Polyhedron 28 (2009) 689–694

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis and spectroscopic characterization of tris(*O*,*O*′-ditolyl dithiophosphato) arsenic/antimony/bismuth(III) compounds: Crystal structures of $[As\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]\cdot 0.5C_6H_{14}$, $[Sb\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$ and $[Bi\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$

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ARTICLE INFO

Article history:
Received 18 October 2008
Accepted 12 December 2008
Available online 27 January 2009

Keywords:
Arsenic(III)
Antimony(III)
Bismuth(III) compounds
O,*O*′-Ditolyl dithiophosphates
Crystal structures

ABSTRACT

Arsenic(III), antimony(III) and bismuth(III) compounds of the type, $[M\{S_2P(OR)_2\}_3]$ (where M = As, Sb and Bi; R = *o*-, *m*-, *p*-C_6H_4Me) were obtained by reactions of MCl_3 with ammonium salts of the corresponding *O*,*O*′-ditolyl dithiophosphate on refluxing in benzene. These compounds were characterized by elemental analysis, IR, ^1H NMR and ^{31}P NMR spectroscopy. The single crystal X-ray structures of three representative compounds were determined. $[As\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]\cdot 0.5C_6H_{14}$ crystallizes as triclinic in the space group $P\bar{1}$ with $a = 10.9396(1)$, $b = 14.1891(2)$, $c = 17.5359(2)$ Å, $\alpha = 70.731(1)$, $\beta = 84.734(1)$, $\gamma = 74.205(1)^\circ$, $Z = 4$, $V = 2472.37(5)$ Å^3. $[Sb\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$ and $[Bi\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$ both crystallize as monoclinic in the space group $P2_1$ with $a = 12.4520(3)$, $b = 22.8760(5)$, $c = 16.2165(4)$ Å, $\beta = 93.022(1)^\circ$, $Z = 4$, $V = 4612.9(2)$ Å^3 and with $a = 12.4903(2)$, $b = 22.9554(4)$, $c = 16.1032(3)$ Å, $\beta = 92.4300(10)^\circ$, $Z = 4$, $V = 4612.96(14)$ Å^3, respectively. In all three molecules, the central metal atom is surrounded by all six sulfur atoms of the three chelating anisobidentate *O*,*O*′-ditolyl dithiophosphate groups in a pseudo trigonally distorted octahedron with a lone pair positioned on one of the triangular octahedral faces. The three metal sulfur bonds adjacent to the lone pair (capped face) are longer than the three furthest from the lone pair (uncapped face). Inter-ligand angles between the longer bonds are greater than those between the shorter bonds.

1. Introduction

Ligands containing the $-S_2P$ grouping are known to exhibit a remarkable diversity in their coordination patterns towards metals which can be classified as monodentate [1,2], bidentate [3,4] and bridging [5]. The most interesting results are obtained when the dithiophosphate ligand is attached to a non-transition metal atom. The presence of a stereochemically active lone pair of electrons on the group 15 elements, arsenic, antimony and bismuth, combined with small ligand bites and molecular associations, adds to the interest in structural variations. Over the past several decades, various dithio ligating systems in, arsenic, antimony and bismuth complexes have been studied with *O*,*O*′-dialkyl [1–10], alkylene [11,12] and mixed ligand [13–15] dithiophosphates. Although only one X-ray structure of an arsenic compound, $[As\{S_2P(OMe)_2\}_3]$ [16], has been reported, there have been several of antimony and bismuth including $[Sb\{S_2P(OMe)_2\}_3]$ [17], $[Sb\{S_2P(OEt)_2\}_3]$ [18], $[Sb\{S_2P\{O(i\text{-}Pr)\}_2\}_3]$ [17], $[Bi\{S_2P(OMe)_2\}_3]$ [6], $[Bi\{S_2P(OEt)_2\}_3]$ [7], $[Bi\{S_2P\{O(i\text{-}Pr)\}_2\}_3]$ [2], $[Bi\{S_2POCHMeCHMeO\}_3]$ [12] and $[Bi\{S_2POCH_2CEt_2CH_2O\}_3]$ [12].

O,*O*′-Dialkyl dithiophosphate derivatives of arsenic, antimony and bismuth are used in industry as analytic reagents [19,20], lubricant additives [21] and show tribological activity to improve anti-friction and antiwear properties [22]. The anticancer activity of $[Ph_2Sb\{S_2P\{O(i\text{-}Pr)\}_2]$ has been investigated [23,24] and the use of $[Sb\{S_2P(OEt)_2\}_3]$ [18] and $[Bi\{S_2P(OEt)_2\}_3]$ [7] as passivation agents for decontaminant metals in the catalytic cracking of petroleum has been reported.

The literature contains substantial amount of work on arsenic, antimony and bismuth derivatives of *O*,*O*′-dialkyl and alkylene dithiophosphates but much less information on their bulky analogous derivatives of *O*,*O*′-(*o*-, *m*-, *p*-ditolyl) dithiophosphate ligands. However, some metal complexes with the *O*,*O*′-ditolyl dithiophosphate ligands have been synthesized and characterized by us [25–27] and, chlorobis(ditolyl dithiophosphate)arsenic(III) compounds were reported recently [28]. $[NMe_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$ [29] and some derivatives of antimony [30] and cobalt [31,32] ditolyl

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doi:10.1016/j.poly.2008.12.017

dithiophosphates have industrial applications and tributyltin(IV)*O*,*O*′-diaryl dithiophosphates are useful in agriculture [33,34].

In this paper, we report the synthesis, characterization and comparative study of *O*,*O*′-ditolyl dithiophosphate complexes of $[As\{S_2P(OR)_2]\}_3]$, $[Sb\{S_2P(OR)_2\}_3]$ and $[Bi\{S_2P(OR)_2\}_3]$ (R = *o*-, *m*-, *p*-C_6H_4Me), along with the single crystal X-ray diffraction of $[As\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]\cdot 0.5C_6H_{14}$, $[Sb\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$ and $[Bi\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$.

2. Results and discussion

Tris(*O*,*O*′-ditolyl dithiophosphato)arsenic(III)/antimony(III)/bismuth(III) have been synthesized by the reactions of the corresponding metal chloride with the ammonium salts of *O*,*O*′-ditolyl dithiophosphoric acid in 1:3 molar ratio. These reactions are quite facile but to ensure completion reaction solutions were refluxed with stirring for 4–5 h in anhydrous benzene.

$$MCl_3 + 3NH_4S_2P(OR)_2 \xrightarrow{4\text{–}5\text{ h refluxing}} [M\{S_2P(OR)_2\}_3] + 3NH_4Cl$$
$$(M = As, Sb, Bi, R = o\text{-}, m\text{-}, p\text{-}C_6H_4Me)$$

These newly synthesized novel derivatives are pale yellow crystalline solids, with the exception of viscous $[As\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$, $[Sb\{S_2P(OC_6H_4Me\text{-}o)_2\}_3]$, $[Sb\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$ and $[Bi\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$. All of these compounds are soluble in common organic solvents such as benzene, chloroform, toluene and acetone, and also in coordinating solvents such as DMSO and DMF and conversely are insoluble in non-polar organic solvents such as carbon tetrachloride and n-hexane. The complexes are moisture sensitive but are stable when kept moisture free in an inert atmosphere. The products were characterized by elemental analysis and IR, ^1H and ^{31}P NMR spectroscopy.

2.1. IR spectra

The relevant assignments of the IR bands have been made on the basis of comparisons with the spectra of ammonium salts of *O*,*O*′-(*o*-, *m*-, *p*-ditolyl) dithiophosphoric acids [35–37] and the analogous tris(*O*,*O*′-dialkyl dithiophosphato)-arsenic(III)/antimony(III)/bismuth(III) compounds [38]. The two strong intensity bands present in the regions 1114-1173 and 900–952 cm^{-1} are assigned to ν[(P)–O–C] and ν[P–O–(C)] stretching vibrations, respectively, in the complexes **1**–**9**. Two strong bands due to ν(P=S) or $\nu(P\text{–}S)_{asym}$ that are observed in the regions 680–690 and 596–598 cm^{-1} in the parent ammonium salts are shifted to lower wave-number in the corresponding tris(*O*,*O*′-ditolyl dithiophosphato)-arsenic(III)/antimony(III)/bismuth(III) compounds consistent with coordination to metal atom. Bands of strong to medium intensities present in the region 510–563 cm^{-1} are due to ν(P–S) or $\nu(P\text{–}S)_{sym}$ stretching vibrations.

2.2. ^1H NMR spectra

The ^1H NMR spectra for complexes **1**–**9** were recorded in $CDCl_3$ solutions at room temperature. The spectral data for tris(*O*,*O*′-ditolyl dithiophosphato)-arsenic(III)/antimony(III)/bismuth(III) compounds are remarkably similar to those of the corresponding ammonium salts of *O*,*O*′-ditolyl dithiophosphoric acids probably due to the large separation between metal and protons. In complexes **1**–**9**, the methyl protons, observed as singlets in the region 2.19–2.31 ppm, display negligible shifts compared to those in the corresponding salts. Similarly, the phenyl protons, which appear in the range 6.61–7.41 ppm, only undergo a negligible downfield shift compared to their positions in the free ligand as a consequence of coordination of the ligand.

2.3. ^{31}P NMR spectra

The proton decoupled ^{31}P NMR spectra of complexes **1**–**9** recorded in $CDCl_3$ all exhibit a sharp singlet, which, is in the region 83.95–85.58 ppm for the compounds of arsenic (**1**–**3**), 87.45–88.70 ppm for those of antimony (**4**–**6**) and 94.23–95.27 ppm for those of bismuth (**7**–**9**). On examining the proton decoupled ^{31}P NMR chemical shifts of a number of metal dialkyldithiophosphates, Glidewell [39] concluded that complexes containing bidentate ligands had signals in the range 82–101 ppm while those with signals less than 82 ppm had monodentate ligands. This suggests that in solution any bidentate coordination of the dithiophosphate groups is relatively strong for bismuth and becomes progressively weaker for antimony and arsenic. The observation of only one sharp singlet for all compounds **1**–**9** reflects the equivalent nature of phosphorous nuclei and the purity of the compound.

2.4. Molecular structures of $[As\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]\cdot 0.5C_6H_{14}$, $[Sb\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$ and $[Bi\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$

$[As\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]\cdot 0.5C_6H_{14}$ (**2**) crystallizes as triclinic in space group $P\bar{1}$ whereas, $[Sb\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$ (**5**) and $[Bi\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$ (**8**) both crystallize as monoclinic in space group $P2_1$. There are two molecules in the asymmetric units of **5** and **8** and in both cases one of the molecules is disordered so for clarity only the molecules that are not disordered are shown in Figs. 2 and 3, respectively. Similarly, for purposes of comparison, the component of n-hexane in the asymmetric unit of **2** is not included in Fig. 1.

$[Sb\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$ (**5**) and $[Bi\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$ (**8**) are isostructural, as are the corresponding analogues $[Sb\{S_2P(OEt)_2\}_3]$ [18] and $[Bi\{S_2P(OEt)_2\}_3]$ [7]. However, $[Sb\{S_2P\{O(i\text{-}Pr)\}_2\}_3]$ [17] and $[Bi\{S_2P\{O(i\text{-}Pr)\}_2\}_3]$ [2] are not isostructural nor are $[As\{S_2P(OMe)_2\}_3]$ [16], $[Sb\{S_2P(OMe)_2\}_3]$ [17] and $[Bi\{S_2P(OMe)_2\}_3]$ [6], but all of these structures consist of similar discrete

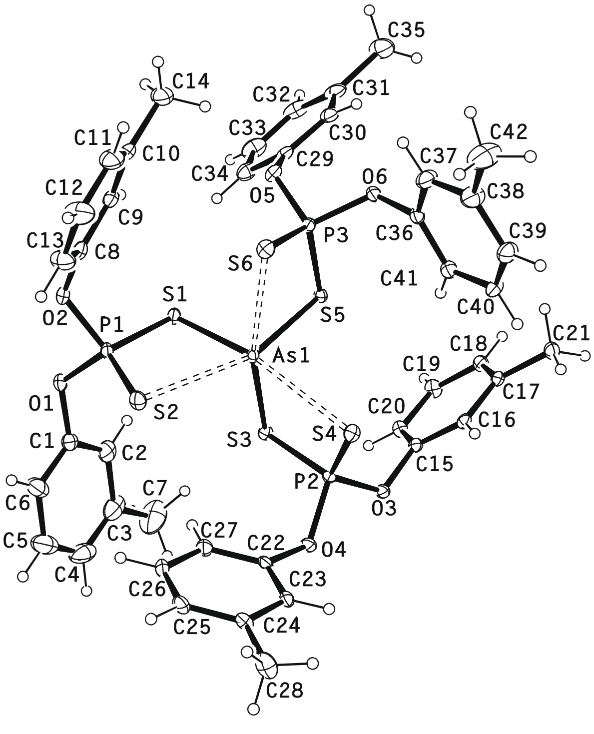

Fig. 1. ORTEP plot of the molecule of $[As\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]\cdot 0.5C_6H_{14}$. The fraction of the C_6H_{14} molecule in the asymmetric unit is omitted for clarity. The non-hydrogen atoms are drawn with 30% probability ellipsoids.

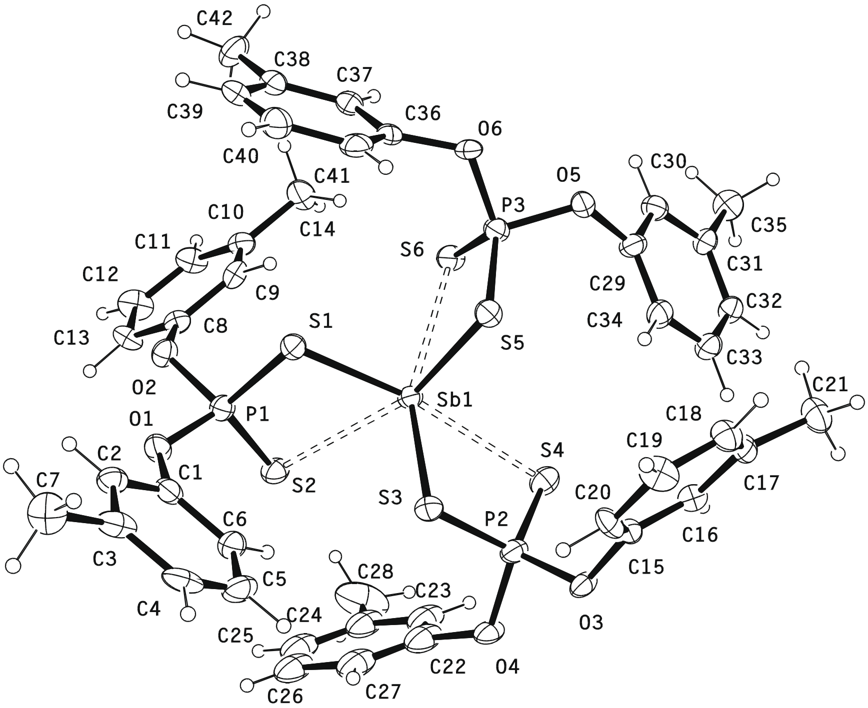

Fig. 2. ORTEP plot of the molecule of [Sb{$S_2P(OC_6H_4Me$-*m*$)_2\}_3$] in the asymmetric unit that is not disordered. The non-hydrogen atoms are drawn with 30% probability ellipsoids.

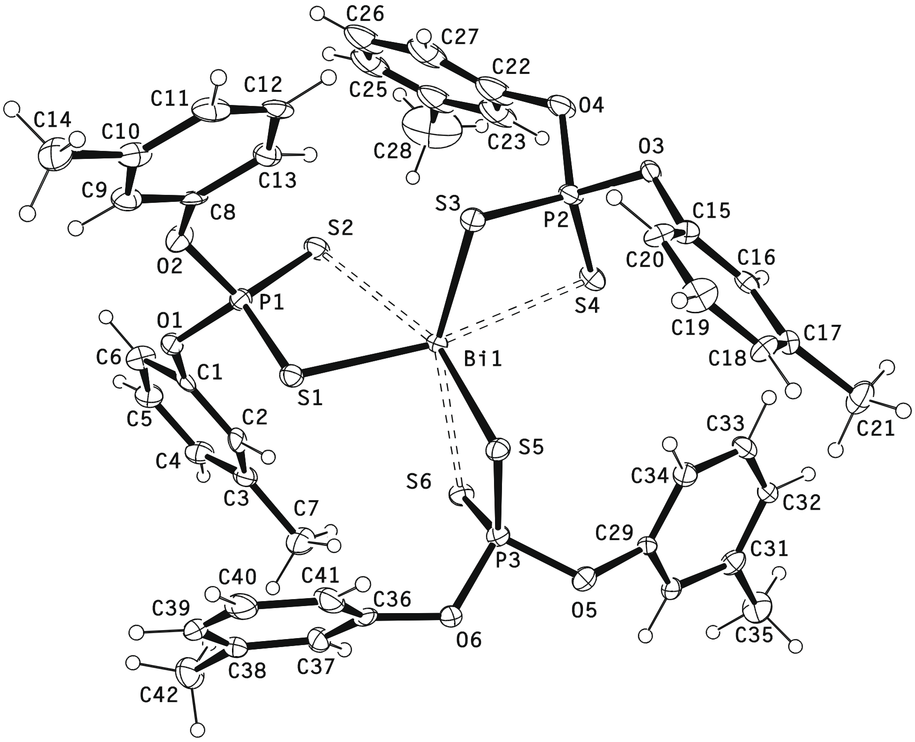

Fig. 3. ORTEP plot of the molecule of [Bi{$S_2P(OC_6H_4$-Me-*m*$)_2\}_3$] in the asymmetric unit that is not disordered. The non-hydrogen atoms are drawn with 30% probability ellipsoids.

[M{$S_2P(OR)_2\}_3$] units with a distorted octahedral arrangement of sulfur atoms. This can be seen in the ORTEP diagrams of **2**, **5** and **8** in Figs. 1–3. These demonstrate the anisobidentate coordination of the phosphorodithioate ligands in **2**, **5** and **8** with the longer (secondary) bonds identified by dashed lines and that there are no inter-molecular associations. The coordination polyhedron on the metal atom can be described as a distorted capped octahedron with a stereochemically active lone pair of electrons in the capping position and approximately on a molecular pseudo triad axis, which passes through the metal atom. The vertices of the distorted octahedron are occupied by the six sulfur atoms of the three anisobidentate phosphorodithioate ligands.

It is assumed that lone pair-bond pair repulsions in the metal coordination sphere [2,7,17,18] result in longer M–S bonds (2.9345(6)–3.0284(6) Å in **2**, 2.980(2)–3.031(2) Å in **5** and 2.926(2)–2.953(2) Å in **8**) for those bonds adjacent to the lone pair and shorter M–S bonds (2.3242(6)–2.3415(6) Å in **2**, 2.543(2)–2.549(2) in **5** and 2.678(2)–2.705(2) Å in **8**) for those more remote. These ranges are consistent with typical values reported for the short and long ligand bonds in [As{$S_2P(OMe)_2$}$_3$] (2.320(1) and 3.029(1) Å) [16], [Sb{$S_2P(OMe)_2$}$_3$] (2.535(2) and 3.006(2) Å) [17], [Sb{$S_2P(OEt)_2$}$_3$] (2.583(1) and 2.86(1) Å) [18], [Sb{S_2P{O(*i*-Pr)}$_2$}$_3$] (2.519(4) and 3.000(5) Å) [17], [Bi{$S_2P(OEt)_2$}$_3$] (2.747(14) and 2.795(12) Å) [7] and [Bi{S_2P{O(*i*-Pr)}$_2$}$_3$] (2.702(6) and 2.8784(6) Å) [2]. The overall difference between long and short M–S distances decreases in the order As (0.65) > Sb (0.47) > Bi (0.25 Å) emphasizing that for **2**, **5** and **8** and other related [M{$S_2P(OR)_2$}$_3$] derivatives, the As compounds are clearly anisobidentate, and possibly close to monodentate. The longest As–S bond for [As{$S_2P(OC_6H_4Me$-*m*$)_2$}$_3$] is 3.0284(6) Å comparable to 3.025(1) Å for [As{$S_2P(OMe)_2$}$_3$] [16] so regardless of whether R is the smallest alkyl group or a relatively large aryl group, the longer As–S distance is essentially unchanged. By contrast, the shorter and longer bonds are relatively similar in length in **8** as well as in [Bi{$S_2P(OEt)_2$}$_3$] [7] and [Bi{S_2P{O(*i*-Pr)}$_2$}$_3$] [2].

The small S–M–S bite angles (75.51(2)–77.47(2)° for **2**), (72.52(7)–72.98(7)° for **5**) and (72.10(6)–72.45(6)° for **8**), which are also similar in the related compounds, might be expected to inevitably result in considerable distortion of the remaining angles from 90.00°. However, this is not the case for the angles involving the three stronger M–S bonds from each ligand in **2** (S(1)–M(1)–S(5), S(3)–M(1)–S(5) and S(1)–M(1)–S(5) which have angles of 91.26(2)°, 91.90(2)° and 92.05(2)°, respectively. This is consistent with the ligands in **2** being close to monodentate. By contrast, the corresponding S–M–S bite angles in **5** and **8** cover a wider range of 84.87(7)–91.81(8)° and 84.45(6)–93.06(7)°, respectively. The interligand angles involving the longer M-S bonds are all considerably larger ranging from 91.74(2)° to 102.46(2)° (for **2**), 94.90(7)–112.29(7)° (for **5**), and 95.27(6)–111.46(6)° (for **8**), with once again values for **5** and **8** being similar and differing from those of **2**.

Finally, unsymmetrical chelation is also reflected in the P–S bond distances which fall into two classes; the shorter distances (ave. 1.927(2) in **2**, 1.940(5) in **5** and 1.961(2) Å in **8**) are associated with S atoms forming the longer M–S interactions while the longer P–S bonds (ave. 2.060(4) in **2**, 2.032(3) in **5** and 2.010(4) Å in **8**) are allied with S atoms forming the shorter bonds to the metal, as is plausible to maintain bond order conservation around sulfur. Notably the largest difference in these bond lengths is for **2** where the difference in the longer and shorter M–S bonds is greatest. Thus the crystal structures provide confirmation of the structural conclusions reached on the basis of the ^{31}P NMR spectra of **2**, **5** and **8** as discussed earlier.

3. Experimental

As_2O_3, $BiCl_3$ and P_2S_5 were purchased from E. Merck and used as such. $SbCl_3$, $SOCl_2$, *o*-, *m*-, *p*-cresols (E. Merck) were distilled prior to use. Solvents (benzene, n-hexane and petroleum ether) were dried and distilled before use. Because the starting materials and newly synthesized compounds readily undergo hydrolysis, stringent precautions were taken to exclude atmospheric moisture throughout all experimental manipulations. Literature methods were used for the preparation of *O,O′*-ditolyl dithiophosphoric acids [35–37]. Ammonium salts of the dithiophosphoric acids were prepared by reaction of the parent acid with ammonia in benzene. $AsCl_3$ was prepared by the reaction of arsenic trioxide and thionyl chloride [40].

Table 1
Crystal data and structure refinement for [As{$S_2P(OC_6H_4Me$-*m*$)_2$}$_3$]·$0.5C_6H_{14}$(**2**), [Sb{$S_2P(OC_6H_4Me$-*m*$)_2$}$_3$] (**5**) and [Bi{$S_2P(OC_6H_4Me$-*m*$)_2$}]$_3$ (**8**).

Compound	2	5	8
Empirical formula	$C_{45}H_{49}O_6P_3S_6As$	$C_{42}H_{42}O_6P_3S_6Sb$	$C_{42}H_{42}O_6P_3S_6Bi$
Formula weight	1046.03	1049.78	1137.01
Temperature (K)	120(2)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1$	$P2_1$
a (Å)	10.9396(1)	12.4520(3)	12.4903(2)
b (Å)	14.1891(2)	22.8760(5)	22.9554(4)
c (Å)	17.5359(2)	16.2165(4)	16.1032(3)
α (°)	70.731(1)		
β (°)	84.374(1)	93.022(1)	92.430(1)
γ (°)	74.2050(1)		
Volume (Å^3)	2472.37(5)	4612.9(2)	4613.0(1)
Z	2	4	4
D_{calc} (g/cm^3)	1.405	1.512	1.637
Absorption coefficient (mm^{-1})	1.083	1.019	4.243
F(000)	1082	2136	2264
Crystal size (mm^3)	0.60 × 0.20 × 0.20	0.24 × 0.12 × 0.08	0.08 × 0.04 × 0.03
θ range for data collection (°)	3.09–25.03	2.93–25.03	2.95–25.03
Index ranges	$-13 \leqslant h \leqslant 13$, $-16 \leqslant k \leqslant 16$, $-20 \leqslant l \leqslant 20$	$-14 \leqslant h \leqslant 14$, $-27 \leqslant k \leqslant 27$, $-19 \leqslant l \leqslant 18$	$-14 \leqslant h \leqslant 14$, $-27 \leqslant k \leqslant 25$, $-18 \leqslant l \leqslant 19$
Reflections collected	49266	50766	38021
Independent reflections [R_{int}]	8694 [0.0438]	16232 [0.1175]	13992 [0.0397]
Max. and min. transmission	0.8126 and 0.5627	0.9230 and 0.7921	0.8833 and 0.7277
Refinement method	Full-matrix least-squares on F^2	Full-matrix least- squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	8694/0/557	16232/2/1017	13992/2/1008
Goodness-of-fit on F^2	1.031	1.024	1.105
Final *R* indices [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.0304$, $wR_2 = 0.0729$	$R_1 = 0.0618$, $wR_2 = 0.1242$	$R_1 = 0.0408$, $wR_2 = 0.0853$
R indices (all data)	$R_1 = 0.0377$, $wR_2 = 0.0767$	$R_1 = 0.1104$, $wR_2 = 0.1457$	$R_1 = 0.0489$, $wR_2 = 0.0901$
Absolute structure parameter		−0.06(2)	0.089(5)
Extinction coefficient	0.0016(3)	0.0044(2)	
Largest difference in peak and hole (e Å^{-3})	0.582 and −0.428	0.783 and −0.724	1.063 and −0.716

Sulfur was estimated gravimetrically as barium sulfate (Messenger's method). Arsenic and antimony were estimated iodometrically and bismuth by titration against standard EDTA solution using xylenol-orange as indicator. IR spectra were recorded on an ABB Bomem FTLA 2000-100 FT-IR spectrometer in KBr pellets in the range (4000–350) cm^{-1}. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker DRX-300 spectrometer in CDCl$_3$ solutions using tetramethylsilane as an internal standard and H$_3$PO$_4$ as an external standard, respectively.

3.1. Preparations

*3.1.1. [As{S$_2$P(OC$_6$H$_4$Me-o)$_2$}$_3$] (**1**)*

Typically, a suspension of NH$_4$S$_2$P(OC$_6$H$_4$Me-*o*)$_2$ (1.13 g, 3.47 mmol) in benzene (10 ml) was added to a benzene solution of arsenic trichloride (0.21 g, 1.15 mmol) in 3:1 molar ratio with constant stirring followed by refluxing for 5 h at room temperature. The precipitate of ammonium chloride was removed by filtration under anhydrous conditions and excess solvent was removed from the filtrate in vacuo resulting in a pale yellow viscous oily liquid, which was crystallized by adding n-hexane and keeping the solution refrigerated for 2–3 days to obtain yellow crystals. Yield: 1.10 g, 94%; m.p. 60 °C. *Anal.* Calc. for $C_{42}H_{42}O_6S_6P_3As$: As, 7.47; S, 19.18. Found: As, 7.60; S, 19.17%. ^{1}H NMR (CDCl$_3$): δ 2.19 (s, CH$_3$, 18H), 6.91–7.10 (m, 24H, OC$_6$H$_4$); ^{31}P NMR (CDCl$_3$): δ 83.95 ppm; IR (KBr) (cm^{-1}): 1114s, ν{(P)–O–C}; 934s, ν{P–O–(C)}; 710s, 664s, ν(P=S); 529m, ν(P–S).

*3.1.2. [As{S$_2$P(OC$_6$H$_4$Me-m)$_2$}$_3$] (**2**)*

Method as above gave yellow needle shaped crystals. Yield: 1.10 g, 90%; m.p. 46 °C. *Anal.* Calc. for $C_{42}H_{42}O_6S_6P_3As$: As, 7.47; S, 19.18. Found: As, 7.58; S, 19.23%.^{1}H NMR (CDCl$_3$): δ 2.30 (s, CH$_3$, 18H), 7.00–7.26 (m, 24H, OC$_6$H$_4$), ^{31}P NMR (CDCl$_3$): δ 84.64 ppm; IR (KBr) (cm^{-1}): 1140s, ν{(P)–O–C}; 952s, ν{P–O–(C)}; 691s, 662s, ν(P=S); 545m, ν(P–S).

*3.1.3. [As{S$_2$P(OC$_6$H$_4$Me-p)$_2$}$_3$] (**3**)*

Method as above gave a yellow oily viscous liquid. Yield: 1.05 g, 86%; *Anal.* Calc. for $C_{42}H_{42}O_6S_6P_3As$: As, 7.47; S, 19.18. Found: As, 7.52; S, 19.27%. ^{1}H NMR (CDCl$_3$): δ 2.21 (s, CH$_3$, 18H), 6.61–7.08 (m, 24H, OC$_6$H$_4$), ^{31}P NMR (CDCl$_3$): δ 85.58 ppm; IR (KBr) (cm^{-1}): 1170s, ν{(P)–O–C}; 940s, ν{P–O–(C)}; 690s, 631s, ν(P=S); 563m, ν(P–S).

*3.1.4. [Sb{S$_2$P(OC$_6$H$_4$Me-o)$_2$}$_3$] (**4**)*

Method as above gave a yellow viscous liquid. Yield: 1.179 g, 99.06%; *Anal.* Calc. for $C_{42}H_{42}O_6S_6P_3Sb$: Sb, 11.60; S, 18.33. Found: Sb, 11.80; S, 18.32%. ^{1}H NMR (CDCl$_3$): δ 2.26 (s, CH$_3$, 18H), 7.04–7.24 (m, 24H, OC$_6$H$_4$), ^{31}P NMR (CDCl$_3$): δ 87.45 ppm; IR (KBr) (cm^{-1}): 1170s, ν{(P)–O–C}; 934s, ν{P–O–(C)}; 709s, 656s, ν(P=S); 533m, ν(P–S).

*3.1.5. [Sb{S$_2$P(OC$_6$H$_4$Me-m)$_2$}$_3$] (**5**)*

Method as above gave a yellow crystalline solid. Yield: 1.2807 g, 88.23%; m.p. 50 °C. *Anal.* Calc. for $C_{42}H_{42}O_6S_6P_3Sb$: Sb, 11.60; S, 18.33. Found: Sb, 11.20; S, 18.30%. ^{1}H NMR (CDCl$_3$): δ 2.31 (s, CH$_3$, 18H), 7.04–7.24 (m, 24H, OC$_6$H$_4$), ^{31}P NMR (CDCl$_3$): δ 88.70 ppm; IR (KBr) (cm^{-1}): 1142s, ν{(P)–O–C}; 948s, ν{P–O–(C)}; 690s, 649s, ν(P=S); 522m, ν(P–S).

*3.1.6. [Sb{S$_2$P(OC$_6$H$_4$Me-p)$_2$}$_3$] (**6**)*

Method as above gave a yellow viscous liquid. Yield: 1.006 g, 90.81%; *Anal.* Calc. for $C_{42}H_{42}O_6S_6P_3Sb$: Sb, 11.60; S, 18.33. Found: Sb, 11.40; S, 18.35%. ^{1}H NMR (CDCl$_3$): δ 2.31 (s, CH$_3$, 18H), 7.00–7.10 (m, 24H, OC$_6$H$_4$), ^{31}P NMR (CDCl$_3$): δ 87.65 ppm; IR (KBr) (cm^{-1}): 1165s, ν{(P)–O–C}; 936s, ν{P–O–(C)}; 700s, 643s, ν(P=S); 510m, ν(P–S).

*3.1.7. [Bi{S$_2$P(OC$_6$H$_4$Me-o)$_2$}$_3$] (**7**)*

Method as above gave a yellow crystalline solid. Yield: 1.12 g, 76%; m.p. 110 °C. *Anal.* Calc. for $C_{42}H_{42}O_6S_6P_3Bi$: Bi, 18.38; S, 16.92. Found: Bi, 13.80; S, 16.32%. ^{1}H NMR (CDCl$_3$): δ 2.30 (s, CH$_3$, 18H), 6.95–7.21 (m, 24H, OC$_6$H$_4$), ^{31}P NMR (CDCl$_3$): δ 94.82 ppm; IR (KBr) (cm^{-1}): 1173s, ν{(P)–O–C}; 900s, ν{P–O–(C)}; 679s, 641m, ν(P=S); 546m, ν(P–S).

Table 2
Selected bond lengths (Å) and angles (°) for [As{S$_2$P(OC$_6$H$_4$Me-*m*)$_2$}$_3$]·0.5C$_6$H$_{14}$ (**2**), [Sb{S$_2$P(OC$_6$H$_4$Me-*m*)$_2$}$_3$] (**5**) and [Bi{S$_2$P(OC$_6$H$_4$Me-*m*)$_2$}$_3$] (**8**).[a]

Compound	**2**	**5**	**8**
M(1)–S(1)	2.3242(6)	2.544(2)	2.678(2)
M(1)–S(2)	3.0284(6)	3.031(2)	2.953(2)
M(1)–S(3)	2.3415(6)	2.549(2)	2.705(2)
M(1)–S(4)	2.9861(6)	2.980(2)	2.926(2)
M(1)–S(5)	2.3278(6)	2.543(2)	2.681(2)
M(1)–S(6)	2.9345(6)	3.025(2)	2.937(2)
S(1)–P(1)	2.0619(8)	2.033(3)	2.010(3)
S(2)–P(1)	1.9270(8)	1.945(3)	1.962(3)
S(3)–P(2)	2.0556(8)	2.031(3)	2.006(3)
S(4)–P(2)	1.9294(8)	1.935(4)	1.962(3)
S(5)–P(3)	2.0615(8)	2.032(3)	2.013(3)
S(6)–P(3)	1.9255(8)	1.940(3)	1.960(3)
P(1)–O(1)	1.594(2)	1.600(6)	1.604(5)
P(1)–O(2)	1.591(2)	1.584(5)	1.597(6)
P(2)–O(3)	1.594(2)	1.589(6)	1.592(6)
P(2)–O(4)	1.594(2)	1.585(6)	1.596(6)
P(3)–O(5)	1.584(2)	1.593(6)	1.590(6)
P(3)–O(6)	1.596(2)	1.595(6)	1.599(6)
S(1)–M(1)–S(2)	75.51(2)	72.69(7)	72.40(6)
S(3)–M(1)–S(4)	76.10(2)	72.98(7)	72.10(6)
S(5)–M(1)–S(6)	77.47(2)	72.52(7)	72.45(6)
S(1)–M(1)–S(3)	91.90(2)	91.81(8)	93.06(7)
S(1)–M(1)–S(5)	91.26(2)	84.87(7)	84.45(6)
S(3)–M(1)–S(5)	92.05(2)	86.90(7)	86.93(6)
S(1)–M(1)–S(4)	167.38(2)	164.67(8)	165.16(7)
S(3)–M(1)–S(6)	167.13(2)	155.87(7)	155.14(6)
S(5)–M(1)–S(2)	162.13(2)	157.46(7)	156.82(6)
S(1)–M(1)–S(6)	95.73(2)	98.56(8)	98.45(7)
S(3)–M(1)–S(2)	100.21(2)	91.56(7)	92.99(6)
S(5)–M(1)–S(4)	93.03(2)	92.25(7)	94.39(6)
S(2)–M(1)–S(4)	102.46(2)	108.80(7)	107.66(6)
S(2)–M(1)–S(6)	91.74(2)	112.29(6)	111.46(6)
S(4)–M(1)–S(6)	96.79(2)	94.90(7)	95.27(6)
P(1)–S(1)–M(1)	94.14(3)	92.8(1)	90.08(8)
P(1)–S(2)–M(1)	77.44(3)	80.9(1)	83.37(9)
P(2)–S(3)–M(1)	93.00(3)	91.5(1)	89.2(1)
P(2)–S(4)–M(1)	77.84(3)	81.3(1)	83.87(9)
P(3)–S(5)–M(1)	90.73(3)	92.9(1)	89.97(9)
P(3)–S(6)–M(1)	77.07(3)	81.3(1)	83.86(9)
O(1)–P(1)–O(2)	94.76(9)	93.7(3)	94.3(3)
O(1)–P(1)–S(1)	107.12(7)	107.6(3)	110.3(2)
O(1)–P(1)–S(2)	116.14(7)	116.9(3)	112.2(2)
O(2)–P(1)–S(1)	106.56(7)	109.4(3)	109.5(2)
O(2)–P(1)–S(2)	117.54(7)	113.8(2)	114.6(3)
S(1)–P(1)–S(2)	112.85(4)	113.5(1)	114.1(1)
O(3)–P(2)–O(4)	94.56(8)	93.9(3)	95.3(3)
O(3)–P(2)–S(3)	107.00(6)	109.7(3)	110.7(3)
O(3)–P(2)–S(4)	116.33(7)	114.2(3)	112.5(3)
O(4)–P(2)–S(3)	107.47(7)	108.4(3)	109.7(3)
O(4)–P(2)–S(4)	106.71(7)	116.1(3)	113.7(3)
S(3)–P(2)–S(4)	112.94(3)	112.9(1)	113.5(1)
O(5)–P(3)–O(6)	100.89(9)	94.2(3)	94.5(3)
O(5)–P(3)–S(5)	108.47(7)	108.2(2)	109.9(2)
O(5)–P(3)–S(6)	111.04(7)	115.0(3)	113.6(2)
O(6)–P(3)–S(5)	106.36(7)	109.3(2)	109.9(2)
O(6)–P(3)–S(6)	116.14(7)	115.2(2)	113.6(2)
S(5)–P(3)–S(6)	113.04(4)	113.2(1)	113.7(1)

[a] Data are not included in **2** for C$_6$H$_{14}$ and in **5** and **8** for the molecules that are disordered.

3.1.8. $[Bi\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$ (**8**)

Method as above gave a yellow crystalline solid. Yield: 0.95 g, 95%; m.p. 40 °C. *Anal.* Calc. for $C_{42}H_{42}O_6S_6P_3Bi$: Bi, 18.38; S, 16.92. Found: Bi, 14.20; S, 16.94%. ^1H NMR ($CDCl_3$): δ 2.23 (s, CH_3, 18H), 6.65–7.41 (m, 24H, OC_6H_4), ^{31}P NMR ($CDCl_3$): δ 94.23 ppm; IR (KBr) (cm^{-1}): 1139s, ν{(P)–O–C}; 950s, ν{P–O–(C)}; 691s, 634s, ν(P=S); 556m, ν(P–S).

3.1.9. $[Bi\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$ (**9**)

Method as above gave a yellow viscous liquid. Yield: 1.10 g, 93%. *Anal.* Calc. for $C_{42}H_{42}O_6S_6P_3Bi$: Bi, 18.38; S, 16.92. Found: Bi, 14.20; S, 16.93%. ^1H NMR ($CDCl_3$): δ 2.30 (s, CH_3, 18H), 6.69–7.12 (m, 24H, OC_6H_4), ^{31}P NMR ($CDCl_3$): δ 95.27 ppm; IR (KBr) (cm^{-1}): 1167s, ν{(P)–O–C}; 934s, ν{P–O–(C)}; 697s, 639s, ν(P=S); 524s, ν(P–S).

3.2. Crystallography

A colorless block crystal of $[As\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]\cdot 0.5C_6H_{14}$ (**2**), a colorless fragment of $[Sb\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$ (**5**) and a yellow block crystal of $[Bi\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$ (**8**) were mounted on glass fibres. Data were collected on a Bruker–Nonius CCD area detector diffractometers, with φ and ω scans chosen to give a complete asymmetric unit. Cell refinement [41] gave cell constants corresponding to a triclinic cell for **2** and monoclinic cells for **5** and **8** whose dimensions are given in Table 1 along with other experimental parameters. An absorption correction was applied [42].

The structures were solved by direct methods [43] and were refined using the WINGX version [44] of SHELX-97 [45]. All of the non-hydrogen atoms were treated anisotropically. All of the hydrogen atoms were included in idealized positions, with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The 58/42 (for **5**) and 77/23 (for **8**) disorder in one of the two molecules of the asymmetric unit was successfully modelled by placing restraints on distances and thermal parameters within the groups. The final cycle of full-matrix least-squares refinement was based on 8694 for **2**, 16232 for **5** and 13992 for **8** observed reflections (7602 for **2**, 10886 for **5** and 12758 for **8** for $F^2 > 4\sigma(F^2)$) and 557 for **2**, 1017 for **5** and 1008 for **8** variable parameters and converged (largest parameter shift was 0.001 times its esd).

Selected bond distances and angles are given in Table 2 and the molecules are displayed as ORTEP diagrams in Figs. 1–3. Additional material available from the Cambridge Crystallographic Data Centre comprises the final atomic coordinates and thermal parameters for all atoms and a complete listing of bond distances and angles.

4. Concluding comments

We have prepared and characterized the following compounds of the type, $[M\{S_2P(OR)_2\}_3]$ (where M = As, Sb and Bi; R = *o*-, *m*-, *p*-C_6H_4Me). The IR, ^1H and ^{31}P NMR spectral data of these compounds are consistent with the presence of complexes containing bidentate ligands and hence a distorted octahedral structure. The molecular structures of $[As\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]\cdot 0.5C_6H_{14}$, $[Sb\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$ and $[Bi\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$ confirm this to be the case and that in the solid state the ligands are more accurately described as anisobidentate.

Acknowledgements

M.E.L. thanks the UK Engineering and Physical Sciences Council for support of the X-ray facilities at Southampton University. We are also thankful to RSIC, CDRI, Lucknow for the spectral analyses.

Appendix A. Supplementary data

CCDC 703657–703659 contain the supplementary crystallographic data for $[As\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]\cdot 0.5C_6H_{14}$, $[Sb\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$ and $[Bi\{S_2P(OC_6H_4Me\text{-}m)_2\}_3]$, respectively. These data can be obtained free of charge via http://www.ccdc.cam. ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.12.017.

References

[1] H.P.S. Chauhan, G. Srivastava, R.C. Mehrotra, Phosphorus Sulfur Silicon 17 (1983) 161.
[2] S.L. Lawton, C.J. Fuhrmeister, R.G. Hass, C.S. Jarman, F.G. Lohmeyer, Inorg. Chem. 13 (1974) 135.
[3] B.P. Singh, G. Srivastava, R.C. Mehrotra, J. Organomet. Chem. 35 (1979) 171.
[4] J.C. Lefferts, K.C. Molloy, J.J. Zuckerman, I. Haiduc, C. Guta, D. Ruse, Inorg. Chem. 19 (1980) 1662.
[5] I. Haiduc, D.B. Sowerby, S.F. Lu, Polyhedron 14 (1995) 3389.
[6] M. Weiber, M. Shrocef, Phosphorus Sulfur Silicon 102 (1995) 265.
[7] M. Iglesias, C.D. Pino, S.M. Carrera, Polyhedron 8 (1989) 483.
[8] A. Muller, V.V.K. Rao, G. Klinksiek, Chem. Ber. 104 (1971) 1892.
[9] H.P.S. Chauhan, N.M. Shaik, K. Kori, Main Group Met. Chem. 26 (2003) 213.
[10] P.N. Nagar, G. Srivastava, R.C. Mehrotra, Synth. React. Inorg. Met. – Org. Chem. 12 (1982) 749.
[11] H.P.S. Chauhan, G. Srivastava, R.C. Mehrotra, Polyhedron 3 (1984) 1337.
[12] R. Bohra, H.P.S. Chauhan, G. Srivastava, R.C. Mehrotra, Phosphorus Sulfur Silicon 60 (1991) 167.
[13] H.P.S. Chauhan, G. Srivastava, R.C. Mehrotra, Polyhedron 2 (1983) 359.
[14] H.P.S. Chauhan, R.K. Singh, K. Kori, Main Group Met. Chem. 25 (2002) 511.
[15] H.P.S. Chauhan, N.M. Shaik, U.P. Singh, Appl. Organomet. Chem. 19 (2005) 1132.
[16] T. Ito, Acta Crystallogr., Sect. E (60) (2004) 783.
[17] D.B. Sowerby, I. Haiduc, A.B. Rusu, M. Salajan, Inorg. Chim. Acta 68 (1983) 87.
[18] R.O. Day, M.M. Chauvin, W.E. McEwen, Phosphorus Sulfur Silicon 8 (1980) 121.
[19] I.S. Levin, V.V. Sergeeva, I.A. Vorsina, Ser. Khim. Nauk 2 (1975) 107.
[20] I.S. Levin, V.V. Sergeeva, I.A. Vorsina, Chem. Abstr. 83 (1975) 66255.
[21] H.H. Farmer, B.W. Malone, H.F. Tompkis, Lubrication Eng. 23 (1967) 57.
[22] L. Chen, J. Dong, G. Chen, Lubrication Sci. 11 (2006) 1.
[23] C. Silvestru, C. Socacia, A. Bara, I. Haiduc, Anticancer Res. 10 (1990) 803.
[24] C. Socaciu, I. Pasca, C. Silvestru, I. Haiduc, A. Bara, Metal Based Drugs 1 (1994) 291.
[25] L. Awwal, J.E. Drake, M.B. Hursthouse, R. Kumar, M.E. Light, R. Ratnani, K. Saraswat, Polyhedron 26 (2007) 3973.
[26] J.E. Drake, C. Gurnani, M.B. Hursthouse, M.E. Light, M. Nirwan, R. Ratnani, Appl. Organomet. Chem. 21 (2007) 539.
[27] A.L. Bingham, J.E. Drake, M.E. Light, M. Nirwan, R. Ratnani, Polyhedron 25 (2006) 945.
[28] A. Kumar, D. Kumar, S.K. Pandey, Synth, React. Inorg. Met. – Org. Nano-Met. Chem. 37 (2007) 697.
[29] J.A. McCleverty, R.S.Z. Kowalski, N.A. Bailey, R. Mulvaney, D.A. O'Cleirigh, J. Chem. Soc., Dalton Trans. 4 (1983) 627.
[30] W.E. McEwen, V.C. Si, B.J. Kalbacher, Phosphorus Sulfur Silicon Relat. Elem. 11 (1981) 191.
[31] N.N. Glebova, O.K. Sharaev, E.I. Tienyakova, B.A. Dolgoplosk, Vysokomolekul. Soedin. Seriya 37 (1995) 1145.
[32] N.N. Glebova, O.K. Sharaev, E.I. Tienyakova, B.A. Dolgoplosk, Chem. Abstr. 125 (1996) 14337g.
[33] Q. Xie, N. Luo, J. Li, X. Jing, Youji Huaxue 12 (1992) 159.
[34] Q. Xie, N. Luo, J. Li, X. Jing, Chem. Abstr. 117 (1992) 26650w.
[35] R. Ratnani, J.E. Drake, C.L.B. Macdonald, A. Kumar, S.K. Pandey, J. Chem. Crystallogr. 35 (2005) 447.
[36] A.L. Bingham, J.E. Drake, C. Gurnani, M.B. Hursthouse, M.E. Light, M. Nirwan, R. Ratnani, J. Chem. Crystallogr. 36 (2006) 627.
[37] A. Kumar, K.R. Sharma, S.K. Pandey, Phosphorus Sulfur Silicon Relat. Elem. 182 (2007) 1023.
[38] H.P.S. Chauhan, Coord. Chem. Rev. 173 (1998) 1.
[39] C. Glidewell, Inorg. Chim. Acta 25 (1977) 159.
[40] K. Kori, Ph.D. Thesis, Devi Ahilya University, Indore, India, 2005.
[41] A.J.M. Duisenberg, J. Appl. Crystallogr. 25 (1992) 92.
[42] G.M. Sheldrick, SADABS, Version 2007/2, Bruker AXS Inc., Madison, Wisconsin, USA, 2007.
[43] G.M. Sheldrick, Acta Crystallogr. A46 (1990) 467.
[44] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
[45] G.M. Sheldrick, SHELXL97, University of Göttingen, Germany, 1997.