DOI:10.7598/cst2015.1112
ISSN:2278-3458

Chemical Science Transactions
2015, **4(4),** 1083-1091

RESEARCH ARTICLE

Synthesis of Derivatives of Organoheterotrimetallic dibutyl-[Al(III), Sn(IV), Ti(IV)]-*μ*-oxoisopropoxide-*μ*-oxo-*n*-propoxide with Salicylates

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Received 1 August 2015 / Accepted 12 August 2015

Abstract: Tin diacetate and aluminium isopropoxide in equimolar proportion in xylene affords the complex $[(OAc)SnOAl(OPr^i)_2]$ which on reaction with $Ti(OPr^n)_4$ in 1:1 molar ratio yielded a new organoheterotrimetallic-*μ*-oxoisopropoxide-*μ*-oxo-*n*-propoxide $[SnO_2TiAl(OPr^i)_2(OPr^n)_3]$ with continuous liberation of isopropyl acetate and propyl acetate formed during the course of reaction. The preparation of some important salicylates (methyl salicylate, chloro methyl salicylate, phenyl salicylate, phenyl 2-hydroxy 5-chloro benzoate) derivatives of compound $[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_3]$ have been carried out in different molar ratios(1:1 and 1:2) in refluxing benzene. The complexes were further characterized by spectral analysis (IR, ^1H, ^{13}C, ^{119}Sn, ^{27}Al NMR and mass spectra).The spectral studies confirmed the proposed framework of the new organoheterotrimettalic complexes and indicated a tetrahedral geometry around the central metal atom.

Keywords: Tin diacetate, Aluminium isopropoxide, Titanium, Methyl salicylate, Chloromethyl salicylate, Phenyl salicylate, Phenyl 2-hydroxy 5-chloro benzoate

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 metallic[1,2]. Multimetallic oxides cover an always wider range of applications in electronics, optics[3-5], magnetism[6-8], catalysis[9] and environmental issues[10]. High-tech applications rely on materials in high purity and/or in a variety of shapes, formulations or microstructures (nano-particles, coatings, porous matrices, *etc*.) and these requirements needed 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 ‘‘Chimie douce’’ 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 them[11]. 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[12,13]. Coordination, solvation, aggregation and redistribution equilibria play an important role in the chemistry of the modified titanium alkoxides, and organic side reactions have to be taken into account[14].

Experimental

The μ-oxo compound has been synthesized in two steps. In first step the $Bu_2Sn(OAc)_2$ (2.135 g, 6.083 mmol) reacts with $Al(OPr^i)_3$ (1.242 g, 6.083 mmol) in same molar ratio which results into formation of the μ-oxo compound $[(OAc)Bu_2SnOAl(OPr^i)_2]$. In second step $[(OAc)Bu_2SnOAl\ (OPr^i)_2]$ undergoes thermal condensation with $Ti(OPr^n)_4$ (1.729 g, 6.083 m mol) in equal molar ratio in xylene to form a new organoheterotrimetallic -μ-oxoisopropoxide-μ-oxo-*n*-propoxide $[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_3]$. The contents were refluxed for about 8 h on a fractionating column and the propyl acetate formed during the reaction was distilled off continuously from 102 ^oC to boiling point of xylene[15,16] (139 ^oC).

Step-I

$$Bu_2Sn(OAc)_2+Al(OPr^i)_3 \xrightarrow[139^oC,\ 5\ h]{\text{Refluxing xylene}} Bu_2Sn(OAc)OAl(OPr^i)_2+Ac(OPr^i)$$

Step-II

$$Bu_2Sn(OAc)OAl(OPr^i)_2+Ti(OPr^n)_4 \xrightarrow[139^oC,\ 8\ h]{\text{Refluxing xylene}} Bu_2SnO_2Al(OPr^i)_2\ Ti(OPr^n)_3+Ac(OPr^n)$$

The solvent xylene was completely removed at (~70 ^oC/1 mm) yielding a yellow solid. The product was redissolved in benzene and slow evaporation of benzene resulted in a pale yellow glassy viscous liquid. The μ-oxo compound was found to be soluble in common organic solvent such as benzene, chloroform and hexane, highly susceptible to hydrolysis and decomposed on heating above ~ 180 ^oC. [Yield: 96%; Anal.: Found: OPr^i, 18.48; OPr^n, 27.74; Bu, 17.88; Al, 4.21; Sn, 18.57; Ti,7.46 and Calculated: OPr^i, 18.52; OPr^n, 27.78; Bu, 17.91; Al, 4.23; Sn, 18.61; Ti,7.50] for $[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_3]$. Table 1 shows the molecular weight determination of $[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_3]$.

Table 1. Molecular weight determination of $[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_3]$

S.No.	Wt. of Comp. g	Wt. of Benzene, g	Temp. Diff. ^oC	Mol.Wt.
1	0.20	0.60	1.34	1273.63
2	0.40	1.20	1.35	1264.20
3	0.60	1.80	1.36	1254.90

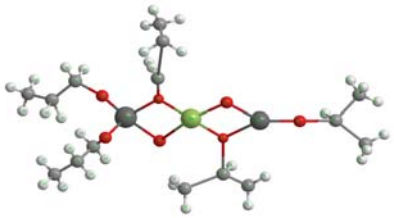

Figure 1. Structure of $[SnO_2TiAl(OPr^i)_2(OPr^n)_3]$

Results and Discussion

Reaction for the Synthesis of derivatives of organoheterotrimetallic dibutyl-[Al(III), Sn (IV),Ti (IV)]-μ-oxoisopropoxide μ-oxo n-propoxide with salicylates

In order to gather more information regarding the nature of dibutyl $[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_3]$ *i.e*. effect of chelation on the stability and solubility, the reaction of μ-oxo mixed propoxide and some important salicylates[17,18] like methyl salicylate, chloro methyl salicylate, phenyl salicylate, phenyl 2-hydroxy 5-chloro benzoate have been carried out in different molar ratios (1:1and 1:2) in refluxing benzene. The reaction scheme can be depicted as follows:

$$Bu_2SnO_2AI(OPr^i)_2\,Ti(OPr^n)_3 + xHRsal \xrightarrow{\text{Refluxing benzane}} Bu_2SnO_2AI(OPr^i)_2Ti(OPr^n)_{3-x}\,Rsal_x + x(Pr^nOH)$$

(x=1, 2; HRSal= methyl salicylate, chloro methyl salicylate, phenyl salicylate, phenyl 2-hydroxy 5-chloro benzoate).

It has been observed that only two OPr^n groups of the [Al(III),Sn(IV),Ti(IV)]-μ-oxoisopropoxide-μ-oxo-*n*-propoxide could be replaced by salicylate group, resulting in the formation of salicylate derivatives of the type $[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_2(RSal)]$ and $[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)(RSal)_2]$ (1:1 and 1:2 molar ratio). The reactions proceed with the formation of *n*-propanol. Further replacements of the groups could not be achieved even with an excess amount 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 are replaced. This also indicates that probably the bridging alkoxy groups could not be replaced[19]. Literature survey indicates that only the more reactive terminal *n*-propoxy groups were replace[20] by salicylates. The salicylate derivatives obtained are yellowish brown transparent semi-solids, highly susceptible to hydrolysis, decomposed on heating above ~ 190 ^oC. The salicylate derivatives are soluble in common organic solvents like chloroform, toluene, benzene and xylene.

The various spectral studies of the salicylate derivatives are performed like IR, ^1H NMR, ^{13}C NMR, ^{119}Sn NMR, ^{27}Al and mass spectra to get the insight of the complex and mode of bonding.

IR spectra

The broad band for ν(O-H) in the region ~3120 cm^{-1} have been found to be absent in 1:1 and 1:2 salicylate derivatives of[Al(III);Sn(IV);Ti(IV)]-μ-oxoisopropoxide-μ-oxo-*n*-propoxide which clearly indicates the deprotonation of O-H group of ligand. The downward shift of ν(C=O) band appearing in salicylates by 15-25 cm^{-1} at ~1640 cm^{-1} indicates the coordination of carbonyl oxygen of salicylate to the metal atom[17]. The upward shift of ν(C-O) band of phenolic group of salicylates in the complexes by 15-20 cm^{-1} at ~1250 cm^{-1} indicates the bond formation between metal atom and oxygen[21]. The absorption bands in the region 1072-1085 cm^{-1} in chloro salicylate derivatives for ν(C-Cl) stretching. The spectrum of the compound shows absorption bands in the region 1377-1383 cm^{-1} and 1147-1161 cm^{-1} which were characteristics of gem-dimethyl and ν(C-O+OPr^i) portion of isopropoxy group (Figure 2) respectively[22]. The bands observed in the region between 2850- 2950 cm^{-1} are due to the different types of ν(C-H) stretching's present in the salicylate derivatives[23]. Bands in the region 1070-1100 cm^{-1} assigned to ν(C-O) stretching of terminal *n*-propoxide. The band for the ν(C-H) of butyl group[24] appears in the region between 2985-2850 cm^{-1}. Bands appearing

in the region at ~ 855-877 cm^{-1} and 957-963 cm^{-1} have been assigned to ν(C-O) stretching of bridging *n*-propoxy[25] and isopropoxy group[22]. The bands at 1021-1029 cm^{-1} have been assigned to ν(C-O) –Ti[26] stretching. A number of vibrations were observed in the region below 700 cm^{-1} has been assigned to M-O stretching vibrations (at 681-685 cm^{-1} due to Al-O[27] and 617-624 cm^{-1} for Ti-O[28]) for the complexes. The characteristic IR data of the salicylate derivatives are listed in Table 2 and Table 3 shows elemental analysis

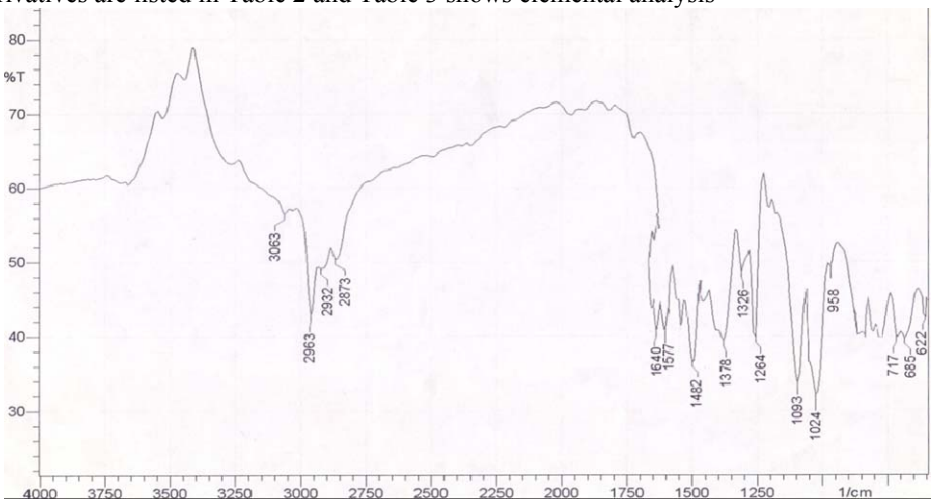

Figure 2. IR Spectrum of $[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_2(PhSal)]$

Table 2. IR spectra (cm^{-1}) of salicylate derivatives of $[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_3]$

Compound	ν(C=O)	ν(C-Cl)	ν(C=C) Sym.	ν(C=C) Asym	ν(C-O) Sym	ν(C-O) Asym	ν(gem di methyl)	ν(C-O) Phenolic	ν(C-O Ti)	ν(C-O Pr^i)	ν(Al-O)	ν(Ti-O)
$[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_2(MeSal)]$	1655	-	1578	1480	1327	1089	1381	1263	1021	963	684	621
$[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)(MeSal)_2]$	1648	-	1580	1477	1332	1088	1379	1261	1024	961	681	619
$[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_2(MeClSal)]$	1662	1078	1582	1483	1333	1091	1382	1271	1023	961	685	618
$[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)(MeClSal)_2]$	1658	1072	1586	1487	1336	1103	1378	1274	1027	959	683	617
$[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_2(PhSal)]$	1640	-	1577	1482	1326	1093	1378	1264	1024	958	685	622
$[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)(PhSal)_2]$	1646	-	1579	1486	1329	1095	1382	1261	1026	955	688	619
$[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)(PhClSal)]$	1668	1082	1581	1487	1331	1095	1377	1271	1027	957	682	624
$[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)(PhClSal)_2]$	1672	1085	1584	1489	1334	1091	1383	1274	1029	951	683	618

^{1}H NMR spectra

The ^{1}H NMR spectra of the salicylate derivatives of μ-oxo compound were carried out in $CDCl_3$. Peak in the region δ 9.5-10.3 ppm for the OH group has been found absent in all the salicylate compound shows the deprotonation of phenolic group and bonding takes place

through phenolic oxygen[29]. A multiplet centred at δ 4.0-4.8 ppm has been assigned to the methine proton of isopropoxy group[32] and a triplet at δ 3.1-3.9 ppm has been assigned to *α*-protons of *n*-propoxy group[20] in all the salicylate derivatives (Figure 3).

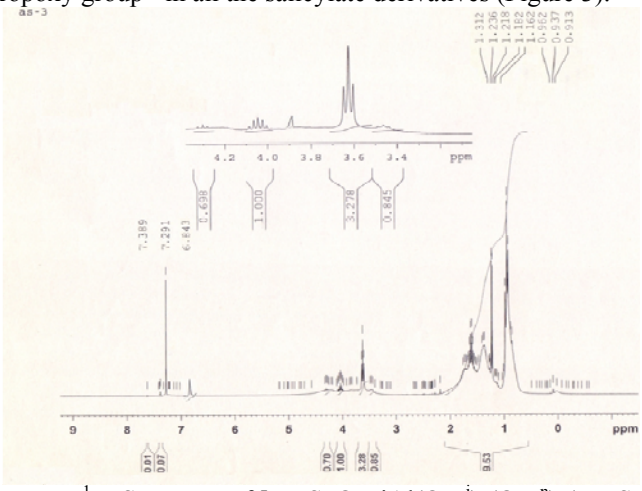

Figure 3. ^{1}H Spectrum of $[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_2(Me\ Sal)]$

Table 3. Elemental analysis of salicylate derivatives of $[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_3]$

Compound g, mmol	Ligand g, mmol	Molar ratio	Refluxing time	Product g, (%)	Found (Calculated), %				
					Sn	Ti	Al	C	H
$Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_3$0.623 (0.982)	HSA1 0.149 (0.982)	1:1	4	$[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_2$(SA1)] 0.599 (83.8)	16.28 (16.33)	6.54 (6.59)	3.67 (3.71)	46.30 (46.23)	7.32 (7.29)
$Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_3$0.554(0.873)	HSA1 0.266 (1.746)	1:2	6	$[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)$(SA1)$_2$] 0.593(82.7)	14.44 (14.50)	5.81 (5.85)	3.26 (3.29)	48.41 (48.36)	6.51 (6.47)
$Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_3$0.620(0.980)	HSA2 0.183 (0.980)	1:1	4	$[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_2$(SA2)] 0.6352 (84.7)	15.53 (15.60)	6.25 (6.29)	3.51 (3.54)	44.21 (44.14)	6.87 (6.83)
$Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_3$0.676(1.065)	HSA2 0.398 (2.130)	1:2	6	$[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)$(SA2)$_2$] 0.7943 (83.9)	13.30 (13.37)	5.34 (5.39)	3.01 (3.04)	44.67 (44.61)	5.78 (5.74)
$Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_3$0.597(0.941)	HSA3 0.202 (0.941)	1:1	4	$[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_2$ (SA3)] 0.5788(77.8)	14.99 (15.05)	6.01 (6.07)	3.39 (3.42)	50.26 (50.20)	7.02 (6.97)
$Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_3$0.639(1.007)	HSA3 0.431 (2.014)	1:2	6	$[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)$(SA3)$_2$] 0.7148 (76.1)	12.65 (12.71)	5.07 (5.12)	2.86 (2.89)	55.30 (55.24)	6.14 (6.10)
$Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_3$0.706(1.112)	HSA4 0.2766 (1.112)	1:1	4	$[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_2$ (SA4)] 0.7052(76.9)	14.33 (14.42)	5.78 (5.81)	3.24 (3.28)	48.17 (48.10)	6.61 (6.56)
$Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_3$0.658(1.037)	HSA4 0.5157 (2.074)	1:2	6	$[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)$(SA4)$_2$] 0.7869 (74.2)	11.70 (11.73)	4.68 (4.73)	2.64 (2.67)	51.05 (50.99)	5.48 (5.43)

^{1}H NMR spectra of all salicylate compound shows number of peaks centred between δ 0.8-1.4 ppm have been assigned to the intermixing of methyl protons of isopropoxy and protons of *n*-propoxy groups[31-33] with protons of the butyl groups bonded to tin atom[33]. Further, the peaks observed in the region δ 6.9-7.8 ppm in salicylate derivatives of μ-oxo compound have been assigned to the phenyl ring protons[30].

^{13}C NMR spectra

The ^{13}C NMR spectra of the salicylate derivatives were carried out in $CDCl_3$. ^{13}C NMR spectra of 1:1 and 1:2 salicylate derivatives of μ-oxo compound show prominent peaks between δ 28.0-28.6 ppm assignable to the methyl carbon of bridging isopropoxy group. Peaks at δ 47.4 and 48.6, 26.5 and 27.7, 16.3 and 17.4 of C-1,C-2 and C-3 of terminal and bridging *n*-propoxide respectively have been present in 1:1 salicylate derivatives whereas peaks for terminal *n*-propoxide have been found to be absent in 1:2 salicylate derivatives (Figure 4). The peak observed at δ 62.7-63.1 ppm has been assigned to the methine carbon of isopropoxy group in the derivative. Peaks observed in the range δ 174.8-176.3 ppm have been assigned to carbonyl carbon of ligand moiety in all salicylate derivatives. Peaks observed in the range δ 51.9-52.4 ppm have been assigned to methyl carbon of ligand moiety in complexes of methyl salicylate and chloro methyl salicylate.

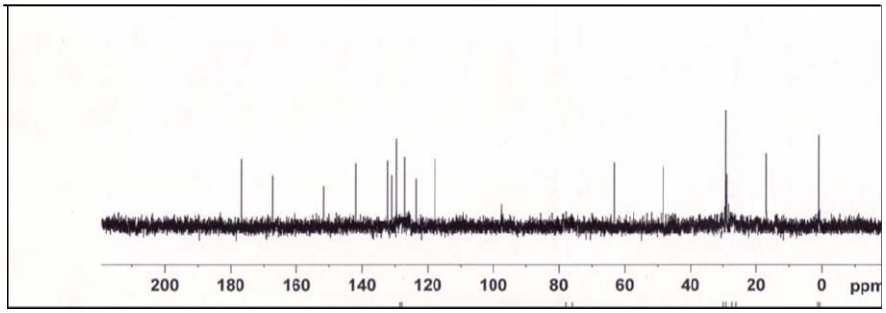

Figure 4. ^{13}C Spectrum of $[Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)(PhClSal)_2]$

The peaks observed at δ 122.0-123.1, 130.2-131.1, 126.9-127.8 and 150.7-151.6 ppm have been assigned to ortho, meta, para and substituted carbon of the phenyl ring in the spectra of phenyl salicylate and Chloro phenyl salicylate derivatives of the μ-oxo mixed propoxide compound respectively[30,31]. The different ^{13}C peaks of 1:1 and 1:2 derivatives of methyl salicylate, chloro methyl salicylate, phenyl salicylate and chloro phenyl salicylate observed are mentioned as follows:-

i) Methyl salicylate derivatives (1:1 and 1:2)
C1-165.6-165.7 ppm; C2-121.7-121.8 ppm; C3-132.5-132.6 ppm; C4-122.6-122.7 ppm; C5-138.5-138.6 ppm; C6-116.3-116.4 ppm

ii) Chloro methyl salicylate derivatives (1:1 and 1:2)
C1-164.3-164.4 ppm; C2-122.6-122.7 ppm; C3-138.5-138.6 ppm; C4-129.7-129.8 ppm; C5-134.2-134.3 ppm; C6-118.9-119.0 ppm

iii) Phenyl salicylate derivatives (1:1 and 1:2)
C1-166.4-166.5 ppm; C2-121.8-121.9 ppm; C3-139.3-139.4 ppm; C4-122.4-122.6 ppm; C5-134.1-134.3 ppm; C6-115.9-116.1 ppm

iv) Chloro phenyl salicylate derivatives (1:1 and 1:2)
C1-165.8-166.0 ppm; C2-122.9-123.1 ppm; C3-142.2-142.3 ppm; C4-129.3-129.5 ppm; C5-131.6-131.8 ppm; C6-118.1-118.3 ppm

^{119}Sn NMR

^{119}Sn NMR spectra of 1:1 and 1:2 salicylate derivatives of μ-oxo compound show prominent peaks at ~ δ -192.0 ppm attributed to the octahedral environment[34] around the Sn in all the salicylate complexes as observed in the μ-oxo compound.

^{27}Al NMR

^{27}Al NMR spectra of salicylate derivativesof [Al(III);Sn(IV);Ti(IV)]-μ-oxoisopropoxide-μ-oxo*n*-propoxide shows broad peak centred at ~δ70.0 ppm consistent with tetrahedral environment of aluminium complex[35-37]. This also supports the dimeric nature of all the salicylate derivatives. On the basis of above studies the following tentative (Figure 5 and 6) structures have been assigned to the salicylate derivatives of[$Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_3$].

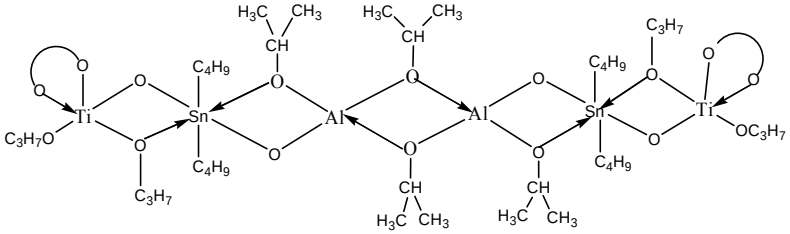

Figure 5. Dimeric structureof [$Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)_2(RSal)$]

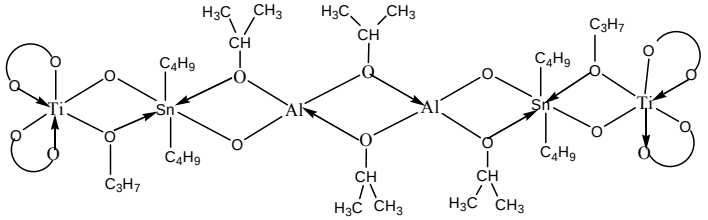

Figure 6. Dimeric structure of [$Bu_2SnO_2TiAl(OPr^i)_2(OPr^n)(RSal)_2$]

Application

These compounds (Metal alkoxides) uses as a catalysts (ziegler natta catalyst, meerwein-ponndorf-verley reduction, nano-particles) so these compounds play an important role in chemistry. Most of the metallic elements are reactive towards oxygen because oxides exist in stable single or mixed phases. Metal alkoxides are very good single source molecular precursor (SSP) due to its molecular structure and high reactivity which depends on the electronegativity of the metal ion, ability to increase the coordination numbers, the steric hindrance in the alkoxy groups which help for the synthesis of corresponding colloidal metal oxides with high homogeneity. The presence of metal ions plays a critical role due to their coordination behavior for controlling a chemical functional behavior, nucleation, growth, orientation and formation of nanostructure material with high performance with the help of tuning the surface–morphology.

Acknowledgement

We wish to express his gratitude to Prof. A. Pal, Chairman, Department of Chemistry, KUK and non-teaching staff for supporting us for this work, providing laboratory facility and feel great pleasure to thank University Grant Commission (UGC), New Delhi, India for financial assistance.

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