Synthesis and Characterization of salicylate derivatives of heterotrimetallic [Al(III);Sn(II);Ti(IV)]-μ-oxo-*iso*propoxide

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Abstract

The reaction of heterotrimetallic [Al(III);Sn(II);Ti(IV)]-μ-oxo-*iso*propoxide 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 [SnO_2TiAl(O-*i*-Pr)$_4$(RSal)] and [SnO_2TiAl(O-*i*-Pr)$_3$(RSal)$_2$] respectively. The salicylate derivatives have been characterized by elemental, liberated isopropanol and spectral analysis (IR, ^{1}H , ^{13}C NMR).

Keywords: Metal alkoxide, Tin, Titanium, Aluminium, Salicylates.

Introduction

The development of materials by soft chemical methods like sol-gel, Metal Organic Chemical Vapour Deposition (MOCVD), Atomic Layer Deposition (ALD), Metal-Organic Decomposition (MOD), etc. has always been closely associated with the chemistry of molecular precursors.[1-6] The molecular engineering to optimize the required properties in the precursors is usually achieved through judicious choice of ligands. Metal derivatives of the alkoxide and β-diketonate ligands have become the predominant single-source precursors for oxide-based ceramic materials, mainly through sol-gel processing and MOCVD, respectively, because of their commercial availability, high solubility in routinely used organic solvents, and easy tunability of their hydrolytic characteristics and mass-transport properties.[7-10] Another important axis of the molecular engineering is the synthesis of bi- and higher metallic derivatives with appropriate properties.[11-18]

Metal oxide nanomaterials are attractive for a variety of applications including catalysis,[19,20] drug delivery,[21,22] photochemistry,[23] sensing[24] and optoelectronics.[25,26] In additional to potentially enhanced properties, structurally well-defined nano-sized oxides can offer a platform to precisely interrogate structure-activity relationships. Therefore, scientists have systematically investigated the properties/activities including conductivity, thermal stability, magnetic behavior, and catalytic performance of the metal oxides with varied surface and/or interface-tuning approaches through regulating the exposed facets, chemical composition, morphology, size, and surface functional groups.[27-32]

The above features underline the importance and utility of μ-oxo compounds, it was therefore considered worthwhile to synthesize salicylate derivatives of heterotrimetallic [Al(III); Sn(II); Ti(IV)] -μ-oxoisopropoxide.

Experimental

All manipulations have been carried out under anhydrous conditions, solvents and the reagents used were of analytical grade and purified by recommended methods.[33] The general techniques and physical measurements were carried out as described elsewhere.[34-36] $[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ was prepared in the laboratory by reported method.[37] 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[38]. Tin, titanium and aluminium in the derivatives were analyzed gravimetrically[36]. 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 heterotrimetallic [Al(III);Sn(II);Ti(IV)]-μ-oxo-isopropoxide

$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ (0.623g,1.200) mmol) and methyl salicylate (0.182g,1.200) were refluxed in benzene (~60 ml) for 3 hrs, on an oil bath (temp. ~100 °C). The reaction can be represented by the following equation:

$$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5] + HRSal \xrightarrow{\text{Reflux, benzene}} [SnO_2TiAl(O\text{-}i\text{-}Pr)_{5-n}(RSal)_n] + nHO\text{-}i\text{-}Pr \quad (n=1;$$

Rsal=deprotonated methyl salicylate)

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.[37,39] 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 $[SnO_2TiAl(O\text{-}i\text{-}Pr)_3(MeSal)_2]$.

The preparation of other salicylate derivatives of $[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 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.

Result and discussion

The reaction of heterotrimetallic [Al(III);Sn(II);Ti(IV)]-µ-oxo-*iso*propoxide 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 $[SnO_2TiAl(O\text{-}i\text{-}Pr)_4(RSal)]$ and $[SnO_2TiAl(O\text{-}i\text{-}Pr)_3(RSal)_2]$ respectively according to the following general reaction :

$$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5] + HRSal \xrightarrow{\text{Reflux, benzene}} [SnO_2TiAl(O\text{-}i\text{-}Pr)_{5-n}(RSal)_n] + nHO\text{-}i\text{-}Pr \quad (n=1\text{-}2;$$

Rsal=deprotonated methyl/ethyl/phenyl salicylate)

The *iso*propanol liberated during the reaction was collected as binary azeotrope of *iso*propanol-benzene. The azeotrope was estimated oxidimetrically to check the progress of reaction.

The salicylates derivatives of heterotrimetallic [Al(III);Sn(II);Ti(IV)]-µ-oxo-*iso*propoxide obtained were pale yellow solids, soluble in common organic solvents (benzene, chloroforms, carbon tetrachloride etc.), susceptible to hydrolysis and decompose on heating above 180 °C.

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 (%)	Ti (%)	Al (%)
1	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.623 (1.200)	HMeSal 0.182 (1.200)	1:1	3	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_4(MeSal)]$ 0.585 (82.0)	0.059 (0.055)	19.31 (16.05)	7.69 (6.17)	4.41 (3.50)
2	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.588 (1.132)	HMeSal 0.344 (2.264)	1:2	$5^{1/2}$	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_3(MeSal)_2]$ 0.635 (83.7)	0.111 (0.101)	16.78 (14.20)	6.68 (5.65)	3.84 (2.95)
3	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.612 (1.179)	HEtSal 0.195 (1.179)	1:1	$3^{1/2}$	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_4(EtSal)]$ 0.591 (82.8)	0.058 (0.052)	18.88 (15.86)	7.52 (6.06)	4.32 (3.40)
4	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.427 (0.822)	HEtSal 0.272 (1.644)	1:2	6	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_3(EtSal)_2]$ 0.479 (84.1)	0.080 (0.076)	16.14 (13.81)	6.42 (5.07)	3.69 (3.05)
5	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.590 (1.136)	HPhSal 0.243(1.36)	1:1	$3^{1/2}$	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_4(PhSal)]$ 0.621 (84.8)	0.056 (0.050)	17.53 (14.87)	6.98 (5.86)	4.01 (3.10)
6	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.379 (0.730)	HPhSal 0.312 (1.46)	1:2	$5^{1/2}$	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_3(PhSal)_2]$ 0.480 (85.4)	0.072 (0.067)	14.26 (12.31)	5.68 (4.76)	3.26 (2.60)

Infrared Spectral Studies

1:1 salicylate derivatives show absorption bands in the region 1360-1330 cm^{-1}, 1160-1150 cm^{-1} and 1120-1090 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.[40,41] 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 [$SnO_2TiAl(O\text{-}i\text{-}Pr)_5$] 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 1240 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 760 cm^{-1} and lower are due to M-O stretching vibrations.[42]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 Spectral Studies

^{1}H NMR spectra

The ^{1}H NMR spectrum of 1:1 derivative show number of peaks in the regions δ 0.7-1.3 ppm are due to methyl protons of the *iso*propoxy groups.[43] A multiplet centered at δ 4.1 ppm in [$SnO_2TiAl(O\text{-}i\text{-}Pr)_5$] due to methine proton of the *iso*propoxy groups[37] 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 [$SnO_2TiAl(O\text{-}i\text{-}Pr)_5$] 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 6.7 –δ 7.7 ppm) in all the derivatives.

^{13}C NMR spectra

The ^{13}C NMR spectra of 1:1 salicylate derivatives of heterotrimetallic [Al(III);Sn(II);Ti(IV)]-μ-oxo-*iso*propoxide shows two prominent peaks at δ ~ 26.5 ppm and δ ~ 28.6 ppm assignable to the methyl carbon of terminal and bridged *iso*propoxy groups. Two different type of methine carbons of *iso*propoxy groups[44] is confirmed by the two signals observed at δ ~ 64.0 ppm and δ ~ 64.4 ppm. 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).[45]

On the basis of above spectral studies following tentative structures **(Fig.1 & 2)** are assigned to 1:1 and 1:2 methyl salicylate derivatives of [$SnO_2TiAl(O\text{-}i\text{-}Pr)_5$]:

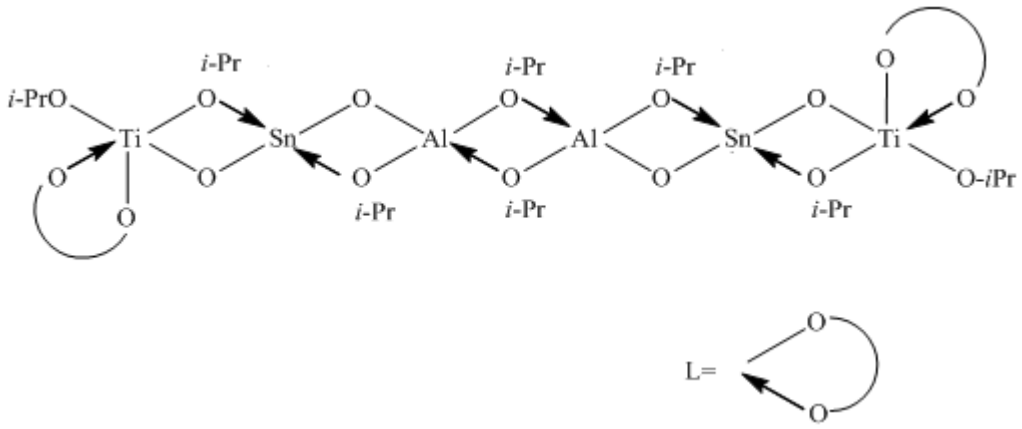

Fig. 1 [$SnO_2TiAl(O\text{-}i\text{-}Pr)_4(MeSal)$]

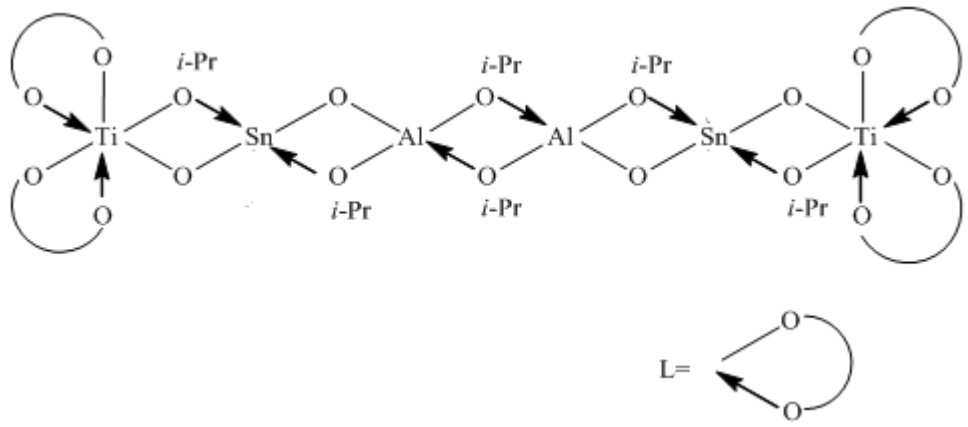

Fig. 2: [$SnO_2TiAl(O\text{-}i\text{-}Pr)_3(MeSal)_2$]

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