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Synthesis and characterization of derivatives of heterotrimetallic[Al(III);Sn(II);Ti(IV)]- μ -oxo-isopropoxide- μ -oxo-*n*-propoxide [SnO₂TiAl (OPrⁱ)₂(OPrⁿ)₃] with cycloalcohols

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ABSTRACT

Tin diacetate and aluminium isopropoxide in equimolar proportion in xylene affords the complex [(OAc)₂SnOAl(OPrⁱ)₂] which on reaction with Ti(OPrⁿ)₄ in 1:1 molar ratio yielded a new organo-heterotrimetallic- μ -oxoisopropoxide- μ -oxon-propoxide [SnO₂TiAl(OPrⁱ)₂(OPrⁿ)₃] with continuous liberation of isopropyl acetate and propyl acetate formed during the course of reaction. The substitution reactions of the above compound with cycloalcohols in different molar ratios (1:1 and 1:2) gave compounds of the type [SnO₂Al(OPrⁱ)₂Ti(OPrⁿ)_{3-x}CA_x] (where X is 1-2 and CA=cyclopentanol, cyclohexanol, cycloheptanol) respectively. The μ -oxoisopropoxide- μ -oxo-*n*-propoxide compound and its cycloalcohols have been characterized by elemental and molecular weight data which suggested that the complexes have 1:1 and 1:2 stoichiometries. The complexes were further characterized by spectral analysis (IR, ¹H, ¹³C, ¹¹⁹Sn, ²⁷Al NMR and mass spectra). The spectral studies confirmed that the proposed framework of the new organo-heterotrimetallic complexes and indicated a tetrahedral geometry around the central metal atom.

Key words: Organo-heterotrimetallic- μ -oxoisopropoxide- μ -oxon-propoxide, Tin, Aluminium, Titanium, cycloalcohols (Cyclopentanol, Cyclohexanol, Cycloheptanol).

INTRODUCTION

The unique characteristics of metal oxides make them the most diverse class of materials, with properties covering almost all aspects of materials science and solid state physics. The great variety of structures and properties made them the primary target in solid state chemistry and still gives inspiration for designing new materials. The crystal structures range from simple rock salt to highly complex incommensurately modulated structures and the nature of the metal-oxygen bonding varies from nearly ionic to covalent or metallic¹⁻². Multimetallic oxides cover an always wider range of applications in electronics, optics³⁻⁵, magnetism⁶⁻⁸, catalysis⁹ and environmental issues¹⁰. High-tech applications rely on materials in high purity and/or in a variety of shapes, formulations or microstructures (nanoparticles, coatings, porous matrices etc.) and these requirements need to move from traditional ceramic routes to chemical routes, more versatile, for their elaboration. The latter deal with inorganic polymerization processes namely hydrolytic or non-hydrolytic sol-gel processing "Chimiedouce" and metal organic deposition (MOD) in solution or chemical vapor deposition (CVD) in the vapor phase. Alkoxy groups are among unique ligands amongst the oxygen containing ones, as they have remarkable flexible bridging tendency between similar as well as dissimilar metal atoms and adjust themselves according to the extent of ramification of the alkyl groups and the atomic sizes of different metal atoms bridged by them¹¹. Special focus is put on structural aspects and on the

possibility to introduce functional organic groups. Such precursors have a high potential for innovative materials synthesis because they permit control of the precursor reactivity in sol-gel processes and the preparation of titanium-based inorganic-organic hybrid materials. Coordination, solvation, aggregation and redistribution equilibrium play an important role in the chemistry of the modified titanium alkoxides and organic side reactions have to be taken into account¹².

MATERIALS AND METHODS

Analytical methods and physical measurements

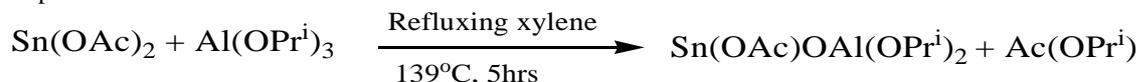
All manipulations have been carried out under anhydrous conditions and the chemicals and solvents used were of analytical grade and purified by recommended method¹³. The tin acetate, aluminium isopropoxide and titanium propoxide were purchased from Aldrich and were used as such cyclopentanol, cyclohexanol, cycloheptanol were used as received. Tin, titanium and aluminium were estimated gravimetrically. The complex $[\text{SnO}_2\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)_3]$ and its cycloalcohols were decomposed in con. HCl and extracted in dil. HCl and further tin was precipitated as sulphide ($\text{P}^{H5} -6$), filtered and estimated as SnO_2 ¹⁴. The H_2S was boiled off completely from the filtrate and titanium was estimated as TiO_2 via the formation of titanium phenazone complex¹⁵. Aluminium was determined gravimetrically as oxinate. Molecular weight determinations were carried out by the Rast Camphor Method. IR spectra were recorded on a Perkin-Elmer model 1710 grating spectrophotometer, in the range 4000–400 cm^{-1} in KBr discs. ^1H , ^{13}C , ^{27}Al and ^{119}Sn NMR spectra were recorded on a Bruker Avance II 400 NMR spectrometer in CDCl_3 using TMS as the internal standard. Mass spectrum was recorded on a Waters QTOF₂ mass spectrometer equipped with Quadrupole and time of flight (TOF) analyser.

2.1. Synthesis of $[\text{SnO}_2\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)_3]$

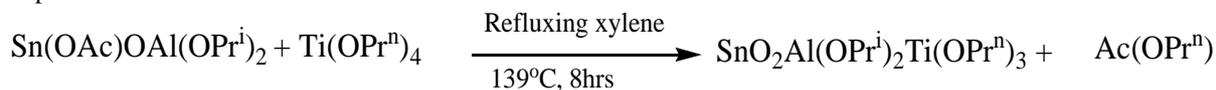
The compound was synthesized in two steps, first the $\text{Sn}(\text{OAc})_2$ (2.335g, 9.864mmol) reacts with $\text{Al}(\text{OPr}^i)_3$ (2.012g, 9.864 mmol) in 1:1 molar ratio in xylene for about 6 hrs on a fractionating column and the isopropyl acetate formed during the reaction was distilled off continuously from 78°C to boiling point of xylene¹⁶ (139°C). The solvent xylene was completely removed at (~70 °C /1mm) which results into formation of the complex $[(\text{OAc})\text{SnOAl}(\text{OPr}^i)_2]$. In second step, this complex undergoes thermal condensation with $\text{Ti}(\text{OPr}^n)_4$ (2.82g, 9.934 mmol) in 1:1 molar ratio in xylene to form a new organohetero-trimetallic- μ -oxoisopropoxide- μ -oxo-n-propoxide $[\text{SnO}_2\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)_3]$. The contents were refluxed for about 8 hrs on a fractionating column and the propyl acetate formed during the reaction was distilled off continuously from 102°C to boiling point of xylene¹⁶ (139 °C). The solvent xylene was completely removed at (~70 °C /1mm) yielding a yellow solid. The product was re-dissolved in benzene and slow evaporation of benzene resulted in a pale yellow glassy solid. The μ -oxo compound was found to be soluble in common organic solvent such as CHCl_3 and C_6H_6 , highly susceptible to hydrolysis and decomposed on heating. [Yield: 95%; Anal.: Found: OPr^i , 22.61; OPr^n , 33.96; Al, 5.16; Sn, 22.77; Ti, 9.16 and Calculated: OPr^i , 22.67; OPr^n , 34.01; Al, 5.19; Sn, 22.80; Ti, 9.19] for $[\text{SnO}_2\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)_3]$.

Preparation of $[\text{SnO}_2\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)_3]$

Step-I



Step-II



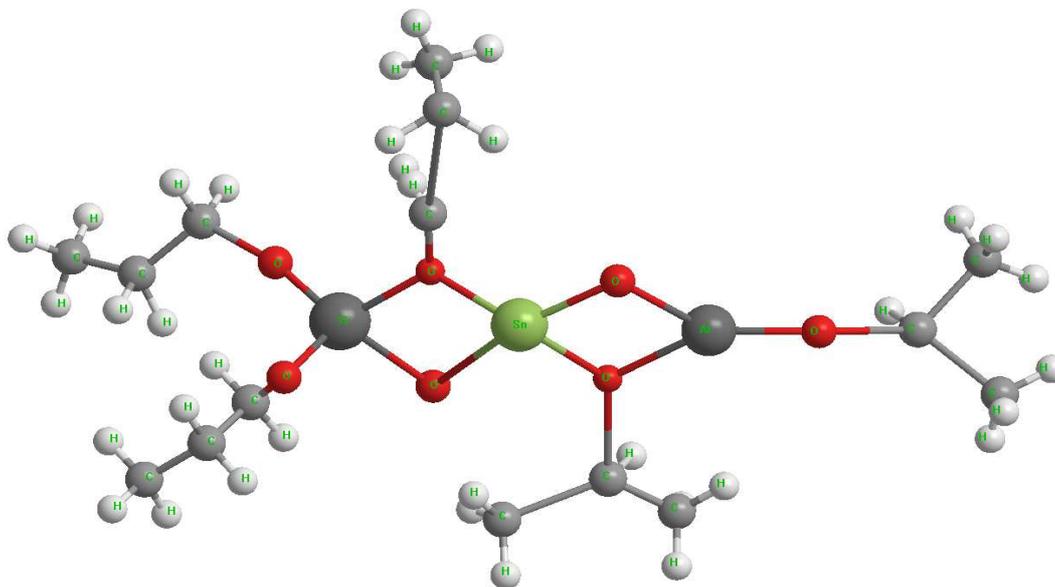
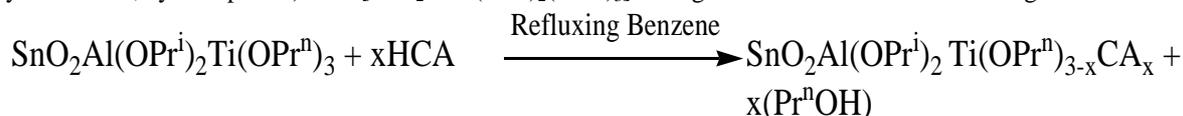


Figure-1: Structure of $[\text{SnO}_2\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)_3]$

Reaction of $[\text{SnO}_2\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)_3]$ with cycloalcohols

The cycloalcohol derivatives of the $[\text{SnO}_2\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)_3]$ complex are prepared in refluxing benzene. A number of reactions are performed by taking various molar ratios (1:1 and 1:2) of the cycloalcohols (cyclopentanol, cyclohexanol, cycloheptanol) with $[\text{SnO}_2\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)_3]$. The general reaction scheme can be given as follows:



(x= 1-2; CA = Cyclopentanol, Cyclohexanol, Cycloheptanol)

It was observed that only two OPr^n groups of the $[\text{Al}(\text{III});\text{Sn}(\text{II});\text{Ti}(\text{IV})]$ - μ -oxo-*isopropoxide*- μ -oxo *n*-propoxide were replaced by cycloalcohol in refluxing benzene resulting in 1:1 and 1:2 molar ratio of the type $[\text{SnO}_2\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)_2\text{CA}]$ and $[\text{SnO}_2\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)\text{CA}_2]$ as yellowish brown colored glassy viscous liquid complexes (Fig. 7-12). The reactions proceed with the formation of propanol. Further replacement of the groups was not achieved even with an excess of ligand and prolonged refluxing time. This indicates the presence of different type of alkoxy groups i.e. terminal and bridging groups and probably, it is only terminal alkoxy group which take part in the reaction and get replaced. This suggests that probably bridging alkoxy groups could not be replaced¹⁷. Literature survey clearly indicates that only the more reactive terminal *n*-propoxy groups were replaced¹⁸ by cycloalcohols. The compounds obtained are highly susceptible to hydrolysis, decomposed on heating above 180 °C. The complexes are soluble in common organic solvents like toluene, benzene and xylene.

The various spectral studies of the complexes are performed like IR, ¹H NMR, ¹³C NMR, ¹¹⁹Sn NMR and ²⁷Al NMR to get the insight of the complexes and mode of bonding.

IR Spectra

In the IR spectrum of the cycloalcohol derivatives, a broad band observed at ~ 3350 cm^{-1} due to $\nu(\text{O-H})$ are found absent¹⁹ which otherwise present in the IR spectrum of pure cycloalcohol ligands. The spectrum of the cycloalcoholic compounds shows absorption bands in the region 1375-1378 cm^{-1} and 1154-1160 cm^{-1} which are characteristics of gem-dimethyl and $\nu(\text{C-O}+\text{OPr}^i)$ portion of *isopropoxy* group respectively²⁰. CH_3 , CH_2 symmetric, CH_2 asymmetric and $\nu(\text{C-O})$ stretching of terminal *n*-propoxide²¹ shows bands in the region 2955-2960 cm^{-1} , 2922-2929 cm^{-1} , 2862-2870 cm^{-1} and 1062-1080 cm^{-1} respectively. Bands appearing in the region at approximately 858-868 cm^{-1} and 964-969 cm^{-1} are assigned to $\nu(\text{C-O})$ stretching of bridging *n*-propoxy²¹ and *isopropoxy* group²⁰. The

bands at 1016-1020 cm^{-1} are assigned to $\nu(\text{C-O})-\text{Ti}^{22}$ and at 1251-1258 cm^{-1} is assigned to $\nu(\text{C-CH}_3)$. A number of vibrations are observed in the region below 700 cm^{-1} has been assigned to M-O stretching vibrations (at 679-684 cm^{-1} due to Al-O²³ and 614-623 cm^{-1} for Ti-O²⁴) for the cycloalcoholic μ -oxocompounds (Fig.-2). The spectrum of the compounds also shows bands at 1073-1103 cm^{-1} and 970-980 cm^{-1} for $\nu(\text{C-O})$ equatorial and $\nu(\text{C-O})$ axial for cycloalcohol group²¹ in the derivatives.

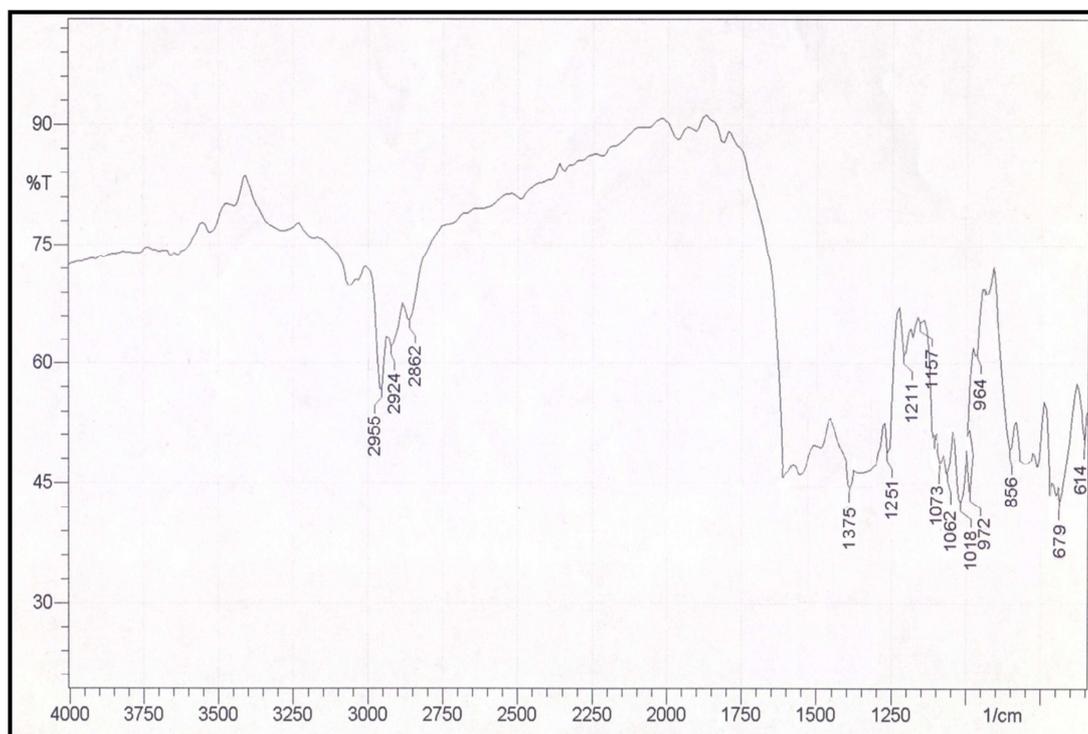


Figure-2: IR of the compound $[\text{SnO}_2\text{TiAl}(\text{OPr})_2(\text{OPrn})(\text{CHex})_2]$

¹H NMR Spectra

The ¹H NMR spectra of the cycloalcoholic compounds of $[\text{Al}(\text{III});\text{Sn}(\text{II});\text{Ti}(\text{IV})]-\mu$ -oxo-*isopropoxide*- μ -oxo-*propoxide* are carried out in CDCl_3 . A multiplet centred at δ 4.3 ppm is observed has been assigned to the methine proton of *isopropoxy* group²⁵ and a triplet at δ 3.4 ppm is assigned to α -protons of *n*-propoxy group²⁶ in all the cycloalcoholic derivatives of μ -oxo alkoxy compound. ¹H NMR spectra of all cycloalcohol derivatives of the compound shows number of peaks between δ 0.8-1.2 ppm has been assigned to the methyl protons of *isopropoxy* and protons of *n*-propoxy groups²⁵⁻²⁷. In cyclopentanol derivatives H (A) gives multiplet at δ 4.1 ppm and H (B, C) shows broad multiplet centred in the region δ 1.4-1.9 ppm. In cyclohexanol derivatives H (A) gives multiplet at δ 3.0 ppm and H (B, C, D) shows broad multiplet centred between δ 1.5-1.7 ppm¹⁹.

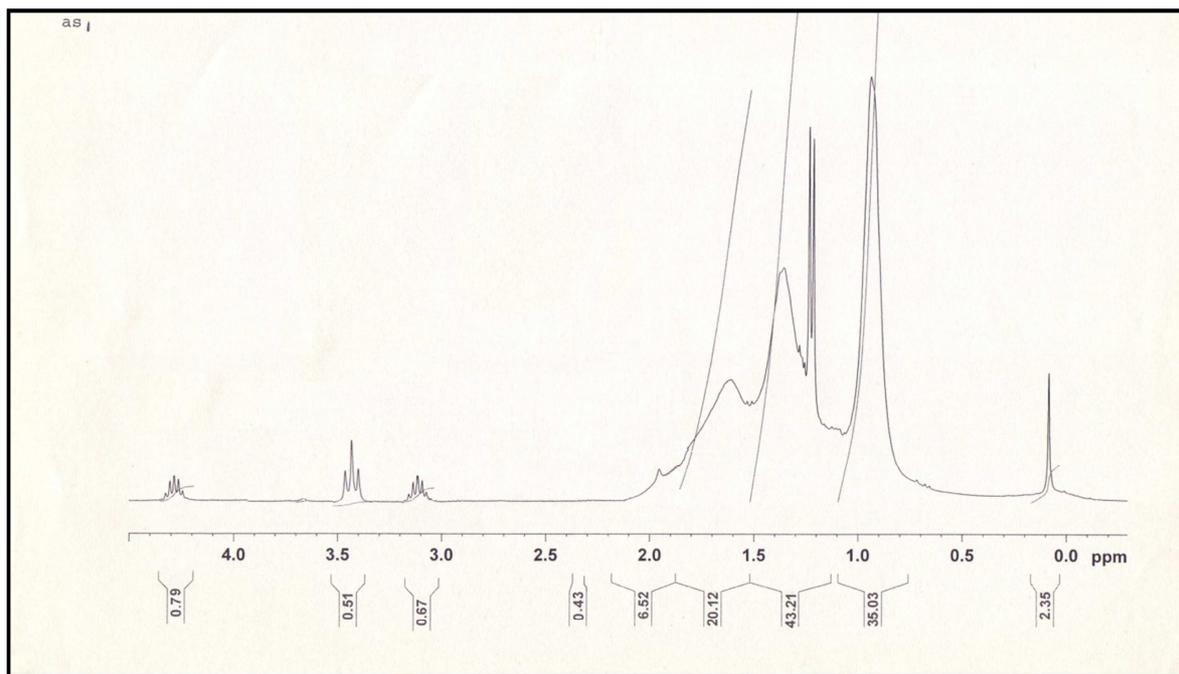


Figure-3: ^1H NMR of the compound $[\text{SnO}_2\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)_2(\text{CHept})]$

In cycloheptanol derivatives H (A) gives multiplet at δ 3.1 ppm (Fig.-3) and H (B, C, D) shows broad multiplet centred in the region δ 1.3-1.6 ppm¹⁹.

^{13}C NMR Spectra

The ^{13}C NMR spectrum of the cycloalcoholic compounds of $[\text{Al}(\text{III});\text{Sn}(\text{II});\text{Ti}(\text{IV})]-\mu\text{-oxo- isopropoxide-}\mu\text{-oxon- propoxide}$ are carried out in CDCl_3 . ^{13}C NMR spectra of 1:1 and 1:2 cycloalcoholic derivatives of compound show prominent peaks between δ 27.9-28.5 ppm assignable to the methyl carbon of bridging *isopropoxy* group. Peaks at δ 47.3 and 48.5, 26.4 and 27.6, 16.2 and 17.5 of C-1, C-2 and C-3 of terminal and bridging *n*-propoxide respectively are present in 1:1 cycloalcoholic derivatives whereas peaks due to terminal *n*-propoxide have been found to be absent in 1:2 cycloalcoholic derivatives (Fig.-4). The peak observed at δ 62.7-63.1 ppm is assigned to the methine carbon of *isopropoxy* group in the derivative. In 1:1 and 1:2 cyclopentanol derivatives show peaks at δ 74.1-74.6 ppm, δ 32.9-33.3 ppm, δ 22.6-23.2 ppm are assigned to C-1, C-2, and C-3 of cyclopentanol respectively. In 1:1 and 1:2 cyclohexanol derivatives show peaks at δ 70.1 ppm, δ 33.3 ppm, δ 26.5 ppm and δ 22.3 ppm are assigned to C-1, C-2, C-3 and C-4 of cyclohexanol respectively¹⁹.

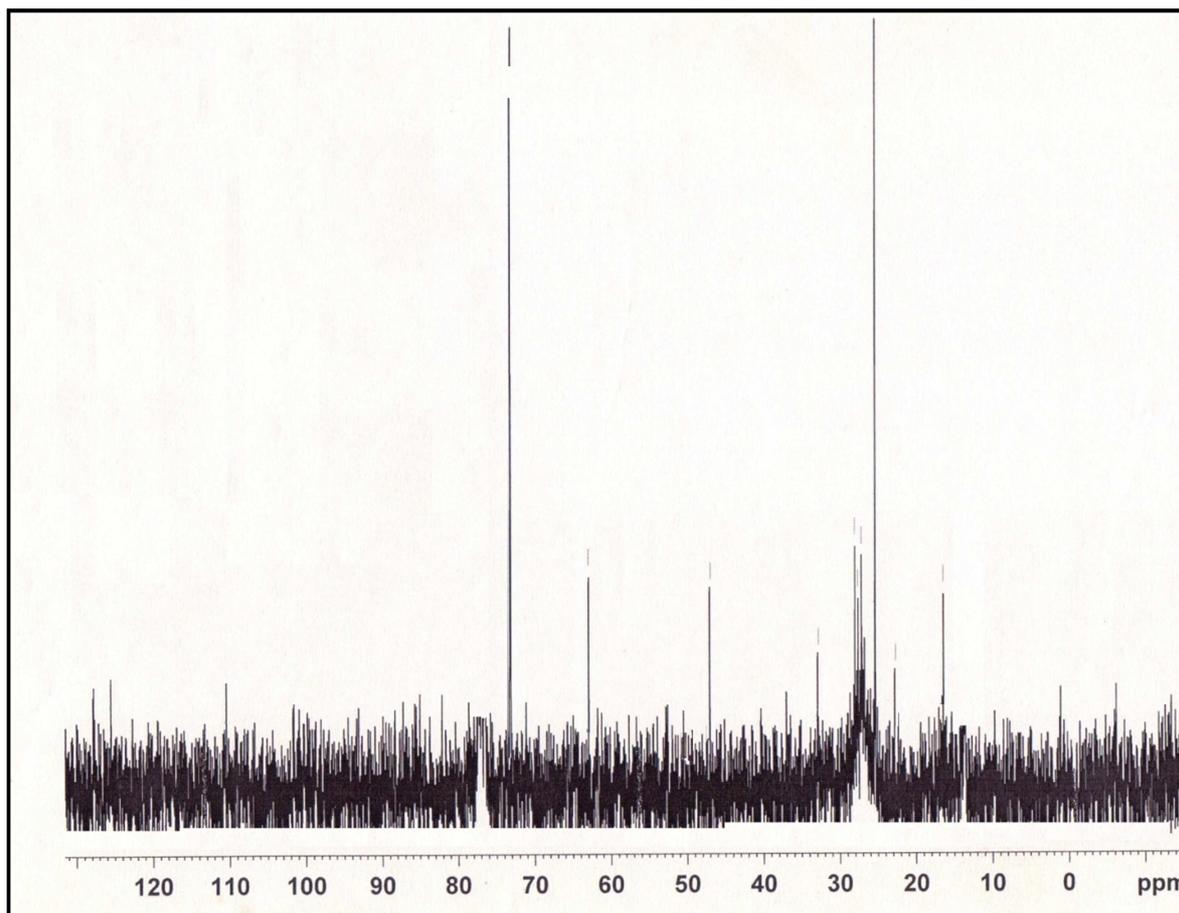


Figure-4: ^{13}C NMR of the compound $[\text{SnO}_2.\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)(\text{CPent})_2]$

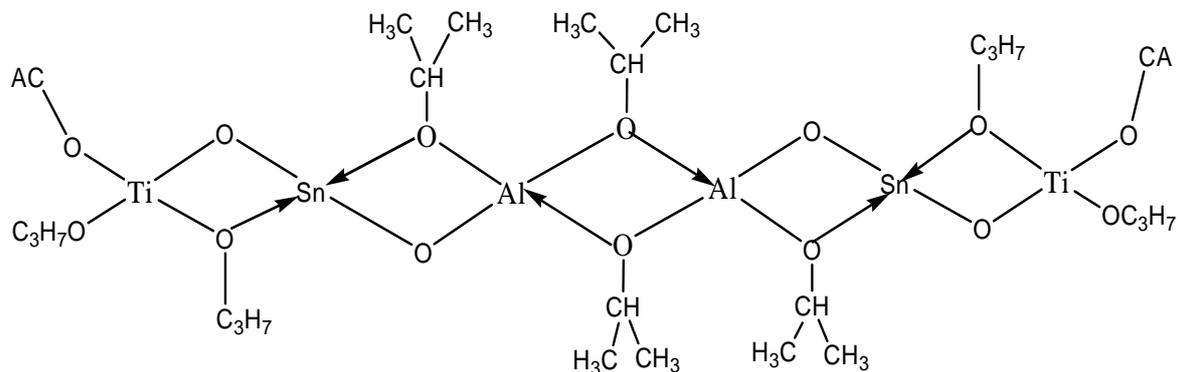
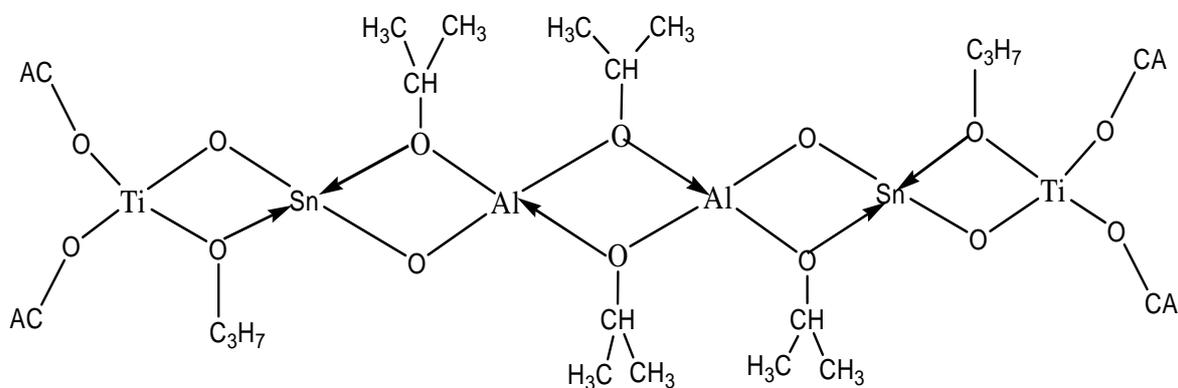
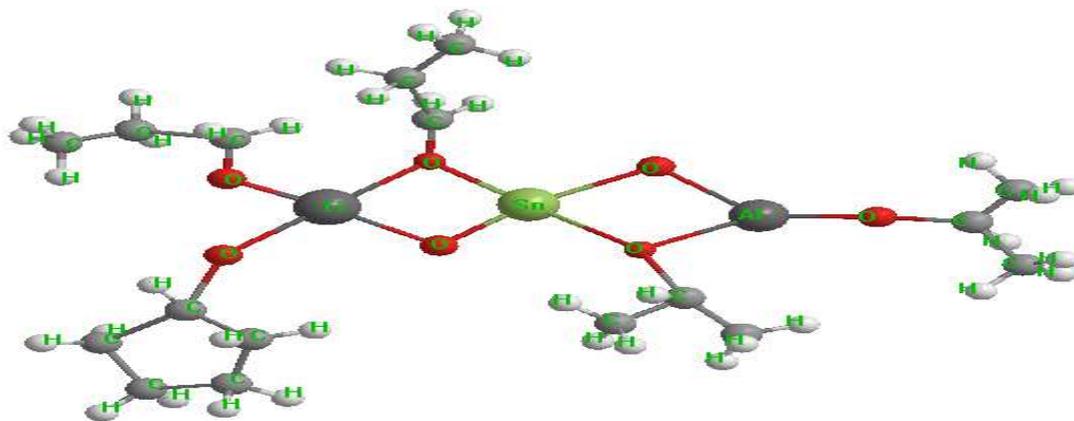
In 1:1 and 1:2 cycloheptanol derivatives show peaks at δ 70.1-70.8 ppm, δ 37.0-37.2 ppm, δ 22.1-22.7 ppm and δ 29.3 ppm are assigned to C-1, C-2, C-3 and C-4 of cycloheptanol respectively¹⁹.

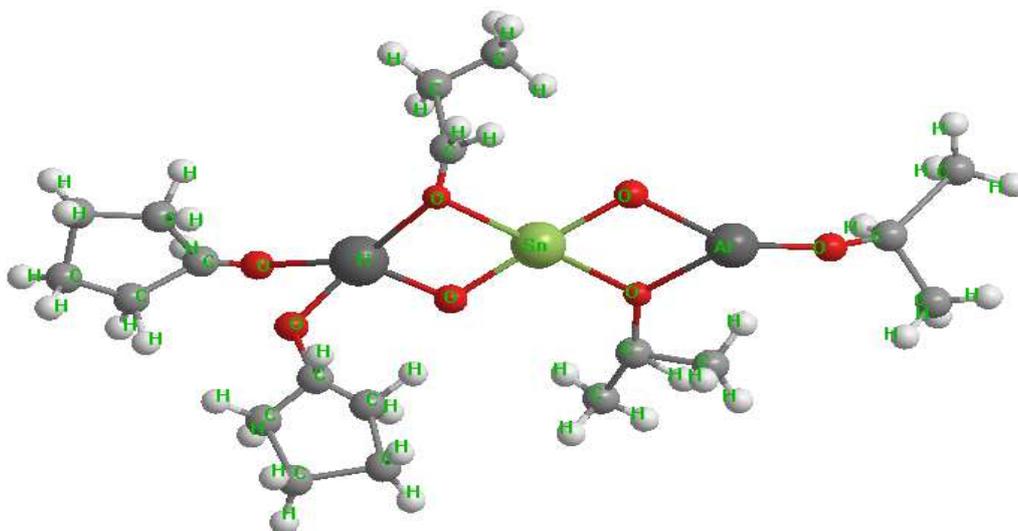
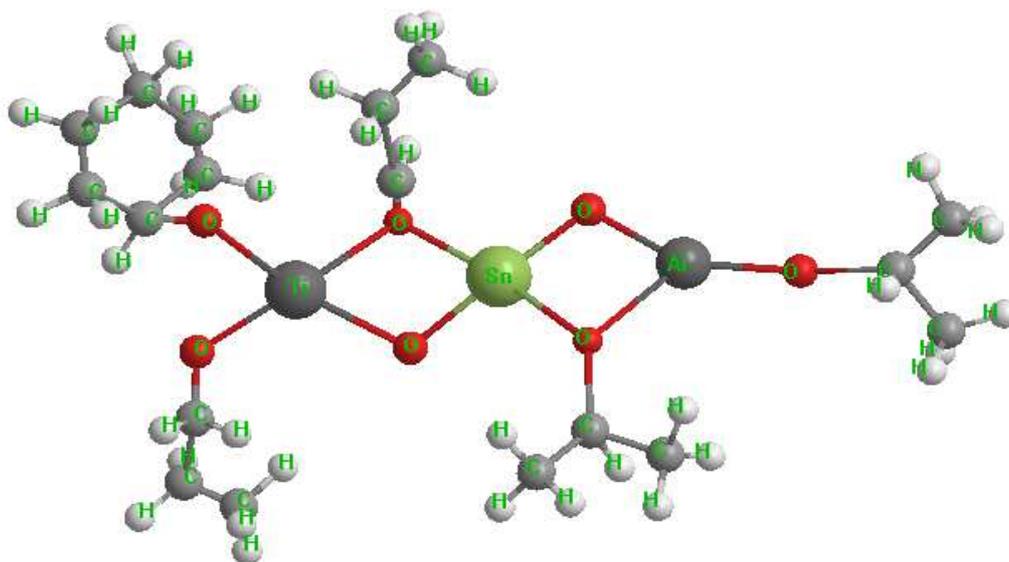
^{119}Sn NMR

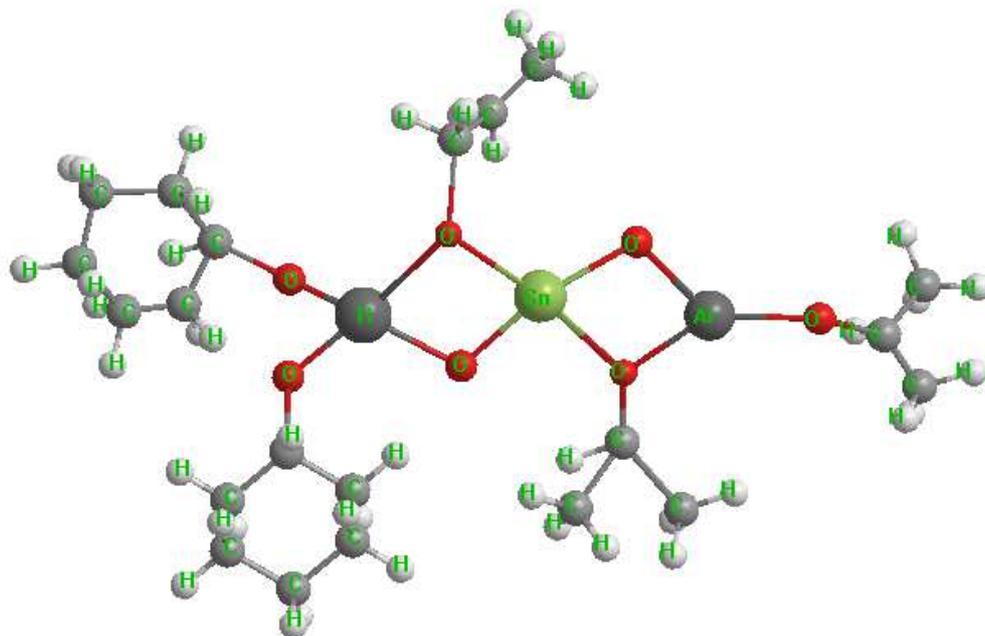
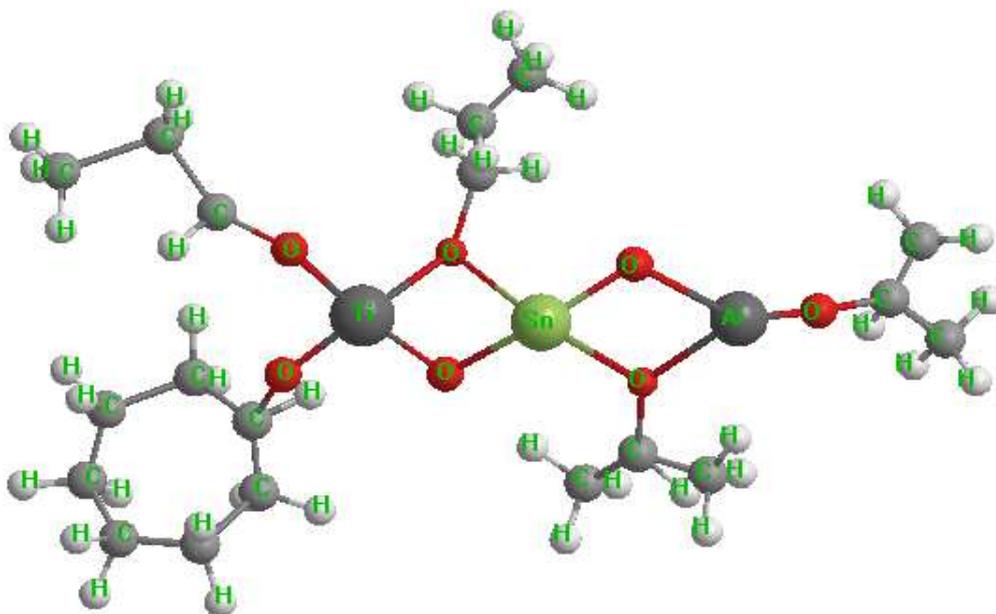
Tetra coordinated environment about Sn atom in the 1:1 and 1:2 cycloalcoholic derivatives of $[\text{Al}(\text{III});\text{Sn}(\text{II});\text{Ti}(\text{IV})]-\mu\text{-oxo- isopropoxide-}\mu\text{-oxon-propoxide}$ confirmed by the ^{119}Sn NMR. Peaks observed at approx δ -76.0 ppm in the spectrum of different cycloalcoholic derivatives attributed to the tetrahedral environment^{27,28}.

^{27}Al NMR

^{27}Al NMR spectrum of 1:1 and 1:2 cycloalcoholic derivatives of $[\text{Al}(\text{III});\text{Sn}(\text{II});\text{Ti}(\text{IV})]-\mu\text{-oxo- isopropoxide-}\mu\text{-oxon-propoxide}$ signal observe at approximately δ 68.0 ppm consistent with tetrahedral environment of aluminium complex³¹⁻³³. This supports the dimeric nature of cycloalcoholic compound. On the basis of above studies, the following tentative dimeric structures have been proposed for cycloalcohol derivatives of $\mu\text{-oxo}$ alkoxide compound in fig 5 and 6.

Figure-5: Dimeric Structure of $[\text{SnO}_2\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)_2\text{CA}]$ Figure-6: Dimeric Structure of $[\text{SnO}_2\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)(\text{CA})_2]$ Figure-7: Structure of $[\text{SnO}_2\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)_2(\text{CPent})]$

Figure-8: Structure of $[\text{SnO}_2\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)(\text{CPent})_2]$ Figure-9: Structure of $[\text{SnO}_2\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)_2(\text{CHex})]$

Figure-10: Structure of $[\text{SnO}_2\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)(\text{CHex})_2]$ Figure-11: Structure of $[\text{SnO}_2\text{TiAl}(\text{OPr}^i)_2(\text{OPr}^n)_2(\text{ChEpt})]$

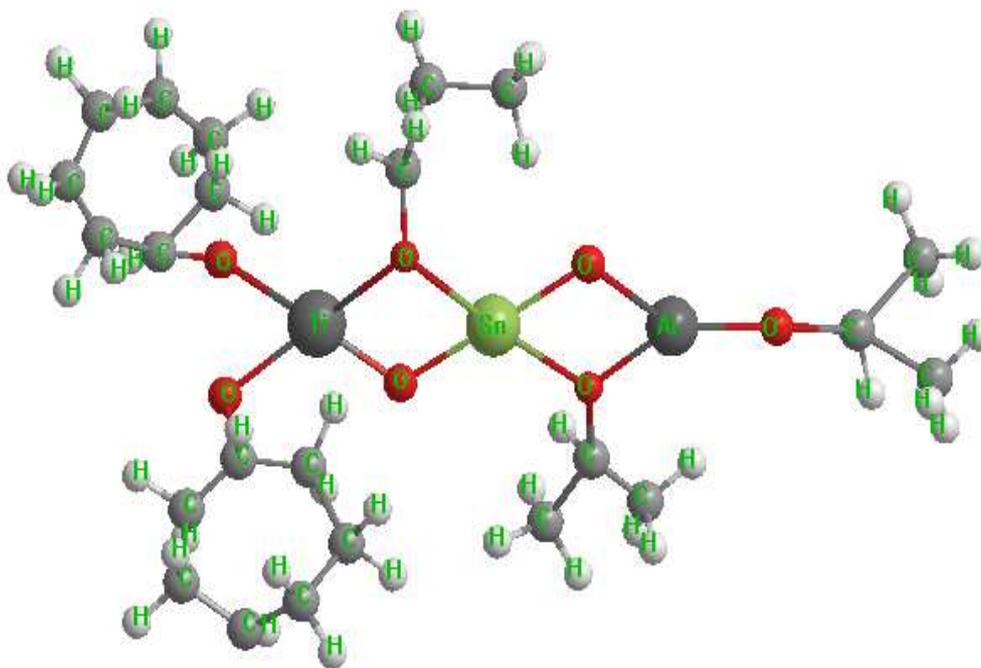


Figure-12: Structure of $[\text{SnO}_2\text{TiAl}(\text{OPr})_2(\text{OPr}^b)(\text{CHept})_2]$

REFERENCES

- [1]. C. N. R. Rao, Transition Metal Oxides, VCH, New York, **1995**.
- [2]. C. N. R. Rao, R. Vaidyanathan, S. Natarajan, *J. Mater. Chem.*, **1999**, 9, 2789.
- [3]. E. Lucas, S. Decker, A. Khaleed, A. Seitz, S. Fultz, A. Ponce, W. Li, C. Carnes, K. Klabunde. *J. Chem. Eur. J.*, **2001**, 7, 2505.
- [4]. L. G. Hubert-Pfalzgraf, *Inorg. Chem. Comm.*, **2003**, 6, 102-120.
- [5]. C. N. R. Rao, A. K. Cheetham, *J. Mater. Chem.*, **2001**, 11, 2887-2894.
- [6]. M. Winter, R. J. Brodd, *Chem. Rev.*, **2004**, 104, 4245-4269.
- [7]. A. S. Arico, P. Bruce, B. Scrosati, J. M. Tarascon, V. Schalkwijk, *Nat. Mater.*, **2005**, 4, 366.
- [8]. M. M. Thackeray, C. S. Johnson, J. T. Vaughney, N. Li, S. A. Hackney, *J. Mater. Chem.*, **2005**, 15, 2257.
- [9]. J. L. G. Fierro, L. L. G. Fierro, Metal Oxides: Chemistry and Applications, Taylor & Francis, CRC, Boca Raton, **2006**.
- [10]. K. L. Chopra, P. D. Paulson and V. Dutta, Progress in Photovoltaics: Research and Applications Special Issue: Progress in Thin-film Solar Cells, **2004**, 12, 69.
- [11]. R. H. Cayton, M. H. Chishlom, E.R. Davidson, V. F. Distasi, D. Ping, J. C. Huffman. *Inorg. Chem.*, **1991**, 30, 1020-1024.
- [12]. U. Schubert, *J. Mater. Chem.* **2005**, 15, 3701-3715.
- [13]. R. S. Ghadwal, M. Sharma, A. Singh and R. C. Mehrotra, *Transition Met. Chem.*, **2004**, 29, 419.
- [14]. A. I. Vogel, A text book of quantitative analysis, London: Longman, **1989**.
- [15]. A. I. Vogel, A text book of quantitative inorganic analysis 5th edn, London: Longman, **1978**.
- [16]. M. Sharma, A. K. Bhagi, H.K. Sharma, Priti, R. Kansal, R. Kumar and P. N. Kapoor, *Indian J. Chem.*, **2005**, 44(A), 256.
- [17]. N. Serpone, P. H. Bird and D. G. Bickley, *J. Chem. Soc., Chem. Comm.*, **1972**, 217.
- [18]. H. Schiff, *Ann. Chem.*, **1864**, 131, 118.
- [19]. W. Clegg, M. R. J. Elsegood, R. J. Errington and J. Havelock, *J. Chem. Soc., Dalton Trans.*, **1996**, 5, 681.
- [20]. R. E. Reeves and L. W. Mazzeno, *J. Am. Chem. Soc.*, **1954**, 76, 2533.
- [21]. A. Yamamoto and S. Kambara, *J. Am. Chem. Soc.*, **1957**, 79, 4344.
- [22]. D. M. Puri and R. C. Mehrotra, *J. Ind. Chem. Soc.*, **1962**, 39, 499.
- [23]. D. M. Puri and R. C. Mehrotra, *J. Less-Common Met.*, **1961**, 3, 167.

- [24]. D. M. Puri and R. C. Mehrotra, *J. Less-Common Met.*, **1961**, 3, 253.
[25]. R. C. Fay and R. N. Lowry, *Inorg. Chem.*, **1967**, 6, 1512.
[26]. N. Serpone and R. C. Fay, *Inorg. Chem.*, **1967**, 6, 1835.
[27]. P. Comba, H. Jakob, B. Nuber and B. K. Keppler, *Inorg. Chem.*, 33, **1994**, 3396.
[28]. D. C. Bradley and C. E. Holloway, *J. Chem. Soc., A*, **1969**, 282.
[29]. G. D. Smith, C. N. Caughlan and J. A. Campbell, *Inorg. Chem.*, **1972**, 11, 2989.
[30]. P. H. Bird, A. R. Fraser and C. F. Lau, *Inorg. Chem.*, **1973**, 12, 1322.