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ScienceDirect
Polyhedron 25 (2006) 2841–2847
POLYHEDRON
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Synthetic, spectroscopic, X-ray structural and antimicrobial studies of 1,3-dithia-2-stibacyclopentane derivatives of phosphorus based dithiolato ligands

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Received 6 March 2006; accepted 10 April 2006
Available online 12 May 2006

Abstract

Some mixed 1,3-dithia-2-stibacyclopentane derivatives with phosphorus based dithiolato ligands of the types $\overline{SCH_2CH_2SS}bS(S)\overline{POGO}$ {where G = —CH(Me)—CH(Me)— and —$C(Me)_2$—$C(Me)_2$—} and $\overline{SCH_2CH_2SS}bS(S)P(OR)_2$ {where R = Pr^n, Bu^n and Ph} have been synthesized by the reaction of 2-chloro-1,3-dithia-2-stibacyclopentane and the ammonium/sodium salt of the corresponding phosphorus based ligands in an equimolar ratio in anhydrous benzene solution. These yellow crystalline solid/semi-solid derivatives have been characterized by elemental analysis (C, H, S and Sb), molecular weights, melting point as well as spectral [UV, IR and NMR (^1H, ^{13}C and ^{31}P)] studies. Single crystal X-ray diffraction analyses of 1,3-dithia-2-stibacyclopentane 2,3-butylenedithiophosphate revealed a monodentate mode of bonding of the dithiophosphate ligand in the complex. The free ligands and their antimony(III) complexes have also been screened for their antibacterial and antifungal activities.

Keywords: 1,3-Dithia-2-stibacyclopentane; Dithiophosphates; IR; NMR spectra; Single crystal X-ray analysis; Antimicrobial activity

1. Introduction

Diorganodithiophosphate derivatives of antimony(III) are well known [1–4] for their utility as analytical reagents, lubricant additives for regeneration of cracking catalysts and antitumour agents. The chemistry of antimony(III) with dialkyldithiophosphate ligands is well explored including the X-ray single crystal structures of a number of compounds [1–4].

Alkylenedithiophosphates and dialkyldithiophosphate ligands behave as versatile dithio ligands and form a variety of complexes with main group [5–11] as well as transition metals [12–16]. *Tris* as well as mixed halide alkylenedithiophosphate and dialkyldithiophosphate derivatives of antimony(III) were reported by us [6,7]. Some corresponding organoantimony(III) derivatives with these ligands and mixed sulfur ligand complexes have also been reported [3,17–19]. The crystal structures of some bismuth(III) [20], nickel [21] and tin [22,23] complexes with these alkylenedithiophosphates have also been reported, which indicate the bidentate behaviour of these alkylenedithiophosphate ligands.

In continuation of our interest in the complexes of group 15 metals with sulfur ligands, we report herein the synthesis, spectral, single crystal X-ray and antimicrobial studies of 1,3-dithia-2-stibacyclopentane derivatives of phosphorus based dithiolato ligands.

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doi:10.1016/j.poly.2006.04.027

2. Experimental

2.1. Materials

Solvents (benzene, alcohols, dichloromethane, *n*-hexane, acetone and diethyl ether, etc.) were dried and purified according to the literature methods [24]. Phosphorous pentasulfide (E. Merck) was used as received. Ethane-1,2-dithiol (E. Merck), antimony trichloride (S. D. Fine), glycols [butane-2,3-diol (E. Merck) and 2,3-dimethylbutane-2,3-diol (Aldrich)] were distilled before use. 2-Chloro-1,3-dithia-2-stibacyclopentane [25] and the alkylene-/diorganodithiophosphoric acids and their sodium/ammonium salts were synthesized by earlier reported methods [2,5].

2.2. Measurements

The elemental analysis (C and H) was performed on a Perkin–Elmer 2400 elemental analyzer. Sulfur was estimated gravimetrically as barium sulfate and antimony was estimated iodometrically titrating against standard sodium thiosulfate solution [6,7]. Molecular weights were determined cryoscopically in benzene. IR spectra were recorded in KBr discs on a Perkin–Elmer 557 spectrophotometer in the region 4000–200 cm^{-1}. The UV spectra were recorded in chloroform solution at room temperature on a Shimadzu UV-1601 UV–Vis spectrophotometer within the range 500–200 nm. ^{1}H, ^{13}C and ^{31}P spectra of all these newly synthesized complexes were recorded in $CDCl_3$ solution using TMS and 85% H_3PO_4 as standards, respectively. The ^{1}H and ^{13}C NMR spectra were operated at 300.13 and 75.49 MHz respectively, on a Bruker AC-300F NMR spectrophotometer at the Sophisticated Analytical Instrument (SAIF) Facility, Punjab University, Chandigarh and ^{31}P NMR spectra were operated at 121.50 MHz on a DRX-300 NMR spectrophotometer, SAIF, Central Drug Research Institute (CDRI), Lucknow.

The single crystal X-ray diffraction analysis was performed on a STOE IPDS (imaging plate system) diffractometer at 25 °C, using graphite monochromated Mo Kα X-ray radiation ($\lambda = 0.71073$ Å). A suitable crystal, grown from a toluene–isopropyl alcohol solution, was sealed in a glass capillary under dry nitrogen atmosphere and mounted on the goniometer head. The data collection was performed at room temperature using the ω–θ scan technique. The crystal structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXS software package for crystal structure solution and refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters in the later cycles of refinement. The hydrogen atoms were placed in idealized positions and refined using the riding model with general isotropic temperature factors. The data collection was performed only up to 27.87°. Selected atomic parameters are collected in Tables 2 and 3, and the crystallographic numbering scheme is shown in Fig. 1.

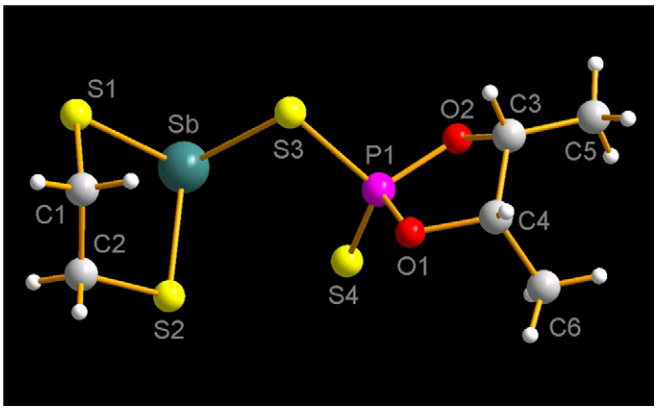
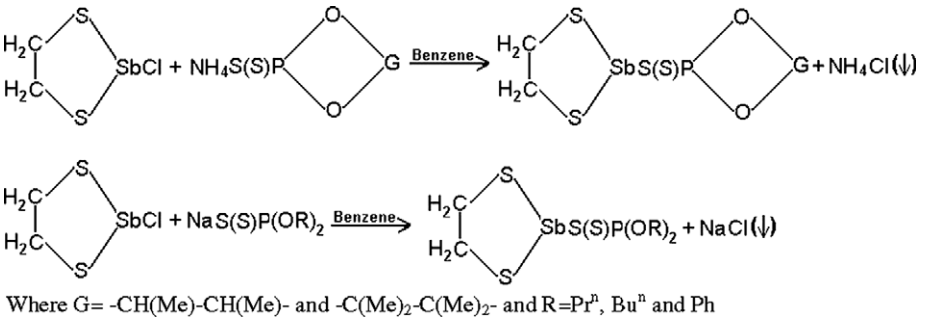


Fig. 1. X-ray single crystal structure of 1,3-dithia-2-stibacyclopentane 2,3-butylenedithiophosphate.

2.3. Antimicrobial studies

The following strains of bacteria and fungi were used: *Staphylococcus aureus* (ATCC 9144), *Bacillus subtilis* (ATCC 6051), *Escherichia coli* (ATCC 9637), *Pseudomonas aeruginosa* (ATCC 25619), *Aspergillus niger* (ATCC 9029) and *Penicillium chrysogenum* (ATCC 10106). Antimicrobial activities were evaluated by the disc diffusion method [27–29] for the tested compounds as follows.

A 0.5 mL (containing 10^6–10^7 microorganisms mL^{-1}) of each of the investigated organisms was added to a sterile agar medium just before solidification, then poured into sterile petri dishes (9 cm in diameter) and left to solidify.



Scheme 1. Reaction of 2-chloro-1,3-dithia-2-stibacyclopentane with sodium/ammonium dithiophosphates in an equimolar ratio.

Using a sterile cork borer (6 mm in diameter), three holes (wells) were made in each dish, then 0.1 ml of tested compounds dissolved in DMF (50, 100 and 200 μg mL^{-1}) were poured into these holes. Finally the dishes were incubated at 37 °C for 24 h (for bacteria) and at 30 °C for 72 h (for fungi), then inhibition zones were detected around each hole.

A quantity of 0.1 ml DMF alone was also tested under the same conditions for each organism and it was found that DMF had no effect on the organisms at the concentrations studied.

2.4. Synthesis of mixed 1,3-dithia-2-stibacyclopentane alkylene-/dialkyl-dithiophosphate derivatives

2.4.1. Synthesis of 1,3-dithia-2-stibacyclopentane 2,3-butylenedithiophosphate

A benzene solution (30 ml) of 2-chloro-1,3-dithia-2-stibacyclopentane (0.72 g, 2.88 mmol) was added to the ammonium salt of 2,3-butylenedithiophosphoric acid (0.58 g, 2.88 mmol) in an equimolar ratio (Scheme 1). The reaction mixture was refluxed with stirring for ~5 h followed by cooling to room temperature. The precipitated ammonium chloride (0.15 g) was removed by filtration. The removal of the solvent from the filtrate under reduced pressure afforded a yellow crystalline compound, which was recrystallised in dichloromethane (yield: 1.13 g, 98%).

The other complexes were synthesized by adopting a similar method. Pertinent analytical and physico-chemical data for these complexes are listed in Table 1.

3. Results and discussion

3.1. Synthesis of antimony(III) complexes

1,3-Dithia-2-stibacyclopentane derivatives with alkylene-/dialkyl-dithiophosphate have been synthesized by the reactions of 2-chloro-1,3-dithia-2-stibacyclopentane with the ammonium/sodium salts of alkylene-/dialkyl-dithiophosphoric acids in an equimolar (1:1) ratio in refluxing benzene ~5 h.

All these newly synthesized derivatives are either yellow crystalline solids or yellow sticky solids and are soluble in common organic solvents like benzene, chloroform, acetone, dichloromethane, DMF and DMSO, etc., but decompose in water.

3.2. Electronic spectra

In the electronic absorption spectra [12–15,26], all the 1,3-dithia-2-stibacyclopentane dithiophosphate derivatives absorb strongly in the region 230–235 nm, corresponding to a π–π^* transition. Another rather weak absorption occurs at 304–309 nm, which may be due to a n–π^* transition. These dithiophosphates also absorb in these regions.

Table 1
Physical and analytical data of the 1,3-dithia-2-stibacyclopentane alkylene-/dialkyl-dithiophosphate complexes

Reactants (g; mmol)		Empirical formula; yield = g (%)	Mol. wt. found (calc.)	Colour and state; m.p. (°C)	Analysis (%) found (calculated)				
	Ligand (dithiophosphates)				C	H	P	S	Sb
0.72 (2.88)	0.58 (2.88)	$C_6H_{12}PO_2S_4Sb$; 1.13 (98)	386 (397.35)	yellow crystalline solid; 85	18.09 (18.14)	2.98 (3.04)	7.64 (7.80)	32.20 (32.28)	30.57 (30.64)
0.56 (2.25)	0.52 (2.25)	$C_8H_{16}PO_2S_4Sb$; 0.93 (97)	410 (425.21)	yellow crystalline solid; 103	22.55 (22.60)	3.72 (3.79)	7.13 (7.29)	30.09 (30.16)	28.59 (28.65)
0.55 (2.20)	$NaS_2P(OPr^n)_2$ 0.52 (2.20)	$C_8H_{18}PO_2S_4Sb$; 0.89 (95)	412 (427.22)	yellow sticky solid;	22.41 (22.49)	4.29 (4.25)	7.14 (7.26)	29.94 (30.02)	28.46 (28.51)
0.69 (2.76)	$NaS_2P(OBu^n)_2$ 0.73 (2.76)	$C_{10}H_{22}PO_2S_4Sb$; 1.23 (97)	439 (455.27)	yellow sticky solid;	26.27 (26.38)	4.79 (4.87)	6.71 (6.81)	28.08 (28.17)	26.68 (26.75)
0.68 (2.71)	$NaS_2P(OPh)_2$ 0.81 (2.70)	$C_{14}H_{14}PO_2S_4Sb$; 1.26 (94)	482 (495.26)	yellow sticky solid;	33.89 (33.95)	2.82 (2.85)	6.12 (6.26)	25.78 (25.89)	24.52 (24.59)

Table 2
Crystal data and refinement details for 1,3-dithia-2-stibacyclopentane 2,3-butylenedithiophosphate

Compound	$\overline{SCH_2CH_2SSb}\overline{S_2POCH(CH_3)CH(CH_3)O}$
Formula	$C_6H_{12}O_2PS_4sSb$
Formula weight	397.12
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.641(2)
b (Å)	10.528(2)
c (Å)	12.472(2)
α (°)	90
β (°)	117.78(3)
γ (°)	90
V (Å^3)	1352.4(4)
Z	4
Crystal size (mm^3)	$0.28 \times 0.2 \times 0.15$
D_c (Mg m^{-3})	1.950
$F(000)$	776
Reflection collected	12095
θ_{max} (°)	2.67–27.87
Maximum and minimum transmission	0.48 and 0.30
Final R indices [$I > 2\sigma$ (I)]	
R_1	0.0366
wR_2	0.1007
R indices (all data)	
R_1	0.0384
wR_2	0.1020
Residual ρ_{max} (e Å^3)	0.928
Residual ρ_{min} (e Å^3)	−0.702

Table 3
Selected bond distances (Å) and bond angles (°) for 1,3-dithia-2-stibacyclopentane 2,3-butylenedithiophosphate

Bond distances	
Sb(1)–S(2)	2.4485(9)
Sb(1)–S(1)	2.4491(10)
Sb(1)–S(3)	2.5566(13)
S(1)–C(1)	1.834(3)
S(2)–C(2)	1.842(3)
S(3)–P(1)	2.0541(12)
S(4)–P(1)	1.9456(16)
P(1)–O(1)	1.602(2)
P(1)–O(2)	1.608(3)
O(1)–C(4)	1.477(4)
O(2)–C(3)	1.481(4)
C(1)–C(2)	1.504(6)
C(3)–C(5)	1.519(5)
C(3)–C(4)	1.525(5)
C(4)–C(6)	1.513(5)
Bond angles	
S(2)–Sb(1)–S(1)	87.80(3)
S(2)–Sb(1)–S(3)	94.83(4)
S(1)–Sb(1)–S(3)	92.17(4)
C(1)–S(1)–Sb(1)	97.97(11)
C(2)–S(2)–Sb(1)	100.36(11)
P(1)–S(3)–Sb(1)	95.79(5)
O(1)–P(1)–O(2)	97.52(13)
O(1)–P(1)–S(4)	116.06(12)
O(2)–P(1)–S(4)	112.98(12)
O(1)–P(1)–S(3)	105.68(10)
O(2)–P(1)–S(3)	109.30(12)
S(4)–P(1)–S(3)	113.89(6)
C(4)–O(1)–P(1)	111.40(19)
C(3)–O(2)–P(1)	109.48(19)
C(2)–C(1)–S(1)	111.6(2)
C(1)–C(2)–S(2)	112.0(3)
O(2)–C(3)–C(5)	109.2(3)
O(2)–C(3)–C(4)	104.1(3)
C(5)–C(3)–C(4)	116.2(3)
O(1)–C(4)–C(6)	109.3(3)
O(1)–C(4)–C(3)	103.5(3)
C(6)–C(4)–C(3)	116.1(3)

3.3. Infra-red spectra

These newly synthesized complexes show medium to strong intensity bands in the regions 1000–1030 cm^{-1} and 830–860 cm^{-1} which are assigned due to ν\{(P)–O–C\} and ν\{P–O–(C)\}, respectively [5–8,17,18]. A broad band in the region 690–720 cm^{-1} (alkylenedithiophosphates) and 660–690 cm^{-1} (dialkyldithiophosphates) due to ν(P=S), present in the free phosphoric acids, is shifted towards lower frequencies in the spectra of all these complexes and is present in the regions 650–660 and 635–645 cm^{-1} respectively, this also overlaps with the ν(C–S) vibrations of dithiolate moieties in these complexes. A sharp band present in the region 925–930 cm^{-1} in the corresponding alkylenedithiophosphate may be assigned to the ring vibrations of the dioxaphospholane ring [30]. The bands of medium to weak intensity in the regions 530–540 and 310–320 cm^{-1} are assigned to ν(P–S) and ν(Sb–S), respectively [17].

3.4. NMR spectral data

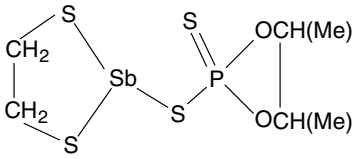
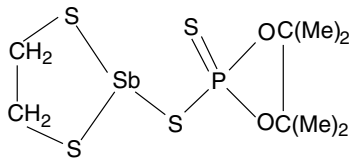
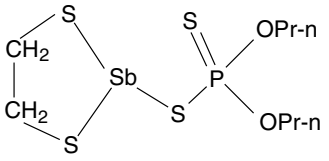
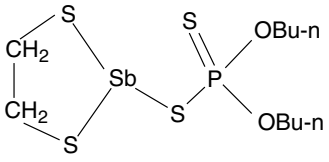
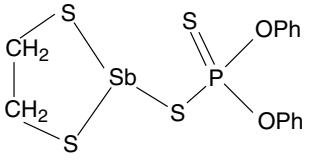
3.4.1. ^{1}H NMR spectra

The chemical shifts corresponding to the protons of mixed 1,3-dithia-2-stibacyclopentane derivatives with alkylene-/dialkyl-dithiophosphate are listed in Table 4. In the ^{1}H NMR spectra of these compounds, a sharp singlet observed in the region δ 3.61–3.74 ppm is due to four CH_2S protons of the 1,3-dithia-2-stibacyclopentane ring [17,18], indicating that these protons are equivalent. In addition, these compounds also exhibit the characteristic proton resonances [5–18] for the corresponding protons of dithiophosphate moieties (Table 4). In a few of the alkylene-/dialkyl-dithiophosphate derivatives, OCH and OCH_2 protons couple with ^{31}P nuclei and appear as a multiplets and doublets of triplets.

3.4.2. ^{13}C NMR spectra

The ^{13}C NMR spectra of the ethane-1,2-dithiolate moiety show only one sharp singlet signal in the region δ 41.41–42.40 ppm due to SCH_2 carbons [17,18] indicating that these two carbon atoms are magnetically equivalent, thus supporting the results of the ^{1}H NMR spectra. In addition, these derivatives also exhibit the expected signals due to the carbons of dithiophosphate moieties [5–17]. The methylene carbons attached to P–O and P–O–C groups

Table 4
^{1}H, $\{^{1}H\}^{13}C$ and ^{31}P NMR spectral data of 1,3-dithia-2-stibacyclopentane alkylene-/dialkyl-dithiophosphate complexes

Compound (No.)	^{1}H Chemical shifts (δ ppm)	^{13}C Chemical shifts (δ ppm)	^{31}P Chemical shifts (δ ppm)
 (1)	1.31 (6H, d ($J = 6.3$ Hz), CH_3) 3.71 (4H, s, CH_2S) 4.65–4.70 (2H, m, OCH)	15.46 (s, Me) 42.40 (s, CH_2S) 79.10 (s, OCH)	108.14
 (2)	1.45 (12H, s, $OCMe_2$) 3.74 (4H, s, CH_2S)	24.17 (s, Me_2) 42.14 (s, CH_2S) 90.92 (s, OC)	103.7
 (3)	0.93 (6H, t ($J(CH_3\text{-}CH_2) = 7.35$ Hz), $OCCCH_3$dtp) 1.69 (4H, m, $OCCH_2$-dtp) 3.69 (4H, s, CH_2S) 4.02 {4H, dt ($J(OCH_2\text{-}CH_2) = 6.54$ Hz and $J(PO\text{-}CH_2) = 9.34$ Hz), OCH_2-dtp}	9.73 (s, $OCCCH_3$-dtp) 22.75 (s, $OCCH_2$-dtp) 41.41 (s, CH_2S) 68.67 (s, OCH_2-dtp)	90.90
 (4)	0.88 (6H, t ($J(CH_3\text{-}CH_2) = 7.37$ Hz), $OCCCCH_3$dtp) 1.36 (4H, m, $OCCCH_2$-dtp) 1.64 (4H, m, $OCCH_2$-dtp) 3.67 (4H, s, CH_2S) 4.06 {4H, dt ($J(OCH_2\text{-}CH_2) = 6.49$ Hz and $J(PO\text{-}CH_2) = 9.19$ Hz), OCH_2-dtp}	13.61 (s, $OCCCCH_3$-dtp) 18.76 (s, $OCCCH_2$-dtp) 31.88 (d ($J = 8.60$ Hz), $OCCH_2$-dtp) 42.03 (s, CH_2S) 67.60 (d ($J = 7.17$ Hz), OCH_2-dtp)	90.89
 (5)	3.61 (4H, s, CH_2S) 7.19–7.37 (10H, m, OC_6H_5)	42.26 (s, CH_2S) 122.08 (s, *m*-C of C_6H_5) 125.85 (s, *o*-C of C_6H_5) 129.49 (s, *p*-C of C_6H_5)	88.13

Where b = broad, s = singlet, d = doublet, t = triplet, q = quartet, dt = doublet of triplets and m = multiplet.

give rise to a doublet for compound No. 4 due to the coupling with ^{31}P nuclei [9] (Table 4).

3.4.3. ^{31}P NMR spectra

The proton decoupled ^{31}P NMR spectra show only one sharp singlet between δ 103.7–108.1 ppm (in alkylenedithiophosphate derivatives). Chemical shift values appear to be downfield by about δ 10–13 ppm with respect to their parent alkylene dithiophosphoric acids (δ 93.07–95.49 ppm) indicating the bidentate behaviour of these dithiophosphate ligands. The corresponding complexes with dialkyldithiophosphate ligands show a ^{31}P signal in the region δ 88–91 ppm. Glidewell [31] concluded that diorganodithiophosphate complexes showing their ^{31}P NMR signals in the range δ 82–101 exhibit a bidentate mode of attachment of the ligands, thus indicating the bidentate mode of binding of diorganodithiophosphate ligands in these synthesized complexes. It is valid for many cases, however doubts have been made about the universality of the above generalization [32,33].

3.5. Crystal structure

The solid-state structure of the compound 1,3-dithia-2-stibacyclopentane 2,3-butylenedithiophosphate has been established by single crystal X-ray analysis, which revealed a monomeric unit. The molecular structure of 1,3-dithia-2-stibacyclopentane 2,3-butylenedithiophosphate is shown in

Fig. 1 and selected interatomic parameters are collected in Table 3. The antimony atom forms three close contacts, two to the ethane-1,2-dithiolato sulfur atoms, Sb(1)–S(2) (2.4485 Å) and Sb(1)–S(1) (2.4491 Å), and one to the dithiophosphato sulfur atom, Sb(1)–S(3) (2.5566 Å). If these three close contacts were considered to define the coordination geometry, the dithiophosphate ligand behaves in a monodentate fashion. Considering the observed Sb–S interactions, the environment about the antimony would be best described as trigonal pyramidal with the lone pair of electrons being stereochemically active, but with non-equivalent S–Sb–S bond angles [87.80(3)°, 92.17(4)° and 94.83(4)°] (Table 3) [34]. The phosphorus atom is tetrahedrally coordinated to two sulfur and two oxygen atoms, which are further attached with carbon atoms of the alkylene group (Fig. 1). The crystal structure shows that the heteroalkylene ring is markedly non-planar and that the configuration of the bonds about the antimony atom is nearly orthogonal.

The structure of this compound is unique as in this compound the 2,3-butylenedithiophosphate ligand is exhibiting monodentate behaviour. However, in most alkylenedithiophosphate derivatives of main group metals, bismuth(III) [20] and organotin(IV) [22,23], the bidentate behaviour of these alkylenedithiophosphate ligands has been reported. However, in (2,9-dimethyl-1,10-phenanthroline) *bis*(4,4,5,5-tetramethyl-1,3,2-dioxaphospholane-2-thione-2-thiolato)-nickel(II), one ligand is unidentate and the other one is bidentate [21]. It is also noticeable here that diorganodithiophosphate and dithiophosphinate ligands exhibited a bidentate as well as a bidentate triconnective chelating nature in their antimony(III) complexes [2,3].

3.6. Antimicrobial activity

The free ligands and their antimony(III) complexes were screened to evaluate their antimicrobial activity against *S. aureus*, *B. subtilis*, *E. coli*, *P. aeruginosa*, *A. niger* and *P. chrysogenum* at three different concentrations, and results are listed in Table 5. The antibacterial activities of some earlier reported antibiotics [29] were compared with the free ligands and their antimony(III) complexes.

The results showed that the antimony(III) complexes exhibit higher antibacterial and antifungal activity than the free diorganodithiophosphate ligands (dtp). It is noticeable here that *E. coli* and *P. aeruginosa* are resistant to the free dtp ligands. It may be concluded that the free ligands and antimony complexes inhibit the growth of bacteria to a greater extent as the concentration is increased. Nevertheless, it is difficult to make out an exact structure and activity relationship between microbial activity and the structure of these complexes.

A comparison of the antimicrobial activities of the free ligands and synthesized complexes with some previously investigated antibiotics [29] shows the following results:

(i) The free ligands (dtp) and their antimony(III) compounds show a greater effect towards *S. aureus* compared to amikacin, septrin, cefobid, ampicillin and traivid. However, the free ligands (dtp) and antimony(III) compounds show a lesser effect towards *S. aureus* compared to doxycllin, augmantin, sulperazon, unasyn, nitrofurantion and erythromycin.

Table 5
Antimicrobial activity[a] of the free dithiophosphate ligands and 1,3-dithia-2-stibacyclopentane alkylene-/dialkyl-dithiophosphate complexes

Compounds	Fungi						Gram (+ve) bacteria						Gram (−ve) bacteria					
	A. niger			*P. chysogenum*			*S. aureus*			*B. subtilis*			*E. coli*			*P. aeruginosa*		
	Conc. (μg/mL)			Conc. (μg/mL)			Conc. (μg/mL)			Conc. (μg/mL)			Conc. (μg/mL)			Conc. (μg/mL)		
	50	100	200	50	100	200	50	100	200	50	100	200	50	100	200	50	100	200
$(CH_3CH_2CH_2O)_2PS_2Na$	+	+	++	+	+	++	+	+	+	+	+	+	0	0	0	0	0	0
$(CH_3CH_2CH_2CH_2O)_2PS_2Na$	+	+	++	+	+	++	+	+	+	+	+	+	0	0	0	0	0	0
$(C_6H_5O)_2PS_2NH_4$	+	+	++	+	+	++	+	+	+	+	+	++	0	0	0	0	0	0
	+	+	++	+	+	+	+	+	+	+	+	++	0	0	0	0	0	0
$\overline{OCH(CH_3)CH(CH_3)O}PS_2NH_4$	+	+	+	+	+	+	+	+	+	+	+	+	0	0	0	0	0	0
$\overline{OC(CH_3)_2C(CH_3)_2O}PS_2NH_4$																		
(1)	+	++	+++	+	++	+++	++	+++	+++	+	+++	+++	+	++	+++	+	++	+++
(2)	+	++	+++	+	++	+++	++	+++	+++	+	++	+++	+	++	+++	+	++	+++
(3)	+	++	+++	+	++	+++	++	+++	+++	+	++	+++	+	++	+++	+	++	+++
(4)	+	++	++	+	++	++	++	++	+++	++	++	+++	+	+	+	++	++	+++
(5)	+	++	++	+	++	++	+	++	++	++	++	+++	+	+	+	+	+	++
Chloroamphenicol	−	−	−	−	−	−	+	+	++	+	+	++	+	++	+++	+	++	+++
Terbinafin	+	++	++	+	++	++	−	−	−	−	−	−	−	−	−	−	−	−

[a] The test was done using the diffusion agar technique, well diameter = 6 mm, inhibition values beyond control are + = 1–5 mm, ++ = 6–10 mm, +++ = 11–15 mm, 0 = not active and − = not tested.

(ii) The antimony(III) compounds show a greater antibacterial effect towards *P. aeruginosa* than doxycillin, augmantin, unasyn, septrin, cefobid, nitrofurantion, traivid, erythromycin and free dtp ligands. However, the antimony(III) compounds show a lesser effect towards *P. aeruginosa* compared to amikacin, sulperazon and chloroamphenicol.
(iii) The antimony(III) complexes show a greater effect towards *E. coli* compared to unasyn, cefobid, ampicillin, erythromycin and dtp ligands (resistance to *E. coli*). However, the antimony(III) compounds show a lesser effect towards *E. coli* compared to amikacin, doxycllin, augmantin, sulperazon, nitrofurantion, traivid and chloroamphenicol.
(iv) Some of the antimony(III) compounds exhibit an equal antimicrobial effect as that of some antibiotics.

From all of the above results we can conclude that some of the free ligands and their antimony complexes show greater antibacterial effects to some of the investigated antibiotics.

4. Conclusions

Present study describes a series of 1,3-dithia-2-stibacyclopentane complexes with alkylene-/dialkyl-dithiophosphate. On the basis of physico-chemical and spectroscopic data we propose a monodentate behaviour of these ligands in these complexes, which is further confirmed by the X-ray crystal structure of 1,3-dithia-2-stibacyclopentane 2,3-butylenedithiophosphate.

Biological activity of the free ligands and their antimony(III) derivatives has been studied by the disc diffusion method on various microorganisms. All antimony(III) complexes exhibit greater antimicrobial activity compared to that of the free ligands. The free alkylene-/dialkyldithiophosphate and their mixed antimony compounds exhibited a higher antibacterial effect than the some of the previously investigated antibiotics.

5. Supplementary materials

Crystallographic data, tables of atomic coordinates, thermal parameters, bond lengths and bond angles of the structure have been deposited with the Cambridge Crystallographic Data Centre, with the deposition number: 604201. Copies of this are available free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Elemental analyses as well as spectral studies were carried out at the SAIF of the CDRI, Lucknow and Punjab University, Chandigarh. The authors are also thankful to S. Srivastava, Holkar Science College, for providing facilities for antimicrobial studies and to Dr. D. Buddhi for UV–Vis spectra.

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