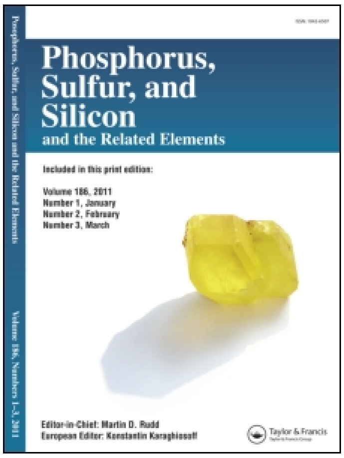

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O,O'-Dialkyldithiophosphate Ligand Based Heterobinuclear Derivatives of Antimony(III): Synthetic and Spectroscopic Studies

Pankaj Kumar Sharma[a]; Yashpal Singh[a]
[a] Department of Chemistry, University of Rajasthan, Jaipur, India

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O,*O*′-Dialkyldithiophosphate Ligand Based Heterobinuclear Derivatives of Antimony(III): Synthetic and Spectroscopic Studies

Pankaj Kumar Sharma
Yashpal Singh
Department of Chemistry, University of Rajasthan, Jaipur, India

*The interaction of sodium tetraisopropoxoborate, $NaB(OPr^i)_4$ with mixed chlorobis(dialkyldithiophosphato)antimony(III), $[(RO)_2P(S)S]_2SbCl$ compounds in a 1:1 molar ratio in refluxing benzene solution yields the corresponding heterobinuclear derivatives of antimony(III) and boron of the type $[(RO)_2P(S)S]_2Sb(\mu\text{-}OPr^i)_2B(OPr^i)_2$, [where R = Me(**1**), Et(**2**), Pr^i(**3**), Pr^n(**4**), and Bu^n(**5**)]. These novel heterobinuclear coordination compounds have been characterized by elemental analyses and molecular weight measurements. Probable structure for them have been suggested on the basis of IR and NMR (^1H, ^{13}C, ^{31}P, and ^{11}B) spectral studies.*

Keywords Bidentate ligands; chlorobis(dialkyldithiophosphato)antimony(III); hexacoordinated antimony; tetracoordinated boron

INTRODUCTION

Initially, considered as "alkoxosalts," the formation of heterobinuclear alkoxides of antimony of the type $NaSb(OR)_4$ and $NaSb(OR)_6$ have been reported during the titration of sodium and corresponding antimony alkoxides in parent alcohols.[1] Although during the last two decades there has been significant development concerning heterobimetallic alkoxides of antimony(III) involving a transition metal center,[2–6] the number of published studies concerning binuclear alkoxides of antimony involving a main group metal center is limited.[7–12] Also heterobinuclear alkoxides of antimony containing deprotonated dithiophosphates and isopropoxometallate group appear to not have been reported so far; though mixed ligand dialkyldithiophosphate derivatives of

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Address correspondence to Yashpal Singh, Department of Chemistry, University of Rajasthan, Jaipur 302 004, India. E-mail: yp_singh07@yahoo.co.in

antimony(III), $[(RO)_2P(S)S]_2SbX$ (where R = Et, Pr^n, Pr^i, and Bu^i) have already been reported earlier.[13–15]

We, therefore, for the first time report herein the synthesis and characterization of a new type of heterobinuclear alkoxide derivatives of antimony(III) with boron based on dithiophosphate ligands.

RESULTS AND DISCUSSION

These heterobinuclear derivatives of antimony and boron have been synthesized by the direct reactions of sodium tetraisopropoxoborate, $NaB(OPr^i)_4$ with corresponding chlorobis(dialkyldithiophosphato)-antimony(III) compounds, $[(RO)_2P(S)S]_2SbCl$ [prepared by the reactions of $SbCl_3$ with sodium salts of dilkyldithiophosphoric acids in a 1:2 molar ratio[13] (compounds with R = Me and Bu^n have been prepared for the first time using the same method)] in a 1:1 molar ratio in refluxing benzene solution for ~2 h [Eq. (1)].

$$[(RO)_2P(S)S]_2SbCl + NaB(OPr^i)_4 \xrightarrow[\text{Reflux}]{C_6H_6} \underset{\mathbf{1\text{-}5}}{[(RO)_2P(S)S]_2\,Sb(\mu - OPr^i)_2}\,B(OPr^i)_2 + NaCl\downarrow \quad (1)$$

where R = Me(**1**); Et(**2**); Pr^i(**3**); Pr^n(**4**); and Bu^n(**5**).

All these reactions are quite facile and quantitative. The newly synthesized heterobinuclear derivatives **1–5** are yellow colored, nonvolatile, moisture sensitive viscous liquids and soluble in common organic solvents. Cryoscopic molecular weight measurements of these derivatives reveal their monomeric nature in benzene solution.

INFRA-RED SPECTRA

IR data cannot distinguish between the various structural possibilities of dialkyldithiophosphate ligands since it is difficult to assign P=S and P—S stretching frequencies with certainty,[16,18] as these are present in the finger print region. The tentative assignments of the important characteristic bands in the IR spectra of these new heterobinuclear derivatives have been made by comparing them with the IR spectral data reported earlier.[9,13,16–20] A strong band present in the region 620–690 cm^{-1} and tentatively assigned to (P=S) stretching vibrations[13] in the spectra of free dialkyldithiophosphoric acids or their sodium salts is shifted toward lower wave numbers by ~35 cm^{-1} in the spectra of these new derivatives, **1–5**. This shifting may be probably due to the bidentate chelation of dithiophosphate moieties, which is supported by ^{31}P NMR spectra of these derivatives. The bands of medium intensity present in the region 510–625 cm^{-1} may be due to asymmetric and symmetric P—S stretching vibrations.[16] The medium intensity bands present in the region 345–370 cm^{-1} are due to Sb-S stretching vibrations.[17] The medium intensity bands in the regions 955–985 cm^{-1} and 785–830 cm^{-1} have been assigned to [(P)—O—C and [P—O—(C)] stretching modes, respectively.[18,19] These heterobinuclear derivatives also show additional bands in the regions 540–575 cm^{-1} and 1255–1470 cm^{-1} due to Sb—O[9] and B—O[20] stretching vibrations, respectively.

^{1}H NMR SPECTRA

^{1}H NMR spectra of the heterobinuclear derivatives **1–5** (Table I) exhibit two sets of signals for terminal and bridging isopropoxy groups in the regions 1.17–1.21 and 1.33–1.42 ppm (doublets) $\{CH(C\mathbf{H}_3)_2\}$, and 4.22–4.63 and 4.77–4.88 ppm (multiplets) $\{C\mathbf{H}(CH_3)_2\}$, respectively. Variable temperature ^{1}H NMR spectra of one representative compound, (**4**), has been recorded between temperatures ranging from 20°C to −50°C and it does not show any change in the positions of the signals, particularly of terminal and bridging isopropoxy groups. All alkyl protons of the (RO) group attached to P atom are observed at expected positions. Splitting due to coupling between α-protons and phosphorus has been observed in the signals of these alkyl groups attached to OP(S)S group (Table I).

^{13}C NMR SPECTRA

A comparative study of ^{13}C NMR spectra (proton decoupled) of these new heterobinuclear derivatives, **1–5**, with the spectra of parent chlorobis(dialkyldithiophosphato)antimony(III) compounds provides some useful information about the mode of bonding in these derivatives. In the ^{13}C NMR spectra (Table I) of these heterobinuclear derivatives, **1–5**, an upfield shift (∼4–6 ppm) has been observed in the positions of the signals of different alkyl group carbons of the dialkyldithiophosphate moieties as compared to their positions in corresponding parent chlorobis(dialkyldithiophosphato)antimony(III) compounds. This upfield shift may be due to the fact that the coordination number of antimony has increased from five to six. Two sets of signals due to terminal and bridging isopropoxy groups have been observed in the spectra of all the new derivatives **1–5** in the range 21.23–23.45 and 23.65–29.98 ppm $\{CH(\mathbf{C}H_3)_2\}$, and 62.90–70.64 and 71.77–73.92 ppm $\{\mathbf{C}H(CH_3)_2\}$, respectively.

TABLE I ^{1}H NMR Spectral Data (δ ppm) of New Heterobinuclear Derivatives 1–5

Compound	^{1}H NMR chemical shift (δ ppm)*	^{13}C NMR chemical shift (δ ppm)*	^{31}P NMR	^{11}B NMR
1	1.18, d, 12H, $(CH(C\mathbf{H}_3)_2)_T$; $J_{CH3CH}= 6.0$	21.23 $(CH(\mathbf{C}H_3)_2)_T$	88.42	−18.84
	1.37, d, 12H, $(CH(C\mathbf{H}_3)_2)_B$; $J_{CH3CH}= 6.0$	24.70 $(CH(\mathbf{C}H_3)_2)_B$		
	3.81, d, 12H, $(OC\mathbf{H}_3)_{dtp}$; $J_{P-O-CH3} = 13.4$	53.76 $(O\mathbf{C}H_3)_{dtp}$		
	4.63, m, 2H, $(C\mathbf{H}(CH_3)_2)_T$	70.64 $(\mathbf{C}H(CH_3)_2)_T$		
	4.88, m, 2H, $(C\mathbf{H}(CH_3)_2)_B$	73.07 $(\mathbf{C}H(CH_3)_2)_B$		
2	1.21, d, 12H, $(CH(C\mathbf{H}_3)_2)_T$; $J_{CH3CH}= 6.1$	14.77 $(CH_2\mathbf{C}H_3)_{dtp}$	90.75	−20.17
	1.33, t, 12H, $(C\mathbf{H}_3)_{dtp}$; $J_{CH3CH2} = 7.1$	22.20 $(CH(\mathbf{C}H_3)_2)_T$		
	1.42, d, 12H $(CH(C\mathbf{H}_3)_2)_B$; $J_{CH3CH} = 5.9$	24.19 $(CH(\mathbf{C}H_3)_2)_B$		
	4.14, dq, 8H, $(OC\mathbf{H}_2)_{dtp}$; $J_{P-O-CH2} = 9.0$, $J_{CH3-CH2} = 7.1$	61.69 $(O\mathbf{C}H_2)_{dtp}$		
	4.38, m, 2H, $(C\mathbf{H}(CH_3)_2)_T$	62.90 $(\mathbf{C}H(CH_3)_2)_T$		
	4.77, m, 2H, $(C\mathbf{H}(CH_3)_2)_B$	71.77 $(\mathbf{C}H(CH_3)_2)_B$		
3	1.17,d, 12H, $(CH(C\mathbf{H}_3)_2)_T$; $J_{CH3CH} = 6.0$	23.45 $(CH(\mathbf{C}H_3)_2)_T$	87.44	−19.76
	1.33,d, 12H, $(CH(C\mathbf{H}_3)_2)_B$; $J_{CH3CH} = 4.6$	24.36 $(CH(\mathbf{C}H_3)_2)_{dtp}$		
	1.38, d, 24H, $(CH(C\mathbf{H}_3)_2)_{dtp}$; $J_{CH3CH} = 6.2$	24.94 $(CH(\mathbf{C}H_3)_2)_B$		
	4.22, m, 2H, $(C\mathbf{H}(CH_3)_2)_T$	64.47 $(\mathbf{C}H(CH_3)_2)_T$		
	4.68, m, 2H, $(C\mathbf{H}(CH_3)_2)_B$	73.12 $(\mathbf{C}H(CH_3)_2)_{dtp}$		
	4.85, m, 4H, $(OC\mathbf{H})_{dtp}$; $J_{P-O-CH} = 10.5$, $J_{CH3-CH} = 6.2$	73.64 $(\mathbf{C}H(CH_3)_2)_B$		
4	0.98, t, 12H, $(C\mathbf{H}_3)_{dtp}$; $J_{CH3CH2} = 7.3$	10.18 $(\mathbf{C}H_3)_{dtp}$	91.38	−20.67
	1.20, d, 12H, $(CH(C\mathbf{H}_3)_2)_T$; $J_{CH3CH} = 6.9$	23.28 $(CH(\mathbf{C}H_3)_2)_T$		
	1.35, d, 12H, $(CH(C\mathbf{H}_3)_2)_B$; $J_{CH3CH} = 6.2$	23.65 $(CH(\mathbf{C}H_3)_2)_B$		
	1.77, m, 8H, $(C\mathbf{H}_2CH_3)_{dtp}$; $J_{CH3-CH2} = 7.3$	24.94 $(\mathbf{C}H_2CH_3)_{dtp}$		
	4.55, dt, 8H, $(OC\mathbf{H}_2)_{dtp}$; $J_{P-O-CH2} = 8.8$, $J_{CH2-CH2} = 7.3$	69.30 $(O\mathbf{C}H_2)_{dtp}$		
	4.58, m, 2H, $(CH(C\mathbf{H}_3)_2)_T$	69.98 $(\mathbf{C}H(CH_3)_2)_T$		
	4.87, m, 2H, $(CH(C\mathbf{H}_3)_2)_B$	73.92 $(\mathbf{C}H(CH_3)_2)_B$		
5	0.92, t, 12H, $(C\mathbf{H}_3)_{dtp}$; $J_{CH3-CH2} = 5.4$	13.36 $(\mathbf{C}H_3)_{dtp}$	92.17	−19.09
	1.21, d, 12H, $(CH(C\mathbf{H}_3)_2)_T$; $J_{CH3CH} = 6.1$	21.44 $(\mathbf{C}H_2CH_3)_{dtp}$		
	1.35, d, 12H, $(CH(C\mathbf{H}_3)_2)_B$; $J_{CH3CH} = 4.2$	23.23 $(CH(\mathbf{C}H_3)_2)_T$		
	1.44, m, 8H, $(C\mathbf{H}_2CH_3)_{dtp}$; $J_{CH3-CH2} = 5.4$	29.98 $(CH(\mathbf{C}H_3)_2)_B$		
	1.68, m, 8H, $(OCH_2C\mathbf{H}_2)_{dtp}$; $J_{CH3-CH2} = 5.4$	33.19 $(OCH_2\mathbf{C}H_2)_{dtp}$		
	2.90, dt, 8H $(OC\mathbf{H}_2)_{dtp}$; $J_{P-O-CH2} = 7.5$, $J_{CH2-CH2} = 5.4$	65.67 $(O\mathbf{C}H_2)_{dtp}$		
	4.54, m, 2H, $(C\mathbf{H}(CH_3)_2)_T$	72.28 $(\mathbf{C}H(CH_3)_2)_T$		
	4.81, m, 2H, $(C\mathbf{H}(CH_3)_2)_B$	73.12 $(\mathbf{C}H(CH_3)_2)_B$		

*Coupling constants are in Hz ; $_T$ = terminal, $_B$ = bridging, $_{dtp}$ = dialkyldithiophosphate, d = doublet, dq = doublet of quartets, dt = doublet of triplets, m = multiplet, t = triplet.

^{31}P NMR SPECTRA

Some important information about the complexation behavior of dialkyldithiophosphate ligands with central antimony atom and the geometry of these new derivatives has been obtained from proton decoupled ^{31}P NMR spectral data (Table I). The ^{31}P NMR spectra exhibit only one signal in the spectra of each new derivative in the range 87.44–92.17 ppm. The presence of ^{31}P NMR signals in this range has been interpreted in terms of bidentate nature of the dialkyldithiophosphate ligands[21] in the derivatives **1–5**.

^{11}B NMR SPECTRA

^{11}B NMR spectra of the derivatives **1–5** exhibit only one signal for each new derivative in the range –18.84 to 20.67 ppm (Table I). The presence of a ^{11}B NMR signal in this range is indicative of a tetrahedral environment around the boron atom in these heterobinuclear derivatives.[22]

In view of two bidentate dialkyldithiophosphate ligands around the antimony atom, the presence of two types of isopropoxy groups (bridging and terminal), and tetracoordination around the boron atom, the following structure (Figure 1) may be tentatively proposed to the new derivatives **1–5**.

It is quite difficult to comment on the molecular structure of these new heterobinuclear derivatives in solid state without actual X-ray crystal structure analysis of at least one of the compounds.

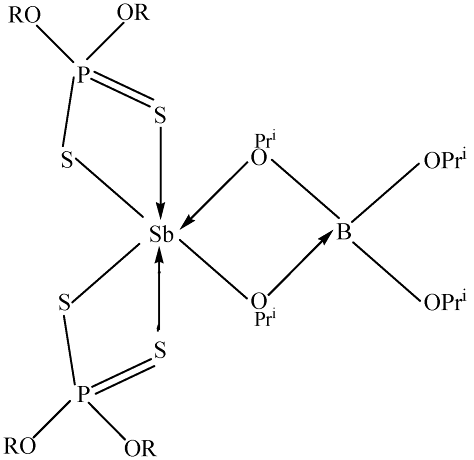

FIGURE 1 Proposed structure of Heterobinuclear derivatives **1–5**, where R = Me (**1**), Et(**2**), Pr^i (**3**), Pr^n (**4**), and Bu^n (**5**).

EXPERIMENTAL

All reactions have been carried out under a moisture-free environment. Solvents (E. Merck, Mumbai-Maharastra, India) were carefully dried by standard methods before use. Mixed chlorobis(dialkyldithiophosphato)antimony(III) derivatives were prepared by the reported method.[13] Sodium tetraisopropoxoborate, $NaB(OPr^i)_4$, was prepared according to the literature method.[23] Sulphur was estimated by Massenger's method.[24] Boron and antimony were determined by the methylborate and iodometric methods, respectively.[24]

Elemental analyses (C and H) were carried out on a Perkin Elmer 2400 C, H, and N analyzer. Molecular weights were determined cryoscopically in freezing benzene solution using a Beckmann's thermometer. The IR spectra were recorded on a Nicolet DX FT IR spectrophotometer as thin films on a CsI cell in the range 4000–200 cm^{-1}. ^1H, ^{13}C, ^{31}P, and ^{11}B NMR spectra were recorded in $CDCl_3$ solution on JEOL FT AL 300 MHz spectrometer. TMS has been used as an internal reference for ^1H and ^{13}C NMR spectra, and for those of ^{31}P and ^{11}B NMR spectra, H_3PO_4 and $B(OCH_3)_3$, respectively, were used as external standards.

Synthesis of Heterobinuclear Derivative 1

Freshly prepared sodium tetraisopropoxoborate, $NaB(OPr^i)_4$ (0.95 g, 3.52 mmol), was mixed with a benzene solution of $[(MeO)_2P(S)S]_2SbCl$ (1.66 g, 3.52 mmol), and the resulting reaction mixture after stirring at r.t. for ~4 h was finally refluxed for ~2 h. The precipitated NaCl (0.20 g, 3.42 mmol) was removed by filtration. Removal of volatile components from filtrate under reduced pressure yielded 2.32 g (96.67%) derivative **1**, which was further purified by a 1:2 mixture of benzene and n-hexane at 0°C to obtain the analytically pure compound **1** in a 91.47% (2.20 g) yield.

A similar procedure was adopted for the synthesis of all other new heterobinuclear derivatives, **2–5**. The physical and analytical data of these derivatives have been summarized in Table II. Amounts of the reactants actually used and the NaCl precipitated follow in brackets.

2. $NaB(OPr^i)_4$ (0.78 g, 2.89 mmol) and $[(EtO)_2P(S)S]_2SbCl$ (1.52 g, 2.88 mmol); NaCl (0.17 g)
3. $NaB(OPr^i)_4$ (0.70 g, 2.59 mmol) and $[(Pr^iO)_2P(S)S]_2SbCl$ (1.52 g, 2.60 mmol); NaCl (0.15 g)
4. $NaB(OPr^i)_4$ (0.79 g, 2.92 mmol) and $[(Pr^n)_2P(S)S]_2SbCl$ (1.71 g, 2.93 mmol); NaCl (0.17 g)

TABLE II **Physical and Analytical Data of the Heterobinuclear Derivatives 1–5**

Compound	Empirical formula and yield (%)	Color/ physical state	Analysis (%) found (calculated)					Mol. wt. found (calcd.)
			Sb	S	B	C	H	
1	$C_{16}H_{40}O_8P_2S_4BSb$	Light yellow/	17.73	18.61	1.49	28.02	5.85	676
	91	viscous liquid	(17.82)	(18.77)	(1.58)	(28.12)	(5.91)	(683.26)
2	$C_{20}H_{48}O_8P_2S_4BSb$	Light yellow/	16.31	17.24	1.37	32.13	6.39	731
	89	viscous liquid	(16.47)	(17.35)	(1.46)	(32.49)	(6.56)	(739.36)
3	$C_{24}H_{56}O_8P_2S_4BSb$	Light yellow/	15.21	15.97	1.28	36.02	7.05	788
	92	viscous liquid	(15.31)	(16.13)	(1.36)	(36.24)	(7.11)	(795.47)
4	$C_{24}H_{56}O_8P_2S_4BSb$	Light yellow/	15.17	15.84	1.28	35.97	7.04	787
	90	viscous liquid	(15.31)	(16.13)	(1.36)	(36.24)	(7.11)	(795.47)
5	$C_{28}H_{64}O_8P_2S_4BSb$	Light yellow/	14.03	14.87	1.19	39.19	7.33	840
	89	viscous liquid	(14.30)	(15.06)	(1.27)	(39.49)	(7.59)	(851.57)

5. $NaB(OPr^i)_4$ (0.66 g, 2.44 mmol) and $[(Bu^nO)_2P(S)S]_2SbCl$ (1.56 g, 2.44 mmol); NaCl (0.14 g)

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