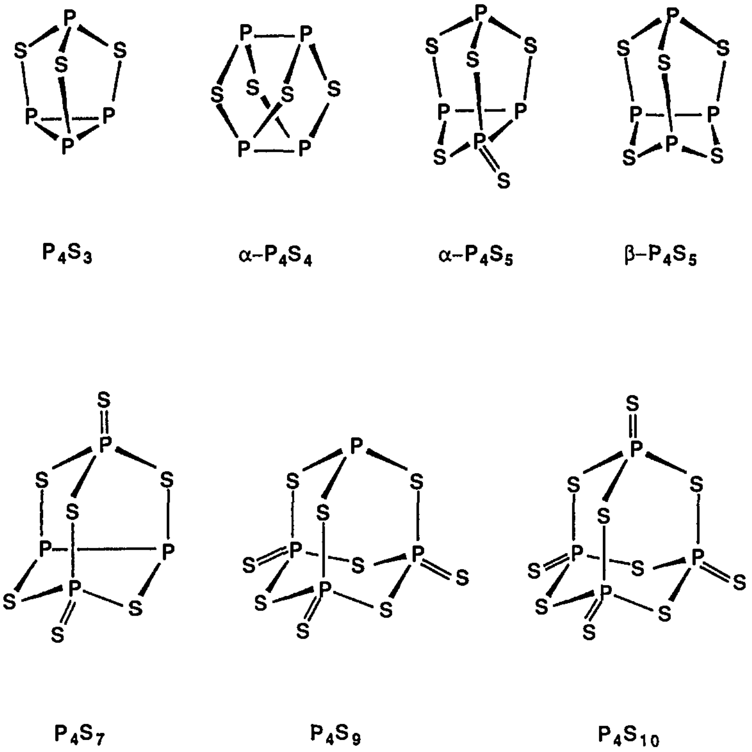
27

Bridging patterns **5** and **6** can also be expected to form supramolecular dimers, higher oligomers or polymers (see Section F.15.b).

It is quite obvious that the diversity of supramolecular associations involving bimetallic biconnective or triconnective, trimetallic triconnective or other types of bridging dithiophosphorus ligands, is much broader and it is not possible to list here all imaginable types. Some other examples will be found in the forthcoming discussion and we can also expect the discovery of new structural motifs.

D. SINGLE AND DOUBLE PHOSPHORUS–SULPHUR BONDS

To identify coordination patterns it is necessary to distinguish between phosphorus–sulphur single and double bonds, as reflected in interatomic distances. Reliable theoretical calculations are scarce. Electron correlated *ab initio* calculations (6–31G* level) predict for $H_3P{=}S$ a double bond length of 1.944 Å, for $H{-}P{=}S$ a bond length of 1.951 Å and for $H_2P{-}SH$ a single bond length of 2.128 Å.[15,16] Experimental values available for comparisons are numerous. The best candidates seem to be phosphorus sulphides, where the phosphorus–sulphur bond lengths are not influenced by other substituents. Crystal structure data for the known phosphorus sulphides[17–29] (Scheme 1) are collected in Table 1. It can be seen that single P—S bonds are in the range of 2.08–2.14 Å and double P═S bonds in the range of 1.89–1.98 Å (average values are not larger than 1.95 Å).



P_4S_3 α-P_4S_4 α-P_4S_5 β-P_4S_5

P_4S_7 P_4S_9 P_4S_{10}

Scheme 1. Molecular structures of binary phosphorus sulphides.

Another useful collection of phosphorus–sulphur bond lengths, for comparison with the values observed in dithiophosphorus ligand complexes, are those measured in dithiophosphoryl- and dithiophosphinyl disulphides (and trisulphides) (Table 2), which contain both single and double bonds. These compounds are closely related to the dithiophosphorus ligands and, in fact, are produced in the oxidation of $X_2PS_2^-$ (X = OR, R) anions (with formation of S—S bonds). The values found in these compounds range from 2.072 to 2.158 Å for single P—S bonds and 1.900 to 1.944 Å for double P═S bonds.[30–40] It is also noteworthy to remember the values of the S—P—S bond angles in these compounds, which range from 103 to 116°.

In compounds containing only P═S double bonds, as in dithiophosphines, $R_2(S{=})P{-}P({=}S)R_2$ (Table 3), the corresponding interatomic distances range between 1.94 and 1.98 Å.[41–47] Among other related compounds investigated (Table 4) it is worth noting the very short P═S double bonds in $(PhS)_3P{=}S$ (1.899 Å)[48] and 1,3,5-$Bu^t_3C_6H_2P({=}S)_2$ (1.90 Å),[49] but more "normal" values in $P\{P({=}S)Me_2\}_3$ (1.96 Å).[50] The single P—S bond length does not seem to be much affected by coordination of a metal to phosphorus[51] (see Table 4).

For comparisons with dimensions of four-membered chelate rings, crystal structure data for cyclic phosphorus–sulphur compounds are collected in Table 5. Exocyclic double bonds are short: 1.92–1.94 Å, compared with the single P—S bonds in the ring (2.11–2.14 Å).[52–56] When the double P═S bond is associated with an exocyclic anionic P—S⁻ bond, in a PS_2^- group, it becomes longer (1.984–1.991 Å) as in the cyclic anions $P_2S_6^{2-}$ present in some salts.[57,58] In the PS_4^{3-} anion, where the negative charge and the π-bond are distributed over four P—S bonds, P—S interatomic distances are in the range 2.02–2.06 Å.[59,60]

All these data seem to indicate that we can safely assume that phosphorus–sulphur bonds of *ca* 2.0 Å and longer can be described as single, and bonds shorter than 1.95 Å as double. Intermediate values, often observed in dithiophosphorus ligand complexes (see below) can be taken to represent delocalized units, as in patterns **4** or **7**.

Table 1. Crystal structure data for binary phosphorus sulphides[a]

Compound	Space group	a b c	α β γ	P—S	P=S	Ref.
P_4S_3	Pmnb	9.660		2.089–2.097		17–19
		10.597				
		13.671				
β-P_4S_4	C2/c	9.771	—	2.106–2.112		20–22
		9.047	102.67			
		8.746	—			
				av. 2.108		
α-P_4S_5	$P2_1$	6.41	—	2.08–2.14	1.94	23
		10.94	111.7			
		6.69	—			
				av. 2.11		
β-P_4S_5	$P2_1/m$	6.389	—	2.105–2.129		24
		10.966	115.65			
		6.613	—			
				av. 2.114		
α-P_4S_7 monoclinic	$P2_1/n$	8.87	—	2.04–2.13	1.93–1.97	25, 26
		17.35	92.7			
		6.83	—			
				av. 2.08	av. 1.95	
β-P_4S_7 othorhombic	Pbcn	8.14	—	2.05–2.13	1.89	27
		11.43	—			
		11.39	—			
				av. 2.09		
P_4S_9	Ia3	17.60	90	2.10–2.14	1.93	28
		17.60	90			
		17.60	90			
				av. 2.12		
P_4S_{10}	$P\bar{1}$	9.07	92.4	2.04–2.13	1.91–1.98	26
		9.18	101.2			
		9.19	110.5			
				av. 2.08	av. 1.95	

[a] The structure diagrams are given in Scheme 1. See also Ref. 29.

It would be of interest to know more about the molecular dimensions in the parent phosphorodithioic and phosphinodithioic acids. Unfortunately, only the crystal structure of diphenyl phosphinodithioic acid, $Ph_2P(=S)SH$, determined both at 140 K and room temperature,[61] has been fully described. The bond lengths are: P—S 2.076 Å (2.077 Å), P=S 1.954 Å (1.950 Å) (at 140 K and room temperature, respectively), and the S—P—S bond angle (108.2°) is practically tetrahedral. Other phosphinodithioic acids, $R_2P(=S)SH$, and phosphorodithioic acids, $(RO)_2P(=S)SH$, have also been investigated, but only the space group and unit cell dimensions are available.[62,63]

E. PHOSPHORODITHIOATES (DITHIOPHOSPHATES)

1. *Group 1: Alkali metals. Other ionic phosphorodithioates*

Two potassium salts, $K^+[S_2P(OR)_2]^-$ ($R = Me$[64] and CH_2Ph[65]) have been investigated by X-ray diffraction. In the anions the P—S interatomic distances are intermediate between single and double bond lengths, suggesting delocalization of the negative charge over the S—P—S fragment. However,

Table 2. Crystal structure data for bis(thiophosphoryl) and bis(thiophospinyl) di(and tri-)sulphides

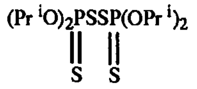
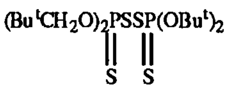
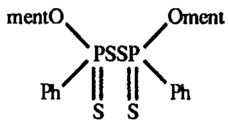
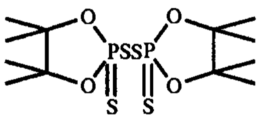
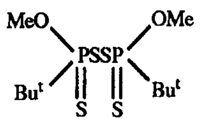
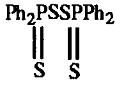
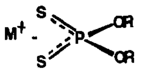
Compound	Space group	*a* *b* *c*	α β γ	P—S	P═S	S—P═S	Ref.
 $(MeO)_2\underset{\substack{\Vert\\ S}}{P}S\underset{\substack{\Vert\\ S}}{S}P(OMe)_2$	C2/c	21.949	—	2.086	1.903	105.4	30
		10.381	100.26	2.091	1.898	106.7	
		12.384	—				
 $(EtO)_2\underset{\substack{\Vert\\ S}}{P}S\underset{\substack{\Vert\\ S}}{S}P(OEt)_2$	P$\bar{1}$	8.388	62.34	2.098	1.906	106.4	31
		11.128	71.93	2.100	1.912	105.4	
		12.518	84.97				
 $(Pr^iO)_2\underset{\substack{\Vert\\ S}}{P}S\underset{\substack{\Vert\\ S}}{S}P(OPr^i)_2$	P$\bar{1}$	8.412	110.70	2.072	1.908	104.8	32
		8.471	94.86				
		8.259	97.91	2.007	1.89		33
 $(Bu^tCH_2O)_2\underset{\substack{\Vert\\ S}}{P}S\underset{\substack{\Vert\\ S}}{S}P(OBu^t)_2$	P$\bar{1}$	9.137	72.26	2.080	1.911	106.7	30
		9.143	73.21				
		9.887	82.58				
 $(PhO)_2\underset{\substack{\Vert\\ S}}{P}S\underset{\substack{\Vert\\ S}}{S}P(OPh)_2$	$P2_12_12_1$	6.618		2.075	1.900	108.4	34
		11.584		2.076	1.898	108.0	
		34.533					
	$P2_12_12_1$	6.629		2.079	1.900	107.7	35
		11.584		2.080	1.901	108.3	
		34.536					
	$P2_12_12_1$	17.083		2.101	1.926	not given	36
		10.952					
		9.586					
	C2	14.913	—	2.082	1.908	103.3	37
		6.847	120.18				
		11.427	—				
	P$\bar{1}$	7.916	110.11	2.093	1.923	101.2	35
		10.501	98.77	2.139	1.913	115.3	
		12.461	99.96				
 $Me_2\underset{\substack{\Vert\\ S}}{P}S\underset{\substack{\Vert\\ S}}{S}PMe_2$	$Pna2_1$	22.046		2.099	1.938	103.7	38
		6.226		2.094	1.941	103.7	
		8.480					

Table 2—*continued.*

Compound	Space group	a b c	α β γ	P—S	P=S	S—P=S	Ref.
 $Et_2\underset{\underset{S}{\|}}{P}SS\underset{\underset{S}{\|}}{P}Et_2$	$P2_1/c$	11.998	—	2.116	1.944	103.8	39
		12.678	115.96	2.112	1.937	103.6	
		12.181	—				
 $Pr^i_2\underset{\underset{S}{\|}}{P}SS\underset{\underset{S}{\|}}{P}Pr^i_2$	$P\bar{1}$	7.661	68.33	2.156	1.931	115.9	38
		11.378	72.61	2.158	1.935	115.1	
		12.403	85.53				
 $Bu^tPh\underset{\underset{S}{\|}}{P}SS\underset{\underset{S}{\|}}{P}PhBu^t$	$C2/c$	20.035	—	2.153	1.938	114.1	35
		9.231	102.30				
		12.978	—				
 $Ph_2\underset{\underset{S}{\|}}{P}SS\underset{\underset{S}{\|}}{P}Ph_2$	$C2/c$	22.268	—	2.139	1.930	114.4	34
		9.039	100.27				
		12.361	—				
 $Cy_2\underset{\underset{S}{\|}}{P}SS\underset{\underset{S}{\|}}{P}Cy_2$ monoclinic	$C2/c$	16.887	—	2.158	1.935	114.8	40
		14.860	100.22				
		12.574	—				
 $Cy_2\underset{\underset{S}{\|}}{P}SS\underset{\underset{S}{\|}}{P}Cy_2$ triclinic	$P\bar{1}$	20.392	68.66	2.111	1.943	105.5	40
		12.302	103.25	2.155	1.932		
		12.749	107.26				
				2.109	1.946	105.0	
				2.151	1.938		

the P—S bond distances seem significantly different [e.g. 1.945(2) and 1.969(2) Å in the benzyl derivative]. The S—P—S bond angle (*ca* 120°) is larger than the tetrahedral value.



28

A tetraphenylarsonium salt,[66] $[AsPh_4]^+[S_2P(OMe)_2]^-$, and a dimethylammonium salt,[67] $[NMe_2H_2]^+[S_2P(OPr^i)_2]^-$, have also been studied. The anions display similar features to those in potassium salts, namely slight differences in the P—S bond lengths and an enlarged S—P—S bond angle. Crystal structure data are collected in Table 6.

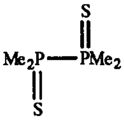
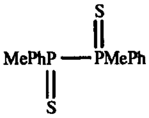
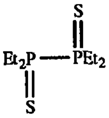
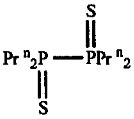
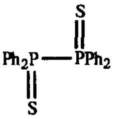
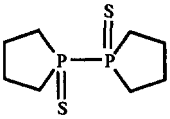
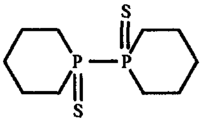
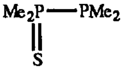
Transition metal phosphorodithioates containing the anion **28**, are listed below and are discussed under the appropriate metal and the literature references are cited there.

$[Mo_3S_4\{S_2P(OEt)_2\}(L)_3]^+[S_2P(OEt)_2]^-$ (L = imidazole)

$[Mn(phen)_3]^{2+}[S_2P(OEt)_2^-]_2$

$[Ni(bipy)\{S_2P(OBu)_2\}]^+[S_2P(OBu)_2]^-$

Table 3. Crystal structure data for tetraorganodithiodiphosphines

	Space group	*a* *b* *c*		P=S	Bond angle P—P=S	Ref.
	C2/m	18.882	—	A		41
		10.703	94.42	1.951	111.2	
		6.984	—	B		
				1.965	112.1	
				1.970	111.9	
	Pbca	17.104	—	1.98	111.8	42
		10.629	—			
		8.592	—			
	P$\bar{1}$	8.98	113.0	1.94	112.8	43a
		6.45	85.2			
		6.15	102.5			
	P2$_1$/n	6.491	—	1.953	112.2	43b
		10.152	100.74			
		13.358	—			
	P2$_1$/c	9.628	—	1.952	112.3	44
		15.798	96.29	1.950	112.0	
		14.304	—			
	P$\bar{1}$	7.65	75.30	1.95	111.1	45
		6.90	104.15			
		5.88	92.36			
	P2$_1$/n	9.44	120.1	1.95	112.7	46
		6.85	99.0			
		6.02	82.4			
	P2$_1$/n	6.314	—	A	115.8	47
		16.252	97.64	1.970		
		8.120	—	B		
				1.979		

$$[\mathrm{Ni(NH_2Bu)_4\{S_2P(OCy)_2\}}]^+[\mathrm{S_2P(OCy)_2}]^-$$

$$[\mathrm{Ni(phen)_3}]^{2+}[\mathrm{S_2P(OMe)_2^-}]_2$$

$$[\mathrm{Ln\{S_2P(OR)_2\}_2(L)_3}]^+[\mathrm{S_2P(OR)_2}]^-$$

with Ln = Sm, R = Et, L = $\mathrm{OPPh_3}$; Ln = Tb and Er, R = Pr^i, L = $\mathrm{PhCONH_2}$.

2. *Group* 2: *Alkaline earths*

No X-ray structure determination has been reported for any alkaline earth metal phosphorodithioate.

Table 4. Crystal structure data for other phosphorus–sulphur compounds

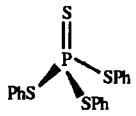
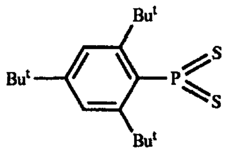
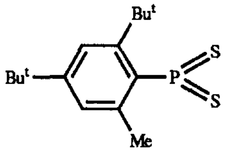
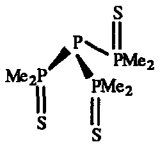
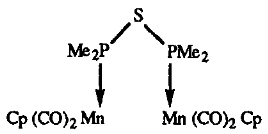
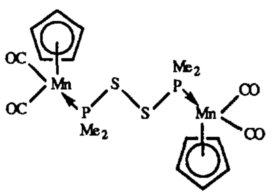
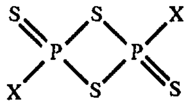
Compound	Space group	*a* *b* *c*	α β γ	P—S	P=S	Bond angle SPS	Ref.
	$P2_1/n$	10.141	—	2.099	1.899	S—P=S	48
		10.195	97.25	2.103		117.7	
		18.870	—	2.103		117.0	
				av. 2.102		116.7	
						S—P—S	
						100.2	
						100.9	
						101.5	
	$P2_1/n$	10.217	—		1.890	S=P=S	49a
		10.324	98.4		1.891	126.0	
		19.102	—				
	$Pna2_1$	15.277	—		1.894	S=P=S	
		11.364	—		1.900	126.3	49b
		9.659	—				
	$P2_1/n$	7.028	—	—	1.956		50
		17.089	101.99		1.964		
		12.850	—				
	Iba2	16.65	—	2.13	—	—	51
		15.64	—	2.12			
		17.49	—				
	C2/c	25.73	—	2.11		—	51
		8.89	116.49	2.16			
		21.23	—				

Table 5. Crystal structure data for other cyclic phosphorus–sulphur compounds



X (trans)	Space group	*a* *b* *c*	α β γ	P—S	P=S	SPS bond angle	Ref.
Me	I2/m	6.793	—	2.141	1.945	S—P—S	52, 53
		7.046	92.25			94.5	
		9.207	—				
						S—P=S	
						116.6	
$\mathrm{Bu^t}$	Cmca	9.872	—	2.121	1.921	S—P—S	54a
		9.594	—			94.0	
		15.488	—				
						S—P=S	
						116.3	
SMe	$\mathrm{P2_1/a}$	8.034	—	endo	1.919	endo	54b, 54c
		8.181	109.98	2.118		S—P—S	
		8.577	—	2.115		93.0	
				exo		exo	
				2.044		S—P—S	
						108.4	
						S—P=S	
						118.5	
SEt	$\mathrm{P2_1/n}$	6.45	—	endo	1.909	endo	54d
		9.96	98.16	2.100		S—P—S	
		10.23	—	2.105		93.1	
				exo		exo	
				2.047		S—P—S	
						110.1	
						S—P=S	
						118.3	
SPh	$\mathrm{P2_1/n}$	6.410	—	endo	1.920	endo	55a
		11.701	101.92	2.112		S—P—S	
		11.409	—	2.107		93.7	
				exo		exo	
				2.080		S—P—S	
						108.2	
						S—P=S	
						116.3	
STol-p	$\mathrm{P\bar{1}}$	6.276	89.81	endo	1.916	endo	55b
		7.262	91.26	2.113		S—P—S	
		10.200	93.52	2.105		93.7	
				exo		exo	
				2.074		S—P=S	
						108.5	
						116.0	

Table 5—*continued.*

X (trans)	Space group	a b c	α β γ	P—S	P═S	SPS bond angle	Ref.
S^-	B2/m	11.210	—	endo		endo	57
(Ag salt)		6.731	—	2.120		S—P—S	
		6.998	126.84			93.7	
				exo		exo	
				2.003		110.8	
				1.984		110.5	
						118.0	
S^-	B2/m	21.410		endo			58
(Zn salt)		6.552		2.124			
		10.680	122.28	2.117			
				2.125			
				2.110			
				exo			
				1.991			
				2.001			
NMe_2	Cmca	7.378	—	2.122	1.926	endo	56
		11.021	—			S—P—S	
		14.407	—			93.1	
cis-Mes	Pbcn	17.878	—	endo	1.916	endo	49b
		15.134	—	2.118		S—P—S	
		13.337	—	2.139		90.1	
						exo	
						S—P═S	
						115.7	
						118.0	

Table 6. Alkali metal, arsonium and ammonium salts

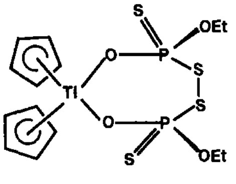
Structure no.	M	R	Space group	a b c	α β γ	P—S	S—P—S	Ref.
28	K	Me	Fddd	17.21	—	1.96	118.2	64
				17.50	—	1.96		
				11.45	—			
28	K	CH_2Ph	$P\bar{1}$	11.468	99.48	1.945	120.1	65
				11.735	98.50	1.969		
				6.542	69.09			
28	$AsPh_4$	Me	$P\bar{1}$	9.637	66.34	1.944	120.1	66
				11.875	68.62	1.954		
				13.119	78.85			
28	NH_2Me_2	Pr^i	$P2_1/c$	14.213	—	1.965	116.6	67
				14.552	101.14	1.974		
				7.129	—			

3. *Group* 3 : Sc, Y

No scandium or yttrium phosphorodithioate has been structurally characterized. Lanthanide and actinide (*f*-element) phosphorodithioates are discussed in Section E.17.

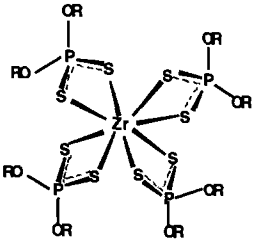
4. *Group* 4 : Ti, Zr, Hf

a. Titanium. Crystal structures of a simple titanium or organotitanium phosphorodithioates have not been reported. Attempts to prepare a bis(cyclopentadienyltitanium) phosphorodithioate by reacting $(\eta^5\text{-}C_5H_5)_2TiCl_2$ with P_4S_{10} in ethanol produced a derivative **29**, containing P—O—Ti and P—S—S—P moieties,[68] obviously formed by hydrolysis and oxidation of the phosphorodithioato ligand presumably formed in the first step of the reaction.



29

b. Zirconium. Zirconium(IV) forms eight-coordinate phosphorodithioates, in which the metal displays distorted dodecahedral geometry, **30**. The ligand is isobidentate, with two practically identical P—S bonds, but the nonequivalent Zr—S bonds can be described as normal covalent (2.653 Å) and dative (2.746 Å) (coordination pattern no. **2**).[69]



30

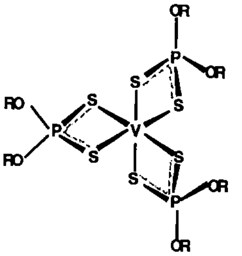
The crystal data and molecular dimensions are listed in Table 7.

Table 7. Crystal structure data for Group 4 and 5 metal phosphorodithioates

Structure no.	R	Space group	a b c	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
30	$\mathrm{Pr^i}$	Fddd	36.850	—	1.976	1.980	2.653	2.746	107.0	91.2	88.3	chel	69
			14.889	—									
			16.593	—									
31	Et	C2/c	8.644	—	1.971	1.989	2.473	2.446	108.1	85.1	85.8	chel	70
			18.487	93.0	1.986	1.986	2.434	2.434	107.7	85.0	85.0		
			17.688	—									
32	$\mathrm{Pr^i}$	Fddd	37.024	—	1.974	1.982	2.626	2.665	105.8	89.7	88.5	chel	69
			14.702	—									
			16.322	—									
33	$\mathrm{Pr^i}$	$P\bar{1}$	7.122	77.38	1.986	2.017	2.651	2.532	105.9	87.4	90.1	chel	71
			11.365	89.08									
			12.532	72.87									
34	$\mathrm{Pr^i}$	$P\bar{1}$	7.251	102.66	1.985	2.000	2.605	2.576	104.6	86.5	87.0	chel	71
			12.386	103.56									
			13.988	94.66									
35	Et	$P2_1/c$	14.564	—	1.935	2.036		2.601	119.5		116.2	uni	72
			17.409	103.62									
			7.506	—									

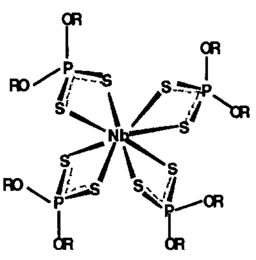
5. *Group* 5: V, Nb, Ta

a. Vanadium. Tris(diethylphosphorodithioato)vanadium(III), $V\{S_2P(OEt)_2\}_3$, contains isobidentate chelating ligands in trigonally distorted octahedral geometry **31**.[70] The S—P—S bond angle is tetrahedral. Molecular dimensions are given in Table 7,



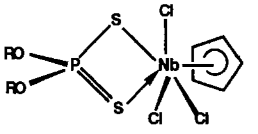
31

b. Niobium. A niobium(IV) diisopropylphosphorodithioate, $Nb\{S_2P(OPr^i)_2\}_4$, has a distorted dodecahedral structure, **32**, like the zirconium(IV) complex **30**, and the four ligands are coordinated as chelating isobidentate (with P—S 1.974 and 1.982 Å).[69]



32

The coordination pattern of the diisopropylphosphorodithioato ligand becomes more asymmetric in two cyclopentadienyl derivatives, **33** and **34** ($R = Pr^i$), where both the Nb—S and P—S interatomic distances differ significantly[71] (see Table 7). This suggests a coordination pattern of type **2**, although the "double P═S bonds" are longer (1.98 Å) than normal values.



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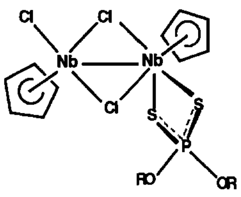
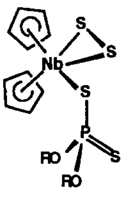


34

In bis(cyclopentadienyl)niobium disulphide diisopropylphosphorodithioate the ligand is monodentate, **35**, and the P—S bond lengths differ accordingly (P—S 2.036 Å and P═S 1.935 Å). The S—P—S angle in the monodentate ligand displays a much larger value (119.5°) than in the chelated vanadium complex,[72] (see Table 7).



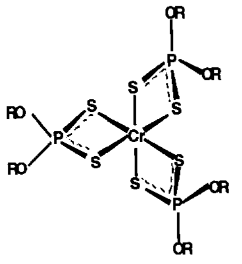
35

The Nb—S bonds also differ, the longer being that to the phosphorodithioato ligand (2.602 Å), compared to the bonds to disulphido group (2.457 and 2.529 Å).

6. *Group* 6: Cr, Mo, W

This triad is well represented and is dominated by molybdenum compounds, which display a great variety of composition and structures.

a. Chromium. All chromium complexes investigated are tris(phosphorodithioato) compounds, $Cr\{S_2P(OR)_2\}_3$, R = Et[73,74] and $(OR)_2$ = OCHMeCHMeO[75,76] with octahedral coordination geometries and isobidentate ligands, **36** (see Table 8).

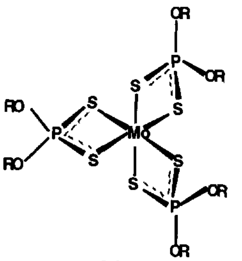


36

The octrahedral geometry is distorted because the S—Cr—S bond angles in the four-membered CrS_2P chelate rings (85°) are smaller than the 90° required by a regular octahedron. A trigonal twist angle (between two parallel triangular faces) of 47° (instead of 60° in the regular octahedron) is also observed.

b. Molybdenum. A large number of mono-, di-, tri- and tetranuclear molybdenum complexes with phosphorodithioato ligands have been investigated structurally. Monodentate, bidentate chelating and bridging coordination patterns were found in molybdenum chemistry. The crystal and molecular dimensions for molybdenum phosphorodithioates are collected in Tables 9–13.

(i) Mononuclear complexes. The octahedral tris(dimethylphosphorodithioato)molybdenum(III) $Mo\{S_2P(OMe)_2\}_3$, **37**, is similar to the analogous chromium(III) and vanadium(III) complexes, with isobidentate chelating ligands.[77]



37

The *p*-tolylimido derivative $Mo\{S_2P(OMe)_2\}_3(N\text{-}C_6H_4Me\text{-}p)$, **38** (R = Me, Ar = NC_6H_4Me-4), contains two bidentate and one monodentate phosphorodithioato ligands,[78] displaying significant differences in the P—S bond lengths and S—P—S bond angles (Table 9). Thus, in the bidentate

Table 8. Crystal structure data for chromium phosphorodithioates

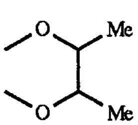
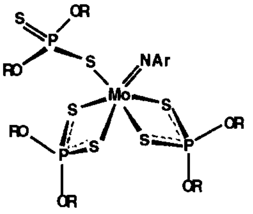
Structure no.	R	Space group	*a* *b* *c*	α β γ	P—S	M—S	S—P—S	M—S—P	Bond type	Ref.
36	Et	C2/c	14.374	—	1.988 1.999	2.423 2.428	106.6	85.7 85.3	chel	73
			13.586	90.51						
			14.270	—						
		C2/c	14.28	—	1.980 2.000	2.423	106.2	85.6 84.9	chel	74
			13.60	89.5	1.995 1.995	2.421	107.0			
			14.35	—						
36	$(RO)_2$=	$P2_12_12_1$	11.699	—	1.972 1.974	2.410 2.424	107.2	85.5 85.1	chel	75, 76
			12.738	—	1.973 1.983	2.438 2.426	107.2	85.1 85.2	chel	
			16.827	—	1.973 1.979	2.420 2.423	107.2	85.4 85.2	chel	

Table 9. Crystal structure data for mononuclear molybdenum phosphorodithioato complexes

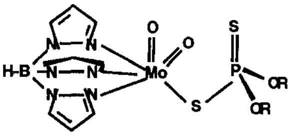
Structure no.	R	Space group	a b c	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
37	Me	$C2/c$	14.342	—	1.990	1.991	2.521	2.501	107.8	85.9	86.5	chel	77
			11.239	77.12	1.994	1.994	2.500	2.500	107.2	96.5	86.5	chel	
			12.945	—									
38	Me	$P2_1/c$	20.421	—	2.001	2.008	2.530	2.448	105.6	86.5	87.5	chel	78
			8.579	93.92	1.986	2.014	2.645	2.492	106.4	86.4	90.0	uni	
			18.449	—	1.940	2.035		2.453	110.7		110.2		
39	Et	$P\bar{1}$	8.421	87.77	1.931	2.047	—	2.048	111.1	—	107.2	uni	79
			12.654	81.36									
			15.240	74.37									
40	Et	$P2_1/c$	17.987	—	1.984	1.993	2.500	2.478	107.0	84.7	84.4	chel	79
			8.219	104.88									
			18.681										
41	Pr^i	$Pbca$	12.703	—	1.992	1.994	2.550	2.559	105.6	89.1	89.8	chel	71
			16.706	—									
			18.398	—									
42	Et						2.599	2.505				chel	80
43	Et	$P2_1/n$	15.479	—	1.986	2.000	2.588	2.564	not given	87.7	88.1	chel	81
			16.718	95.56									
			17.156	—									
44	Et	$P2_1/c$	15.311	—	1.97	2.02	3.06	2.62				chel	82
	R′ = Me		10.231	98.76									
			20.889	—									

ligands P—S bond lengths are in the range 1.986–2.014 Å, while in the monodentate group single (P—S 2.035 Å) and double (P=S 1.940 Å) bonds are clearly distinguished.

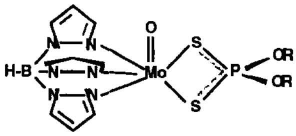


38

Of the two tris(dimethylpyrazolylborato)phosphorodithioato mixed ligand complexes the dioxomolybdenum(VI) derivative **39** contains a monodentate phosphorodithioato ligand, while in the oxomolybdenum(IV) compound, **40**, the ligand is bidentate.[79] As observed before, in the monodentate ligand the S—P—S bond angle is larger (111°) than in the bidentate ligand (107°). The phosphorus–sulphur bond lengths are 2.047 Å (P—S) and 1.931 Å (P=S) in **39**, and 1.984 and 1.993 in **40**, in agreement with the coordination patterns of the ligands.



39



40

The η^5-cyclopentadienylmolybdenum phosphorodithioato complexes **41** (R = Pr^i)[71] and **42** (R = Et)[80] contain isobidentate chelating ligands and in **41** the P—S bond lengths are equal (1.992 and 1.994 Å).

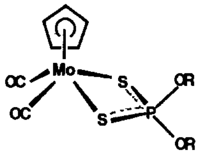
Table 10. Crystal structure data for binuclear molybdenum phosphorodithioato complexes

Structure no and R	R′ R″	Space group	*a* *b* *c*	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
45		P2$_1$/c	8.235	—	2.006	1.956	2.504	2.799	109.3	91.4	84.1	chel	83
Me			16.544	103.7	2.018	1.983	2.453	2.549	105.9	87.9	86.0	chel	
			11.444	—									
45		P2$_1$/n	8.709	—	1.954	2.000	2.800	2.501	110.3	83.4	90.8	chel	84
Et			24.170	112.3	1.988	2.004	2.534	2.457	105.7	86.2	88.0	chel	
			9.942	—									
45	—	P$\bar{1}$	11.36	94.9	1.947	2.010	2.801	2.497	109.2	84.4	91.7	chel	85
Et^a			13.96	103.8	1.983	2.017	2.547	2.442	105.3	86.3	88.4	chel	
			8.66	81.7									
45	—	P$\bar{1}$	10.670	100.1	1.967	2.020	2.534	2.444	105.5	86.7	88.1	chel	86
Pr^n			13.063	92.16	1.932	2.002	2.809	2.501	109.5	—	91.7	chel	
			8.944	80.88									
45	—	P$\bar{1}$	10.898	98.43	1.928	2.012	2.833	2.514	109.8	83.2	90.5	chel	87
Pr^i			12.637	98.67	1.988	2.014	2.529	2.457	105.0	87.1	88.6	chel	
			8.972	86.78									
46	—	Pbca	11.636	—	1.993	1.996	2.547	2.506	107.1	86.0	87.1	chel	88
Et^b			18.290	—	1.988	1.998	2.522	2.489	106.6	86.7	87.4	chel	
			23.904										
47	—	Pbca	22.679	—	1.993	1.999	2.460	2.491	103.5	88.6	88.0	chel	89
Pr^i			16.224	—	1.977	2.010	2.481	2.490	103.9	87.5	86.5	chel	
			15.104	—									
48	—	Pbca	23.021	—	2.015	2.018	2.476	2.505	103.1	87.6	86.7	chel	90
Pr^i			16.030	—	1.999	1.999	2.472	2.501	104.8	88.0	87.2	chel	
			14.792	—									
49	—	P2$_1$/c	14.044	—	1.998	2.008	2.477	2.466	102.3	88.9	89.0	chel	91,92
Et			10.341	112.5	1.980	2.004	2.489	2.475	104.0	88.3	88.2	chel	
			17.821	—									
50	Ar =	P$\bar{1}$	20.026	65.46	1.995	2.008	2.524	2.527	105.0	87.8	87.4	chel	93
Et	Ph		12.360	77.46	1.996	2.009	2.527	2.535	105.5	87.7	87.2	chel	
			12.093	77.54	1.982	2.017	2.544	2.545	107.7	85.6	84.9	chel	
					1.985	2.007	2.527	2.526	106.8	85.1	84.7	chel	
50	Ar =	Pcab	12.514	—	2.011	2.012	2.505	2.459	103.3	86.8	87.2	chel	93
Me	*p*-Tol		13.136	—	1.988	1.996	2.527	0	106.1	86.9	87.2	chel	
			28.009	—				2.510					
51	—	P$\bar{1}$	8.773	69.24	1.964	2.012	2.635	2.459	106.2	86.3	90.2	chel	94
Et			9.712	70.43	1.969	1.999	2.645	2.482	106.2	86.7	90.7	chel	
			13.652	66.87									
52	R′ = CF$_3$	P2$_1$/a	23.569	—	1.987	1.997	2.542	2.577	106.2	87.5	88.1	chel	95
Et	R″ = H		17.176	111.8	1.985	1.998	2.538	2.506	106.7	87.0	87.6	chel	
	Ar = *p*-Tol		10.050	—									
52	R′ = CF$_3$	A2/a	33.891	—	1.994	2.001	2.526	2.518	105.9	87.8	87.8	chel	96
Et	R″ = Me		16.169	90.52	2.000	2.000	2.548	2.493	106.1	86.8	88.3	chel	
	Ar = *p*-Tol		13.902	—									
52	R′ = Me	P2$_1$/c	13.403	—	1.992	1.996	2.511	2.553	106.4	87.2	88.2	chel	97
Et	R″ = SEt		24.817	116.2	1.987	1.988	2.520	2.552	106.8	88.0	87.1	chel	
	Ar = *p*-Tol		13.894	—									
52	R′ = Me	P$\bar{1}$	13.781	104.48	1.995	1.982	2.517	2.550	106.8	87.7	87.1	chel	98
Et	R″ = NH$_2$		14.524	106.39	1.988	1.988	2.510	2.557	106.7	87.9	86.6	chel	
			10.961	107.31									
	Ar = *p*-Tol												
52	R′ = Me	P2$_1$/n	12.473	—	1.996	1.985	2.515	2.515	106.9	87.7	86.9	chel	98
Et	R″ =		28.197	114.81	1.995	1.985	2.504	2.567	106.7	88.2	86.7	chel	
	NCHBu^t		13.568	—									
	Ar = *p*-Tol												
52	R′ = Me	P$\bar{1}$	15.602	91.13	1.993	1.987	2.517	2.560	106.8	88.2	87.1	chel	98
Et	R″ =		15.618	96.25	1.990	1.993	2.515	2.557	106.2	88.5	87.3	chel	
	NCMe$_2$		9.627	117.59									
	Ar = *p*-Tol												
53	C$_7$H$_{15}$	C2/c	28.664	—	1.987	1.989	2.552	2.567	106.8	87.9	87.4	chel	99
Et	Ar =		14.653	122.1									
	p-Tol		32.304	—									

Table 10—*continued.*

Structure no and R	R′ R″	Space group	a b c	α β γ	P—S		M—S		S—P—S	M—S—P		Bond typ	Ref.
54	—	$P2_1/n$	17.316	—	1.987	1.994	2.515	2.525	105.5	88.2	87.8	chel	100
Pr^i			14.560	93.00	1.969	2.003	2.523	2.507	105.8	88.0	87.7	chel	
			2.150	—									
55	—	$P2_1/n$	17.200	—	2.007	2.025	2.538	2.485	105.1	87.0	88.0	chel	100
Pr^i			12.690	111.0	1.997	2.024	2.529	2.495	104.9	87.5	87.9	chel	101
			15.448	—									
56	—	Aa	11.854	—	2.004	2.009	2.512	2.508	104.8	87.9	87.9	chel	102
Pr^i			9.000	93.27	2.008	2.011	2.503	2.498	104.5	87.9	88.0	chel	
			28.849	—									
57	—	$P\bar{1}$	15.279	90.17	1.988	2.014	2.544	2.485	106.5	86.3	87.2	chel	103
Et			17.019	95.51	1.982	2.020	2.630	2.471	106.0	86.5	90.1	chel	
			11.640	74.65	1.929	2.050	—	2.461	111.3	—	107.0	uni	
					2.000	2.012	2.533	2.486	106.2	86.1	87.2	chel	
					1.980	2.009	2.663	2.483	108.3	84.2	88.6	chel	
					1.933	2.051	—	2.466	110.5	—	108.5	uni	

[a] $C_6H_4Cl_2$ solvate.
[b] THF solvate.



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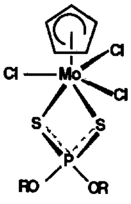

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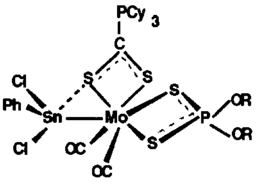
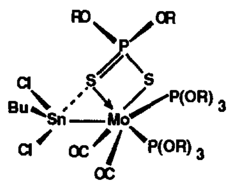
In a bimetallic molybdenum–tin complex **43** (R = Et) the dithiophosphorus ligand is coordinated as monometallic biconnective (isobidentate) only to molybdenum; the tin atom participates only in a secondary interaction (Sn...S 2.999 Å) with the sulphur atom of Cy_3PCS_2 ligand.[81] In a related bimetallic compound **44** (R = Et, R′ = Me) the phosphorodithioato ligand is bimetallic triconnective, with two bonds to molybdenum (Mo—S 2.62 and 2.65 Å) and a weak secondary interaction to tin (Sn... S 3.06 Å).[82] The P—S bonds differ slightly (P—S1 2.02 Å and P—S2 1.97 Å), the longer being that involved in the secondary bond to tin.

Crystal data and molecular dimensions for mononuclear molybdenum phosphorodithioates are given in Table 9.



43



44

(ii) Binuclear complexes. There are at least three types of binuclear molybdenum phosphorodithioato complexes: (a) single bridged (oxo), (b) doubly bridged (oxo/oxo, oxo/thio, oxo/imino) and (c) complexes with a spacer group separating the two metal atoms. Crystal data for binuclear phosphorodithioates are listed in Table 10.

Trioxodimolybdenum(V) phosphorodithioates, $Mo_2O_3\{S_2P(OR)_2\}_4$, are binuclear compounds containing a single oxo bridge and four chelating phosphorodithioato ligands in a *trans*-configuration, as in **45** (R = Me,[83] Et,[84,85] Pr^n,[86] and Pr^i[87]). The difference in the P—S interatomic distances

Table 11. Crystal structure data for trinuclear phosphorodithioato molybdenum complexes (R = Et in compounds **59–74**)

Structure no. and R′	L	Space group	*a* *b* *c*	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
59	imidazole[a]	$P\bar{1}$	14.465	99.36	1.981	1.989	2.580	2.550	107.1	87.1	87.3	chel	104
			14.653	93.11	1.981	1.998	2.597	2.563	107.1	87.8	88.4	chel	
			14.886	114.29	1.976	1.989	2.569	2.567	107.4	87.9	87.7	chel	
					1.952	1.946	—	—	118.7			ionic	
60	H_2O	$P2_1/c$	13.553	—	1.998	1.971	2.564	2.578	107.5	87.66	87.5	chel	105–
			10.066	95.00	2.007	1.977	2.588	2.594	108.5	86.5	85.7	chel	107
			31.014	—	1.966	2.013	2.568	2.533	107.7	86.3	86.3	chel	
					1.979	1.969	2.585	2.586	116.6	109.3	109.2	bridge	
60	BzCN	$P\bar{1}$	15.941	76.41	1.973	1.996	2.597	2.564	106.8	88.0	88.5	chel	108
			15.957	83.87	1.982	1.983	2.564	2.553	108.3	86.3	86.6	chel	
			20.240	74.41	1.980	2.000	2.587	2.580	106.9	88.3	88.0	chel	
					1.989	1.972	2.641	2.655	115.3	105.5	105.9	bridge	
60	oxazole[b]	$P2_1/n$	16.579	—	2.001	1.986	2.565	2.578	106.4	not	not	chel	109
			16.959	94.44	1.999	1.985	2.568	2.591	106.4	given	given	chel	
			16.867	—	1.997	1.971	2.548	2.582	108.7			chel	
					1.969	1.943	2.639	2.594	117.0			bridge	
60	PPh_3[c]	$P\bar{1}$	10.472	74.04	1.982	2.001	2.589	2.574	107.8	86.6	86.7	chel	110,
			14.375	76.50	1.980	1.979	2.586	2.595	109.9	85.9	85.6	chel	111
			21.695	72.22	1.979	1.976	2.608	2.600	107.8	87.9	88.4	chel	
					1.985	1.984	2.599	2.584	116.7	105.1	106.9	bridge	
60	allylthi	$P\bar{1}$	13.944	77.35	1.975	1.989	2.551	2.586	107.4	87.5	88.2	chel	112
	ourea		14.143	69.94	1.993	1.987	2.577	2.592	106.9	88.3	88.0	chel	
			14.233	63.50	1.978	1.989	2.582	2.603	109.3	86.0	86.3	chel	
						1.948	2.583	2.632	117.0	110.4	111.2	bridge	
61	bipy	$P\bar{1}$	13.683	95.57	1.943	1.976	2.585	2.571	107.2	88.3	88.0	chel	115
			13.983	91.87	1.985	1.961	2.544	2.571	107.8	86.7	86.4	chel	
			14.699	117.40	1.976	1.969	2.655	2.674	115.7	105.7	105.3	bridge	
					1.998	1.901	2.573	—	120.8	118.0		ionic	
62	oxazole	$P\bar{1}$	11.931	78.17	1.990	1.992	2.542	2.570	107.1	88.0	87.2	chel	116
			13.203	91.34	1.982	1.992	2.541	2.574	106.7	88.4	87.6	chel	
			15.014	109.63	1.978	1.990	2.543	2.582	107.2	88.3	87.4	chel	
					1.964	—	2.644	—	—	106.1	—	bridge	
										(oxo)			
63	Py	$P\bar{1}$	10.519	93.27	1.981	1.987	2.510	2.561	106.0	88.4	86.8	chel	117
H			12.121	94.63	1.978	1.996	2.559	2.520	106.8	87.1	87.8	chel	
			15.757	105.2	1.977	1.988	2.573	2.549	107.0	87.8	88.2	chel	
63	Py	$P\bar{1}$	9.556	101.41	1.989	1.985	2.531	2.559	107.1	87.9	87.2	chel	117
Me			14.067	101.44	2.000	1.991	2.515	2.563	105.7	88.8	87.6	chel	
			15.914	74.26	1.997	1.983	2.549	2.576	107.9	87.3	86.9	chel	
63	Py[d]	$P2_1/n$	13.158	—	1.995	1.985	2.526	2.554	105.8	88.7	88.2	chel	118
Me			23.153	112.7	2.006	1.986	2.515	2.548	106.5	87.8	87.3	chel	
			16.175	—	2.001	1.985	2.540	2.540	106.6	88.5	87.6	chel	
63	MeCN	$P\bar{1}$	12.877	108.70	1.989	1.974	2.537	2.560	107.0	87.8	87.5	chel	119
Me			12.954	102.05	1.987	1.990	2.571	2.549	106.6	87.8	88.3	chel	
			12.807	71.62	1.998	1.987	2.514	2.549	106.3	88.2	87.4	chel	
63	Py	$P\bar{1}$	12.972	66.22	1.980	1.997	2.549	2.567	108.5	86.8	86.0	chel	120
Et			13.763	101.72	1.996	1.979	2.541	2.567	107.3	87.4	87.1	chel	
			14.515	118.90	1.976	1.998	2.549	2.522	106.5	87.5	87.8	chel	
64	—	$P2_1/c$	12.748	—	1.991	1.994	2.547	2.567	107.7	87.4	86.8	chel	121
			14.320	101.07	1.994	2.012	2.487	2.463	104.0	87.5	87.8	chel	
			23.118	—	1.987	2.023	2.540	2.467	105.2	87.3	87.3	chel	
65	oxazole	$P\bar{1}$	13.175	117.87	1.966	1.975	2.568	2.568	108.8	87.1	86.9	chel	109
			13.372	60.09	1.981	1.981	2.555	2.673	107.0	90.6	87.2	chel	
			16.656	109.03	1.979	1.971	2.559	2.616	108.7	87.1	85.7	chel	
					1.980	1.980	2.581	2.586	115.1	104.9	102.7	bridge	
65	imidazole	$C2/c$	14.954	—	1.961	1.991	2.604	2.561	108.0	87.4	88.0	chel	122
			22.323	98.23	1.969	1.994	2.665	2.571	107.9	87.2	89.3	chel	
			27.003	—	1.963	1.989	2.593	2.592	109.5	86.9	86.4	chel	
					1.983	1.978	2.636	2.607	113.2	102.6	104.8	bridge	

Table 11.—*Continued*

Structure no. and R′	L	Space group	*a* *b* *c*	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
66	thiourea	$P2_1/n$	15.355	—	1.966	1.992	2.574	2.636	109.1	88.0	85.7	chel	105,
			12.718	90.57	1.974	1.990	2.585	2.585	108.2	86.4	87.3	chel	123
			22.806	—	1.973	1.974	2.578	2.578	108.9	87.0	86.9	chel	
					1.946	1.912	2.592	2.592	116.3	108.7	106.4	bridge	
67	Py	$P\bar{1}$	12.921	97.54	1.989	1.954	2.568	2.563	108.2	85.8	86.0	chel	124
Me			14.260	116.66	1.994	1.999	2.562	2.546	106.9	87.4	87.8	chel	
			12.800	100.10	2.000	1.967	2.566	2.554	107.7	86.5	87.5	chel	
68	Py[e]	$P\bar{1}$	11.704	109.94	1.99	1.98	2.56	2.54		86.7	87.1	chel	125
Me			14.169	91.53	1.96	2.00	2.53	2.54		87.8	86.7	chel	
			11.688	91.93									
68	Py	$P2_1/c$	15.057	—	1.978	1.959	2.533	2.534	107.7	87.1	87.5	chel	126
CH_2Ph			13.052	105.97	2.010	1.969	2.547	2.541	107.2	86.8	87.9	chel	
			21.662										
69	X = Cl	$P\bar{1}$	11.570	102.62	1.983	1.998	2.549	2.496	105.1	88.1	89.2	chel	92,
			13.093	102.15	1.985	1.995	2.545	2.499	105.0	88.0	89.0	chel	127
			14.399	111.87	1.984	1.996	2.550	2.502	105.3	88.0	89.1	chel	
69	X = I[f]	$P\bar{1}$	10.350	103.69	1.994	2.004	2.549	2.512	105.2	88.1	88.9	chel	128
			13.931	86.62	1.982	2.001	2.506	2.556	105.4	89.0	88.0	chel	
			16.369	111.99	1.984	1.994	2.552	2.515	105.5	89.1	89.0	chel	
70	X = Cl	$P2_1/n$	8.253	—	1.997	2.003	2.520	2.541	106.0	88.2	87.5	chel	129
			21.018	90.89	2.017	1.959	2.517	2.563	107.6	85.9	85.9	chel	
			21.531	—	2.003	2.003	2.515	2.557	106.1	87.3	88.4	chel	
70	X = I	$P2_1/n$	16.570	—	1.980	1.990	2.543	2.519	107.6	86.7	87.2	chel	130,
			12.370	99.97	1.979	1.999	2.540	2.498	105.8	87.6	88.4	chel	131
			20.007	—	1.983	2.002	2.537	2.512	106.4	87.4	87.7	chel	
71		$P2_1/n$	17.378	—	1.994	1.981	2.513	2.549	106.3	87.1	86.4	chel	132
			19.752	84.50	1.973	2.003	2.498	2.555	106.1	87.5	88.4	chel	
			23.845	—	1.991	1.997	2.506	2.551	105.3	89.1	87.7	chel	
					1.982	1.980	2.507	2.533	105.3	88.8	88.2	chel	
					1.999	1.983	2.497	2.550	105.1	89.2	88.0	chel	
					1.992	2.007	2.500	2.542	105.0	88.9	88.1	chel	
72		$P2_1/n$	17.282	—	1.986	1.989	2.529	2.493	105.9	87.4	88.4	chel	133
			19.543	91.89	1.984	1.991	2.526	2.491	107.0	86.5	87.3	chel	
			23.997	—	2.000	1.999	2.532	2.489	106.2	96.8	88.0	chel	
					1.984	1.977	2.487	2.535	106.3	88.3	87.1	chel	
					1.984	1.996	2.533	2.503	106.7	86.5	87.1	chel	
					1.981	1.993	2.542	2.479	106.3	86.7	88.2	chel	
73		$P6_3/m$	15.492	—	1.978	1.978	2.492	2.492	105.5	88.0	88.0	chel	134
			15.492	—									
			8.530	120									
74		$P\bar{1}$	12.971	100.62	1.980	1.996	2.565	2.546	107.8	86.7	86.9	chel	135
			13.578	114.25	1.985	1.992	2.567	2.510	106.7	86.7	88.2	chel	
			14.135	101.49	2.004	2.003	2.459	2.548	105.6	88.7	85.7	chel	
					1.989	2.005	2.566	2.536	112.2	106.8	106.3	bridge	

[a] Acetone solvate.

[b] Acetonitrile solvate.

[c] 0.86 CH_2Cl_2 solvate.

[d] CH_3COOEt solvate.

[e] 0.5 H_2O solvate.

[f] Toluene solvate.

Table 12. Crystal structure data for tetranuclear molybdenum phosphorodithioates (R = Et in compounds **75**–**85**)

Structure no.	X or R′	Space group	*a* *b* *c*	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
75, α	O	$P\bar{1}$	13.387	72.84	1.968	1.987	2.540	2.529		87.9	87.8	chel	138
			13.997	87.92	1.958	1.968	2.570	2.534		89.0	87.6	chel	
			16.281	84.87	1.963	1.972	2.533	2.545		86.7	86.2	chel	
					1.970	1.983	2.586	2.579		107.9	103.8	bridge	
					1.976	1.966	2.607	2.581		107.9	107.0	bridge	
					1.995	1.977	2.584	2.579		107.0	106.3	bridge	
75, α	O 40% S 60%	$P\bar{1}$	14.031	92.15	1.972	1.989	2.543	2.562	106.6	88.0	88.2	chel	136a
			13.372	72.91	1.964	1.970	2.552	2.559	108.3	87.0	87.1	chel	
			16.272	95.20	1.976	1.988	2.542	2.549	107.7	86.0	86.4	chel	
					1.974	1.990	2.575	2.579	116.7	106.9	97.3	bridge	
					1.987	1.980	2.563	2.588	116.9	108.0	108.5	bridge	
					1.977	1.998	2.565	2.571	116.4	107.3	107.8	bridge	
76, β	O	$P2_1/n$	13.689	—	1.985	1.965	2.556	2.578	107.7	87.3	87.6	chel	139
			30.903	93.07	1.990	1.975	2.542	2.540	106.2	87.3	87.7	chel	
			14.212	—	1.975	1.981	2.528	2.619	107.6	88.7	86.0	chel	
					1.958	1.986	2.546	2.609	108.4	86.7	87.9	chel	
					1.945	1.950	2.542	2.556	115.5	108.8	109.1	bridge	
					1.934	1.939	2.549	2.584	122.8	106.9	111.6	bridge	
76, β	S	$P2/n$	12.827	—	1.985	1.989	2.595	2.598	107.3	88.35	88.14	chel	136a
			17.206	97.12	1.981	1.973	2.549	2.545	105.9	88.63	88.89	chel	136b
			13.507	—	1.900	1.928	2.577	2.551	118.9	111.97	109.36	bridge	
		$P2/c$	17.374	—									137
			17.354	93.20									
			19.963	—									
77, α	O[a]	$R3$	12.852	108.37	1.975	2.009	2.584	2.548	116.2	107.5	107.1	bridge	140
					1.975	1.983	2.549	2.546	106.9	87.9	87.8	chel	
78, β	R′ = Me	$P2/c$	13.176	—	1.976	2.008	2.517	2.543	106.1	87.5	88.3	chel	141
			11.699	116.11	1.987	1.976	2.508	2.542	106.3	88.7	87.2	chel	
			18.526	—									
78	R′ = Me	$Pcab$	18.900		1.978	1.982	2.550	2.481	106.7	86.6	88.4	chel	141, 142
	H adduct		21.678		1.998	1.968	2.563	2.495	107.6	85.6	88.1	chel	
			24.491		1.970	2.006	2.495	2.557	106.7	87.0	87.9		
					1.971	1.997	2.498	2.564	106.0	87.6	87.6		
78	R′ = Me H adduct[b]	$P2/n$	17.271	—	1.976	2.008	2.553	2.500	106.1	86.7	87.5	chel	143
			11.985	105.94	1.987	1.976	2.497	2.557	106.3	87.3	86.8	chel	
			13.061	—									
79	Ar = *p*-tol	$P\bar{1}$	24.179	75.78	1.970	1.975	2.551	2.559	109.2	86.2	85.8	chel	144
			14.413	59.65	1.976	1.997	2.568	2.541	108.4	85.2	85.5	chel	
			12.590	58.35	1.976	1.985	2.557	2.543	108.7	84.3	84.6	chel	
					1.979	1.994	2.567	2.532	107.0	87.4	88.0	chel	
80	Ar = Ph	$P\bar{1}$	20.026	65.46	1.995	2.008	2.524	2.527	105.0	87.8	87.4	chel	93
			12.360	77.46	1.996	2.009	2.527	2.535	105.5	87.7	87.2	chel	
			12.093	77.54	1.982	2.017	2.544	2.545	107.7	85.6	84.9	chel	
					1.985	2.007	2.527	2.526	106.8	85.1	84.7	chel	
81	Ar = *p*-tol R′ = CF_3	$Pcab$	15.343	—	1.997	2.001	2.554	2.498	106.0	88.0	89.3	chel	145
			20.787	—	1.992	2.002	2.550	2.508	105.0	87.3	88.4	chel	
			25.422	—									
82	—	$A2/a$	18.632	—	1.983	1.993	2.679	2.510	107.8	85.6	90.1	chel	146
			24.384	92.16	1.955	2.020	2.662	2.482	108.7	84.9	88.5	chel	
			12.600	—	1.990	2.005	2.636	2.508	108.7	84.9	88.1	chel	
					1.979	2.012	2.661	2.495	108.5	84.9	88.8	chel	

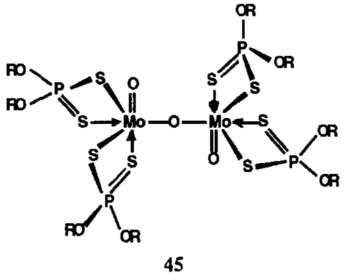
[a] 3MeCN solvate.

[b] Acetone solvate.

Table 13. Crystal data for heterometallic molybdenum phosphorodithioato complexes

Structure no. and R′	L	Space group	*a* *b* *c*	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
83	Py	$P\bar{1}$	11.460	112.35	1.976	1.980	2.535	2.567	107.2	88.3	87.3	chel	147
H			14.237	90.09	1.978	1.993	2.547	2.498	107.5	86.8	85.8	chel	
			15.046	111.77	1.983	1.998	2.498	2.543	106.3	86.9	88.4	chel	
83	H_2O	$P\bar{1}$	10.146	110.42	2.0035	1.982	2.491	2.552	106.4	88.1	86.9	chel	148
Me			12.978	106.86	2.004	1.981	2.495	2.542	105.8	88.5	87.6	chel	
			16.132	91.31	1.977	2.000	2.527	2.558	108.1	84.3	84.8	chel	
83	DMSO	$P\bar{1}$	12.183	72.87	1.980	1.995	2.489	2.550	106.2	87.0	88.4	chel	148
Me			12.551	71.24	1.994	1.977	2.513	2.541	106.4	88.0	87.6	chel	
			15.979	67.48	1.979	1.985	2.577	2.530	109.2	85.1	86.3	chel	
83	DMF	$P\bar{1}$	12.639	108.78	1.966	1.995	2.570	2.542	107.7	87.3	86.7	chel	149
Me			13.722	106.36	1.979	2.002	2.561	2.507	106.3	87.8	86.4	chel	
			14.644	102.54	1.987	1.989	2.541	2.501	105.8	87.0	87.7	chel	
83	MeCN	$P\bar{1}$	11.723	75.40	1.996	2.000	2.543	2.504	106.4	86.9	87.9	chel	150
CCl_3			14.353	69.13	2.006	2.000	2.548	2.553	108.0	86.2	86.2	chel	
			15.333	64.93	1.943	2.029	2.533	2.490	107.1	87.0	86.3	chel	
83	Py	$P2_1/c$	14.779	—	1.979	2.001	2.540	2.502	105.9	87.6	88.2	chel	148
Ph			13.736	93.26	2.003	1.981	2.494	2.548	105.8	88.4	87.4	chel	
			23.073	—	2.000	1.981	2.512	2.578	107.8	87.4	86.0	chel	
84	Py	$P\bar{1}$	13.781	98.37	1.997	1.960	2.526	2.547	107.9	86.8	86.9	chel	151
Me			14.523	109.41	1.995	1.964	2.525	2.546	108.6	86.2	86.3	chel	
			12.098	105.00	1.999	1.988	2.556	2.564	107.5	87.3	87.4	chel	
84	DMF	$P\bar{1}$	13.215	106.06	1.994	1.998	2.524	2.557	106.9	87.0	88.0	chel	151
Me			17.81	109.78	1.993	1.982	2.518	2.555	107.6	87.4	86.6	chel	
			9.783	82.00	2.009	1.964	2.567	2.569	109.0	85.5	86.5	chel	
85	oxazole	$P\bar{1}$	10.342	76.27	1.993	1.984	2.527	2.596	106.8	89.0	87.0	chel	152,
			11.994	88.55	1.981	1.990	2.579	2.513	106.2	87.6	89.3	chel	153
			21.352	73.26	1.982	2.004	2.584	2.519	107.6	86.0	87.2	chel	
85	EtOH	$P2_1/n$	13.250	—	1.963	1.964	2.537	2.590	108.4	86.5	87.9	chel	152,
			17.296	92.41	1.966	1.966	2.555	2.562	108.1	86.8	87.0	chel	154
			23.223	—	1.931	2.005	2.541	2.577	109.2	86.2	85.7	chel	
					1.963	1.988	2.569	2.582	115.9	108.3	108.7	bridge	

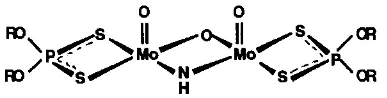
(Table 10) suggest a formulation with single and double phosphorus–sulphur bond lengths. A shorter P—S bond is associated with a longer Mo—S bond and *vice versa*.



45

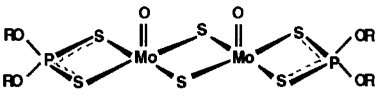
The Mo—S bond *trans* to Mo═O is the longest, followed by that *trans* to the bridging oxygen. A difference in the P—S and Mo—S(—S) bond lengths in the chelate rings, and the presence of short phosphorus–sulphur bond lengths (as low as 1.932 Å in $Mo_2O_3\{S_2P(OPr^n)_2\}_4$,[86] or 1.928 Å in $Mo_2O_3\{S_2P(OPr^i)_2\}_4$,[87] corresponding to double bonds) suggests that the formulation **45**, with a coordination pattern of type **2**, satisfactorily reflects the nature of bonding in these compounds.

The compound $Mo_2O_3(NH)\{S_2P(OEt)_2\}_2 \cdot THF$ is an oxo-imino doubly bridged binuclear compound **46**, with two isobidentate chelating ligands (see Table 10 for geometric parameters).[88]



46

There are several similar compounds containing oxomolybdenum, thiooxomolybdenum and aryliminomolybdenum coordination centres, connected by double sulphur or oxosulphur bridges, **47**–**50** and two terminal chelating ligands. All contain five-coordinate molybdenum(V). In these compounds the phosphorodithioato ligands are isobidentate, with practically equal P—S bonds, and a diminished S—P—S bond angle imposed by the formation of the four-membered MoS_2P chelate rings. Molecular dimensions for compounds **47** (R = Pr^i),[89] **48** (R = Pr^i),[90] **49** (R = Et),[91,92] and **50** (R = Me, Et, Ar = Ph, *p*-tolyl)[93] are collected in Table 10.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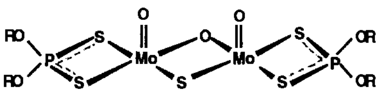
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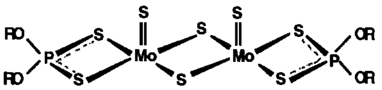
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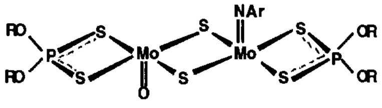
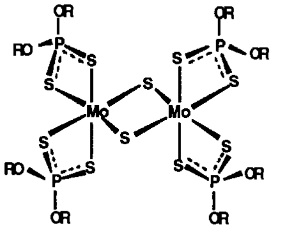
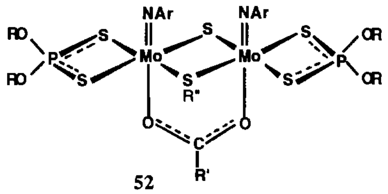

50

A doubly bridged compound with four chelating ligands, $Mo_2S_2\{S_2P(OEt)_2\}_4$, **51** (R = Et),[94] contains six-coordinate molybdenum(IV). The phosphorus–sulphur bonds are slightly differing (1.96 and 2.00 Å), suggesting some double bond character in the shorter ones. A *trans* influence of bridging sulphur atoms in the Mo_2S_2 nucleus can be invoked to explain these differences.


51

Another type of dinuclear complex contains an additional carboxylato bridge, connecting the two molybdenum atoms, as in structures **52** (R = Et, R′ = CF_3, R″ = H,[95] Me,[96]; R′ = Me, R″ = SEt,[97] NH_2, $NCMe_2$ and $NCHBu^{t}$[98]) and **53** (R = Et, R′ = C_7H_{15}),[99] with terminal isobidentate chelating phosphorodithioates, and *p*-tolylimino groups bonded to molybdenum. Molecular dimensions are listed in Table 10.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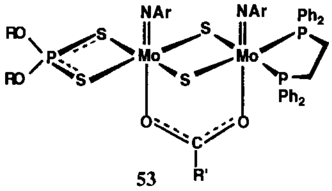
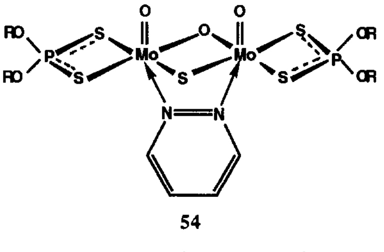

53

The pyridazine molecule in $Mo_2SO_3\{S_2P(OPr^i)_2\}_2$·pyridazine, **54**,[100] and pyridine in Mo_2SO_3 $\{S_2P(OPr^i)_2\}_2$·pyridine, **55**,[100,101] also form bridges between molybdenum centres, while the phosphorodithioato ligand forms terminal isobidentate chelating groups. The bridging mode of pyridine in **55** is rather unusual and surprising.[102]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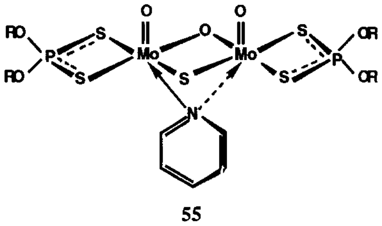
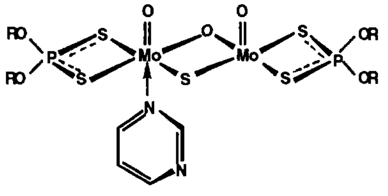
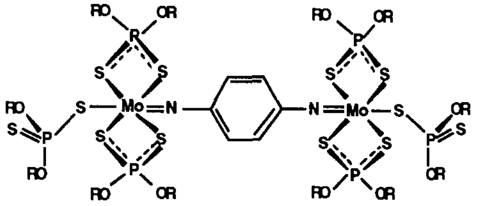

55

A pyrimidine adduct $Mo_2SO_2\{S_2P(OPr)_2\}_2$·pyrimidine has been formulated as **56**, with the pyrimidine molecule coordinated to only one molybdenum atom, with a long Mo—N distance (2.861 Å). The ligand is isobidentate chelating.



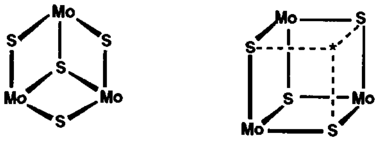
56

In the complex $Mo_2\{S_2P(OPEt)_2\}_6 \cdot NC_6H_4N$ the *p*-phenylenediimino group acts as a spacer bridge between two molybdenum atoms. Of the six phosphorodithioato ligands two are monodentate terminal groups, while the other four are chelating, as shown in **57**.[103]



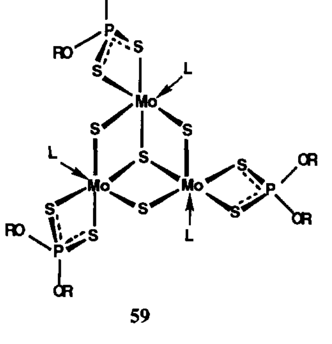
57

(iii) Trinuclear complexes. A large number of trinuclear molybdenum phosphorodithioato complexes are built around a cyclic $Mo_3S_4^{4+}$ core, **58a**. The Mo_3S_3 unit also contains three Mo—Mo bonds and is capped by a fourth sulphur atom; it can also be regarded as an incomplete cubane structure, with one of the four corners (marked by an asterisk) missing, as shown in **58b**. This site (*) can be occupied in some compounds by a fourth metal (hetero)atom, e.g. molybdenum, copper or antimony, to form a complete cubane structure.



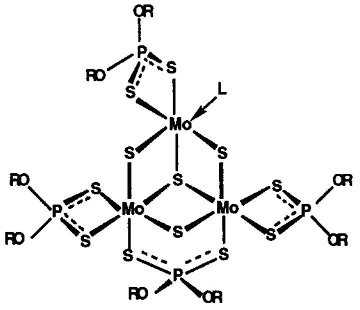
58a,b

The $Mo_3S_4^{4+}$ core is coordinatively unsaturated, each molybdenum atom displaying the tendency to become octahedral, six-coordinated (if Mo—Mo bonds are ignored, as we will do throughout this review, for simplicity). Thus, each molybdenum atom possesses three available coordination sites. If a phosphorodithioato ligand forms a chelate ring at each molybdenum site, and an additional monodentate ligand is coordinated to each molybdenum atom, structure **59** results. This has been found in the compound $[Mo_3S_4\{S_2P(OEt)_2\}_3(L)_3]^+[(EtO)_2PS_2]^-$ (L = imidazole),[104] where the positive charge of the trinuclear complex is neutralized by a fourth phosphorodithioate group acting as a non-coordinated counter ion. The chelating ligands are all isobidentate (P—S 1.976–1.998 Å; S—P—S 107.2°). In the free anion $(EtO)_2PS_2^-$ the P—S bonds are shorter (1.946 and 1.952 Å) and the S—P—S bond angle larger (118.7°).[104]



59

A pair of the monodentate ligands L can be replaced by a fourth phosphorodithioato group, acting as a bridge and spanning across the Mo—S—Mo bridge, to form a structure of type **60**.

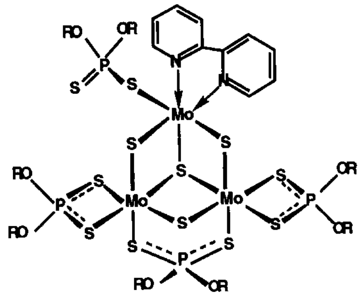


60

These compounds contain three chelating and one bridging phosphorodithioato ligands and several such complexes, with L = H_2O,[105–107] $PhCH_2CN$,[108] oxazole,[109] PPh_3,[110,111] and allylthiourea,[112] have been reported. The ligand L is weakly bonded and can be easily interchanged with various groups. The position occupied by L has been called "a loose coordination site", reflecting this mobility.[113,114]

The differences between the two coordination patterns of phosphorodithioato ligands in **60** are reflected in the different values of the S—P—S bond angle (see Table 11). Thus, formation of a four-membered chelate ring MoS_2P, forces a diminished value of this angle, which is in the range 105–108° (compared with the ideal tetrahedral value of 109°), while bridging $S_2P(OR)_2$ ligand displays a broader S—P—S angle (115–117°).

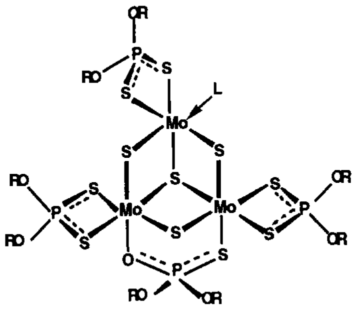
If the "loose coordination site" is occupied by a strong bidentate donor, like bipyridyl, this can force the phosphorodithioato ligand coordinated to the same site to become monodentate, as in **61**, a structure found in $Mo_3S_4\{S_2P(OEt)_2\}_4\cdot$bipy.[115] This is a rare, if not unique, example of a compound containing simultaneously three different types of coordinated phosphorodithioate ligand in the same molecule: monodentate, bidentate chelating and bridging.



61

The P—S bond lengths and S—P—S bond angles in the three types of ligand (Table 11) differ in agreement with the coordination patterns. Thus, in the monodentate ligand P—S 1.998 Å, P=S 1.901 Å; S—P—S 120.8°; in the bidentate ligands P—S bond lengths are in the range 1.943–1.985 Å and S—P—S 107.5° (av.), while in the bridge P—S 1.969 and 1.976 Å and S—P—S 115.7°.[115]

The bridging phosphorodithioato group in **61** can be replaced by other ligands, notably monothiophosphato (phosphorothioato) groups, as in **62**, or carboxylato groups, as in **63**. While compounds of type **62**, e.g. $Mo_3S_4\{S_2P(OEt)_2\}_3\{SOP(OEt)_2\} \cdot L$ (L = oxazole)[116] may have been formed by accidental hydrolysis of tetrakis(phosphorodithioato) complexes,



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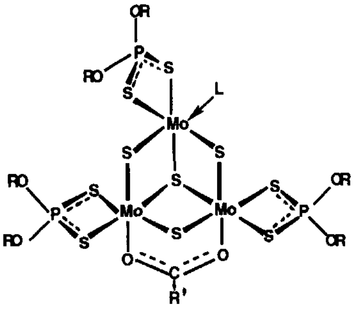
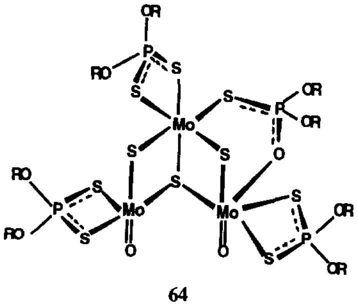


63

carboxylato-bridged complexes **63**, $Mo_3S_4\{S_2P(OEt)_2\}_3(\mu_2\text{-}R'COO)(L)$, with R′ = H, L = pyridine,[117] R′ = Me, L = pyridine,[117,118] MeCN,[119] and R′ = Et, L = pyridine,[120] have been prepared and studied in a systematic way. For crystal data and molecular dimensions see Table 11.

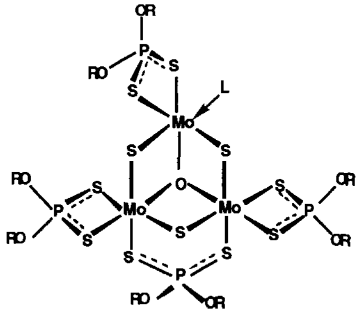
Oxidation of trinuclear complexes may lead to ruptured structures such as **64**, which contain a monothiophosphato (phosphorothioato) bridge and two oxomolybdenum centres, in addition to the chelating phosphorodithioates. Such a structure has been found in the compound $Mo_3S_3O_2\{S_2P(OEt)_2\}_3\{SOP(OEt)_2\}$. The phosphorodithioato ligands are chelating and the phosphoro(mono)thioato group is bridging.[121]



64

A related family of trinuclear phosphorodithioato complexes is based upon the Mo_3S_3O core, in which the central, triply bridging sulphur atom in a capping position, has been replaced by oxygen.

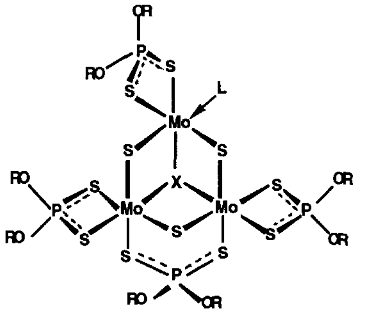
Thus, complexes of type **65**, with L = oxazole[109] and imidazole,[122] have been structurally investigated. The available crystal data are listed in Table 11.



65

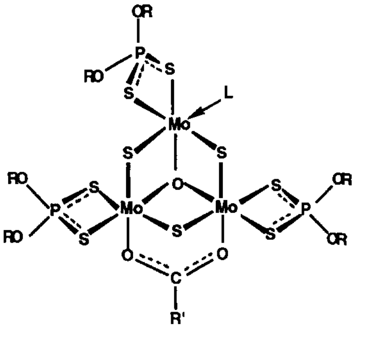
Here, the two different coordination patterns of the phosphorodithioato ligands lead to differing P—S interatomic distances and S—P—S bond angles, as found in Mo_3S_4 derivatives above.

Mixed species, with approximately 50–50% degree of occupancy of the central site X by oxygen and sulphur, **66**, have also been described, e.g. $Mo_3S_3(O,S)\{S_2P(OEt)_2\}_4 \cdot L$ with L = thiourea.[105,123]



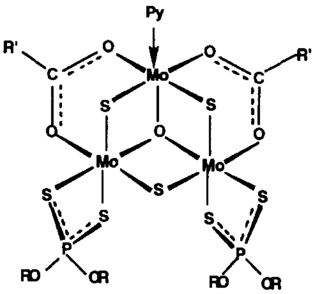
66

The phosphorodithioato bridge can be replaced by a carboxylato bridge, as illustrated by $Mo_3S_3O\{S_2P(OEt)_2\}_3(OAc)Py$ (**67**).[124]



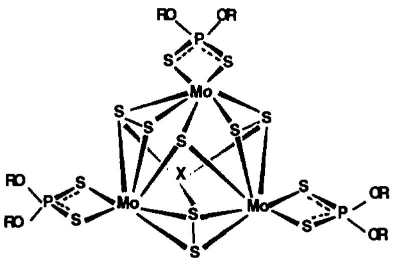
67

A further development is a structural change in the trinuclear complexes, where the bridging and one of the chelating phosphorodithioato ligands are replaced by two carboxylato bridges. This results in a structure such as **68**, with two chelating ligands. Examples are $Mo_3S_3O\{S_2P(OEt)_2\}_2(OAc)_2Py$,[125] and $Mo_3S_3O\{S_2P(OEt)_2\}_2(BzCOO)_2Py$.[126]



68

More complex structures, but related to those discussed above, are formed with three disulphido bridges between the molybdenum atoms. While maintaining the main features of previous structures, an additional halogen atom weakly interacts with three sulphur atoms, as observed in $Mo_3(S_2)_3S(X)\{S_2P(OEt)_2\}_3$ (**69**) with X = Cl,[92,127] and X = I,[128] and $Mo_3(S_2)_3(O)(X)\{S_2P(OEt)_2\}_3$ (**70**) with X = Cl,[129] and X = I.[130,131] The structures could also be shown as complete cubes, with a site occupied by a halogen (**69a** and **70a**).



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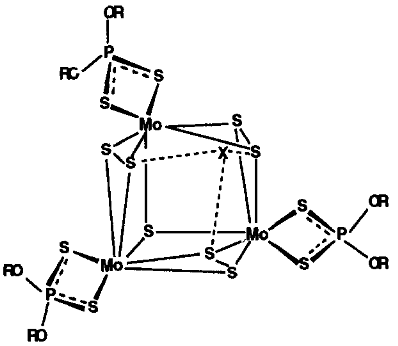
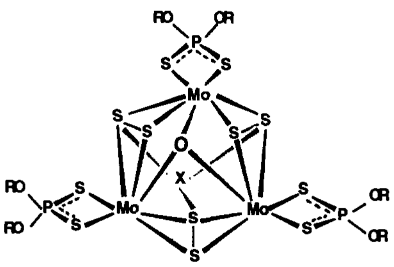


69A



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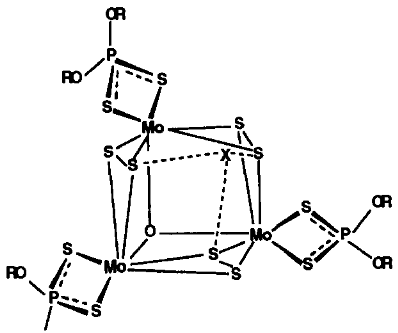
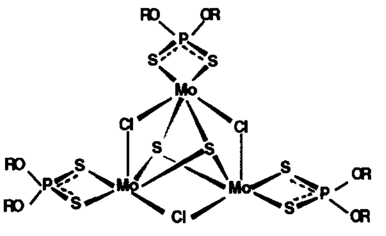


70A

Double trinuclear units, as in $Cl[Mo_3S_7\{S_2P(OEt)_2\}_3]_2[FeCl_4]$ (**71**)[132] and the related oxo derivative $Cl[Mo_3S_6O\{S_2P(OEt)_2\}_3]_2$ $[FeCl_4]$ (**72**),[133] are formed by sharing a chlorine atom via S...Cl (semi)bonds (2.936–3.145 Å).

Trinuclear molybdenum phosphorodithioato complexes are also known, in which halogen bridges are part of the central core bonding the molybdenum atoms together. Thus, in $Mo_3S_2Cl_3\{S_2P(OEt)_2\}_3$ the phosphorodithioato ligands occupy only chelating positions (structure **73**)[134] while in Mo_3S_2 $Cl_3\{S_2P(OEt)_2\}_4$ an additional bridging phosphorodithioato ligand forces one chlorine atom into a monodentate position (structure **74**).[135]



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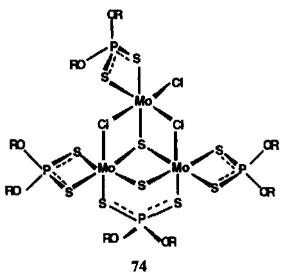
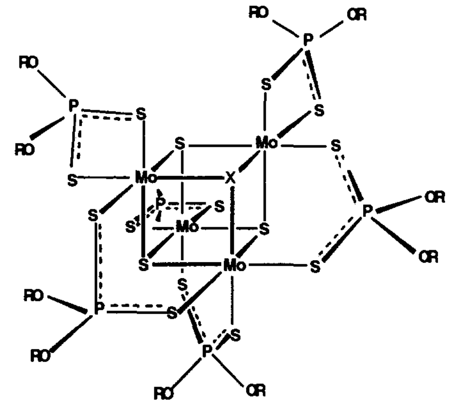


74

(iv) Tetranuclear complexes. A fairly large number of phosphorodithioato molybdenum complexes are formed about a central Mo_4S_4 or Mo_4S_3O cubane core, with the general composition $Mo_4S_3X\{S_2P(OR)_2\}_6$ (where X = S or O).[136] Two isomeric forms are possible: an α-isomer, with three bridging and three chelating phosphorodithioato ligands, α-$Mo_4S_3X\{\mu$-$S_2P(OR)_2\}_3\{S_2P(OR)_2\}_3$, **75**, and the β-isomer, with two bridging and four chelating phosphorodithioato ligands, β-$Mo_4S_3X\{\mu$-$S_2P(OR)_2\}_2\{S_2P(OR)_2\}_4$, **76**. The β-$Mo_4S_4\{S_2P(OEt)_2\}_6$ complex has been reported by two groups.[136,137]



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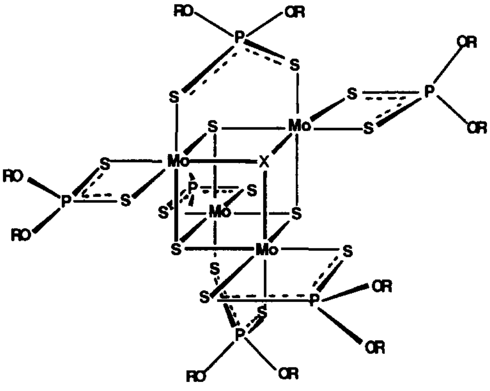

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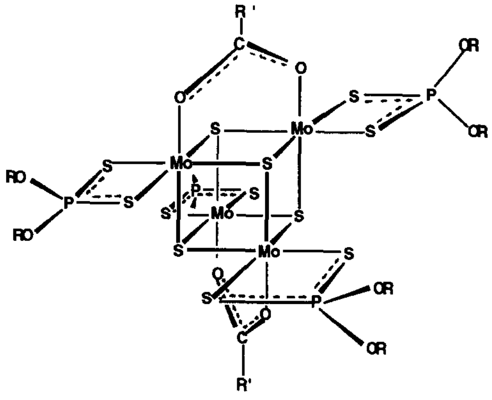
Similar compounds with X = O, i.e. α-$Mo_4S_3O\{S_2P(OEt)_2\}_6$ (structure **75**, X = O),[138] β-$Mo_4S_3O\{S_2P(OEt)_2\}_6$ (structure **76**, X = O),[139] and α-$Mo_4S_3O\{S_2P(OEt)_2\}_6\cdot 3MeCN$ (**77**)[140] have been reported.

Compounds whose structures have been established by X-ray diffraction are listed in Table 12 which shows the obvious differences between the molecular dimensions of the bridging and chelating ligands.

The two bridges of the β-structure can be replaced by carboxylato bridges, resulting in formation of $Mo_4S_4\{S_2P(OR)_2\}_4(\mu$-$RCOO)_2$, **78**. Several such compounds are known, including Mo_4S_4

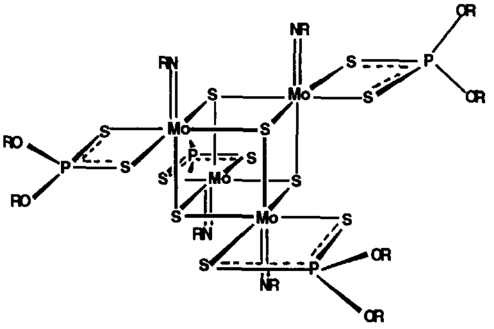
$\{S_2P(OEt)_2\}_4(\mu\text{-}OAc)_2$,[141] $Mo_4S_4\{S_2P(OEt)_2\}_4(\mu\text{-}OAc)_2H$,[142] and $Mo_4S_4\{S_2P(OEt)_2\}_4(\mu\text{-}PhCOO)_2$[143] (see Table 12).



78

The exchange of bridging phosphorodithioato ligands for carboxylato ligands, while the chelating groups are maintained, suggests that the latter are more strongly bound.

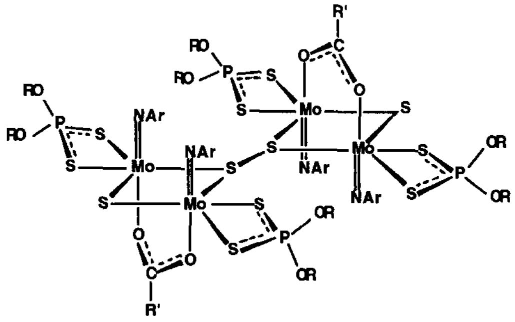
The compound $Mo_4S_4\{S_2P(OEt)_2\}_4(NC_6H_4Me\text{-}p)_4$ also contains a cubic core, but the structure is constructed differently. Each molybdenum atom forms a chelate MoS_2P ring and a Mo=N bond with the arylimido group, as shown in **79**.[144]



79

A related compound, $Mo_4S_4O_2\{S_2P(OEt)_2\}_4(NC_6H_4Me\text{-}p)_2$, **80**, has also been reported.[93] It differs from **79** only by replacement of two NAryl by two oxo groups.

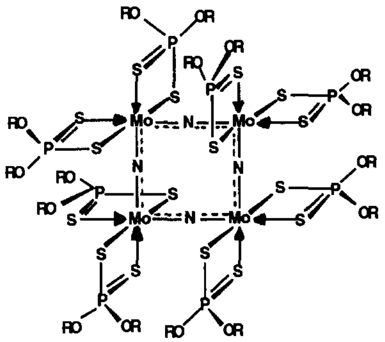
A completely different structure was found in the compound $Mo_4S_4\{S_2P(OEt)_2\}_4(NC_6H_4Me\text{-}p)_4(\mu\text{-}OOCCF_3)_2$.[145] This complex is in fact a dimer consisting of two dinuclear units, joined by an S—S bond, **81** (R' = CF_3). Compound **81** contains only chelating phosphorodithioato ligands.



81

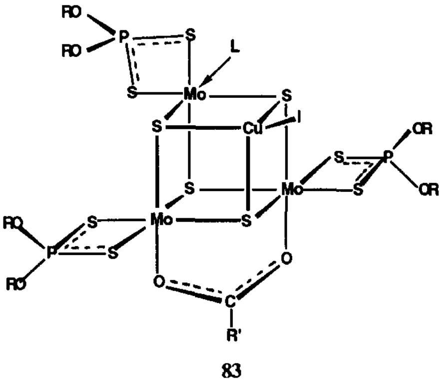
The compound $Mo_4N_4\{S_2P(OEt)_2\}_8$ is based upon on a rare monocyclic Mo_4N_4 skeleton, **82**. The square Mo_4N_4 ring is almost planar and each molybdenum atom participates in two additional MoS_2P chelate rings. The Mo—N bond lengths are practically equal (1.862–1.870 Å) and indicate some degree of double bonding, while the Mo—S and P—S interatomic distances are nonequivalent.[146] Short Mo—S bonds (range 2.469–2.510 Å) are associated with long P—S bonds (range

1.993–2.020 Å) and long Mo—S bonds (range 2.637–2.680 Å) pair with short P—S bonds (range 1.955–1.990 Å).[146] Therefore, coordination pattern **2** probably best describes the ligand structure here.



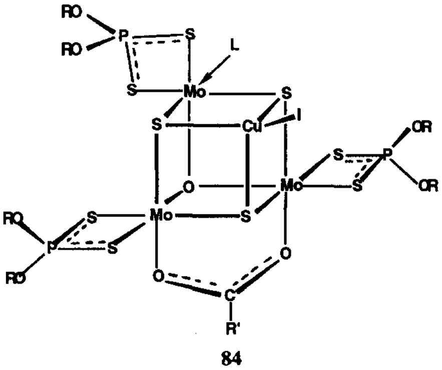
82

(v) Heterometallic molybdenum phosphorodithioates. Trinuclear molybdenum complexes can be converted into complete cubanes by inserting a metal atom in the vacant position of structure **58b**. Several cubane structures **83** in which one corner of the cube is occupied by a CuI unit have been reported, e.g. $Mo_3CuS_4(I)\{S_2P(OEt)_2\}_3(\mu\text{-}R'COO)(L)$, with R′ = H, L = Py,[147] R′ = Me, L = H_2O,[148] DMF,[149] DMSO;[148] R′ = CCl_3, L = MeCN[150] and R′ = Ph, L = Py.[148] Their structures contain only chelating phosphorodithioato ligands. Molecular dimensions are listed in Table 13.



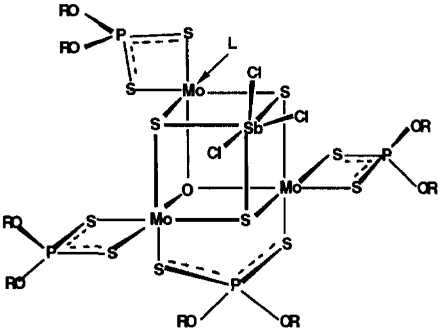
83

One of the sulphur atoms of the cubane unit can be replaced by oxygen, to form $Mo_3CuS_3O(I)\{S_2P(OEt)_2\}_3$ (μ-OAc)(L), (**84**) L = Py, DMF.[151]



84

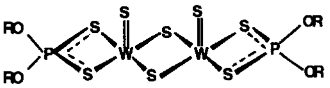
An $SbCl_3$ molecule can also be inserted in the corner of the cube, as shown in **85**, and the compounds $Mo_3S_4SbCl_3\{S_2P(OEt)_2\}_4 \cdot 2H_2O$,[152] $Mo_3S_4SbCl_3\{S_2P(OEt)_2\}_4 \cdot$ oxazole[152,153] and $Mo_3S_4SbCl_3\{S_2P(OEt)_2\}_4 \cdot EtOH$[152,154] have been investigated.



85

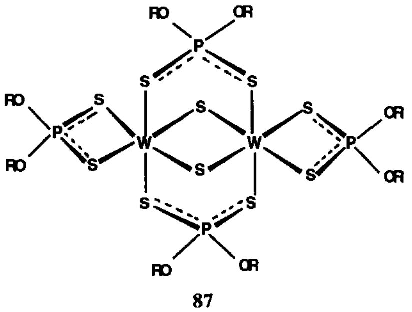
c. Tungsten. The chemistry of tungsten phosphorodithioato complexes appears very similar to that of molybdenum, but far fewer compounds have been investigated structurally. Some structural differences are, however, observed.

The dinuclear compound $W_2S_4\{S_2P(OEt)_2\}_2$ contains a double sulphur bridge and two chelating phosphorodithioato ligands, **86**,[91,155] and is similar to its molybdenum analogue. Two crystalline forms of this compound were obtained, depending on the synthesis method used.[156]



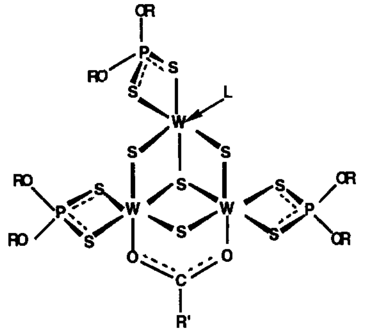
86

A compound of composition $W_2S_2\{S_2P(OEt)_2\}_4$ differs from its molybdenum counterpart in that the tungsten compound contains two bridging and two chelating ligands, **87**,[157] whereas the molybdenum compound (structure **51**) contains only chelating ligands. In **87** the chelating ligands are isobidentate and the bridging groups are symmetric (coordination pattern **10**). Unlike the four-membered chelate WS_2P rings, the five-membered W_2S_2P rings present in this structure are not planar. The W—S bonds to chelating ligands (av. 2.57 Å) are longer than those to bridging ligands (av. 2.48 Å). As usual, the bridging S—P—S bond angle (114.4°) is larger than the chelating S—P—S bond angle (106.70).[157]



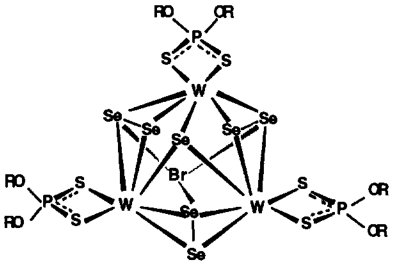
87

A trinuclear compound $W_3S_4\{S_2P(OEt)_2\}_3(\mu\text{-}OAc)(pyridine)$[158] has structure **88** (R′ = Me, L = Py), which is reminiscent of the molybdenum analogue.



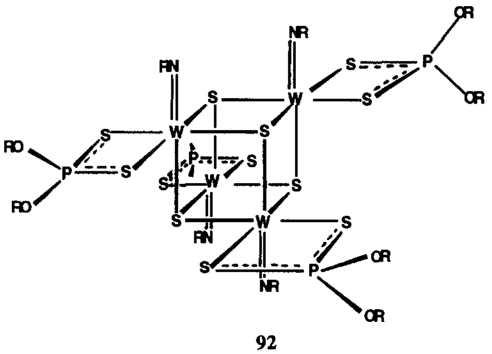
88

The trinuclear compound $W_3Se_7Br\{S_2P(OEt)_2\}_3$ has no molybdenum counterpart in terms of composition (no molybdenum–selenium core of this type in a phosphorodithioate) but the structural type **89** is similar to **69**. The ligand is isobidentate.[159]



89

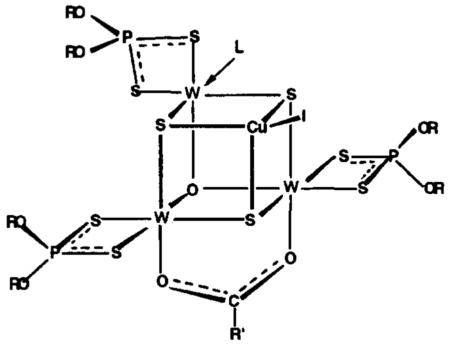
Cubane clusters (both α- and β-isomers) similar to those of molybdenum are also known for tungsten, i.e. $\alpha\text{-}W_4S_4\{S_2P(OEt)_2\}_6$ (**90**),[160] $\beta\text{-}W_4S_4\{S_2P(OEt)_2\}_6$ (**91**),[136] and $W_4S_4\{S_2P(OEt)_2\}_4(NC_6H_4Me\text{-}p)_4$ (**92**).[161]



92

Several cubane structures containing tungsten and copper, of the general formula $W_3CuS_4(I)\{S_2P(OEt)_2\}_3(\mu\text{-}R'COO)(L)$, with R′ = Me, L = MeCN,[162] Py;[163,164] R′ = CCl_3, L = MeCN[165] and R′ = Ph, L = MeCN,[166] have been investigated crystallographically. Their structure of type **93** is similar to that of molybdenum analogues (structure **83**).

Crystal data and molecular dimensions of tungsten phosphorodithioato complexes are collected in Table 14.

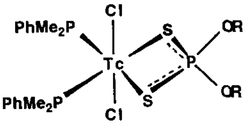


93

7. *Group* 7 : Mn, Tc, Re

Attempts to prepare manganese phosphorodithioato complexes resulted in the formation of ionic $[Mn(phen)_3][S_2P(OEt)_2]_2$ (**94**), in which the metal is octahedrally coordinated only by *ortho*-phenanthroline, leaving the phosphorodithioate as counter-ion, outside the coordination sphere.[167] The P—S bonds in the anion are in the range 1.942–1.956 Å and the S—P—S bond angle (av. 118.50°) is broader than tetrahedral.

In spite of the rarity of technetium compounds, a phosphorodithioato complex of this metal, $TcCl_2\{S_2P(OMe)_2\}(PMe_2Ph)_2$ (**95**) has been investigated by X-ray diffraction. The compound displays an octahedral coordination geometry with isobidentate chelating phosphorodithioate (Tc—S 2.475 Å, P—S 1.992 Å).[168]



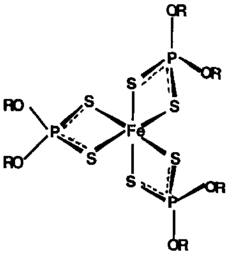
95

The crystal data are collected in Table 15.

No rhenium phosphorodithioate crystal structure has been reported so far in the literature.

8. *Group* 8 : Fe, Ru, Os

a. Iron. The iron(III) phosphorodithioato complexes investigated by X-ray diffraction Fe $[S_2P(OR)_2]_3$ with R = Me[169] and Pr^i,[170] display an octahedral geometry, **96**, with three isobidentate chelating ligands. The octahedron is distorted by a twist angle of 20° between the two triangular faces of the octahedron (compared with a twist angle of 60° for the ideal octahedron).



96

The iron(II) complex $NMe_4[FeCl\{S_2P(OMe)_2\}_2]$ displays trigonal bipyramidal geometry **97** with practically isobidentate ligands.[169] As expected axial Fe—S bonds (2.570 and 2.603 Å) are somewhat longer than equatorial Fe—S bonds (2.427 and 2.450 Å) and this induces some asymmetry in the P—S bonds as well (1.971–1.990 Å).

Table 14. Crystal structure data for tungsten phosphorodithioato complexes (R = Et in compound **86**)

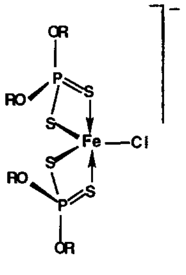
Struc-ture no.	R′ L	Space group	*a* *b* *c*	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
86	form A	$P2_1/n$	10.122	—	2.005	2.003	2.471	2.476	102.0	89.7	89.8	chel	155
			12.813	90.25	2.009	1.997	2.467	2.487	102.9	89.0	88.7	chel	
			18.267	—									
	form A	$P2_1/n$	18.230	—	2.012	2.022	2.483	2.473	102.3	89.2	89.4	chel	156
			12.905	90.5	1.992	2.022	2.498	2.473	103.8	88.3	88.2	chel	
			10.153	—									
	form B	$P2_1/a$	14.045	—	2.002	2.011	2.467	2.466	101.5	89.5	89.3	chel	91
			10.341	113.09	1.993	2.009	2.482	2.475	102.6	89.1	89.0	chel	
			17.994										
	form B	$P2_1/a$	13.844	—	2.000	2.016	2.438	2.430	100.3	89.7	89.6	chel	156
			10.280	113.2	2.019	1.998	2.480	2.477	101.7	89.5	90.0	chel	
			17.907	—									
87		$P2_1/n$	10.905	—	1.988	2.002	2.561	2.582	106.8	88.7	87.5	chel	157
			13.784	110.48	2.012	2.009	2.507	2.461	114.4	103.9	105.6	bridge	
			13.360	—									
88	Me, Py	$P\bar{1}$	13.939	101.08	1.975	1.999	2.551	2.509	106.1	87.7	88.4	chel	158
			16.018	105.69	1.979	1.997	2.569	2.535	107.4	87.1	87.7	chel	
			9.627	77.64	1.953	1.986	2.557	2.507	106.5	87.8	88.5	chel	
89		$P2_1/c$	13.169	—	1.983	1.972	2.515	2.531	103.1	90.4	90.2	chel	159
			22.651	121.09	2.034	2.025	2.553	2.548	103.5	89.4	89.7	chel	
			15.067	—	2.040	2.040	2.568	2.548	107.3	86.2	88.0	chel	
90		$P\bar{1}$	14.063	92.06	1.961	2.000	2.543	2.560	106.4	88.0	88.4	chel	160
			16.289	95.24	1.990	1.980	2.546	2.547	106.8	87.3	87.7	chel	
			13.377	73.06	1.970	1.985	2.542	2.552	107.5	86.0	86.6	chel	
					1.967	1.990	2.564	2.574	116.9	107.2	107.7	bridge	
					1.970	2.010	2.561	2.567	116.7	107.5	107.6	bridge	
					2.000	1.987	2.558	2.577	117.0	107.7	108.8	bridge	
91		$P2/n$	12.807	—	2.019	1.979	2.559	2.556	107.5	86.7	87.6	chel	136a
			17.195	97.33	1.960	1.988	2.585	2.539	107.3	87.5	88.2	chel	
			13.488	—	1.926	1.926	2.546	2.546	123.2	111.2	111.2	bridge	
					2.047	2.047	2.580	2.580	103.6[a]	123.2[a]	123.2[a]	bridge	
92	Ar =	$P\bar{1}$	14.650	101.82	1.985	1.987	2.539	2.538	107.1	87.3	87.2	chel	161
	p-Tol		19.133	104.61	1.983	1.988	2.557	2.535	107.6	85.6	86.1	chel	
			13.073	75.92	1.992	1.996	2.561	2.543	107.7	85.2	85.6	chel	
					1.987	1.994	2.523	2.559	106.5	88.3	87.2	chel	
93	Me,	$P\bar{1}$	10.152	111.00	1.973	1.992	2.554	2.499	106.7	87.1	88.0	chel	162
	MeCN		14.325	104.43	1.994	1.980	2.521	2.559	107.3	86.6	85.8	chel	
			15.935	97.89	1.983	1.995	2.543	2.496	105.8	87.5	87.5	chel	
93	Me, Py	$P2_1/n$	14.196	—	1.984	2.003	2.554	2.506	105.8	87.7	88.6	chel	163,
			17.203	86.02	1.998	2.000	2.573	2.526	106.5	86.8	88.1	chel	164
			18.075	—	1.981	2.005	2.562	2.499	105.7	87.5	88.8	chel	
93	CCl_3,	$P\bar{1}$	11.684	103.88	1.971	2.014	2.567	2.504	107.0	86.5	87.4	chel	165
	MeCN		14.243	109.01	1.984	2.008	2.537	2.476	104.9	87.9	89.1	chel	
			15.455	65.64	1.981	1.997	2.533	2.487	105.6	87.3	88.2	chel	
93	Ph,	$P\bar{1}$	11.645	96.15	2.004	1.985	2.521	2.563	106.7	87.7	86.9	chel	166
	MeCN		18.565	113.65	1.959	2.007	2.496	2.556	107.3	86.9	87.4	chel	
			11.292	93.77	2.002	1.971	2.487	2.549	105.8	87.3	86.2	chel	

[a] Because of large thermal parameters of the phosphorus atom these data are of low quality.

Table 15. Crystal structure data for Group 7 metal (Mn, Tc, Re) phosphorodithioato complexes

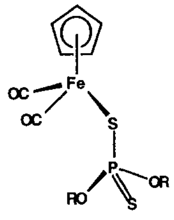
Structure no.	R	Space group	a b c	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
94[a]	Et	$P\bar{1}$	17.340	84.66	1.946	1.924	—	—	118.3	—	—	ionic	167
			12.738	115.46	1.942	1.956	—	—	118.7	—	—	ionic	
			12.651	115.94									
95	Me	Pbcn	16.207	—	1.992	1.992	2.475	2.475	106.1	86.9	86.9	chel	168
			10.445	—									
			14.878	—									

[a] Amended data.



97

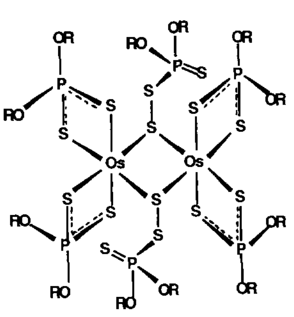
Three cyclopentadienyliron dicarbonyl phosphorodithioates, η^5-CpFe(CO)$_2${S$_2$P(OR)$_2$} with Cp = C$_5$H$_5$, R = Et,[171] Pr^i[172] and Cp = C$_5$Me$_5$, R = Pr^i[173] contain monodentate ligands in a typical piano-stool structure **98**. Molecular dimensions are given in Table 16.



98

b. Ruthenium. No ruthenium phosphorodithioate crystal structure has been determined.

c. Osmium. The only relevant osmium compound which has been investigated by X-ray diffraction, contains two trithio (Pr^{i}O)$_2$(S)PSS ligands in an unusual bridging configuration **99** and four phosphorodithioato chelating ligands.[174,175]



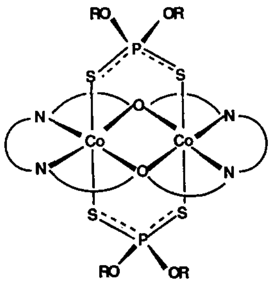
99

The molecular dimensions are listed in Table 16.

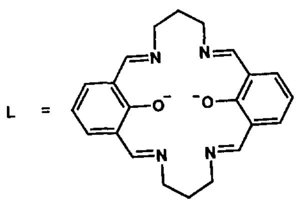
9. *Group* 9 : Co, Rh, Ir

a. Cobalt. The octahedral Co{S$_2$P(OMe)$_2$}$_3$ complex (**100**) displays a twofold symmetry axis through Co and P(1) and the ligands are isobidentate chelating.[176] A hemihydrate Co{S$_2$P(O Et)$_2$}$_3$ · 1/2H$_2$O (**101**) has also been investigated.[177]

A mixed ligand dinuclear complex $Co_2\{S_2P(OEt)_2\}_2 \cdot L$ (**102**) where L = 11,23-dimethyl-3,7,15,19-tetraazatricyclo($19^{3.1.1}$-9^{13})-hexacosa-2,7,9,11,13(26),14,19,21(25)22,24-decaene-25,26-diolate, containing two phosphorodithioato symmetrical bridges (coordination pattern **7**), has been described.[178]

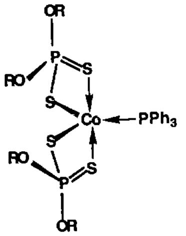


102



102

Cobalt(II) phosphorodithioates can be stabilized as five- and six-coordinate adducts or anions. Thus, five-coordinate $Co\{S_2P(OMe)_2\}_2 \cdot PPh_3$ displays a trigonal bipyramidal geometry, **103**, with non-equivalent axial (Co—S 2.569 and 2.664 Å) and equatorial bonds (Co—S 2.325 and 2.333 Å).[179,180] The usual long M—S/short P—S bond pairing is observed in this compound, which imposes non-equivalence on the P—S bonds (short 1.941 and 1.961 Å; long 1.997 and 2.010 Å).

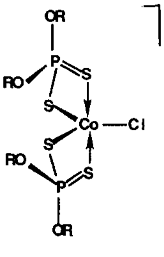


103

Table 16. Crystal structure data for Group 8 metal phosphorodithioates (Fe, Ru, Os)

Structure no.	R	Space group	*a* *b* *c*	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
96	Me	C2/c	14.211	—	1.991	1.994	2.491	2.465	107.9	85.7	85.1	chel	169
			11.115	97.23	1.994	1.994	2.465	2.465	107.0	86.0	86.0	chel	
			12.823	—									
96	Pr^i	C2/c	11.030	—	1.998	1.998	2.461	2.461	105.7	86.8	86.8	chel	170
			27.110	87.50	1.985	2.007	2.491	2.472	108.5	94.9	85.0	chel	
			11.657	—									
97	Me	$P\bar{1}$	7.165	83.98	1.990	1.973	2.427	2.570	110.9	85.2	81.8	chel	169
			8.628	85.32	1.985	1.971	2.450	2.603	110.3	86.2	82.4	chel	
			16.526	89.80									
98	Et	$P2_1/n$	7.440	—	1.933	2.018	—	2.304	112.1	—	111.2	uni	171
			14.545	94.42									
			14.454	—									
98	Pr^i	$P2_1/c$	13.189	—	1.944	2.026	—	2.322	112.5	—	109.1	uni	172
			8.636	94.19									
	Cp=		16.113	—									
	C_5Me_5												
98	Pr^i	$P2_1/c$	13.718	—	1.940	2.021	—	2.312	111.9	—	112.0	uni	173
	Cp =		11.090	98.16									
	C_5Me_5		14.985	—									
99	Pr^i	$P\bar{1}$	13.695	97.4	1.994	2.014	2.469	2.472	104.0	88.4	87.9	chel	174,
			13.747	97.6	1.981	2.010	2.384	2.454	102.0	88.3	85.7	chel	175
			10.707	117.4									

Five-coordinate cobalt(II) is also present in $[\mathrm{NMe_4}][\mathrm{CoCl\{S_2P(OMe)_2\}_2}]$, which displays trigonal bipyramidal geometry **104**.[169] The non-equivalence of P—S (short 1.964 and 1.965 Å, long 1.996 and 2.000 Å) and Co—S bonds (long 2.615 and 2.651 Å, short 2.337 and 2.358 Å) is similar to that noted in the neutral triphenylphosphine adduct cited above.



104

Six-coordinate cobalt(II) occurs in $\mathrm{Co\{S_2P(OEt)_2\}_2 \cdot 2Py}$ (**105**).[181] Molecular dimensions of cobalt complexes are listed in Table 17.

b. Rhodium. No rhodium phosphorodithioato complexes seem to have been structurally investigated by X-ray diffraction.

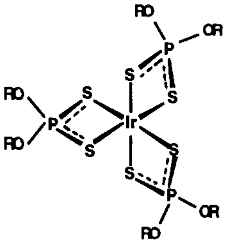
c. Iridium. Only one iridium phosphorodithioate, $\mathrm{Ir\{S_2P(OPr^i)_2\}_3}$, **106**, has been investigated by X-ray diffraction,[182] which shows the presence of two independent molecules in the unit cell. The ligand is anisobidentate and the molecular dimensions are given in Table 17. A curiosity of this compound is the non-equivalence of the three ligands in the coordination octahedron, as seen from

Table 17. Crystal structure data for Group 9 (Co, Rh, Ir) metal phosphorodithioato complexes

Structure no.	R	Space group	*a* *b* *c*	*α* *β* *γ*	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
100	Me	C2/c	13.895	—	1.981	1.983	2.315	2.340	103.5	86.6	85.9	chel	176
			11.084	97.81	1.986	1.986	2.312	2.312	102.3	86.8	86.8	chel	
			13.020	—									
101	Et	$P\bar{1}$	9.805	89.46	2.007	1.992	2.321	2.313	103.2	85.5	86.1	chel	177
			9.812	89.42	2.007	2.003	2.314	2.326	103.0	85.7	86.2	chel	
			14.271	86.95	2.004	2.017	2.318	2.320	102.8	85.8	86.0	chel	
102	Et	$P\bar{1}$	18.644	84.99	1.968	1.970	2.680	2.650	118.1	110.7	108.1	bridge	178
			11.694	82.61	1.950	1.969	2.642	2.622	119.1	110.0	109.6	bridge	
			9.487	73.48									
103	Me	$P2_1/n$	26.712	—	1.941	2.010	2.569	2.325	109.0	81.4	86.5	chel	179,
			9.495	95.43	1.961	1.997	2.664	2.333	111.6	78.6	86.6	chel	180
			11.180	—									
104	Me	$P\bar{1}$	7.164	84.59	2.000	1.965	2.337	2.615	111.1	86.3	79.6	chel	169
			8.612	84.63	1.996	1.964	2.358	2.651	110.4	87.5	80.3	chel	
			16.504	89.41									
105	Et	$P2_1/c$	8.117	—	1.975	1.976	2.506	2.524	111.1	84.3	83.9	chel	181
			17.183	104.19									
			9.901	—									
106	Pr^i	$P\bar{1}$	8.970	98.54	A[a]								182
			10.513	88.87	1.949	1.957	2.436	2.394	104.7	87.4	88.4	chel	
			19.107	98.18	2.014	2.034	2.373	2.334	102.1	86.6	87.2	chel	
					2.003	2.054	2.382	2.390	101.1	88.9	87.7	chel	
					B[a]								
					2.062	2.085	2.376	2.341	99.0	88.2	88.6	chel	
					1.978	1.984	2.417	2.456	103.3	89.4	88.1	chel	
					1.965	2.032	2.413	2.413	104.2	87.8	86.3	chel	

[a] Two independent molecules in the unit cell.

the P—S and Ir—S bond lengths and the S—P—S bond angles. From the P—S distances it appears that two of the ligands are reasonably symmetrically coordinated in each independent molecule, but the third is in each case anisobidentate. It is a curious compound though with such a variation in P—S lengths between ligands.

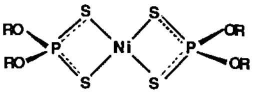


106

10. *Group* 10: Ni, Pd, Pt

a. Nickel. Nickel(II) phosphorodithioates seem to be another class of complexes favoured by crystallographers, as they are surpassed only by the number of molybdenum compounds investigated. Crystal data and molecular dimensions for nickel phosphorodithioato complexes are collected in Table 18.

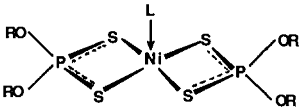
Square planar nickel(II) complexes, **107**, were among the first metal phosphorodithioates to be investigated by X-ray diffraction and now the structures of Ni$\{S_2P(OR)_2\}_2$ with R = Me,[183] Et,[184–186] Pr^n,[187] Pr^i [188,189] cyclo-C_6H_{11},[190] are known. Derivative of diols, such as 1,1′-biphenyl-2,2′-diol[191] and 1,1′-binaphthyl-2,2′-diol[192] have also been studied.



107

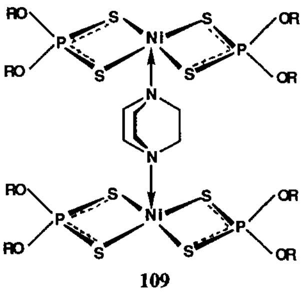
The nickel(II) phosphorodithioates display the tendency to coordinate one or two additional donor molecules, forming five- and six-coordinate adducts, respectively.

Five-coordinate complexes are obtained with bulky or sterically demanding donor molecules. Thus, tertiary phosphine adducts Ni$\{S_2P(OR)_2\}_2 \cdot$L with R = Me, L = PMe_3,[193] and R = Et, L = PPh_3[194] are square pyramidal compounds, **108**, with the metal atom *ca* 0.5 Å above the basal plane of four sulphur atoms from the two basically isobidentate ligands.



108

Other five-coordinate adducts investigated are Ni$\{S_2P(OMe)_2\}_2 \cdot$quinoline (tetragonal pyramidal, **108**, L = quin)[195] and 2Ni$\{S_2P(OEt)_2\}_2 \cdot$DABCO (binuclear with two distorted tetragonal pyramidal coordination centres) **109**.[196]

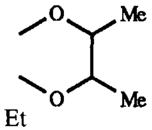


109

Table 18. Crystal structure data for nickel phosphorodithioato complexes

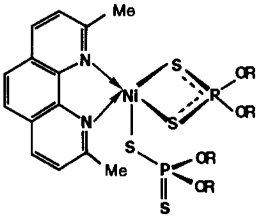
Structure no.	R	L	Space group	*a* *b* *c*	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
107	Me		Pbca	10.290	—	1.979	1.984	2.225	2.219	1.027	84.4	84.5	chel	183
				8.640	—									
				16.356	—									
107	Et		P2$_1$/c	10.48	—	1.947	1.986	2.213	2.208	103.1	84.7	83.9	chel	185
				10.22	102.50									
				8.62	—									
107	Et		P2$_1$/c	10.493	—	1.986	1.993	2.230	2.236	103.1	84.3	84.0	chel	186
				10.300	102.59									
				8.760	—									
107	Pr^n		P2$_1$/n	8.165	—	1.978	1.999	2.220	2.230	102.5	84.8	84.1	chel	187
				8.706	103.76									
				14.935	—									
107	Pr^i		Bb	14.160	—	2.002	2.006	2.214	2.247	102.5	84.6	83.7	chel	188
				18.094	—	1.985	2.003	2.231	2.214	102.2	84.6	84.6	chel	
				10.323	61.02									
107	Pr^i		C2/c	14.047	—	1.991	1.993	2.227	2.216	101.7	84.9	85.2	chel	189
				10.338	109.71									
				16.807	—									
107	Cy		P2$_1$/n	11.802	—	1.982	1.993	2.221	2.216	101.7	84.9	85.0	chel	190
				9.336	96.72									
				14.177	—									
107	(RO)$_2$= biph		P2$_1$/c	9.990	—	1.972	1.977	2.226	2.243	105.0	82.8	83.2	chel	191
				7.827	99.71									
				16.483	—									
107	(RO)$_2$= binaph		P2$_1$2$_1$2$_1$	9.630	—	1.971	1.975	2.242	2.233	106.1	81.9	82.1	chel	192
				10.171	—	1.966	1.967	2.249	2.239	106.9	79.9	80.2	chel	
				37.489	—									
108	Me	PMe$_3$	P$\bar{1}$	13.001	99.483								chel	193
				9.418	84.150									
				13.780	98.979									
108	Et	PPh$_3$	P$\bar{1}$	12.985	99.58	1.969	1.969	2.395	2.433	107.2	84.4	83.7	chel	194
				13.748	99.10	1.960	1.977	2.436	2.391				chel	

Table 18—*continued.*

Structure no.	R	L	Space group	*a* *b* *c*	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
108	Me	quin	C2/c	15.61 10.11 29.75	— 101.3 —	1.99 1.99	2.00 2.01	2.42 2.43	2.42 2.39	106.8 105.5	84.8 85.2	84.7 84.6	chel chel	195
109	Et		$P\bar{1}$	13.171 8.333 10.602	105.15 102.32 90.93	1.969 1.977	1.995 1.978	2.426 2.437	2.450 2.441	109.1 110.4	83.6 83.0	82.4 92.9	chel chel	196
110	Me		$P2_1/c$	7.86 14.51 21.79	— 92.50 —	1.913 1.937	1.968 1.962	2.583 —	2.300 2.419	111.1 116.8	80.2 —	86.7 114.7	chel uni	195
110	$(RO)_2=$ 		$P2_1/c$	20.007 11.599 14.929	— 107.65 —	1.936 1.955	2.003 1.979	2.398 2.499	— 2.344	117.2 108.0	— 83.0	111.3 86.7	uni chel	197
111	Et	Py	$P2_1/c$	8.11 17.89 9.94	— 104.8 —	1.98	1.99	2.49	2.50	110.4	84.2	83.7	chel	198
111	Bu^n	Py	$P2_1/c$	13.753 9.256 15.306	113.8	1.971	1.972	2.486	2.511	111.7	82.0	82.6	chel	199
111	Cy	Py	$P\bar{1}$	8.438 14.885 6.366	99.25 93.46 92.01	1.821	1.827	2.302	2.303	118.8	83.1	83.0	chel	200
111	Cy	$BzNH_2$	P2/c	9.620 19.553 12.274	— 110.36 —	1.976	1.988	2.490	2.504	110.9	82.6	82.7	chel	201
112	Bu^n		$P2_1/n$	12.770 16.756 17.135	— 111.67 —	1.961 1.959	1.973 1.966	2.590 2.565	2.488 2.464	111.1 111.8	81.0 82.4	83.4 85.0	chel chel	202
113	Me	bipy	C2/c	12.131 15.102 13.972	— 121.06 —	1.970	1.973	2.519	2.485	111.8	82.2	83.0	chel	203
113	Bu^n	bipy	$P\bar{1}$	9.469 14.638 14.637	69.64 71.16 89.99	1.951 1.944	1.980 1.979	2.466 2.463	2.524 2.522	112.1 111.9	82.5 82.7	83.4 83.6	chel chel	204

113	Me	phen	$P2_1/c$	6.61	—	1.97	1.97	2.50	2.47	110.8	83.4	84.2	chel	195
		(yellow		18.57	100.17	1.97	1.97	2.52	2.48	111.6	83.0	84.1	chel	
		green)		18.86	—									
113	Me	phen	$P2_1/c$	14.914	—									205
		(bright		9.333	135.95									
		green)		23.359	—									
113	Et	phen	$C2/c$	15.500	—	1.959	1.972	2.509	2.471	110.2	84.1	84.8	chel	206
				17.400	101.21									
				10.347	—									
113	Et	TMED	$P2_1/n$	22.281	—	1.969	1.969	2.504	2.547	110.8	85.2	84.1	chel	207
				21.597	126.42	1.967	1.972	2.500	2.543	109.8	86.0	84.6	chel	
				13.237	—	1.965	1.976	2.502	2.554	109.6	86.5	84.8	chel	
						1.964	1.980	2.493	2.547	110.3	85.7	84.0	chel	
113	Et	DPED	$C2/c$	13.96	—	1.974	1.981	2.459	2.505	110.4	84.6	83.3	chel	208
				17.89	96.43									
				11.88	—									
114	Bu^n		$P2_1/n$	16.806	—	1.960	1.984	2.496	2.499	111.1	82.7	83.2	chel	209
				12.720	98.154	1.894	1.943	—	—	120.0	—	—	ionic	
				21.248	—									
115	Cy	R′ = Bu^n	$P\bar{1}$	13.513	95.66	1.953	1.960	2.549	2.624	111.1	84.0	85.9	chel	210
				16.040	90.23	1.960	1.969	—	—	117.6	—	—	ionic	
				12.891	75.46									
116	Me		$C2/c$	24.885	—									205
				11.313	131.65									
				19.771	—									
117	Et		$P\bar{1}$	9.029	108.9	1.939	1.999	2.264	2.247	105.1	83.7	82.8	chel	211
				13.432	90.2									
				17.246	109.4									

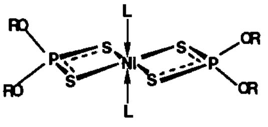
In the adduct with 2,9-dimethyl-phenanthroline, $\mathrm{Ni\{S_2P(OMe)_2\}_2\cdot 2,9\text{-}Me_2phen}$, the dinitrogen ligand displaces one sulphur from the coordination sphere, with the formation of an unusual complex containing both didentate and monodentate phosphorodithioato ligands, **110**. The coordination geometry is intermediate between square pyramidal and trigonal bipyramidal.[195]



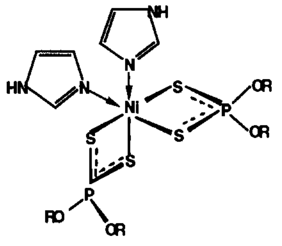
110

A similar geometry was found in $\mathrm{Ni\{S_2P(OCMe_2CMe_2O)\}_2\cdot 2,9\text{-}Me_2phen}$.[197]

Trans-octahedral complexes of type **111**, e.g. $\mathrm{Ni\{S_2P(OR)_2\}_2\cdot 2Py}$ with R = Et,[198] Bu^n,[199] Cy[200] and $\mathrm{Ni\{S_2P(OCy)_2\}_2\cdot 2PhCH_2NH_2}$[201] have been investigated, but surprisingly, the bisimidazole adduct $\mathrm{Ni\{S_2P(OBu^n)_2\}_2\cdot 2imidazole}$ is a *cis*-complex **112**.[202]

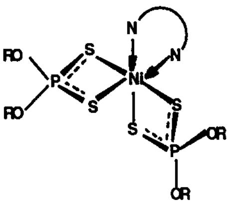


111



112

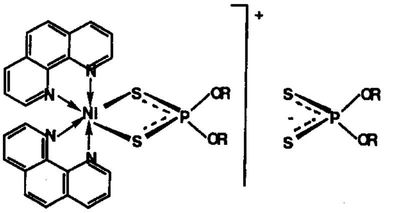
A *cis*-configuration of type **113** is imposed by polycyclic tertiary amines such as bipyridyl and orthophenanthroline, and has been found in $\mathrm{Ni\{S_2P(OR)_2\}_2\cdot bipy}$ with R = Me[203] and Bu^n,[204] and in $\mathrm{Ni\{S_2P(OR)_2\}_2\cdot phen}$ with R = Me[195,205] and Et.[206] Similarly, the adducts of substituted ethylenediamines $\mathrm{Ni\{S_2P(OEt)_2\}_2\cdot TMED}$[207] and $\mathrm{Ni\{S_2P(OEt)_2\}_2\cdot DPED}$,[208] are also *cis*-octahedral complexes.



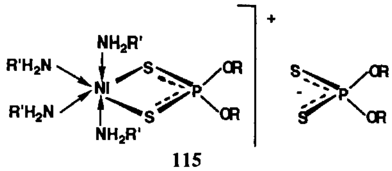
113

In all the nitrogen-base *cis*-adducts and Ni—S bonds become non-equivalent, as a result of *trans*-influence of the nitrogen donors. The data listed in Table 18 illustrate this tendency, showing differing Ni—S interatomic distances.

Occasionally, the nitrogen donor can displace the phosphorodithioato ligand, with formation of ionic complexes. Those investigated by X-ray diffraction include two six-coordinate complexes, $\mathrm{[Ni\{S_2P(OBu^n)_2\}(phen)_2]^+[\cdot S_2P(OBu^n)_2]^-}$, **114** ($\mathrm{R = Bu^n}$)[209] and $\mathrm{[Ni\{S_2P(OCy)_2\}(BuNH_2)_4]^+[S_2P(OCy)_2]^-}$, **115** (R = Cy),[210] as well as products of complete expulsion of the phosphorodithioate ligand from the coordination sphere, like $\mathrm{[Ni(phen)_3]\,[S_2P(OMe)_2]_2}$ (**116**).[205]

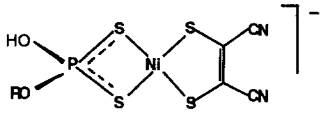


114



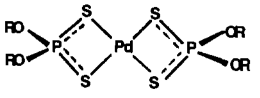
115

In the complex $[\mathrm{NBu_4}][\mathrm{Ni\{S_2P(OEt)(OH)\}S_2C(CN)_2}]$, **117**, an ethyl group has been lost (hydrolysis) during the preparation,[211] but the coordination of the phosphorodithioate ligand has been maintained.



117

b. Palladium. Only two palladium square planar phosphorodithioates, **118**, have been investigated, namely $\mathrm{Pd\{S_2P(OPr^i)\}_2}$[212] and $\mathrm{Pd\{S_2P(OC_6H_3Me_2)_2\}}$.[213] The molecular dimensions are listed in Table 19. In both compounds the ligands are isobidentate and the S—P—S bond angles of 103–105° suggest minor strain in four-membered chelate ring.



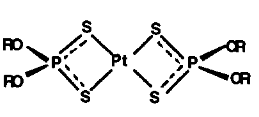
118

c. Platinum. Platinum(II) forms a square planar four-coordinate complex, with two isobidentate ligands, $\mathrm{Pt\{S_2P(OPr^i)_2\}_2}$, **119**,[214] and a cation with two coordinated phosphine ligands, in $[\mathrm{Pt\{S_2P(OPr^i)_2\}(PMe_2Ph)_2}]^+[\mathrm{PF_6}]^-$, **120**.[215]

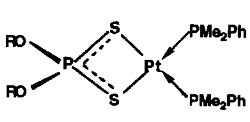
Table 19. Crystal structure data on palladium and platinum phosphorodithioato complexes

Structure no.	R	Space group	a b c	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
118	Pr^i	$P\bar{1}$	6.379	99.89	1.998	1.994	2.346	2.334	103.4	86.1	86.5	chel	212
			8.449	97.04									
			10.977	99.42									
118	$\mathrm{OC_6H_3}$-$\mathrm{Me_2}$	$P2_1/a$	16.075	115.46	1.984	1.992	2.346	2.344	104.9	82.4	82.3	chel	213
			8.353										
			14.268										
119	Pr^i	$P\bar{1}$	6.346	100.29	2.003	2.010	2.332	2.341	101.9	87.3	86.9	chel	214
			8.470	96.79									
			10.956	99.21									
120	Pr^i	$P\bar{1}$	10.913	93.59	A[a]								
			11.432	91.79	2.001	2.003	2.383	2.381	104.3	86.1	86.1	chel	215
			29.463	106.60									
					B[a]								
					1.997	2.012	2.364	2.367	102.6	87.4	87.0	chel	
121	Et	$P\bar{1}$	12.291	113.06	1.926	2.019	(3.954)	2.324	120.7	106.1	—	uni	216
			13.064	100.71	1.974	1.999	2.388	2.337	103.6	85.9	86.8	chel	
			13.679	114.72									
122	Et	$P2_1$	10.107	—	1.928	2.036	—	2.342	119.1	—	104.5	uni	217a
			20.002	114.23	1.993	2.011	2.373	2.328	102.4	86.2	87.0	chel	
			11.278	—									
123	Pr^i	$P2_1/c$	8.467	—	1.994	2.001	2.434	2.341	105.0	87.8	87.1	chel	217b
			15.846	98.03									
			21.540										

[a] Two independent molecules in the unit cell.

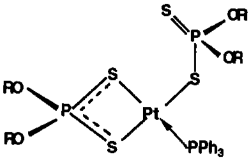


119



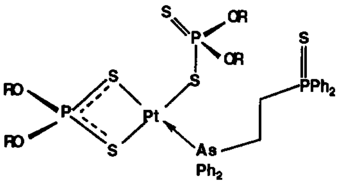
120

In the triphenylphosphine adduct, Pt$\{S_2P(OEt)_2\}_2 \cdot PPh_3$, **121**, one ligand is forced to become monodentate.[216] The differing *trans*-effects of phosphorus (from PPh_3) and sulphur (from the monodentate phosphorodithioate) produce slight differences in the Pt—S interatomic distances: Pt—S 2.388 Å *trans* to PPh_3, Pt—S 2.337 Å *trans* to sulphur from the monodentate phosphorodithioate and Pt—S 2.324 Å *trans* to sulphur from the chelating ligand.

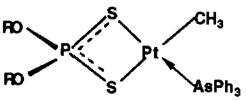


121

A second complex containing both chelating and mondentate phosphorodithioato ligands is Pt$\{S_2P(OEt)_2\}_2 \cdot$ApeS (ApeS = $Ph_2AsCH_2CH_2P({=}S)Ph_2$) which displays square planar geometry, **122**, with coordination by one arsenic and three sulphur atoms.[217a] The monodentate phosphorodithioato ligand in **121** and **122** can be replaced by an organic group and a methylplatinum compound **123** has been reported.[217b]



122

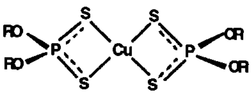


123

Molecular dimensions for platinum compounds are given in Table 19.

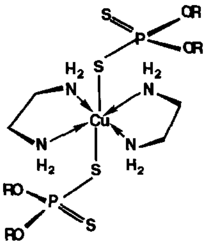
11. *Group* 11: Cu, Ag, Au

a. Copper. Copper(II) phosphorodithioates are difficult to obtain, because of internal oxidation of the ligand to bis(thiophosphoryl)disulphide, with concomitant reduction of the metal to copper(I). Therefore, only copper(II) compounds investigated by X-ray diffraction can be considered as authentic examples. In fact, the only copper(II) phosphorodithioate is Cu$\{S_2P(OC_6H_4Me\text{-}2)_2\}$, a square planar complex **124** with isobidentate ligands.[218] The Cu—S bonds average 2.33 Å.

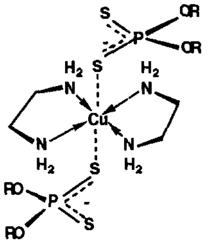


124

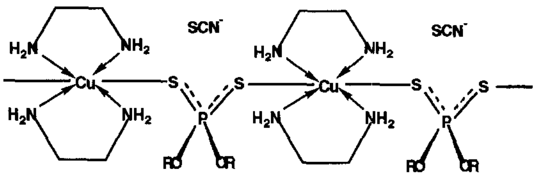
In two other copper(II) complexes, namely $Cu(en)_2\{S_2P(OEt)_2\}_2$,[219] and $Cu(en)_2\{S_2P(OEt)_2\}(SCN)$,[219] the Cu—S distance of *ca* 3.0 Å suggests that in the actual complex the square planar cation $[Cu(en)_2]^{2+}$, weakly interacts with phosphorodithioato anions. The original paper describes the phosphorodithioato ligand in $Cu(en)_2\{S_2P(OEt)_2\}_2$ as monodentate, (structure **125**) with Cu—S 3.04 and 2.90 Å, P—S 1.93–1.94 Å in one ligand and 1.98 and 2.01 Å in the second ligand.[219] In $Cu(en)_2\{S_2P(OEt)_2\}(SCN)$ the phosphorodithioato ligand is described as bridging (structure **126**) with Cu—S 3.09 and 2.99 Å, P—S 1.96 and 1.97 Å.[219]



125



125a

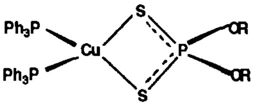


126

The SCN— anions are free in the lattice (non-coordinated). The abnormally long Cu—S distances make this description debatable. Probably a more correct description would be to consider packing of square planar $[Cu(en)_2]^{2+}$ cations and $(EtO)_2PS_2^-$ anions in the lattice. The equivalence of the P—S bonds in **125** supports this idea, and $Cu(en)_2\{S_2P(OEt)_2\}_2$ could then be reformulated as **125a**.

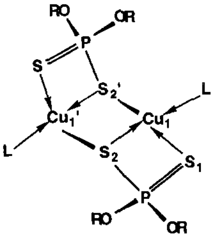
All other copper phosphorodithioates are copper(I) derivatives.

Mononuclear copper(I) phosphorodithioates are known only as triphenylphosphine adducts, $CuS_2P(OR)_2 \cdot 2PPh_3$ with R = Et[220] (structure **127**) and $(OR)_2 = OCH_2CMe_2CH_2O$.[221a] The coordination geometry is distorted tetrahedral.



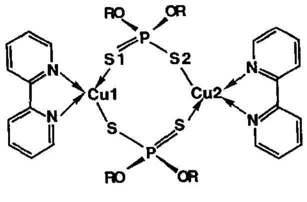
127

The mono(triphenylphosphine) adduct is a tricyclic dimer, $[(Ph_3P)Cu\{S_2P(OEt)_2\}]_2$ **128** (R = Et, L = PPh_3). The transannular Cu1—S2 distance (2.553 Å) is only slightly longer than the ring Cu1—S1 (2.455 Å) and Cu1—S2′ (2.357 Å) distances. Thus, the dimeric structure is of type **22**, with dative transannular bonds. The P=S(1) double bonds (1.969 Å) are somewhat elongated, due to participation of the sulphur atoms in an additional dative bond. The single P—S(2) bond (2.004 Å) displays a normal interatomic distance.[221b]



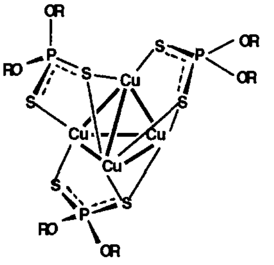
128

The bipyridine adduct is a cyclic dimer, $[Cu\{S_2P(OEt)_2\} \cdot bipy]_2$, with bridging phosphorodithioato ligands. The copper–sulphur bonds in the dimer are Cu1—S1 2.347 and Cu2—S2 2.323 Å, and phosphorus–sulphur bonds are P—S1 1.969 and P—S2 1.984 Å. The non-equivalence of the bond pairs supports formulation **129**, with the ligand displaying coordination pattern **8** and an eight-membered ring skeleton of type **20**.



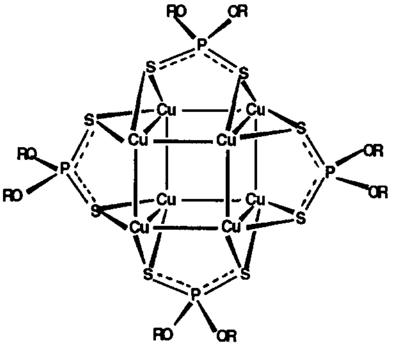
129

In the absence of an additional donor ligand, copper(I) phosphorodithioates are polynuclear, cluster complexes. Thus, copper(I) diisopropylphosphorodithioate is a tetramer **130**, containing a Cu_4 tetrahedron,[222–224] with a triconnective phosphorodithioate (coordination pattern **18**) on each face (in **130** the ligand on the rear Cu_3 face is omitted for clarity).



130

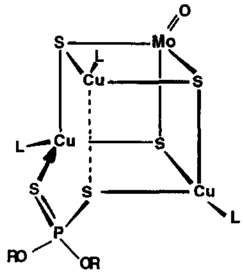
Two cubic Cu_8 cluster complexes $Cu_8S\{S_2P(OEt)_2\}_6$[223] and $Cu_8Cl_2\{S_2P(OEt)_2\}_6$[224a] have been reported. In $Cu_8S\{S_2P(OEt)_2\}_6$ the Cu_8 cube contains an encapsulated sulphur atom in the centre and a tetrametallic tetraconnective phosphorodithioato ligand (coordination pattern **19**) on each face (only four are shown in diagram **131** for clarity). In $Cu_8Cl_2\{S_2P(OEt)_2\}_6$ one chlorine is encapsulated and occupies an internal position in the centre of the cube, while the second is external, and forms a bridge connecting pairs of cubes in a supramolecular chain structure.[224a] The Cu … Cu interatomic distances of 2.95–3.00 Å in the sulphur-centred compound and 3.18–3.44 Å in the chlorine-centred compound, indicate weak metal–metal interactions. The Cu—S(—P) distances of 2.25–2.28 Å are shorter (indicating stronger bonds) than the eight $Cu—S_{central}$ bonds (2.54–2.63 Å).[223]



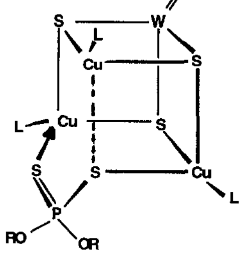
131

These two compounds are the only known examples of tetrametallic tetraconnective coordination of phosphorodithioato ligands.

Two heterometallic compounds, derived from a cubane skeleton, $Cu_3MoS_3O(PPh_3)_3\{S_2P(OEt)_2\}$, **132**,[224b] and $Cu_3WS_3O(PPh_3)_3\{S_2P(OEt)_2\}$, **133**,[224c] have similar structures. The ligand is anisobidentate and displays distinct single P—S and double P═S bonds, e.g. 2.002 and 1.964 Å, respectively, in **132**.[224b]



132

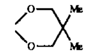


133

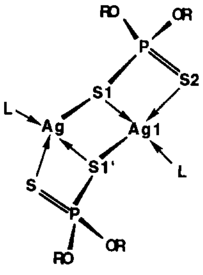
Crystal and molecular data for copper phosphorodithioates are listed in Table 20.

b. Silver. A triphenylphosphine adduct was found to be a dimer, $[Ag\{S_2P(OEt)_2\}(PPh_3)]_2$, **134** (R = Et, L = PPh_3) with bimetallic triconnective coordination (pattern **14**).[225] The Ag—S bonds

Table 20. Crystal structure data for Group 11 (Cu, Ag, Au) phosphorodithioato complexes

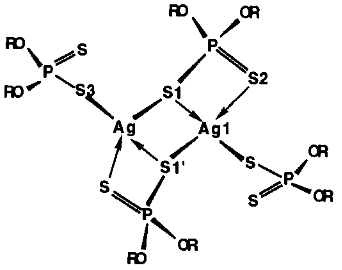
Structure no.	R	X or L	Space group	a b c	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
124	2-Me-		$P2_1/n$	9.128	—	1.976	1.986	2.317	2.330	106.9	83.4	82.8	chel	218
	C_6H_4			13.633	91.08	1.982	1.982	2.346	2.312	106.7	83.1	84.0	chel	
				24.204	—									
125	Et		$P2_1$	13.597	—	1.94	1.98	(3.04)		119.0			ionic	219
				6.945	121.22	1.93	2.10	(2.90)		118.9			ionic	
				16.071	—									
126	Et		$P2_1/c$	8.529	—	1.96	1.97	(3.09)	(2.99)	118.3			ionic	219
				19.247	122.67									
				13.696	—									
127	Et		$P2_1/n$	11.88	—	1.967	1.973	2.440	2.453	112.7	78.4	78.0	chel	220
				14.70	91.0									
				22.09	—									
127	$(OR)_2$=		$P2_1/n$	18.159	—	1.957	1.979	2.466	2.457	114.4	80.2	80.0	chel	221a
				12.234	108.75									
				18.656	—									
128	Et	PPh_3	$P\bar{1}$	9.716	78.16	1.969	2.004	2.456	2.553	114.7	81.8	78.7	bridge	221b
				11.026	102.64				2.537			101.5		
				12.475	114.34									
129	Et		$P\bar{1}$	9.388	95.88	1.969	1.984	2.347	2.323	118.4	108.6	100.4	bridge	220
				10.208	68.44									
				10.704	115.94									
130	Pr^i		$P2_12_12_1$	11.311	—	1.963	2.050	2.278	2.290	119.1	101.8	110.6	bridge	218
				12.428	—				2.262			102.9		
				33.923	—	1.966	2.059	2.230	2.291	118.8	102.7	110.3	bridge	
									2.268			101.0		
						1.980	2.065	2.286	2.267	118.0	99.5	105.4	bridge	
									2.283			104.5		
						1.969	2.050	2.275	2.305	117.1	99.2	106.0	bridge	
									2.260			107.7		
				11.283	—	2.009	2.049	2.277	2.263	116.5	103.2	115.5	bridge	222
				12.380	—				2.268			102.4		
				33.825	—	1.982	2.021	2.266	2.247	119.1	101.1	103.6	bridge	
									2.283			110.7		
						1.962	2.045	2.265	2.256	117.9	98.5	106.5	bridge	
									2.289			105.8		
						1.973	2.038	2.283	2.252	118.1	99.2	105.6	bridge	
									2.256			104.7		
131	Et	X=S	$R\bar{3}$	12.667	111.42	1.986	2.013	2.251	2.280	119.5	103.1	110.8	bridge	223
131	Et	X=Cl	$P\bar{1}$	11.578	55.54	2.002	2.022	2.269	2.287	121.2	108.3	102.7	bridge	224a
				12.663	57.35	2.000	2.028	2.267	2.305	120.9	102.4	113.3		
				14.317	72.23	2.012	2.020	2.264	2.298	120.5	102.5	102.8	bridge	
											108.5	113.4		
											108.4	103.1	bridge	
											102.6	113.6		
132	Et	X = O	$P\bar{1}$	13.810	99.42	1.964	2.002	2.342	2.481				bridge	224b
		L = PPh_3		19.753	107.24									
				11.719	88.05									
133	Et	X = O	$P\bar{1}$	13.808	99.27	1.973	2.001	2.337	2.472	118.3	103.4	107.1	bridge	224c
		L = PPh_3		19.764	107.8									
				11.696	88.12									
134	Et	PPh_3	$P2_1/c$	14.965	—	1.957	2.000	2.810	2.502	117.3	82.3	102.8	chel	225
				9.753	119.0				2.821			81.4		
				18.438	—									
135	Et		$P2_1/c$	12.966	—			2.517	2.728				uni	226
				16.159	106.0			2.868	2.679					
				12.898	—									
136	Et	X = S	$P\bar{1}$	13.600	101.19	1.981	2.000	2.622	2.684	117.1	98.7	95.0		227
		L = PPh_3		20.636	107.22				2.689			107.9		
				11.700	77.17									
136	Et	X = O	$P\bar{1}$	14.275	98.58	1.968	1.975	2.735	2.583	115.6	98.0	105.1	chel	228
		L = PPh_3		19.960	107.68				2.656		107.3			
				11.746	87.88									
137	Pr^i		$P\bar{1}$	12.495	99.33	2.001	2.028	2.284	2.253	116.7	102.2	103.0	bridge	229
				17.251	102.17	1.944	2.036	2.326	2.223	117.3	104.7	103.4	bridge	
				12.167	72.79	1.970	2.019	2.267	2.292	118.1	109.2	100.7	bridge	
						1.983	2.017	2.297	2.276	118.4	101.6	107.8	bridge	

are non-equivalent (Agl—S1 2.821 Å, Agl—S1′ 2.502 and Ag—S2 2.810 Å) and the phosphorus–sulphur bonds are close to single (P—S1 2.000 Å) and double (P—S2 1.957 Å). This leads to a (quasi)tricyclic structure **134** consisting of an $\mathrm{Ag_2S_4P_2}$ ring with two dative transannular S → Ag interactions, i.e. a molecular skeleton of type **22**.



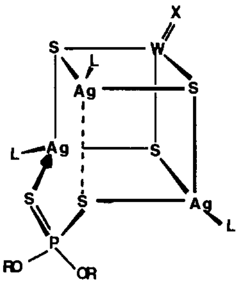
134

The bis(diethylphosphorodithioato) anion is also dimeric, $[\mathrm{Ag}\{\mathrm{S_2P(OEt)_2}\}_2]_2^{2-}$ (in its tetramethylammonium salt $[\mathrm{NMe_4^+}]_2$ $[\mathrm{Ag}\{\mathrm{S_2P(OEt)_2}\}_2]_2^{2-}$, and the phosphorodithioato ligands are distinctly nonequivalent, showing monodentate (monoconnective) and bimetallic triconnective behaviour (structure **135**).[226] The strongest silver–sulphur bond is to the monodentate ligand (Agl—S3 2.517 Å), while in the eight-membered $\mathrm{Ag_2S_4P_2}$ ring the Ag—S bonds are somewhat weaker (Agl—S2 2.728 Å and Agl—S1′ 2.679 Å). Transannular dative bonds S1 → Agl again transform the structure into a tricyclic system **135**, based again upon a molecular skeleton of type **22**.



135

Mixed polynuclear tungsten-silver compounds, with phosphorodithioato ligands attached only to silver, $\mathrm{WAg_3S_4}$ $\{\mathrm{S_2P(OEt)_2}\}$ $(\mathrm{PPh_3})_3$ and $\mathrm{WAg_3S_3O}$ $\{\mathrm{S_2P(OEt)_2}\}$ $(\mathrm{PPh_3})_3$ have been reported.[227,228] These are polycyclic cages, consisting of $\mathrm{WS_2Ag}$, $\mathrm{WS_3Ag_2}$ and $\mathrm{PS_3Ag_2}$ rings, with external oxo and thiooxo groups attached to tungsten. They bear some relation with the cubane structures, as illustrated by the idealized diagram **136** (X = S or O, L = $\mathrm{PPh_3}$).

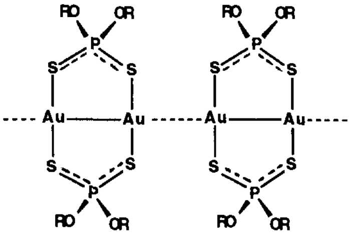


136

Silver atoms are tetracoordinate (distorted tetrahedral geometry) and the phosphorodithioato ligand displays trimetallic triconnective bridging (pattern **13**) which can be seen as connected to a triangular face in a $\mathrm{WAg_3}$ tetrahedron. The P—S bonds seem to be intermediate between single and double, and the S—P—S bond angles of 117.1° (X = S) and 115.6° (X = O) are enlarged, probably because of spanning two silver atoms. Perhaps for the same reason, the Ag—S—P angles (95.0–107.9° for X = S and 98.0–107.3° for X = O) also display significantly larger values than in bidentate phosphorodithioato complexes.

Crystal and molecular data of silver complexes are collected in Table 20.

c. Gold. Only one gold(I) phosphorodithioate, $[AuS_2P(OPr^i)_2]_n$, has been structurally investigated.[229] It consists of binuclear Au—Au units, connected through secondary bonds in supramolecular chains, **137**. The somewhat unsymmetric phosphorodithioato ligand is bridging. The crystal and molecular dimensions are listed in Table 20. The S—P—S bond angles are enlarged to 116.7–118.4°, due to the bridging function of the ligands.

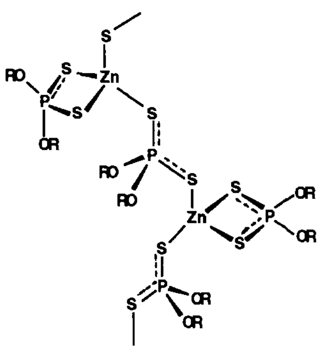


137

12. *Group* 12: Zn, Cd, Hg

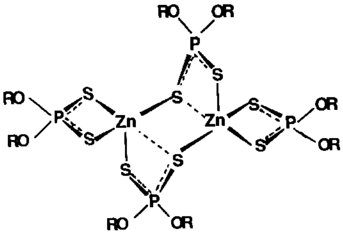
a. Zinc. Zinc (dialkyl)phosphorodithioates are important engine oil lubricant additives, and as such have received much attention. Since amines are also introduced in the composition of lubricant oils, a number of amine adducts have also been investigated.

Zinc(II) diethylphosphorodithioate is a polymeric compound, $[Zn\{S_2P(OEt)_2\}_2]_n$, which displays symmetrically bridging ligands (coordination pattern **7**) as shown in diagram **138**, with an additional chelating ligand at each metal atom.[230] The Zn—S bonds in the polymeric chain (2.337 and 2.345 Å) are comparable to those in the chelate rings (2.350 and 2.401 Å), but the P—S interatomic distances are different, i.e. 1.992 and 2.001 Å in the bridging groups and 1.973 and 1.987 Å in the chelating phosphorodithioato ligands. Geometry about zinc is basically tetrahedral.[230]



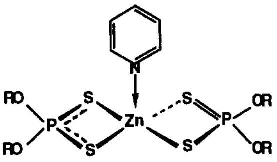
138

The diisopropylphosphorodithioato complex is a dimer, $[Zn\{S_2P(ORPr^i)_2\}_2]_2$,[231] containing an eight-membered ring, formed by two bridging ligands and two four-membered chelate rings, **139**. In the bridging group P—S bond lengths are 1.956 and 1.972 Å, while in the chelate rings the P—S distances are 1.968 and 1.984 Å. The S—P—S bond angles are 117.3° and 109.7°, respectively. The transannular Zn...S distance of 3.347 Å indicates a weak interaction, making the system quasi-tricyclic, of type **23**. The bridging ligands can be considered symmetric (coordination pattern no. **7**) and the chelating ligands practically isobidentate.



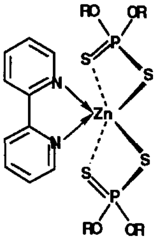
139

In the nitrogen base adducts the initial tetrahedral geometry is disturbed by the additional ligand. Thus, in the pyridine adduct $Zn\{S_2P(OPr^i)_2\}_2 \cdot Py$ (**140**)[232,233] one of the phosphorodithioato ligands is forced to become anisobidentate (coordination pattern **3**) and the P1—S2 separation (1.948 Å) is significantly shorter than P1—S1 (2.010 Å), P2–S3 (2.007 Å) and P2—S4 (1.971 Å). The Zn—S bonds are longer in the chelate ring (Zn—S3 2.352 Å, Zn—S4 2.496 Å) than the primary bond to the anisobidentate ligands, Zn—S1 (2.273 Å); a secondary Zn...S interaction (Zn...S2 3.041 Å) underscores the difference between the coordination patterns of the two ligands.

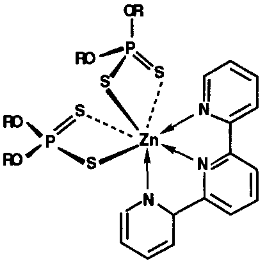


140

A dinitrogen ligand, bipyridyl, in $Zn\{S_2P(OPr^i)_2\}_2 \cdot bipy$ (**141**)[233] forces one phosphorodithioato ligand to become anisobidentate, with Zn...S 2.711 Å (coordination pattern **3**), while the three nitrogen atoms of terpyridine in the adduct $Zn\{S_2P(OPr^i)_2\}_2 \cdot terpy$ (**142**)[233] force both phosphorodithioato ligands to become basically monodentate (Zn...S 3.523 and 3.977 Å). A clear distinction between double and single phosphorus–sulphur bonds can be made on the basis of the respective interatomic distances (P=S 1.925 and 1.926 Å in **141**; 1.892 and 1.936 Å in **142**; P—S 1.997 and 2.005 Å in **141**; 1.968 and 2.012 Å in **142**).[233]

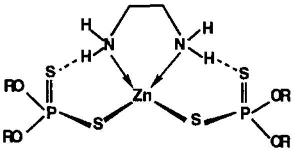


141



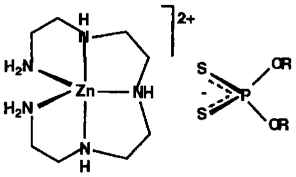
142

Aliphatic amines produce similar structural changes. Thus, in the adduct $Zn\{S_2P(OPr^i)_2\}_2 \cdot en$ (structure **143**)[232] the metal is four-coordinate (distorted tetrahedral) and the phosphorodithioato ligands are each monodentate, engaging in hydrogen bonding with the diamine.



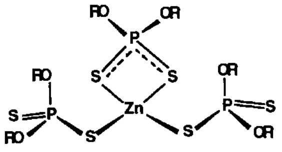
143

A pentaamine, such as 1,11-diamino-3,6,9-triazaundecane (abbreviated datau) occupies five coordination sites around the metal (trigonal bipyramidal geometry) in $Ni\{S_2P(OEt)_2\}_2 \cdot datau$ (structure **144**)[233] and displaces both phosphorodithioato ligands from the coordination sphere, making them outer-sphere counter ions.



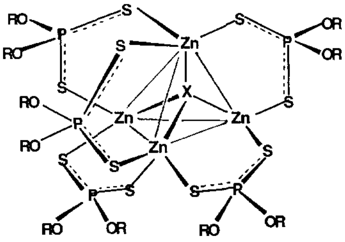
144

An anionic tris(phosphorodithioato) complex $[NMe_4][Zn\{S_2P(OC_6H_4Me\text{-}4)_2\}_3]$ contains, unexpectedly, a tetrahedrally coordinated central atom with one isobidentate chelating and two monodentate ligands (structure **145**).[234,235] Obviously, the zinc atom is too small to accommodate six sulphur atoms and become six-coordinate. In the chelate ring P—S bonds are 1.961 and 1.978 Å, while in the monodentate ligands one can distinguish double P═S bonds (1.921 and 1.926 Å) and single P—S bonds (1.986 and 1.987 Å). The S—P—S bond angle in the four-membered chelate ring is 113.2°, and less strained (119.1°) in the monodentate ligands.



145

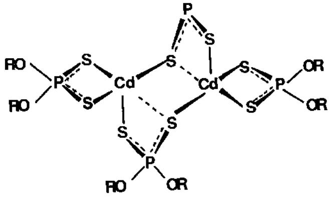
Tetranuclear zinc complexes with an encapsulated central sulphur or oxygen atom, i.e. $Zn_4S\{S_2P(OEt)_2\}_6$[236] and $Zn_4O\{S_2P(OBu^n)_2\}_6$ (EXAFS[237] and X-ray diffraction[238]) both contain a tetrahedron of zinc atoms (without metal–metal bonds) with practically isobidentate phosphorodithioato ligands bridging between pairs of metal atoms along the tetrahedron edges (structure **146**, X = S or O). There are no metal–metal bonds in these complexes; one ligand has been omitted for clarity.



146

Crystal and molecular dimensions of zinc phosphorodithioates are listed in Table 21.

b. Cadmium. Cadmium bis(diisopropylphosphorodithioate) is a cyclic dimer,[231] $[Cd\{S_2P(OPr^i)_2\}_2]_2$, **147**, like its zinc analogue, with an eight-membered ring of type **23**.

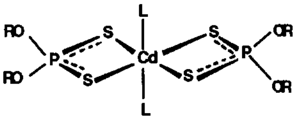


147

Cadmium can achieve six-coordination and this was found in the urotropine (hexamethylene tetramine) adduct $Cd\{S_2P(OEt)_2\}_2 \cdot 2urotr$[239] with a *trans*-octrahedral structure **148** (R = Et, L = urotr).

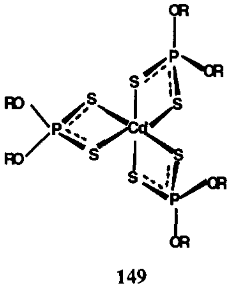
Table 21. Crystal structure data for zinc phosphorodithioato complexes

Structure no.	R	Space group	a b c	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
138	Et	$P2_1/a$	12.084	—	1.973	1.987	2.401	2.350	109.7	81.5	82.5	chel	230
			19.840	113.99	1.992	2.001	2.345	2.337	108.0	101.8	106.4	bridge	
			8.463	—									
139	Et	$C2/c$	10.934	—	1.968	1.984	2.409	2.351	109.7	81.4	82.6	chel	231
			17.098	99.23	1.956	1.972	2.306	2.302	117.3	100.7	104.1	bridge	
			25.587	—									
140	Pr^i	$P2_1/n$	21.28	—	1.946	2.017	(3.032)	2.269	113.5	—	93.5	uni	232
			8.35	99.5	1.975	1.999	2.502	2.358	111.3	79.9	83.1	chel	
			16.27	—									
			16.289	—	1.948	2.010	(3.041)	2.273	113.8	—	93.6	uni	233
			8.331	99.56	1.971	2.007	2.496	2.352	111.0	80.2	83.2	chel	
			21.316	—									
141	Pr^i	$P\bar{1}$	9.020	83.12	1.925	2.005	(3.822)	2.327	117.5	—	97.8	uni	233
			8.502	97.96	1.926	1.997	2.711	2.365	112.0	79.6	87.5	chel	
			21.267	103.46									
142	Pr^i	$P2_1/n$	8.847	—	1.936	2.012	(3.523)	2.334	117.4	—	99.3	uni	233
			25.215	90.74	1.892	1.968	(3.977)	2.339	120.7	—	114.0	chel	
			15.740	—									
143	Pr^i	$P2_1/c$	13.402	—	1.913	2.003	—	2.292	117.1	—	104.9	uni	232
			16.470	99.00	1.898	1.975	—	2.331	118.8	—	99.2	uni	
			12.294	—									
144	Et	$P2_1/c$	8.183	—	1.947	1.955	—	—	117.9	—	—	ionic	233
			25.161	99.72	1.937	1.962	—	—	120.4	—	—	ionic	
			14.981	—									
145	p-Tol	$P2_1/a$	29.311	—	1.961	1.978	2.423	2.423	113.2	80.8	80.4	chel	234,
			11.032	106.83	1.921	1.986	3.565	2.308	119.1		102.3	uni	235
			17.515	—	1.921	1.987	3.511	2.296	119.1		100.6	uni	
146	Et	$R\bar{3}$	20.776	—	1.983	1.994	2.335	2.337	120.5	109.9	106.6	bridge	236
			20.776	—	1.968	1.981	2.341	2.353	121.1	108.6	106.6	bridge	
	X = S		11.560										
146	Bu^n	$P\bar{1}$	12.522	112.13								bridge	237,
			14.514	106.72									238a,
	X = O		14.528	106.65									238b



148

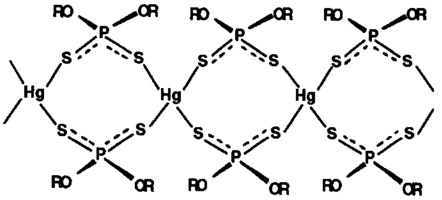
Unlike the zinc analogue which is four-coordinate, the tris(diisopropylphosphorodithioato)cadmium complex anion in $[NMe_4][Cd\{S_2P(OPr^i)_2\}_3]$ is six-coordinate, with isobidentate ligands (structure **149**).[240] Because of a twist of 44° the coordination geometry is intermediate between octahedral and trigonal prismatic.



149

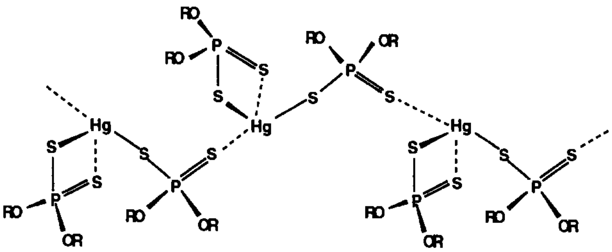
Molecular dimensions for cadmium compounds are listed in Table 22.

c. Mercury. Mercury(II) phosphorodithioates are polymeric materials, containing bridging ligands and two types have been identified by X-ray diffraction. Bis(diethylphosphorodithioato)mercury(II), is a double chain polymer, $[Hg\{S_2P(OEt)_2\}_2]_n$, with each ligand acting as a bridging group (structure **150**).[241,242] The two P—S bonds are 2.12 and 2.13 Å, therefore the ligand is symmetric (coordination pattern **7**) and the metal is tetrahedrally coordinated (Hg—S 2.56 Å).



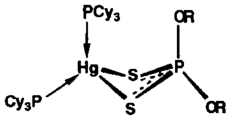
150

In polymeric bis(diisopropylphosphorodithioato)mercury(II), $[Hg\{S_2P(OPr^i)_2\}_2]_n$ there are both chelating and bridging ligands. The structure is supramolecular (polymeric), with chelate HgS_2P ring units connected into a helical chain of type **27** by asymmetric phosphorodithioato bridges (coordination pattern **9**).[243] Formulation **151** is supported by the clear non-equivalence of P—S and Hg—S interatomic distances. Thus, in the chelate ring P—S is 2.024 and P═S 1.934 Å, in the bridge P—S is 2.006 Å and P═S 1.954 Å. The Hg—S interatomic distances are 2.888 and 2.390 Å in the chelate ring, and 2.388 and 2.748 Å in the bridge.[243] The long P—S bond is always associated with a short Hg—S bond and *vice versa*.



151

The only monocylic chelate ring mercury derivative is the salt of bis(tricyclohexylphosphine)(diisopropylphosphorodithioato)mercury(II), $[Hg\{S_2P(OP^i)_2\}(PCy_3)]^+CF_3SO_3^-$, which contains an isobidentate ligand (structure **152**). Although the P—S bonds are nearly equal (1.982 and 1.989 Å), there is a difference in the Hg—S bond lengths (2.707 and 2.821 Å).[244]



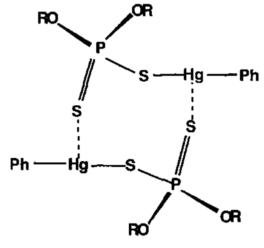
152

An organomercury(II) phosphorodithioate is a cyclic dimer, $[PhHg\{S_2P(OEt)_2\}]_2$, **153** (R = Et), with very asymmetric bridging ligands.[245] The double and single phosphorus–sulphur bonds in the ligand (P═S 1.924 Å and P—S 2.028 Å) are associated with long (secondary) and short (covalent)

Table 22. Crystal structure data for cadmium and mercury phosphorodithioato complexes

Structure no.	R	L	Space group	a b c	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
147	Pr^i		C2/c	10.964	—	1.972	1.974	2.591	2.552	112.2	83.4	84.4	chel	231
				16.906	99.91	1.956	1.962	2.486	2.600	116.0	96.9	102.2	bridge	
				26.490	—									
148	Et	urotr	P2$_1$/n	16.310	—	1.979	1.982	2.682	2.704	115.8	83.7	83.1	chel	239
				6.777	96.13									
				14.576	—									
149	Pr^i		R$\bar{3}$	15.414	50.68	1.976	1.982	2.658	2.777	113.4	87.5	84.1	chel	240
150	Et		I4$_1$a	20.33		2.13	2.12	2.56		114.6		95.4	bridge	241, 242
				20.33										
				4.37										
151	Pr^i		C2/c	31.70	—	1.934	2.024	2.888	2.390	112.0	79.7	91.6	chel	243
				8.66	129.34	1.945	2.006	2.748	2.388	109.2	103.2	103.7	bridge	
				22.34	—									
152	Pr^i		P2$_1$/c	10.440	—	1.982	1.989	2.707	2.821	112.6	87.1	83.8	chel	244
				22.615	93.05									
				21.904	—									
153	Et		P2$_1$/c	7.330	—	1.924	2.028	3.323	2.383	116.1	94.9	—	bridge	245
				18.085	105.96									
				11.552	—									

mercury–sulphur bonds (Hg...S 3.323 Å and Hg—S 2.383 Å),[245] to form the eight-membered ring of type **21**.

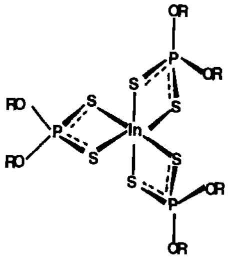


153

The molecular dimensions of mercury phosphorodithioates are listed in Table 22.

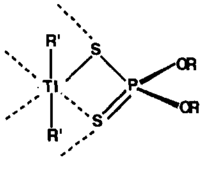
13. *Group* 13: Al, Ga, In, Tl

No structure of aluminium or gallium phosphorodithioates has been determined. Tris-(diethylphosphorodithioato)indium(III), In$\{S_2P(OEt)_2\}_3$, is an octahedral complex with three anisobidentate chelating ligands,[246] which can be formulated as **154**. The low accuracy of the structure determination ($R = 12\%$) prevents any further comments.



154

Organothallium phosphorodithioates were found to be supramolecular, polymeric associates, $[Me_2Tl\{S_2P(OR_2)\}]_n$ (R = Me, Et, Cy). Monomeric units, **155**, containing nearly linear $TlMe_2$ coordination centres and anisobidentate phosphorodithioato ligands, are connected through intermolecular Tl...S secondary interactions (coordination pattern no. **17**), leading to complex two-dimensional structures. The full details of the work will be soon published.[247]



155

Crystal and molecular structure data are given in Table 23.

14. *Group* 14: Si, Ge, Sn, Pb

a. Silicon. No silicon phosphorodithioate has been structurally investigated.

b. Germanium. In the germanium phosphorodithioates studied, the ligand is always monodentate. Thus, the phosphorodithioates $Ge\{S_2P(OMe)_2\}_4$ (**156**),[248] $[GeS\{S_2P(OMe)_2\}_2]_2$ (**157**),[248] $Ph_3Ge\{S_2P(OMe)_2\}$ (**158**),[249] $Ph_2Ge\{S_2P(OMe)_2\}_2$ (**159**)[249] and $PhGe\{S_2P(OMe)_2\}_3$ (**160**) (only partially solved structure)[250] are all molecular compounds, with no intermolecular metal–ligand interactions. The bond lengths and angles are listed in Table 24. The data clearly distinguish between single and double phosphorus–sulphur bonds.

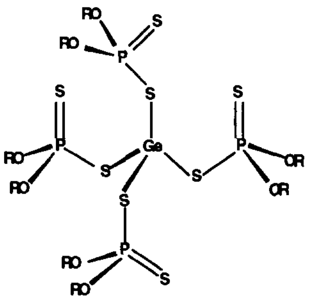
Table 23. Crystal structure data for Group 13 (Al, Ga, In, Tl) phosphorodithioato complexes

Structure no.	R	Space group	*a* *b* *c*	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
154	Et	Cc	8.61	—	1.952	2.037	2.633	2.591	111.0	85.2	85.8	chel	246
			18.81	92.20	1.902	2.137	2.578	2.607	109.5	88.5	83.0	chel	
			17.85	—	1.874	2.066	2.609	2.628	111.8	87.7	83.7	chel	
155	Me				1.919	1.973	2.982	3.029				bridge	247a, 247b
R′ = Me							3.326						
							3.236						
155	Et				1.95	1.99	3.029	2.983				bridge	247a, 247b
R′ = Me							3.209						
					1.916	2.030	3.015	2.984				chel	
155	Cy				1.96	1.97	2.811	2.97				bridge	247a, 247b
R′ = Me								3.19					
					1.982	2.01	3.157	2.951				bridge	

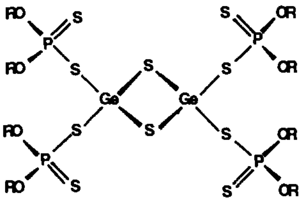
Table 24. Crystal structure data for germanium phosphorodithioates

Structure no.	R	Space group	*a* *b* *c*	α β γ	P—S		M—S		S—P—S	M—S—P	Bond type	Ref.
156	Me	$P2_1/c$	11.230	—	1.900	2.081	—	2.218	106.9	104.9	uni	248
			23.044	113.59	1.909	2.080	—	2.230	107.9	105.9	uni	
			12.086	—	1.917	2.071	—	2.236	108.2	105.9	uni	
					1.890	2.100	—	2.224	118.6	104.9	uni	
157	Me	$P2_1/c$	10.344	—	1.915	2.065	3.402	2.222	115.7	100.7	uni	248
			12.860	104.44	1.914	2.064	3.417	2.223	116.1	102.3	uni	
			12.443	—								
158	Me	$P\bar{1}$	10.311	101.47	1.923	2.060	(5.253)	2.285	109.1	109.0	uni	249
			11.282	113.68								
			11.517	110.31								
159	Me	$P\bar{1}$	9.813	89.04	1.898	2.043	—	2.257	111.9	103.7	uni	249
			10.345	85.28	1.904	2.045	—	2.253	112.4	105.6		
			11.837	82.29								
160	Me	$Pn2_1a$	13.673	[a]								250
			14.566									
			13.154									

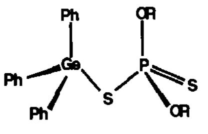
[a] Molecular structure not completely solved; no further information available.



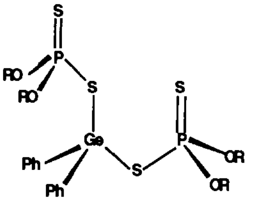
156



157

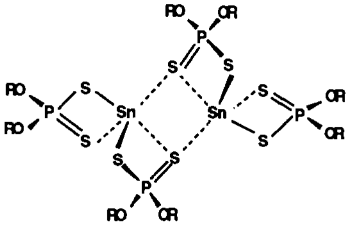


158



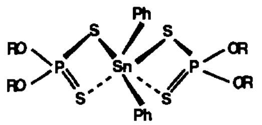
159

c. Tin. Only one tin(II) compound has been investigated, namely dimeric $[\mathrm{Sn}\{S_2P(OPh)_2\}_2]_2$. The compound contains two chelating and two bridging (bimetallic triconnective) ligands, as shown in **161**. Both the chelate and bridging ligands are asymmetric, and short (double) and long (single) phosphorus–sulphur bonds are observed: P=S 1.967 Å and P—S 2.002 Å in the chelating ligands and P=S 1.964 Å and P—S 2.006 Å in the bridging ligands. The secondary Sn...S interactions (3.391 Å) leading to dimerization are substantially longer than the intrachelate ring Sn...S interactions (2.830 and 3.043 Å).[251,252] The structure can be regarded as based upon a molecular skeleton of type **24**.

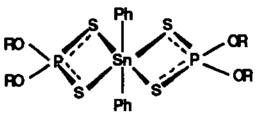


161

Two types of structure have been identified for diorganotin phosphorodithioates: an asymmetric structure **162**, with anisobidentate ligands, and a symmetric structure **163**, with isobidentate phosphorodithioates.



162



163

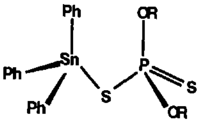
The asymmetric structure **162** is illustrated by diphenylbis(diethylphosphorodithioato)tin(IV), $Ph_2Sn\{S_2P(OEt)_2\}_2$.[253] In the anisobidentate ligand, the phosphorus–sulphur bonds are unequal (P=S 1.919 and 1.942 Å; P—S 2.036 and 2.029 Å) and the secondary Sn...S interactions bring the two atoms to 3.20 and 3.23 Å. The bond angles C—Sn—C (135°), S1—Sn—S3 (84.5°) and S2...Sn...S4 (136.9°) determine a coordination geometry which can be described as intermediate between distorted tetrahedral (if only the primary bonds are considered) and distorted octahedral (if the secondary Sn...S bonds are also included).

The symmetric structure **163** of $Ph_2Sn\{S_2P(OPr^i)_2\}_2$ is so far unique. The ligands are isobidentate (P—S 1.998 and 2.000 Å) and the Sn—S bonds are identical and of intermediate length (2.678–2.689 Å) between those of the primary and secondary bonds cited above for the unsymmetric $Ph_2Sn\{S_2P(OEt)_2\}_2$. The coordination geometry around tin is octahedral (centrosymmetric).[254]

The dramatic structural differences between the two diphenyltin phosphorodithioates which occur when peripheral OR groups are changed (OEt/OPr^i) are rather puzzling. Crystal packing effects can be invoked to explain these differences, but this seems still unsatisfactory.

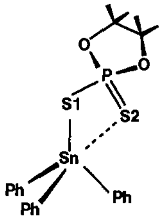
The structures of the two other diorganotin phosphorodithioates, namely $Me_2Sn\{S_2P(OCMe_2CMe_2O)\}_2$[255] and $Bu_2Sn(OAc)\{S_2P(OCH_2CMe_2CH_2O)\}$[256] are also asymmetric, with anisobidentate ligands (as in **162**).

(Diethylphosphorodithioato)triphenyltin, $Ph_3Sn\{S_2P(OEt)_2\}$, is an illustration of the unidentate coordination **164** in organotin compounds. The P—S bond lengths (2.054 and 1.931 Å) clearly indicate single and double bond character, respectively, and the orientation of the P═S bond, away from tin, underscores the unidentate character of the ligand. Coordination around tin is distorted tetrahedral.[257]



164

The structure is different in the 2-thiooxo-1,3,2-dioxophospholane-2-thiolato derivative $Ph_3Sn\{S_2P(OCMe_2CMe_2O)\}$. Although the phosphorus–sulphur bond distances (2.039 and 1.903 Å) would indicate a unidentate coordination, the orientation of the doubly bonded sulphur (S2) towards the metal and its distance to the tin atom (Sn ... S2 3.411 Å), suggesting a weak secondary interaction, makes the ligand anisobidentate. This determines a coordination geometry at tin, which is intermediate between tetrahedral and trigonal bipyramidal, as shown in **165** (R = Ph).[258]



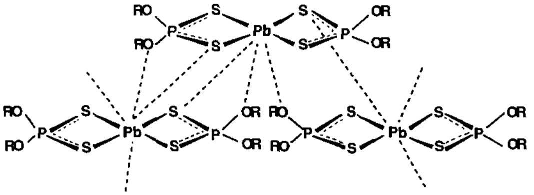
165

Triorganotin structures can be compared with that of S═P(S—SnMe$_3$)$_3$. Single (2.076–2.080 Å) and double (1.948 Å) phosphorus–sulphur bonds are observed in the latter, with a four-coordinate tin atom.[259] The S═P—S bond angles are larger than tetrahedral (114.3–114.7°), while S—P—S bond angles (103.4–104.8°) are diminished, illustrating the effects of valence shell electron repulsions.

Crystal data and molecular dimensions for tin phosphorodithioates are collected in Table 25.

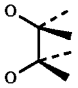
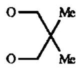
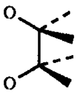
d. Lead. The structures of four lead(II) phosphorodithioates, $[Pb\{S_2P(OR)_2\}_2]_n$, with R = Et,[260,261] Pr^i,[262] Bu^i[261] and Ph[261] have been determined, and each one is different.

Bis(diethylphosphorodithioato)lead(II)[260,261] is built up of distorted tetragonal pyramids, with the apical lead atom 1.48 Å above the basal plane and the ligands anisobidentate (P—S 1.969 and 1.995 Å; 1.968 and 1.991 Å; Pb—S 2.996 and 2.754 Å; 3.022 and 2.790 Å). Additional Pb ... O and Pb ... S (3.409 and 3.483 Å) interactions (two of each) lead to supramolecular association, **166** (R = Et), with the coordination geometry around lead becoming square-antiprismatic. This is one of the rare examples (in fact only two are known, see Section E.17 for the second) when oxygen atoms of P—OR groups of the phosphorodithioato ligand participate in coordination to the metal.

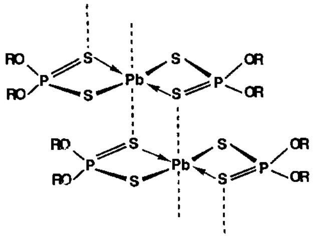


166

Table 25. Crystal structure data for tin phosphorodithioato complexes

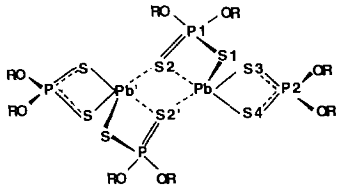
Structure no.	R	Space group	a b c	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
161	Ph	$P\bar{1}$	10.499	99.18	1.967	2.002	2.830	2.623	112.3	82.9	87.9	chel	251,
			13.948	95.71	1.964	2.006	3.043	2.631	115.5	96.1	94.3	bridge	252
			9.291	91.80			3.391			74.8		chel	
162	Et	$P2_1/c$	14.137	—	1.942	2.029	3.23	2.492	112.4	—	97.5	uni	253
			14.299	112.33	1.919	2.036	3.20	2.481	113.2	—	97.7	uni	
			15.759	—									
163	Pr^i	$P2_1/n$	17.517	—	1.998	2.006	2.689	2.678	111.3	86.3	85.4	chel	254
			14.212	100.63									
			6.340	—									
162	$(OR)_2=$	Pccn	16.830	—	1.932	2.031	3.130	2.495	112.4	79.1	95.0	chel	255
			11.407	—									
			12.829	—									
162	$(OR)_2=$	$P\bar{1}$	6.942	71.16	1.931	2.032	3.174	2.528	114.7	77.1	93.1	chel	256
			12.992	78.12	1.930	2.034	3.172	2.526	114.6	77.2	93.1	chel	
			16.804	74.50									
164	Et	$P\bar{1}$	12.647	98.59	1.931	2.054	—	2.458	112.3	—	103.8	uni	257
			9.961	91.51									
			9.437	96.12									
165	$(OR)_2=$	$P2_1/n$	14.511	—	1.903	2.039	3.411	2.436	114.8	—	102.1	chel	258
			11.536	94.32									
			15.435	—									

In bis(diisopropylphosphorodithioato)lead(II) there are only lead–sulphur interactions.[262] Each $Pb\{S_2P(OPr^i)_2\}_2$ molecule forms two pairs of additional lead–sulphur Pb...S bonds with two neighbouring molecules, resulting in a supramolecular structure **167** ($R = Pr^i$). Each phosphorodithioato ligand is bimetallic triconnective and the lead atoms are six-coordinate. The coordination geometry around lead is ψ-pentagonal bipyramidal, with possibly a lone pair occupying an equatorial position.



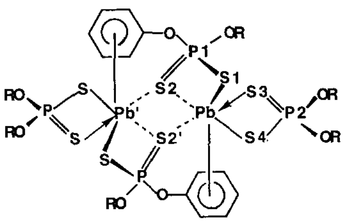
167

Bis(diisobutylphosphorodithioato)lead(II) forms dimeric associates $[Pb\{S_2P(OBu^i)_2\}_2]_2$.[261] In each monomeric building unit one ligand is isobidentate chelating (monometallic biconnective) (Pb—S3 2.768, Pb—S4 2.762 Å), the other is bimetallic triconnective and participates in the formation of the dimer. The interunit Pb′...S2 secondary bonds (3.444 Å) are longer than the intraunit Pb...S2 secondary bonds (3.127 Å), which is reflected in the formulation **168** ($R = Bu^i$), based upon a molecular skeleton of type **24**. This is also supported by the P—S bond lengths: P1—S1 1.994 Å, P1—S2 1.951 Å; P2—S3 1.985 Å and P2—S4 1.986 Å. The coordination geometry around lead is ψ-pentagonal pyramidal.



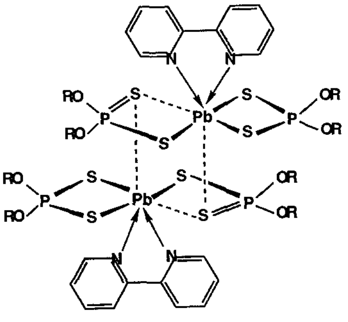
168

Bis(diphenylphosphorodithioato)lead(II) is also a supramolecular dimer, $[Pb\{S_2P(OPh)_2\}_2]_2$[261] but the interunit Pb... S4′ distance (3.215 Å) is slightly shorter than the intraunit Pb... S4 distance (3.323 Å), leading to the formation of an eight-membered quasicyclic species, as shown in **169** (R = Ph). Additional η^6-C_6H_5-Pb interactions between two different units seem to stabilize the dimer. The phosphorus–sulphur bond length differentiation (P1—S1 1.984, P1—S2 1.960 Å ; P2—S3 1.958, P2—S4 1.993 Å) are in agreement with formulation **169**.



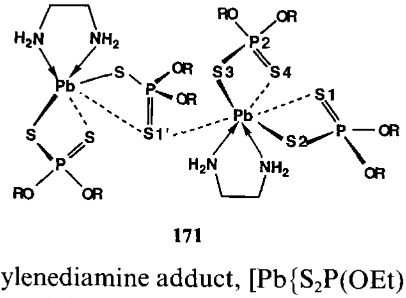
169

Supramolecular association of lead(II) phosphorodithioates is obviously the result of the tendency of the large lead atom to achieve a higher coordination number. This tendency can also be satisfied by coordination of additional donor molecules, i.e. adduct formation. In the bipyridine adduct $[Pb\{S_2P(OEt)_2\}\cdot bipy]_2$ dimerization still occurs,[263] and the lead atom is seven-coordinate, as shown in **170** (R = Et).



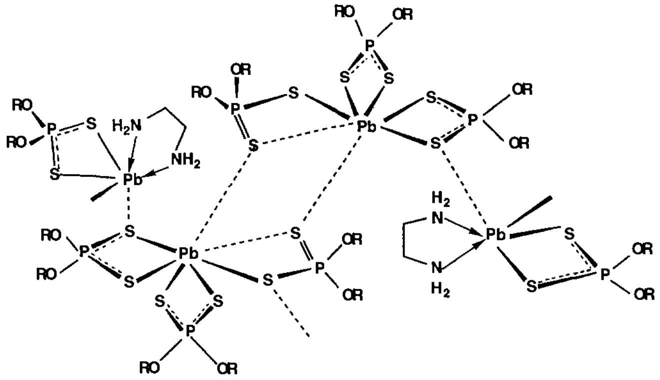
170

The ethylenediamine adduct, on the other hand, is a supramolecular chain polymer $[Pb\{S_2P(OEt)_2\}_2\cdot en]_n$ **171** (R = Et), with chelating ethylenediamine and phosphorodithioato (isobidentate) ligands and phosphorodithioato (bimetallic triconnective) bridges. The metal atom is again seven-coordinate.[263]



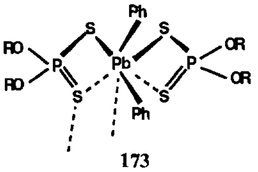
171

The structure of a second ethylenediamine adduct, $[Pb\{S_2P(OEt)_2\}_2\cdot 1/2en]_n$, is more complex.[263] It contains tetranuclear units interlinked to produce a chain-like supramolecular structure. These are formed from dimeric $[Pb\{S_2P(OEt)_2\}_3]_2$ units, doubly bridged by $Pb\{S_2P(OEt)_2\} \cdot en$ units, as shown in **172**.



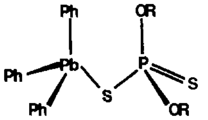
172

The structures of organolead(IV) phosphorodithioates are much simpler, because fewer coordination sites are available around the organometallic R_nPb coordination centres. Thus, in bis(dibenzylphosphorodithioato)diphenyllead(IV), $[Ph_2Pb\{S_2P(OCH_2Ph)_2\}_2]_2$, the unit molecule contains anisobidentate ligands and six-coordinate lead in distorted octahedral geometry, as shown in **173** ($R = CH_2Ph$). In the crystal, adjacent molecules are connected in pairs by weak Pb... S interactions (3.69 Å), and the lead coordination geometry becomes distorted pentagonal bipyramidal.[264]



173

The presence of a larger number of organic groups around the metal reduces coordination possibilities. In (diethylphosphorodithioato)triphenyllead(IV), $Ph_3Pb\{S_2P(OEt)_2\}$, the ligand is monodentate (P═S 1.924 Å, P—S 2.034 Å)) and coordination around lead is reduced to (distorted) tetrahedral, **174** (R = Et). The Pb—S bond (2.554 Å) is shorter than in the diphenyllead derivative or than in any lead(II) phosphorodithioates. The phosphorus–sulphur bond lengths (P—S 2.035 Å and P═S 1.923 Å) are in agreement with monodentate coordination.[264]



174

Crystal structure data, including bond lengths angles are collected in Table 26.

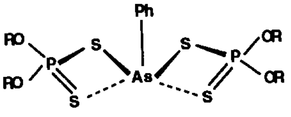
15. *Group* 15: As, Sb, Bi

a. Arsenic. Only one structure of an arsenic phosphorodithioate has been reported. Thus, bis(diisopropylphosphorodithioato)phenylarsenic(III), $PhAs\{S_2P(OPr^i)_2\}_2$, is a molecular monomeric compound, containing anisobidentate ligands, in tetragonal pyramidal coordination **175** ($R = Pr^i$).[265] The coordination geometry can also be described as ψ-octahedral, with a stereochemically active lone pair of electrons occupying a position *trans* to the phenyl group. The presence of single P—S (2.09–2.10 Å) and double P═S bonds (1.90 Å) is worth underscoring. The

Table 26. Crystal structure data for lead phosphorodithioato complexes

Structure no.	R	Space group	a b c	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
166	Et	$P\bar{1}$	10.102	99.82	1.969	1.995	2.996	2.754	115.4	83.5	89.8	chel	260,
			10.366	109.91	1.968	1.991	3.022	2.790	116.2	83.1	89.1	chel	261
			9.702	86.17									
167	Pr^i	$P2_1/n$	5.290	—	2.000	1.982	2.761	2.985	113.8			bridge	262
			10.067	95.97				3.232				chel	
			9.335	—	1.958	1.944	2.772	3.027	114.6			bridge	
								3.175				chel	
168	Bu^i	$P\bar{1}$	17.426	91.73	1.985	1.986	2.768	2.762	112.0	87.4	87.5	chel	261
			14.377	93.87	1.994	1.951	2.755	3.127	113.9	92.6	82.8	chel	
			6.237	65.67				3.444				bridge	
169	Ph	$P\bar{1}$	14.178	95.61	1.993	1.958	2.732	2.896	113.7	88.0	84.1	chel	261
			9.332	91.86	1.984	1.960	2.753	3.323	115.1	92.9	77.5	chel	
			10.507	99.10				3.215			80.7	bridge	
170	Et	$P2_1/c$	14.727	—	1.95	1.98	3.000	3.118	116.5	84.7	88.4	chel	263
			14.490	110.72	1.97	1.99	—	3.212			99.6	bridge	
			11.616	—			2.949	2.929	113.2	88.8	89.0	chel	
171	Et	$P\bar{1}$	10.933	103.58	1.955	1.958	3.173	3.074	115.2	86.1	88.9	chel	263
			13.257	132.24				3.190			102.5	bridge	
			13.705	91.50	1.945	1.957	3.177	2.967	116.8	85.9	91.8	chel	
172	Et	$P\bar{1}$	9.997	98.54	1.98	1.99	3.05	2.82	113.0	86.0	92.3	chel	263
			19.875	100.77	1.96	1.96	2.96	2.93	113.0	89.1	90.0	bridge	
			15.000	95.64	1.96	1.97	3.21	3.11	116.2	93.2	91.4	bridge	
					1.97	1.95						chel	
173	Bz	$P\bar{1}$	11.760	80.14	1.93	1.98	2.940	2.723	112.4	86.3	91.4	chel	264
			12.532	111.46	1.93	2.01	2.957	2.679	114.0	84.0	90.3	chel	
			16.263	112.41									
174	Et	$P\bar{1}$	9.579	101.62	1.924	2.034	—	2.554	111.0	—	104.6	uni	264
			10.602	99.55									
			12.710	100.72									

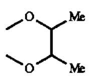
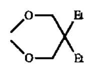
As—S bonds are 2.310–2.317 Å (primary bonds) and 3.125 and 3.187 Å (secondary interactions). For other molecular dimensions see Table 27.



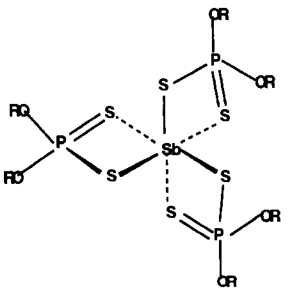
175

b. Antimony. The molecular structures of $Sb\{S_2P(OR)_2\}_3$ with R = Me,[266] Et[267] and Pr^i,[266] have been determined. All three compounds are monomeric tris chelates, with anisobidentate ligands,

Table 27. Crystal structure data for Group 15 (As, Sb, Bi) metal phosphorodithioato complexes

Structure no.	R	Space group	*a* *b* *c*	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
175	Pr^i	$P2_1/c$	12.454	—	1.90	2.10	3.125	2.310	111.5	78.2	97.4	chel	265
			26.693	109.40	1.90	2.09	3.187	2.317	112.0	77.3	77.3	chel	
			8.901	—									
176	Me	$P2_1/n$	9.313	—	1.941	2.029	3.008	2.522	112.2	81.5	93.4	chel	266
			8.506	99.09	1.941	2.036	3.006	2.535	112.3	81.7	93.1	chel	
			28.528	—	1.927	2.033	3.002	2.531	112.8	81.7	92.9	chel	
176	Et	$P2_1$	8.624	—	1.984	1.992	2.785	2.590	108.4	86.2	91.8	chel	267
			9.707	92.83	1.979	1.983	2.838	2.629	109.9	86.0	91.67	chel	
			17.521	—	1.927	1.976	2.856	2.583	109.7	86.0	92.9	chel	
176	Pr^i	$P2_1/n$	11.293	—	1.945	2.029	3.031	2.521	111.2	82.1	94.9	chel	266
			10.659	97.22	1.933	2.034	3.013	2.531	111.6	82.2	93.7	chel	
			31.195	—	1.949	2.044	3.000	2.519	111.2	82.1	93.8	chel	
177	Pr^i	$P2_1/c$	12.451	—	1.947	2.039	3.056	2.516	111.0	82.2	95.5	chel	265
			26.681	109.70	1.941	2.048	3.067	2.529	110.9		95.3	chel	
			9.026										
178	Pr^i	$P2_1/c$	10.714	—	1.942	2.044	3.684	2.555	116.1	100.5	63.6	bridge	268
			18.205	97.44			3.172						
			22.010	—	1.943	2.035	3.934	2.531	115.3	103.3	72.5		
							3.266						
179	Et	$P2_1$	8.618	—	1.925	1.972	2.820	2.750	112.3	87.8	88.9	chel	269
			9.698	92.95	1.972	2.002	2.778	2.795	112.1	88.2	87.1	chel	
			17.569	—	1.964	1.980	2.747	2.747	112.1	88.3	87.1	chel	
179	Pr^i	$P2_1/c$	20.096	—	1.959	1.997	2.886	2.714	112.6	85.7	89.8	chel	270
			9.086	114.71	1.948	1.991	2.878	2.702	112.2	85.8	90.0	chel	
			21.619	—	1.955	2.011	2.858	2.690	111.7	86.1	89.7	chel	
179	(OR)$_2$=	$C2/c$	16.684	—									271
			13.682	98.45									
			11.930	—									
179	(OR)$_2$=	$P2_1/c$	9.591	—	1.932	1.978	2.836	2.758	115.4	85.4	86.7	chel	271
			10.059	90.51	1.968	2.023	2.856	2.712	114.2	84.3	87.2	chel	
			36.170	—	1.934	1.995	2.873	2.745	114.2	85.6	88.0	chel	

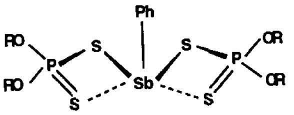
displaying distorted octahedral coordination geometry, **176**, determined by the three primary Sb—S bonds (2.52–2.63 Å) and the three secondary Sb…S interactions (*ca* 3 Å).



176

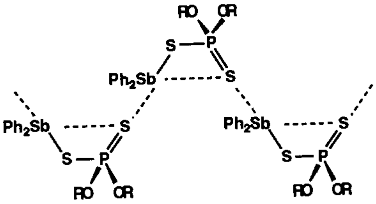
The molecular dimensions are listed in Table 27. It can be seen that the ethyl derivative differs somewhat from the methyl and isopropyl phosphorodithioato complexes, both in terms of P—S, Sb—S bond lengths and S—P—S bond angles, and in the ethyl complex the ligand becomes more closely isobidentate.

Bis(diisopropylphosphorodithioato)phenylantimony(III), PhSb$\{S_2P(OPr^i)_2\}_2$, is monomeric, with structure **177** (R = Pr^i), and is structurally very similar to the phenylarsenic analogue.[265]



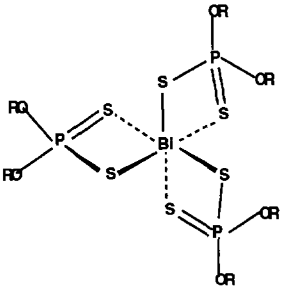
177

(Diisopropylphosphorodithioato)diphenylantimony(III), $[Ph_2Sb\{S_2P(OPr^i)_2\}]_n$, is a supramolecular polymer, **178** (R = Ph, R′ = Pr^i), with secondary Sb...S bonds (3.172 and 3.266 Å) connecting the monomeric units into a polymeric chain. The ligand is bimetallic triconnective (P—S 2.044 Å, P═S 1.942 Å) and the sulphur atom doubly bonded to phosphorus participates in intraunit secondary Sb... S bonding (3.934 and 3.684 Å). It is worth noting that the intermolecular secondary Sb... S interactions are shorter than the Sb... S interactions within the chelate building units.[268]



178

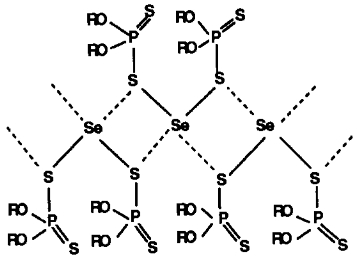
c. Bismuth. All four bismuth tris(phosphorodithioates) whose structures have been determined by X-ray diffraction, Bi$\{S_2P(OR)_2\}_3$, with R = Et,[269] Pr^i[270] and $(OR)_2$ = OCHMeCHMeO and $OCH_2CEt_2CH_2O$[271] are monomeric, distorted octrahedral complexes, **179**, with anisobidentate ligands, like the antimony analogues. The molecular dimensions are given in Table 27.



179

16. *Group* 16: Se, Te

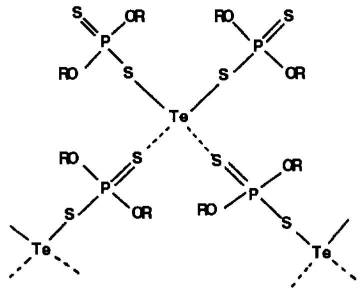
a. Selenium. A selenium(II) phosphorodithioate can be regarded as an analogue of the bis(thiophosphoryl) trisulphides, but their structures are completely different. The structure of $[Se\{S_2P(S)(OEt)_2\}_2]_n$ determined at −135°C contains double (1.912 Å) and single (2.094–2.099 Å) phosphorus–sulphur bonds, and intermolecular secondary Se...S interactions (3.342–3.523 Å) leading to supramolecular association, **180** (R = Et). The coordination geometry around selenium thus becomes trapezoidal planar.[272]



180

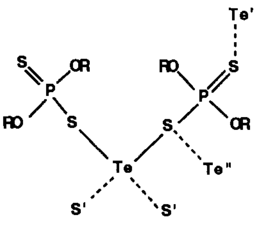
For crystal data and molecular dimensions see Table 28.

b. Tellurium. Several tellurium(II) and tellurium(IV) phosphorodithioates have been investigated by X-ray diffraction. In bis(dimethylphosphorodithioato)tellurium(II), $[Te\{S_2P(OMe)_2\}_2]_n$, the molecules are associated into a supramolecular two-dimensional structure through Te...S secondary interactions, as shown schematically in **181** (R = Me). The P=S double bond (1.92 Å) of the ligand is involved in intermolecular secondary interactions (Te...S 3.31 Å). The other P—S bond of the ligand is a single bond (2.09 Å). The tellurium atom lies on a two-fold axis.[273]

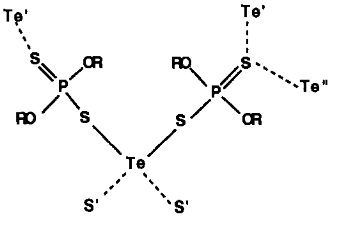


181

The structure of $[Te\{S_2P(OEt)_2\}_2]_n$ (**182**) is also associated, but in a more complex way, leading to a three-dimensional supramolecular array.[274] The asymmetric unit contains three molecules, with the ligand in each showing single (P—S 2.076–2.089 Å) and double (P=S 1.919–1.939 Å) bonds. The P=S double bonds not involved in secondary interactions are the shortest (1.927 and 1.919 Å) ; some double bonds participate in secondary interactions with tellurium atoms, **182a**, while one is connected by secondary interactions simultaneously to two other tellurium atoms, **182b**. The intermolecular, secondary bonds, are in the range from 3.209 to 3.541 Å (the sum of van der Waals radii for Te and S is *ca* 3.8 Å). If the secondary bonds are considered, the coordination geometry around tellurium is trapezoidal planar.[273]



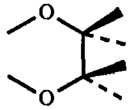
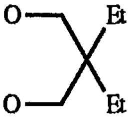
182a



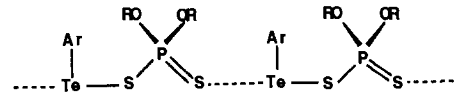
182b

Two organotellurium(II) derivatives, e.g. $[p\text{-}MeOC_6H_4Te\ S_2P(OMe)_2]_n$[275] and $[p\text{-}EtOC_6H_4Te\ S_2P(OMe)_2]_n$[276a] are also supramolecular associates, forming single strand polymeric chains **183**. The primary Te—S bonds are in the normal range (2.439–2.443 Å) and the secondary Te...S bonds (3.309 and 3.262 Å) are significantly shorter than van der Waals distances. In $[PhTe\ S_2P(OMe)_2]_n$ the primary Te—S bonds are 2.418 Å and the secondary Te...S bonds were determined as 3.405 Å.[276b]

Table 28. Crystal structure data for selenium and tellurium phosphorodithioato complexes

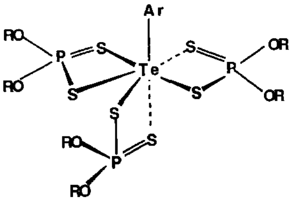
Structure no.	R	Space group	*a* *b* *c*	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
180	Et	P$\bar{1}$	8.364	63.28	2.099	1.912	2.209	3.342	107.1	—	102.0	bridge	272
			10.755	70.78	2.094	1.912	2.210	3.523	105.7	—	103.0	bridge	
			12.387	83.93				—					
181	Me	Pbcn	10.37	—	1.92	2.09	2.44	3.31	106.8	—	105.1	bridge	273
			11.51	—									
			12.56	—									
182	Et	P$\bar{1}$	12.247	101.69	A[a]								
			12.656	103.29	1.927	2.079	2.420	—	107.7	—	103.2	bridge	275
			20.135	104.72	1.939	2.077	2.430	—	109.6	—	102.1	bridge	
					B[a]								
					1.929	2.082	2.435	—	107.5	—	103.6	bridge	
					1.919	2.089	2.387	—	106.9	—	104.1	bridge	
					C[a]								
					1.949	2.070	2.424	—	106.7	—	100.8	bridge	
					1.930	2.070	2.421	—	106.9	—	104.7	bridge	
183	Me	P2_1/n	9.976	—	1.933	2.051	3.262	2.443	107.9	—	103.3	bridge	275
	Ar = *p*-		12.023	97.22									
	MeOC$_6$H$_4$		12.333	—									
183	Et	P2_1/n	10.176	—	1.927	2.052	3.309	2.439	107.9	—	102.9	bridge	276a
	Ar = *p*-		12.407	97.40									
	EtOC$_6$H$_4$		12.234	—									
183	Me	P2_1/c	10.324	—	1.919	2.060	3.405	2.418	107.2	—	106.1	bridge	276b
	Ar = Ph		8.519	101.83									
			14.929	—									
184	Ph	P2_1/c	10.392	—	1.933	2.009	3.292	2.651	113.6	97.7	80.8	chel	276c
			10.379	95.273	1.909	2.069	3.374	2.481	116.4	74.9	97.0	chel	
			42.050	—	1.934	2.013	3.106	2.613	113.5	94.4	81.9	chel	
185	Me	P2_1/c	7.820	—	1.934	2.045	3.383	2.619	115.1	98.1		chel	277
			15.356	92.84	1.928	2.022	3.362	2.625	116.3			chel	
			20.317	—									
185	Et	P$2_12_12_1$	8.297	—	1.931	2.043	3.367	2.609	114.4	79.4	99.2	chel	278a
	R′ = Ph		16.311	—	1.929	2.020	3.365	2.620	115.9	78.6	100.0	chel	
			21.117	—									
185	(RO)$_2$=	P2_1/c	12.707	—	1.939	2.045	3.349	2.604	113.8	99.1		chel	278b
			11.482	98.00	1.944	2.038	3.341	2.661	113.6	95.9		chel	
			16.782	—									
	R = Me												
185	(RO)$_2$=	P$\bar{1}$	12.580	91.28	1.917	2.060	3.490	2.597	116.4	97.4		chel	278b
			13.313	104.94	1.920	2.052	3.516	2.660	116.7	99.4		chel	
			8.206	78.52									
	R = Me												
186	Et	P2_1/n	11.637	—	1.951	1.962	3.150	3.286	117.9	87.3	91.4	chel	278c
			15.159	111.84									
			14.688	—									
187	Et	P2_1/c	10.856	—	1.901	2.036	3.493	2.627	116.1	98.9	76.4	bridge	279
			19.876	98.31	1.903	2.021	3.447	2.621	114.3	101.5	79.3		
			12.206	—									
188	Et	P$2_12_12_1$	6.653	—	1.927	2.027	3.438	2.742	116.0	78.4	96.5	chel	280
			9.876	—									
			36.347	—									
189	Et	P$\bar{1}$	9.078	69.28	1.992	1.815	3.436	2.708		99.3	80.5	chel	281
			11.823	88.29									
			14.941	89.40									
190	Me	P2_1/n	9.694	—	1.993	2.009	2.728	2.632	110.6	85.6	88.0	chel	277
	Ar=		13.679	110.65									
	p-MeOC$_6$H$_4$		13.879	—									
191	Et	P$\bar{1}$	14.287	85.30	1.933	2.000	3.477	2.691	116.9	73.1	93.6	chel	282
			14.579	84.36	1.960	1.972	3.410	2.684	116.2	77.0	97.4	chel	
			14.652	60.20	1.908	1.995	3.413	2.772	116.3	75.7	93.6	chel	

[a] Three crystallographically independent molecules in the unit cell.



183

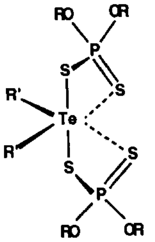
Only one monoorganotellurium(IV) tris(phosphorodithioate), **184** (Ar = Ph, R = Ph), has been structurally investigated. The compound displays pentagonal bipyramidal geometry and the ligands are anisobidentate, with short (P=S 1.933, 1.934 and 1.909 Å) and long (P—S 2.009, 2.013 and 2.069 Å) phosphorus–sulphur bonds. The tellurium–sulphur distances indicate primary bonds (2.651, 2.613 and 2.481 Å, all in the equatorial plane) and secondary interactions (3.292 and 3.106 Å—equatorial, and 3.374 Å—axial). The aryl group is in apical position, *trans* to the longest Te... S distance. The S—P—S bond angles (113.6°, 113.5° and 116.4°) are wider than tetrahedral, in keeping with the weak chelating character of the ligands.[276c]



184

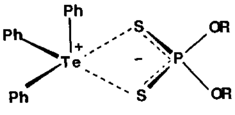
In bis(dialkylphosphorodithioato)diphenyltellurium(IV), $Ph_2Te\{S_2P(OR)_2\}_2$, with R = Me[277] and Et,[278a] the ligands are strongly anisobidentate, with single (P—S 2.020 and 2.045 Å) and double (P=S 1.928 and 1.934 Å) bonds. The tellurium coordination geometry is ψ-trigonal bipyramidal, with phenyl groups in equatorial positions, **185**, R′ = Ph. The sulphur atoms doubly bonded to phosphorus, which are involved in secondary interactions with tellurium (Te... S 3.35–3.38 Å) are well above and below the equatorial plane, and were not considered in the description of the coordination geometry.

Dimethyltellurium derivatives of cyclic alkylene phosphorodithioates, $Me_2Te\{S_2P(OCMe_2CMe_2O)\}_2$ and $Me_2Te\{S_2P(OCH_2CEt_2CH_2O)\}_2$ display similar structures.[278b]



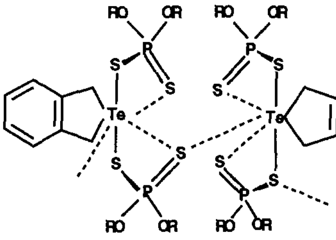
185

Triphenyltellurium(IV) diethylphosphorodithioate, $Ph_3Te\{S_2P(OEt)_2\}$, displays an uncommon structure **186**, in which both tellurium–sulphur bonds are unusually long (3.286 and 3.150 Å), of the order of magnitude of secondary interactions. The P—S bonds in the phosphorodithioato ligand (1.951 and 1.962 Å)[278c] are of the same order of magnitude as found in ionic phosphorodithioates. Perhaps, this compound can be best described as containing discrete Ph_3Te^+ cations and $(EtO)_2PS_2^-$ anions, connected through secondary Te... S interactions. This view is also supported by the wide S—P—S bond angle (117.9°).



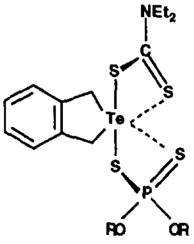
186

The heterocyclic tellurium(IV) bis(diethylphosphorodithioate) $[C_6H_4(CH_2)_2Te\{S_2P(OEt)_2\}_2]_n$ has a supramolecular structure **187**, in which the molecules are connected into zig-zag chains by weak secondary Te...S bonds (3.729 Å). In the molecular unit the ligands are clearly anisobidentate: P—S 2.021 and 2.036 Å; P=S 1.901 and 1.903 Å; Te—S 2.621 and 2.627 Å; Te...S 3.447 and 3.393 Å. The weak intrachelate Te...S impose little strain upon the S—P—S bonds, which are rather wide (114.3 and 116.1°).[279]



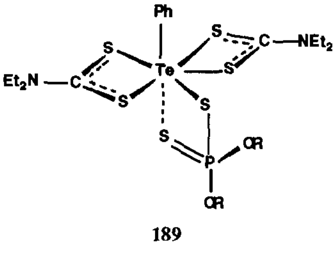
187

The mixed ligand complex $C_6H_4(CH_2)_2Te\{S_2C\text{-}NEt_2\}\{S_2P(OEt)_2\}$ (structure **188**) is worth mentioning, because the primary Te—S bonds are clearly different: Te—S_{dtc} 2.521 Å and Te—S_{dtp} 2.742 Å, suggesting that the dithiocarbamato ligand is more strongly bound to tellurium than the phosphorodithioate. The secondary bonds are also shorter for dithiocarbamate (Te... S_{dtc} 3.103 Å) than for the phosphorodithioate (Te... S_{dtp} 3.438 Å).[280]



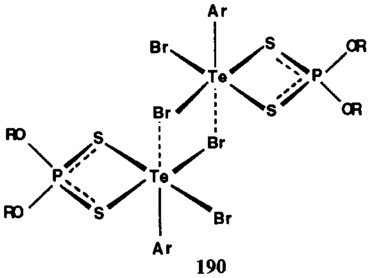
188

A related mixed ligand complex, $PhTe\{S_2C\text{-}NEt_2\}_2\{S_2P(OEt)_2\}$, displays pentagonal bipyramidal geometry, **189**, with five sulphur atoms in the equatorial plane (Te—S distances in the range 2.674–2.708 Å). The phenyl group occupies an axial position, perpendicular to the pentagonal plane, while the second axial position is occupied by a sulphur atom, doubly bonded to phosphorus in a phosphorodithioato ligand.[281] This axial distance (Te...S 3.436 Å) is much longer than the equatorial Te—S bonds (2.690–2.708 Å). The phosphorodithioato ligand is anisobidentate (coordination pattern no. 3) with P—S 1.992 Å and 1.815 Å (unusually short) and Te—S 2.708 and 3.436 Å. This compound is closely related to the tris(phosphorodithioate) **184** cited above.



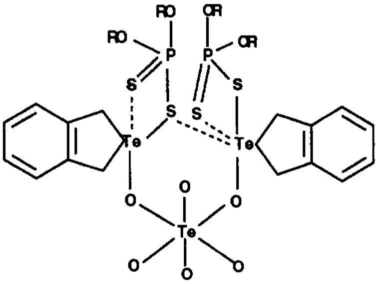
189

The compound $[p\text{-}MeOC_6H_4Te\{S_2P(OMe)_2\}Br_2]_2$ contains a practically isobidentate chelating ligand (rare in tellurium chemistry), with P—S 1.993 and 2.009 Å; Te—S 2.728 and 2.632 Å in tetragonal pyramidal coordination **190** (R = Me). However, if the intermolecular Te...Br secondary interactions (3.810 Å) are also considered, the coordination geometry becomes distorted octahedral.[277]



190

A unique mixed valence compound $Te^{VI}[OTe^{IV}(CH_2)_2C_6H_4\{S_2P(OEt)_2\}]_6$ contains six Te^{IV} heterocyclic units, each with an anisobidentate phosphorodithioato ligand, connected *via* Te^{IV}—O—Te^{VI} bonds to the central tellurium(VI) atom, as shown in **191** (R = Et). Secondary interactions between different units are also present.[282]



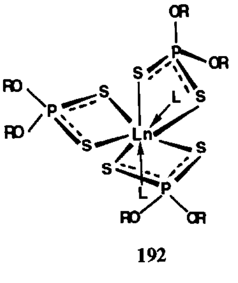
191

Crystal data and molecular dimensions for tellurium compounds are collected in Table 28.

17. *Lanthanides*

There are four types of lanthanide phosphorodithioato complex, whose structures have been established by X-ray diffraction: (a) neutral tris(dialkylphosphorodithioato) metal(III) adducts, $Ln\{S_2P(OR)_2\}_3 \cdot 2L$; (b) anionic tetrakis(dialkylphosphorodithioato) metallates, $(Ln\{S_2P(OR)_2\}_4]^-$; (c) cationic bis(dialkyl-phosphorodithioato) metal complexes, with a non-coordinated phosphorodithioato counter ion, $[Ln\{S_2P(OR)_2\}_2 \cdot 3L]^+[S_2P(OR)_2^-]$; and (d) mixed cationic–anionic complexes (combination of types (b) and (c)), like $[Ln\{S_2P(OR)_2\}_2 \cdot 3L]^+$ $[Ln\{S_2P(OR)_2\}_4]^-$.

In the neutral complexes $Ln\{S_2P(OR)_2\}_3 \cdot 2L$ investigated, with Ln = La, R = Et, L = $OPPh_3$;[283] L = $OS(CH_2Ph)_2$;[284] R = Pr^i, L = DMSO;[285] L = $MeCONMe_2$;[286] Ln = Nd, R = Pr^i, L = $PhCONH_2$,[287] the metal is eight-coordinate (distorted square antiprism or dodecahedral), **192**, and the ligands are isobidentate, occupying six of the coordination sites. The other two site are occupied by a neutral oxygen donor ligand L. Solid state molecular dimensions are listed in Table 29.



192

In the anionic tetrakis(dialkylphosphorodithioato) complexes, $[Ph_4As]^+[Ln\{S_2P(OR)_2\}_4]^-$ with Ln = La, R = Et;[288] Ln = Ce, R = Me;[289a] Ln = Nd, R = Pr^i,[289a] Ln = Ho, R = Pr^i;[289a] Ln = Er, R = Me,[289a] Et[288] and $[Ph_4P^+][Pr\{S_2P(OMe)_2\}_4]^-$ [289b] dodecahedral geometry is achieved by coor-

Table 29. Crystal structure data on lanthanide phosphorodithioato complexes

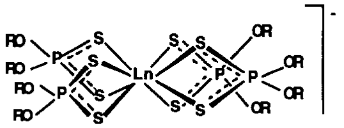
Structure no.	R	L	Space group	*a* *b* *c*	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
192	Et	$OPPh_3$	$P2_1/c$	19.66	—	1.936	1.976	3.048	3.075	114.5	91.0	89.4	chel	283
La				12.54	94.16	1.966	1.986	2.981	3.092	114.3	90.9	87.4	chel	
				24.11	—	1.957	1.971	3.037	3.092	115.1	90.3	88.5	chel	
192	Et	$OSBz_2$	$P\bar{1}$	13.300	92.79	1.959	1.969	2.992	3.023	114.9	89.2	88.1	chel	284
La				19.816	114.92	1.961	1.964	3.008	3.018	112.8	90.9	90.5	chel	
				11.257	75.40	1.955	1.969	3.091	3.013	115.0	88.6	90.6	chel	
192	Pr^i	DMSO	$P2_1/n$	17.354	—	1.959	1.966	3.003	3.013	112.9	90.7	90.3	chel	285
La				23.336	96.04	1.971	1.972	3.008	3.015	113.6	89.8	89.7	chel	
				10.955	—	1.949	1.950	3.011	2.984	114.2	89.4	90.2	chel	
192	Pr^i	DMA	$P\bar{1}$	23.071	120.0	1.965	1.987	3.046	3.009	112.8	90.3	91.0	chel	286
La				11.060	97.2	1.970	1.985	3.012	2.988	113.1	89.3	89.7	chel	
				10.793	88.9	1.974	1.981	3.013	3.029	113.1	90.2	89.6	chel	
192	Pr^i	$PhCONH_2$	C2/c	28.887	—	A^a								287
Nd				28.913	106.72	1.961	1.971	2.987	2.984	114.3	89.3	89.2	chel	
				24.814	—	1.946	1.989	2.900	2.972	112.2	91.3	88.4	chel	
						1.939	1.953	2.962	2.895	113.4	88.7	90.4	chel	
						B^a								
						1.950	1.957	2.971	2.895	113.0	88.8	90.8	chel	
						1.970	1.970	2.983	2.983	114.4	89.1	89.1	chel	
						C^a								
						1.929	1.969	2.898	2.969	112.4	91.3	88.8	chel	
						1.967	1.967	2.993	2.993	114.3	89.3	89.3	chel	
193	Et		$P2_1/c$	20.053	—	1.956	1.974	3.011	2.997	114.4	89.0	89.2	chel	288
La				15.207	112.02	1.968	1.974	2.973	3.002	113.8	90.0	89.0	chel	
				20.389		1.962	1.973	2.975	2.958	111.4	91.0	91.2		
						1.976	1.986	2.989	3.002	112.0	90.5	89.9		
193	Me		Cc	14.762	—	1.948	1.966	2.964	2.965	114.1	89.5	89.1		289a
Ce				16.780	101.09	1.960	1.972	2.952	2.986	114.1	89.6	88.5	chel	
				19.890	—	1.961	1.970	2.952	2.999	112.5	91.1	89.6	chel	
						1.968	1.970	2.998	2.939	111.7	90.0	91.6	chel	

193	Pr^i		P2$_1$/c	12.868	—	1.972	1.975	2.955	2.968	112.3	90.4	90.0	chel	289a
Nd				24.966	102.32	1.960	1.996	2.941	2.938	111.7	90.6	90.0	chel	
				21.420	—	1.974	1.990	2.947	2.927	111.8	89.3	89.6	chel	
						1.945	1.968	2.979	2.929	113.7	88.9	89.9	chel	
193	Pr^i		P2$_1$/n	14.400	—	1.970	1.973	2.837	2.878	112.1	88.9	87.6	chel	289a
Ho				32.427	93.46	1.956	1.962	2.921	2.837	111.9	88.5	90.8	chel	
				15.167	—	1.966	1.986	2.877	2.825	110.4	89.6	90.7	chel	
						1.974	1.987	2.894	2.848	110.8	88.4	89.5	chel	
193	Me		Cc	14.626	—	1.946	1.975	2.840	2.886	112.0	90.3	88.4	chel	289a
Er				16.760	100.89	1.963	1.972	2.893	2.904	112.4	89.5	89.0	chel	
				19.718	—	1.956	1.973	2.804	2.906	110.2	92.2	88.8	chel	
						1.960	1.993	2.887	2.729	109.4	88.3	92.2	chel	
193	Et		P2$_1$/c	19.972	—	1.966	1.968	2.904	2.833	111.5	88.3	90.3	chel	288
Er				15.148	112.27	1.960	1.978	2.910	2.823	112.1	88.0	90.2	chel	
				20.244		1.960	1.969	2.871	2.802	110.2	89.4	91.3	chel	
						1.963	1.969	2.816	2.900	111.1	90.5	88.0	chel	
193	Me		Pca2$_1$	19.857	—	1.96	2.06	2.888	3.015	112.9	85.4	90.8	chel	289b
Pr				11.422	—	1.99	2.01	2.942	2.982	112.7	89.0	87.6	chel	
				19.077	—	2.01	2.02	3.056	2.985	112.0	87.7	89.5	chel	
						1.99	2.01	3.010	2.932	111.3	88.5	90.6	chel	
194	Et	OPPh$_3$	P2$_1$	17.90	—	1.89	2.06	2.92	2.89	110.3	92.3	89.6	chel	283
Sm				16.84	99.98	1.95	2.01	2.97	2.93	113.3	89.2	89.0	chel	
				12.54	—	1.89	1.98			118.5			ionic	
194	Pr^i	PhCONH$_2$	P2$_1$/n	25.076	—	1.966	1.988	2.805	2.816	110.9	89.4	88.6	chel	290
Tb				15.446	100.77	1.978	1.988	2.805	2.816	112.1	88.4	88.4	chel	
				14.579	—	1.961	1.964			117.9			ionic	
194	Pr^i	PhCONH$_2$	P2$_1$/n	25.036	—	1.973	1.981	2.781	2.790	110.9	88.9	88.5	chel	290
Er				15.338	99.50	1.973	1.986	2.815	2.819	111.3	88.9	88.5	chel	
				14.805	—	1.946	1.964			118.3			ionic	
193/194	Pr^i	OSBu$_2$	An	23.696	—	Cation	**194:**							
				23.466	111.22	1.950	1.966	2.895	2.889	112.2	89.7	89.5	chel	291
				20.208	-/n	1.927	1.994	2.916	2.908	113.5	89.4	88.4	chel	
Nd						Anion	**193:**							
						1.948	1.966	2.937	2.911	113.4	88.9	89.3	chel	
						1.949	1.964	2.904	2.940	112.5	90.3	88.9	chel	
						1.954	1.983	2.933	2.928	111.6	90.7	90.2	chel	
						1.977	1.988	2.882	2.951	111.8	90.9	88.7	chel	

Table 29—*continued.*

Structure no.	R	L	Space group	a b c	α β γ	P—S		M—S		S—P—S	M—S—P		Bond type	Ref.
193/194	Pr^i	DMSO	P2$_1$/n	29.846	—	Cation	**194**:							
				20.070	92.13	1.952	1.955	2.884	2.891	112.3	89.5	89.2	chel	285
				14.057	—	1.949	1.982	2.872	2.875	112.3	89.6	88.9	chel	
Eu						Anion	**195**:							
						1.943	1.974	2.897	2.881	112.4	88.9	88.8	chel	
						1.934	1.953	2.908	2.872	113.0	88.9	89.6	chel	
						1.967	1.970	2.876	2.891	110.1	91.2	90.7	chel	
						1.948	1.951	2.912	2.883	112.0	89.6	90.4	chel	
195	Me		P2$_1$/n	10.601	—	1.960	1.960	2.909	2.922				chel	292
Sm				17.946	101.90	1.960	1.960	3.047	2.918				bridge	
				12.407	—									

dination of eight sulphur atoms from four isobidentate ligands, **193**. Molecular dimensions are given in Table 29.



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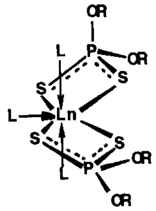
The complexes $[Ln\{S_2P(OR)_2\}_2 \cdot 3L]^+[S_2P(OR)_2]^-$ with Ln = Sm, R = Et, L = $OPPh_3$; Ln = Tb, Er, R = Pr^i, L = $PhCONH_2$,[290] contain a cation of pentagonal bipyramidal geometry, with two isobidentate chelating phosphorodithioato ligands and the three additional neutral oxygen donor ligands; one phosphorodithioate is anionic, as shown in **194**.



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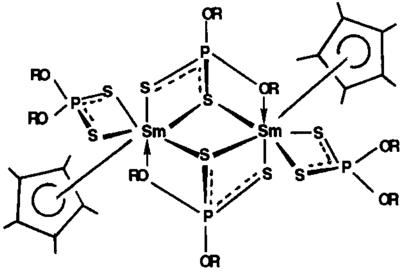
Finally, the complexes $[Ln\{S_2P(OR)_2\}_2 \cdot 3L]^+[Ln\{S_2P(OR)_2\}_4]^-$ (**193/194**) with Ln = Nd, R = Pr^i, L = $OSBu_2$,[291] and Ln = Eu, R = Pr^i, L = DMSO,[285] combine in the same compound a cation **194** and an anion **195** of the types discussed above. Note again that the metal is eight-coordinate in the anion and seven-coordinate in the cation.

Interatomic distances and bond angles are listed in Table 29.

The only organolanthanide compound investigated by X-ray diffraction is the dimeric η^5-pentamethylcyclopentadienyl samarium complex, $(\eta^5\text{-}C_5Me_5)Sm\{S_2P(OMe)_2\}_2$. This has an unusual structure **195** (R = Me) and is the second complex in which the oxygen atom of the phosphorodithioato ligand participates in bonding.[292]



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