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Synthesis of salicylate derivatives of heterobimetallic [Sn(II);Ti(IV)]-μ-oxo-*iso*propoxide

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Abstract: The reaction of heterobimetallic [Sn(II);Ti(IV)]-μ-oxo-*iso*propoxide with salicylates (HRSal) such as methyl salicylate (HMeSal), ethyl salicylate (HEtSal) and phenyl salicylate (HPhSal) in different molar ratios were carried out in refluxing benzene yielded derivatives of the type $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_5(RSal)]$, $[SnO_2Ti(O\text{-}i\text{-}Pr)4(RSal)_2]$, $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_3(RSal)_3]$ and $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_2(RSal)_4]$. The salicylate derivatives have been characterized by elemental, liberated isopropanol and spectral analysis (IR, ^1H , ^{13}C NMR).

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

Introduction

Preparation of oxides from heterometallic alkoxides has advantages over those obtained by traditional routes such as those using metal carbonates, oxides, and oxalates etc. which require heating to higher temperatures.[1] These advantages include low temperature of formation low crystallization temperatures, better compositional uniformity at the molecular level and high purity conformal coverage in the case of thin films. The metal alkoxides and alkoxide precursor solutions of this invention have particular use in the production of nanocrystalline metal oxide films on large-area glass panels. The films are of high quality, transparent and suitable for use in electrochromic devices. They have valuable application in other areas of industry and technology, such as in catalysts and electronic devices. The investigation and the use of hetero-metallic alkoxides as single-source molecules precursors for synthesis of oxides have seen a rapid growth during the last more than one and half decade. The control of particle size and the morphology of the oxide are of crucial importance nowadays both from the fundamental and industrial point of view. Heterometallic-μ-oxo alkoxides are often associated with more accessible precursors such as carboxylates, Schiff bases and β-diketonates in chemical routes to intricate mixed metal oxides. The mixed metal oxides obtained from heterometallic-μ-oxo alkoxides precursors have found use to new ceramics and medicinally important such as for absorbing harmful chemicals and gases.[2]

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.[3-7] 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[8] in a single molecule show the rich synthetic and structural chemistry of metal alkoxides.[9]

Metal alkoxides are frequently employed as sol-gel molecular precursors in the fabrication of nanomaterials. The addition of chelating ligands to metal alkoxide precursors greatly increases their stability. This, in turn, slows the otherwise rapid hydrolysis–condensation kinetics.[10-12] The condensation rate is slowed because bidentate or multidentate chelates also occupy other coordination sites on the metal center as well as tethering alkoxy groups that are prone to water attack.[13]

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

Experimental

Due to highly hygroscopic nature of metal alkoxides, stringent precautions were taken to exclude moisture throughout the study using glasswares with interchangeble joints, solvents and the reagents used were of analytical grade and purified by recommended methods.[14] The general techniques and physical measurements were carried out as described elsewhere.[15-17,] $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ was prepared in the laboratory by reported method.[18] 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[19]. Tin, titanium and aluminium in the derivatives were analyzed gravimetrically[17]. Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer over the range of 4000-400 cm^{-1}. The ^{1}H 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 heterobimetallic [Sn(II);Ti(IV)]-µ-oxo-isopropoxide

$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.623 (1.041) and methyl salicylate 0.159 (1.041) 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:

$$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6] + n\ HRSaL \xrightarrow[Reflux]{Benzene} [SnO_2Ti_2(O\text{-}i\text{-}Pr)_{6-n}(RSal)_n + n\ HO\text{-}i\text{-}Pr$$

(n=1; Rsal=deprotonated methyl salicylate)

The freed isopropanol was gathered constantly at 72-78^{0}C as a double azeotrope of isoproponol-benzene. The isopropanol in azeotrope was assessed oxidimetrically to check the consummation of the reaction.[18,20,] The excess of solvent was removed at 40 °C/1 mm pressure. A pale yellow solid product was obtained.

The preparation of other salicylate derivatives of $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ in 1:1,1:2, 1:3 and 1:4 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.

Result and discussion

The reaction of heterobimetallic [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 different molar ratios of 1:1,1:2, , 1:3 and 1:4 carried out in refluxing benzene yielded derivatives of the type $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_5(RSal)]$, $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_4(RSal)_2]$, $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_3(RSal)_3]$ and $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_2(RSal)_4]$.respectively according to the following general reaction : $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6] +$

$$n\ HRSaL \xrightarrow[Reflux]{Benzene} [SnO_2Ti_2(O\text{-}i\text{-}Pr)_{6-n}(RSal)_n + n\ HO\text{-}i\text{-}Pr$$

(n=1-2; 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 heterobimetallic [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.

Infrared Spectral Studies

1:1 to 1:3 salicylate derivatives show absorption bands in the region 1350-1330 cm^{-1}, 1165-1150 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.[21,22] The absence of band at ~ 1165-1150 cm^{-1} in 1:4 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 $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ indicates the deprotonation of these ligands. The ν(C=O) band appearing in salicylates at ~1645 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.[23] 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.

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 (%)
1	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.623 (1.041)	HMeSal 0.159 (1.041)	1:1	3	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_5(MeSal)]$ 0.585 (84.6)	0.060 (0.055)	17.07 (16.05)	13.60 (12.17)
2	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.588 (0.927)	HMeSal 0.283 (1.854)	1:2	4	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_4(MeSal)_2]$ 0.610 (77.8)	0.053 (0.47)	15.05 (14.30)	11.99 (10.65)
3	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.612 (1.023)	HMeSal 0.469 (3.069)	1:3	$4^{1/2}$	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_3(MeSal)_3]$ 0.720 (82.0)	0.047 (0.040)	13.45 (12.86)	10.72 (9.56)
4	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.427 (0.714)	HMeSal 0.436 (2.856)	1:4	6	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_2(MeSal)_4]$ 0.790 (81.4)	0.043 (0.038)	12.16 (11.61)	9.69 (8.27)
5	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.590 (0.986)	HEtSal 0.164 (0.986)	1:1	$3^{1/2}$	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_5(EtSal)]$ 0.579 (82.1)	0.062 (0.055)	16.73 (15.87)	13.33 (12.06)
6	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.379 (0.597)	HEtSal 0.199 (1.194)	1:2	4	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_4(EtSal)_2]$ 0.629 (78.4)	0.057 (0.052)	14.71 (13.31)	11.72 (10.26)
7	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.379 (0.633)	HEtSal 0.317 (1.899)	1:3	$4^{1/2}$	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_3(EtSal_)_3]$ 0.735 (79.9)	0.052 (0.045)	12.84 (11.71)	10.22 (9.36)
8	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.487 (0.814)	HEtSal 0.543 (3.256)	1:4	$5^{1/2}$	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_2(EtSal)_4]$ 0.829 (80.8)	0.048 (0.039)	11.50 (10.31)	9.16 (8.05)
9	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.510 (0.852)	HPhSal 0.183 (0.852)	1:1	3	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_5(PhSal)]$ 0.621 (82.4)	0.058 (0.050)	15.67 (14.31)	12.46 (11.26)

10	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.395 (0.660)	HPhSal 0.283 (1.32)	1:2	4	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_4(PhSal)_2]$ 0.735 (81.0)	0.050 (0.042)	12.99 (11.61)	10.35 (9.30)
11	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.555 (0.928)	HPhSal 0.598 (2.784)	1:3	$5^{1/2}$	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_3(PhSal)_3]$ 0.856 (80.5)	0.045 (0.037)	11.10 (10.31)	8.84 (7.40)
12	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.465 (0.777)	HPhSal 0.668 (3.108)	1:4	6	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_2(PhSal)_4]$ 0.965 (79.2)	0.041 (0.036)	9.68 (8.59)	7.71 (6.33)

NMR Spectral Studies

^{1}H NMR spectra

The ^{1}H NMR spectrum of 1:1 to 1:3 derivative show number of peaks in the regions δ 0.7-1.5 ppm are due to methyl protons of the *iso*propoxy groups .[24] A multiplet centered at δ 4.1 ppm in $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 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 $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6$ 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 to 1:3 salicylate derivatives of heterobimetallic [Sn(II);Ti(IV)]-μ-oxo-*iso*propoxide shows two prominent peaks at δ ~ 26.5 ppm and δ ~ 28.7 ppm assignable to the methyl carbon of terminal and bridged *iso*propoxy groups. Two different type of methine carbons of *iso*propoxy groups[25] is confirmed by the two signals observed at δ ~ 64.1 ppm and δ ~ 64.4 ppm. The 1:4 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).[26]

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 $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$:

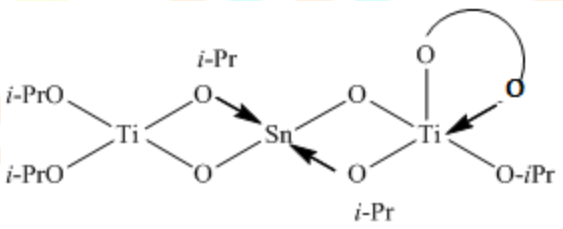

Fig. 1 $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_5(MeSal)]$

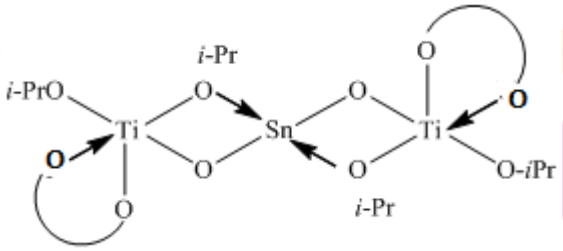

Fig. 2: $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_4(MeSal)_2]$

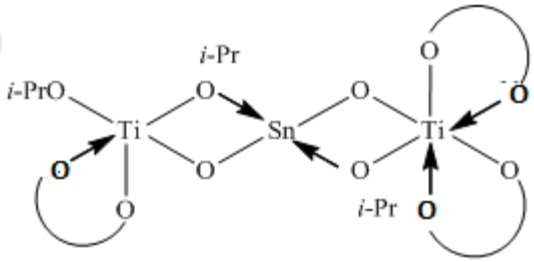

Fig.3 $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_3(MeSal)_3]$

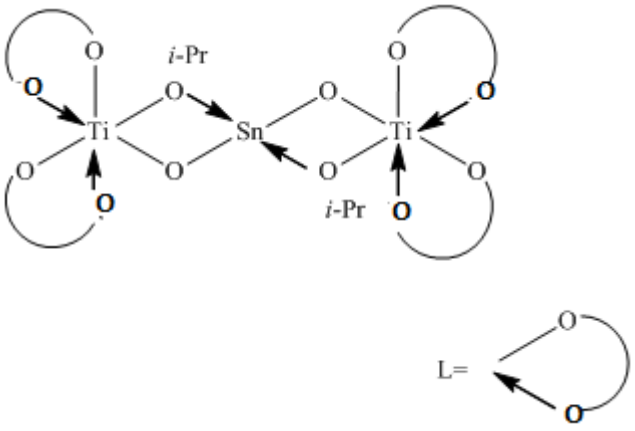

Fig.4 $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_2(MeSal)_4]$

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CONCLUSION : The study concluded that all the salicylate derivatives exhibited pale yellow solids . They were soluble in organic solvents but prone to hydrolysis.

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