

Synthesis and Characterization of Derivatives of Dibutyl Sn(IV)-Ti(IV)- μ -Oxoisopropoxide with Schiff Bases

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(Received August 24, 2011; Accepted December 16, 2011)

ABSTRACT. New Schiff base derivatives of organoheterobimetallic- μ -oxoisopropoxide $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_6]$ have been synthesized by the thermal condensation μ -oxoisopropoxide compound with Schiff bases in different molar ratios (1:1-1:4) yielded the compounds of the type $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_{6-n}(\text{SB})_n]$ (where n is 1-4 and SB=Schiff base anion) respectively. The μ -oxoisopropoxide derivatives have been characterized by elemental, spectral analysis (IR, ^1H , ^{13}C , ^{119}Sn NMR) and molecular weight measurement. The studies reveal that the derivative compounds show monomeric nature. Further these are found less susceptible to hydrolysis as compared to parent compound and may prove excellent precursors for the mixed metal oxides.

Key words: Bimetallic oxoalkoxides, Tin, Titanium, Schiff bases

INTRODUCTION

Strontium titanate finds applications in varistors, while thin strontium titanate films are used in tunable HTS (high temperature superconducting) microwave filters. This synthetic contribution to the field has been the combination of first-row transition metal i.e. titanium(IV) and tin to provide precursor for mixed metal oxides. To achieve the goal its Schiff base derivatives were synthesized because of their less tendency to undergo hydrolysis and prevent the phase separation problem in forming the multicomponent oxides. In the context of the search for environment-respectful, lead- and bismuth-free chemical compounds for devices such as actuators, SnTiO_3 (ST) is investigated from first principles within density functional theory. The equation of state describes the equilibrium volume of SnTiO_3 is smaller than ferroelectric PbTiO_3 (PT) in agreement with a smaller Sn^{2+} radius. While ionic displacements exhibit similar trends between ST and PT, a larger tetragonality (c/a ratio) for ST results in a larger polarization. Within ST analyzes of site projected density of states and chemical bonding indicate a reinforcement of the bond covalence with respect to Pb homologue. Both PT and ST exhibit anomalous large effective charges and the dielectric constant of ST is calculated larger than PT.¹ 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.² The synthesis of

homogeneously dispersed bimetallic oxides in nano crystalline or amorphous form has been reported by Klabunde *et al.*³ Apart from their role as precursors for mixed metal oxides the bimetallic- μ -oxoalkoxides of transition metals have been found to rank among the best catalysts for the polymerization of heterocyclic monomers like lactones, oxiranes, thiranes and epoxides.^{4,5} Molybdenum and tungsten alkoxides in their middle oxidation state have been used as a model for reductive cleavage of carbon monoxide to carbides and oxides via the Fisher-Tropsch reaction.⁶ Owing to the ever-growing importance of heterometallic alkoxides and oxoalkoxides it was considered worthwhile to synthesize the Schiff base derivatives of $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_6]$.

EXPERIMENTAL

Instrumentation

The general technique and physical measurement were carried out as described elsewhere.⁷⁻⁹ The Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer over the range of 4000-400 cm^{-1} . The ^1H , ^{13}C , and ^{119}Sn NMR spectra were recorded in CDCl_3 on Bruker Avance II 400 NMR spectrometer.

Reagents

All reagents used were of analytical grade. All manipulations have been carried out under anhydrous conditions and the solvents and reagents used were purified and

dried by standard methods.¹⁰ The reagents dibutyl tin diacetate and titanium(IV) isopropoxide were purchased from Aldrich and used as received. Benzene was purchased from Ranbaxy, kept in presence of sodium wire for two days and distilled twice before use to ensure the complete removal of moisture.

Procedure

[Bu₂SnO₂Ti₂(OPrⁱ)₆] and Schiff bases were prepared in laboratory by reported methods.¹¹ The isopropoxy groups in the μ -oxoisopropoxide compound and liberated isopropanol formed in preparation of Schiff base derivatives were estimated oxidimetrically.¹¹ Tin and titanium were estimated gravimetrically.¹⁰ The derivatives were decomposed in conc. HCl and extracted in dil. HCl, tin was precipitated as sulphide (pH 5-6), filtered and estimated as SnO₂.¹⁰ The H₂S was boiled off completely from the filtrate and titanium was estimated as TiO₂ via the formation of titanium-phenazone complex.¹⁰

Synthesis of derivatives of dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide with Schiff bases

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

The compound [Bu₂SnO₂Ti₂(OPrⁱ)₆] (0.383 g, 0.536 mmol) and salicylidene-aniline (0.106 g, 0.536 mmol) were refluxed in (~50) ml benzene for 4 hrs at ~100 °C in a flask connected to short distillation column. The liberated isopropanol was collected continuously at 72-78 °C as a binary azeotrope of isopropanol-benzene.¹² The isopropanol in azeotrope was estimated oxidimetrically to check the completion of the reaction. The excess of the solvent was then removed at reduced pressure (45 °C/1 mm Hg) yielding a yellowish red highly viscous product.

Similar procedure was adopted for the preparation of other derivatives of [Bu₂SnO₂Ti₂(OPrⁱ)₆] with schiff bases (HSB) i.e. Salicylidene-aniline (HSB¹), Salicylidene-*o*-toluidene (HSB²) and Salicylidene *p*-chloroaniline (HSB³) in stoichiometric ratio of 1:1, 1:2, 1:3 and 1:4 molar ratios.

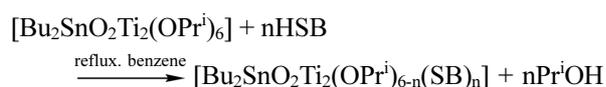
The details are given in (Table 1) along with analytical data.

Table 1. Analytical data

S. No.	Compound g (mmol)	Ligand g (mmol)	Molar ratio	Refluxing time hrs	Product g (%)	Anal. Calcd. (found)		
						HOPr ⁱ g	Sn (%)	Ti (%)
1.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.383 (0.536)	HSB ¹ 0.106 (0.536)	1:1	4	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₅ (SB ¹)] 0.386 (84.6)	0.07 (0.07)	13.97 (13.83)	11.24 (11.22)
2.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.390 (0.545)	HSB ¹ 0.215 (1.09)	1:2	6	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₄ (SB ¹) ₂] 0.457 (84.7)	0.12 (0.12)	12.03 (11.87)	9.68 (9.47)
3.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.385 (0.539)	HSB ¹ 0.318 (1.617)	1:3	8	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₃ (SB ¹) ₃] 0.516 (85.1)	0.16 (0.15)	10.57 (10.61)	8.51 (8.39)
4.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.372 (0.520)	HSB ¹ 0.410 (2.08)	1:4	9	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₂ (SB ¹) ₄] 0.572 (87.0)	0.19 (0.18)	9.42 (9.36)	7.58 (7.46)
5.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.382 (0.534)	HSB ² 0.113 (0.534)	1:1	4	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₅ (SB ²)] 0.384 (83.1)	0.07 (0.07)	13.7 (13.72)	11.06 (11.02)
6.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.387 (0.541)	HSB ² 0.228 (1.082)	1:2	7	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₄ (SB ²) ₂] 0.463 (84.1)	0.12 (0.11)	11.70 (11.56)	9.42 (9.35)
7.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.385 (0.539)	HSB ² 0.341 (1.617)	1:3	8	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₃ (SB ²) ₃] 0.535 (85.2)	0.15 (0.15)	10.19 (10.22)	8.20 (8.15)
8.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.371 (0.519)	HSB ² 0.438 (2.076)	1:4	9	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₂ (SB ²) ₄] 0.582 (85.0)	0.18 (0.17)	9.02 (9.04)	7.26 (7.14)
9.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.362 (0.506)	HSB ³ 0.117 (0.506)	1:1	4	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₅ (SB ³)] 0.358 (79.7)	0.07 (0.07)	13.42 (13.36)	10.80 (10.73)
10.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.370 (0.518)	HSB ³ 0.240 (1.036)	1:2	7	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₄ (SB ³) ₂] 0.461 (84.2)	0.11 (0.10)	11.25 (11.28)	9.05 (9.03)
11.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.365 (0.511)	HSB ³ 0.385 (1.533)	1:3	8	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₃ (SB ³) ₃] 0.527 (83.9)	0.15 (0.15)	9.68 (9.56)	7.79 (7.80)
12.	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₆] 0.389 (0.544)	HSB ³ 0.504 (2.176)	1:4	9	[Bu ₂ SnO ₂ Ti ₂ (OPr ⁱ) ₂ (SB ³) ₄] 0.680 (89.2)	0.17 (0.17)	8.49 (8.37)	6.83 (6.79)

RESULTS AND DISCUSSION

Many reactions of dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide with bidentate schiff bases (HSB) i.e. salicylidene aniline (HSB¹), salicylidene-*o*-toluidene (HSB²), salicylidene *p*-chloroaniline (HSB³) are performed in different molar ratios in refluxing benzene, in which the products of type [Bu₂SnO₂Ti₂(OPrⁱ)₅(SB)], [Bu₂SnO₂Ti₂(OPrⁱ)₄(SB)₂], [Bu₂SnO₂Ti₂(OPrⁱ)₃(SB)₃] and [Bu₂SnO₂Ti₂(OPrⁱ)₂(SB)₄] are formed. The general reaction can be given as follows.



Where $n=1-4$ and HSB=schiff bases

The isopropanol liberated during the course of reaction is collected azeotropically (isopropanol-benzene) and estimated oxidimetrically to check the progress of the reaction and it has been observed that only four out of six of isopropoxy groups of dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide could be replaced with Schiff base. Further replacement of fifth and sixth isopropoxy groups could not be achieved even with an excess of ligand (Schiff base) and prolonged refluxing time (approx. 20 hours).

All the Schiff base derivatives of dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide are found to be brownish yellow from gel type to solid product, soluble in common organic solvents (benzene, chloroform, hexane), susceptible to hydrolysis and decompose on heating strongly.

Infrared spectral studies

The spectra of the 1:1 to 1:3 Schiff base derivatives of [Bu₂SnO₂Ti₂(OPrⁱ)₆] show absorption bands in the region 1360-1340 cm⁻¹ and 1165-1150 cm⁻¹ are the characteristics of *gem*-dimethyl portion and combination band $\nu(\text{C}-\text{O}+\text{OPr}^i)$ of the terminal and bridging isopropoxy group respectively.¹³ No peak is observed at 1165 cm⁻¹ in the spectrum of 1:4 schiff base derivatives indicates the absence of terminal isopropoxy group. A band appeared at approximately 950 cm⁻¹ is due to $\nu(\text{C}-\text{O})$ stretching of bridging isopropoxy group. However all these bands are also observed in 1:5 and 1:6 Schiff base derivatives as that found in 1:4 β -Schiff base derivatives of μ -oxoisopropoxide compound reveals the presence of bridging isopropoxy group even in the 1:6 Schiff base derivatives.

The $\nu(\text{O}-\text{H})$ band occurring in the region ~3400-3100 cm⁻¹ in the schiff bases disappears completely in the derivatives, indicating the deprotonation of these ligands. Schiff bases show intense bands at ~1565 cm⁻¹ and ~1260 cm⁻¹

due to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{O})$ vibrations of azomethine and phenolic groups respectively. The downward shift in $\nu(\text{C}=\text{N})$ stretch by ~15-25 cm⁻¹ indicating the coordination of azomethine nitrogen of the ligand to the metal atom and upward shift in $\nu(\text{C}-\text{O})$ by ~20-30 cm⁻¹ suggesting the bond formation of phenolic oxygen of the Schiff base to the metal in the derivatives.¹⁴ A number of peaks are observed in the region 700-400 cm⁻¹ due to M-O and M-N stretching vibrations in μ -oxo compounds which is difficult to assign exactly due to the overlapping of bands in this region.¹⁵

NMR Spectral Studies

¹H NMR

¹H NMR spectra of all the Schiff base derivatives of dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide show broad multiplet centered between δ 0.8-1.2 ppm due to the intermixing of methyl protons of isopropoxy groups along with butyl groups on tin.¹⁶ A broad multiplet centered at δ 4.1 is due to the methine proton of isopropoxy groups in the spectra of all derivatives. These signals are also observed in 1:5 and 1:6 Schiff base derivatives indicate the presence of bridging isopropoxy group.

In the ¹H NMR spectra of all derivatives, the signals observed at δ 6.8-7.8 ppm are due to phenyl ring protons. A peak observed at δ 11.2 ppm due to phenolic (O-H) protons of Schiff base is disappeared by the formation of its derivative of dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide indicative of the deprotonation of phenolic group. In the case of salicylidene-*o*-toluidene derivatives an additional signal at δ 2.3 ppm has been observed due to methyl protons substituted on the benzene ring.

¹³C NMR

The ¹³C NMR spectra of 1:1 to 1:3 Schiff base derivatives of dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide shows two prominent peaks at δ ~ 27.4 and δ ~ 27.9 ppm assignable to the methyl carbon of terminal and intermolecularly bridged isopropoxy moiety and two different type of methine carbons of isopropoxy group is confirmed by the two signals observed at δ ~ 62.6 ppm and δ ~ 62.8 ppm.¹⁷ The other peaks are found at 25.44, 25.27, 24.1 and 13.43 due to C-1, C-2, C-3 and C-4 of the butyl group.¹⁸ Further the 1:4 schiff base derivatives of μ -oxoisopropoxide show the absence of terminal isopropoxy group. These signals are also observed in 1:5 and 1:6 schiff base derivatives of μ -oxo compound indicating non-removal of the bridging isopropoxy group. Two signals observed in the range δ 160.3-164.0 ppm and δ 150-147 ppm are due to carbonyl carbon and methine carbon attached to nitrogen of ligand

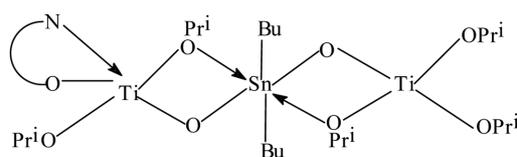
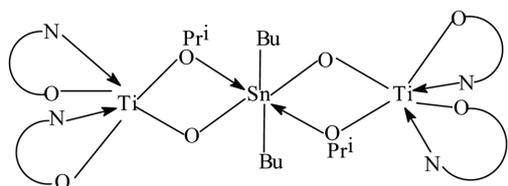
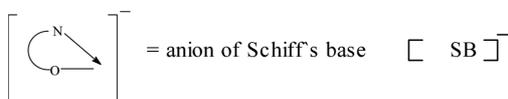
(a) Proposed structure of $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_5(\text{SB})]$ (b) Proposed structure of $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_2(\text{SB})_4]$ 

Fig. 1. (a) Proposed Structure of mono derivative of dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide with bidentate schiff bases (HSB). (b) Proposed Structure of tetra derivative of dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide with bidentate schiff bases (HSB).

moiety in all the Schiff derivatives of μ -oxoisopropoxide compound. Moreover, a number of signals are observed between δ 133-117 ppm due to the different carbons of two phenyl rings.

^{119}Sn NMR

A sharp signal around at δ -192.4 ppm in the ^{119}Sn NMR spectrum of derivatives of dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide is attributed to the hexacoordination about Sn atom in the all compound.¹⁹

Molecular Weight Determination

The molecular weight measurement of the Schiff base derivatives of dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide shows these are monomeric in nature.

CONCLUSION

The aforesaid spectral study and elemental analysis suggest the tentative structures of the Schiff base derivatives of dibutyl Sn(IV)-Ti(IV)- μ -oxoisopropoxide of the type $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_5(\text{SB})]$, $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_4(\text{SB})_2]$, $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_3(\text{SB})_3]$ and $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPr}^i)_2(\text{SB})_4]$.

Acknowledgments. Authors are gratefully acknowledging the Haryana Institute of Engineering & Technol-

ogy, Kaithal and Kurukshetra University, Kurukshetra for providing the necessary facilities to complete this research work.

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