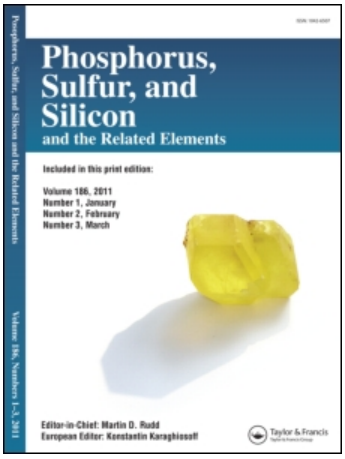

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Some Homo- and Hetero-Dinuclear Complexes of Antimony(III) Derived from Schiff Base Ligands

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Some Homo- and Hetero-Dinuclear Complexes of Antimony(III) Derived from Schiff Base Ligands

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The reactions of a series of bifunctional tridentate Schiff base ligands LH_2 *(*$R'C(NYOH)CHC(R)OH$*]* $R=R'=CH_3$, $Y=(CH_2)_2 L^1H_2$; $R=CH_3$, $R'=C_6H_5$, $Y=(CH_2)_2$ L^2H_2; $R=R'=CH_3$, $Y=(CH_2)_3$ L^3H_2; $R=CH_3$, $R'=C_6H_5$, $Y=(CH_2)_3$ L^4H_2 *with* $Sb(OPr^i)_3$ *in 2:1 molar ratio yield SbLLH (1a–1d) type of precursor derivatives. Reactions of these precursor derivatives with* $Sb(OPr^i)_3$ *and* $(Me_3Si)_2NH$ *in 1:1 and 2:1 molar ratio respectively yield new type of ligand bridged homo- (2a–2d) and hetero-(3a–3d) dinuclear derivatives respectively. These complexes have been characterized on the basis of elemental analyses, molecular weight measurements and a plausible structure has been suggested on the basis of spectral [IR,NMR{*^1H, ^{13}C, ^{29}Si*}] and FAB-mass studies.*

Keywords ^1H, ^{13}C, and ^{29}Si NMR; FAB Mass studies; homodinuclear and heterodinuclear compounds; Schiff base compounds of antimony

INTRODUCTION

In recent years, the chemistry of organoantimony(III) complexes has attracted considerable attention due to the striking structural possibilities ranging from discrete monomeric structures to supramolecular assemblies.[1–7] Although, alkoxobridged heterometallic derivatives of antimony[8–14] have been investigated, examples of ligand bridged homo- and hetero-dinuclear derivatives of antimony are rare.[15–17]

In addition, a great many possible applications in catalysis[18,19] and materials science can be foreseen for heterometal complexes.

In view of the above, we report herein for the first time the synthesis and spectroscopic characterization of a new series of ligand bridged homo- and hetero-dinuclear antimony(III) complexes.

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EXPERIMENTAL

All the experiments have been carried out under strictly anhydrous conditions. Solvents (E. Merck) have been dried by the literature method.[20] $Sb(OPr^i)_3$ was prepared by the method reported earlier.[21] Schiff bases (LH_2) were prepared by the equimolar condensation reactions of β-diketones and appropriate aminols.[22] Hexamethyl disilazane (Aldrich) has been distilled prior to use. Isopropyl alcohol in the azeotrope and isopropoxy group in the complexes was determined oxidimetrically.[23] Antimony was estimated iodometrically.[24] The ^1H (300 MHz), ^{13}C (300 MHz), and ^{29}Si (59.6 MHz) NMR spectra in $CDCl_3$ solution were recorded on JEOL FT Al 300 Spectrometer. ^1H and ^{13}C NMR spectra were recorded using TMS as internal reference and ^{29}Si NMR recorded using Me_3SiCl as external reference. IR spectra have been recorded as nujol mull, using KBr cells in the range 4000–400 cm^{-1} on FTIR spectrophotometer model 8400s Shimadzu. The FAB-mass spectra were recorded on a MICROMASS QUATTRO II triple quadruple mass spectrometer. C, H and N were analyzed on a Perkin Elmer-2400 C, H, N analyzer.

Since all the derivatives of each series (homo- and hetero- dinuclear) have been synthesized by similar methods, the synthesis of only one representative compound of each series is being discussed here and the synthetic and analytical data of rest of the compounds is summarized in Table I and II.

(a) Synthesis of SbL^1L^1H (1a)

The reaction mixture containing $Sb(OPr^i)_3$ (2.58 g, 8.63 mmol) and L^1H_2 (2.47 g, 17.26 mmol) in benzene was refluxed for ~20 h. The liberated Pr^iOH during this period was fractionated out azeotropically and determined periodically to monitor the progress and completion of the reaction. When the azeotrope showed the negligible amount of isopropanol, the reaction was stopped, and the excess solvent was removed under reduced pressure to obtain a brown viscous liquid compound. The compound was purified by dissolving it in benzene to get a clear solution. To this solution n-hexane was added slowly until an oily layer begins to separate. The solution was stored overnight at $-5^\circ C$. An oily layer is separated out, then the excess solvent was decanted and the compound was dried under reduced pressure. The analysis of SbL^1L^1H was found to have Sb, 29.11; C, 41.61; H, 5.59; N, 6.17 calculated for $C_{14}H_{23}SbN_2O_4$; Sb, 30.07; C, 41.52; H, 5.68; N, 6.92%.

TABLE I Synthetic and Analytical Data of the Complexes SbLLH (1a–1d)

S. No.	Reactants, g (mmol)		Empirical formula, color (yield) %	Pr^iOH found (Calcd.)	Analysis % found (Calcd.)				Mol.wt. found (Calcd.)
	$Sb(OPr^i)_3$	LH_2			Sb	C	H	N	
1a	2.58	2.47	$C_{14}H_{23}SbN_2O_4$ Brown	1.55	29.11	41.61	5.59	6.17	421.18
	(8.63)	(17.26)	Viscous Liquid (96.60)	(1.56)	(30.07)	(41.52)	(5.68)	(6.92)	(404.9)
1b	3.82	5.28	$C_{24}H_{27}SbN_2O_4$	2.27	22.18	54.42	5.00	4.93	490.29
	(12.84)	(25.7)	Reddish-Brown Viscous Liquid (93.63)	(2.32)	(23.01)	(54.48)	(5.10)	(5.29)	(529.0)
1c	4.24	4.45	$C_{16}H_{27}SbN_2O_4$ Brown	2.40	27.55	44.33	6.26	6.20	389.11
	(14.17)	(28.32)	Viscous Liquid (97.33)	(2.45)	(28.12)	(44.39)	(6.24)	(6.47)	(432.9)
1d	2.42	3.55	$C_{26}H_{31}SbN_2O_4$ Brown	1.40	20.25	54.15	5.32	4.13	551.81
	(8.09)	(16.18)	Viscous Liquid (97.15)	(1.46)	(21.1)	(54.12)	(5.37)	(4.85)	(577.1)

TABLE II Synthetic and Analytical Details of Compounds 2a–2d and 3a–3d.

Compound	Reactants, g		Empirical formula, color, physical state, yield (%)	Pr^iOH found (observed)	Analysis % found (Calcd.)					Mol. Wt. found (Calcd.)
	SbLLH	$Sb(OPr^i)_3$/ $(Me_3Si)_2NH$			Sb	OPr^i	C	H	N	
2a	1.05	0.77	$C_{20}H_{36}Sb_2N_2O_6$, Brown	0.13	37.82	18.35	33.09	5.41	4.35	668.91
	(2.59)	(2.58)	Viscous Liquid (95.76)	(0.15)	(37.45)	(18.54)	(33.22)	(5.45)	(4.08)	(643.83)
2b	1.35	0.76	$C_{30}H_{40}Sb_2N_2O_6$, Brown	0.14	31.88	15.07	47.28	5.29	3.21	750.11
	(2.57)	(2.57)	Viscous Liquid (80.99)	(0.15)	(31.71)	(15.39)	(46.91)	(5.21)	(3.65)	(767.97)
2c	1.12	0.77	$C_{22}H_{40}Sb_2N_2O_6$, Brown	0.14	36.59	17.21	39.84	5.68	4.40	683.88
	(2.58)	(2.57)	Viscous Liquid (97.91)	(0.15)	(36.24)	(17.59)	(39.32)	(5.95)	(4.17)	(671.90)
2d	1.28	0.66	$C_{32}H_{44}Sb_2N_2O_6$, Brown	0.12	28.11	14.06	47.81	5.14	3.28	825.75
	(2.21)	(2.22)	Viscous Liquid (98.99)	(0.13)	(29.84)	(14.48)	(47.09)	(5.39)	(3.43)	(816.04)
3a	1.17	0.23	$C_{17}H_{31}SbSiN_2O_4$, Brown	—	25.47	—	42.81	4.40	5.74	489.15
	(2.88)	(1.42)	Viscous Liquid (98.12)		(25.52)		(42.79)	(4.49)	(5.87)	(477.10)
3b	2.11	0.32	$C_{27}H_{35}SbSiN_2O_4$, Brown	—	20.09	—	53.84	5.77	4.71	591.84
	(3.98)	(1.98)	Viscous Liquid (97.47)		(20.25)		(53.93)	(5.82)	(4.66)	(601.24)
3c	1.12	0.20	$C_{19}H_{35}SbSiN_2O_4$, Brown	—	23.89	—	45.04	7.02	5.67	520.78
	(2.59)	(1.30)	Viscous Liquid (94.61)		(24.10)		(45.17)	(6.93)	(5.54)	(505.16)
3d	1.99	0.28	$C_{29}H_{39}SbSiN_2O_4$, Brown	—	18.84	–	53.51	5.94	4.24	675.47
	(3.44)	(1.73)	Viscous Liquid (98.17)		(18.75)		(53.64)	(6.01)	(4.31)	(649.30)

(b) Preparation of 2a

A benzene solution (~20 ml) of $Sb(OPr^i)_3$ (0.77 g, 2.58 mmol) was added to the benzene solution (~30 ml) of 1a (1.05 g, 2.59 mmol). The resulting reaction mixture was refluxed for ~10 h. The liberated isopropanol was fractionated off azeotropically and estimated. When the liberation of isopropanol ceased, the reaction was stopped and the solution was allowed to cool to room temperature. Removal of the excess solvent under reduced pressure yielded a brown viscous liquid compound. The compound was purified by benzene and n-hexane mixture. The analysis of 2a was found to have Sb, 37.82; OPr^i, 18.35; C, 33.09; H, 5.41; N, 4.35 calculated for $C_{20}H_{36}Sb_2N_2O_6$; Sb, 37.45; OPr^i, 18.54; C, 33.22; H, 5.45; N, 4.08%.

(c) Preparation of 3a

A benzene (~50 ml) solution of SbL^1L^1H (1.17 g, 2.88 mmol) and hexamethyldisilazane (0.23 g, 1.42 mmol) was refluxed for ~8 h, until the evolution of ammonia ceases. After the completion of the reaction, the excess solvent was removed under reduced pressure yielding brown viscous liquid complex 3a. The compound was purified by the similar method adopted for the purification of 2a. The analysis of 3a was found to have Sb, 25.47; C, 42.81; H, 4.40; N, 5.74 calculated for $C_{17}H_{31}SbSiN_2O_4$; Sb, 25.52; C, 42.79; H, 4.49; N, 5.87%.

RESULTS AND DISCUSSION

Reactions of $Sb(OPr^i)_3$ with $LH_2[R'C(NYOH)CHC(R)OH]$ in 1:2 molar ratio yield mononuclear precursor derivatives (1a–1d).

$$Sb(OPr^i)_3 + 2LH_2 \xrightarrow[\text{reflux}]{\text{benzene}} SbLLH + 3Pr^iOH \quad (1)$$

$LH_2 = L^1H_2$ {R = R' = CH_3, Y = $(CH_2)_2$} 1a,
$LH_2 = L^2H_2$ {R = CH_3, R' = C_6H_5, Y = $(CH_2)_2$} 1b,
$LH_2 = L^3H_2$ {R = R' = CH_3, Y = $(CH_2)_3$} 1c,
$LH_2 = L^4H_2$ {(R = CH_3, R' = C_6H_5, Y = $(CH_2)_3$} 1d.

Interactions of 1a–1d with $Sb(OPr^i)_3$ in equimolar ratio in benzene solution gave homodinuclear antimony complexes (2a–2d).

$$SbLLH + Sb(OPr^i)_3 \xrightarrow[\text{reflux}]{\text{benzene}} SbLLSb(OPr^i)_2 + Pr^iOH \quad (2)$$

Reactions of 1a–1d with hexamethyldisilazane in 2:1 molar ratio in refluxing benzene yield heterodinuclear derivatives of antimony with

silicon atom (3a–3d).

$$2\ \mathrm{SbLLH} + (\mathrm{Me_3Si})_2\mathrm{NH} \xrightarrow[\text{reflux}]{\text{benzene}} 2\mathrm{SbLLSiMe_3} + \mathrm{NH_3} \quad \uparrow \qquad (3)$$

L = L^1 = 2a & 3a, L = L^2 = 2b & 3b, L = L^3 = 2c & 3c, L = L^4 = 2d & 3d.

All these derivatives are brown viscous liquids, soluble in organic solvents and depict monomeric nature in benzene solution.

Spectral Studies

IR Spectra

The broad band for νOH present in the region 3200–3400 cm^{-1} in the spectra of 1a–1d disappears in the spectra of homo- and hetero-dinuclear derivatives (2a–2d and 3a–3d), respectively, and the formation of Sb-O bond and the coordination of C=N to Sb is supported by the appearance of bands in the region 550–585 cm^{-1} and 430–445 cm^{-1} (in the spectra of 1a–1d, 2a–2d, and 3a–3d) νSb–O[21,25] and νSb←N[26] respectively, and a shift of ~15 cm^{-1} in the position of νC=N (1610–1625 cm^{-1}). These bands show a smaller shift (10 cm^{-1}) towards lower wave number as compared to their position in the spectra of 1a–1d. The band observed in the region 865–872 cm^{-1} may be assigned to νSi–O[27] in the spectra of 3a–3d.

The band observed in the region 1575–1594 cm^{-1} in the spectra of 2a–2d and 3a–3d for νC–O shows a small shift towards lower wave number as compared their position in the spectra of 1a–1d.

New bands appearing in the region 990–1012 cm^{-1} (in the spectra of 2a–2d) and 1240 $\pm$ 10 (in the spectra of 3a–3d) may be attributed to νC–O of isopropoxy and ν(Si–Me) deformation, respectively.

^{1}H NMR Spectra

The characteristic signals in the spectra of 1a–1d, 2a–2d and 3a–3d are summarized in Tables III and IV.

Absence of –OH signal in the spectra of 1a–1d at δ 4.06–4.34 ppm indicates the deprotonation of hydroxy group of amino alcohol present in the ligand. Endic –OH group present at δ 10.76–11.47 ppm in the spectra of 1a–1d is found to be absent in the spectra of 2a–2d and 3a–3d, suggesting the formation of homo- and hetero-dinuclear derivatives.

Presence of two sets of signals for methine and methyl protons of ligand moiety in the spectra of 2a–2d and 3a–3d suggests the two different types of ligand environments (with small downfield shift as compared to 1a–1d). This may be explained by the fact that one ligand is attached to Sb only and another ligand bridges the two metals Sb and Si. One

TABLE III ^{1}H and ^{13}C NMR Spectra of New Complexes 1a–1d

Complex	^{1}H NMR	^{13}C NMR			
		C=O	C=N	Aromatic carbon	Alkylene carbon
1a	3.59–3.76 (t,2CH_2O), 3.25–3.44 (t,2CH_2N), 5.14 (s,CHCO), 5.10 (s, C**H**COH), 2.10 (s, CH_3CO), 2.00 (s, 2CH_3CN), 1.90 (s, C**H**$_3$COH), 10.89 (CH_3CO**H**)	194.32, 192.78	163.47, 162.28	—	95.34 (**C**HCO), 95.12 (**C**HCOH), 65.89–65.11 (CH_2O), 61.12 (CH_2N), 28.71 (**C**H$_3$CO), 25.45 (**C**H$_3$CN), 19.03 (**C**H$_3$COH)
1b	3.71–3.72 (t, 2CH_2O), 3.26–3.46 (t, 2CH_2N), 5.78 (s, CHCO), 5.61 (s, C**H**COH), 2.13 (s, CH_3CO), 2.01 (s, C**H**$_3$COH), 7.33–8.03 (m, 2C_6H_5), 11.49 (s, CH_3CO**H**)	190.15, 189.71	164.89, 163.58	125.75–130.11	91.15 (**C**HCO), 91.01 (**C**HCOH), 63.25 (CH_2O), 59.19 (CH_2N), 28.15 (**C**H$_3$CO), 25.01 (**C**H$_3$CN), 18.19 (**C**H$_3$COH)
1c	3.57–3.74 (t, 2CH_2O), 3.39–3.41 (m, 2C**H**$_2$$CH_2O$), 3.35–3.37 (t, 2$CH_2N$), 4.97 (s, CHCO), 4.94 (s, C**H**COH), 2.08 (s, CH_3CO), 2.03 (s, 2CH_3CN), 1.84 (s, C**H**$_3$COH), 10.89 (s, CH_3CO**H**)	190.79, 189.15	160.96, 161.71	—	93.15(**C**HCO), 92.69 (**C**HCOH), 62.89 (CH_2O), 61.71 (**C**H$_2$$CH_2O$) 59.25 ($CH_2N$), 28.15 (**C**H$_3$CO), 26.64 (**C**H$_3$CN), 16.82 (**C**H$_3$COH)
1d	3.62–3.67 (t, 2CH_2O), 3.43–3.50 (m, 2C**H**$_2$$CH_2O$), 3.20–3.27 (t,2$CH_2N$), 5.69 (s, CHCO), 5.66 (s, C**H**COH), 2.07 (s, CH_3CO), 1.84 (s, C**H**$_3$COH), 7.33–7.82 (m, 2C_6H_5), 11.43 (s, CH_3CO**H**)	186.12, 184.82	163.87, 163.15	125.14–128.79	91.01 (**C**HCO), 90.02 (**C**HCOH), 62.17 (CH_2O), 61.81 (**C**H$_2$$CH_2O$), 56.72 ($CH_2N$), 31.36 (**C**H$_3$CO), 29.15 (**C**H$_3$CN), 17.77 (**C**H$_3$COH)

TABLE IV ^{1}H, ^{13}C and ^{29}Si NMR Spectra of New Complexes 2a–2d and 3a–3d

Complex	^{1}H NMR	^{13}C NMR				^{29}Si NMR
		C=O	C=N	Aromatic carbon	Alkylene carbon	
2a	3.44–3.46(t, 2C**H**$_2$O), 3.40–3.42 (t, 2CH$_2$N), 4.97(s, CHCO), 4.91 (s, CHCOSb), 3.90–3.98 (septet, 2OC**H**(CH$_3$)$_2$), 1.18–1.21 (d, 2OCH(C**H**$_3$)$_2$, 1.98 (s, CH$_3$CO), 1.96 (s, 2CH$_3$CN)	190.79, 189.75	164.89, 163.15	—	93.05 (**C**HCO), 92.78 (**C**HCOSb), 63.25 (CH$_2$O), 62.89 (CH$_2$N), 59.25 (O**C**H(CH$_3$)$_2$), 29.17 (**C**H$_3$CO), 25.47 (**C**H$_3$CN), 25.88 (OCH(**C**H$_3$)$_2$), 19.75 (**C**H$_3$COSb)	—
2b	3.79–3.83 (t, 2CH$_2$O), 3.45–3.51 (t, 2CH$_2$N), 5.68 (s, CHCO), 5.47 (s, CHCOSb), 4.0–4.04(septet, 2OC**H**(CH$_3$)$_2$), 1.19–1.21 (d, 2OCH(C**H**$_3$)$_2$), 2.08 (s, CH$_3$CO), 2.06 (s, CH$_3$COSb), 7.26–7.86 (m, 2C$_6$H$_5$)	186.92, 186.48	165.32, 164.98	126.68–130.27	91.95 (**C**HCO), 91.27 (**C**HCOSb), 63.28 (CH$_2$O), 60.98 (CH$_2$N), 59.47 (O**C**H(CH$_3$)$_2$), 31.13 (**C**H$_3$CO), 25.31 (OCH(**C**H$_3$)$_2$), 19.58 (**C**H$_3$COSb)	—
2c	3.83–3.91 (t, 2CH$_2$O), 3.61–3.64 (m, 2C**H**$_2$CH$_2$O), 3.36–3.55 (t, 2CH$_2$N), 5.04 (s, CHCO), 5.0 (s, CHCOSb), 3.93–3.99 (septet, 2OC**H**(CH$_3$)$_2$), 2.16 (s, CH$_3$CO), 1.17–1.20 (d,2OCH(C**H**$_3$)$_2$), 1.96 (s, 2CH$_3$CN), 1.89 (s, CH$_3$COSb)	188.75, 187.91	164.55, 164.08	—	91.81 (**C**HCO), 91.46 (**C**HCOSb), 65.94 (CH$_2$O), 65.60 (**C**H$_2$CH$_2$O), 65.17 (CH$_2$N), 58.80 (O**C**H(CH$_3$)$_2$), 31.85 (**C**H$_3$CO), 25.11 (**C**H$_3$CN), 24.85 (OCH(**C**H$_3$)$_2$), 18.74 (**C**H$_3$COSb)	—
2d	3.97–3.99 (t, 2CH$_2$O), 3.51–3.55 (m, 2C**H**$_2$CH$_2$O), 3.46–3.49 (t, 2CH$_2$N), 5.67 (s, CHCO), 5.65 (s, CHCOSb), 4.0–4.04 (septet, 2OC**H**(CH$_3$)$_2$), 1.18–1.23 (d, 2OCH(C**H**$_3$)$_2$), 2.09 (s, CH$_3$CO), 2.01 (s, CH$_3$COSb), 7.27–7.86 (m, 2C$_6$H$_5$)	186.76, 186.02	164.55, 164.21	126.29–129.81	91.46 (**C**HCO), 91.28 (**C**HCOSb), 65.94 (CH$_2$O), 65.17 (**C**H$_2$CH$_2$O), 63.24 (CH$_2$N), 58.36 (O**C**H(CH$_3$)$_2$), 31.85 (**C**H$_3$CO), 25.11 (OCH(**C**H$_3$)$_2$), 18.77 (**C**H$_3$COSb)	—

3a	3.70–3.89 (t, $2CH_2O$), 3.66–3.68 (t, $2CH_2N$), 4.99 (s, CHCO), 4.97 (s, CHCOSi), 2.11 (s, CH_3CO), 2.01 (s, CH_3CN), 1.97 (s, CH_3COSi), 0.08–0.11 (s, $OSi(CH_3)_3$)	195.45, 195.26	164.23, 163.77	—	96.36 (**C**HCO), 96.16 (**C**HCOSi), 62.22 (CH_2O), 61.65 (CH_2N), 29.46 ($\mathbf{C}H_3CO$), 26.00 ($\mathbf{C}H_3CN$), 19.70 ($\mathbf{C}H_3COSi$), 2.68 ($OSi(CH_3)_3$)	22.71
3b	3.94–3.98 (t, $2CH_2O$), 3.65–3.69 (t, $2CH_2N$), 5.53 (s, CHCO), 5.52 (s, CHCOSi), 2.02 (s, CH_3CO), 1.98 (s, CH_3COSi), 0.06–0.18 (s, $OSi(CH_3)_3$), 7.19–7.74 (m, $2C_6H_5$)	187.49, 187.31	164.87, 164.80	126.66–130.21	92.22 (**C**HCO), 92.17 (**C**HCOSi), 61.87 (CH_2O), 60.78 (CH_2N), 25.49 ($\mathbf{C}H_3CO$), 19.38 ($\mathbf{C}H_3COSi$), 1.87 ($OSi(CH_3)_3$)	20.18
3c	3.65–3.73 (t, $2CH_2O$), 3.40–3.42 (m, $2C\mathbf{H}_2CH_2O$), 3.33–3.38 (t, $2CH_2N$), 5.08 (s, CHCO), 4.96 (s, CHCOSi), 2.02 (s, CH_3CO), 2.0 (s, $2CH_3CN$), 1.91 (s, CH_3COSi), 0.04–0.11 (s, $OSi(CH_3)_3$)	193.97, 193.84	163.37, 162.94	—	94.99 (**C**HCO), 94.02 (**C**HCOSi), 58.90 (CH_2O), 58.37 ($\mathbf{C}H_2CH_2O$), 58.05 (CH_2N), 32.94 ($\mathbf{C}H_3CO$), 28.63 (CH_3CN), 18.68 (CH_3COSi), 2.47 ($OSi(CH_3)_3$)	21.57
3d	3.59–3.63 (t, $2CH_2O$), 3.55–3.57 (m, $2C\mathbf{H}_2CH_2O$), 3.30–3.32 (t, $2CH_2O$), 5.74 (s, CHCO), 5.54 (s, CHCOSi), 2.13 (s, CH_3CO), 1.95 (s, CH_3COSi), 0.07–0.19 (s, $OSi(CH_3)_3$), 7.23–7.93 (m, $2C_6H_5$)	187.86, 187.76	165.98, 165.84	127.33–130.88	92.49 (**C**HCO), 92.02 (**C**HCOSi), 59.67 (CH_2O), 59.46 ($\mathbf{C}H_2CH_2O$), 59.01 (CH_2N), 33.32 ($\mathbf{C}H_3CO$), 19.90 ($\mathbf{C}H_3COSi$), 2.44 ($OSi(CH_3)_3$)	21.87

set of signals appeared as doublet ($CH(CH_3)_2$) and as septet ($CH(CH_3)_2$) at δ1.17–1.23 and 3.90–4.04 ppm, respectively, for isopropoxy group[16] in the spectra of 2a–2d showing the presence of only one type of isopropoxy group. $(CH_3)_3Si$ protons appear as singlet at δ 0.04–0.19 ppm in the spectra of 3a–3d.

^{13}C NMR Spectra

In the ^{13}C NMR spectra (Table IV) of 2a–2d and 3a–3d exhibit two sets of signals for each of the C—O (δ 186.92–195.45 and 186.02–195.26 ppm) and CH=C (δ 91.46–96.36 and 91.27–96.16 ppm) groups, which is consistent with the presence of two different ligand environment and two metals. These signals appeared with small downfield shift as compared to its position as in the spectra of 1a–1d.

The signals in the region (δ 163.37–165.95 and 162.94–165.84 ppm) have been observed for C=N in the spectra of 2a–2d and 3a–3d with small downfield shift as compared to its position in the spectra of 1a–1d, suggesting the involvement of C=N group in coordination.

The signals for carbons of isopropoxy group $CH(CH_3)_2$ and $CH(CH_3)_2$ in the spectra of 2a–2d have been observed in the region δ 58.36–59.47 and 24.85–25.88 ppm, respectively. Presence of only one set of signals supports the presence of only one type of isopropoxy group in the homodinuclear complexes. The signal for $Si(CH_3)_3$has been observed in the region δ 1.87–2.68 ppm in the spectra of 3a–3d.

^{29}Si NMR Spectra

^{29}Si NMR signal in the spectra of compounds (3a–3d) is observed in the range δ 20.18–22.71 ppm. Presence of ^{29}Si signal in this range

TABLE V Fragmentation Mode of $C_6H_5(NCH_2CH_2O)\overline{CHC(CH_3)OSbO}$-$CH_2CH_2NC(C_6H_5)CHC(CH_3)OSb(OCH(CH_3)_2)_2$ (2b)

Complex	m/e
$C_6H_5C(\overline{NCH_2CH_2O)CHC(CH_3}\overline{)}OSbOCH_2CH_2NC(C_6H_5)CHC(CH_3)OSb(OCH(CH_3)_2)_2$	767
$C(\overline{NCH_2CH_2O)CHC(CH_3}\overline{)}OSbOCH_2CH_2NC(C_6H_5)CHC(CH_3)OSb(OCH(CH_3)_2)_2$	690
$C(\overline{NCH_2CH_2O)CHC}OSbOCH_2CH_2NC(C_6H_5)CHC(CH_3)OSb(OCH(CH_3)_2)_2$	675
$C(\overline{NCH_2CH_2O)CH}SbOCH_2CH_2NC(C_6H_5)CHC(CH_3)OSb(OCH(CH_3)_2)_2$	647
$NCH_2CH_2OSbOCH_2CH_2NC(C_6H_5)CHC(CH_3)OSb(OCH(CH_3)_2)_2$	622
$CH_2OSbOCH_2CH_2NC(C_6H_5)CHC(CH_3)OSb(OCH(CH_3)_2)_2$	594
$CH_2OSbOCH_2CH_2NC(C_6H_5)CHCOSb(OH)(OCH(CH_3)_2)$	537
$CH_2OSbOCH_2CH_2NC(C_6H_5)CHCOSb(OH)_2$	495
$CH_2OSbOCH_2CH_2NCCHCOSb$	384
Sb_2O_3	293
SbO_2	156

TABLE VI Fragmentation Mode of $C_6H_5(NCH_2CH_2O)CHC(CH_3)$-$OSbOCH_2CH_2NC(C_6H_5)CHC(CH_3)OSi(OCH(CH_3)_2)_2$(3b)

Complex	m/e
$C_6H_5C(NCH_2CH_2O)CHC(CH_3)OSbOCH_2CH_2NC(C_6H_5)CHC(CH_3)OSi(CH_3)_3$	602
$C_6H_5C(NCH_2CH_2O)CHC(CH_3)OSbOCH_2CH_2NC(C_6H_5)CHC(CH_3)OSi$	557
$C_6H_5C(NCH_2CH_2O)CHC(CH_3)OSbOCH_2CH_2NC(C_6H_5)CHC(CH_3)O$	529
$C_6H_5C(NCH_2CH_2O)CHC(CH_3)OSbOCH_2CH_2NC(C_6H_5)CH$	486
$C_6H_5C(NCH_2CH_2O)CHC(CH_3)OSbOCH_2CH_2N$	384
$C_6H_5C(NCH_2CH_2O)CHC(CH_3)OSbOCH_2$	356
$C(NCH_2CH_2O)CHC(CH_3)OSbOCH_2$	279
$C(NCH_2CH_2O)CHC(CH_3)SbOCH_2$	263
$C(NCH_2CH_2O)CHC(CH_3)Sb$	233
$C(NCH_2CH_2O)CHSb$	206
$C(NCH_2CH_2O)CH$	85

indicates the presence of tetracoordinated Silicon atom[28,29] in these compounds.

FAB-Mass Spectra

FAB-Mass spectra of two compounds (one from each series) of the homodinuclear compound (2b) and heterodinuclear compound (3b) has been recorded which shows the monomeric nature of these compounds. The mass spectral fragmentation pattern of compound 2b and 3b is summarized in Tables V and VI, respectively.

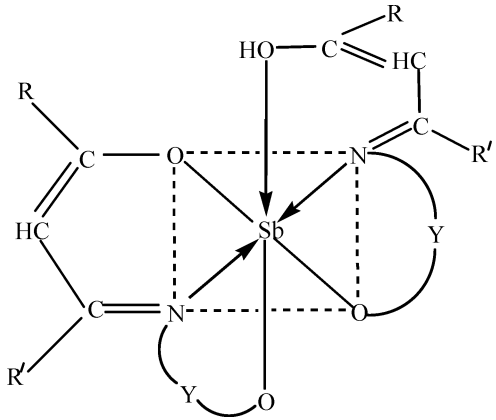

FIGURE 1 Proposed structure for 1a–1d .

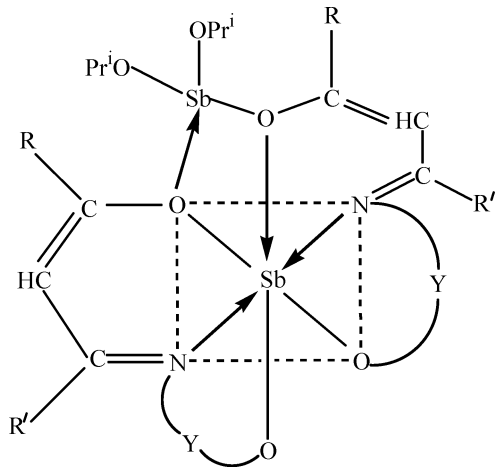

FIGURE 2 Proposed structure for 2a–2d.

In view of the bifunctional tridentate ligand and hexacoordinated antimony Fig. 1 for 1a–1d and presence of hexa and tetracoordinated antimony Fig. 2 for 2a–2d and on the basis of spectral studies, hexacoordinated antimony and tetracoordinated silicon atom Fig. 3 for 3a–3d may be proposed.

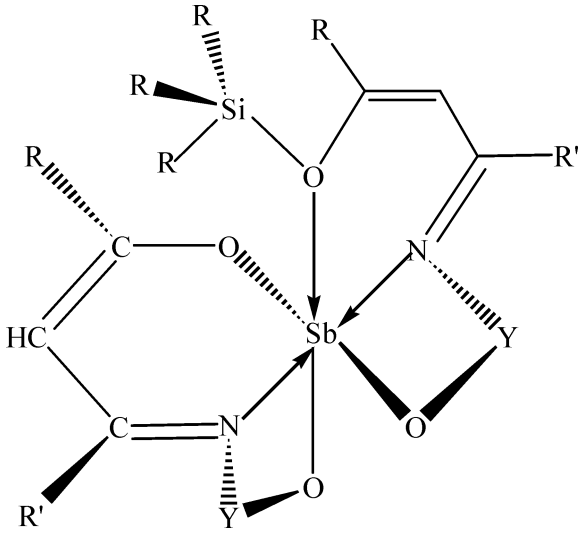

FIGURE 3 Proposed Structure for 3a–3d.

REFERENCES

[1] H. J. Breunig and R. Rösler, *Coord. Chem. Rev.*, **163,** 33 (1997).
[2] H. J. Breunig and R. Rösler, *Chem. Soc. Rev.*, **29,** 403 (2000).
[3] B. Ross, J. Belz, and M. Niger, *Chem. Ber.*, **123,** 975 (1990).
[4] R. E. DesEnfants, II, J. A. Gavney, Jr., R. K. Hayashi, A. D. Rae, L. F. Dahl, and A. Bjarnason, *J. Organomet. Chem.*, **383,** 543 (1990).
[5] A. Gutpa, R. K. Sharma, R. Bohra, V. K. Jain, J. E. Drake, M. B. Hursthouse, and M. E. Light, *Polyhedron*, **21,** 2387 (2002).
[6] S. Eller, S. Dülsen, and R. D. Fischer, *J. Organomet. Chem.*, **390,** 309 (1990).
[7] M. Nunn, M. J. Begley, and D. B. Sowerby, *Polyhedron*, **15**(19), 3167 (1996).
[8] N. Tempel, W. Schwarz, and J. Weidlein, *Z. Anorg. Allgem Chem.*, **474,** 157 (1981).
[9] H. Fleischer, H. Bayran, S. Elzner, and N. W. Mitzel, *J. Chem. Soc., Dalton Trans.*, 373 (2001).
[10] A. K. Sen Gupta, R. Bohra, and R. C. Mehrotra, *Indian J. Chem.*, **31A,** 23 (1992).
[11] T. Athar, R. Bohra, and R. C. Mehrotra, *Indian J. Chem.*, **28A,** 302 (1989).
[12] T. Athar, R. Bohra, and R. C. Mehrotra, *Main Group Met. Chem.*, **10,** 399 (1987).
[13] T. Athar, R. Bohra, and R. C. Mehrotra, *Synth. React. Inorg. Met.-Org.Chem.*, **19,** 195 (1989).
[14] S. M. Biros, B. M. Bridgewater, A. E. Villages, J. M. Tanski, and G. Perkin, *Inorg. Chem.*, **41,** 4051 (2002).
[15] M. E. Gress and R. A. Jacobson, *Inorg. Chim. Acta*, **8,** 209 (1974).
[16] N. B. Sharma, R. S. Ghadwal, A. Singh, and R. C. Mehrotra, *Heteroatom Chemistry*, in press (2007).
[17] S. Arnold, V. Mansel, and G. Klar, *Z. Naturforsch, B : Chem. Sci.*, **45,** 369 (1990).
[18] D. L. Mckay and Fr. Demande, 2, 363, 207 (1978); *Chem. Abstr.*, **90,** 41,172 (1979).
[19] G. H. Dale and D. L. Mckay, *Hydrocarbon Process*, 97 (1977).
[20] D. D. Perrin, W. L. F. Armarege, and D. R. Perrin, *Purification of Laboratory Chemicals;* Pergamon Press: Oxford, U.K. (1986).
[21] T. B. Brill and N. C. Campbell, *Inorg. Chem.*, **12,** 1884, (1973).
[22] J. P. Tandon and H. B. Singh, *Synth. React. Inorg. Met.-Org. Chem.*, **7,** 547 (1977).
[23] D. C. Bradley, F. M. A. Halim, and W. J. Wardlaw, *J. Chem Soc.*, 3450 (1950).
[24] A. I. Vogel, *A Text Book of Quantitative Chemicals Analysis;* Longman: London (1998).
[25] H. A. Meinema and J. G. Noltes, *J. Organomet. Chem.*, **25,** 139 (1970).
[26] G. N. Chremos and R. A. Zingaro, *J. Organomet. Chem.*, **22,** 647 (1970).
[27] A. Marchand and J. Valade, *J. Organomet. Chem.*, **12,** 305 (1968).
[28] R. C. Mehrotra and P. Bajaj, *J. Organomet. Chem.*, **22,** 41 (1971).
[29] M. Goyal, S. Mishra, and A. Singh, *Phosphorous, Sulphur, Silicon and Related Elements*, **175,** 143 (2001).