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Synthesis and characterization of salicylate derivatives of dibutyl [Al(III);B(III);Sn(IV)]-µ-oxoisopropoxide

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Abstract: The isopropoxy substitution reactions of dibutyl [Al(III);B(III);Sn(IV)]-µ-oxoisopropoxide with salicylates (HRSal) such as methyl salicylate (HMeSal), ethyl salicylate (HEtSal) and phenyl salicylate (HPhSal) in the molar ratios 1:1 and 1:2 carried out in refluxing benzene yielded derivatives of the type $[Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_3(Rsal)]$ and $[Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_2(Rsal)_2]$ respectively. The derivatives have been characterized by elemental, liberated isopropanol and spectral analysis (IR, ^1H , ^{13}C NMR).

Introduction

The chemistry of metal alkoxides and their applications to biology and materials science[1–3] are very attractive and fast growing research areas. Among the many aspects being studied, the preparation of heteronuclear molecules potential single-source precursors of high technology mixed-metal oxides is one of the most challenging.

A large number of heterometallic alkoxides which can be used as single-source precursors for the synthesis of oxide ceramics are known in the literature.[4] In addition to homoleptic {MM′(OR)x}, heteroleptic {MM′(OR)x(X)y where X = OAc, OR′, halide) and oxo alkoxide species {MM′O(OR)x} or {MM′(OR)x(X)y}, alkoxide derivatives with different metal combinations and up to three different metals[5] in a single molecule show the rich synthetic and structural chemistry of metal alkoxides.[6]

Volatile organometallic alkoxides are among the best precursors for the synthesis mixed metal oxides because they can be used in metal-organic-chemical-vapor-deposition (MOCVD), in sol-gel synthesis or in solid synthesis.[7] To overcome the problem of very fast rate of hydrolysis of metal alkoxides attempts are being made to provide modified precursor the alkoxy groups have been substituted by other ligands for example such as salicylates which may undergo hydrolysis at slower rate, and to get information about structural features, solubilities and effect of chelating group on the stability of µ-oxo compounds, their salicylate derivatives have been synthesized. Owing to the ever-growing importance of hetero metallic

alkoxides and oxoalkoxides it was considered worthwhile to synthesize the salicylate derivatives of [$Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_4$].

Experimental

All manipulations have been carried out under anhydrous conditions, solvents and the reagents used were of analytical grade and purified by recommended methods.[8] The general techniques and physical measurements were carried out as described elsewhere.[9-11].Methyl salicylate, ethyl salicylate were distilled under reduced pressure before use. Phenyl salicylate (Hi-media) was used as received. The estimation of isopropyl alcohol liberated in synthesis of salicylate derivatives were carried out oxidimetrically[12]. Tin, titanium and aluminium in the derivatives were analyzed gravimetrically[11]. Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer over the range of 4000-400 cm^{-1}. The ^1H and ^{13}CNMR spectra were recorded in $CDCl_3$ on Bruker Avance II 400 NMR spectrometer. Elemental analysis was carried on Perkin Elmer 2400 CHN Elemental Analyser.

Synthesis of 1:1 methyl salicylate derivative of dibutyl [Al(III);B(III);Sn(IV)]-µ-oxo-isopropoxide

[$Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_4$] (0.749 g,(1.38) mmol) and methyl salicylate (0.210g, 1.38 mmol) were refluxed in benzene (~60 ml) for 3 hrs, on an oil bath (temp. ~100 °C). The liberated *iso*propanol was continuously fractionated at 72-78 °C as binary azeotrope of *iso*propanol-benzene. The azeotrope formed during the course of reaction was collected and checked for completion of the reaction.[13] The excess of solvent was removed at 40 °C/1 mm pressure. A pale yellow solid product was obtained. Similar reaction was carried in 1:2 molar ratio resulting in [$Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_3(MeSal)_1$].

The preparation of other salicylate derivatives of [$Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_4$] in 1:1 and 1:2 molar ratios were carried out by similar procedure and their analytical data along with metal and liberated *iso*propanol estimation have been summarized in the **(Table 1).** All the derivatives were found to be pale yellow in color soluble in common organic solvents (benzene, chloroform benzene, hexane), susceptible to hydrolysis and decompose on heating above ~ 180 ^oC.

Results and discussion

The reaction of $[Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_4$ with salicylates (HRSal) such as methyl salicylate (HMeSal), ethyl salicylate (HEtSal) and phenyl salicylate (HPhSal) in the molar ratios 1:1 and 1:2 carried out in refluxing benzene yielded derivatives of the type $[Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_3(RSal)]$ and $[Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_2(RSal)_2]$ respectively.The isopropanol liberated during the reaction collected azeotropically (isopropanol-benzene) and estimated oxidimetrically to check the progress of the reaction. It was observed that only two out of the four of isopropoxy groups of dibutyl [Al(III); B (III); Sn (IV)] -μ-oxoisopropoxide could be replaced by salicylates. Further replacement of isopropoxy groups could not be achieved even with an excess of ligand and prolonged refluxing time in benzene (approx. 16h). This suggests that probably bridging isopropoxy groups could not be replaced.

The salicylate derivatives of dibutyl [Al(III); B (III); Sn (IV)] - μ-oxoisopropoxide are found to be yellow to brownish-yellow colored solids. All derivatives show appreciable solubility in common organic solvents (benzene, chloroform, hexane), susceptible to hydrolysis and decompose on heating strongly above ~ 180^{o}C.

Infrared Spectral Studies

1:1 salicylate derivatives show absorption bands in the region 1360-1340 cm^{-1}, 1165-1150 cm^{-1} and 1125-1090 cm^{-1} are characteristics of *gem*-dimethyl portion and combination band *ν*(C-O + O-*i*-Pr) of the terminal and bridging *iso*propoxy groups respectively.[14,15] The absence of band at ~ 1165-1150 cm^{-1} in 1:2 salicylate derivatives indicating complete replacement of terminal *iso*propoxy groups. A broad band in the region ~3100cm^{-1} due to *ν*(O-H) in salicylates is found absent in derivatives of $[Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_4]$ indicates the deprotonation of these ligands. The *ν*(C=O) band appearing in salicylates at ~1650 cm^{-1} shows a downward shift of 15-25 cm^{-1} in the derivatives, indicating the coordination of the carbonyl oxygen of the salicylate to the metal atom. A strong band observed at 1245 cm^{-1} in salicylates due to phenolic *ν*(C-O)) vibration is shifted 15-20 cm^{-1} higher in the derivatives indicating bond formation of phenolic oxygen of salicylates to the metal atom. Some bands observed in salicylate derivatives at 765 cm^{-1} and lower are due to M-O stretching vibrations.[16] The bands related to phenyl groups in the derivatives are observed at their usual positions in the IR spectra. The IR spectra of the derivatives indicate that salicylates behave as monobasic bidentate ligands.

NMR Spectra Studies

^{1}H NMR spectra

The ^{1}H NMR spectrum of 1:1 derivative show number of peaks in the regions δ 0.7-1.2 ppm are due to intermixing of methyl protons of the *iso*propoxy groups and protons of the butyl groups bonded to tin atom.[17] A multiplet centered at δ 4.1 ppm in [Bu_2SnO_2AlB(O-*i*-Pr)$_4$] due to methine proton of the *iso*propoxy groups[18] is found to overlap with the peak observed at ~ δ 3.8 ppm and a quartet centered at ~ δ 3.6 ppm are assigned to methyl and methylene protons in 1:2 derivative of [Bu_2SnO_2AlB(O-*i*-Pr)$_4$] with methyl and ethyl salicylates respectively. A broad singlet at ~δ 12.8 ppm due to phenolic proton in the salicylate is found absent in the derivatives confirms their deprotonation. The signals due to phenyl ring protons of salicylate moiety are observed at their usual positions (δ 6.8 –δ 7.8 ppm) in all the derivatives.

^{13}C NMR spectra

The ^{13}C NMR spectra of 1:1 salicylate derivatives of dibutyl [Al(III); B(III);Sn(IV)]-μ-oxo-*iso*propoxide shows two prominent peaks at δ ~ 26.6 ppm and δ ~ 28.8 ppm assignable to the methyl carbon of terminal and bridged *iso*propoxy groups. Two different type of methine carbons of *iso*propoxy groups[19] is confirmed by the two signals observed at δ ~ 64.1 ppm and δ ~ 64.5 ppm. The other peaks at δ 26.1 ppm, δ 25.6 ppm, δ 15.5 ppm and δ 14.0 ppm are assignable to C-1, C-2, C-3 and C-4 respectively of the butyl group.[18] The 1:2 salicylate derivatives of μ-oxo-*iso*propoxide show the absence of terminal *iso*propoxy groups. The peaks observed in the region δ125.2-136.7 ppm are due to carbon atoms on benzene ring; however, the peak observed at about δ168.2 ppm is due to ring carbon linked to the ester group and a peak observed at about δ186.4 ppm is due to carbon of the ester group (-COOR).[20]

On the basis of above spectral studies and analytical studies (**Table 1**) the following tentative structures have been assigned to 1:2 salicylate derivative of [Bu_2SnO_2AlB(O-*i*-Pr)$_4$]

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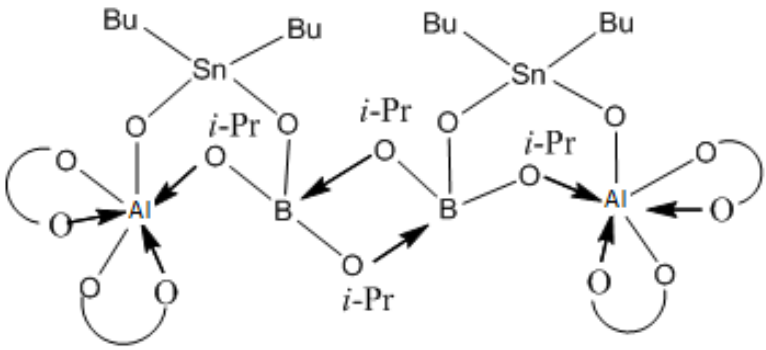

Fig. $[Bu_2SnO_2AlB(i\text{-}OPr)_2L_2]$

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Table-1: Analytical data

S.No	Compound g(mmol)	Ligand g(mmol)	Molar Ratio	Refluxing time	Product g(%)	Anal. Calcd. (found)			
						HO-*i*-Pr g	Sn (%)	B (%)	Al (%)
1	$[Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_4]$ 0.749 (1.38)	HMeSal 0.210 (1.38)	1:1	3	$[Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_3(MeSal)]$ 0.585 (82.0)	0.059 (0.055)	18.50 (18.05)	1.71 (1.17)	4.72 (4.50)
2	$[Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_4]$ 0.749 (1.38)	HMeSal 0.420 (2.76)	1:2	5	$[Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_2(MeSal)_2]$ 0.635 (83.7)	0.111 (0.101)	17.48 (17.10)	1.85 (1.25)	4.30 (3.95)
3	$[Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_4]$ 0.738 (1.36)	HEtSal 0.225 (1.36)	1:1	4	$[Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_3(EtSal)]$ 0.591 (82.8)	0.058 (0.052)	16.03 (15.86)	1.46 (1.06)	3.65 (3.20)
4	$[Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_4]$ 0.738 (1.36)	HEtSal 0.450 (2.72)	1:2	6	$[Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_2(EtSal)_2]$ 0.479 (84.1)	0.080 (0.076)	15.92 (15.01)	1.65 (1.07)	4.25 (3.65)
5	$[Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_4]$ 1.026 (1.31)	HPhSal 0.260 (1.31)	1:1	4	$[Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_3(PhSal)]$ 0.621 (84.8)	0.056 (0.050)	15.05 (14.87)	1.07 (0.86)	4.43 (4.10)
6	$[Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_4]$ 1.026 (1.31)	HPhSal 0.520 (2.62)	1:2	6	$[Bu_2SnO_2AlB(O\text{-}i\text{-}Pr)_2(PhSal)_2]$ 0.480 (85.4)	0.072 (0.067)	14.59 (13.91)	1.08 (0.76)	4.57 (4.10)

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