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Supramolecular associations, secondary bonds, quasi-cyclic structures and heterogeometrism in metal derivatives of phosphorus- and arsenic-based thioacids and oxo analogs

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Contents

Abstract

The structural features of complexes involving thiophosphorus and thioarsenic ligands bound to transition metal and Main Group elements are described. Intermolecular associations are very common and are discussed in the context of supramolecular chemistry. © 1997 Elsevier Science S.A.

Keywords: Phosphorus-based thioacid; Arsenic-based thioacid

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1. Introduction

1.1. Definitions

1.1.1. Supramolecular chemistry

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" [1,2]. Intermolecular forces leading to supramolecular structures can be secondary bonds, hydrogen bonds, donor–acceptor (Lewis acid–base type) interactions or ionic interactions. Such forces are important in host–guest complexation, in the control of aggregation states and are fundamental for what is now called "crystal engineering" [3]. The formation of supramolecular structures occurs mostly as a spontaneous process (self-assembly) rather than through stepwise mechanisms and involves a process known as 'molecular recognition'. According to Lehn, "supramolecular chemistry is a generalized coordination chemistry" [1].

In supramolecular compounds one can distinguish three levels of structural organization: a primary structure (at the molecular level); a secondary structure consisting of associated molecules (i.e. supramolecular entities resulted from intermolecular interactions); a tertiary structure (crystal packing of the secondary or supramolecular entities). This differs from common molecular crystals based upon simple crystal packing of the molecular entities, without an intermediate level of structural organization.

So far, the concepts of supramolecular chemistry have been mostly applied to biological and organic structures or to metal coordination compounds [4], but have been much less used in organometallic chemistry. Supramolecular structures, in agreement with the definition cited above [1,2], are frequently encountered in Main Group metal compounds, and this review will concentrate upon derivatives of phosphorus-based acids.

The data obtained by our research group, correlated with those of others, suggest a promising working hypothesis: when the preferred coordination number of the central metal is larger then the number of coordination sites occupied by the organic groups and the donor ligands in organometallic and inorganic compounds of Main Group metals, self-organized supramolecular associations may occur.

The degree of association and the structure of a compound cannot be predicted, and this makes interesting the investigation of such systems. To get information about the relationship between the coordination number of the metal, the functionality of the metal-centered core and self-organized supramolecular association in organometallic compounds, it is necessary to synthesize new compounds which satisfy the working hypothesis just cited and to study their crystal structure.

It should be noted that the supramolecular structures to be discussed contain a central inorganic core wrapped in external organic groups. The self-organization in organic solutions, followed by crystallization, is probably due to the tendency of polar inorganic parts to join together, exposing to the outside environment of the organic solvent the nonpolar hydrocarbon part. This is comparable with the formation of miceles or of the interface layers between a lipophilic and a hydrophilic phase in a system made up of two immiscible, polar/nonpolar solvents: the polar part of dissolved molecules is in the hydrophilic phase and the nonpolar (hydrocarbon chain) in the organic lipophilic phase (see Ref. [5]). A better understanding of the factors controlling the self-assembly and self-organization of supramolecular associates may be useful for crystal engineering techniques, i.e. design of pre-established structures.

Organometallic compounds with ordered, self-organized supramolecular structures, could be of interest as precursors for advanced materials, since such compounds may contain components in the right stoichiometric proportion and required space arrangement to permit the synthesis of some materials with desired composition and pre-established structure, after removal of the organic part, e.g. by thermal processes. The exploration of this field might lead to new precursors for oxides, sulfides, arsenides, phosphides and other materials required by advanced technologies. Therefore, the investigation of basic processes leading to ordered, self-organized supramolecular structures may be of more than academic interest.

1.1.2. Secondary bonding

This term (introduced by Alcock) describes "weak bonds between Main Group metal atoms, longer than single covalent bonds but shorter than van der Waals interatomic distances" [6,7]. It is obvious from this definition that semibonding interactions can be identified only by crystal structure determinations with the aid of diffraction methods. Usually these bonds are not strong enough to survive in solution, but they can have spectacular effects in the building of a crystal structure (crystal engineering).

Typically, secondary bonding (or semibonding) interactions occur as a basically linear X–A···Y system in which A–X is a normal covalent bond and A···Y is the secondary bond, The explanation advanced by Alcock suggests that the secondary bond is formed either by donation from the lone pair on X into an s* orbital of the A–Y bond, or (alternatively and equivalently) as an asymmetric three-center system, with three s symmetry atomic orbitals on A, X and Y, combined to form three molecular orbitals: one filled bonding molecular orbital located between A and X, one filled nonbonding or weakly bonding orbital located between A and Y, and one empty antibonding orbital [6,8,9].

To facilitate comparisons, expected covalent bond and van der Waals interatomic distances for several bonds to sulfur are presented in Table 1. Two sets of covalent bond atomic radii and van der Waals radii, given in Tables 2 and 3 respectively, were used. Atomic radii are from Refs. [7,10]. Since van der Waals radii are more difficult to estimate, two sets of values are also given, one from a much cited paper by Bondi [7,11] and a second one more recently recommended by Batsanov [12]. Batsanov's values are slightly smaller than those suggested by Bondi. It has been noted that covalent and dative bonds (Lewis acid–base or donor–acceptor interactions) between the same atoms (i.e. for a given pair of elements) are not identical; the dative bonds are slightly longer. Sometimes it may be useful to keep this distinction in mind [13].

Table 1
Expected covalent bond and van der Waals interatomic distances (Å)

Bond	Sum of covalent radii		Sum of van der Waals radii	
	Ref. [7]	Ref. [10]	Refs. [7,11]	Ref. [12]
Ga–S	2.302	2.28	—	—
In–S	2.462	2.49	—	—
Tl–S	—	2.47	—	—
Ge–S	2.272	2.222	3.75	3.86
Sn–S	2.442	2.406	3.9	4.05
Pb–S	—	2.44	—	4.15
P–S	2.14	2.123	3.6	3.75
As–S	2.248	2.238	3.65	3.86
Sb–S	2.422	2.356	3.85	4.05
Bi–S	—	2.45	3.95	4.25
Se–S	2.255	2.183	3.7	3.8
Te–S	2.443	2.376	3.86	4.01

Table 2
Covalent bond atomic radii (Å)

Element	Ref. [7]	Ref. [10]
B	0.83	0.817
C	0.767	0.767
N	0.702	0.726
O	0.659	0.745
Al	1.18	1.202
Si	1.09	1.169
P	1.088	1.103
S	1.052	1.02
Ga	1.25	1.26
Ge	1.22	1.202
As	1.196	1.218
Se	1.203	1.163
In	1.41	1.47
Sn	1.39	1.386
Sb	1.37	1.336
Te	1.391	1.356
Tl	—	1.45
Pb	—	1.42
Bi	—	1.43

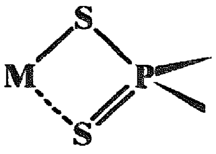
1.1.3. Quasi-cyclic structures

Rings formed through secondary bonds were called quasi-cyclic structures [14]. This type of compound can be illustrated with phosphor-1,1-dithiolato ligands, which display a great diversity of coordination patterns [15,16]. Bidentate (monometallic biconnective) coordination of these ligands to a metal center leads to cyclization (chelate ring formation). In Main Group metal compounds, cyclization frequently

Table 3
Van der Waals radii (Å)

Element	Refs. [7,11]	Ref. [12]
C	1.7	1.7
N	1.55	1.6
O	1.52	1.5
Si	2.1	1.95
P	1.8	1.9
S	1.8	1.85
Ge	1.95	2.01
As	1.85	2.01
Se	1.9	1.95
Sn	2.1	2.2
Sb	2.05	2.2
Te	2.06	2.15
Pb	—	2.3
Bi	2.15	2.4

occurs through secondary bonds, as shown in **1**. This type of chelating differs from **2**, where the cyclization occurs through dative bonds (of the same order of magnitude, but slightly longer than covalent bonds) or from **3**, where symmetrical chelating coordination occurs through basically covalent bonds. Since the secondary M···S interaction is not an authentic chemical bond, a chelate ring of type **1** is called a quasi-cyclic structure.



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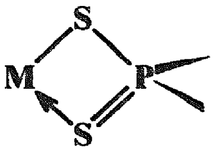

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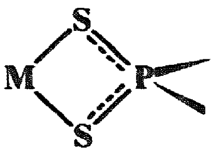

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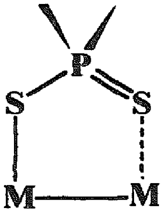
Other types of quasi-cyclic structure are formed by unsymmetrical bridging of phosphor-1,1-dithiolates as in **4**, by dimerization of phosphor-1,1-dithiolates as in **5**, or by unsymmetrical coordination of dithioimidodiphosphinates as in **6**.

Each type will be illustrated in Sections 2 and 3.

1.1.4. Heterogeometrism

Compounds of the same general formula, i.e. members of the same class, differing only in the nature of the peripheral (organic) groups (substituents) often display different coordination geometries around the metal coordination center. Such compounds were called ‘heterogeometric analogs,’ and the phenomenon ‘heterogeometrism’ [14]. Thus, diorganotin(IV) phosphor-1,1-dithiolates display either capped tetrahedral (**7**) or regular octahedral (**8**) coordination geometries. Nickel complexes



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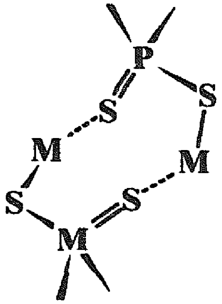

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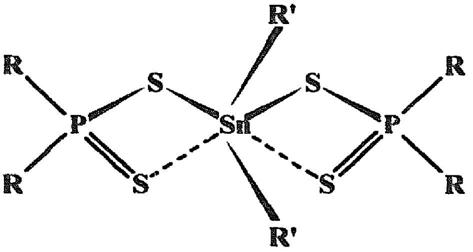
belonging to the same class can be either tetrahedral or square planar. Such examples will be discussed in more detail below. (Remember, isomerism is the situation when compounds of identical composition display different molecular structures.)



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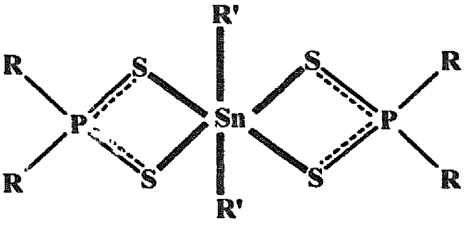

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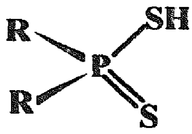
1.2. The ligands

1.2.1. Phosphor-1,1-dithiolates (phosphorodithioates, phosphinodithioates) and arsenic analogs

This review covers a large number of Main Group metal compounds with phosphorus-based ligands, **9**–**11**, derived from dithio- and monothiophosphoric and phosphinic acids, i.e. phosphorodithioates (dithiophosphates or dithiophosphoric acid *O*,*O*-diesters, **9**, R = alkoxy, aroxy), phosphinodithioates (dithiophosphinates, **9**, R = alkyl, aryl), phosphorothioates (monothiophosphates, **10**, R = alkoxy, aroxy) and phosphinothioates (monothiophosphinates, **10**, R = alkyl, aryl), as well as their sulfur-free oxo analogs (phosphoric acid *O*,*O*-diesters and phosphinates, **11**). Similar arsenic compounds, **12**–**14**, are also known but much less investigated.

The coordination patterns of the ligands derived from phosphor-1,1-dithiolates display a broad diversity [15,16]. Monodentate (monometallic monoconnective) coordination is rare (e.g. in $Ph_3Sn\{S_2P(OEt)_2\}$ [17], $Ge\{S_2P(OMe)_2\}_4$ [18],



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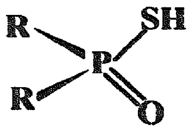

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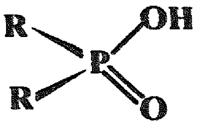

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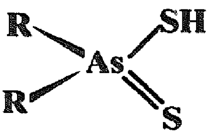

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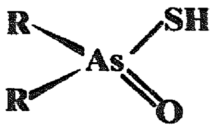

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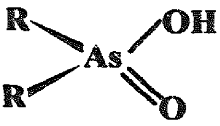
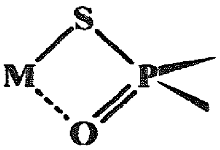


14

$Ge_2S_2\{S_2P(OMe)_2\}_4$ [18], $Ph_3Ge\{S_2P(OMe)_2\}$ [19], $Ph_2Ge\{S_2P(OMe)_2\}_2$ [19], $Ph_3GeS_2PR_2$, R = Me and Ph [20], $Ph_3Pb\{S_2P(OEt)_2\}$ [21]); bidentate symmetrical (isobidentate) and bidentate unsymmetrical (anisobidentate) (both monometallic biconnective) and bridging (bimetallic biconnective, etc.) coordination patterns are the most common, and lead to a great richness of structure types [16].

The anions derived from oxothio acids **15**, **16** are ambident nucleophiles, as they can form primary bonds through either sulfur or oxygen:



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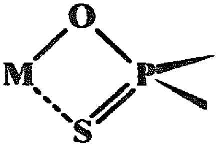


16

The anions derived from these acids can be combined with 'naked' metal atoms or with organometallic moieties of various functionalities, serving as coordination centers, e.g.

monofunctional:

RZn(II)
RCd(II)
RHg(II)

R_2Al(III)
R_2Ga(III)
R_2Tl(III)

R_2As(III)
R_2Sb(III)
R_2Bi(III)

R_3Ge(I)
R_3Sn(IV)
R_3Pb(IV)

RTe(II)
R_3Te(IV)

difunctional:

RAl(III)
RGa(III)
RTl(III)

R_2Ge(IV)
R_2Sn(IV)
R_2Pb(IV)

RAs(III)
RSb(III)
RBi(III)

R_3As(V)
R_3Sb(V)
R_3Bi(V)

R_2Te(IV)

trifunctional:

RGe(IV)
RSn(IV)
RPb(IV)

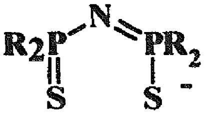
$R_2As(V)$
$R_2Sb(V)$
$R_2Bi(V)$

etc.

The number of possible intercombinations between these moieties and the ligands cited above is legion. In the work done and published so far, only a few of these possibilities have been explored.

1.2.2. 1,3-Dichalcogenoimidodiphosphinates

These ligands, conventionally formulated as **17–19**, are the inorganic analogs of acetylacetonates and their thio analogs. They result by facile deprotonation of bis(chalcogenophosphinyl)imines, $R_2(X{:})P{-}NH{-}P({:}X)R_2$ (X = S, Se or O) in strongly basic media. Some of the dithio salts, $M^+[SPh_2PNPPh_2S]^-$, with potassium [22], potassium-18-crown-6-ether [23] and PPN cations [24] have been investigated by X-ray diffraction and suggest considerable delocalization of the negative charge over the S–P–N–P–S fragment, in metal compounds; however, the electron delocalization is sometimes limited to the P–N–P fragment or is even absent.



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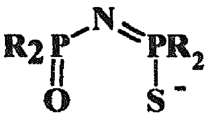

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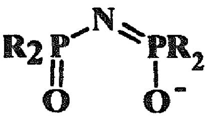
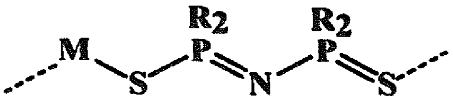


19

These ligands have a larger bite (ca. 3.7 Å) than phosphor-1,1-dithiolates and tend to coordinate as bidentate chelating, to form six-membered, inorganic (carbon-free) chelate rings **20** [25]; occasionally they may form bridges, leading to dimeric, large ring systems (as in gold(I) or phenyltellurium(II) derivatives) or to supramolecular, polymeric structures **21** (as in the case of the trimethyltin derivative) (see below).

20



M = SnMe3 R = Ph

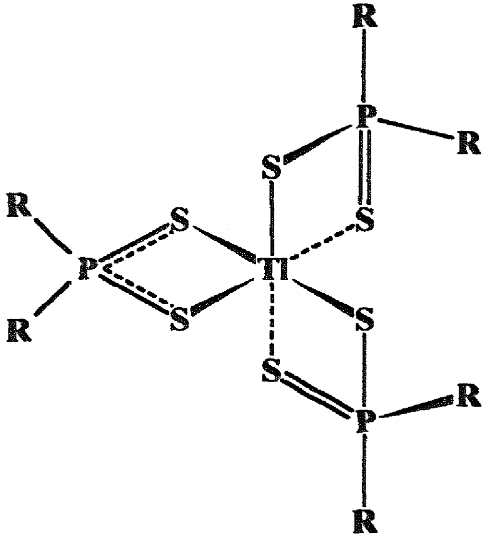
21

The coordination is generally symmetrical (particularly in transition metal complexes), but in Main Group metal compounds a certain degree of asymmetry is sometimes observed, suggesting their description as quasi-cyclic structures.

2. Secondary bonds in mononuclear quasi-cyclic compounds

Mononuclear complexes are formed when the coordinated ligands, together with the organic group attached to the central metal atom in organometallic derivatives, allow for coordinative saturation. The phosphor-1,1-dithiolato ligands have a small bite and tend to act as bidentate. Symmetrical (isobidentate) coordination leads to four-membered chelate ring formation; unsymmetrical (anisobidentate) coordination, consisting in a primary M–S (basically covalent) bond and a secondary M···S interaction, leads to formation of quasi-cyclic four-membered systems. Isobidentate coordination of dithiophosphorus ligands is rare in Main Group metal chemistry, but it is predominant in transition metal chemistry [16].

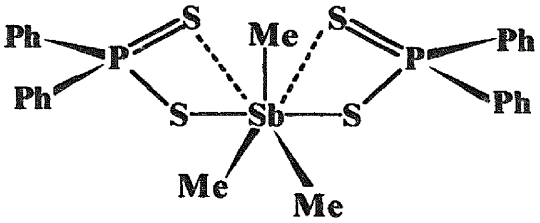
A nice compound illustrating in the same molecule the difference between isobidentate and anisobidentate dithio-phosphorus ligands is provided by thallium(III) tris(dicyclohexylphosphinodithioate), $Tl(S_2PCy_2)_3$, obtained by protodephenylation of $TlPh_3$ with dicylohexylphosphinodithioic acid, $Cy_2P(S)SH$ [26]. This compound contains a symmetrically coordinated (isobidentate) ligand and two unsymmetrically coordinated (anisobidentate) ligands, as illustrated in **22**. The isobidentate ligand forms a regular four-membered chelate ring, whereas the two anisobidentate ligands form two four-membered quasi-cyclic systems.



22

Apparently, a similar case is displayed by tris(diethylphosphorodithioato)indium(III), $In\{S_2P(OEt)_2\}_3$, but the accuracy of this structure determination is rather low ($R=0.12$) [27].

Trigonal bipyramidal coordination, typical for antimony(V), can be achieved in trimethylantimony(V) bis(diphenylphosphinodithioate) (**23**) with three organic groups and two ligand moieties; therefore, there is no need for association and, not surprisingly, the compound $Me_3Sb(S_2PPh_2)_2$ is monomeric. The small bite of the ligand is probably the cause of two weak secondary Sb···S interactions (3.744 and 3.842 Å) in addition to the primary Sb–S bonds (2.611 Å) [28]. The sum of van der Waals radii for antimony–sulfur is 4.05 Å (Bondi) or 3.89 Å (Batsanov).



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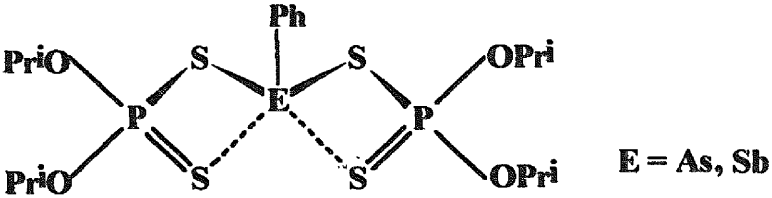
Phenylarsenic(III) and phenylantimony(III) bis(diisopropylphosphorodithioates), $PhE\{S_2P(O^iPr)_2\}_2$ (E = As, Sb) are also monomeric, distorted square pyramidal complexes, **24**, with the aromatic group in axial position and chelate quasi-cyclic units in the basal plane (As–S 2.310 and 2.317 Å; As···S 3.125 and 3.187 Å; Sb–S 2.516 and 2.529 Å, Sb···S 3.056 and 3.067 Å) [29]. The sum of van der Waals radii for arsenic–sulfur is 3.85 Å (Bondi) or 3.65 Å (Batsanov).

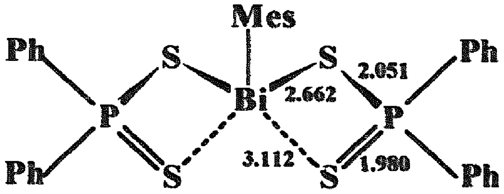


24

The mesitylbismuth(III) derivative, $MesBi(S_2PPh_2)_2$, is a five-coordinate monomer, **25**, probably as a result of the steric demands of the bulky mesityl group, which prevent intermolecular association; the coordination geometry is distorted square pyramidal, and primary Bi–S bonds (2.622 Å) and secondary Bi···S interactions (3.112 Å) are observed in the chelate quasi-cyclic systems [30]. The sum of van der Waals radii for bismuth–sulfur is 4.25 Å (Bondi).

Phenyltellurium tris(diphenylphosphorodithioate), $PhTe\{S_2P(OPh)_2\}_3$, displays pentagonal bipyramidal geometry **26**, and the anisobidentate ligands form three four-membered quasi-cyclic systems, with primary Te–S bonds in the equatorial plane (2.651, 2.613 and 2.481 Å) and secondary Te···S bonds (3.292 and 3.106 Å equatorial and 3.374 Å axial) [31]. The sum of van der Waals radii for tellurium–sulfur is 4.00 Å (Bondi) and 3.86 Å (Batsanov).

Secondary bonds leading to formation of quasi-cyclic systems are present in tellurium compounds. Thus, in diphenyltellurium bis(dialkylphosphorodithioates),



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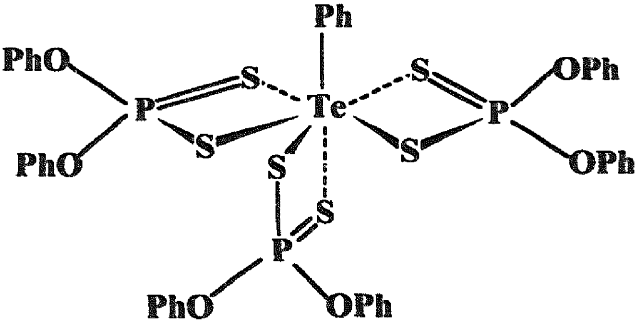

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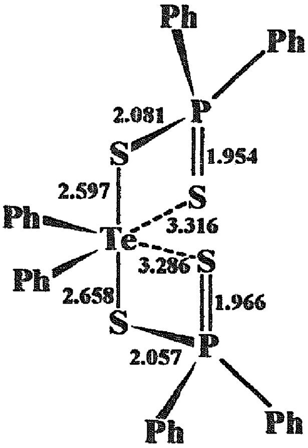
$Ph_2Te\{(S_2P(OR)_2\}_2$, R = Me [32] and Et [33], and diphenylphosphinodithioate, $Ph_2Te(S_2PPh_2)_2$, each anisobibentate ligand forms a primary Te–S and a secondary Te···S bond with the central atom, with formation of quasi-cyclic four-membered chelate rings. The molecular dimensions are illustrated for the phosphinodithioate, **27**. Similar structures have been found in dimethyltellurium alkylenedithiophosphates [34]. Some other related compounds have been reviewed [35].

The structure of $Te_2(S_2PPh_2)_2$ is, in many respects, unique. First, it contains two fused five-membered quasi-cycles, based on a shared Te–Te bond; secondly, the bicyclic units are connected through Te···Te secondary bonds into a supramolecular polymeric structure, **28**. This deep red compound has been serendipitously obtained in the reaction of TeO_2 with diphenylphosphinodithioic acid, $Ph_2P(S)SH$, in refluxing acetone. The ligands contain single P–S (2.066 Å) and double P=S (1.983 Å) bonds, and clear distinction can be made between primary Te–S bonds (2.471 and 2.439 Å) and secondary Te···S interactions (2.989 and 3.066 Å) [36].

Another particular type of quasi-cyclic structure is one in which the metal is attached to a chelating anion through two secondary bonds. This has been identified in triphenyltellurium phosphorodithioates (**29**, R = OEt. Te···S 3.286 and 3.150 Å; P–S 1.951 and 1.962 Å) [37], phosphinodithioates (**29**, R = Ph, Te···S 3.331 and 3.655 Å; P–S 2.004 and 1.975 Å) [38] and dithioimidodiphosphinates (**30**, R = Ph, Te···S 3.264 and 3.451 Å; P–S 1.983 and 1.974 Å) [38]. Please note some tendency of asymmetry of tellurium–sulfur interatomic distances. These are significantly longer



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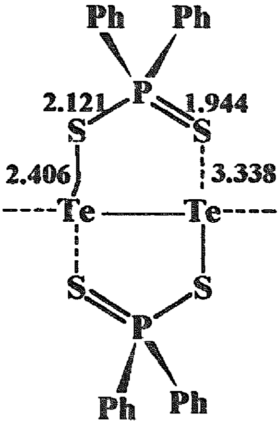

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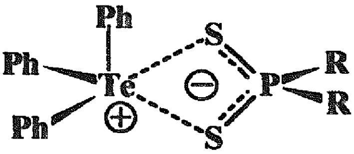
than the normal covalent (primary bonds) Te–S distances in mono- and diorganotellurium compounds of the same ligands [35].



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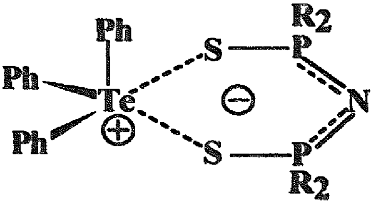

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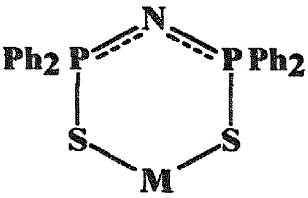
The tetraphenyldithioimidodiphosphinato ligand, with its larger bite, forms presumably strain-free six-membered rings. In transition metal complexes, basically symmetrical chelates, **31**, are formed [25,39] which can be described as authentic rings. In Main Group metal derivatives a variable degree of asymmetry, as shown in **32** is observed.

The asymmetry is most dramatic in the selenium compound $Se(SPh_2PNPPh_2S)_2$ (**33**) [40], but is also significant in the lead compound $Pb(SPh_2PNPPh_2S)_2$ (**34**) [41] and cannot be ignored in the bismuth compound $Bi(SPh_2PNPPh_2S)_3$ (**35**) [42], as illustrated by the differences measured between the metal–sulfur interatomic distances Δ_{M-S}. Thus, such rings can be described as quasi-cyclic systems. Note that M···S secondary bonds in these compounds are much shorter than the sums of van der Waals radii.

By comparison with the selenium(II) compound, it seems curious that in the spirobicyclic tellurium(II) compound, $Te(SPh_2PNPPh_2S)_2$, **36**, the coordination is



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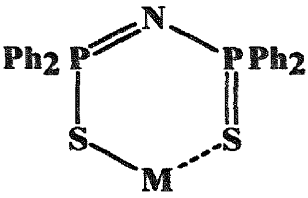

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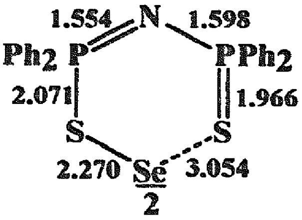
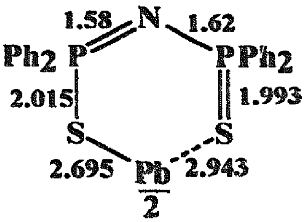


$\Delta_{Se\text{-}S} = 0.784$ Å

33



$\Delta_{Pb\text{-}S} = 0.352$ Å

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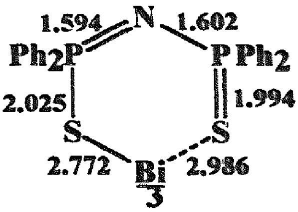
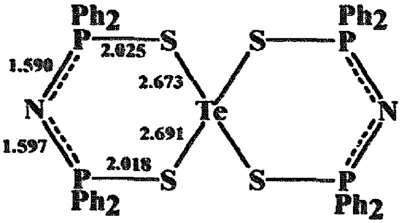


$\Delta_{Bi\text{-}S} = 0.214$ Å

35

rather symmetrical (Te–S between 2.675 and 2.699 Å) [43]. However, when the ligand is bridging, as in the dimeric phenyltellurium(II) derivative, $[PhTe(SPh_2PNPPh_2S)]_2$, **37**, the coordination is less symmetrical, as illustrated by the Te–S and P–S interatomic distances [44].



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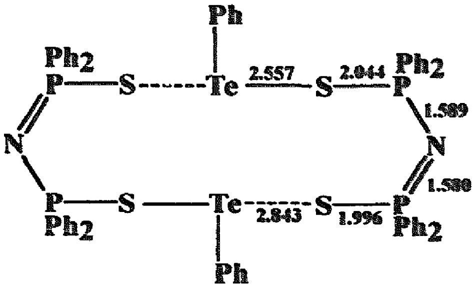

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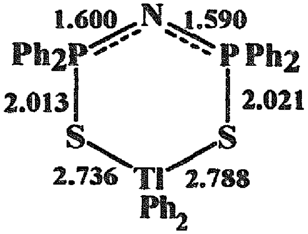
Since sterical crowding caused by either two or three voluminous ligands could be invoked to explain the observed asymmetry in **33**–**35**, it would be of interest to compare metal–sulfur interatomic distances in monocyclic compounds. In the diphenylthallium(III) derivative, $Ph_2Tl(SPh_2PNPPh_2S)$ **38**, [45], the ring is basically symmetric. In the monocyclic copper compound, $Ph_3P \cdot Cu(SPh_2PNPPh_2S)$ 39, [46], the degree of asymmetry observed is still less, and it is interesting to compare the Cu–S interatomic distances (2.215 and 2.258 Å) with those observed in the tetranuclear compound $[Cu_4(SPh_2PNPPh_2S)_3]^+[CuCl_2]^- \cdot CCl_4$ (Cu–S between 2.257 and 2.278 Å) [47]. In another monocyclic compound, a gold(III) derivative, $AuCl_2(SPh_2PNPPh_2S)$, the Au–S bonds are also very close (2.314 and 2.303 Å) [48].



$\Delta_{Tl\text{-}S} = 0.053$ Å

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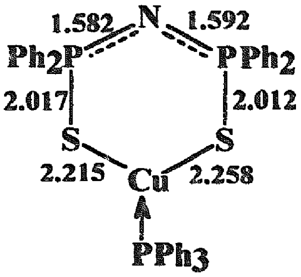
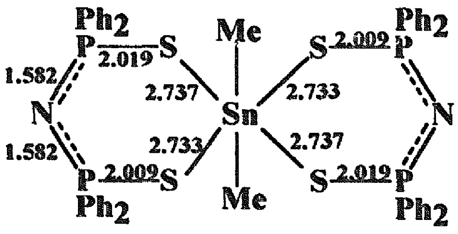


$\Delta_{Cu\text{-}S} = 0.043$ Å

39

Symmetrical and unsymmetrical bonding of the dithioimidodiphosphinato ligand achieved with the same metal, as shown above for tellurium(II), can be illustrated more dramatically with di- and triorganotin derivatives [49] Thus, in the octahedral dimethyltin(IV) derivative, $Me_2Sn(SPh_2PNPPh_2S)_2$ 40, [50], the coordination is symmetrical and the Sn–S bond lengths are equal (av. 2.735 Å), but in the



$\Delta_{Sn\text{-}S} = 0.004$ Å

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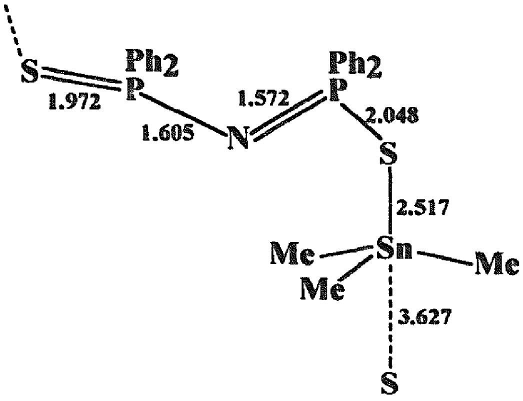
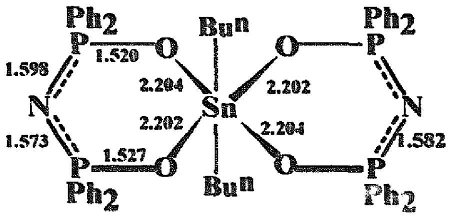


$\Delta_{Sn\text{-}S} = 1.110$ Å

41

trimethyltin(IV) derivative, $Me_2Sn(SPh_2PNPPh_2S)$, **41**, ring closure does not occur and the bonding of the ligand in the supramolecular chain formed (containing trigonal bipyramidal tin) is totally unsymmetrical, with intramolecular Sn–S primary bonds (2.517 Å) and intermolecular Sn···S secondary bonds (3.627 Å) [51]. The sum of van der Waals radii for tin–sulfur is 4.05 Å (Bondi).

Oxo analogs are more symmetric. Thus, in the octahedral dibutyltin(IV) derivative, $^nBu_2Sn(OPh_2PNPPh_2O)_2$, **42**, the coordination is totally symmetric (Sn–O 2.204 and 2.202 Å) [52]. The inorganic tin(IV) derivative $SnI_2(OPh_2PNPPh_2O)_2$ (also octahedral) is symmetric as well [53]. On the contrary, in the ψ-trigonal bipyramidal tin(II) compound, $Sn^{II}(OPh_2PNPPh_2O)_2$, the Sn–O bond lengths differ in the same ring, as shown in **43**: axial Sn–O bonds are longer than equatorial Sn–O bonds [53].



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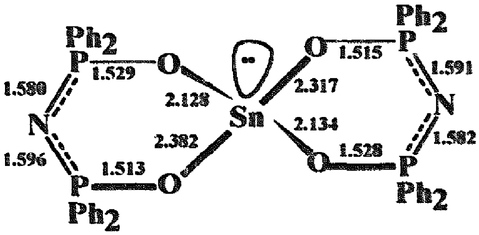

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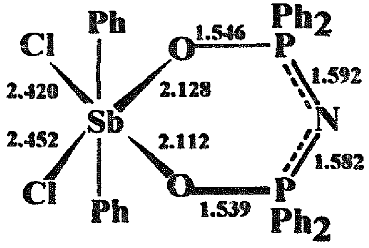
In the diphenylantimony(V) compound, $Ph_2SbCl_2(OPh_2PNPPh_2O)$, the degree of asymmetry is almost negligible, as shown in **44**. In the oxo-thio analog $Ph_2SbCl_2(OPh_2PNPh_2S)$ (**45**) both antimony–chalcogen bond lengths are in the range expected for normal covalent bonds. The octahedral coordination geometry is, however, severely distorted because of the significant difference in the Sb–O and Sb–S bond lengths [54]. Both these ring systems are authentic chelate rings; no secondary bonding participates in their formation.



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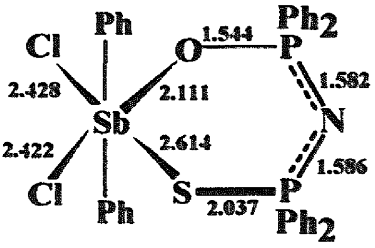

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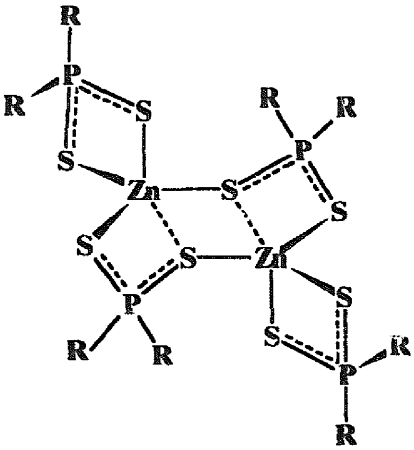
3. Secondary bonds in cyclic and quasi-cyclic dimers

Cyclic dimers of zinc phosphoro- and phosphinodithioates, $[Zn(S_2PR_2)_2]_2$ (**46**, R = Et [55], ${}^{n}Pr$ [56], $O^{i}Pr$ [57]) and cadmium analogs $[Cd(S_2PR_2)_2]_2$ (**47**, R = Ph [58], $O^{i}Pr$ [59]) have been known for quite some time. The association can be assigned to Lewis acid–base (donor–acceptor) interactions, since intermolecular M–S bond lengths are only slightly longer than intramonomeric M–S bond lengths; thus, for example, in $[Zn(S_2PEt_2)_2]_2$ all Zn–S distances are in the range 2.302–2.454 Å, indicating primary bonds [55]. Similarly, in $[Cd(S_2PPh_2)_2]_2$ the Cd–S distances are in the range 2.528–2.641 Å, suggesting that all are primary bonds [58]. Secondary bonds are, however, present as transannular M···S interactions, as demonstrated by interatomic distances such as Cd···S 3.078 Å in $[Cd(S_2PPh_2)_2]_2$.



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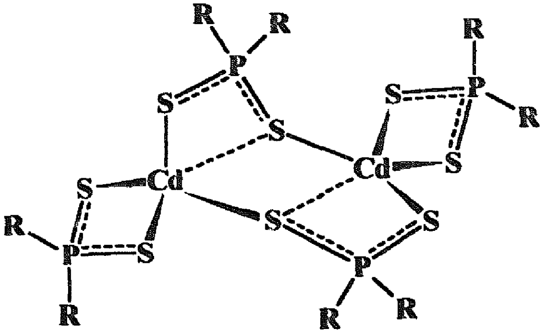

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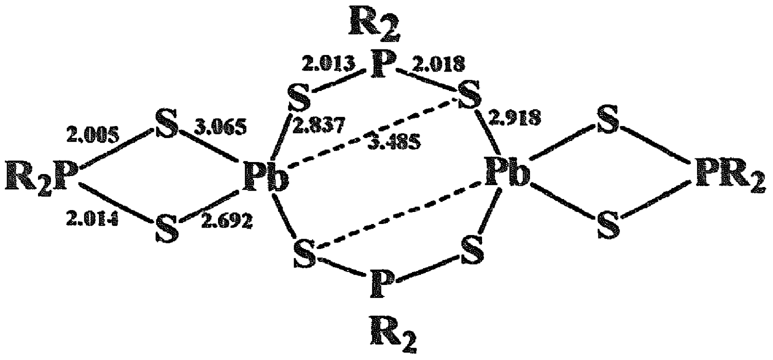
This type of dimeric structure is also found in lead(II) bis(dimethylphosphinodithioate), $Pb(S_2PMe_2)_2$, [60], where the Pb–S bonds forming the eight-membered $Pb_2S_4P_2$ ring are primary bonds, differing from other lead dimers cited below (quasi-cyclic system). The dimeric units **48** are associated via secondary Pb···S bonds to form a supramolecular structure (see below, structure **63**).

A different mode of dimer formation acts in tin(II) bis(diphenylphosphorodithioate), $[Sn\{S_2P(OPh)_2\}_2]_2$ [61]; in this compound, two molecules are associated through secondary Sn···S bonds (3.043 Å) into a supramolecular pair **49**. Note that the intermolecular Sb···S secondary bonds (3.043 Å) are shorter (stronger) than intrachelate Sb···S bonds (3.391 Å).

This type of structure is repeated by some lead(II) phosphorodithioates, i.e. $[Pb\{S_2P(O^{i}Bu)_2\}_2]_2$ **50** (primary Pb–S 2.768 and 2.762 Å; secondary Pb···S 3.444 and 3.127 Å) [62], and $[Pb\{S_2P(OPh)_2\}_2]_2$ (primary Pb–S 2.732, 2.753 and 2.896 Å; secondary Pb···S 3.215 and 3.323 Å) [62]. The sum of van der Waals radii for lead–sulfur is estimated as 4.15 Å (Bondi). The bipyridine adduct,



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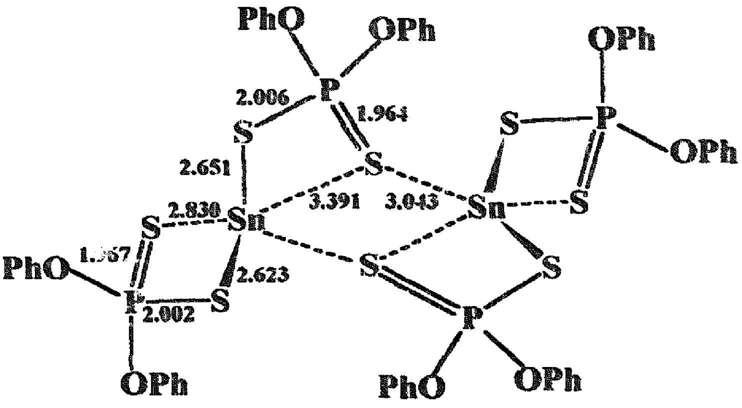

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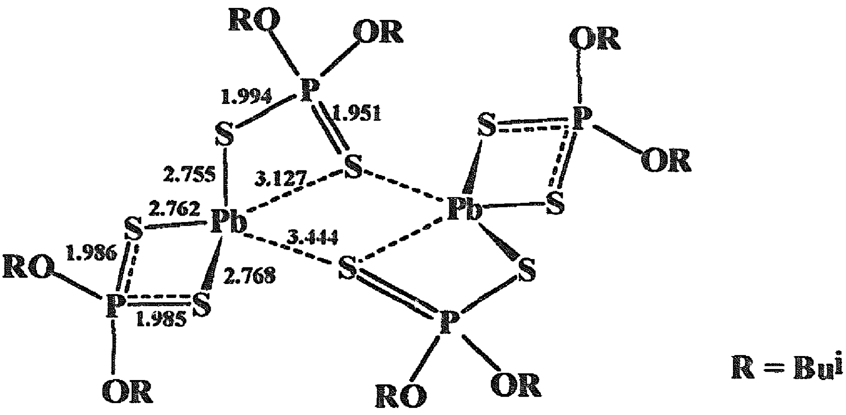
Pb$\{S_2P(OEt)_2\}_2$·Bipy is also a dimer, with seven-coordinate lead [63]. Pentagonal-bipyramidal, seven-coordinate lead is also found in the dimeric compound, diphenyllead(IV) bis(benzylphosphorodithioate), $[Ph_2Pb\{S_2P(OCH_2Ph)_2\}_2]_2$ [64].

Two dimeric, quasi-cyclic organomercury compounds have been identified, namely a phosphorodithioate, $[PhHg\{S_2P(OEt)_2\}]_2$ (**51**) [65], and a phosphinodithioate, $[MeHg(S_2PPh_2)]_2$ (**52**) [66]. The dimers are formed through secondary Hg···S interactions (3.323 and 3.152 Å respectively). The transannular mercury–sulfur interatomic distances of 3.633 Å in **51** and 3.869 Å in **52**, are longer than the sum of van der Waals radii (estimated as 3.5 Å), and thus the ring systems can be considered as quasi-monocyclic.

Diphenylantimony(III) diphenylphosphinodithioate dimerizes through Sb···S secondary bonds (3.474 Å) to form an eight-membered ring, **53**; transannular Sb···S secondary bonds (3.440 Å) transform the structure into a quasi-tricyclic system [67]. The sum of van der Waals radii for antimony–sulfur is 4.05 Å (Bondi) or 3.89 Å



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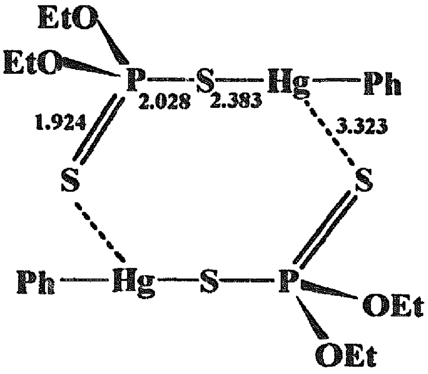

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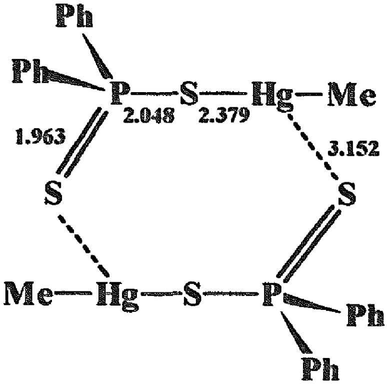

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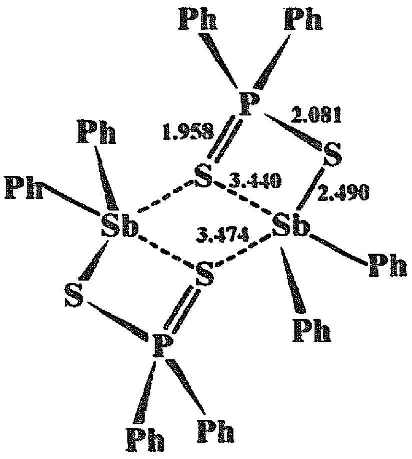
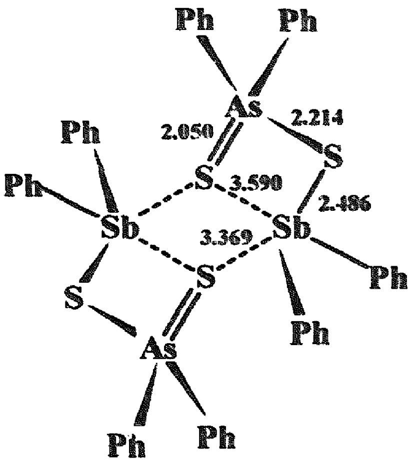
(Batsanov). The primary Sb–S bonds (2.490 Å) are in range of the sum of covalent radii (2.42 Å). A similar quasi-tricyclic structure **54** is observed for dimeric diphenylantimony(III) diphenylarsinodithioate, $[Ph_2SbS_2AsPh_2]_2$ [67].

By contrast with structure **53** above, in $(p\text{-Tol})_2SbS_2PEt_2$ the transannular Sb$\cdots$S interatomic distances are much larger (3.940 and 4.013 Å), falling in the range of the sum of Van der Waals radii, estimated as 4.05 Å (Bondi) or 3.89 Å (Batsanov); thus secondary interactions can be neglected and the structure can be described as quasi-monocyclic. Within the eight-membered ring contour, there is an alternation of primary Sb–S bonds (2.485 and 2.509 Å) and secondary Sb$\cdots$S interactions (3.556 and 3.318 Å) [68].

Perhaps it is worth mentioning here that diorganoantimony phosphinodithioates





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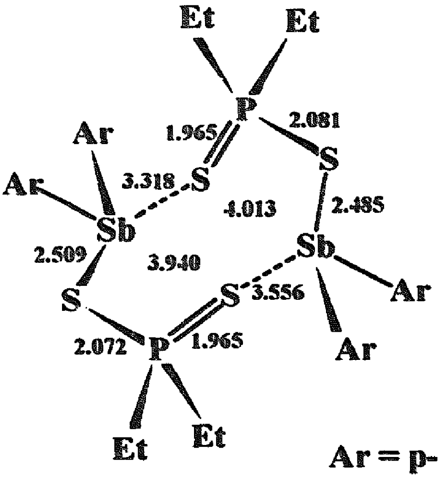


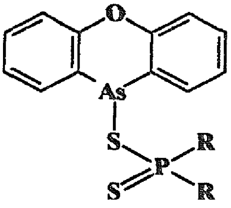
Ar = p-tolyl

55

exhibit antitumor activity, comparable or higher than that of the better known diorganotin analogs [69].

Phenoxarsinyl-10-diphenylphosphinodithioate (**56**) is an unexpected dimer, **57**, associated through As···S secondary bonds (3.402 Å), $[C_{12}H_8OAsS_2PPh_2]_2$; the dimer also contains transannular As···S secondary bonds (3.381 Å) and strongly anisobidentate phosphinodithioato ligands (P–S 2.091 Å; P=S 1.955 Å) [70]. The sum of van der Waals radii for arsenic–sulfur is estimated as 3.85 Å (Bondi) or

3.65 Å (Batsanov). The quasi-tricyclic system displays a chair conformation **58** of the eight-membered ring contour or, alternatively, a ladder-type conformation.



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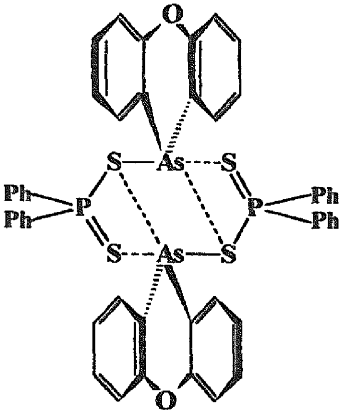

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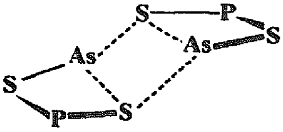

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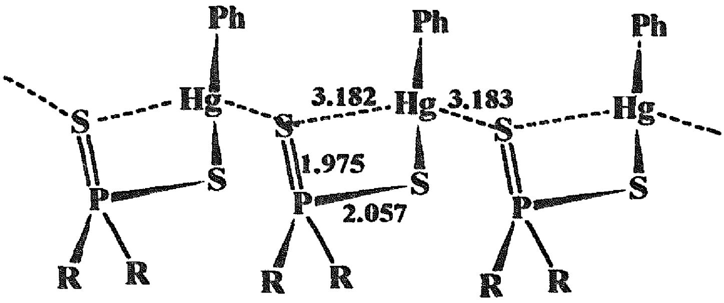
4. Supramolecular polymeric structures formed through secondary bonds

The formation of supramolecular polymeric structures through secondary bonds is observed when a large-sized metal coordination center (either as 'naked' metal atom or organometallic group) cannot achieve coordinative saturation only with the coordinated anionic ligands which neutralize its positive charge.

Phenylmercury(II) diethylphosphinodithioate is a polymer, $[PhHgS_2PEt_2]_x$, **59**, containing Hg···S secondary bonds both within the four-membered quasi-cycle of the monomeric unit (3.182 Å) and as intermolecular bonds (3.183 Å) leading to polymerization [71]; the phosphorus–sulfur bonds are nonequivalent (2.057 and 1.975 Å).



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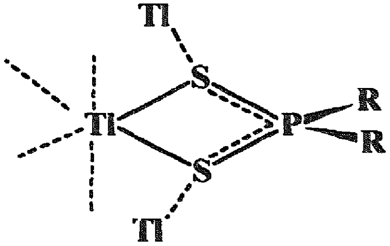
In neutral complexes, thallium(I) and diorganothallium(III) coordination centers, bearing only one ligand, are coordinatively unsaturated; therefore, such compounds will enter additional interactions to increase the coordination number of the metal and will be associated. Thus, in thallium(I) diethylphosphinodithioate, $[TlS_2PEt_2]_x$, four-membered chelate rings with isobidentate ligands (P–S 1.983 Å) are formed, and monomeric units **60** are interconnected into a two-dimensional layer via secondary Tl···S bonds (3.453 and 3.429 Å) which are significantly longer than the Tl–S primary bonds (3.056 Å) [72].



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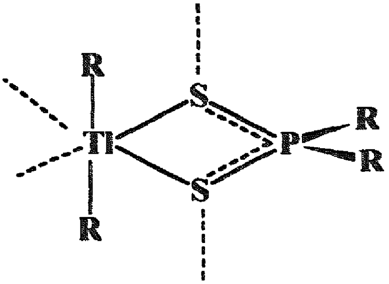

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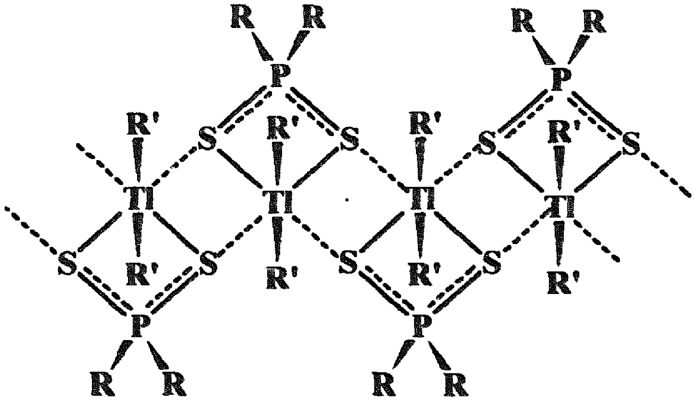
In polymeric dimethylthallium(III) diphenylphoshinodithioate, $[Me_2TlS_2PPh_2]_n$, the four-membered chelate rings **61** are again connected into a two-dimensional layer structure via Tl···S secondary interactions (3.147 and 3.364 Å). The ligand is slightly anisobidentate [73].

The dicyclohexylphosphinodithioate, $[Ph_2TlS_2PCy_2]_n$, forms monodimensional ribbons **62** by association of the chelate rings through pairs of Tl···S secondary bonds [73].

Lead(II) phosphorodithioates and phosphinodithioates investigated so far are all



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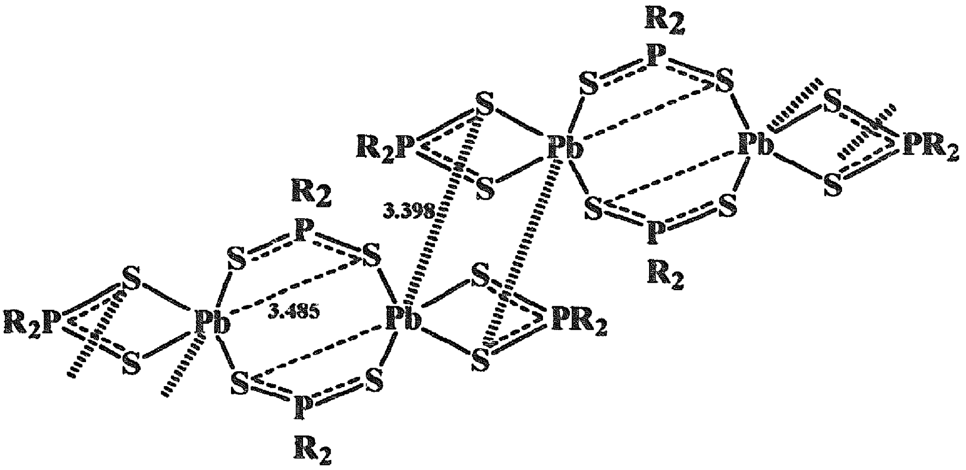
polymeric, and display a different structure for each peripheral group R at phosphorus.

Lead(II) bis(dimethylphosphinodithioate), Pb(S$_2$PMe$_2$)$_2$, forms cyclic dimers (48) containing an eight-membered Pb$_2$S$_4$P$_2$ ring with two bridging ligands and two four-membered rings of two chelating ligands; these units are further associated into a supramolecular structure 63 via Pb···S secondary interactions (3.398 Å) [60].



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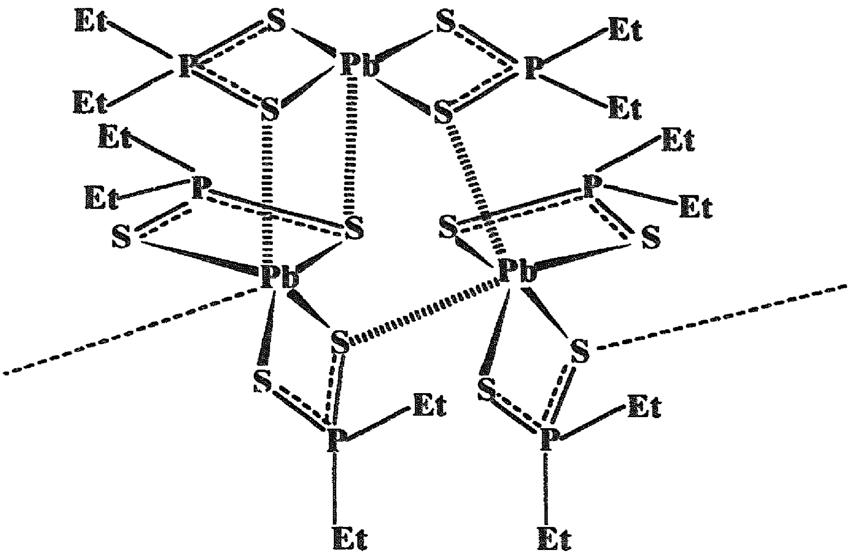
Lead(II) bis(diethylphosphinodithioate), Pb(S$_2$PEt$_2$)$_2$, contains anisobidentate ligands which form four-membered quasi-cyclic rings, involved in additional secondary bonds leading to supramolecular association. The molecular units are first organized in trimeric aggregates, which in turn form a polymeric structure 64. The Pb···S secondary bonds are in the range 3.100–3.269 Å and a six-membered quasi-cyclic Pb$_3$S$_3$ is readily distinguished in this supramolecular structure; the coordination geometry about lead has been described as pseudopentagonal bipyramidal, with a lone electron pair located in an equatorial position [74].

The structure of lead(II) bis(diphenylphosphinodithioate), Pb(S$_2$PPh$_2$)$_2$, consists of pairs of molecular units, connected through secondary Pb···S interactions (3.27 Å); these are further associated into a supramolecular ribbon structure 65 through additional, somewhat weaker (3.448 Å), Pb···S secondary interactions [75].

Complex polymeric structures formed through secondary Pb···S bonds are also observed in ethylenediamine adducts Pb{S$_2$P(OEt)$_2$}$_2$·en and Pb{S$_2$P(OEt)$_2$}$_2$·$\frac{1}{2}$en (en = ethylenediamine) [63].

Several diorganoantimony(III) supramolecular polymeric structures have also been identified. Thus, diphenylantimony(III) diisopropylphosphorodithioate, [Ph$_2$SbS$_2$P(O^{i}Pr)$_2$]$_x$ is a chain polymer 66 made up from four-membered quasi-cyclic units (Sb–S 2.531 and 2.555 Å Sb···S 3.684 and 3.934 Å; P–S 2.044 Å, P=S 1.942 Å) interconnected through Sb···S secondary bonds (3.172 and 3.266 Å) [76].

In polymeric [Me$_2$SbS$_2$PMe$_2$]$_n$ the primary Sb–S bonds (1.555 Å) alternate with



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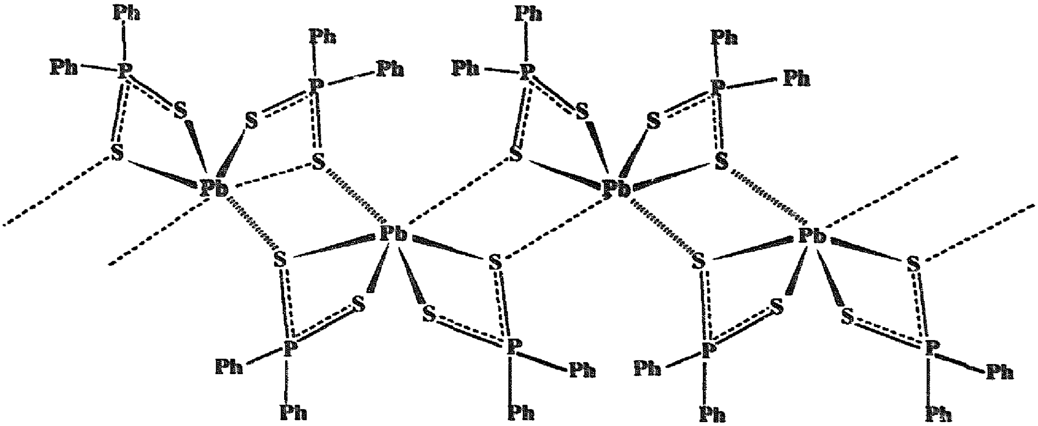
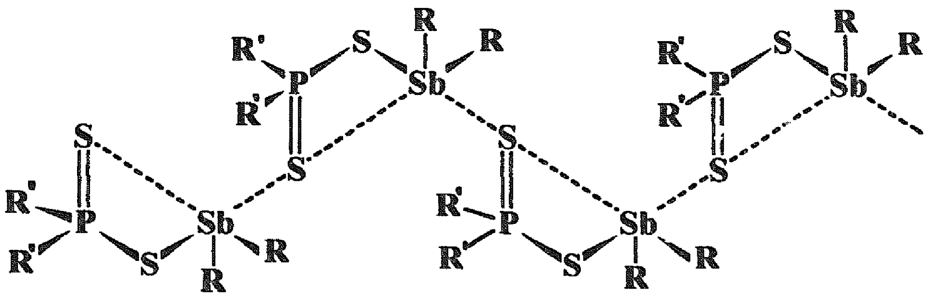


65

intermonomeric secondary bonds (Sb···S 3.158 Å); a longer intramonomeric contact (Sb···S 3.822 Å) serves to close quasi-cyclic SbS_2P chelate rings [77].

A similar supramolecular structure has 67 been found in the dimethylarsinodithioate $Ph_2SbS_2AsMe_2$ [78]. The quasi-cyclic chelates SbS_2As (Sb–S 2.655, Sb···S 3.652 Å) are interconnected through relatively strong secondary bonds (Sb···S 2.830 Å); the arsenic–sulfur interatomic distances are intermediate between single



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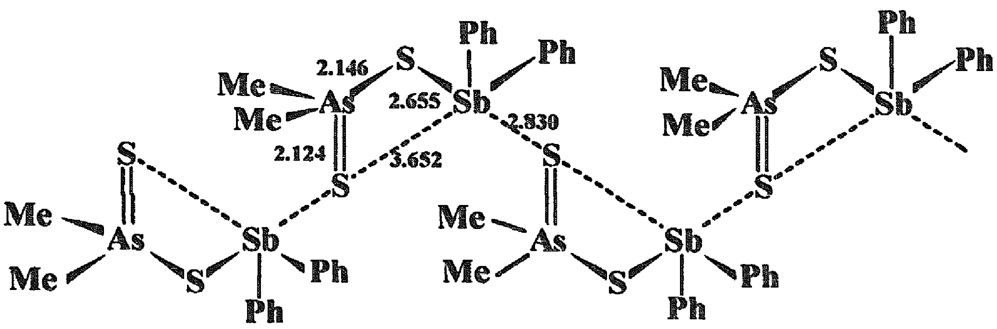

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and double bond lengths. Considering the Sb···S secondary bonds, the coordination geometry around antimony is distorted square pyramidal.

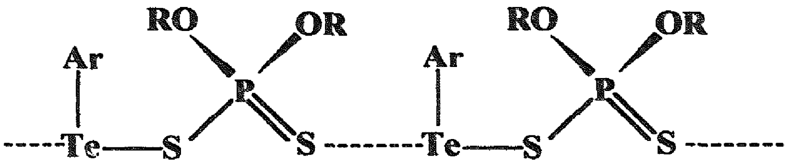
Tellurium(II) bis(diorganophosphorodithioates), Te$\{S_2P(OR)_2\}_2$, R = Me [79] and Et [80] are associated through secondary Te···S bonds (interatomic distances in the range 3.209 to 3.541 Å; estimated sum of van der Waals radii 4.00 Å (Bondi) or 3.86 Å (Batsanov)) in complex supramolecular structures.

Aryltellurium phosphorodithioates, $ArTeS_2P(OR)_2$, Ar = p-$MeOC_6H_4$, R = Me [81], Ar = p-$EtOC_6H_4$, R = Me [82] and Ar = Ph, R = Me [83], are linear polymers **68** formed through secondary Te···S bonds between individual molecules. The primary Te–S bonds are in the range 2.439–2.443 Å, and the secondary bonds in the range 3.309–3.262 Å. The ligands are anisobidentate bridging, with distinct single and double P–S bonds.

Among aryltellurium phosphinodithioates, $ArTeS_2PR_2$, Ar = Ph, p-tolyl, R = Me, Et, Ph, prepared by oxidative addition of thiophosphoryl disulfides to ditellurides

$$ArTe{-}TeAr + R_2(S)P{-}S{-}S{-}P(S)R_2 \rightarrow 2ArTeS(S)PR_2$$

the thermochromic $PhTeS_2PPh_2$ has been analyzed by X-ray diffraction both at low temperature, 173 K (yellow form) and room temperature, 273 K (red form) [84].



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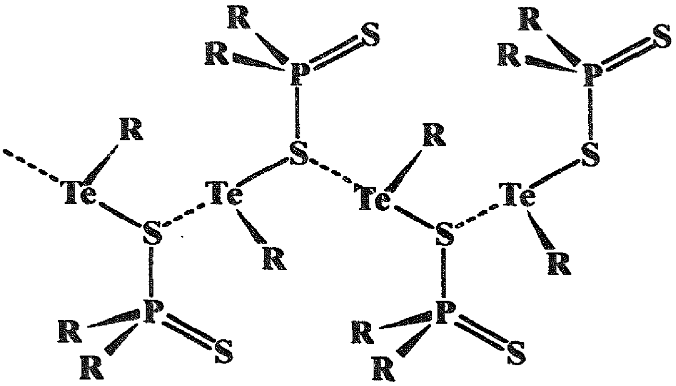
Both forms display a supramolecular polymeric structure **69**, in which the molecules are associated through Te···S secondary bonding in a novel mode; thus, the sulfur atom singly bonded to phosphorus (P–S 2.121 Å in yellow form, 2.118 Å in red form) is involved in secondary bonding to the tellurium atom of a symmetry-related molecule (Te–S(–P) 2.406, Te···S′(–P′) 3.383 Å in the yellow form, and Te–S(–P) 2.401 and Te···S′(–P′) 3.422 Å in the red form); the sulfur atom doubly bonded to phosphorus (P=S 1.944 Å in yellow form, 1.934 Å in red form) is not involved in coordination to tellurium. This coordination pattern is unique for phosphinodithioates.



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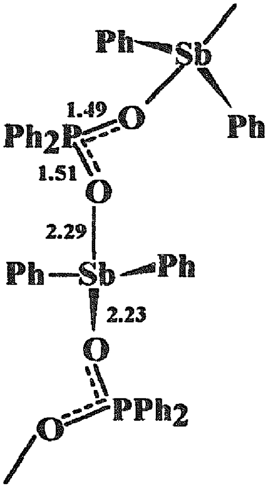
Replacement of sulfur by oxygen does not much change the ability to associate. Thus, $Ph_2SbOSPPh_2$ (**70**) and $Ph_2SbO_2PPh_2$ (**71**) are also polymeric [85], but the intermolecular bonds are dative bonds (Lewis acid–base donor–acceptor type) as suggested by the intermolecular Sb–O and Sb–S interatomic distances.

A beautiful supramolecular chain structure **72** has been found in dimethylthallium diphenylphosphinothioate; the $[Ph_2TlOSPPh_2]$ chelate ring units are associated through O→Tl Lewis acid–base interactions, and S···Tl secondary interactions between chain segments lead to formation of quasi-cyclic fragments in the structure [86].



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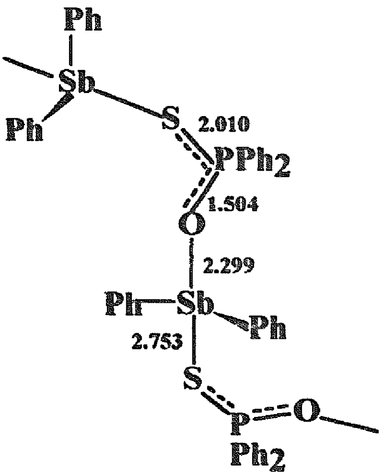

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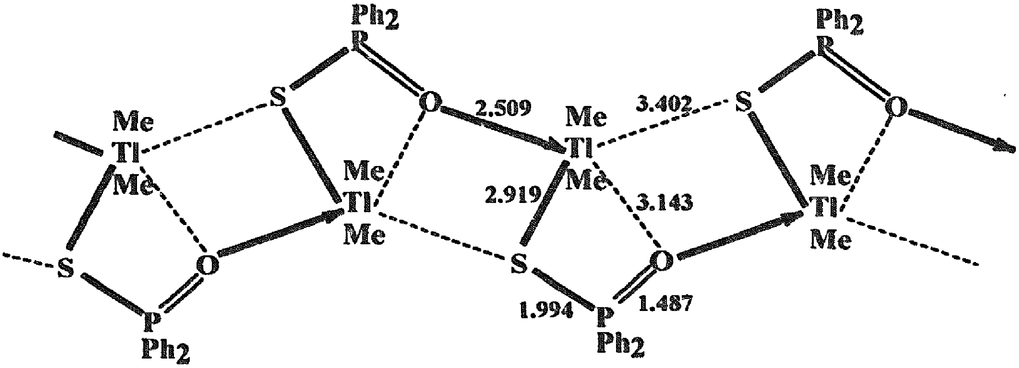

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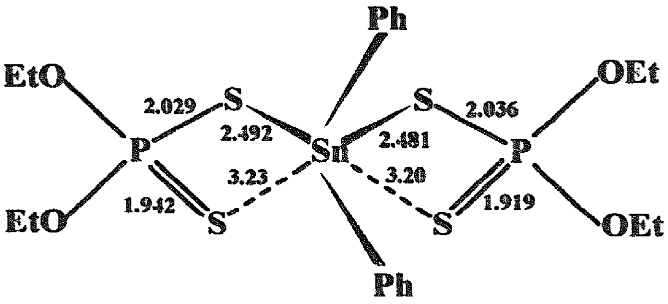
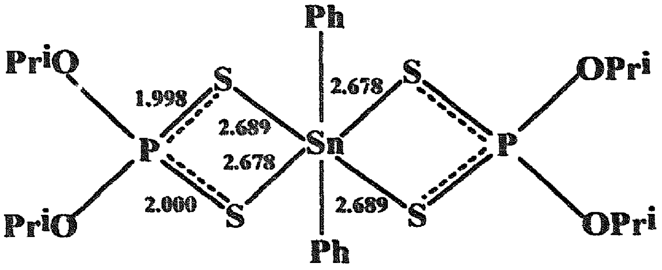
5. Heterogeometrism

Under the definition of heterogeometrism above, diorganotin bis(dialkylphosphorodithioates) were cited as an example. Thus, $Ph_2Sn\{S_2P(OEt)_2\}_2$ contains unsymmetrically coordinated (anisobidentate) phosphorodithioato ligands and the coordination center can be described as displaying a capped tetrahedral geometry, **73a**, if the secondary bonds are considered [87]. The symmetrical, octahedral structure **73b** is displayed by $Ph_2Sn\{S_2P(O^iPr)_2\}_2$ [88].

A bicapped tetrahedral structure, similar to **73a** has been found for $Me_2Sn(S_2PMe_2)_2$ [89], $Me_2Sn(S_2PEt_2)_2$ (Sn–S 2.476 Å, Sn···S 3.336 Å, P–S 2.054 Å,



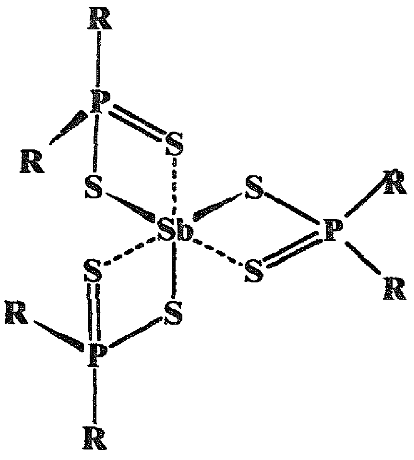
73a



73b

P=S 1.91 Å) [90] and $Me_2Sn(S_2AsMe_2)_2$ [91], but the symmetrical octahedral geometry **73b** is so far unique for a phosphor-1,1-dithiolato diorganotin complex.

Another example of heterogeometrism is provided by antimony(III) tris(phosphorodithioates) and their phosphinodithioato analogs. Thus, the phosphorodithioates $Sb[S_2P(OR)_2]_3$ with R = Me, ^{i}Pr are distorted octahedral complexes **74** with anisobidentate ligands (R = Me, Sb–S 2.522–2.535 Å, Sb···S 3.002–3.008 Å, P–S 2.029–2.036 Å, P=S 1.927–1.941 Å; R = ^{i}Pr, Sb–S 2.519–2.531 Å, Sb···S 3.000–3.031 Å, P–S 2.029–2.044 Å, P=S 1.932–1.945 Å) [92] (for R = Et, see Ref. [93]). Antimony(III) tris(diethylphosphinodithioate), $Sb(S_2PEt_2)_3$, is also a distorted octahedral complex with anisobidentate ligands (Sb–S 2.503–2.583 Å, Sb···S 2.907–3.137 Å, P–S 2.054–2.057 Å, P=S 1.960–1.968 Å) [94]. In contrast, antimony(III) tris(diphenylphosphinodithioate), $Sb(S_2PPh_2)_3$, displays a rare pentagonal pyramidal geometry, **75**, with two ligands in the basal plane and the third spanning a basal and the apical position. The three ligands are strongly anisobidentate [95].



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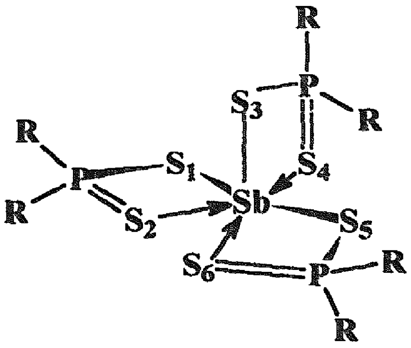

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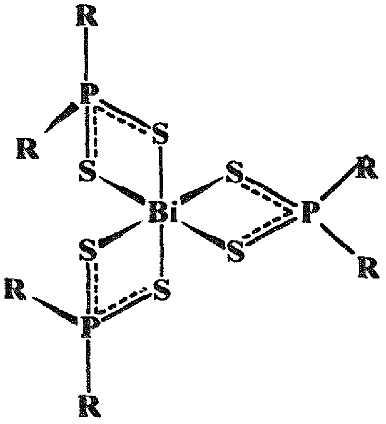
Bismuth(III) tris(phosphorodithioates), $Bi\{S_2P(OR)_2\}_3$, with R=Et [96], ^{i}Pr [97] and $(OR)_2=OCHMeCHMeO$ and $OCH_2CEt_2CH_2O$ [98] are monomeric, distorted octahedral complexes **76**. Among phosphinodithioates, $Bi(S_2PR_2)_3$, only the ethyl derivative (R=Et) displays a similar structure [99,100], but the methyl (R=Me0 [101] and phenyl (R=Ph) [95] derivatives are dimers **77**, with seven-coordinate bismuth, formed through secondary Bi···S interactions.



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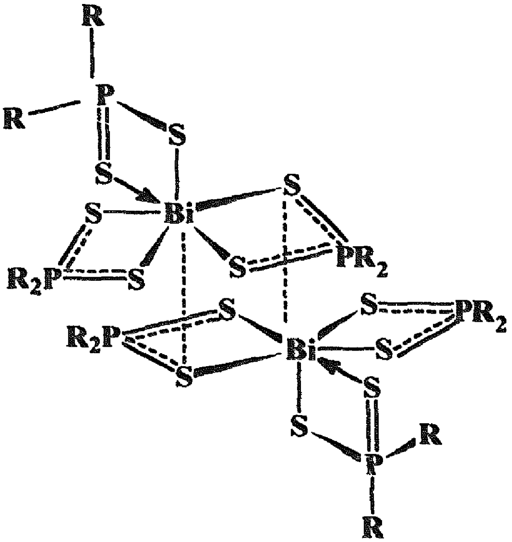

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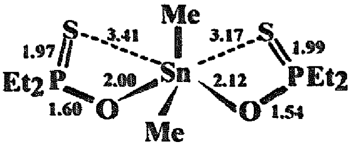
Another case of heterogeometrism can be cited for the pair of monothiophosphinates, $Me_2Sn(OSPEt_2)_2$ and $Me_2Sn(OSPPh_2)_2$. The former is a monomeric, molecular compound, **78**, with chelating ligands, displaying capped tetrahedral coordination geometry at tin [102], whereas the latter is a polymeric compound, associated through secondary Sn···S interactions and displaying trigonal pyramidal coordination geometry at tin [103]. Not surprisingly, the structure of the trimethyltin(IV) derivative $Me_3SnOSPMe_2$ is also polymeric (with trigonal bipyramidal five-coordinate tin) [104], but the association of a diorganotin phosphinothioate is unexpected, and so is the monodentate coordination (dangling) of lateral $OSPPh_2$ groups in $Me_2Sn(OSPPh)_2$.



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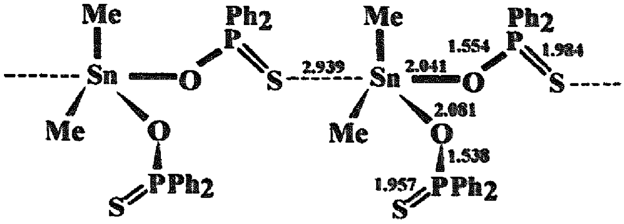

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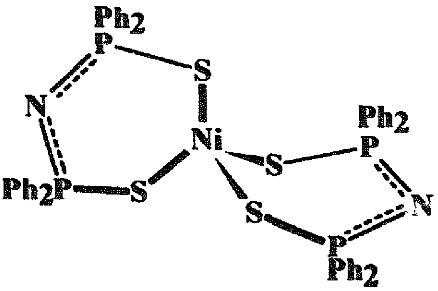
A surprising example of heterogeometrism is provided by nickel(II) dithioimidodiphosphinates. Thus, the symmetrically substituted bis(chelates) nickel(II) tetramethyldithioimidodiphosphinate, $Ni(SMe_2PNPMe_2S)_2$ [105,106], and nickel(II) tetraphenyldithioimidodiphosphinate, $Ni(SPh_2PNPPh_2S)_2$ [107,108] display a tetrahedral coordination geometry (**80**), while the unsymmetrically substituted analog, nickel(II) 1,1-dimethyl-3,3-diphenyl-1,3-dithioimidodiphosphinate, $Ni(SMe_2PNPPh_2S)_2$, is a square planar complex (**81**) [108]. The reason for this case of heterogeometrism is not clear.



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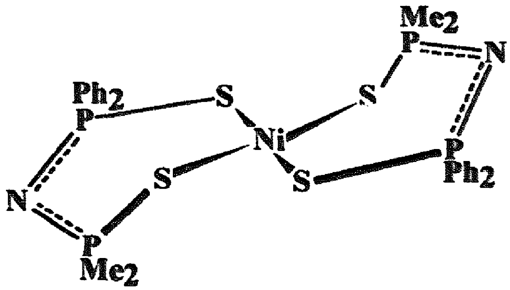

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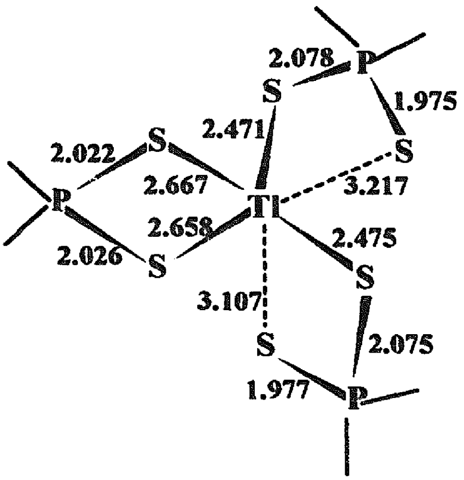
6. Concluding remarks

The structure of Main Group metal complexes of phosphorus- and arsenic-based anionic ligands is determined by the size of the central atom, by the presence or absence of organic groups attached to the metal, and possibly by the bulkiness of the ligand. It is almost generally observed that minor changes in the nature of the peripheral substituents attached to phosphorus (or arsenic), away from the coordination site, produce dramatic changes in the coordination geometry (leading to heterogeometrism), or association degree (leading to cyclic or quasi-cyclic dimers or chain-like polymers) in chemically similar (analogous) compounds.



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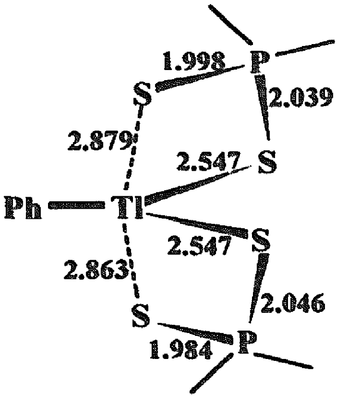

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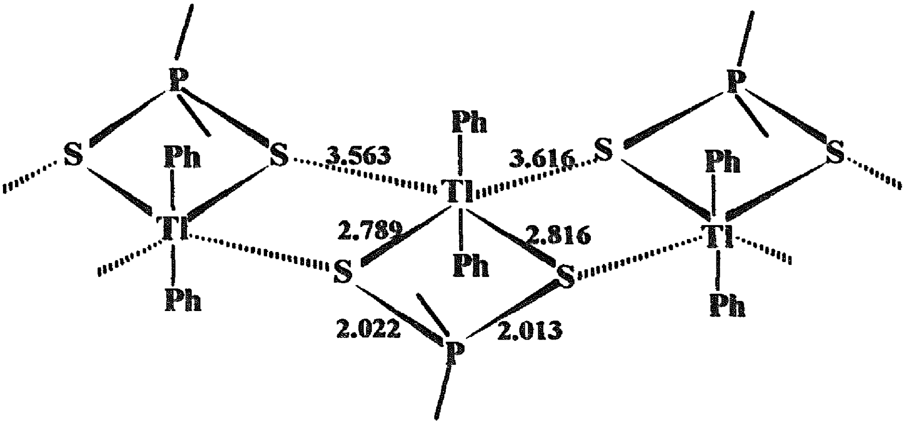

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If a monovalent organic group (alkyl, aryl) is attached to the central metal atom, in the resulting organometallic coordination center this group will occupy only one coordination site, whereas potentially bidentate phosphorus- and arsenic-based ligands discussed here tend to occupy two coordination sites (either as isobidentate or as anisobidentate ligands). As a result, the need for intermolecular (supramolecular) association may arise in organometallic derivatives, as a way to achieve coordinative saturation of the central metal atom.

An interesting comparison, illustrating the effect of occupying a bonding site with a monodentate (monofunctional) organic group instead of a bidentate (chelating) dithio ligand, can be made in the series $Tl(S_2PCy_2)_3$, $PhTl(S_2PCy_2)_2$ and $Ph_2Tl(S_2PCy_2)$ [26]. The metal is six-coordinate in monomeric $Tl(S_2PCy_2)_3$ (**82**), if secondary bonds are considered, with a symmetric chelate ring (isobidentate ligand) and two quasi-cyclic fragments (anisobidentate ligands). In the monoorganothallium derivative $PhTl(S_2PCy_2)_2$ (**83**) both ligands are anisobidentate and form quasi-cyclic chelates, the metal being five-coordinate. The diorganotallium compound, $Ph_2Tl(S_2PCy_2)$ (**84**) is polymeric, associated through secondary Tl···S bonds. It is interesting to note the significant variations in the lengths of the primary Tl–S bonds with increasing charge of the metal coordination center: the shortest bonds are observed in the Tl^{3+} compound (av. 2.473 Å), followed by $PhTl^{2+}$ derivatives (2.547 Å) and Ph_2Tl^+ derivative (2.789 and 2.816 Å).

In a similar manner, in the antimony series $Sb(S_2PR_2)_3$, $R'Sb(S_2PR_2)_2$ are monomeric and $R'_2Sb(S_2PR_2)$ are polymeric (or dimeric).

Supramolecular associations, secondary bonds, quasi-cyclic structures and heterogeometrism are by no means limited to thio phosphorus and arsenic-based ligands. Similar examples can be found with dithiocarbamates, xanthates, carboxylates and thiocarboxylates and other ligands (see for example Refs. [109–111]), but we limited our discussion to a field with which we are more familiar. It is also possible that many supramolecular associations have been ignored if the crystal structure determination was limited only to the molecular unit, without investigating the intermolecular relations.

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