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Organoheterometallic [$Bu_3Sn(IV)$-$Ti(IV)$]-μ-oxoisopropoxide and its Salicylate Derivatives: Synthesis, Spectral and Thermal Studies

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ABSTRACT

Tributyl Sn(IV)-Ti(IV)-μ-oxoisopropoxide [$Bu_3SnOTi(OPr^i)_3$] prepared by refluxing equimolar amounts of tributyl tin acetate and titanium isopropoxide in xylene. The reactions of [$Bu_3SnOTi(OPr^i)_3$] with methyl/ethyl/phenyl salicylates in 1:1 and 1:2 molar ratios resulted in derivatives of the type [$Bu_3SnOTi(OPr^i)_2(Rsal)$] and [$Bu_3SnOTi(OPr^i)(RSal)_2$] (where RSal is deprotonated methyl/ethyl/phenyl salicylate) respectively. The [$Bu_3SnOTi(OPr^i)_3$] characterization has been made by elemental analysis, molecular weight measurements, thermal and spectral studies (^1H, ^{13}C, ^{119}Sn NMR and IR). The salicylate derivatives of parent compound have been characterized by elemental analysis, molecular weight measurements, and spectral studies (^1H, ^{13}C, ^{119}Sn NMR and IR). The studies reveal that the compound [$Bu_3SnOTi(OPr^i)_2$ and its salicylate derivatives are dimeric in nature.

KEYWORDS: Bimetallic-μ-oxoalkoxides, Titanium, Tin, salicylates, Volatile

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INTRODUCTION

SnO_2 and TiO_2 are potential candidates for a wide range of applications, as catalyst, gas sensors, adsorption materials and micro- synthesized powders and microwave dielectric ceramics.[1] Full substitution of Pb by the smaller Sn atom to get $SnTiO_3$ gives a tetragonal ground state, with the rhombohedral phase at ~12.6 meV at higher energy.[2] The environmentally 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. Moreover, $SnTiO_3$ materials is used in micropumps in medical field.[2] Strontium titanate finds applications in varistors, while thin strontium titanate films are used in tunable high temperature superconducting microwave filters.[3] Titanium−tin mixed oxide $(Ti,Sn)O_2$ with anatase structure synthesized based on a sol−gel technique using titanium tetra-isopropoxide and tin tetrachloride as precursors.[4] The relaxor antiferroelectric $(Pb,La)(Zr,Sn,Ti)O_3$ powders were synthesized by conventional mixed oxide method and co-precipitation method. Both the samples exhibit typical antiferroelectric double hysteresis loops. Compared to the conventional mixed oxide method, lower coercive field, higher saturated polarization and better squareness of hysteresis loop can be obtained from ceramics by co-precipitation due to the homogeneity.[5] Recently, β-diketiminate derivative zinc alkoxide exhibits the highest rate of polymerization with better stereoselectivity in the formation of polylactic from the rac-lactide with aggregation and narrow polydisperties[6]. 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[7]. Volatile organometallic alkoxides are among the preeminent precursors for the synthesis of mixed metal oxides because they can be used in metal-organic-chemical-vapor-deposition (MOCVD), in sol-gel synthesis or in solid synthesis.[8,9] Synthesis of homogeneously dispersed bimetallic oxides in nano crystalline or amorphous form has been reported by Klabunde *et al.*[10] 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 heterocyclic monomers like lactones, oxiranes, thiranes and epoxides[11-13]. 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. Therefore, heterobimetallic tributyl Sn(IV)-Ti(IV)-μ-oxoisopropoxide was prepared and its salicylate derivatives were synthesized to gain insight the structure of parent compound. The study reveals salicylate derivatives undergo hydrolysis with slower rate in comparison to parent compound and prevent the phase secretion problem in forming the multicomponent oxides.

EXPERIMENTAL

Instrumentation

The general technique and physical measurement were carried out as described elsewhere.[9-11] The molecular weights are determined in dry benzene using cryoscopic method. The infrared spectra recorded as direct film on a Perkin Elmer 1710 FTIR spectrometer, over a range 4000-400 $cm^{-l.}$ The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra recorded in $CDCl_3$ on Bruker Avance II 400 NMR spectrometer. TG study has been made on Diamond TG/DTA Perkin Elmer instrument.

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. The titanium isopropoxide and tributyl tin acetate (both from Aldrich) are used as received. The methyl/ethyl/phenyl salicylates were prepared in laboratory, dried and purified prior to their use.[14] 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

The complex $[Bu_3SnOTi(OPr^i)_3]$ and its salicylate derivatives were prepared in laboratory by reported methods.[15,16] The isopropyl acetate and isopropanol formed during the synthesis of $[Bu_3SnOTi(OPr^i)_3]$ and its salicylate derivatives respectively were estimated oxidimetrically.[15,16] Tin and titanium were estimated gravimetrically.[17] The parent complex and its salicylate derivatives were decomposed in conc. HCl and extracted in dil. HCl, tin is precipitated as sulphide (*p*H 5-6), filtered and estimated as SnO_2.[17] The H_2S was boiled off completely from the filtrate and titanium is estimated as TiO_2 via the formation of titanium-phenazone complex.[17]

Synthesis of [$Bu_3SnOTi(OPr)_3$]

$Bu_3Sn(OAc)$ (3.589 g, 10.28 mmol) and $Ti(OPr^i)_4$ (2.910 g, 10.28 mmol) are refluxed in 1:1 moar ratio in xylene (~80 ml) for 6 hrs on an oil bath (temperature ~150 °C). The liberated isopropyl acetate continuously removed from ~78 °C to the boiling point of xylene (139 °C). The isopropyl acetate formed during the course of reaction collected and estimated oxidimetrically[15-18] to check the completion of the reaction. The excess of solvent removed at reduced pressure to give the μ-oxo compound as pale yellow highly viscous product, soluble in common organic solvents such as $CHCl_3$, and C_6H_6, highly susceptible to hydrolysis and decomposed on heating (~180 °C). The product re-dissolved in benzene and slow evaporation of benzene resulted in a pale yellow highly thick liquid. (Yield=98%).

Table 1- Analytical data

SNo.	Compound g (m mol)	Ligand g (m mol)	Molar Ratio	Refluxing time (Hrs)	Product (%)	Anal found (calcd)		
						Pr^iOH(g)	Sn %	Ti %
1.	[$Bu_3SnOTi(OPr^i)_3$] 1.000(1.89)	HMeSal 0.287(1.89)	1:1	4	[$Bu_3SnOTi(OPr^i)_2$(MeSal)] (80.3)	0.16 (0.11)	19.10 (19.13)	7.49 (7.55)
2.	[$Bu_3SnOTi(OPr^i)_3$] 0.692(1.30)	HMeSal 0.397(2.61)	1:2	$8^1/_2$	[$Bu_3SnOTi(OPr^i)$$(MeSal)_2$] (79.8)	0.18 (0.16)	16.54 (16.66)	6.49 (6.58)
3.	[$Bu_3SnOTi(OPr^i)_3$] 0.913(1.72)	HEtSal 0.286(1.72)	1:1	4	[$Bu_3SnOTi(OPr^i)_2$(EtSal)] (81.2)	0.10 (0.10)	18.66 (18.71)	7.45 (7.38)
4.	[$Bu_3SnOTi(OPr^i)_3$] 0.771(1.45)	HEtSal 0.483(2.90)	1:2	8	[$Bu_3SnOTi(OPr^i)$$(EtSal)_2$] (79.5)	0.16 (0.17)	16.05 (16.03)	6.29 (6.33)
5.	[$Bu_3SnOTi(OPr^i)_3$] 0.892(1.68)	HPhSal 0.362(1.68)	1:1	$3^1/_2$	[$Bu_3SnOTi(OPr^i)_2$(PhSal)] (80.7)	0.12 (0.10)	17.33 (17.37)	6.70 (6.86)
6.	[$Bu_3SnOTi(OPr^i)_3$] 0.787(1.48)	HPhSal 0.639(2.97)	1:2	$8^1/_2$	[$Bu_3SnOTi(OPr^i)$$(PhSal)_2$] (78.8)	0.14 (0.18)	13.9 (14.14)	5.54 (5.59)

HMeSal = Methyl salicylate;HEtSal = Ethyl salicylate; HPhSal = Phenyl salicylate

Reaction of [$Bu_3SnOTi(OPr^i)_3$] *with methyl salicylate* (HMesal) *in 1:1 molar ratio*

[$Bu_3SnOTi(OPr)_3$] (1.000 g, 1.89 mmol) and methyl salicylate (0.287 g, 1.89 mmol) refluxed in benzene (~60 ml) for 4 hrs on an oil bath (temperature ~100 ºC). The liberated isopropanol continuously fractionated at 72-78 ºC as binary azeotrope of isopropanol-benzene. The azeotrope formed during the course of reaction collected and checked for completion of the reaction.[18,19] The excess of solvent removed at 40 ºC/1 mm pressure and a pale yellow amorphous solid product was obtained. The preparation of other salicylate derivatives of [$Bu_3SnOTi(OPr^i)_3$] in 1:1 and 1:2 molar ratios carried out

by a similar procedure and their analytical data along with metal and liberated isopropanol estimations have been summarized in the Table-1.

RESULTS & DISCUSSION

$[Bu_3SnOTi(OPr^i)_3]$ has been synthesized by refluxing tributyl tin acetate and titanium isopropoxide in 1:1 molar ratio according to the following reaction scheme-1.

$$Bu_3Sn(OAc) + Ti(OPr^i)_4 \xrightarrow[139\ ^oC]{\text{refluxing xylene}} [Bu_3SnOTi(OPr^i)_3] + AcOPr^i$$

Scheme-1

To further gain an insight the structure, solubility and rate of hydrolysis, many reactions of tributyl Sn(IV)-Ti(IV)-μ-oxoisopropoxide are performed with different salicylates in various molar ratios in refluxing benzene. The reactions yielded compounds of the type $[Bu_3SnOTi(OPr^i)_2(RSal)]$ and $[Bu_3SnOTi(OPr^i)(RSal)_2]$ following reaction scheme-2.

$$Bu_3SnOTi(OPr^i)_3] + nHRSal \xrightarrow[78\ ^oc]{\text{refluxing benzene}} [Bu_3SnOTi(OPr^i)_{3-n}(RSal)_n] + nPr^iOH$$

(n = 1-2; HRSal= methyl/ethyl/phenyl salicylate)

Scheme-2

The molecular weight measurement of the compound $[Bu_3SnOTi(OPr^i)_3]$ and its salicylate derivatives shows these are dimeric in nature and is probably linked through oxygen bridges.

IR Spectra

The sharp bands at 1595 and 1435 cm^{-1} due to ν_{assym} (C=O) and ν_{sym} (C=O) respectively in tributyl tin acetate have been found to be absent in the parent compound indicating the removal of acetyl group.[20] The spectra of the μ-oxoisopropoxide and its 1:1 derivatives show absorption bands at ~1360 cm^{-1} and ~1165 cm^{-1} are the characterstics of *gem*-dimethyl portion and combination band ν(C-O+OPr^i) of the bridging and terminal isopropoxy group respectively.[21] No peak is observed at 1165 cm^{-1} in the spectrum of 1:2 salicylate derivatives indicates the absence of terminal isopropoxy group. A band appeared at approximately 950 cm^{-1} is due to ν(C-O) stretching of bridging isopropoxy group.[22] However, all the bands of 1:2 salicylate derivatives of parent compound are also observed in the spectra of compounds obtained on performing the reaction in 1:3 molar ratio of parent compound and salicylates. This suggests non-removal of bridging isopropoxy group in salicylate derivatives. A broad

band in the region ~3100 cm^{-1} due to ν(O-H) in salicylates is found absent in all salicylate derivatives of parent compound indicates the deprotonation of salicylates. The ν(C=O) band appearing in salicylates at ~1650 cm^{-1} shows a downward shift by 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) vibrations is shifted by 15-20cm^{-1} higher in the derivatives indicating bond formation of phenolic oxygen of salicylate to the metal atom.[23] A number of bands observed in μ-oxo and its derivatives in the region 700- 400 cm^{-1} 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.

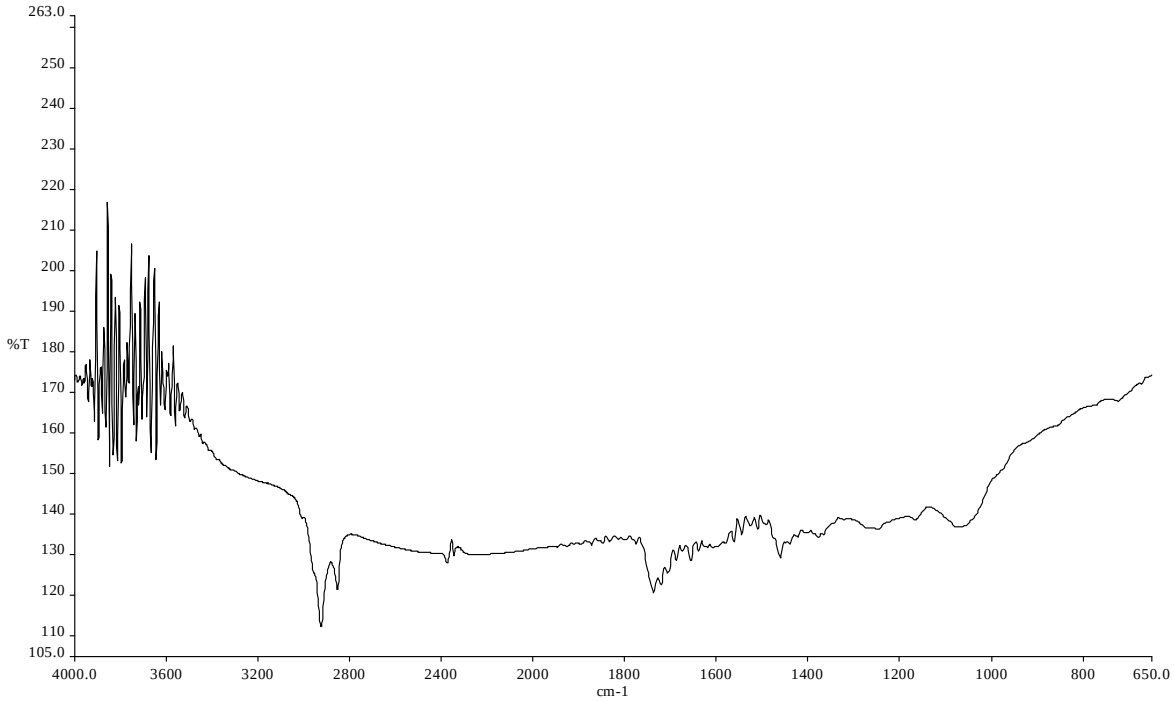


Fig.1 IR Spectra of Oxoisopropoxide and its derivatives

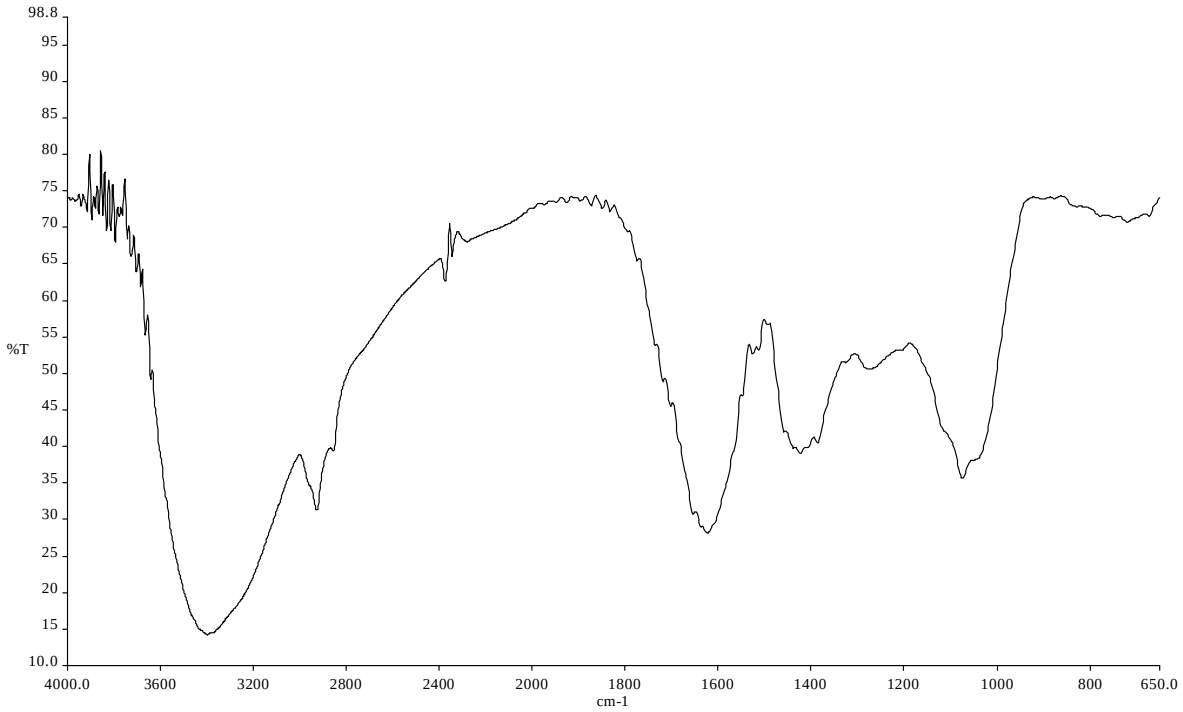


Fig.2 IR Spectra of salicylates derivatives

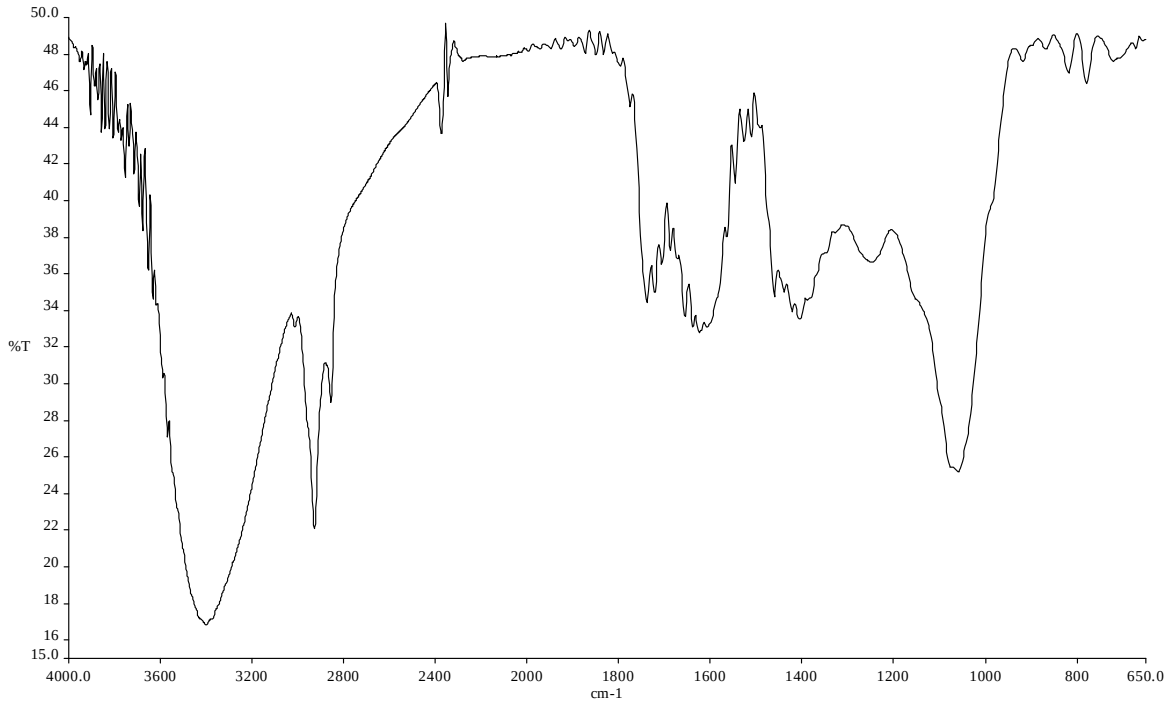


Fig.3 IR Spectra of tributlyl oxoisopropoxide

^{1}H NMR spectra

A peak observed at δ 2.3 ppm in tributyl tin acetate due to methyl protons of the acetate group found absent in the parent μ-oxo compound, confirms the replacement of the acetyl group. The ^{1}H NMR spectrum of the tributyl Sn(IV)-Ti(IV)-μ-oxoisopropoxide and its 1:1 derivative show number of peaks in the region δ 0.7-1.2 ppm due to inter mixing of methyl protons of the isopropoxy groups and protons of the butyl groups bonded to tin atom.[24] A multiplet centered at δ 4.1 ppm assigned due to methine protons of the isopropoxy groups in parent μ-oxo compound and its 1:1 derivative found overlap with ~ δ 3.8 ppm due to methyl protons and methylene protons of methyl salicylate and ethyl salicylate in 1:1 derivative respectively. A sharp singlet 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 tributyl Sn(IV)-Ti(IV)-μ-oxoisopropoxide with methyl and ethyl salicylates respectively. This confirms the substitution of both terminal isopropoxy groups. A broad singlet at ~δ 12.8 ppm due to phenolic proton in the salicylate found absent in all derivatives confirms their deprotonation. The signals due to phenyl ring protons of salicylate moiety are observed at their usual positions (δ 6.4–7.6 ppm) in all the derivatives.

^{13}C NMR

The ^{13}C NMR spectra of Tributyl Sn(IV)-Ti(IV)-μ-oxoisopropoxide and its 1:1 salicylate derivatives show two prominent peaks at ~ δ 27.4 and ~ δ 27.9 ppm assignable to the methyl carbon of terminal and bridging isopropoxy groups and two different type of methine carbons of isopropoxy group confirmed by the two signals observed at δ ~ 62.6 ppm and δ ~ 62.8 ppm.[25] The other peaks found at 25.49, 25.29, 23.21 and 13.39 are due to C-1, C-2, C-3 and C-4 of the butyl group.[26] Further the 1:2 salicylate derivatives of μ-oxoisopropoxide show the absence of terminal isopropoxy group. However, all peaks of ^{13}C NMR spectra of 1:2 salicylate derivatives of parent compound are also observed in the spectra of compounds obtained on performing the reaction in 1:3 molar ratio of parent compound and salicylates.. The peaks observed in the region δ124-138 ppm are due to carbon atoms on benzene ring, however, the peak observed at about δ170 ppm is due to ring carbon linked to the ester group and a peak observed at about δ188 ppm is due to carbon of the ester group (-COOR).[27]

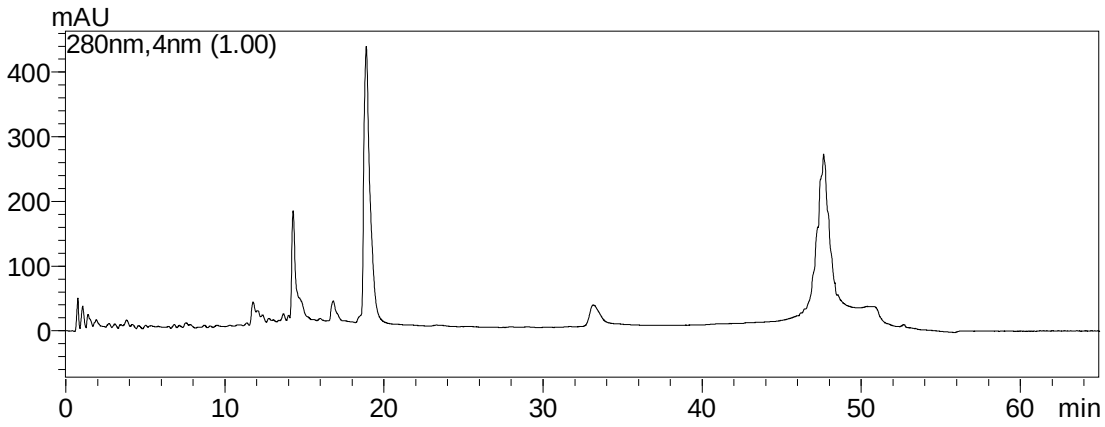


Fig.4 Profiling of oxoisopropoxides and spectral analysis

^{119}Sn NMR

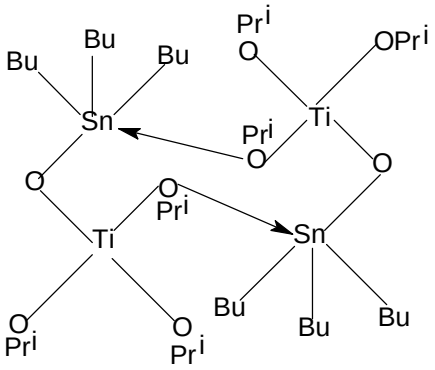
The ^{119}Sn NMR spectra of [$Bu_3SnOTi(OPr^i)_3$] and its derivatives exhibits a sharp signal at ~δ 150-158 ppm assignable to the penta-coordination about tin.[28]

Thermal analysis

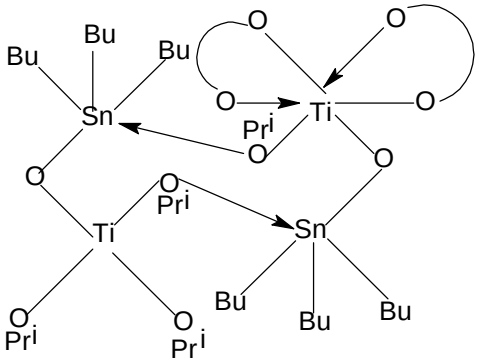
Thermogravimetric (TG) analysis of [$Bu_3SnOTi(OPr^i)_3$] has been performed up to 700 ^oC at 10^oC/min. The total weight loss of 93.740 % was observed from 65 to 350 ^oC. A small weight loss between 65 to 170^o C is probably due to the presence of moisture and traces of solvent in the μ-oxo compound. A rapid weight loss observed between ~ 170 to 350 ^oC indicates the volatile nature of μ-oxo compound. Further, the remaining weight 6.260 % observed is due to the decomposition of partially hydrolysed μ-oxo compound in to mixed metal oxide.[29]

CONCLUSION

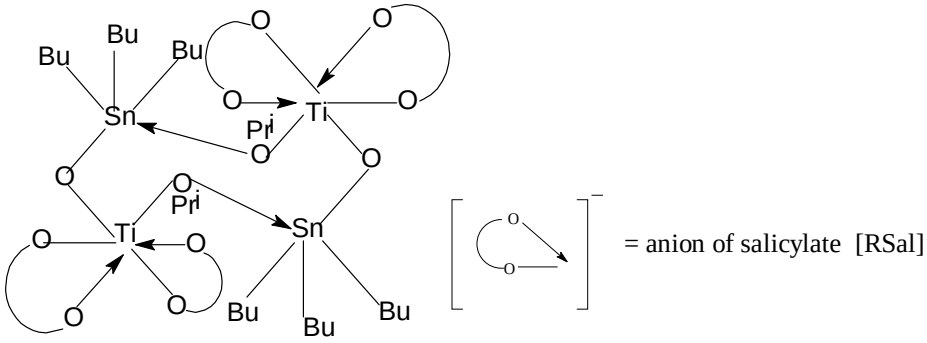
The aforesaid studies suggest the tentative structures of the [$Bu_3SnOTi(OPr^i)_3$] and its salicylates of the type [$Bu_3SnOTi(OPr^i)_2(RSal)$] and [$Bu_3SnOTi(OPr^i)(RSal)_2$]. TG study reveals the volatile nature of μ-oxo compound and its hydrolysed product fabricate the metal oxides. It is shown the derivatives of parent compound are found more stable and less prone to hydrolysis as compared to parent compound. The proposed structures of parent compound and its 1:1 and 1:2 salicylate derivatives are shown as Fig.5 (a), (b) and (c) respectively.



(a) Proposed structure of [$Bu_3SnOTi(OPr^i)_3$]



(b) Proposed structure of [$Bu_3SnOTi(OPr^i)_2(RSal)$]



(c) Proposed structure of [$Bu_3SnOTi(OPr^i)(RSal)_2$]

Fig.5 **(a) Proposed structure of [$Bu_3SnOTi(OPr^i)_3$] and (b) Proposed structure of [$Bu_3SnOTi(OPr^i)_2(RSal)$] (c) Proposed structure of [$Bu_3SnOTi(OPr^i)(RSal)_2$]**

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REFERENCES

1. Cava RJ. Dielectric materials for applications in microwave communications. J. Mater. Chem. **2001;** 11:54-62.
2. Cohen R, Ganesh P. Class of pure piezoelectric materials.US Patent. 2011; 8039131.

3. Matar SF, Baraille I et al. First principles studies of $SnTiO_3$ perovskite as potential environmentally benign ferroelectric material. Chemical Physics.2009; 355: 43-49.
4. Marcela MO, Danielle CS et al. Ability for the facile transportation of electrons and protons.Chem. Mater .2003**;** 15:1903.
5. Athar T, Hakeem Aet al. Synthesis of β-dikitiminate derivatives of zinc alkoxides. J. Chil. Chem. Soc.2011; 56: 887.
6. Hench L. L, West JK. The sol-gel process.Chem.Rev.1990; 90:33-72.
7. Kapoor PN, Heroux D et al. High surface area homogeneous nanocrystalline bimetallic oxides obtained by hydrolysis of bimetallic μ-oxo alkoxides J. Mater.Chem.2003**;** 13:410-414.
8. Heuschen J, Jerome R et al. Polycaprolactone-based block copolymers.Macromolecules.1981; 14: 242-246.
9. Hamitou A, Jerome R et al.A new catalyst for the living polymerization of lactones to polyesters. Macromolecules.1973;6:651-652.
10. Ouhadi T,Hamitou A et al.Soluble bimetallic μ-oxoalkoxides. VII. Characteristics and mechanism of ring-opening polymerization of lactones. J. Polymer. Sci.1977; 15: 865-873.
11. Sharma HK, Kapoor PN. Synthesis of new bimetallic [Al(III), Mg(II)]-μ-oxoisopropoxide and its β-diketone derivatives**.**Polyhedron**.**1988**;** 7: 1389.
12. Sharma HK, Kumar R. Synthesis of organoheterobimetallic [Bu_2Sn(IV)-Ti(IV)]-μ-oxoisopropoxide and its β-diketonates.Indian J. Chem. 2008; 47A: 854-858.
13. Sharma M, Bhagi AK et al. Precursors for mixed metal oxide nanoparticles: Synthesis and characterization of μ-oxoalkoxides of some bivalent metals and their β-diketonates.Indian J. Chem. 2005; 44: 256-260.
14. Kumar R. Synthesis and Pyrolytic Studies of Schiff Base Derivatives of Heterotrinucleic[AlIII-SnII-BIII]-μ-oxoisopropoxide .E-J. Chem., 2012; 9:387-395.
15. Sawyer AK. Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry**.**Organotin Compounds.1971; 2:347-349**.**
16. Nakamoto K. Infrared and Raman Spectra of Inorganic and Coordination Compounds. John Wiley and Sons. 1986;138.
17. Kumar R, Sharma HK. Synthesis and Characterization of Derivatives of Dibutyl Sn(IV)-Ti(IV)-*μ*-Oxoisopropoxide with Schiff Bases. J. Korean Chem. Soc. 2012;56:54-57.

18. Ouhadi T, Hamitou A et al. Soluble Bimetallic μ-Oxo-alkoxides. 8. Structure and Kinetic Behavior of the Catalytic Species in Unsubstituted Lactone Ring-Opening Polymerization. Macromolecules. 1976**;**9:927-931.
19. Shiner V J et al. The chemistry of metal alkoxides and their applications to biology. J. Am. Chem. Soc. 1963; 85: 2318.
20. Singh RV, Joshi SC et al.Studies of biologically potent organotin(IV) and organosilicon(IV) complexes of a sulfur donor ligandderivedfromacetylferrocene.Appli.Organomet.Chem.2002;16: 713-720.
21. Mirzaee M, Amini MM et al. Preparation and characterizationof boehmite,CuO,TiO2 and Nb2O5 by hydrothermal assisted sol-gel processing of metal alcoxides.Ceram.Silikáty.2005;49: 40-47.