Preparation and characterisation of new types of metallic- and heterodimetallic–butyltin glycolates

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Reactions of $BuSn(OPr^i)_3$ with two equivalents of a number of glycols (HOGOH, where G = CMe_2CMe_2, CH(Me)CH(Me), CMe_2CH_2CHMe, and $CMe_2CH_2CH_2CMe_2$), with varying steric bites yield metallic glycolate complexes (**1**), (**2**), (**3**), and (**4**) with one residual hydroxy group; these on reacting with $Al(OPr^i)_3$ and $Nb(OPr^i)_5$ in a 1:1 molar ratio yield interesting heterodimetallic compounds of the general formulae $BuSn(OGO)_2Al(OPr^i)_2$ and $BuSn(OGO)_2Nb(OPr^i)_4$. All of these derivatives have been characterised by elemental analyses, spectroscopic (IR; NMR: ^1H, ^{27}Al, and ^{119}Sn) studies and molecular weight determinations.

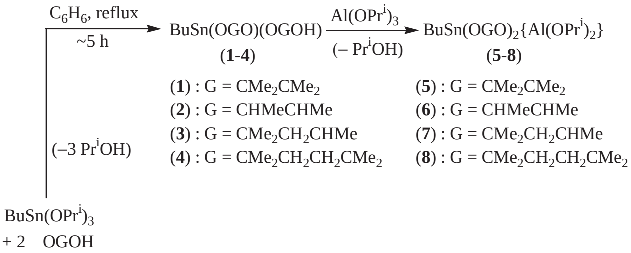
Keywords: heterodimetallic glycolates, butyltin glycolates, glycolate complexes

Mixtures of metal alkoxides, in general, and heterometallic alkoxides in particular have been found to be excellent precursors for the synthesis of novel oxide-ceramic materials via the sol-gel process.[1-6] During 1980 to 2000, work on heterometallic alkoxide systems was centred around chelating alkoxometallate ligands[5-13] such as $Al(OPr^i)_4^-$, $Nb(OPr^i)_6^-$, $Ta(OPr^i)_6^-$, $Zr_2(OPr^i)_9^-$, and $Sn_2(OPr^i)_9^-$. However, recently heterometallic alkoxides of a novel variety have been synthesised by treating the products obtained from the reactions between excess of glycols with metals like Ba, Mg, Ca and Sr[14] and alkoxides of other metals such as Al[14] and Nb.[15] This paper reports for the first time the results of investigations on similar homo and heterometallic glycolate derivatives based on an organometallic moiety like butyltin(IV).

The homometallic derivatives of the type BuSn(OGO)(OGOH) have been synthesised by the 2 : 1 reactions of glycols with $BuSn(OPr^i)_3$, which was successfully[16-17] synthesised for the first time in our laboratories by the simple metathetic 1 : 3 reaction of $BuSnCl_3$ with $NaOPr^i$ in benzene.

Results and discussion

Reactions of $BuSn(OPr^i)_3$ with glycols in 1 : 2 molar ratio in benzene afford soluble derivatives, which on heating with $Al(OPr^i)_3$ and $Nb(OPr^i)_5$ in a 1:1 molar ratio afford heterometallic butyltin glycolate-isopropoxide derivatives according to the Scheme 1.



Scheme 1

For testing the generality of the latter type of reactions yielding heterometallic products (**5–8**), (**1**) was reacted with $Nb(OPr^i)_5$ also in 1:1 molar ratio, yielding the product $[BuSn(OCMe_2CMe_2O)OCMe_2CMe_2ONb\text{-}(OPr^i)_4]$ (**9**).

An interesting feature of homoleptic glycolates is that (**1**) and (**2**) on attempted distillation under reduced pressure liberated free glycol along with a bis(butyltin)trisglycolate derivative, whereas the heterobimetallic analogues (**5**) and (**6**) prepared from undistilled (**1**) and (**2**) are stable molecules which distilled *in vacuo* unchanged in analysis.

All these colourless, moisture-sensitive new complexes (**1-9**) are soluble in common organic solvents (*e.g.*, C_6H_6, CH_2Cl_2, $CHCl_3$, CCl_4, THF, *etc.*). The molecular weight determinations (cryoscopically in benzene) of freshly prepared samples of (**1**)–(**9**) show that they are monomeric in solution. However, all of these exhibit a tendency to dimerisation and/or higher molecular association on aging. The increase in molecular complexity of the aged samples is a common feature in metal alkoxides.[6]

Spectral studies: IR studies on derivatives (**1**)–(**4**) exhibit important IR absorptions (Table 1) at 3000–2940m ν(O–H), 1080–1000m ν(C–O), 590–580m and 520–510m ν(Sn–C), and 558–573m ν(Sn–O) cm^{-1}. Heterodimetallic derivatives (**5**)–(**9**) exhibit absorptions at 1175–1125s $\nu(OPr^i)$, 1080–1000m ν(C–O), 680–610m ν(Al–O), 580m ν(Nb–O), 590–570m and 539–510m ν(Sn–C), and 575–560m ν(Sn–O) cm^{-1}; the appearance of two ν(Sn–C) bands (Table 1) for derivatives (**1**) to (**9**) may be ascribed to conformational isomers as reported[18] earlier also.

^1H NMR spectra (δ, ppm) (Table 1) of (**1**)–(**9**) exhibit complex multiplets due to BuSn protons in the region: 0.90–1.70. The derivatives (**1**)–(**4**) show a broad peak at 1.99–3.19 due to the residual OH group. The heterodimetallic derivatives (**5**)–(**9**) exhibit characteristic signals of butyltin and glycolate moieties (Table 1) as well as a doublet and a multiplet for methyl and methine protons of the isopropoxy groups at 1.20–1.28 and 4.06–4.35, respectively.

The appearance of ^{27}Al NMR (δ, ppm) signals for derivatives (**5**)–(**8**) in the range 33–60 is consistent with four-coordinate[19] aluminium (Fig. 1).

Freshly prepared derivatives (**1**) to (**4**) exhibit two sharp ^{119}Sn NMR signals almost in equal (9 : 10) relative intensities at: δ –336.7/–351.2, –336.5/–352.9, –347.73/–367.46, and –332.67/–342.76, respectively. The appearance of two signals is likely to be due to the presence of two penta-coordinate[20] species arising from the butyl group occupying equatorial as well as axial positions. Derivatives (**5**),(**6**),(**7**), and (**8**), when freshly prepared, exhibit sharp signals at δ –345 ± 10 which support the structural formulation shown in Fig. 1, with Sn(IV) in a five-coordinate environment.

It is worth mentioning that the aged samples of (**5**)–(**8**) show an additional ^{119}Sn NMR signal at *ca* δ — 450, indicating structural variation and the adoption of an octahedral environment around the central tin atom.

Experimental

All manipulations were performed under a moisture-free environment. Benzene and *n*-hexane (Qualigenes, India) were dried by refluxing over sodium benzophenone ketyl and distilled prior to use. Isopropyl alcohol (S.d. fine, India) was made anhydrous by

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Table 1 IR (cm^{-1}) and NMR (^1H, ^{119}Sn and ^{27}Al) (δ, ppm) spectral studies of metallic- and heterodimetallic derivatives of butyltin glycolates

Compound no.	ν(OH)	ν(OPr^i)	ν(C–O)	ν(Al–O)	ν(Sn–C)	ν(Sn–O)	^1H	^{119}Sn	^{27}Al
1	2900s	–	1080m	–	510m, 590m	566m	^{1}**H** : 0.92 (m, 3H, $Sn(CH_2)_3\mathbf{Me}$); 1.28 (s, 24H, $C\mathbf{Me}_2$); 1.60 (br, 6H, $Sn(C\mathbf{H}_2)_3CH_3$); 1.99 (br, 1H, O**H**)	–336.7 –351.2	–
2	2950s	–	1049m	–	512m, 580m	570m	^{1}**H** : 0.90 (m, 3H, $Sn(CH_2)_3\mathbf{Me}$); 1.16 (d, 12H, HC**Me**); 1.68 (br, 6H, $Sn(C\mathbf{H}_2)_3Me$); 3.20 (br, 1H, O**H**); 3.75 (br, 4H, C**H**Me)	–336.5 –352.9	–
3	2960s	–	1055m	–	510m, 590m	575m	^{1}**H** : 0.91-1.00 (m, 3H, $Sn(CH_2)_3\mathbf{Me}$); 1.19 (s, 6H, $C\mathbf{Me}_2$); 1.25 (s, 6H, $C\mathbf{Me}_2$); 1.30 (d (J = 6.11 Hz); 6H, CH**Me**); 1.55-1.59 (m, 10H, $Sn(C\mathbf{H}_2)_3Me+C\mathbf{H}_2$); 3.19 (br, 1H, O**H**); 4.24 (m, 2H, $C\mathbf{H}Me_2$)	–347.73 –367.46	–
4	3000s	–	1040m	–	520m, 580m	558m	^{1}**H** : 0.95-1.10 (m, 3H, $Sn(CH_2)_3\mathbf{Me}$); 1.26 (s, 24H, $C\mathbf{Me}_2$); 1.59(br, 6H, $Sn(C\mathbf{H}_2)_3Me$); 1.65 (s, 8H, $C\mathbf{H}_2$); 2.18 (br, 1H, O**H**)	–332.67 –342.76	–
5	–	1125m, 1166m	1049m	617m	539m, 570m	560m	^{1}**H** : 0.93 (m, 3H, $Sn(CH_2)_3\mathbf{Me}$); 1.23 (m, 36H, $C\mathbf{Me}_2$ + $CH\mathbf{Me}_2$); 1.65 (br, 6H, $Sn(C\mathbf{H}_2)_3Me$); 4.28 (m, 2H, C**H** Me_2)	–352.3	33
6	–	1130m, 1155m	1005m	625m	520m, 585m	570m	^{1}**H** : 0.93 (m, 3H, $Sn(CH_2)_3\mathbf{Me}$); 1.20 (br, 24H, CH**Me** + $CH\mathbf{Me}_2$); 1.68 (br, 6H, $Sn(C\mathbf{H}_2)_3Me$); 3.48 (br, 4H, $C\mathbf{H}Me_2$); 4.05 (m, 2H, $C\mathbf{H}Me_2$)	–353.4	36
7	–	1133m, 1166m	1066m	616m	515m, 583m	575m	^{1}**H** : 0.92 (m, 3H, $Sn(CH_2)_3\mathbf{Me}$); 1.10-1.40 (m, 30H, $C\mathbf{Me}_2$ + CH**Me** + $CH\mathbf{Me}_2$); 1.50 (br, 4H, $C\mathbf{H}_2$); 1.70 (br, 6H, $Sn(C\mathbf{H}_2)_3Me$); 4.35(br, 4H, C**H**Me + $C\mathbf{H}Me_2$)	–355.33	33
8	–	1110m, 1175m	1078m	650m	510m, 590m	560m	^{1}**H** : 0.95 (m, 3H, $Sn(CH_2)_3\mathbf{Me}$); 1.15-1.28 (m, 36H, $C\mathbf{Me}_2+CH\mathbf{Me}_2$); 1.50 (br, 8H, $C\mathbf{H}_2$); 1.64 (br, 6H, $Sn(C\mathbf{H}_2)_3Me$); 4.31 (m, 2H, $C\mathbf{H}Me_2$)	–340.1	59
9	–	1110m, 1160m	1040m	572m ν(Nb-O)	515m, 590m	568m	^{1}**H** : 0.92 (m, 3H, $Sn(CH_2)_3\mathbf{Me}$); 1.25 (br, 48H, $C\mathbf{Me}_2+CH\mathbf{Me}_2$); 1.65 (br, 6H, $Sn(C\mathbf{H}_2)_3Me$); 4.18 (m, 4H, $C\mathbf{H}Me_2$)	–319.98	–

Table 2 Preparative and analytical details of metallic- and heterodimetallic derivatives of BuSn(IV)

	Reactants (g, mmol)	Liberated Pr^iOH Found (Calcd.)	Product B.p.[a]/°C/mm; colour and state yield[b]/g, (%)	Analysis Found (Calcd.) %				Mol. Wt.[d] Found (Calcd.)
				Sn	Al	C	H	
$BuSn(OPr^i)_3$	$HOCMe_2CMe_2OH$	2.43	$BuSn(OCMe_2CMe_2O).(OCMe_2CMe_2OH)$ (**1**)	28.98	–	46.77	8.67	430
(4.81, 13.62)	(3.22, 27.25)	(2.45)	Colourless waxy solid 4.55, (99)[c]	(29.00)		(46.96)	(8.37)	(409)
$BuSn(OPr^i)_3$	HOCHMeCHMeOH	2.18	BuSn(OCHMeCHMeO)(OCHMeCHMeOH) (**2**)	33.10	–	39.96	7.25	367
(4.31, 12.20)	(2.20, 24.41)	(2.20)	White solid 4.25, (99)[c]	(33.62)		(40.82)	(7.42)	(353)
$BuSn(OPr^i)_3$	$HOCMe_2CH_2CHMeOH$	2.90	$BuSn(OCMe_2CH_2CHMeO)(OCMe_2CH_2CHMeOH)$ (**3**)	28.85	–	46.85	8.39	425
(5.70, 16.14)	(3.81, 32.23)	(2.91)	192,0.1; Colourless viscous liquid 5.75, (87)	(29.00)		(46.96)	(8.37)	(409)
$BuSn(OPr^i)_3$	$HOCMe_2CH_2CH_2CMe_2OH$	1.91	$BuSn(OCMe_2CH_2CH_2CMe_2O)(OCMe_2CH_2CH_2CMe_2OH)$ (**4**)	25.05	–	51.51	9.35	470
(3.76, 10.64)	(3.11, 21.26)	(1.92)	199,0.2; Colourless waxy solid 4.26, (86)	(25.50)		(51.61)	(9.09)	(465)
1	$Al(OPr^i)_3$	0.45	$BuSn(OCMe_2CMe_2O)_2\{Al(OPr^i)_2\}$ (**5**)	21.13	4.88	47.51	9.15	565
(3.08, 7.52)	(1.54, 7.53)	(0.45)	245/0.2; Colourless waxy solid 3.54, (85)	(21.44)	(4.87)	(47.74)	(8.56)	(553)
2	$Al(OPr^i)_3$	0.72	$BuSn(OCHMeCHMeO)_2\{Al(OPr^i)_2\}$ (**6**)	23.49	5.42	43.24	7.91	502
(4.31, 12.20)	(2.49, 12.18)	(0.73)	240,0.2; White solid 5.33, (88)	(23.86)	(5.43)	(43.47)	(7.90)	(497)
3	$Al(OPr^i)_3$	0.31	$BuSn(OCMe_2CH_2CHMeO)_2\{Al(OPr^i)_2\}$ (**7**)	21.42	4.82	47.39	9.05	575
(2.19, 5.35)	(1.09, 5.33)	(0.32)	198,0.2; Colourless viscous liquid 2.63, (89)	(21.44)	(4.87)	(47.74)	(8.56)	(553)
4	$Al(OPr^i)_3$	0.63	$BuSn(OCMe_2CH_2CH_2CMe_2O)_2\{Al(OPr^i)_2\}$ (**8**)	19.01	4.44	50.89	9.11	699
(4.96, 10.66)	(2.18, 10.67)	(0.64)	210,0.2; Colourless waxy solid 5.72, (88)	(19.47)	(4.42)	(51.23)	(9.09)	(609)
1	Nb(OPri)5	0.38	BuSn(OCMe2CMe2O)2{Nb(OPri)4}(9)	28.45	–	45.66	8.18	756
(2.64, 6.45)	(2.51, 6.46)	(0.38)	186,0.05; Colourless waxy solid 4.08, (86)	(28.68)		(45.56)	(8.33)	(737)
				Sn+Nb				

[a]All distilled under reduced pressure unchanged in analysis except the derivatives (**1**) and (**2**), which yielded $(BuSn)_2$ $(OCMe_2CMe_2O)_3$ (b.p. 220°C/0.2 mm) and $(BuSn)_2$ $(OCHMeCHMeO)_3$ (b.p. 225°C/0.2 mm), respectively along with some parent glycol. [b]Yield refers to distilled product unless otherwise indicated. [c]Undistilled product. [d]For freshly prepared compound.

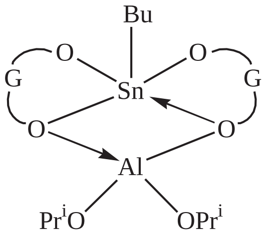
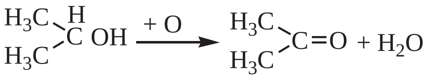


Fig. 1 Proposed structure for the derivatives (**5**)–(**8**).

refluxing over $Al(OPr^i)_3$ followed by distillation. 2,3-Dimethyl-2,3-butanediol(pinacol), *meso*-2,3-butanediol, and 2-methyl-2,4-pentanediol (hexylene glycol) were dried and purified by refluxing over $Al(OPr^i)_3$ followed by fractional distillation at 171°C/755 mm, 182°C/758 mm, and 197°C/755 mm, respectively. 2,5-Dimethyl-2,5-hexanediol was purified by sublimation under reduced pressure at 82°C/0.1 mm. $BuSn(OPr^i)_3$,[17] $Al(OPr^i)_3$,[21] and $Nb(OPr^i)_5$[22] were prepared by literature methods. Tin and niobium were determined as their oxides,[23] while aluminium was determined by the oxinate method.[23] Isopropyl alcohol in the azeotrope was determined by an oxidimetric method,[24] this procedure is based on quantitative oxidation of isopropyl alcohol to acetone by $K_2Cr_2O_7$ in 12.5% H_2SO_4; benzene present in the azeotrope does not interfere in the above procedure for quantitative estimation of isopropyl alcohol:



$$(H_3C)_2CH\text{–}OH \xrightarrow{+\,O} (H_3C)_2C{=}O + H_2O$$

^{1}H NMR (89.55 MHz), ^{27}Al NMR (23.79 MHz), and ^{119}Sn NMR (33.35 MHz) spectra were recorded on a JEOL FX 90Q spectrometer. ^{1}H NMR spectra in $CDCl_3$ were referenced with internal TMS ($\delta = 0$). ^{27}Al and ^{119}Sn NMR spectra in C_6H_6 were referenced with external $Al(NO_3)_3.xH_2O$ and Me_4Sn, respectively. IR (4000–200 cm^{-1}) spectra were recorded as Nujol mulls on a Nicolet Magna-550 spectrophotometer using CsI optics. Microanalyses (C and H) were performed using a Perkin Elmer 2400 CHNS/O analyzer. Molecular weights were determined cryoscopically in benzene.

Synthesis of homometallic butyltin glycolates

As the synthetic procedures for all the four homometallic butyltin glycolates are similar, the synthetic procedure for only one derivative is described in detail.

$BuSn(OCMe_2CMe_2O)(OCMe_2CMe_2OH)$ **(1) :** To a benzene (~ 25 ml) solution of meso-$HOCMe_2CMe_2OH$ (3.22 g, 27.25 mmol), a benzene (~ 30 ml) solution of freshly prepared $BuSn(OPr^i)_3$ (4.81 g, 13.62 mmol) was added and the resulting colourless solution was refluxed under a fractionating column with continuous azeotropic distillation of the alcohol for ~5 h. Isopropyl alcohol liberated during the above period was collected and estimated (2.43 g). On completion of the reaction as evidenced by the absence of isopropyl alcohol in the distillate, the refluxing was stopped. The solvent (benzene) was removed from the resulting solution under reduced pressure to afford a colourless waxy solid (5.55 g, 99%).

The apparently facile nature of the reaction as indicated by the reaction time required for the formation of product (**1**), prompted us to try the reaction directly at room temperature.

After addition of meso-$HOCMe_2CMe_2OH$ (0.989 g, 8.29 mmol) to a benzene (~25 ml) solution of $BuSn(OPr^i)_3$ (1.46 g, 4.13 mmol), the resulting reaction mixture was stirred at room temperature (32°C) for 4 h. The removal of volatile components under reduced pressure afforded the product (**1**) in 1.67 g (99%) yield.

The other derivatives (**2**), (**3**), and (**4**) in quantitative yields were also prepared conveniently by the alternative procedure adopted for (**1**). Preparative and analytical details are listed in Table 2.

Synthesis of heterobimetallic glycolates of BuSn(IV)

Novel heterobimetallic butyltin(IV) glycolates have been prepared by the reactions of homometallic glycolates BuSn(OGO)(OGOH) with different metal alkoxides. Due to the similarity in the synthetic procedure, preparative details of only one typical derivative are described below :

*$BuSn(OCMe_2CMe_2O)\{Al(OPr^i)_2\}$***(5):** To freshly prepared solution of $BuSn(OCMe_2CMe_2O)(OCMe_2CMe_2OH)$ (3.08 g, 7.52 mmol) in benzene (~ 20 ml), $Al(OPr^i)_3$ (1.54 g, 7.53 mmol) was added and the resulting reaction mixture was refluxed for ~4 h, during which the liberated isopropyl alcohol was continuously fractionated out and estimated periodically until the distillate showed the absence of isopropyl alcohol. The volatile material from the colourless solution was then removed under reduced pressure to yield a colourless waxy solid product, the analysis of which corresponded to the title compound (**5**). Further purification was carried out by distillation (b.p. 245°C/0.2 mm) to obtain the analytically pure compound (3.54 g, 85 % yield) as a colourless waxy solid.

Derivatives (**6**)–(**9**) were prepared in an analogous manner. Preparative and analytical details are listed in Table 2.

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