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

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Abstract: The isopropoxy substitution reactions of dibutyl [Sn(IV); B(III)]-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 $[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_3(Rsal)]$ and $[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_2(Rsal)_2]$ respectively. The derivatives have been characterized by elemental, liberated isopropanol and spectral analysis (IR, ^1H , ^{13}C NMR).

Introduction

Mixed metal alkoxides are ideal precursors to technologically important ceramic oxides via chemical vapor deposition (CVD), sol-gel processes, and more recently nanocrystal fabrication.[1-8] These so-called "single-source" precursors are of interest since they can greatly simplify processing, control stoichiometry of final materials and increase throughput.

The design and synthesis of heterobimetallic complexes have attracted considerable attention because sometimes they show multiple functionalities and prominent catalytic activity, selectivity over monometallic complexes, and can potentially even achieve chemical transformations that are unprecedented with monometallic catalysts.[9] For example, heterobimetallic complexes (e.g., Fe, Mo, and Co) at the active site of the enzyme of nitrogenase play a key role in the fixation of atmospheric nitrogen gas.[10] The bimetallic-µ- oxoalkoxide have amazingly high solubility in common organic solvents which makes them excellent precursors for the synthesis of mixed metal oxides by sol-gel processes[11]. Due to high solubility of metal and bimetallic alkoxide in organic solvents they could also used as model for exploring the frontiers between heterogeneous and homogeneous catalysts[12].

The heterobimettalic-µ-oxo-alkoxides are found to be associated in organic solvent like the simple metal alkoxides.[13,14] The association results from the tendency of metals to fulfill their coordination number by forming inter and intra molecular oxygen-metal bonds. The mean degrees of association of these compounds have been obtained from cryoscopic measurement and other spectroscopic studies. The

chemical reactivity, solubility and molecular association of the bimetallic-μ-oxo-alkoxides are largerly affected by the nature of alkoxy groups (steric factors).

The above features underline the importance and utility of μ-oxo compounds, it was therefore considered worthwhile to synthesis salicylate derivatives of dibutyl [Sn (IV); B (III)] -μ-oxoisopropoxide. Importance of these derivatives lies in the fact that they can also be used as an excellent single precursor for the preparation of mixed metal oxide in homogeneous phase.

Experimental

All manipulations have been carried out under anhydrous conditions and solvents and the reagents used were of analytical grade and purified by recommended methods.[15]The general technique and physical measurement were carried out as described elsewhere.[16-18] $[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_4]$ was synthesized by reported method.[19] The estimation of isopropyl alcohol liberated in synthesis of salicylate derivatives were carried out oxidimetrically.[20] Tin and boron in the derivatives were analysed gravimetrically.[18]

The Infrared spectra were recorded on a Perkin- Elmer 1710 FTIR spectrometer over the range of 4000-400 cm^{-1}. The ^{1}H, ^{13}C, ^{119}Sn and ^{11}B NMR 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 $[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_4]$

The compound $[Bu_2SnO_2B(O\text{-}i\text{-}Pr)_4]$ (0.320 g, 0.625 mmol) and and methyl salicylate (0.210g, 1.38 mmol) were refluxed in ~ 50 ml benzene in a flask connected to short distillation column on an oil bath for about 4 h. The isopropanol liberated at 72-78 ^{o}C was fractionated as the binary azeotrope of isopropanol-benzene[21] was collected and checked for completion of the reaction. The excess of the solvent was then removed under reduced pressure (45 ^{o}C /1mm) yielding a yellowish brown solid. Similar reaction was carried in 1:2 molar ratio resulting in $[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_2(MeSal)_2]$.

The preparation of other salicylate derivatives of $[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_4]$ 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 ^{o}C.

Results and discussion

The reaction of $[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_4$ 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 $[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_3(RSal)]$ and $[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_2(RSal)_2]$ respectively according to the following general reaction :

(n= 1-2, HL = Meth/Et/Phe salicylate)

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 [Sn (IV); B (III)] -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 [Sn (IV); B (III)]- 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.

The absorption bands in the region 1360– 1340, 1165– 1150 and 1135- 1115 cm^{-1} in the IR spectra of 1:1 salicylate derivatives of $[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_4$ are assigned to the *gem*-dimethyl portion and combination band ν(CO + O-*i*-Pr) of the terminal and bridging isopropoxy groups respectively.[22,23] Absence of peak at 1165 cm^{-1} in the spectrum of 1:2 derivatives indicates the absence of terminal isopropoxy groups. A broad band in the region 3100 cm^{-1} due to ν(O-H) in salicylate is found absent in derivatives indicates the deprotonation of these ligands.the ν(C=O) band in salicylates at 1625 cm^{-1} show a downward shift of 15-25 cm^{-1} in the derivatives indicating the coordination of carbonyl oxygen of salicylate to metal atom. A number of bands assigned in the region 700– 400 cm^{-1} due to M-O stretching vibrations[24] in salicylate derivatives of μ-oxoisopropoxide compound.

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.[25] A multiplet centered at δ 4.1 ppm in $[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_4]$ due to methine proton of the *iso*propoxy groups[26] 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 $[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_4]$ 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 [Sn(IV);B(III)]-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[27] 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.[26] 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).[28]

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 [$Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_4$]

Table- 1 Analytical data

S.No	Compound g(mmol)	Ligand g (mmol)	Reflux time (hr)	Product g(%)	Anal. Found (calcd.)				
					i –Opr(g)	Sn(%)	B(%)	C(%)	H(%)
1	$[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_4]$ 0.320 (0.532)	HMeSal 0.053 (0.53)	4	$[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_3(MeSal)]$ 0.323 (94.9)	0.03 (0.03)	18.45 (18.53)	3.90 (3.98)	37.26 (37.47)	6.05 (6.55)
2	$[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_4]$ 0.315 (0.524)	HMeSal 0.105 (1.05)	6	$[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_2(MeSal)_2]$ 0.337 (94.4)	0.05 (0.06)	17.35 (17.44)	3.72 (3.76)	38.52 (38.79)	5.75 (6.17)
3	$[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_4]$ 0.315 (0.524)	HEtSal	4	$[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_3(EtSal)]$	0.05 (0.06)	17.35 (17.44)	3.72 (3.76)	38.52 (38.79)	5.75 (6.17)
4	$[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_4]$ 0.315 (0.524)	HEtSal	6	$[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_2(EtSal)_2]$	0.05 (0.06)	17.35 (17.44)	3.72 (3.76)	38.52 (38.79)	5.75 (6.17)
5	$[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_4]$ 0.160 (0.267)	HPhSal 0.0433 (0.267)	5	$[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_3(PhSal)]$ 0.178 (95.0)	0.02 (0.02)	16.85 (16.90)	3.61 (3.65)	42.65 (42.70)	5.98 (6.26)
6	$[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_4]$ 0.130 (217)	HPhSal 0.0703 (0.434)	7	$[Bu_2SnO_2B_2(O\text{-}i\text{-}Pr)_2(PhSal)_2]$ 0.163 (93.6)	0.03 (0.03)	14.64 (14.75)	3.17 (3.20)	47.57 (47.73)	5.20 (5.71)

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