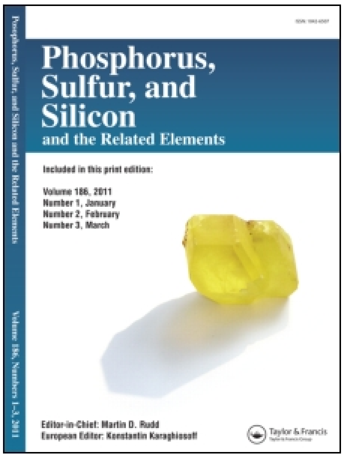

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MIXED DITHIOLATO ALKYLENE DITHIOPHOSPHATE DERIVATIVES OF ARSENIC(III) AND ANTIMONY(III)

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MIXED DITHIOLATO ALKYLENE DITHIOPHOSPHATE DERIVATIVES OF ARSENIC(III) AND ANTIMONY(III)

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Mixed dithiolato alkylene dithiophosphate derivatives of arsenic(III) and antimony(III) with the general formula

(where, G = -$CH_2C(CH_3)_2CH_2$-; -$CH_2C(C_2H_5)_2CH_2$-)

have been synthesized for the first time by the replacement reactions of ethane-1,2-dithiolatoarsenic(III) chloride, ethane-1,2-dithiolatoantimony(III) chloride, toluene-3,4-dithiolatoantimony(III) chloride, respectively with sodium alkylenedithiophosphates in equimolar ratios in benzene. These new compounds are soluble in common organic solvents like benzene, chloroform and carbon tetrachloride. These have been characterised by elemental analysis, melting points as well as spectroscopic (IR and ^{1}H. ^{13}C and ^{31}P NMR) studies and probable structures have been proposed.

Keywords: Dithiophosphate; Arsenic; Antimony

INTRODUCTION

Diorganodithiophosphate derivatives of arsenic(III) and antimony(III) are well known[1–5] for their utility as analytical reagents, as lubricant addi-

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tives, for regeneration of cracking catalysts and antitumour agents. The chemistry of arsenic(III) and antimony(III) with dialkyldithiophosphate ligands is well explored including the x-ray single crystal structures of a number of compounds[1-5].

O,O-alkylenedithiophosphate ligands, the cyclic analog of O,O-dialkyldithiophosphoric acids[6], behave as versatile dithio ligands and form a variety of complexes with non-transition[7-10] as well as transition elements[11-13]. Tris as well as mixed halide (alkylenedithiophosphate) derivatives of arsenic(III) and antimony(III) were reported by us[7], but the corresponding mixed dithiolato alkylenedithiophosphate derivatives are still unknown. In view of the exciting chemistry of corresponding mixed dithiolatoantimony(III) dialkyldithiophosphate derivatives, it was thought of interest to synthesize some mixed dithiolato alkylenedithiophosphate derivatives of arsenic(III) and antimony(III) and to characterize them by various physico-chemical techniques.

EXPERIMENTAL

Materials

Moisture was carefully excluded throughout the experimental manipulations. Solvents (benzene, hexane, alcohols) were dried by standard methods. Arsenic trichloride (b.p. 130°C), antimony trichloride (b.p. 223°C) 2,2-dimethylpropane-1,3-diol and 2,2-diethylpropane 1–3 diol were distilled before use. Ethane-1,2-dithiol (Fluka) and toluene-3–4-dithiol (Fluka) were used as received. Ethane-1,2-dithiolatoarsenic(III) chloride, ethane-1,2-dithiolato-antimony(III) chloride, Toluene-1,2-dithiolatoantimony(III) chloride[15,16] and alkylene dithiophosphoric acid[6] and their sodium salts[6,7] were prepared by reported methods.

Product Analyses

Sulphur was estimated gravimetrically as barium sulphate. Arsenic and antimony were estimated[7,18] iodometrically titrating against standard sodium thiosulphate solution. Carbon and hydrogen were analysed at

Regional Sophisticated Instrumentation Centre of Central Drug Research Institute, Lucknow.

Measurements

IR spectra were recorded as Nujol mulls on a Pye Unican SP3 300 spectrophotometer in the range 4000 – 200 cm^{-1}, ^1H and ^{13}C NMR spectral data were recorded in $CDCl_3$ solutions (for comp. Nos. 3 and 4 in Table II, the ^1H NMR spectra were recorded in $CDCl_3$ and DMSO mixture) using tetramethylsilane as internal standard on EM-360 and Jeol FX-90 spectrophotometers. ^{31}P NMR spectra in $CDCl_3$ solutions were recorded at RSIC, IIT, Bombay using H_3PO_4 as an internal standard.

GENERAL METHODS FOR THE SYNTHESIS OF VARIOUS DITHIOLATOARSENIC(III) AND DITHIOLATOANTIMONY(III) ALKYLENE DITHIOPHOSPHATES

(1) Reaction between sodium 2,2-dimethylene dithiophosphate and ethane-1,2-dithiolatoarsenic(III) or ethane-1,2 -dithiolatoantimony(III) chloride in 1:1 molar ratio

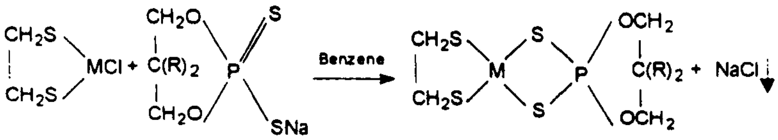
To the benzene solution (~40 ml) of ethane-1,2-dithiolatoarsenic(III) chloride or ethane-1,2-dithiolatoantimony(III) chloride was added sodium 2,2-dimethylpropylene dithiophosphate in equimolar ratio and the contents were refluxed for ~ 3 hours. The precipitated sodium chloride was removed by filtration and the crystalline solid product was obtained on removing excess of solvent from the filtrate.

(2) Reaction between sodium 2,2-diethylpropylene dithiophosphate and toluene-3,4-dithiolatoantimony(III) chloride in 1:1 molar ratio

Equimolar amount of toluene-3,4-dithiolatoantimony(III) chloride dissolved in benzene (~30 ml), was added dropwise to sodium 2,2-diethyl propylene dithiophosphate in a round bottom flask. The contents were stirred for ~4 hours at 50–60°C. The precipitated sodium chloride was separated by filtration and the solvent was removed from the filtrate under reduced pressure to give a shiny yellow crystalline solid.

RESULTS AND DISCUSSION

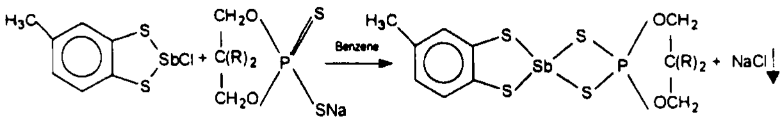
Ethane dithiolato alkylenedithiophosphate derivatives of arsenic(III) and antimony(III) have been synthesized by the replacement reaction of ethane-1,2-dithiolato metal chloride and sodium alkylenedithiophosphate in 1:1 molar ratios in refluxing benzene.



(M = As and Sb; R = CH_3, C_2H_5)

The mixed ethane dithiolate alkylenedithiophosphate derivatives of arsenic(III) are white solids, however, the corresponding derivatives of antimony(III) are pale yellow solids.

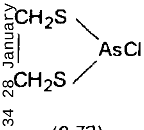
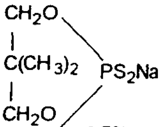
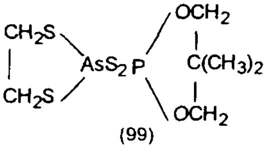
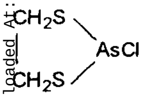
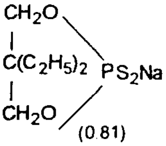
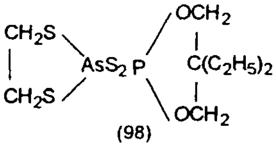
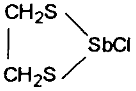
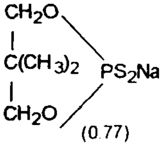
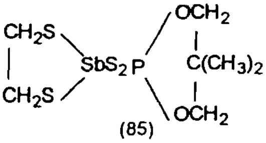
Toluene-3,4-dithiolatoantimony(III) chloride reacts with sodium alkylenedithiophosphate in 1:1 molar ratio in anhydrous benzene at 50–60°C to give mixed toluene dithiolatoantimony(III) alkylenedithiophosphates.

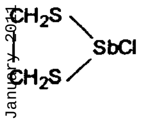
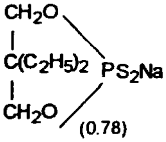
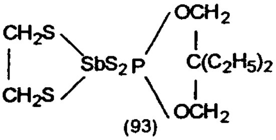
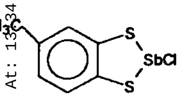
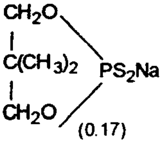
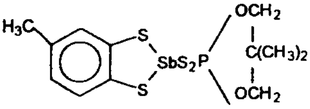
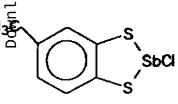
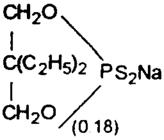
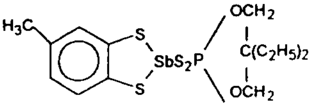


(R = CH_3, C_2H_5)

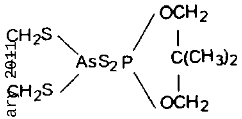
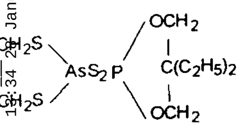
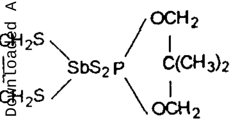
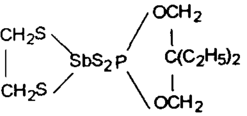
These derivatives are shiny yellow crystalline solids. All these derivatives are low melting and soluble in common organic solvents like benzene, chloroform, dichloromethane, carbon tetrachloride etc. They are characterised by elemental as well as spectral analysis.

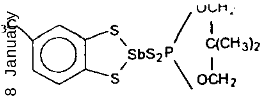
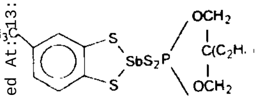
action of sodium alkylene dithiophosphates with 2-chloro-1,3-dithia-2 metallo cyclopentane and with toluene-3,4-dithiolato antim

Reactants (g)		Product % Yield	M P °C	Elemental analysis found (Calcd		
				As/Sb	S	C
 (0 72)	 (0 79)	 (99)	118	22.02 (20.53)	34.52 (35.02)	22.62 (22.98)
 (0.66)	 (0.81)	 (98)	90	19.42 (19.06)	32.82 (32.61)	27.36 (27.51)
 (0.87)	 (0.77)	 (85)	120	29.36 (29.62)	30.68 (31.14)	19.77 (20.43)

Reactants (g)		Product % Yield	M P °C	Elemental analysis found (Calcd			
				As/Sb	S	C	
 (0.79)	 (0.78)	 (93)	120	27.50 (27.71)	28.62 (29.12)	24.06 (24.57)	4 (4
 (0.24)	 (0.17)	 (84)	65	25.18 (25.78)	26.78 (27.05)	29.98 (30.44)	3. (3
 (0 22)	 (0 18)	 (97)	52	23.74 (24.24)	25.12 (25.54)	33.10 (33.52)	4. (3

LE II ^1H, ^{13}C and ^{31}P NMR spectral data of mixed dithiolato alkylene dithiophosphate derivatives of arsenic(III) and antimony(III)

Compound	*^1H Chemical shift (δppm)*	*^{13}C Chemical shift (δppm)*	*^{31}P C shift (*
	0.87, s, 6H (CH_3) 3.51, s, 4H (CH_2S) 4.04, d, 4H (OCH_2); J(P-OCH_2)=7.0Hz	21.30 (CH_3) 32.50 (Quarternary carbon atom) 43.88 (CH_2S) 77.47 (CH_2O)	85
	0.88, t, 6H (CH_3); J(CH_3-CH_2)=7.5Hz 1.68, q, 4H (CH_2); J(CH_2-CH_3)=7.5Hz 3.62, s, 4H (CH_2S) 4.09, d, 4H (CH_2O); J(P-OCH_2)=7.5Hz	–	86
	0.88, s, 6H(CH_3) 2.65, s, 4H(CH_2S) 2.96, d, 4H(CH_2O); J(P-OCH_2)=7.0 Hz	21.62 (CH_3) 32.50 (Quarternary carbon atom) 42.46 (CH_2S) 77.51 (CH_2O)	89
	0.76, t, 6H(CH_3); J(CH_3-CH_2)=7.6 Hz 1.20, q, 4H(CH_2); J(CH_2-CH_3)=7.6 Hz 2.84, s, 4H(CH_2S) 3.06, d, 4H(CH_2O); J(P-OCH_2)=7.0 Hz		90

Compound	*^1H Chemical shift (δppm)*	*^{13}C Chemical shift (δppm)*	*^{31}P C shift (*
	1.04, s, 6H (CH_3) 2.30, s, 3H (ring CH_3) 4.05, d, 4H (CH_2O; J(P-OCH_2)=7.0Hz 6.83–6.86, m, 1H (ring proton) 7.26–7.36, m, 2H (ring protons)	–	88
	0.83, t, 6H (CH_3); J(CH_3-CH_2)=6.8 Hz 1.42, q, 4H (CH_2); J(CH_2-CH_3)=6.8Hz 2.31, s, 3H (CH_3 ring) 4.06, d, 4H (CH_2O); J(P-OCH_2)=7.0Hz 6.84–6.86, m. 1H (ring proton) 7.26–7.36, m. 2H (ring protons)	–	89

d = doublet, t = triplet, q = quartet and m = multiplet.

Infra-red Spectra

Infra red spectra of these complexes have been recorded in the region 4000–200 cm^{-1} with the assignments, made on the basis of previous reports[6–8,14].

The bands present in the region 990 – 950 cm^{-1} and 850 – 810 cm^{-1} have been assigned to (P)-O-C and P-O-(C) stretching modes respectively. The bands at 940–910 cm^{-1} may be attributed to the dithiophosphorinanes ring vibrations[19]. A strong band due to ν(P=S) present in the spectra of sodium salt of alkylenedithiophosphoric acid in the region 690 – 665 cm^{-1} is shifted towards lower frequencies in the spectra of all these derivatives and is present as 660 – 640 cm^{-1}. The shifting indicates most probably a strong bidentate chelation of dialkylenedithiophosphate ligand with metal. Bands of weak to medium intensities present in the region 540 – 510 cm^{-1}, 390 – 380 cm^{-1} and 320 - 310 cm^{-1}due to (P-S), (As-S) and (Sb-S) stretching vibrations respectively[20,21]. The bands due to (C-S) stretching vibrations of the dithiolate moieties probably overlap with ν(P=S) vibrations in the region 660 – 640 cm^{-1}.

NMR Spectra

The ^1H NMR spectra of mixed dithiolato alkylene dithiophosphate derivatives of arsenic(III) and antimony(III) have been recorded in $CDCl_3$ "(compound No. 3 and 4; Table II have been recorded in the mixture of $CDCl_3$ and DMSO)" solutions. The ethane dithiolate derivatives of arsenic exhibit a sharp singlet in the region 3.51 – 3.62 δppm due to dithiocyclopentane (CH_2S) ring protons[14,22], thus indicating that these protons are equivalent. The corresponding toluene dithiolate derivatives of antimony show complex pattern in the regions 6.81 – 6.86 δppm and 7.26 – 7.36 δppm due to aromatic ring protons and a singlet at 2.30 – 2.31 δppm due to ring methyl protons.

The ^1H NMR spectra of ethane dithiolate derivatives of antimony (Compound No. 3 and 4; Table II) recorded in $CDCl_3$ and DMSO mixture, exhibit a singlet and a doublet at 2.65 – 2.84 δppm and 2.96 – 3.06 δppm due to CH_2S and CH_2O groups respectively. This shifting of signals towards high field may be due to the solvent effect of DMSO[23,24].

In addition, the spectra also exhibit the characteristic proton resonances for the corresponding alkylene moieties[7–10]. Dimethylpropylene dithiophosphate derivatives of arsenic and antimony exhibit a sharp singlet at 0.87 – 1.04 δppm due to methyl protons. Ethyl protons of diethylpropylene dithiophosphate derivatives appear as a triplet at 0.76 - 0.88 δppm and a quartet at 1.20 – 1.68 δppm. Due to coupling with phosphorus OCH_2 protons of these complexes appear as a doublet at 4.04 – 4.09 δppm.

The ^{13}C NMR spectra[23,24] of only two representative compounds ethane dithiolatometal(III) 2,2 dimethyl propylene dithiophosphates (metal = As, Sb) have been recorded and listed with the assignments (Table-II, Comp. No. 1,3).

The proton decoupled ^{31}P NMR spectral data for these derivatives (Table II) exhibit only one ^{31}P chemical shift in the region 85–91 δppm for each compound. whereas. the parent alkylene dithiophosphoric acids exhibit only one ^{31}P chemical shift at 77 – 79 δppm[7]. The ^{31}P chemical shift values are shifted towards down field (by 8 – 12 ppm) in these complexes indicating the bidentate behaviour of alkylenedithiophosphate ligands towards arsenic and antimony[7,25].

It is very difficult to comment on the actual structure of these compounds in the solid state without single crystal x-ray structure of at least one of the compounds. The observations based on the spectral data are consistent with trigonal bipyramidal geometry of these complexes. The ^{31}P NMR data and shifting of ν(P=S) towards lower frequencies indicate bidentate nature of alkylene dithiophosphate ligand to the metal. The four coordinated central metal atom surrounded by a bifunctional bidentate dithiol and a monofunctional bidentate dithiophosphate moiety. The stereochemically active lone pair occupies one of the equitorial positions. However, the intermolecular associations may give rise to dimeric or polymeric species[26,27], the possibility of which can not be ignored only on the basis of these data for which single crystal x-ray studies would be required.

Acknowledgements

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