

Chemistry of arsenic, antimony and bismuth compounds derived from xanthate, dithiocarbamate and phosphorus based ligands

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Abstract

The chemistry of both tri- and penta-valent compounds of arsenic, antimony and bismuth derived from xanthate, dithiocarbamate and phosphorus based ligands have been reviewed. Synthesis, properties, structural aspects and applications of their compounds have been described.

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Keywords: Arsenic; Antimony; Bismuth; Xanthates; Dithiocarbamates; Phosphorus based acids

1. Introduction

The chemistry of arsenic, antimony and bismuth compounds derived from xanthates, dithiocarbamates and phosphorus based ligands has been an active area of research for more than four decades. There are several reasons for the sustained interest in these compounds. These compounds show great structural diversity which ranges from monomeric to polymeric supramolecular assemblies and find extensive applications as biocides, catalysts, additives for lubricants, etc. The Group V chalcogenide (V–VI) materials (e.g. band gap of their

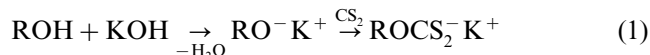
Abbreviations: Me, methyl; Et, ethyl; Prⁿ, *n*-propyl; Prⁱ, *iso*-propyl; Buⁿ, *n*-butyl; Buⁱ, *iso*-butyl; Bu^s, *sec*-butyl; c-Oct, cyclo-octyl; Octⁱ, *iso*-octyl; Ph, phenyl; tol, *p*-tolyl; Ar, aryl; Am, amyl; c-Hx, cyclohexyl; Bz, benzyl; Mes, mesityl; Ac, acetyl; deadtc, *N,N'*-iminodiethanol diithiocarbamate, (HOCH₂CH₂)₂NCS₂⁻; dtc, diethyldithiocarbamate; Medtc, dimethyldithiocarbamate; bipy, bipyridyl; phen, 1,10-phenanthroline; exa, ethyl xanthate.

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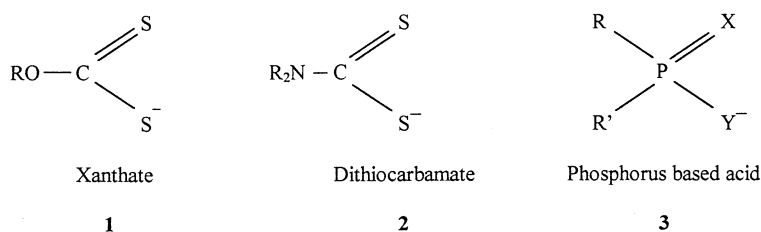
sulfides M_2S_3 2.36 (As), 1.7 (Sb) and 1.3 (Bi) eV) and their ternary compounds (e.g. $CuSbS_2$) are used in solar cells, photolithography, holographic recording, optical memory devices, photoconductors and as thermoelectric generators and coolers [1,2]; Bi_2Te_3 being the best room temperature thermoelectric material [1]. Although metal xanthates, dithiocarbamates and dithiophosphates are used as molecular precursors in CVD processes [3], the role of As, Sb and Bi derivatives as precursors for preparation of metal sulfides is emerging [4].

Xanthate, dithiocarbamate and phosphorus based acid ligands can be represented as **1–3** and can bind



2.2. Dialkyldithiocarbamate ligands

Dithiocarbamic acid (H_2NCS_2H , unstable in free state) yields stable salts. Substituted derivatives are prepared by the reaction of primary or secondary amines with carbon disulfide in the presence of sodium or potassium hydroxide (Eq. (2)) [8]. The R_2NCS_2Na .



(R' = R or OR; R = alkyl or aryl, include all possible combinations)

R'	X	Y	Name of the phosphorus based acid
R	O	O	diorganophosphinic acid
R	O	S	diorganothiophosphinic acid
R	S	S	diorganodithiophosphinic acid
OR	O	O	diorganophosphoric acid
OR	O	S	diorganothiophosphoric acid
OR	S	S	diorganodithiophosphoric acid

the metal center in several ways.

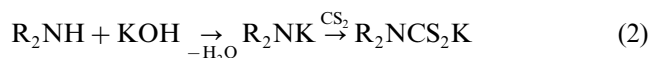
Although some aspects of arsenic, antimony and bismuth compounds with these ligands have been reviewed [5–7] an updated comprehensive review may fill the gaps and may further accelerate work in this area.

2. General synthetic routes to ligands

2.1. Xanthate ligands

The alkyl derivatives of dithiocarbamic acid ($HOCS_2H$, free acid is unknown) often referred as xanthates are usually prepared by the reaction between potassium hydroxide, alcohol and carbon disulfide (Eq. (1)) [8,9].

nH_2O (R = Me or Et) are commercially available.



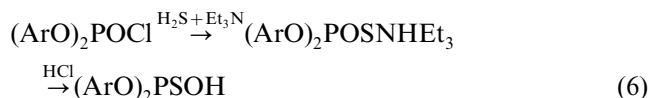
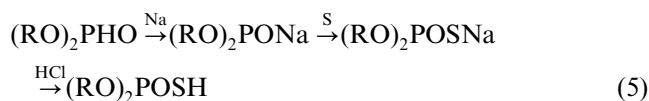
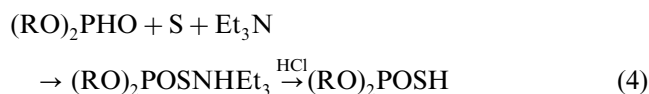
2.3. Phosphorus based acid ligands

Diphenylphosphinic acid, Ph_2POOH [10] and related phosphinic acids [11,12] are obtained by oxidation of R_2PCL with dilute HNO_3/H_2O_2 mixture. The dialkylphosphoric acids such as $(RO)_2PO_2K$ (R = Pr^i or Bu^t) are prepared by oxidation of $(RO)_2POH$ with potassium permagnate [13].

Diphenylthiophosphinic acid, Ph_2POSH , is obtained by the reaction of Ph_2PCL with sulfur in toluene/water suspension (Eq. (3)) [14],



Dialkylthiophosphates are prepared readily by employing reaction routes 4–6 [15,16].



Diphenyldithiophosphinic acid is obtained by the modified Friedel Crafts synthesis using P_2S_5 and benzene in the presence of AlCl_3 [17]. Sodium dialkyldithiophosphinates are obtained by the reaction of $\text{R}_2\text{P(S)P(S)R}_2$ with sulfur and sodium sulfide [18,19].

Dialkyldithiophosphoric acids are prepared by the reactions of P_2S_5 with an appropriate alcohol [20,21].

3. Chemistry of trivalent compounds

3.1. Synthesis

Both classical and organometallic derivatives of xanthates, dithiocarbamates and phosphorus based acids are prepared in several ways. In general, reactions of metal halides with sodium, ammonium, lead or silver salt of ligands have been employed for the synthesis of these complexes (Scheme 1). Reactions between metal halides and free acids, particularly dithiophosphorus acids, have also been employed [6]. Metal acetates instead of halides can also be used for the preparation of these complexes [24].

A large number of tris derivatives of the type ML_3 derived from phosphorus based acids [22–40], dithio-



$\text{M} = \text{As or Sb}$

$\text{R} = \text{Me, Et, Ph}$

$\text{M}' = \text{NH}_4, \text{Na, K or } \frac{1}{2} \text{Pb}$

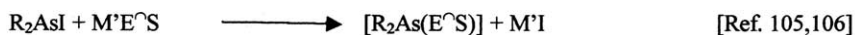
$\text{S}^\wedge\text{S} = \text{S}_2\text{COR}'$ ($\text{R}' = \text{Me, Et, Pr}^n, \text{Pr}^i, \text{allyl, Bu}^n$)

$\text{S}_2\text{CNR}''_2$ ($\text{R}'' = \text{Me or Et}$)

$\text{S}_2\text{P}(\text{OR}''')_2$ ($\text{R}''' = \text{Et, Pr}^n, \text{Pr}^i, \text{Ph, etc.}$)



$(\text{R} = \text{Me, Et, Ph}; \text{R}' = \text{Et, Pr}^n, \text{Pr}^i, \text{Bu}^n)$



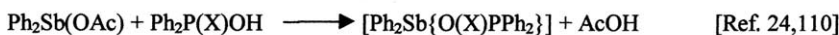
$\text{R} = \text{Me, Et, Ph}$

$\text{E}^\wedge\text{S} = \text{S}_2\text{COEt}; \text{S}_2\text{CNR}'_2$ ($\text{R}' = \text{Me, Et}$)

$\text{SOP}(\text{OR}')_2; \text{S}_2\text{P}(\text{OR}')_2$



$(\text{R} = \text{Me, Et, Ph})$



$(\text{X} = \text{O or S})$



$(\text{R} = \text{Me, Et, } \frac{1}{2} \text{ piperidyl})$

Scheme 1.

carbamates [41–61] and xanthates [62–73] have been synthesized. The M and L in these complexes include the following:

concomitant formation of disulfide [83,84]. The $\text{SbCl}(\text{S}_2\text{CNR}_2)_2$ reacts with neutral nitrogen donor ligands, L (L = Et_3N , py, Phen) in dichloromethane to

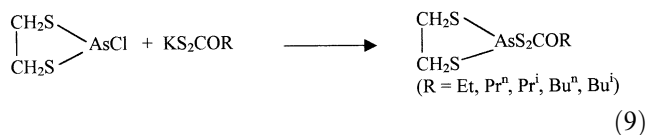
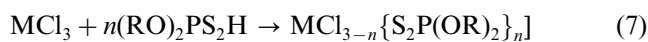
M	L	Reference
Sb	$\text{O}(\text{S})\text{PR}_2$; R = Me, Ph, c-Hx	[23]
As, Sb, Bi	S_2PR_2 ; R = Me, Et, Ph	[22,27,31–33,35,38,39]
As, Sb, Bi	$\text{S}_2\text{P}(\text{OR})_2$ (R = Me, Et, Pr^i , Bu^n , Bu^i , Bu^s , Ph, $\text{CH}_2\text{CEt}_2\text{CH}_2\text{O}$)	[22,25,26,28–30,34,36,40]
As, Sb, Bi	$\text{RR}'\text{NCS}_2$; R = Et, $\text{R}' = m\text{-tolyl}$	[49]
Sb	R = $\text{R}' = \text{Bz}$, Oct^i , Pr^i , $\text{CH}_2\text{CH}_2\text{OH}$; R = Bu^n , $\text{R}' = \text{N}(\text{CH}_2\text{CH}_2)$; RR' = $(\text{CH}_2)_4$, $(\text{CH}_2)_5$, $\text{CH}_2\text{CH}_2\text{OC}_2\text{H}_4$	[56]
Bi	RR' = $(\text{CH}_2)_4$, $(\text{CH}_2)_5$, $(\text{CH}_2)_6$	[50]
Sb	RR' = 1-pyrrolidinyl, 4-phenyl-1-piperazinyl, 4-morpholinyl	[48]
As, Sb, Bi	NH_4L = ammoniumtetramethylene dithiocarbamate	[51]
Sb	HL = 4-aminophenazenedithiocarbamic acid	[52]
Sb, Bi	Thiomorpholine-4-carbodithioate	[53]
Bi	Piperidine-1-carbodithioate	[54]
As, Sb, Bi	HL = monomethylpiperidinodithiocarbamic acid	[55]
As, Sb	HL = 2-alkylaminocyclopentene-1-carbodithioc acid (alkyl = H, Me, Et, Bu)	[57]
Bi	HL = 2-alkylaminocyclopentene-1-carbodithioc acid (alkyl = H, Me, Et, Bu)	[58]
As	HL = <i>N</i> -methylaminoethanoldithiocarbamic acid	[59]
As, Sb, Bi	HL = <i>N</i> -methylaminoethanoldithiocarbamic acid, <i>N,N'</i> -iminodiethanoldithiocarbamic acid	[60,61]
As, Sb, Bi	(ROCS_2^-) , R = Me	[66,71]
	Et	[62,63,67,69,70,73]
	Pr^i	[68]
Bi	c-Hx, Bz	[72]

Several organometallic derivatives of the general formulae $[\text{R}_2\text{M}(\text{S}_2\text{COR}')] (M = \text{As}, R = \text{Me}, R' = \text{Et}, \text{Pr}^i, \text{Am}, \text{allyl}, \text{c-Hx}, \text{C}_{12}\text{H}_{25}; R = \text{Ph}, R' = \text{Et}, \text{Pr}^i; R = p\text{-O}_2\text{NC}_6\text{H}_4, R' = \text{Et}$ [25], $M = \text{Bi}, R = \text{Me}, \text{Ph}, R' = \text{Me}, \text{Et}, \text{Pr}^n, \text{Pr}^i, \text{Bu}^n, \text{Bu}^i$ [74,75], $\text{MeBi}(\text{S}_2\text{COR})_2$, (R = Me, Et, Pr^i) [76], $\text{RSb}(\text{S}_2\text{CNET}_2)_2$ (R = Me, Et, Bu, Ph) [77], $\text{Ph}_2\text{Sb}(\text{S}_2\text{CNET}_2)$ [77], $\text{RBi}(\text{S}_2\text{CNR}'_2)_2$ (R = Ph or Me; $\text{R}' = \text{Me}, \text{Et}$) [42,47], $[\text{PhSb}(\text{S}_2\text{PR}_2)_2]$ (R = Et, Ph) [78], $[\text{Ph}_{3-n}\text{Sb}\{\text{S}_2\text{P}(\text{OR})_2\}_n]$ ($n = 1$ or $2, \frac{1}{2}\text{R} = \text{CMe}_2\text{CMe}_2, \text{CH}_2\text{CMe}_2\text{CH}_2, \text{CMe}_2\text{CH}_2\text{CHMe}$) [79] and $[\text{O}(\text{C}_6\text{H}_4)_2\text{As}(\text{S}_2\text{PR}_2)]$ (R = Me, Et, Ph) [80,81] have been prepared and characterized. Binuclear complexes $(\text{SbL}_2)_2\text{CH}_2$ [L = S_2CNR_2 (R = Me, Et), S_2COR (R = Et, Pr^i), $\text{S}_2\text{P}(\text{OR})_2$] have been synthesized by the reaction of $(\text{SbCl}_2)_2\text{CH}_2$ with sodium salt of the acid [82].

A myriad of mixed ligand complexes have been reported [83–88]. The chloro derivatives of the general formula $[\text{MCl}_{3-n}\{\text{S}_2\text{P}(\text{OR})_2\}_n]$ (Eq. (7)) ($M = \text{As}$ or Sb , $n = 1$ or 2 ; R = Et, $\text{Pr}^n, \text{Pr}^i, \text{Bu}^i$) [86], $[\text{AsBr}(\text{S}_2\text{CNET}_2)_2]$ [120], $[\text{SbPh}(\text{Cl})(\text{S}_2\text{COR})]$ (R = Me, Et, Pr^n, Pr^i) [89] have been synthesized. Reaction of $\text{M}(\text{S}_2\text{CNR}_2)_3$ with bromine or iodine readily affords $[\text{MX}(\text{S}_2\text{CNR}_2)_2]$ (X = Br or I; M = As, Sb, Bi; R = Et, Bu^i, Bz) with

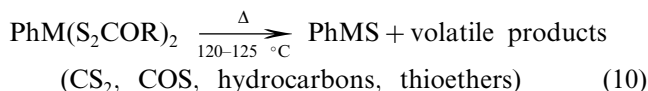
yield 1:1 adducts, $[\text{SbCl}(\text{S}_2\text{CNR}_2)_2\text{L}]$ [90a]. Beside chloro ligands, alkoxo and several other bidentate ligands have also been employed. Mixed alkoxo/aryldithiophosphonate derivatives of the type $[(\text{RO})_2\text{E}\{\text{S}_2\text{PAr}(\text{OR}')\}] (E = \text{As}, \text{Sb}, \text{Bi})$ have been prepared by Nizamov et al. [90b–90i]. Glycols and dithiolates are usually the ligands of choice and complexes of the types $[(\text{OGO})\text{As}\{\text{S}_2\text{P}(\text{OR})_2\}] (G = -\text{CH}_2\text{CH}_2-, -\text{MeCH}-\text{CH}_2-, -\text{Me}_2\text{C}-\text{CH}_2\text{CHMe}-, -\text{CH}_2-\text{CH}=\text{CHCH}_2-, -\text{Me}_2\text{CCMe}_2-; R = \text{Et}, \text{Pr}^n, \text{Pr}^i, \text{Bu}^s, \text{Ph})$ [85], $[(\text{SCH}_2\text{CH}_2\text{S})\text{Sb}\{\text{S}_2\text{P}(\text{OR})_2\}]$ (Eq. (8)) (R = Et, Pr^i, Bu^i) [87], $[(\text{RO})_2\text{PS}_2]_2\text{SbSCH}_2\text{CH}_2\text{SSb}\{\text{S}_2\text{P}(\text{OR})_2\}_2]$ (R = Et, Pr^i, Bu^i) [87], $[(\text{SCH}_2\text{CH}_2\text{S})\text{E}(\text{S}_2\text{COR})]$ (E = As or Sb; R = Et, $\text{Pr}^i, \text{Bu}^n, \text{Bu}^i$) (Eq. 9) [91,92] and $[(\text{SCH}_2\text{CH}_2\text{S})\text{M}(\text{S}_2\text{CNR}_2)] (M = \text{As}$ or $\text{Sb}; R = \text{pyrrolidyl}, 3\text{-pyrrolyl}, 4\text{-morphoyl}, 3\text{-methylpiperidyl})$ [93] have been isolated. Several complexes containing a combination of xanthates, dithiocarbamates and phosphorus based acids with the general formulae $[\text{M}(\text{S}_2\text{COMe})(\text{S}_2\text{COEt})_2]$ (M = Sb or Bi) [94], $[\text{M}(\text{S}_2\text{CNR}_2)_2(\text{S}_2\text{CNR}')]$ (As, Sb) [95], $[\text{Sb}(\text{S}_2\text{CNR}_2)_2\{\text{S}_2\text{P}(\text{OR})_2\}_2]$ [96] and $[\text{Sb}\{\text{S}_2\text{P}(\text{OR}')_2\}_2(\text{S}_2\text{COR}')] (R' = \text{Et}, \text{Pr}^n, \text{Pr}^i, \text{Bu}^s, \text{Bu}^i)$ [88]

have been synthesized.



3.2. Properties

Xanthate complexes, $\text{PhM}(\text{S}_2\text{COR})_2$ ($\text{M} = \text{As}$ or Sb) tend to decompose on heating (ca. 120 °C) to $[\text{PhMS}]$ (Eq. (10)) as revealed by TG analysis [97,98].



Mass spectra of several of these complexes have been reported [80,97–106]. The mass spectra of diorganoarsenic derivatives, $[\text{Me}_2\text{As}(\text{S}_2\text{CNMe}_2)]$ (m/z 225), $[\text{Me}_2\text{As}\{\text{SOP}(\text{OEt})_2\}]$ (m/z = 274) and $[\text{Ph}_2\text{As}\{\text{SOP}(\text{OR})_2\}]$ show molecular ion peaks with the exception of the xanthate derivatives, e.g. $[\text{Me}_2\text{As}(\text{S}_2\text{COEt})]$ for which molecular ion peak is not observed. The mass spectra of mono-organocomplexes of As or Sb (xanthates, dithiocarbamates, mono- and dithio-phosphates) show similar behaviour. None of the spectra exhibit molecular ion peak indicating pyrolytic decomposition. Two prominent decomposition pathways appear to operate with the loss of metal-alkyl/phenyl group or one of the ligand moieties [97–100,104–106].

The TG and DT analysis on $\text{M}(\text{S}_2\text{COR})_3$ ($\text{R} = \text{Me, Et, Pr}^i, \text{Bu}^n, \text{c-Hx, Bz}$; $\text{M} = \text{As, Sb}$ or Bi) and antimony dithiocarbamates have been reported [52,64,107]. The $\text{As}(\text{S}_2\text{COR})_3$ ($\text{R} = \text{Bu}^n$ or Bz) are volatile while other arsenic derivatives are volatile with decomposition [64]. The antimony and bismuth complexes decompose in

two stages, in the first stage (100–290 °C) M_2S_3 ($\text{M} = \text{Sb}$ or Bi) is formed [64].

Electronic spectra of $\text{M}(\text{S}_2\text{COEt})_3$ ($\text{M} = \text{As, Sb, Bi}$) exhibit four absorptions (ca. 230, 260, 285 and 360 nm). These bands have been assigned to inter ligand (ca. 230, 260, 285 nm) and charge transfer (ca. 360 nm) bands [65]. The solid state electronic spectra of $\text{M}(\text{S}_2\text{CNR}_2)_3$ [46,55] and $\text{MX}(\text{S}_2\text{CNR}_2)_2$ ($\text{M} = \text{Sb}$ or Bi , $\text{X} = \text{Cl, Br}$ or I) exhibit three bands. The most intense band (228–255 nm) is assigned to the intramolecular charge transfer in the ligand ($\pi-\pi^*$ in $\text{N}=\text{C}=\text{S}$ group). The band in halo derivatives is blue shifted relative to the corresponding tris-dithio complex. The position of this band is sensitive to the central metal atom. The second band appears as a shoulder (290–300 nm) and is assigned to $\pi-\pi^*$ transition in the $\text{N}=\text{C}=\text{S}$ group. The third band of low intensity, often absent in Sb complexes, is attributed to $n-\pi^*$ or charge transfer transition [46].

Xanthate, dithiocarbamate and dithiophosphate complexes of As(III) and Bi(III) have been studied by polarography [108]. The shift of half wave potential depends on the nature of ligand and follow the trend, dithiophosphate < xanthate < dithiocarbamate.

The IR band positions in these complexes depends on the oxidation state of metal atom, nature of ligand and the coordinating atom as well as ligand bonding mode. Usually, a shift in band positions is observed after the complexation for bonds near to coordinating atom. The IR data on dithiophosphate complexes cannot distinguish between various structural possibilities. The absorptions in the region 544–520 cm^{-1} are the result of $\nu_{\text{sym}}\text{PS}$ and $\nu_{\text{sym}}\text{PO}$ coupling as inferred from normal coordinate analysis of $\text{Ni}\{\text{S}_2\text{P}(\text{OR})_2\}_2$ ($\text{R} = \text{Me}$ or Et) [109]. The $\nu_{\text{As-S}}$ absorption has been assigned in the region 310–390 cm^{-1} [27,80,102]. The alkyl-arsenic compounds exhibit an absorption in the region 450–480 cm^{-1} attributable to $\nu_{\text{As-C}}$ [104]. However, the difference between P-S (460–535 cm^{-1}) and P=S (585–640 cm^{-1}) falling in the range 50–70 and 70–90 cm^{-1} has been used to determine the coordination behaviour of Ph_2PS_2^- and are due to *iso*- and *aniso*-bidentate mode of bonding, respectively. The values greater than 95 cm^{-1} imply unidentate coordination [110,111].

Table 1
 ^1H - and ^{13}C -NMR resonance for the methylselenic(III) complexes

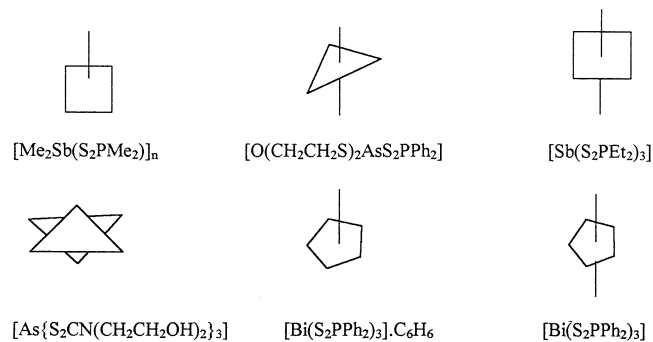
MeAs(III) complexes	MeAs NMR resonance		Me ₂ As(III) complexes	Me ₂ As NMR resonance	
	^1H	^{13}C		^1H	^{13}C
$[\text{MeAs}(\text{S}_2\text{COEt})_2]$	1.93	17.4	$[\text{Me}_2\text{As}(\text{S}_2\text{COEt})]$	1.44	13.6
$[\text{MeAs}(\text{S}_2\text{CNMe}_2)_2]$	2.05	23.2	$[\text{Me}_2\text{As}(\text{S}_2\text{CNMe}_2)]$	1.47	12.4
$[\text{MeAs}(\text{S}_2\text{CNEt}_2)_2]$	2.04	23.2	$[\text{Me}_2\text{As}(\text{S}_2\text{CNEt}_2)]$	1.46	12.5
$[\text{MeAs}\{\text{S}_2\text{P}(\text{OEt})_2\}_2]$	1.98	20.3	$[\text{Me}_2\text{As}\{\text{S}_2\text{P}(\text{OEt})_2\}]$	1.49	14.8
$[\text{MeAs}\{\text{S}_2\text{P}(\text{OPr}^i)_2\}_2]$	2.03	21.3	$[\text{Me}_2\text{As}\{\text{S}_2\text{P}(\text{OPr}^i)_2\}]$	1.48	14.7
$[\text{MeAs}\{\text{SOP}(\text{OEt})_2\}_2]$	2.19	21.1	$[\text{Me}_2\text{As}\{\text{SOP}(\text{OEt})_2\}]$	1.56	15.4

Table 2
Structures of trivalent compounds determined by X-ray diffraction

Compound	Ligand bonding mode	Structure/geometry around metal atom	Reference
[As(S ₂ COMe) ₃] (Fig. 6)	Aniso-bidentate	Shows polymorphism α , β forms, distorted octahedral	[66,71]
[As(S ₂ COEt) ₃]	Aniso-bidentate	Geometry intermediate between trigonal prismatic and octahedral As–S = 2.3069(6), 2.9560(7) Å	[62,67]
[As(S ₂ COPr ^f) ₃]	Aniso-bidentate	Distorted octahedral As–S = 2.305(2), 2.978(2) Å	[68]
[Sb(S ₂ COMe) ₃]	Aniso-bidentate	Loosely held dimer, weak intermolecular M··S interactions	[71]
[Sb(S ₂ COEt) ₃]	Aniso-bidentate	Distorted octahedral Sb–S = 2.511(2), 3.002(3) Å	[63,69,70]
[Sb(S ₂ COPr ^f) ₃]	Aniso-bidentate	Distorted octahedral Sb–S = 2.508(1), 3.006(1) Å	[68]
[Bi(S ₂ COMe) ₃]	Aniso-bidentate	Loosely held dimer, weak intermolecular M··S interactions	[71]
[Bi(S ₂ COEt) ₃]	Aniso-bidentate	Distorted pentagonal bipyramidal, ladder like structure	[73]
[Bi(S ₂ COPr ^f) ₃]	Aniso-bidentate and a bridging S-atom from the neighbouring molecule	Polymeric structure, seven-coordinated bismuth	[68]
[Bi(S ₂ COBz) ₃]	Chelating and bridging	Centrosymmetric dimer, bismuth atom seven-coordinated	[72]
[Bi{S ₂ CO(c-Hx)} ₃]	Chelating and bridging	Centrosymmetric dimer, bismuth atom seven-coordinated	[72]
[As{S ₂ CNEt ₂ } ₃]	Aniso-bidentate	Discrete monomer, C ₃ -symmetry, mean As–S = 2.84(9), 2.34(9) Å	[116]
[As{S ₂ CN(Me)CH ₂ CH ₂ OH} ₃]	Aniso-bidentate	Monomer, C ₃ -symmetry, mean As–S = 2.320(3) and 2.927(2) Å	[59]
[As{S ₂ CN(CH ₂ CH ₂ OH) ₂ } ₃]	Aniso-bidentate	Distorted trigonal antiprism, mean As–S = 2.34(2) and 2.84(2) Å	[61]
[Sb{S ₂ CNEt ₂ } ₃]	Aniso-bidentate	C ₃ -symmetry, Sb–S = 2.487(4)–2.631(4) Å; Sb··S = 2.886(4)–2.965(4) Å	[117]
[Sb{S ₂ CNPr ^f } ₃]	Aniso-bidentate, weak intermolecular interaction	C ₃ -symmetry, Sb–S = 2.465(4)–2.857(4), 2.737(5)–2.822(5) Å, intermolecular Sb··S = 3.471(4) Å	[118]
[Sb{S ₂ CN(CH ₂ CH ₂ OH) ₂ } ₃]	Aniso-bidentate	Distorted pentagonal pyramid	[61]
[Bi{S ₂ CNEt ₂ } ₃]	Aniso-bidentate	C ₃ -symmetry, Bi–S = 2.595(5)–2.775(5); 2.956(5)–2.964(4) Å; weak intermolecular Bi··S = 3.210(4) Å	[117]
[Bi{S ₂ CN(CH ₂ CH ₂ OH) ₂ } ₃] ₂	Chelating triconnective	Centrosymmetric dimer, distorted square antiprism	[61]
[Sb(OSPPh ₂) ₃]	Monometallic biconnective + Bimetallic triconnective	Irregular seven-vertex polyhedron (ψ -irregular eight-vertex polyhedron, dimer)	[23]
[Sb{OSP(c-Hx)} ₂ } ₃]	Monometallic biconnective	Distorted octahedron (ψ -capped octahedron)	[23]
[Sb(S ₂ PEt ₂) ₃]	Aniso-bidentate	Distorted octahedral Sb–S = 2.503(2)–2.583(3), 2.907(3)–3.137(3) Å	[39]
[Sb(S ₂ PPh ₂) ₃]	Monometallic biconnective (aniso-bidentate)	ψ -Pentagonal bipyramidal, (distorted pentagonal pyramid), Sb–S _{ap} = 2.456(1) Å, Sb··S _{eq} = 3.187(1) Å, Sb–S _{eq(av.)} = 2.595(5) Å, Sb··S _{eq(av.)} = 2.95(4) Å	[31,33]
[Sb{S ₂ P(OMe) ₂ } ₃] (Fig. 2)	Monometallic biconnective	Distorted octahedral (ψ -octahedron), monomer, mean Sb–S = 2.53(1), 3.005(3) Å	[22]
[Sb{S ₂ P(OEt) ₂ } ₃]	Monometallic biconnective	Distorted octahedral (ψ -capped octahedron), monomer, mean Sb–S = 2.60(2), 2.83(4) Å	[30]
[Sb{S ₂ P(OPr ^f) ₂ } ₃]	Monometallic biconnective	Distorted octahedral (ψ -capped octahedron), monomer, Sb–S = 2.52(1), 3.02(2) Å	[22]
[Bi(S ₂ PMe ₂) ₃] (Fig. 1)	Bimetallic biconnective and Bimetallic triconnective	Centrosymmetric dimer in which pentagonal bipyramidal monomeric units are held together by Bi··S interaction	[38]
[Bi(S ₂ PEt ₂) ₃]	Isobidentate	Distorted octahedral, monomer	[35]
[Bi(S ₂ PEt ₂) ₃]·C ₆ H ₆	Isobidentate	Octahedral ↔ trigonal prism, monomer	[115]
[Bi(S ₂ PPh ₂) ₃]	Bimetallic triconnective	Dimeric, pentagonal bipyramidal	[33]
[Bi{S ₂ P(OMe) ₂ } ₃]	Bidentate	Dimeric, eight-membered ring system	[40]
[Bi{S ₂ P(OEt) ₂ } ₃]	Bidentate chelating	Distorted octahedral, monomer	[34]
[Bi{S ₂ P(OPr ^f) ₂ } ₃]	Bidentate chelating	Distorted octahedral (ψ -capped octahedron), monomer	[27a]
[Bi{S ₂ P(OCH(Me)CH(Me)O)} ₃]	Bidentate chelating (isobidentate)	Less distorted octahedral, monomer	[36]
[Bi{S ₂ P(OCH ₂ CEt ₂ CH ₂ O)} ₃]	Bidentate chelating	Distorted octahedral	[36]
[AsBr ₂ (S ₂ CNEt ₂) ₂]	Bidentate	Dimeric with halogen bridges, five-coordinate As atom	[124]
[SbBr(S ₂ COEt) ₂] (Fig. 7)	Bidentate chelating	Zig-zag chain containing six-coordinate Sb atom	[121]
[SbI{S ₂ CN(CH ₂) ₄ } ₂]	Bidentate chelating	Infinite polymeric chain stabilized by I-bridges	[122]
[Sb(S ₂ CN ⁿ Bu ⁿ) ₂ Cd ₂ I ₆]	Asymmetric chelating	Pseudotrigonal bipyramidal	[146]
[BiCl ₂ (S ₂ CNEt ₂) ₂]	Bidentate chelating	Infinite polymer, Bi atoms bridged by two halides and one S-atom	[126]

Table 2 (Continued)

Compound	Ligand bonding mode	Structure/geometry around metal atom	Reference
[BiCl ₂ (S ₂ CNEt ₂)py ₃]		Bi atom in pseudo pentagonal bipyramidal environment with axial halogen substituents	[128]
[BiI ₂ (S ₂ CNEt ₂)py ₃]		Bi atom in pseudo pentagonal bipyramidal environment with axial halogen substituents	[128]
[BiBr ₂ (S ₂ CNEt ₂)]	Bidentate chelating	Infinite polymer, Bi atom bridged by two halides and one S-atom	[126]
[BiI ₂ (S ₂ CNEt ₂)]	Bidentate chelating	Infinite polymer, Bi atoms are bridged by iodine and ligand sulfur atom	[127]
[BiBr(S ₂ CNEt ₂) ₂]	Bidentate chelating	Tetranuclear centrosymmetric unit	[123]
[BiI(S ₂ CNEt ₂) ₂]	Bidentate chelating	Infinite polymeric chain stabilized by I-bridges, hexa-coordinated Bi atom	[123]
[As(S ₂ C ₂ H ₄)(S ₂ CN–morphyl-4)]	Monodentate		[93]
[O(CH ₂ CH ₂ S) ₂ As{S ₂ CN–(CH ₂ CH ₂) ₂ O}]	Aniso-bidentate weak transannular secondary interactions	Tetragonal pyramidal or distorted trigonal bipyramidal, As–S = 2.280(2) Å	[133]
[S(SCH ₂ CH ₂ S) ₂ As(S ₂ CNEt ₂)]	Aniso-bidentate	Tetragonal pyramidal or distorted trigonal bipyramidal, As–S = 2.305(1) Å	[133]
[S(SCH ₂ CH ₂ S) ₂ AsS ₂ P(OMe) ₂]	Aniso-bidentate	'AsS ₂ C ₄ S' ring in boat–chair conformation, As–S = 2.245–2.375(1) Å	[133a]
[O(CH ₂ CH ₂ S) ₂ AsS ₂ PPh ₂]	Aniso-bidentate	Trigonal bipyramidal	[102]
[S(CH ₂ CH ₂ S) ₂ AsS ₂ PPh ₂]	Aniso-bidentate	Trigonal bipyramidal	[102]
[Sb(oxine) ₂ (S ₂ COEt)]	Bidentating chelating	Pentagonal bipyramidal, Sb–S = 3.059(2), 3.175(2) Å	[70]
[PhAs(S ₂ COPr ^f) ₂]	Aniso-bidentate	Square pyramidal with phenyl group at apical position, As–S = 2.298 and 3.041 Å	[139]
[MeSb(S ₂ COEt) ₂]	Isobidentate	Pentagonal bipyramidal	[140]
[PhSb(S ₂ COEt) ₂]	Asymmetric chelating	Pseudopentagonal bipyramid, Sb–S = 2.5377(19), 2.4987(17) Å; Sb···S = 3.1051(15), 2.9981(16) Å, intermolecular secondary Sb···S = 3.905(2) Å	[141]
[PhBi(S ₂ COMe) ₂]	Bidentate chelating	Square pyramidal	[145]
[MeAs(S ₂ CNEt ₂) ₂] (Fig. 14)	Monodentate, weak secondary interaction	Pyramidal/skewed trapezoidal bipyramidal, As–S = 2.337(2), 2.326(3) Å, As···S = 2.943(3), 2.878(3) Å	[106]
[PhAs(S ₂ CNEt ₂) ₂]	Monodentate, weak secondary interaction	Pyramidal, As–S = 2.323(2), 2.344(2); As···S = 2.840(2), 2.921(2) Å	[106,136]
[MeAs(S ₂ CNMe ₂) ₂]		Quadrilateral pyramidal	[138]
[MeSb(S ₂ CNEt ₂) ₂]	Aniso-bidentate and triconnective	Centrosymmetric dimer, Sb–S = 2.554(2), 2.538(2); 2.960(2), 2.904(2) Å; weak secondary Sb···S = 3.847(2) Å	[137]
[MeBi(S ₂ CNEt ₂) ₂]	Aniso-bidentate	Slightly distorted pentagonal pyramidal, dimeric structure, weak intermolecular Bi···S interaction	[143]
[PhBi(S ₂ CNEt ₂) ₂]	Aniso-bidentate	Centrosymmetric dimer, coordination around Bi is pseudo pentagonal bipyramidal	[144]
[Py–C ₆ H ₄ Bi(S ₂ CNEt ₂) ₂]	Biconnective	Pseudo-pentagonal bipyramidal	[144]
[PhAs{S ₂ P(OPr ^f) ₂] ₂] (Fig. 13)	Bidentate chelating	Distorted square-pyramid (distorted ψ-octahedron), monomer	[100]
[PhSb{S ₂ P(OPr ^f) ₂] ₂] (Fig. 13)	Monometallic biconnective (bidentate chelating)	Distorted square-pyramid (distorted ψ-octahedron)	[100]
[MesBi(S ₂ PPh ₂) ₂]	Monometallic biconnective	Distorted square-pyramid (distorted ψ-octahedron) Bi–S = 2.662(2) Å, Bi···S = 3.123(3) Å	[142]
[O(C ₆ H ₄) ₂ As(S ₂ CN(CH ₂ CH ₂) ₂)]	Monodentate	Pyramidal, As–S = 2.277(1) Å	[134]
[O(C ₆ H ₄) ₂ As(S ₂ PMe ₂)]	Monodentate	Pyramidal, As–S = 2.286(2) Å	[81]
[O(C ₆ H ₄) ₂ As(S ₂ PEt ₂)]	Aniso-bidentate	Pyramidal, dimeric quasi-tricyclic structure, As–S = 2.318(2) Å	[81]
[O(C ₆ H ₄) ₂ As(S ₂ PPh ₂)]	Monodentate	Pyramidal, dimeric quasi-tricyclic structure	[80]
[Ph ₂ Sb(O ₂ PPh ₂)] (Fig. 10)	Bimetallic biconnective	Distorted ψ-trigonal bipyramid, infinite chain	[24]
[Ph ₂ Sb(OSPPh ₂)] (Fig. 11)	Bimetallic biconnective	Distorted ψ-trigonal bipyramid, infinite chain	[24]
[Me ₂ Sb(S ₂ PMe ₂) _n]	Bimetallic triconnective	Distorted square pyramid (distorted ψ-octahedron)	[135]
[Ph ₂ Sb(S ₂ PMe ₂)]	Bridging bidentate	Centrosymmetric dimer	[103]
[Ph ₂ Sb(S ₂ PPh ₂)] (Fig. 12)	Bimetallic triconnective	Distorted square pyramid (distorted ψ-octahedron), dimer	[110]
[(<i>p</i> -tol) ₂ Sb(S ₂ PEt ₂)]	Bidentate bridging (bimetallic biconnective)	Distorted ψ-trigonal bipyramid, cyclic dimer	[111]
[Ph ₂ Sb{S ₂ P(OPr ^f) ₂] _n]	Bimetallic triconnective	Distorted square pyramid (distorted ψ-octahedron), infinite chain	[37]
[Ph ₂ Bi(S ₂ COPr ^f)]	Bridging	Trigonal bipyramidal, loosely associated polymeric chain	[74]



Scheme 2. Stereochemistries generally encountered for trivalent arsenic, antimony and bismuth compounds.

NMR spectra (¹H, ¹³C and ³¹P) of several of these complexes have been investigated [37,80,101–106]. The ¹H-, ¹³C- and ³¹P-NMR spectra of organoarsenic complexes exhibit single set of resonances characteristic of metal-alkyl/phenyl group and the ligand fragmentation. The ¹³C-NMR spectra (Table 1) of the RAs group in the dithiocarbamate complexes is deshielded compared with the corresponding xanthate complexes, consistent with the stronger coordination of the former ligand [105,106]. The ³¹P-NMR data of monothiophosphate complexes suggests that they are bonded to arsenic atom through sulfur in a monodentate fashion [104]. A series of arsenic, antimony and bismuth tris-xanthates have been studied by solid state ¹³C-NMR spectroscopy [112]. The spectrum of the bismuth complex, Bi(S₂-COEt)₃ exhibits five resonances in the ratio 1:1:2:1:1. The data have been interpreted as being consistent with the presence of two polymorphs of the complex (see later, Fig. 7) [112].

³¹P-NMR spectra of several bi- and tri-valent metal complexes with diisopropyl monothiophosphates have been investigated by Glidewell [113]. The chemical shifts have been interpreted in terms of nature of bonding, and the following trend has been proposed.

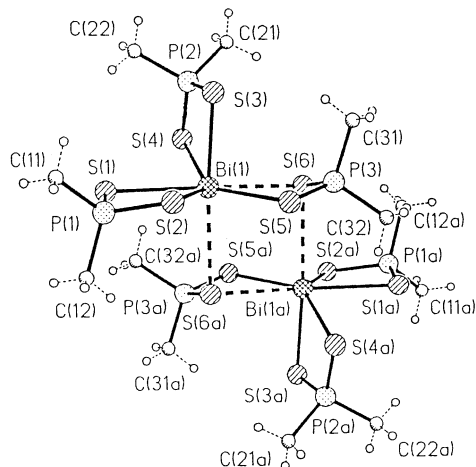


Fig. 1. Structure of [Bi(S₂PMe₂)₃] reproduced from Ref. [38].

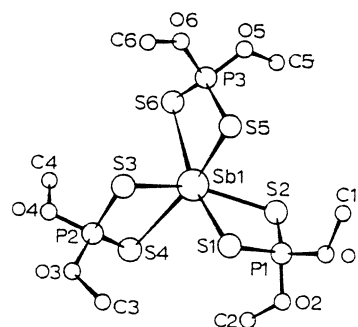


Fig. 2. Structure of [Sb(S₂P(OMe)₂)₃] reproduced from Ref. [22].

$\delta^{31}\text{P} \sim 30$ ppm: bonding through sulfur

$\delta^{31}\text{P} \sim 58$ ppm: bonding through oxygen

$\delta^{31}\text{P}$ 30–58 ppm: anisobidentate bonding.

The ¹²¹Sb Mössbauer spectra of a number of dithiocarbamate complexes have been reported [114] and an attempt has been made to rationalize the Mössbauer parameters with the structure of the molecule. The isomer shifts for antimony(III) have negative values, while organoantimony(V) have positive values. The large quadrupole coupling constants for RSb(S₂CNEt₂)₂ (R = Me or Ph) have been attributed to disposition of sulfur atoms in the equatorial plane and an excess of electron density in the axial position.

3.3. Structures

The structures of several classical and organometallic derivatives have been elucidated by single crystal X-ray diffraction analyzes (Table 2). These investigations have usually involved compounds containing dithio ligands.

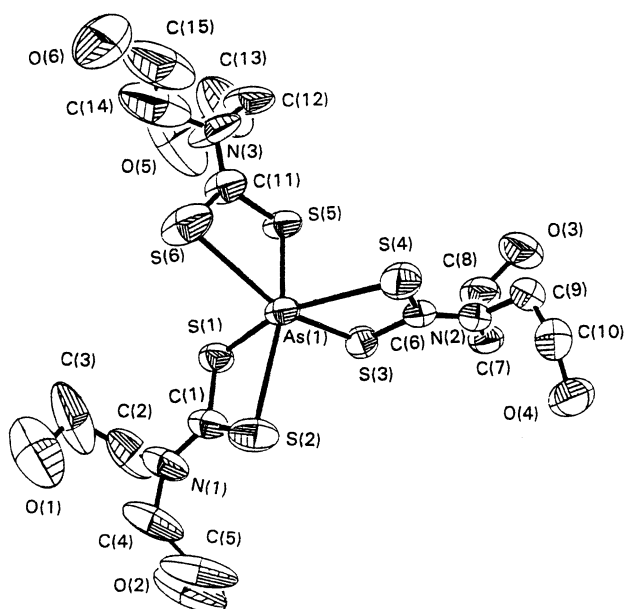


Fig. 3. Molecular structure of As(deadtC)₃ reproduced from Ref. [61a].

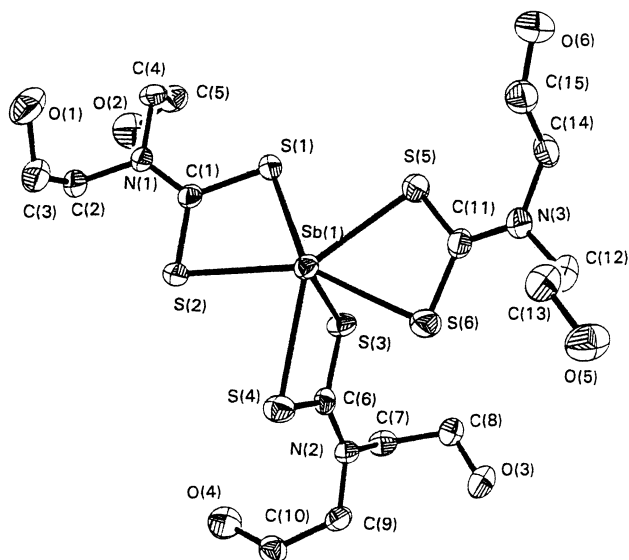


Fig. 4. Molecular structure of Sb(deadtc)₃ reproduced from Ref. [61a].

Unlike the oxo ligands, the dithio derivatives usually prefer discrete monomeric structures and the secondary interactions, if there are any, are generally very weak inhibiting the formation of large molecular aggregates in a true sense. The S[∧]S ligands are often asymmetrically chelated (anisobidentate) with the difference between the two M–S distances decreasing in the order, As > Sb > Bi. The stereochemical activity of the ns^2 [$n = 4(\text{As}), 5(\text{Sb}), 6(\text{Bi})$] lone pair causes these elements to adopt several different coordination geometries. When the lone pair is suppressed by hybridization with p- and d-orbitals, these atoms adopt a regular octahedral geometry. However, this is not often observed and usually distorted octahedral geometries (particularly for ML₃ complexes having short M–S bonds *trans* to long bonds) are encountered. This results in coordination environments that resemble a trigonal pyramid, a square pyramid, trigonal bipyramid or antiprism. The R groups attached to the metal center as well as ligand, in addition to the contribution from electron pair, also play very important role in determining the overall geometry of a molecule. Various stereochemistries generally observed for these compounds are depicted in Scheme 2.

The ligand moiety in [Sb(OSPR₂)₃] (R = Ph, c-Hx) complexes acts as monometallic biconnective in c-Hx derivative and as monometallic biconnective with bimetallic triconnective in phenyl derivative [23]. The complexes [M(S₂PEt₂)₃] (M = Sb [39], Bi [35,115]) show a distorted octahedral geometry with asymmetrically chelated Et₂PS₂⁻ ligands. Distortion is attributed to the ligand bite. However, the phenyl derivatives, [M(S₂PPh₂)₃] adopt an usual pentagonal bipyramidal configuration either as discrete monomer as in the case of Sb [31,33] or through dimerization via intermolecular

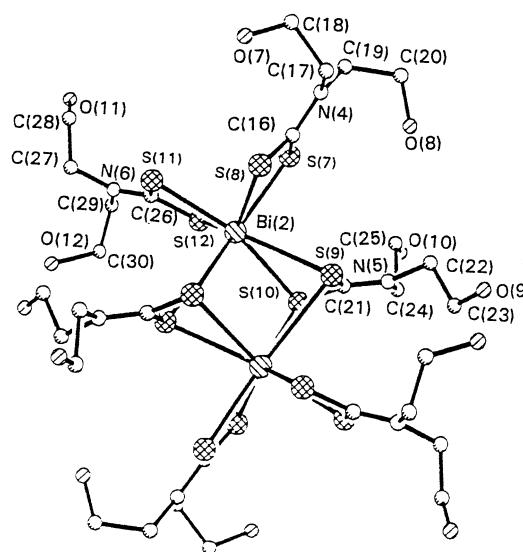


Fig. 5. Molecular structure of Bi(deadtc)₃ reproduced from Ref. [61a].

metal–sulfur contacts as in the case of Bi [33]. A dimeric structure is also reported for [Bi(S₂PMe₂)₃] (Fig. 1) [38] in which dimerization occurs through Bi···S secondary interactions. Structures of tris-dialkyldithiophosphates of antimony and bismuth [M{S₂P(OR)₂}₃] (M = Sb or Bi; R = Me, Et, Prⁱ, Buⁿ, Buⁱ, Bu^s, CH(Me)CH(Me)O, CH₂CEt₂CH₂O) [22,27b,28,30,34,36,40] have been reported. All are monomeric discrete molecules (Fig. 2)

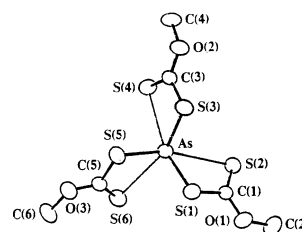


Fig. 6. Structure of [As(S₂C(OMe)₃)₃] reproduced from Ref. [71].

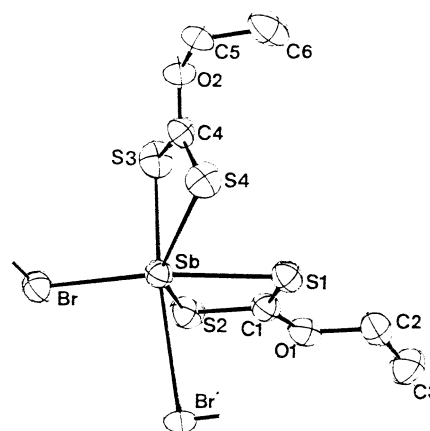


Fig. 7. Structure of [SbBr(S₂COEt)₂] reproduced from Ref. [121].

except for $[\text{Bi}\{\text{S}_2\text{P}(\text{OMe})_2\}_3]$ which dimerizes through bridging dithiophosphate ligand, contain distorted octahedral metal atoms, with asymmetrically chelated ligands; two M–S distances differing by ca. 0.5 Å for Sb and ca. 0.15 Å for Bi complexes.

The structures of tris-dithiocarbamate complexes, $[\text{M}(\text{S}_2\text{CNR}_2)_3]$ (M = As or Sb or Bi; R = Et, Prⁿ, *N*-methylaminoethanol, *N,N'*-iminodiethanol) have been reported [59,61,116–118]. The three ligands are asymmetrically chelated. Distortion from ideal geometry is often observed owing to the presence of the stereochemically active lone pair. Such distortions are evident in the structures of $[\text{M}\{\text{S}_2\text{CN}(\text{CH}_2\text{CH}_2\text{OH})_2\}_3]$ (M = As, Sb, Bi) (Figs. 3–5) [61]. The arsenic derivative has a distorted trigonal antiprismatic geometry with three strong (As–S = 2.33–2.35(2) Å) and three weak (As–S = 2.82–2.86(2) Å) As–S bonds, whereas the corresponding antimony complexes has a distorted pentagonal pyramid coordination. The bismuth complex, in contrast, is a centrosymmetric dimer and has a distorted square antiprism geometry. The two bidentate ligands are bridged in such a way that each sulfur atom is simultaneously bound to both metal atoms [61]. Weak intermolecular interactions between S and Sb have been reported for $[\text{Sb}(\text{S}_2\text{CNPr}_2)_3]$ [118].

Overwhelming structural data on tris-xanthate complexes reveal that the ligands, like other dithiolates, are asymmetrically chelated [62,66,68–73]. The complex $[\text{As}(\text{S}_2\text{COMe})_3]$ shows polymorphism. The compound crystallizes into two different forms, viz. trigonal (α) [66] and monoclinic (β) [71] (Fig. 6). In both forms arsenic exists in a distorted octahedral geometry [66,71] comprising three short and three long As–S bonds. Although the corresponding antimony and bismuth compounds are isomorphous, these are associated molecules and form loosely held dimers through weak intermolecular M–S interactions [66,71]. $[\text{As}(\text{S}_2\text{COEt})_3]$ exists in enantiomeric pairs of discrete molecules

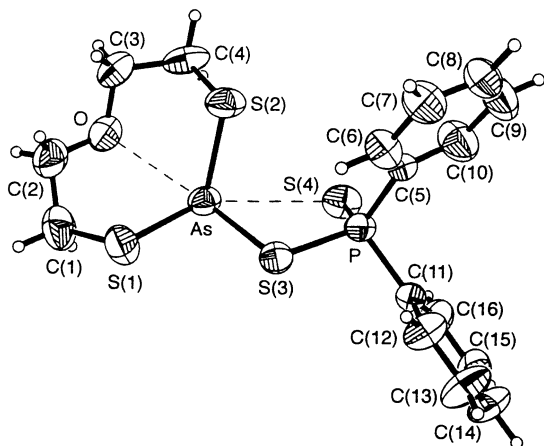


Fig. 8. Structure of $[\text{O}(\text{CH}_2\text{CH}_2\text{S})_2\text{AsS}_2\text{PPh}_2]$ reproduced from Ref. [102].

which are centered about a threefold axis [62,67]. The Bi atom in $[\text{Bi}(\text{S}_2\text{COEt})_3]$ adopts a highly distorted pentagonal bipyramidal configuration with one S atom and the electron pair occupying axial positions [73]. Contrary to this, $[\text{Bi}(\text{S}_2\text{COPr}^i)_3]$ forms a polymeric array in which Bi atoms are seven coordinated (MS_7 environment) through three asymmetrically chelated dithio ligands and a bridging sulfur atom from the neighbouring molecule [119]. Similar seven coordination environments (MS_7) are reported for $[\text{Bi}(\text{S}_2\text{COR})_3]$ (R = Bz, c-Hx) but the molecules are centrosymmetric dimers [72].

Structures of mono- and di-halo complexes have also been elucidated. These complexes usually have associated structures with halogen bridges although molecular weight determination in CHCl_3 reveal their monomeric nature [83]. Aggregation increases as one descends down the group i.e. $\text{As} < \text{Sb} < \text{Bi}$. The structures of $[\text{AsBr}(\text{S}_2\text{CNEt}_2)_2]$ has been reported [120]. The structure of $[\text{SbBr}(\text{S}_2\text{COEt})_2]$ shows a zig-zag chain in which antimony atoms acquire hexa-coordination with bromine bridges (Fig. 7) [121]. The complex $[\text{SbI}\{\text{S}_2\text{CN}(\text{CH}_2)_4\}_2]$ has an infinite polymeric chain of $\text{Sb}(\text{S}^\ominus\text{S})_2$ units stabilized by iodo-bridges. The Sb and I atoms alternate along the axis. The Sb atom is coordinated by four S atoms and two I atoms resulting in an irregular polyhedron [122]. A similar structure is reported for $[\text{BiI}(\text{S}_2\text{CNEt}_2)_2]$ [123], however, the iodine atoms are in the *cis* positions of the bismuth octahedron. The bromo derivative $[\text{BiBr}(\text{S}_2\text{CNEt}_2)_2]$ consists of a tetranuclear centrosymmetric unit with the Bi atoms bridged by two and three coordinated Br atoms [123].

The complex $[\text{AsBr}_2(\text{S}_2\text{CNEt}_2)]$ is dimeric with penta coordinate arsenic atoms which are held together by two halogen bridges [124]. The electron pair is stereochemically active. The X-ray crystal analysis of $[\{\text{Cl}_2\text{SbO}_2\text{P}(\text{OMe})_2\}_2]$ has revealed a dimeric structure [125]. The complexes $[\text{BiX}_2(\text{S}_2\text{CNEt}_2)]$ (X = Cl [126], Br [126], I

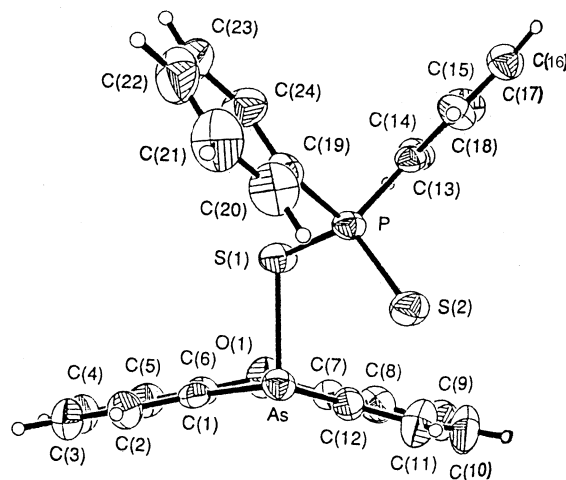
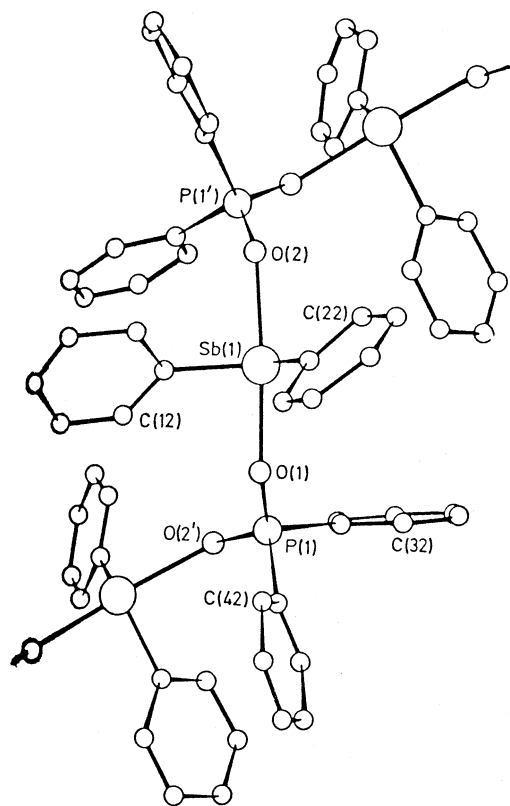
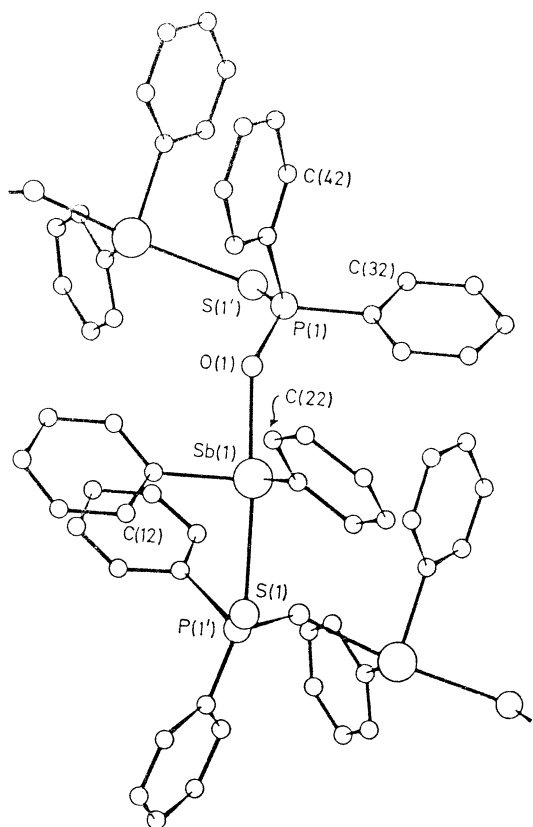
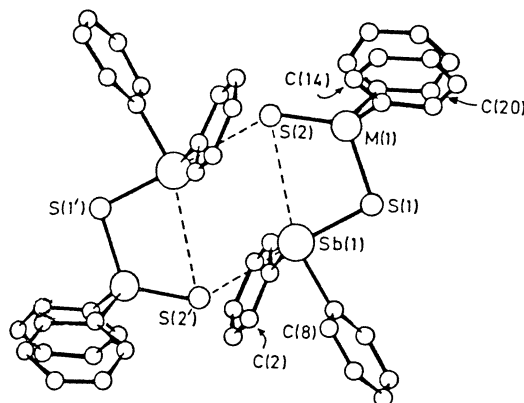
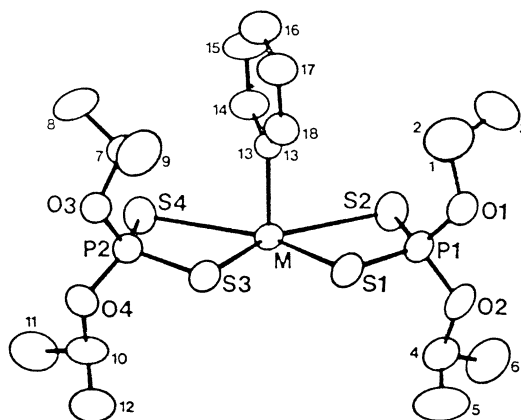


Fig. 9. Molecular structure of $[\text{O}(\text{C}_6\text{H}_4)_2\text{AsS}_2\text{PPh}_2]$ reproduced from Ref. [80].

Fig. 10. Structure of $[\text{Ph}_2\text{Sb}(\text{O}_2\text{PPh}_2)]$ reproduced from Ref. [24].Fig. 11. Structure of $[\text{Ph}_2\text{Sb}(\text{OSPPH}_2)]$ reproduced from Ref. [24].Fig. 12. Structure of $[\text{Ph}_2\text{Sb}(\text{S}_2\text{PPh}_2)]$ reproduced from Ref. [110].

[127] form infinite linear polymeric chain in which successive Bi atoms are bridged by the halides and one sulfur atom of the dithio ligand which is also chelated with each Bi. These infinite chains can be cleaved either by addition of neutral ligands to give mononuclear derivative $[\text{BiX}_2(\text{S}_2\text{CNET}_2)(\text{py})_3]$ [128], binuclear halobridged $[\text{Bi}_2(\text{S}_2\text{CNET}_2)(\text{bipy})]$ complex [129] or by tetraalkylammonium halide to generate bismuthate anion as in $[\text{Et}_4\text{N}]_2[\text{BiI}_2\text{X}(\text{S}_2\text{CNET}_2)_2]$ ($\text{X} = \text{Cl}$ or Br) [130]. A few cationic complexes have been reported. Thus, the compound $[\text{Bi}(\text{dtc})_2(\text{NO}_3)(\text{H}_2\text{O})]$ have been characterized by IR and X-ray powder diffraction and its possible structure is given [131]. The X-ray crystal structure of $[\text{NET}_4][\text{Bi}(\text{exa})_4]$ reveals a dodecahedral coordination environment around bismuth [132].

Structures of some mixed ligand complexes have also been elucidated. The dithiocarbamate moiety in $[\text{As}(\text{S}_2\text{CN-morphyl-4})(\text{S}_2\text{C}_2\text{H}_4)]$ [93] is monodentate. The structures of arsocane and stibocanes, $[\{\text{X}(\text{CH}_2\text{CH}_2\text{S})_2\}\text{E}(\text{S}^\wedge\text{S})]$ ($\text{X} = \text{O}$ or S ; $\text{E} = \text{As}$ or Sb ; $\text{S}^\wedge\text{S} = \text{S}_2\text{CNR}_2$, S_2PR_2 , $\text{S}_2\text{P}(\text{OR})_2$) have been described [101,102,133]. In these compounds there is transannular $\text{E} \cdots \text{X}$ interaction. The transannular interaction with S

Fig. 13. Molecular structure of $[\text{PhM}\{\text{S}_2\text{P}(\text{OPr}')_2\}_2]$ ($\text{M} = \text{As}$ or Sb) reproduced from Ref. [100].

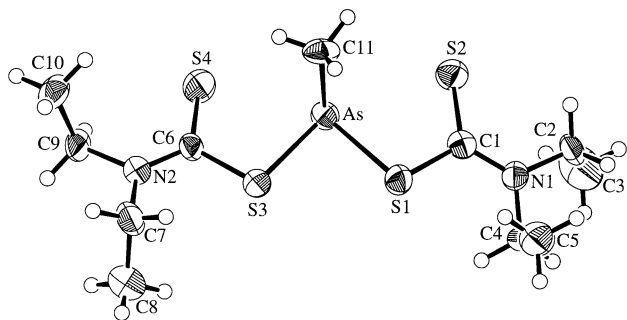


Fig. 14. Molecular structure of $[\text{MeAs}(\text{S}_2\text{CNEt}_2)_2]$ reproduced from Ref. [106].

($\text{X}=\text{S}$) is weaker than oxygen ($\text{X}=\text{O}$). The pendent sulfur of the dithio ligand also shows a weak secondary interaction (Fig. 8), with the arsenic atom acquiring penta coordination.

The complexes $[\text{O}(\text{C}_6\text{H}_4)_2\text{As}(\text{S}_2\text{PR}_2)]$ ($\text{R}=\text{Me}$ [81], Et [81] and Ph (Fig. 9) [80] and $[\text{O}(\text{C}_6\text{H}_4)_2\text{As}\{\text{S}_2\text{CN}(\text{CH}_2\text{CH}_2)_2\}]$ [134] are all discrete monomeric molecules with the phenoxarsine moiety folded over the $\text{As}\cdots\text{O}$ axis. The magnitude of folding is dependent on the dithio ligand with values of $154.4\text{--}176.1^\circ$. The dithio ligand in $[\text{O}(\text{C}_6\text{H}_4)_2\text{As}(\text{S}_2\text{PMe}_2)]$ functions as a monodentate ligand leading to pyramidal geometry of As. The ethyl and phenyl derivatives possess a quasi-tricyclic structure based upon intra and inter molecular $\text{As}\cdots\text{S}$ secondary bonds. In these compounds the dithio ligand is asymmetrically chelated.

The compound $[\text{Ph}_2\text{Sb}(\text{O}_2\text{PPh}_2)]_n$ forms an infinite chain of Ph_2Sb groups held together by bridging diphenylphosphinate moiety (Fig. 10) [24]. The antimony atom adopts a pseudo trigonal bipyramidal geometry defined by equatorially placed two phenyl groups while axial positions are occupied by two oxygen atoms and a stereochemically active lone pair [24]. A similar chain structure has been reported for $[\text{Ph}_2\text{Sb}(\text{OSPPH}_2)]_n$ [24] in which Ph_2Sb groups are bridged through OSPPH_2 ligands (Fig. 11). Molecular structures of $[\text{Me}_2\text{Sb}(\text{S}_2\text{PMe}_2)]_n$ [135], $[\text{Ph}_2\text{Sb}(\text{S}_2\text{PMe}_2)]$ [103], $[\text{Ph}_2\text{Sb}(\text{S}_2\text{PPh}_2)]$ (Fig. 12) [110], $[(p\text{-tol})_2\text{Sb}(\text{S}_2\text{PEt}_2)]$ [111] and $[\text{Ph}_2\text{Sb}\{\text{S}_2\text{P}(\text{OPr}^i)_2\}]$ [37] reveal their associated nature. $[\text{Ph}_2\text{Sb}(\text{S}_2\text{PMe}_2)]$ is weakly associated dimer in the solid state. Similarly $[\text{Ph}_2\text{Sb}(\text{S}_2\text{PPh}_2)]$ is dimeric containing a distorted square pyramidal antimony atom. The eight-membered Sb_2S_4 ring is formed due to transannular $\text{Sb}\cdots\text{S}$ interactions [110]. The complex $[(p\text{-tol})_2\text{Sb}(\text{S}_2\text{PEt}_2)]$ is a cyclic dimer in which the fragments are held together by weak $\text{Sb}\cdots\text{S}$ interactions. Antimony in $[\text{Ph}_2\text{Sb}\{\text{S}_2\text{P}(\text{OPr}^i)_2\}]$ is strongly bonded to ligand through one S atom besides two other weaker $\text{Sb}\cdots\text{S}$ contacts which results in the formation of infinite chains [37]. The structure of $[\text{Ph}_2\text{Bi}(\text{S}_2\text{COPr}^i)]$ consists of a loosely associated polymeric chain [74].

The crystal structures of $[\text{PhM}\{\text{S}_2\text{P}(\text{OPr}^i)_2\}_2]$ ($\text{M}=\text{As}, \text{Sb}$) are isomorphous and consist of discrete molecules (Fig. 13) [100]. The two dithiophosphate ligands form an approximate basal plane and the phenyl group occupies an axial position in the central atom's square pyramidal environment. The overall geometry of the central metal atom is consistent with the presence of a stereochemically active lone pair of electrons occupying an axial position, *trans* to the phenyl group, in the octahedral distribution of six electron pairs. The ligands chelate the central metal atom with unequal M–S bonds. The difference between the short and long M–S bonds in Sb of ca. 0.54 \AA is significantly less than the difference of ca. 0.8 \AA found in As derivative.

Structures of $[\text{PhAs}(\text{S}_2\text{CNR}_2)_2]$ ($\text{R}=\text{Me}$ [136], Et [106] and $[\text{MeAs}(\text{S}_2\text{CNEt}_2)_2]$ (Fig. 14) [106] have been established. The arsenic atom forms three close contacts, one with the R group at $1.968(6)\text{ \AA}$ and two to sulfur atoms. However, the two remaining sulfur atoms are in close proximity to arsenic having $\text{As}\cdots\text{S}$ $2.84(2)\text{--}2.92(2)\text{ \AA}$ which are within the sum of van der Waals radii of arsenic and sulfur of 3.74 \AA . The coordination would be based on a skewed trapezoidal pyramid with one site vacant, i.e. occupied by a lone pair of electrons. Structure of $[\text{MeSb}(\text{S}_2\text{CNEt}_2)_2]$ has been reported by Wieber et al. [137]. The structure of $[\text{MeAs}(\text{S}_2\text{CNMe}_2)_2]\text{I}_2$ [138] consists of $-\text{I}_2-\text{As}-\text{I}_2-\text{As}-$ chains cross linked by $-\text{I}-\text{As}-\text{I}-\text{As}-$ chain to form two dimensional network [138].

Structure of $[\text{PhAs}(\text{S}_2\text{COPr}^i)_2]$ has been reported [139]. The antimony atom in $[\text{RSb}(\text{S}_2\text{COEt}_2)]$ ($\text{R}=\text{Me}$ [140], Ph [141]) is coordinated with one carbon atom of R group and five sulfur atoms from xanthate ligands. Two sulfur atoms form primary bonds, and intramolecular secondary bonds making the ligand asymmetrically chelated. The final contact is a weak intermolecular secondary bond. The geometry can be described as

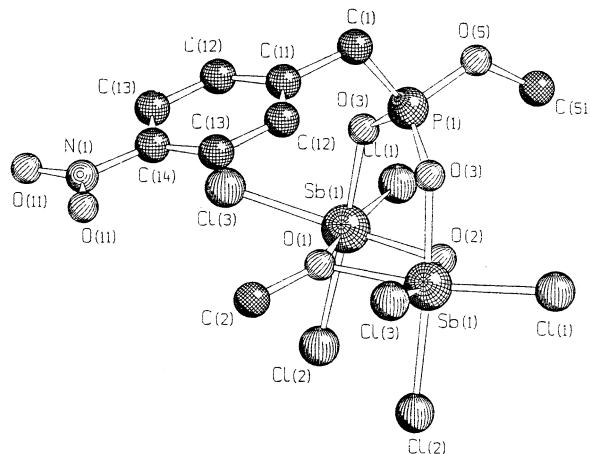
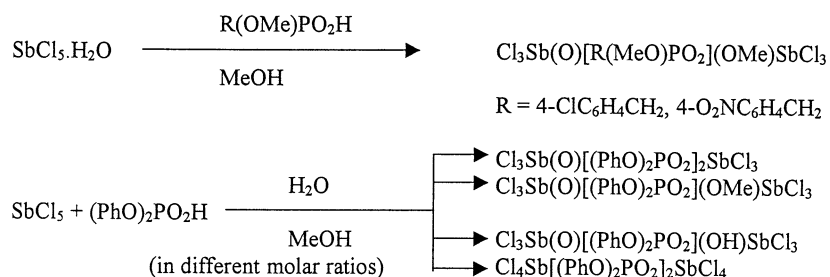


Fig. 15. Structure of $[\text{SbCl}_3(\text{O})\{4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2(\text{MeO})\text{PO}_2\}]\text{SbCl}_3(\text{OMe})$ reproduced from Ref. [150].



Scheme 3.

Table 3
Structures of pentavalent compounds determined by X-ray diffraction

Compound	Ligand bonding mode	Structure/geometry around central metal atom	Reference
$[\text{Cl}_3\text{Sb(O)}\{\text{ClC}_6\text{H}_4\text{CH}_2(\text{MeO})\text{PO}_2\}\text{SbCl}_3(\text{OMe})]$	Bridging phosphonato group, O-links between Sb-atoms	Binuclear	[150]
$[\text{Cl}_3\text{Sb(O)}\{\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2(\text{MeO})\text{PO}_2\}\text{SbCl}_3(\text{OMe})]$ (Fig. 15)	Bridging phosphonato group, O-links between Sb-atoms	Binuclear	[150]
$\{[\text{SbCl}_3(\text{O}_2\text{PEt}_2)]_2(\mu\text{-O})\}$	Biconnective bridging	Distorted octahedral	[150a]
$\{[\text{SbCl}_3]_2(\mu\text{-O})(\mu\text{-OH})(\mu\text{-O}_2\text{PEt}_2)\}$	Biconnective bridging	Distorted octahedral	[150a]
$\{[\text{SbCl}_3]_2(\mu\text{-O})(\mu\text{-OMe})(\mu\text{-O}_2\text{PEt}_2)\}$	Biconnective bridging	Distorted octahedral	[150a]
$[\text{SbCl}_3\{\text{O}_2\text{PMe}_2\}]_2\text{O}$	Bimetallic biconnective	Distorted octahedral	[148]
$[\text{SbCl}_3\{\text{O}_2\text{P(OPh)}_2\}]_2\text{O}$	Bridging	Binuclear	[152]
$[\text{SbCl}_3(\text{O})\{\text{O}_2\text{P(OPh)}_2\}]\text{SbCl}_3(\text{OMe})$	Bridging	Binuclear	[152]
$[\text{SbCl}_3(\text{O})\{\text{O}_2\text{P(OPh)}_2\}]\text{SbCl}_3(\text{OH})$	Bridging	Binuclear	[152]
$[\text{Cl}_3\text{Sb(O)}(\text{OH})(\text{C}_6\text{H}_5\text{CH}_2)\text{RPO}_2]\text{SbCl}_3 \cdot \text{H}_2\text{O}$; (R = OMe, OEt)	Bridging	Octahedral, Sb–O = 1.992–2.036(2) Å	[153]
$\{[\text{SbCl}_3]_2(\mu\text{-O})(\mu\text{-OH})(\mu\text{-O}_2\text{PF}_2)\}$	Bridging	Octahedral, Sb–O = 1.972–2.127(5) Å	[153]
$[\text{SbCl}_4\{\text{O}_2\text{PMe}_2\}]_2$ (Fig. 16)	Bimetallic biconnective	Distorted octahedral	[154]
$[\text{SbCl}_4\{\text{O}_2\text{PEt}_2\}]_2$	Bimetallic bridging	Distorted octahedral	[154a]
$[\text{SbCl}_4\{\text{O}_2\text{PCL}_2\}]_2$	Bridging	Centrosymmetric eight-membered ring	[155]
$[\text{SbCl}_4\{\text{O}_2\text{P(OMe)}_2\}]_2$	Bimetallic biconnective	Distorted octahedral, dimer	[125]
$[\text{SbCl}_4\{\mu\text{-O}_2\text{P(NMe}_2)_2\text{-O, O}\}\text{SbCl}_4]$	Bridging	Binuclear	[156]
$[\text{SbCl}_4\{\text{O}_2\text{P(OPh)}_2\}]_2$	Bridging	Binuclear	[152]
$[\text{SbCl}_5\{\text{O}_2\text{P(NMe}_2)(\text{NHMe}_2)\}]$	Bridging	Binuclear	[156]
$[\text{Ph}_2\text{SbCl}\{\text{O}_2\text{P(c-Hx)}_2\}]_2\text{O}$ (Fig. 17)	Bridging	Octahedral	[158]
$[\text{Ph}_2\text{Sb}\{\text{O}_2\text{P(c-Hx)}_2\}\text{O}]_2 \cdot 2\text{CH}_2\text{Cl}_2$	Bridging	Dimeric, hexa coordinated Sb, four-membered Sb_2O_2 ring	[159]
$[\text{Ph}_2\text{Sb}\{\text{O}_2\text{P(c-Oct)}_2\}\text{O}]_2 \cdot 2\text{CH}_2\text{Cl}_2$	Bridging	Dimeric, hexa coordinated Sb, four-membered Sb_2O_2 ring	[159]
$[\text{Ph}_8\text{Sb}_4\text{O}_4(\text{OH})_2\{\text{O}_2\text{P(c-Hx)}_2\}]_2 \cdot \text{AcOH} \cdot \text{CH}_2\text{Cl}_2$	Bridging	Tetranuclear Sb_4O_4 cages, hexa-coordinated Sb	[159]
$[\text{Me}_3\text{Sb}(\text{OH})\{\text{O}_2\text{PPh}_2\}]_n$	Monodentate	Distorted trigonal bipyramidal, Sb–O(H) = 1.967(3) Å	[161]
$[\text{Bu}_3\text{Sb}(\text{OH})\{\text{O}_2\text{PPh}_2\}]$ (Fig. 18)	Monodentate	Distorted trigonal bipyramidal, polymeric chain self assembly through intermolecular H-bonding	[162]
$\{[\text{Me}_3\text{Sb}(\text{O}_2\text{PMe}_2)]_2\text{O}\}$	Bridging	Octahedral	[163]
$\{[\text{Ph}_3\text{Sb}(\text{O}_2\text{PMe}_2)]_2\text{O}\}$ (Fig. 19)	Bridging	Octahedral	[163]
$\{[\text{tol}_3\text{Sb}(\text{O}_2\text{PMe}_2)]_2\text{O}\}$	Triply bridging	Octahedral	[163]
$[\text{Me}_3\text{Sb}(\text{OSPPH}_2)]$ (Fig. 20)	Monodentate (through O-atoms)	Distorted trigonal bipyramidal, discrete monomer, Sb–O(1) = 2.107(5) Å, Sb–O(2) = 2.114(5) Å	[167]
$[\text{Me}_4\text{SbOSPMe}_2]$	Monodentate (through O-atoms)	Distorted trigonal bipyramidal, Sb–O = 2.532(4) Å	[170]
$[\text{Me}_3\text{Sb}(\text{S}_2\text{PPh}_2)_2]$	Monodentate	Distorted trigonal bipyramidal	[78]
$[\text{Me}_3\text{Sb}(\text{S}_2\text{CNMe}_2)_2]$	Monodentate	Distorted trigonal bipyramidal	[173]
$[\text{Ph}_4\text{As}][\text{S}_2\text{PPr}'_2]$	Ionic	Salt both anion and cation have tetrahedral geometry	[175]
$[\text{Ph}_4\text{As}][\text{S}_2\text{P(OMe)}_2]$	Ionic	Salt both anion and cation have tetrahedral geometry	[175]

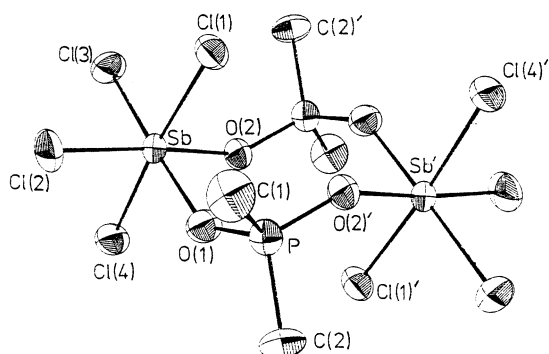


Fig. 16. Structure of $[\text{SbCl}_4(\text{O}_2\text{PMe}_2)_2]_2$ reproduced from Ref. [154a].

distorted pentagonal bipyramidal, one of the sites being occupied by the electron pair.

The structure of $[\text{MesBi}(\text{S}_2\text{PPh}_2)_2]$ is monomeric. The dithio ligand is anisobidentate with Bi–S distances 2.662(2) and 3.123(3) Å. The geometry around bismuth is square pyramidal with the metal atom lying 0.333 Å above the basal plane formed by four sulfur atoms [142]. The axial position is occupied by the carbon atom of the mesityl group bound to Bi [142]. The complex $[\text{MeBi}(\text{S}_2\text{CNEt}_2)_2]$ is dimeric formed due to Bi–S interactions. The central bismuth atom acquires a distorted pentagonal pyramidal geometry in which electron pair is directed opposite to the apical carbon atom [143]. The structure of $[\text{PhBi}(\text{S}_2\text{CNEt}_2)_2]$ [144] has also been reported. The structure of $[\text{PhBi}(\text{S}_2\text{COMe}_2)]$ reveals

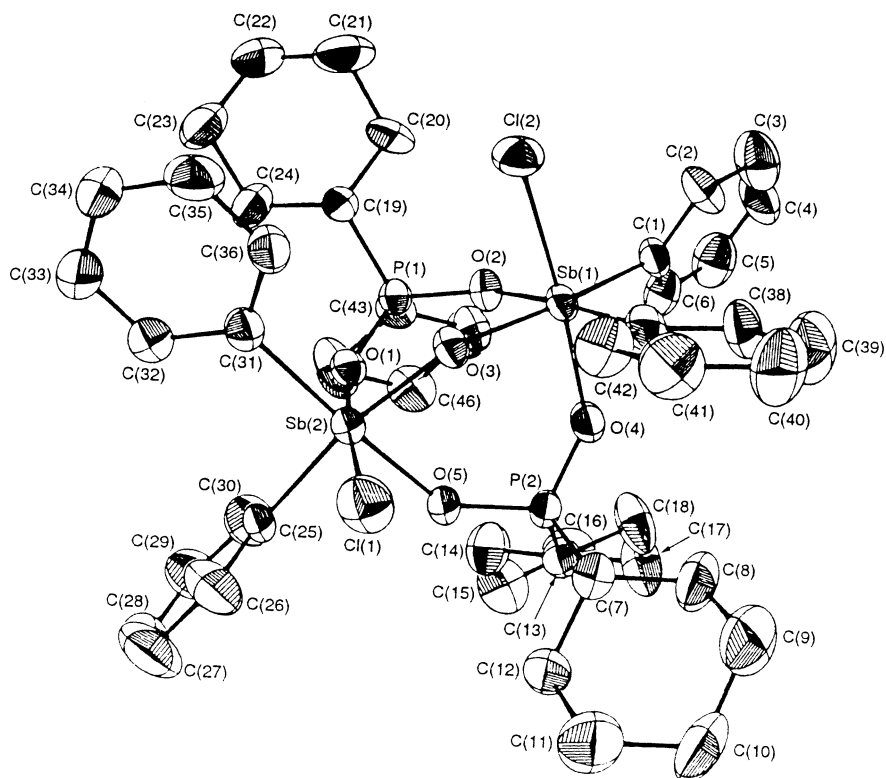
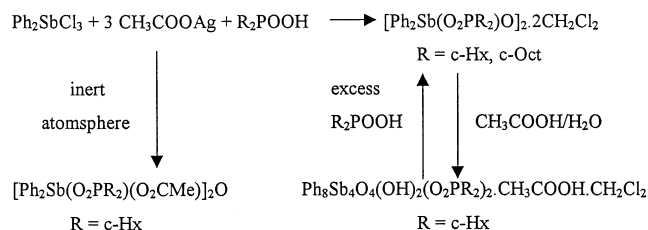


Fig. 17. Molecular structure of $[\text{Ph}_2\text{SbCl}\{\text{O}_2\text{P}(\text{c-Hx})_2\}]_2\text{O}$ reproduced from Ref. [158].



Scheme 4.

that Bi is in square pyramidal geometry [145]. The antimony atom in $[\text{Sb}(\text{Budtc})_2]_2\text{Cd}_2\text{I}_6$ acquires a pseudo trigonal bipyramidal geometry with the lone pair of electron lying at the equatorial position [146].

4. Chemistry of pentavalent compounds

The chemistry of these elements in the pentavalent state is dominated by antimony compounds for which both inorganic and organometallic derivatives are reported. With sulfur ligands the redox process becomes important and reduction of antimony(V) compounds to antimony(III) is often quite facile. There is hardly any report on Bi(V) compounds with these ligands.

Schmidt and co-workers [147–152] have reported several chloroantimony compounds with phosphorus based acids. These compounds are often associated with phosphate ligand bridging antimony atoms. The reac-

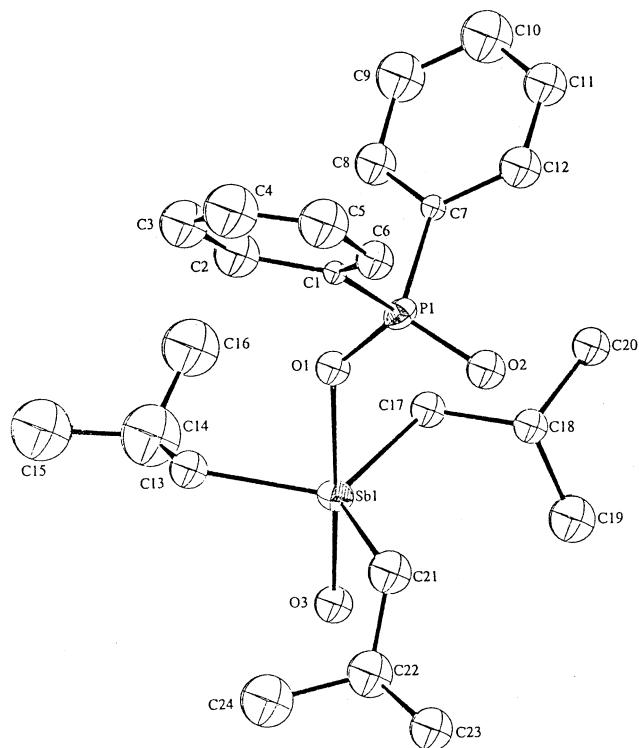


Fig. 18. Molecular structure of $[\text{Bu}_3\text{Sb}(\text{OH})(\text{O}_2\text{PPh}_2)]$ reproduced from Ref. [162].

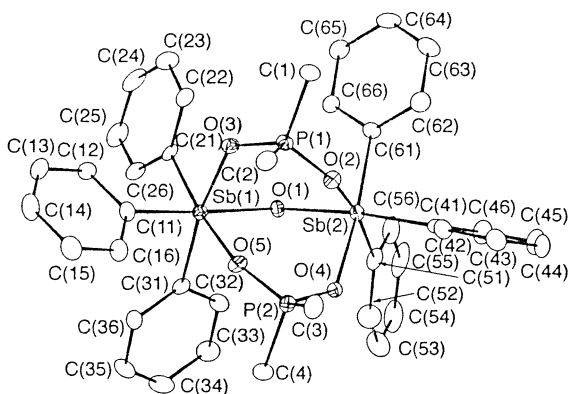


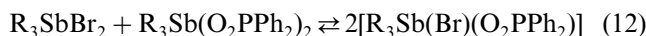
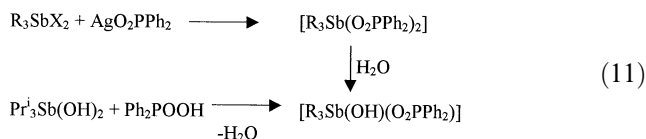
Fig. 19. Structure of $[\{\text{Ph}_3\text{SbO}_2\text{PMe}_2\}_2\text{O}]\cdot\frac{1}{2}\text{CH}_2\text{Cl}_2$ reproduced from Ref. [163].

tion of $\text{SbCl}_5\cdot\text{H}_2\text{O}$ with benzylmethoxophosphinic acid in methanol affords $[\text{SbCl}_3(\text{O})\{\text{R}(\text{OMe})\text{PO}_2\}\text{SbCl}_3(\text{OMe})]$ (Fig. 15) ($\text{R} = 4\text{-ClC}_6\text{H}_4\text{CH}_2$, $4\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2$ [150]) (Scheme 3). Oxygen bridges antimony atoms which are also bridged by bidentate phosphonate ligands. The treatment of SbCl_5 with $\text{Bz}(\text{RO})\text{PO}_2\text{H}$ in water yields $\text{Cl}_3\text{SbO}(\text{OH})[\text{Bz}(\text{RO})\text{PO}_2]\text{SbCl}_3\cdot\text{H}_2\text{O}$ ($\text{R} = \text{Me}$, Et) [153]. In solution there is rapid intermolecular exchange of protons. The structures of a few tetrachloroantimony(V) compounds have been established by X-ray diffraction [125,152,154–156] (Table 3). The compounds $[\text{SbCl}_4(\text{O}_2\text{PR}_2)]_2$ (Fig. 16) ($\text{R} = \text{Me}$, Cl , OMe ,

OPh) are dimeric and all possess bridging PO_2^- group so as to form eight-membered $\text{Sb}_2(\text{O}_2\text{P})_2$ rings. Schimidt and co-workers have reported $[\text{SbX}_3(\text{Medtc})_2]$ ($\text{X} = \text{Cl}$ or Br) [157].

Diphenylantimony(V) phosphinates have been reported by Kumaraswamy and co-workers [158]. The reaction of Ph_2SbCl_3 with AgO_2PR_2 ($\text{R} = \text{c-Hx}$, c-Oct) in 1:2 stoichiometry gave $[\text{Ph}_2\text{SbCl}(\text{O}_2\text{PR}_2)]_2\text{O}$ [158]. The structure of cyclohexylphosphinate shows that the antimony atom is hexacoordinated with bridging phosphinate group (Fig. 17). These workers have also reported several dinuclear and tetranuclear cages of oxodiphenylantimony phosphinates [159]. Thus, the dimeric $[\text{Ph}_2\text{Sb}\{\text{O}_2\text{PR}'_2\}_2\text{O}]\cdot 2\text{CH}_2\text{Cl}_2$ ($\text{R}' = \text{c-Hx}$, c-Oct) and tetrameric $[\text{Ph}_8\text{Sb}_4\text{O}_4(\text{OH})_2\text{O}_2\text{P}(\text{C}_6\text{H}_{11})_2)_2]\cdot\text{CH}_3\text{COOH}\cdot\text{CH}_2\text{Cl}_2$ have been characterized by single crystal X-ray analysis. All these compounds contain four-membered Sb_2O_2 rings with hexacoordinated antimony. The mixed phosphinate–acetate, $[\text{Ph}_2\text{Sb}\{\text{O}_2\text{P}(\text{C}_6\text{H}_{11})_2\}\{\text{O}_2\text{CMe}\}_2\text{O}]\cdot\text{H}_2\text{O}$ have also been reported by the same group [159], (Scheme 4).

Synthesis of triorgano-arsenic and -antimony(V) diphenylphosphinate involves the reaction of R_3EX_2 with AgO_2PPh_2 [160]. The FAB MS of organoantimony compounds indicate them to be dimeric whereas the analogous arsenic derivatives are monomeric. Partial hydrolysis affords hydroxo derivatives $[\text{R}_3\text{Sb}(\text{O-H})(\text{O}_2\text{PPh}_2)]$ (Eq. 11) (Fig. 18) which can also be obtained by the reaction of $\text{R}_3\text{Sb}(\text{OH})_2$ with the free acid [161,162]. The structure of $[\text{R}_3\text{Sb}(\text{OH})(\text{OPPh}_2)]$ ($\text{R} = \text{Me}$ or Bu^t) reveals that the antimony atom acquires a distorted trigonal bipyramidal geometry with R_3 groups in equatorial positions. The molecules are associated into a polymeric zig-zag chain formed through intermolecular hydrogen bonds between the hydrogen of the hydroxo group and oxygen double bonded to phosphorus. Attempts to prepare $[\text{R}_3\text{SbBr}(\text{O}_2\text{PPh}_2)]$ results in a dynamic equilibrium between R_3SbBr_2 , $\text{R}_3\text{SbBr}(\text{O}_2\text{PPh}_2)$ and $\text{R}_3\text{Sb}(\text{O}_2\text{PPh}_2)_2$ (Eq. 12) [162]. The synthesis and structures of a few oxo compounds, $[\{\text{Me}_3\text{Sb}(\text{O}_2\text{PMe}_2)_2\text{O}]\cdot\frac{1}{2}\text{CH}_2\text{Cl}_2$, $[\{\text{Ph}_3\text{Sb}(\text{O}_2\text{PMe}_2)_2\text{O}]\cdot\frac{1}{2}\text{CH}_2\text{Cl}_2$ (Fig. 19), $[\{\text{tol}_3\text{Sb}(\text{O}_2\text{PMe}_2)_2\text{O}]\cdot\frac{1}{2}\text{CH}_2\text{Cl}_2$ have been reported [163]. These complexes are obtained by the reaction of $(\text{R}_3\text{SbBr})_2\text{O}$ with NaO_2PR_2 . In these compounds two antimony atoms have triple bridges, two with phosphinate groups and one with an oxygen atom.



Compounds of general formula $[\text{R}_3\text{Sb}\{\text{O}_2\text{PHR}'\}_2]$

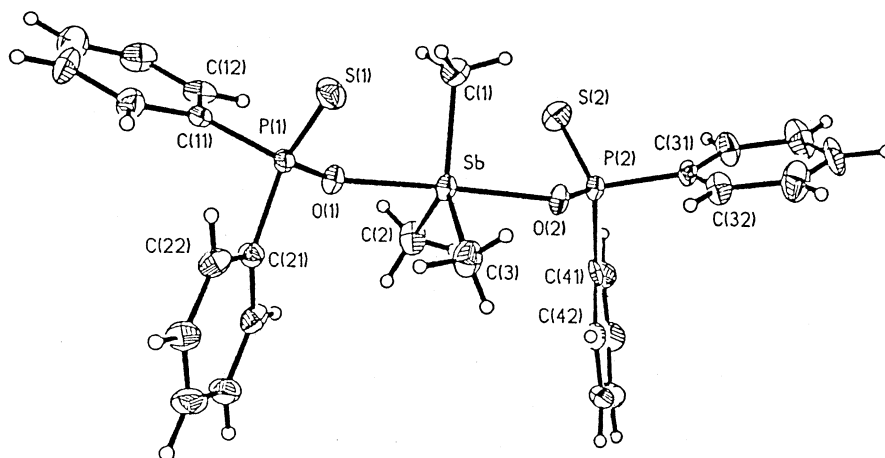


Fig. 20. Structure of $[\text{Me}_3\text{Sb}(\text{OSPPh}_2)_2]$ reproduced from Ref. [167].

($\text{R} = \text{Me}, \text{Ph}$; $\text{R}' = \text{Ph}, \text{CH} = \text{CHPh}$) [164] have been synthesized and characterized. Tetraorganoantimony(V) with phosphonic acids, $[\text{Me}_4\text{Sb}\{\text{O}_2\text{P}(\text{OH})\text{R}\}]$ ($\text{R} = \text{Me}, \text{Ph}$) are associated molecules in which the OH group is involved in hydrogen bonding [165,166].

Monothiophosphate complexes of triorganoantimony(V), $[\text{R}_3\text{Sb}(\text{OSPR}'_2)]$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^n, \text{Pr}^i, \text{Ph}$; $\text{R}' = \text{Me}, \text{Et}, \text{Ph}, \text{OEt}, \text{OPr}^n, \text{OPr}^i$) have been prepared by the reaction of R_3SbCl_2 with ammonium salts of thiophosphoric acids [167,168]. The FAB MS of $\text{Me}_3\text{Sb}(\text{OSPR}_2)_2$ ($\text{R} = \text{Me}, \text{Et}$) exhibits molecular ion peak [167]. The ^1H -, ^{13}C - and ^{31}P -NMR spectra exhibit a single set of resonances [168]. The presence of Sb–O stretching in the region $410\text{--}460\text{ cm}^{-1}$ in their IR spectra indicates bonding through oxygen. These compounds are discrete monomeric molecules in which the ligand is bonded to antimony through oxygen in a monodentate fashion. The structure of $\text{Me}_3\text{Sb}(\text{OSPPH}_2)_2$ (Fig. 20) shows that the antimony is in a trigonal bipyramidal configuration in which SbC_3 unit is planar [167]. The tetraorganoantimony(V) compound $[\text{Me}_4\text{Sb}][\text{SOPMe}_2]$ has been initially thought to be ionic [169,170]. The structure of $\text{Me}_4\text{SbOSPM}_2$ later reveals a distorted trigonal bipyramidal configuration around Sb atom. The thiophosphate ligand is bonded through oxygen to antimony in a monodentate fashion [170].

Although triorganoantimony(V) complexes with dithio ligands have been prepared and fully characterized, reduction to antimony(III) is quite facile (Eq. (13)). Similarly reaction of Ph_2SbOBr with $\text{R}_2\text{PS}_2\text{Na}$ ($\text{R} = \text{Me}, \text{Et}, \text{Ph}$) results in reduction of Sb(V) to Sb(III) [103].



Triorganoantimony(V) bis dithiolates (dithiophosphate [78], xanthates [171,172] and dithiocarbamates [171,172]) have been prepared by the reactions of R_3SbX_2 with sodium salts of dithio ligand. The structures of $[\text{Me}_3\text{Sb}(\text{S}_2\text{PPh}_2)_2]$ [78], $[\text{Me}_3\text{Sb}(\text{S}_2\text{CNMe}_2)_2]$

[173] established by single crystal X-ray diffraction methods show that antimony acquires a distorted trigonal bipyramidal configuration with a planar SbC_3 unit. The stabilization of the pentavalent state for antimony with a sulfur ligand comes from σ -electron donating methyl groups. Several trimethylantimony derivatives of the type $[\{\text{Me}_3\text{Sb}(\text{S}^\ominus\text{S})\}_2\text{O}]$ ($\text{S}^\ominus\text{S} = \text{S}_2\text{P}(\text{OR}')_2$, $\text{R} = \text{Me}, \text{Et}$; S_2CNR_2 , $\text{R} = \text{Me}, \text{Et}$; S_2COR , $\text{R} = \text{Me}, \text{Et}$) have been investigated [151,174].

Tetraorganoarsenic compounds with dithiophosphinic acids, $[\text{R}_4\text{As}][\text{S}_2\text{PR}'_2]$ ($\text{R} = \text{Me}$ or Ph ; $\text{R}' = \text{Pr}^i, \text{OMe}$) are ionic derivatives [175]. Both cations and anions are tetrahedral and the two P–S bond lengths are equal [152,175,176]. Tetraorganoantimony(V) dithiocarbamates, $[\text{Me}_4\text{Sb}(\text{S}_2\text{CNR}_2)_2]$, ($\text{R} = \text{Me}, \text{Et}$) and $[\text{Ph}_4\text{Sb}(\text{S}_2\text{CNET}_2)_2]$ have been reported.

5. Applications

Arsenic, antimony and bismuth derivatives of phosphorus based acids, dithiocarbamates and xanthates find extensive applications in the petroleum industry either as catalysts or lubricant additives, as biocides and as analytical reagents. Trivalent compounds have often been used for the purpose.

Antimony complexes with dithio ligands have shown catalytic activity [177–184]. Antimony(III) phosphoro- and phosphinodithioates, e.g. $[\text{Sb}\{\text{S}_2\text{P}(\text{OPr}^i)_2\}_3]$ [184], are used as catalysts for decontamination in petroleum cracking [178,179]. The compound $[\text{Sb}(\text{S}_2\text{CNPr}_2)_3]$, however, shows improved catalytic efficiency [184]. Metal tris(*N,N*-diethyldithiocarbamates), $[\text{M}(\text{S}_2\text{CN-Et}_2)_3]$ act as inhibitors in the oxidation of hydrocarbons [185,186]. Antimony tris-dialkyldithiocarbamates, $[\text{Sb}(\text{S}_2\text{CNR}_2)_3]$ ($\text{R} = \text{C}_{1-10}$ alkyls) accelerate vulcanization of rubber [187,188]. Organoantimony compounds

have been used as passivating agents [189]. Bismuth dithiocarbamates have been used as stabilizers to improve the shelf life of photosensitive resins without lowering their sensitivity [190].

Applications of dithioates of arsenic, antimony and bismuth as lubricant additives have been reported in patent literature [191–204]. *O,O*-dialkyldithiophosphoric acid complexes have been used as oil additives [199]. Anti-friction, -wear and extreme pressure performance as additives in lubricants of bismuth dioctyl diithiocarbamate, $[\text{Bi}\{\text{S}_2\text{CN}(\text{Oct})_2\}_3]$ has been evaluated [204]. These compounds showed improved anti-friction and -wear properties of lubricants and greases.

Biocidal activities of several trivalent dithio compounds have been evaluated [205–219]. Haiduc and co-workers [208–213] have investigated anti-cancer activities of antimony complexes. In vivo and in vitro tests indicate that $[\text{Ph}_2\text{SbS}_2\text{PPh}_2]$ and $[\text{Ph}_2\text{SbS}_2\text{P}(\text{OPr}^i)_2]$ are effective against Ehrlich ascites tumor [211]. The latter complex is more effective than the former while both of them show greater activity than the corresponding organotin derivatives [211]. Dialkyldithiophosphoric acid complexes have also been employed as pesticides [199,205]. Organoarsenic dithiophosphates $[\text{R}_2\text{AsS}_2\text{P}(\text{OR}')_2]$ ($\text{R} = \text{Me, Et, Ph}$; $\text{R}' = \text{Me, Et}$), dithiocarbamates $[\text{MeAs}(\text{S}_2\text{CNR}_2)_2]$ and xanthates (e.g. $[\text{Me}_2\text{As}(\text{S}_2\text{COPr}^i)]$ $[\text{RAs}(\text{S}_2\text{COR}')_2]$, $[\text{As}(\text{S}_2\text{COR}')_3]$) have been reported as agricultural bactericides, insecticides, nematocides, fungicides and herbicides [206,214–219].

These complexes have been extensively employed as analytical reagents [220–255]. Traces of As(III) and Sb(III) have been determined by radiochemical methods employing isotope exchange between labeled metal diethyldithiocarbamates in CCl_4 and an aqueous solution containing metal to be determined [223]. The selectivity of the method is high as other common metal ions usually do not interfere in the determination. Bismuth diethyldithiocarbamate, $[\text{Bi}(\text{S}_2\text{CNET}_2)_3]$ has been employed for the polarographic determination of mercury [226] and determination of copper in pure Fe, Co and Ni [227]. The complex has also been used for selective extraction of gold and mercury from sea water at $\text{pH} \leq 1$ [244]. A complete separation of ^{210}Pb , ^{210}Bi , ^{210}Po has been achieved by $\text{Bi}(\text{S}_2\text{CNET}_2)_3$ [241]. For neutron activation analysis palladium from natural sample is extracted by $\text{Bi}(\text{S}_2\text{CNET}_2)_3$ [250]. Clark and Qazi [234] have reported a modified colorimetric method for the determination of malathion. Alkaline hydrolysis of malathion in the presence of Bi gives bismuth dimethyldithiophosphate, a yellow colored complex, which is determined colorimetrically (absorbs at 325 nm). Similarly, bismuth diethyldithiocarbamate has been studied [236].

Solid–liquid separation method have been used for some metals after liquid–liquid extraction [228]. The method involves treatment of metals with various

complexing agents to get water insoluble colored complexes which are quantitatively extracted into molten naphthlene at $> 81^\circ\text{C}$. The solidified mixture of metal complexes and naphthalene is separated, dried, dissolved in DMF and the amount of trace metals is determined spectrophotometrically.

Arsenic(III) is selectively extracted in the presence of Zn(II), Ni(II) and other metals using decomposition of diisooctyldithiophosphate [229]. Thin layer chromatographic behaviour of *N,N*-disubstituted dithiocarbamates of As, Sb, Bi in different solvents has been studied. Mobilities of different types of tris complexes follow the order $\text{Morp}\cdot\text{dtc} \ll \text{Dime}\cdot\text{dtc} < \text{Pip}\cdot\text{dtc} < \text{Die}\cdot\text{dtc} < \text{MePh}\cdot\text{dtc} < \text{Dipr}\cdot\text{dtc} < \text{Dibut}\cdot\text{dtc} < \text{Dibenz}\cdot\text{dtc}$. The mobility of As and Sb derivatives is comparable while for the corresponding Bi complexes it is slow [245].

6. Concluding remarks

This review describes salient features on synthesis, spectroscopic, and structural aspects of arsenic, antimony and bismuth complexes of xanthate, dithiocarbamate and phosphorus based acids. A variety of structural patterns and different bonding modes of ligands have been observed in these complexes. It is found that arsenic compounds are monomeric in nature, whereas antimony and bismuth derivatives are often associated leading to supramolecular assemblies. These compounds find many applications such as lubricating oil additives, passivating agents, pesticides, etc. The trivalent derivatives with dithio ligands may also prove important molecular precursors for the preparation of metal sulfide (M_2S_3) films and nanopaticles.

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