Synthesis of Derivatives of Heterobimetallic [Sn(II);Ti(IV)]-µ-oxo-*iso*propoxide with Schiff Bases

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ABSTRACT

With an aim to enhance the stability and volatility of the heterometallic **[**Sn(II);Ti(IV)]-µ-oxo-*iso*propoxide a number of substitution reactions of the complex are carried out with different schiff bases viz Salicylidene aniline (HSB^1), Salicylidene-*o*-toluidene (HSB^2) and Salicylidene-*p*-chloroaniline (HSB^3) have been performed in different molar ratios in refluxing benzene resulting in to the formation of products of the type $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_5(SB)]$, $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_4(SB)_2]$, $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_3(SB)_3]$ and $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_2(SB)_4]$. The schiff base derivatives have been characterized by elemental, liberated isopropanol and spectral analysis (IR, ^1H , ^{13}C NMR).

Keywords: Metal alkoxide, schiff base, Tin, Titanium**.**

INTRODUCTION

Interest in the synthesis and properties of the molecular precursors for metal oxide and nonoxide nanomaterials are due to their inherent advantages during materials processing *via* soft chemical routes [Sol-Gel, Metal-Organic Chemical Vapor Deposition (MOCVD), Metal-Organic Decomposition (MOD)][1-8].Design and synthesis of heterometallic derivatives with suitable properties can be used as single source precursors for generating advanced complex materials containing more than one metal[9-18]. Classical or functional metal alkoxides, which have appropriate hydrolysis and condensation characteristics, are the preferred single-source precursors for oxide ceramic materials *via* sol-gel processing. [19-29]

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. [30-32] 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. [33]

The catalytic properties of metal alkoxides have also been well established. The µ-oxo alkoxides have been reported to be amongst the best catalysts for polymerization of heterocyclic monomers like lactones, oxiranes, thiiranes and epoxides.[34,35] The alkoxides of molybdenum and tungsten in their middle oxidation states have been used as model for reductive cleavage of carbon monoxide to carbides and oxides *via* Fisher-Tropsch reaction.[36]

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

RESULT AND DISCUSSION

A number of reactions of heterobimetallic [Sn(II);Ti(IV)]-µ-oxo-*iso*propoxide with bidentate Schiff bases (HSB) i.e. Salicylidene aniline (HSB^1), Salicylidene-*o*-toluidene (HSB^2) and Salicylidene-*p*-chloroaniline (HSB^3) have been performed in different molar ratios in refluxing benzene resulting in to the formation of

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products of the type $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_5(SB)]$, $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_4(SB)_2]$, $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_3(SB)_3]$ and $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_2(SB)_4]$. The general reaction can be given as follows:

$$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6] + nHSB \xrightarrow[Reflux]{Benzene} [SnO_2Ti_2(O\text{-}i\text{-}Pr)_{6-n}(SB)n] + nHO\text{-}i\text{-}Pr \quad (73)$$

Where n=1-4 and HSB =Schiff bases

The *iso*propanol liberated during the course of reaction is collected azeotropically (*iso*propanol-benzene) and estimated oxidimetrically to check the progress of the reaction and it has been observed that only four out of six of *iso*propoxy groups could be replaced by Schiff bases. Further replacement of *iso*proxy groups could not be achieved even with an excess of ligand (Schiff base) and prolonged refluxing time (approx. 20 hours) in benzene.

All the Schiff base derivative of [Sn(II);Ti(IV))]-µ-oxo-*iso*propoxide are found to be brownish yellow highly viscous liquid to gel type, soluble in common organic solvents (benzene, chloroform, hexane), susceptible to hydrolysis and decompose on heating above 200^0C.

Infrared Spectral Studies

The spectra of the 1:1 to 1:3 Schiff base derivative of $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ shows absorption bands in the region 1360-1340 cm^{-1}, 1165-1150 cm^{-1} and 1090-1020 cm^{-1} are the characteristics of *gem*-dimethyl[37] portion and combination bands *v*(C-O +O-*i*-Pr) of the terminal and bridging *iso*propoxy groups respectively. No peak is observed at 1165 cm^{-1} in the spectrum of 1:4 schiff base derivative indicates the absence of terminal *iso*propoxy groups. This suggest that probably bridging isopropoxy groups could not be replaced. A band appeared at approx. 950cm^{-1} is due to *v*(C-O) stretching of bridging *iso*propoxy group.[37,38]

The IR spectra of Schiff base display a broad band at ~3400-3100 cm^{-1} due to *v*(O-H) stretch. Further these ligands show intense bands in the region ~1565 cm^{-1} and 1270-1240 cm^{-1} due to *v*(C=N) of azomethine group and *v*(C-O) vibrations of the phenolic group respectively. Disappearance of *v*(O-H) stretch at ~ 3400-3100 cm^{-1} in the IR spectra of Schiff base derivatives and downward shift in *v*(C=N) stretch and upward shift in *v*(C-O) i.e. ~ 1565 cm^{-1} by ~ 15-25 cm^{-1} and 1240-1270 cm^{-1} by ~20-30 cm^{-1} respectively indicate that azomethine 'N'is coordinated to metal atom and bond formation of phenolic oxygen[39] to the metal atom. While some vibrations are observed below700 cm^{-1} are due to M-O and M-N stretching vibrations in the Schiff base derivatives which are difficult to assign exactly due to the overlapping of bands in this region.

NMR Spectral Studies

^{1}H NMR Spectra

^{1}H NMR spectraof all the Schiff base derivatives of heterobimetallic [Sn(II);Ti(IV))]-µ-oxo-*iso*propoxide show a number of peaks centered between δ 0.6-1.5 ppm due to the intermixing of methyl protons of terminal and bridging*iso*propoxy groups. A multiplet at 4.2 ppm is due to the methine proton of *iso*propoxy groups in the spectra of all derivatives.

In the ^{1}H NMR spectra of all derivatives, the signals observed between δ 7.1-7.8 ppm are due to phenyl ring proton. Apeak observed in the ^{1}H NMR spectra of Schiff base at δ 11.2 ppm due to phenolic (O-H) proton is found absent in its derivative of heterobimetallic [Sn(II);Ti(IV))]-µ- oxo-*iso*propoxide indicates the deprotonation of these ligands. In the case of salicylidene-*o*-toluidene derivatives an additional signal at δ 2.3 ppm has been observed due to methyl protons[39,40] substituted on the benzene ring.

^{13}C NMR Spectra

The ^{13}C NMR spectra of 1:1 to 1:3 Schiff base derivative of heterobimetallic [Sn(II);Ti (IV))]-µ- oxo-*iso*propoxide compound shows two prominent peaks at δ ~26.9 ppm and δ ~27.4 ppm assignable to the methyl

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carbon of terminal and bridged *iso*propoxy moiety and two different types of methine carbons of *iso*propoxy groups is confirmed by the two signals observed at δ ~62.6-62.8 ppm and δ~63.1-63.3 ppm. Further the 1:4 schiff base derivatives of μ- oxo-*iso*propoxide indicate the absence of terminal *iso*propoxy groups.

Two signal observed in the range δ 160.3-164.0 ppm and δ 148.0-150.16 ppm are due to carbonyl carbon and methine carbon attached to nitrogen of ligand moiety in all the Schiff derivatives of μ- oxo-*iso*propoxide compound.[39] A number of peaks are observed between δ 128.0-125.0 ppm in ^{13}C NMR spectrum of schiff base derivatives are due to different types of phenyl ring carbons.

Experimental

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

Synthesis of 1:1 salicylidene-aniline derivative of μ-oxo compound.

The compound $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ (0.383g, 0.637mmol) and salicylidene-aniline (0.106g, 0.536 mmol) were refluxed in (~50ml) benzene for 4 hrs at ~100 °C in a flask connected to short distillation column. The liberated *iso*propanol was collected continuously at 72-78 °C as a binary azeotrope of *iso*propanol-benzene. The reaction can be depicted as:

$$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6] + nHSB^1 \xrightarrow{\text{Reflux, Benzene}} [SnO_2Ti_2(O\text{-}i\text{-}Pr)_{6-n}(SB)n] + nHO\text{-}i\text{-}Pr$$

Where n=1-4 and HSB =Salicylidene-aniline

The *iso*propanol in azeotrope was estimated oxidimetrically to check the completion of the reaction. The excess of the solvent was then removed under reduced pressure (45 °C/ 1mm) yielding a yellowish red highly viscous product.

Similar procedure was adopted for the preparation of other derivatives of $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ with Schiff bases (HSB) i.e. Salicylidene-aniline (HSB^1), Salicylidene-*o*-toluidene (HSB^2) and Salicylidene *p*-chloroaniline (HSB^3) in different stoichiometric ratio of 1:1, 1:2, 1:3 and 1:4. All the derivatives were found to be brownish yellow highly viscous liquid to gel type product, soluble in common organic solvents (benzene, chloroform, hexane), susceptible to hydrolysis. The details are given in **(Table-1)** along with the analytical data.

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	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.383 (0.637)	HSB^1 0.106 (0.536)	1:1	4	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_5(SB^1)]$ 0.409 (87.0)	0.038 (0.030)	16.09 (15.83)	12.98 (12.60)
2	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.390 (0.649)	HSB^1 0.215 (1.09)	1:2	6	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_4(SB^1)_2]$ 0.493 (86.7)	0.078 (0.072)	13.57 (13.05)	10.95 (10.60)
3	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.385 (0.641)	HSB^1 0.318 (1.617)	1:3	8	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_3(SB^1)_3]$ 0.559 (86.3)	0.011 (0.095)	11.73 (11.42)	9.46 (9.05)
4	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.372 (0.619)	HSB^1 0.410 (2.08)	1:4	9	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_2(SB^1)_4]$ 0.611 (85.9)	0.148 (0.140)	10.33 (9.98)	8.33 (7.94)
5	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.382 (0.636)	HSB^2 0.113 (0.534)	1:1	4	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_5(SB^2)]$ 0.421 (86.4)	0.038 (0.032)	15.43 (15.10)	12.47 (12.12)
6	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.387 (0.644)	HSB^2 0.228 (1.082)	1:2	7	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_4(SB^2)_2]$ 0.524 (87.1)	0.077 (0.071	12.70 (12.11)	10.24 (9.85)

ISSN No. 2321-2705 | DOI: 10.51244/IJRSI |Volume XII Issue X October 2025

7	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.386 (0.642)	HSB^2 0.341 (1.617)	1:3	8	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_3(SB^2)_3]$ 0.604(85.4)	0.196 (0.189)	10.77 (10.22)	8.69 (8.15)
8	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.371 (0.617)	HSB^2 0.438 (2.076)	1:4	9	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_2(SB^2)_4]$ 0.666 (85.0)	0.148 (0.142)	9.35 (9.04)	7.55 (7.14)
9	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.362 (0.603)	HSB^3 0.117 (0.506)	1:1	4	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_5(SB^3)]$ 0.394(84.8)	0.036 (0.030)	15.37 (14.95)	12.40 (11.89)
10	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.370 (0.616)	HSB^3 0.240 (1.036)	1:2	7	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_4(SB^3)_2]$ 0.495 (85.3)	0.074 (0.069)	12.58 (12.26)	10.14 (9.79)
11	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.365 (0.608)	HSB^3 0.385 (1.533)	1:3	8	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_3(SB^3)_3]$ 0.584 (86.2)	0.109 (0.098)	10.64 (10.24)	8.58 (8.13)
12	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_6]$ 0.389 (0.648)	HSB^3 0.504 (2.176)	1:4	9	$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_2(SB^3)_4]$ 0.740 (88.9)	0.155 (0.148)	9.22 (8.87)	7.44 (7.16)

On the basis of aforesaid spectral studies and elemental analysis the following tentative structures (**Fig. 1-4**) of the Schiff base derivatives of heterobimetallic [Sn(II);Ti(IV))]-µ-oxo-*iso*propoxide of the type $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_5(SB)_1]$,$[SnO_2Ti_2(O\text{-}i\text{-}Pr)_4(SB)_2]$, $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_3(SB)_3]$ and $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_2(SB)_4]$ has been depicted:

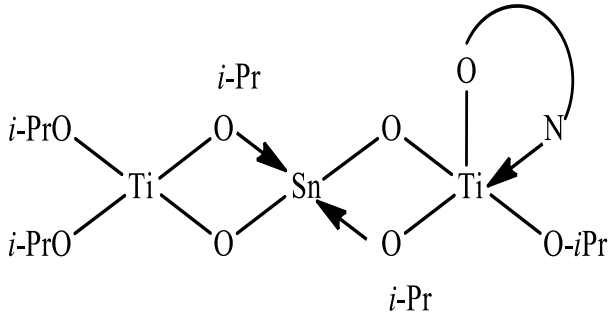

Fig. 1: $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_5(SB)_1]$

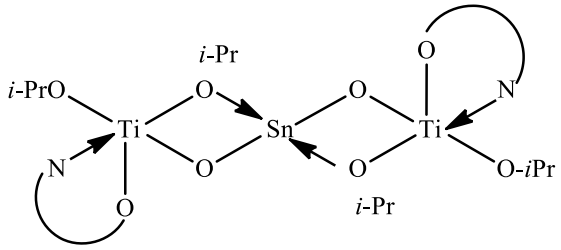

Fig. 2: $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_4(SB)_2]$

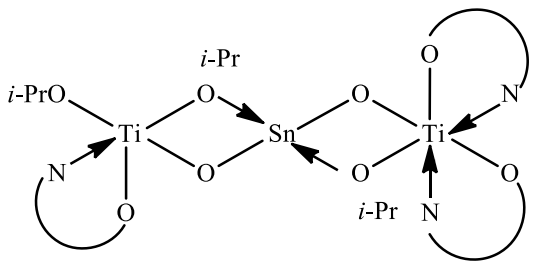

Fig. 3: $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_3(SB)_3]$

ISSN No. 2321-2705 | DOI: 10.51244/IJRSI |Volume XII Issue X October 2025

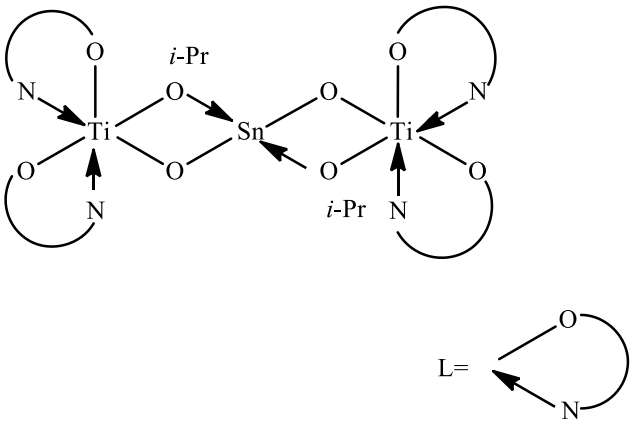

Fig. 4: $[SnO_2Ti_2(O\text{-}i\text{-}Pr)_2(SB)_4]$

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