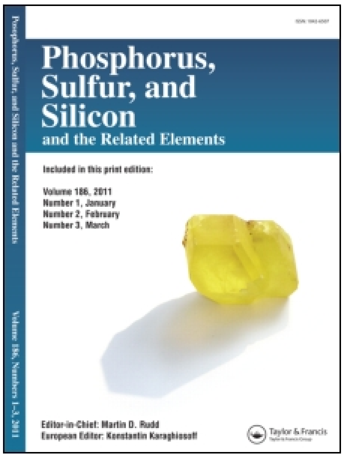


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Spectroscopic Studies of Alkoxoantimony(V) Schiff Base Complexes and Heterobinuclear Complexes of Antimony(V) with Boron

Durgashanker[a]; Yashpal Singh[a]
[a] Department of Chemistry, University of Rajasthan, Jaipur, India

To cite this Article Durgashanker and Singh, Yashpal(2009) 'Synthesis and Spectroscopic Studies of Alkoxoantimony(V) Schiff Base Complexes and Heterobinuclear Complexes of Antimony(V) with Boron', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 1, 45 — 57

To link to this Article: DOI: 10.1080/10426500802077572

URL: http://dx.doi.org/10.1080/10426500802077572

Phosphorus, Sulfur, and Silicon, 184:45–57, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802077572

Synthesis and Spectroscopic Studies of Alkoxoantimony(V) Schiff Base Complexes and Heterobinuclear Complexes of Antimony(V) with Boron

Durgashanker and Yashpal Singh
Department of Chemistry, University of Rajasthan, Jaipur, India

*Reactions of $Sb(OPr^i)_5$ (prepared in situ by the reaction of $NaOPr^i$ and $SbCl_5$) with one equivalent of benzothiazoline ligands, $HNC_6H_4SC(R)CH{:}C(OH)COOCH_3$ in refluxing benzene yield the corresponding derivatives of the type $[OPr^i]_3Sb[SC_6H_4NC(R)CH{:}C(O)COOCH_3]$ (**1a–1e**). The reactions proceed with the opening of benzothiazoline ring. The equimolar reactions of the compounds **1a–1e** with $PhB(OH)_2$ have been carried out in refluxing benzene resulting in the heterobinuclear derivatives $PhB(\mu\text{-}O)_2Sb[SC_6H_4NC(R)CH{:}C(O)COOCH_3][OPr^i]$ (2a-2e). All the compounds have been characterized by the elemental analysis and molecular weight determinations, and probable structure has been proposed on the basis of IR and NMR (^1H, ^{13}C, and ^{11}B) spectroscopic evidences.*

Keywords Antimony(V); benzothiazoline; boron; heteronuclear compounds

INTRODUCTION

During the last two decades, there has been significant development concerning heteromettalic alkoxides and oxoalkoxides of antimony(III) involving transition metals[1–7] as well as main group metal centers[7–16] due to their applications as precursors in sol-gel technology of oxide materials, which are based on hydrolysis of alkoxides and oxoalkoxides. Although a number of heterometallic compounds of antimony(III) have been reported, little work has been reported on heteronuclear alkoxide derivatives of antimony(V), which are mainly limited to alkoxo-bridged compounds of the type $MSb(OEt)_5$ [M = Mn, Fe, Co, Ni(II)][10] and $MSb(OR)_5$ [M = Li, Na, K; R = Me, ^{i}Pr, ^{n}Pr, ^{n}Bu, ^{t}Bu].[14] Moreover, heterobinuclear alkoxide derivatives of antimony(V) appear to not have been reported so far. We therefore, for the first time, report the synthesis and characterization of a new type of oxobridged heterobinuclear

Received 16 January 2008; accepted 8 February 2008.

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

alkoxo derivatives of antimony(V) with boron(III) based on benzothiazoline ligands.

RESULTS AND DISCUSSION

The equimolar reactions of $Sb(OPr^i)_5$ (prepared in situ) with benzothiazoline ligands $[HNC_6H_4SC(R)CHC(OH)COOCH_3$, where $R = C_6H_5$ (L^1H_2), $4\text{-}BrC_6H_4(L^2H_2)$, $4\text{-}ClC_6H_4(L^3H_2)$, $4\text{-}CH_3OC_6H_4(L^4H_2)$, $4\text{-}CH_3C_6H_4(L^5H_2)]$ have been carried out in refluxing benzene. The reactions proceed with rearrangement of benzothiazoline ring and yield colored, solid antimony(V) derivatives, $[OPr^i]_3Sb[SC_6H_4NC(R)CHC(O)COOCH_3]$ (**1a–1e**).

$$Sb(OPr^i)_5 + HNC_6H_4SC(R)CHC(OH)COOCH_3 \xrightarrow{\text{Benzene}} [OPr^i]_3Sb[SC_6H_4NC(R)CHC(O)COOCH_3] + 2Pr^iOH$$

$$[R = C_6H_5(1a),\ 4\text{-}BrC_6H_4(1b),\ 4\text{-}ClC_6H_4(1c),\ 4\text{-}CH_3OC_6H_4(1d),\ 4\text{-}CH_3C_6H_4(1e)].$$

The reactions of these compounds (**1a–1e**) have been carried out with $PhB(OH)_2$ in a 1:1 molar ratio in refluxing benzene. Isopropanol liberated during the reaction was fractionated off azeotropically with benzene. The progress and completion of the reaction was checked by estimating isopropanol in the azeotrope.

After completion of the reaction, excess solvent was distilled off and the last traces of solvent were removed under vacuum, leading to colored compounds as viscous liquid. These compounds are soluble in common organic solvents.

$$[OPr^i]_3Sb[SC_6H_4NC(R)CHC(O)COOCH_3] + PhB(OH)_2 \xrightarrow[\text{Reflux}]{\text{Benzene}} PhB(\mu\text{-}O)_2Sb[SC_6H_4NC(R)CHC(O)COOCH_3][OPr^i] + 2Pr^iOH$$

$$[R = C_6H_5\ (2a),\ 4\text{-}BrC_6H_4\ (2b),\ 4\text{-}ClC_6H_4\ (2c),\ 4\text{-}CH_3OC_6H_4\ (2d),\ 4\text{-}CH_3C_6H_4\ (2e)].$$

Molecular weight measurements of these compounds reveal their monomeric nature in refluxing benzene.

Spectroscopic Studies

Infrared Spectra

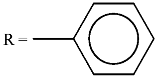
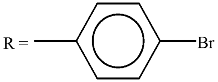
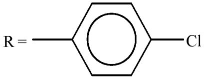
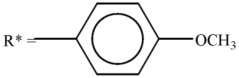
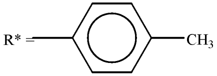
The important characteristic bands in the IR spectra of the newly synthesized antimony(V) complexes (**1a–1e**) have been assigned tentatively comparing them with IR spectral data of the free ligands. A broad band present in the spectra of free ligands in the range 3325–3225 cm^{-1} due to νN-H group disappeared in the spectra of the corresponding antimony compounds (**1a–1e**). The spectra of **1a–1e** exhibit new bands in the range 1630–1625 cm^{-1}, 410–403 cm$^{-1,}$ and 425–420 cm^{-1}, which have been assigned to ν(C=N), ν(Sb—S)[17,18] and ν(Sb—N),[19] respectively. Disappearance of NH absorption band and appearance of C=N, Sb—S, and Sb—N bands indicate the rearrangement of the benzothiazoline ring during complexation and subsequent formation of C=N, Sb—S, and Sb—N bonds. A broad band observed in the range 3638–3417 cm^{-1} due to the –OH group in the spectra of free ligands is found to be absent in the spectra of corresponding antimony derivatives. A new band is observed in the spectra of these complexes at 575–562 cm^{-1}, which has been assigned to the Sb-O absorption band.[20] Disappearance of the OH absorption band and appearance of the Sb-O absorption band indicate deprotonation of the —OH group and subsequent formation of the Sb—O bond. In addition to all the bands present in the spectra of the complexes (**1a–1e**), some new bands have also been observed at 1320–1315 cm^{-1} and 760–750 cm^{-1} due to νB-O[21] and νSb-O,[22] respectively, in the spectra of the complexes (**2a–2e**). The vibration modes for ν**Sb-O**[CH(CH$_3$)$_2$][23] appear in the range 620–610 (symmetric stretching), 550–520 (asymmetric stretching), and 450–425 (symmetric bending) cm^{-1} in the spectra of these complexes.

^{1}H NMR Spectra

The characteristic signals in the spectra of **1a–1e** and **2a–2e** are summarized in Tables I and II.

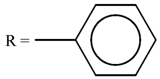
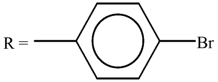
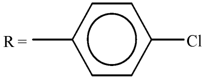
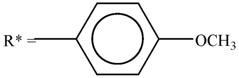
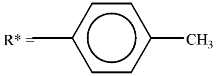
The signals observed at δ15.10–15.35 ppm and δ3.90–4.40 ppm due to enolic –OH and –NH group protons in the spectra of free ligands, respectively, are found to be absent in the spectra of corresponding derivatives (**1a–1e**). Absence of the signals indicates the deprotonation of –OH and –NH groups during complex formation. A small downfield shift in the position of the =CH proton as compared to its position in the free ligand is observed in the spectra of these derivatives. The deprotonation of –OH group and downfield shift of =CH protons indicate the involvement of >C—OH group in bonding. The substituted phenyl ring protons are observed in the range δ 6.16–8.20 ppm. The methyl (ester) group is observed as a singlet in the range δ 2.55–2.60 ppm. A multiplet and a doublet at δ 4.01–4.09 ppm and δ 1.22–1.25 ppm have been assigned to —OCH and —CH$_3$ protons of isopropoxy groups, respectively.

TABLE I ^{1}H NMR Spectral Data (δ ppm) of the Complexes $[OPr^i]_3Sb[SC_6H_4NC(R)CH{:}C(O)COOCH_3]$(1a–1e)

S. No.	Complexes	R	$—NC_6H_4S—$	$=CH$	OCH_3 (ester)	$CH(OPr^i)$	$CH_3(OPr^i)$ (J in Hz)
1	 (1a)	7.10–7.40 (m, 5H)	7.50–8.20 (m, 4H)	9.02 (s, 1H)	2.60 (s, 3H)	4.09 (m, 3H)	1.25 (d, 18H) (6.39)
2	 (1b)	6.16–7.37 (m, 4H)	7.44–8.17 (m, 4H)	9.02 (s, 1H)	2.59 (s, 3H)	4.02 (m, 3H)	1.22 (d, 18H) (5.85)
3	 (1c)	6.91–7.31 (m, 4H)	7.43–8.17 (m, 4H)	9.01 (s, 1H)	2.60 (s, 3H)	4.04 (m, 3H)	1.21 (d, 18H) (5.31)
4	 (1d)	6.86–7.26 (m, 4H)	7.36–8.16 (m, 4H)	9.01 (s, 1H)	2.56 (s, 3H)	4.01 (m, 3H)	1.19 (d, 18H) (5.59)
5	 (1e)	7.24–7.28 (m, 4H)	7.46–8.17 (m, 4H)	9.01 (s, 1H)	2.59 (s, 3H)	4.10 (m, 3H)	1.22 (d, 18H) (5.49)

*The $—OCH_3$ and $—CH_3$ group protons appeared as singlet at δ 3.87 (**1d**) and 2.42 (**1e**) ppm respectively. s = singlet, d = doublet, m = multiplet.

TABLE II ^{1}H NMR Spectral Data (δ ppm) of the Complexes $PhB(\mu\text{-}O)_2Sb[SC_6H_4NC(R)CH{:}C(O)COOCH_3][OPr^i]$(2a–2e)

S. No.	Complexes	R	$—NC_6H_4S—$	=CH	OCH_3 (ester)	$CH(OPr)^i$	$CH_3(OPr)^i$ (J in Hz)	Ph-B
1	 (2a)	7.26–7.43 (m, 5H)	7.75–8.16 (m, 4H)	9.00 (s, 1H)	2.59 (s, 3H)	4.60 (m, 1H)	1.16 (d, 6H) (6.03)	7.44–7.61 (m, 5H)
2	 (2b)	7.15–7.35 (m, 4H)	7.68–8.07 (m, 4H)	8.90 (s, 1H)	2.46 (s, 3H)	4.50 (m, 1H)	1.12 (d, 6H) (6.20)	7.41–7.48 (m, 5H)
3	 (2c)	7.31–7.39 (m, 4H)	7.81–8.15 (m, 4H)	9.00 (s, 1H)	2.55 (s, 3H)	4.60 (m, 1H)	1.23 (d, 6H) (6.03)	7.42–7.58 (m, 5H)
4	 (2d)	6.79–7.34 (m, 4H)	7.46–8.06 (m, 4H)	8.90 (s, 1H)	2.44 (s, 3H)	4.48 (m, 1H)	1.13 (d, 6H) (6.03)	7.37–7.43 (m, 5H)
5	 (2e)	7.15–7.27 (m, 4H)	7.47–8.08 (m, 4H)	8.99 (s, 1H)	2.50 (s, 3H)	4.52 (m, 1H)	1.15 (d, 6H) ()	7.35–7.46 (m, 5H)

*The $—OCH_3$ and $—CH_3$ group protons appeared as singlet at δ 3.76 (**2d**) and 2.32 (**2e**) ppm respectively. s = singlet, d = doublet, m = multiplet.

In the spectra of **2a–2e**, in addition to all the signals present in the spectra of **1a–1e**, a new multiple at δ 7.35–7.61 ppm is also observed. This is assigned to the phenyl group attached to boron.

^{13}C NMR Spectra

In the ^{13}C NMR spectra of the antimony (V) complexes (**1a–1e**), the signal observed at δ 158.68–160.07 ppm due to the CN group in the spectra of free ligands shows a downfield shift, indicating the rearrangement of the benzothiazoline ring on complexation. A small downfield shift observed in the position of the signals of =CH and >C—O (as compared to free ligands) indicates the involvement of the >C—O group in bonding during complex formation. The signals for >C=O (ester), CH_3 (ester) and $-NC_6H_4S-$ groups are observed at their expected positions (Table III). Two sets of signals appeared in the range δ 60.01–61.82 ppm, and δ 25.30–25.50 ppm have been assigned to —OCH and $-CH_3$carbons of isopropoxy groups. In ^{13}C NMR spectra of the heterodinuclear complexes (**2a–2e**), a new set of signals appeared at δ 122.29–139.32 ppm, which has been assigned to the carbons of phenyl ring attached to boron. The signals for other groups of these complexes are summarized in Table IV.

^{11}B NMR spectra of the heteronuclear complexes (**2a–2e**) exhibit only one signal for each compound in the range of δ 9.56–9.72 ppm with reference to $B(OMe)_3$. Presence of ^{11}B signal (Table IV) in this range indicates the presence of tricoordinated boron atom in these complexes.[24,25]

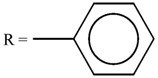
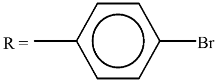
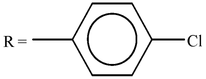
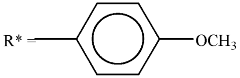
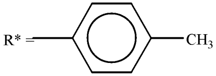
On the basis of the above spectral evidence, it is clear that the ligand behaves as a bifunctional tridentate moiety in these complexes. Structure (1) for **1a–1e** may be suggested in which the Sb atom is hexacoordinated (Figure 1). Structure (2) may be proposed for the complexes 2a-2e in which Sb atom is hexacoordinated and B atom is tricoordinated (Figure 2).

EXPERIMENTAL

Materials and Methods

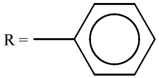
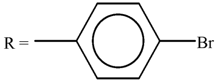
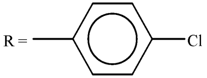
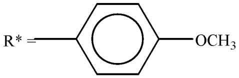
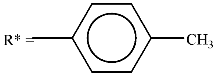
All the chemicals used were of reagent grade. Care was taken to exclude moisture throughout experimental work. The solvents were dried by literature method.[26] The benzothiazoline ligands were prepared by reported method.[27] Antimony[28] was estimated by iodometric method. Liberated isopropanol and isopropoxy groups were estimated oxidimetrically using 1N $K_2Cr_2O_7$ solution in 25% H_2SO_4.[29] Nitrogen and sulfur were estimated by Kjeldhal's[28] and Messenger's[28] methods,

TABLE III ^{13}C NMR Spectral Data (δ ppm) of the Complexes $[OPr^i]_3Sb[SC_6H_4\ NC(R)CH{:}C(O)COOCH_3]$ (1a–1e)

S. No	Complexes	R	—NC_6H_4S—	CN	C—O	=CH	C=O	OCH_3 (ester)	CH (OPr^i)	CH_3 (OPr^i)
1	 (1a)	134.85 132.51 127.81 126.23	153.52, 133.72, 128.32, 127.50, 125.01, 124.09	161.45	165.01	96.75	197.18	27.55	61.82	25.36
2	 (1b)	133.60 128.75 126.77 123.46	153.50, 136.65, 131.95, 127.55 125.29, 122.37	161.75	164.65	96.68	197.06	26.85	60.01	25.50
3	 (1c)	132.50 131.41 126.79 123.64	153.11, 135.38 128.61, 126.19 125.57, 121.90	160.01	165.22	96.51	196.30	27.05	61.52	61.52
4	 (1d)	133.51, 130.61, 130.49 123.47	155.00, 140.01, 129.13, 126.52, 125.09, 121.56	161.80	165.11	97.53	195.90	25.37	61.45	24.40
5	 (1e)	134.50 130.0 128.46, 125.55	153.0, 137.50, 133.59, 129.0, 126.17, 121.89	160.20	165.12	96.33	196.50	27.00	60.62	25.39

*The OCH_3 and CH_3 group carbons appeared at δ 55.20 (**1d**) and 26.50 (**1e**) ppm respectively.

TABLE IV ^{13}NMR and ^{11}B NMR Spectral Data (δ ppm) of the Complexes, PhB(μ-O)$_2$Sb[SC$_6$H$_4$NC(R)CH: C(O)COOCH$_3$][OPr^i] (2a–2e)

S. No	Complexes	R	—NC$_6$ H$_4$S—	CN	C—O	=CH	C=O	OCH$_3$(ester)	CH(OPr^i)	CH$_3$(OPr^i)	Ph-B	^{11}B
1	 (2a)	135.70 132.56 127.48 125.98	152.97, 134.30, 129.16, 127.15, 124.54, 122.93	162.91	167.55	96.11	196.85	26.50	65.54	25.37	133.82 130.02 125.30 122.29	9.56
2	 (2b)	133.65 132.82 128.23 126.10	153.99, 135.68, 129.78 125.86, 123.56, 121.83	162.82	167.01	97.79	196.88	26.45	66.11	24.69	131.78 129.18 127.67 125.48	9.63
3	 (2c)	139.43 133.64 129.68 127.68	153.09, 135.32, 128.78, 125.50, 123.55, 121.62	163.05	167.10	97.40	196.63	26.36	66.12	25.37	139.32 129.21 128.73 126.12	9.67
4	 (2d)	133.68 130.54 125.97 129.22	154.18, 136.01, 127.69, 125.49, 123.54,121.84	163.44	167.58	97.50	196.47	25.68	66.08	24.70	132.88 130.21 126.09 124.78	9.57
5	 (2e)	143.74 132.86 129.22 127.69	153.15,134.63, 128.42, 126.10, 123.54, 121.84	163.05	166.50	97.60	197.66	25.53	66.11	24.70	133.67 129.27 129.17 125.49	9.72

*The OCH$_3$ and CH$_3$ group carbons appeared at δ 55.25 (2d) and 26.44 (2e) ppm respectively.

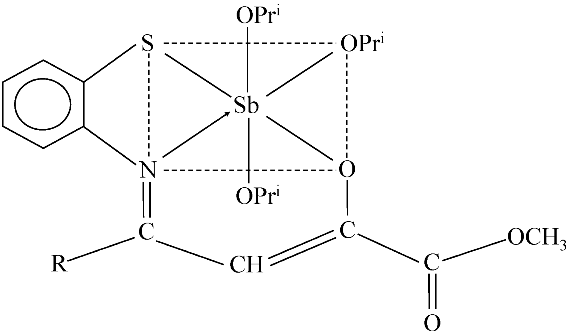


FIGURE 1 Proposed structure of the complexes (**1a–1e**).

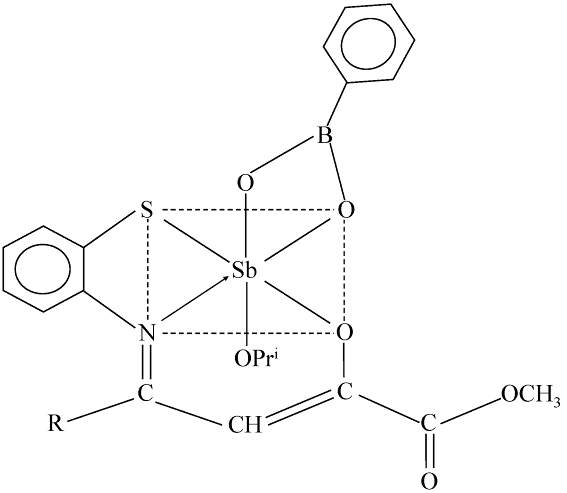


FIGURE 2 Proposed structure of the complexes (**2a–2e**).

respectively. Molecular weight of the complexes has been determined ebuilioscopically in benzene solution using Beckman's thermometer.

The IR spectra were recorded on a FT-IR spectrophotometer model 8400 S Shimadzu as liquid films on KBr optics and as pallet using KBr in the range 4000–400 cm^{-1}. ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded in CDC1$_3$ solution on a JEOL FT AL 300 MHz spectrometer. ^{1}H and ^{13}C NMR were recorded using TMS as internal and external references, respectively. ^{11}B NMR was recorded with reference to B(OMe)$_3$as an external reference.

Since similar methods have been used for the synthesis of these complexes (**1a–1e** and **2a–2e**), synthetic detail of only one complex of

TABLE V Synthetic and Analytical Data of the Complexes $[OPr^i]_3Sb(SC_6H_4NC(R)CH{:}C(O)COOCH_3]$ (1a–1e)

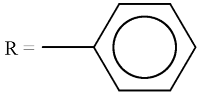
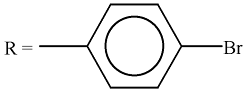
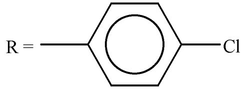
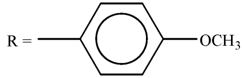
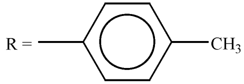
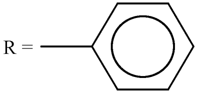
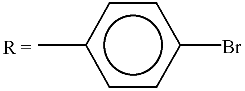
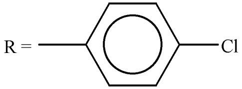
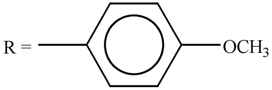
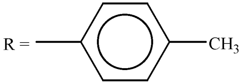
S. No.	Complexes	Reagents g (mmol)			Molecular formula, Color, Physical state, and Yield (%)	NaCl Found (Calc.)	Analyses % Found (Calculated)				Molecular Weight Found (Calc.)
		Na	$SbCl_5$	Ligands			Sb	n	S	-OPr^i	
1	 (1a)	0.35 (15.2)	0.91 (3.04)	0.95 (3.03) (L^1H_2)	$C_{25}H_{34}NO_6SSb$ Yellow Solid 90%	0.85 (0.89)	19.75 (19.95)	2.25 (2.29)	5.15 (5.25)	29.01 (29.04)	601.82 (610.38)
2	 (1b)	0.40 (17.40)	1.04 (3.48)	1.36 (3.47) (L^2H_2)	$C_{25}H_{33}NO_6SBrSb$ Dark yellow Solid 87%	1.01 (1.02)	17.52 (17.66)	2.01 (2.03)	4.60 (4.65)	25.50 (25.72)	675.14 (689.27)
3	 (1c)	0.42 (18.27)	1.09 (3.64)	1.27 (3.65) (L^3H_2)	$C_{25}H_{33}NO_6SClSb$ Yellow Solid 88%	1.02 (1.07)	18.51 (18.88)	2.14 (2.17)	4.85 (4.97)	27.12 (27.49)	640.04 (644.82)
4	 (1d)	0.39 (16.96)	1.01 (3.38)	1.16 (3.38) (L^4H_2)	$C_{26}H_{36}NO_7SSb$ Brown Solid 82%	0.98 (0.99)	18.91 (19.01)	2.15 (2.19)	4.99 (5.01)	27.23 (27.68)	628.78 (640.40)
5	 (1e)	0.47 (20.44)	1.22 (4.08)	1.34 (4.09) (L^4H_2)	$C_{26}H_{36}NO_6SSb$ Yellow Solid 86%	1.14 (1.19)	19.42 (19.50)	2.20 (2.24)	5.11 (5.14)	28.06 (28.39)	620.12 (624.40)

TABLE VI Synthetic and Analytical Data of the Complexes PhB(μ-O)$_2$Sb[SC$_6$H$_4$NC(R)CH:C(O)COOCH$_3$] [OPr^i], (2a–2e)

		Reagents g (mmol)		Molecular formula, Color, Physical state, and Yield (%)	Pr^{i}OH (g) Found (Calc.)	Analyses % Found (Calc.)				Mol. Wt. Found (Calc.)
S. No.	Complexes	(OPr^i)$_3$SbL	PhB(OH)$_2$			Sb	n	S	OPr^i	
1	 (2a)	1.5 (2.46) (1a)	0.30 (2.46)	C$_{26}$H$_{25}$NO$_6$SBSb Dark yellow Liquid 92%	0.29 (0.30)	19.71 (19.89)	2.21 (2.29)	5.18 (5.24)	9.55 (9.65)	602.12 (612.12)
2	 (2b)	2.31 (3.35) (1b)	0.41 (3.36)	C$_{26}$H$_{24}$NO$_6$SBBrSb Brown Liquid 93%	0.40 (0.40)	17.43 (17.62)	2.01 (2.03)	4.60 (4.64)	8.49 (8.55)	684.80 (691.01)
3	 (2c)	1.90 (2.95) (1c)	0.36 (2.95)	C$_{26}$H$_{24}$NO$_6$SBClSb Dark yellow Liquid 90%	0.36 (0.35)	18.61 (18.83)	2.11 (2.16)	4.88 (4.96)	9.04 9.14	640.56 (646.56)
4	 (2d)	1.78 (2.78) (1d)	0.34 (2.79)	C$_{27}$H$_{27}$NO$_7$SBSb Brown yellow Liquid 88%	0.32 (0.33)	18.78 (18.96)	2.15 (2.18)	4.89 (4.99)	9.12 (9.20)	632.39 (642.14)
5	 (2e)	2.15 (3.44) (1e)	0.42 (3.44)	C$_{27}$H$_{27}$NO$_6$SBSb Dark yellow Liquid 87%	0.40 (0.41)	19.34 (19.45)	2.18 (2.24)	5.06 (5.12)	9.40 (9.44)	622.79 (626.14)

each series is given. Synthetic and analytical data of the complexes are summarized in Tables V and VI.

Synthesis of $[OPr^{i}]_3Sb[(SC_6H_4NC(C_6H_5)CH{:}C(O)COOCH_3]$

A weighed amount of sodium metal (0.35 g, 15.2 mmol) was added to ~25 mL of well dried isopropanol, and the mixture was stirred for 1 h. A benzene solution of $SbCl_5$ (0.91 g, 3.04 mmol) was added dropwise. The mixture was refluxed for about 2 h. After cooling the solution, a benzene solution of ligand (0.95 g, 3.03 mmol) was added to it, and the mixture was refluxed again for 3–4 h. NaCl thus precipitated was filtered off, and volatile components were removed from filtrate at reduced pressure to yield a yellow colored solid compound with 90% yield, which was purified by dissolving the compound in benzene, and n-hexane was added to this clear solution until a precipitate begin to separate. The solution was heated to dissolve precipitate and cooled. A yellow solid compound was obtained, the solvent was decanted, and the compound was dried under reduced pressure.

Synthesis of $PhB\,(\mu\text{-}O)_2Sb[SC_6H_4NC(C_6H_5)CH{:}C(O)COOCH_3][OPr^{i}]$

A benzene solution (~20 mL) of the compound (**1a**) (1.5 g, 2.46 mmol) and a benzene solution of $PhB(OH)_2$(0.30 g, 2.46 mmol) (~20 mL) were mixed and the mixture was refluxed on a fractionating column for ~4 h. The liberated isopropanol was fractionated periodically as azeotrope with benzene and estimated to monitor the progress as well as completion of the reaction. After completion of reaction, the excess solvent was removed under reduced pressure, and for the purification, the compound was dissolved in benzene, and to this clear solution n-hexane was added until an oily layer of the compound begin to separate. This solution was cooled at low temperature. After decanting off the solvents, the compound was dried under reduced pressure to yield brownish-yellow colored viscous liquid in 92% yield.

REFERENCES

[1] U. Bemm, R. Norrestam, M. Nygren, and G. Westin, *Inorg. Chem.*, **31,** 2050 (1992).

[2] U. Bemm, R. Norrestam, M. Nygren, and G. Westin, *Inorg. Chem.*, **32,** 1597 (1993).

[3] G. Westin and M. Nygren, *J. Mater. Chem.*, **4,** 1275 (1994).

[4] U. Bemm, R. Norrestam, M. Nygren, and G. Westin, *Acta. Cryst.*, **C 51,** 1260 (1995).

[5] U. Bemm, R. Norrestam, M. Nygren, and G. Westin, *Inorg. Chem.*, **34,** 2367 (1995).

[6] A. M. Pohl, L. G. Westin, and M. Kritikos, *Chem. Eur. J.*, **7,** 3438 (2001).

[7] N. Y. Turova, *Russ. Che. Rev.*, **73**(11), 1041 (2004).
[8] T. Athar, R. Bohra, and R. C. Mehrotra, *Main Group Met. Chem.*, **10,** 39 (1987).
[9] T. Athar, R. Bohra, and R. C. Mehrotra, *Synth. React. Inorg. Met.-Org. Chem.*, **19,** 195 (1989).
[10] G. Westin and M. Nygren, *J. Mater. Sci.*, **27,** 1617 (1992).
[11] U. Bemm, K. Lashgari, R. Norrestam, M. Nygren, and G. Westin, *J. Solid State Chem.*, **103,** 366 (1993).
[12] U. Bemm, K. Lashgari, R. Norrestam, M. Nygren, and G. Westin, *J. Solid State Chem.*, **108,** 283 (1994).
[13] M. Veith, E.-C. Yu, and V. Huch, *Chem. Eur. J.*, **1,** 26 (1995).
[14] T. Athar, R. Bohra, and R. C. Mehrotra, *Ind. J. Chem.*, **28A,** 302 (1989).
[15] U. Bemm, R. Norrestam, M. Nygren, and G. Westin, *J. Solid State Chem.,* **134,** 312 (1997).
[16] M. Baier, P. Bissinger, J. Blumel, and H. Schmidbaur, *Chem. Ber.,* **126,** 947 (2006).
[17] T. B. Brill and N. C. Campbell, *Inorg. Chem.*, **12,** 1884 (1973).
[18] E. Maslowsky, Jr., *J. Organomet. Chem.*, **70,** 153 (1974).
[19] R. G. Goyal, E. Maslowsky, Jr., and C. R. Senoff, *Inorg. Chem.*, **10,** 2572 (1971).
[20] A. K. S. Gupta, R. Bohra, and R. C. Mehrotra, *Inorg. Chim. Acta.*, **170,** 191 (1990).
[21] G. O. Doak, G. G. Long, and L. D. Freedman, *J. Organomet. Chem.*, **4,** 82 (1965).
[22] N. B. Colthup, L. H. Daly, and S. E. Wiberby, *Inroduction to IR and Raman Spectroscopy*, 2nd ed., P335, Academic Press, New York (1975).
[23] T. Athar, R. Bohra, and R. C. Mehrotra, *J. Indian Chem. Soc.*, **67,** 535 (1990).
[24] M. P. Groziak, A. D. Ganguly, and P. D. Robinson, *J. Am. Chem. Soc.*, **116,** 7597 (1994).
[25] M. P. Hughes and B. D. Smith, *J. Org. Chem.*, **62,** 4492 (1997).
[26] D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd ed., Pergamon Press, New York (1980).
[27] D. Shanker, R. K. Sharma, J. Sharma, A. K. Rai, and Y. P. Singh, *Phosphorus, Sulfur, and Silicon*, **180,** 141 (2005).
[28] A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, 5th ed., Longmans, London (1989).
[29] D. C. Bradley, R. C. Mehrotra, and F. M. Abd-el-Halim, *J. Chem. Soc.*, 4609 (1952).