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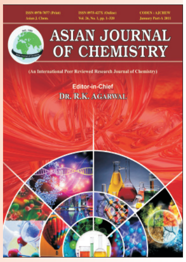

Synthesis and Characterization of Organoheterotrimetallic Dibutyl-[Sn(IV), Ti(IV), Al(III)]-μ-oxoisopropoxide and Its β-Diketonates

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Thermal condensation of dibutyl tin diacetate and aluminium isopropoxide in 1:1 molar ratio in refluxing xylene affords [(AcO)Bu_2SnOAl(*i*-$OPr)_2$] which on reaction with titanium isopropoxide in 1:1 molar ratio yields a new organoheterotrimetallic dibutyl [Sn(IV), Ti(IV), Al(III)]-μ-oxoisopropoxide with continuous liberation of isopropyl acetate. The isopropoxy substitution reactions of μ-oxoisopropoxide compound with β-diketones in different molar ratios (1:1-1:2) gives compounds of the type [Bu_2SnO_2TiAl(*i*-$OPr)_{5-n}L_n$] (where n is 1-2 and L = acetylacetonate/benzoylacetonate anion). The μ-oxoisopropoxide compound has been characterized by elemental, spectral analysis (IR, ^1H, ^{13}C, ^{119}Sn and ^{27}Al NMR) and molecular weight measurement. The β-diketonates of [Bu_2SnO_2TiAl (*i*-$OPr)_5$] have been characterized by elemental, liberated isopropanol and spectral analysis (IR, ^1H, ^{13}C NMR).

Keywords: Tin, Titanium, Aluminium, Acetylacetonate, Benzoylacetonate.

INTRODUCTION

The ready availability, steric tunability and hard-donor properties have made alkoxides amongst the most versatile σ-bonding ligand in chemistry[1]. Alkoxides are outstanding ligands for early transition metals because electron-rich oxygen atoms complement these chemically hard, electron poor metals exceedingly well alkoxides have played a prominent role in the chemistry of the group 4-6 metals, particularly as ligands for multiple metal-metal bonded species[2]. More recently, the use of metal alkoxides as precursors for binary or ternary metal oxides has stimulated much interest in these compounds[3].

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[4,5]. 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[6].

Alkoxides are considered to be suitable precursors for super or semi-conducting, ferroelectric, dielectric and even biocompatible oxide materials[7,8] over other precursors such as metal nitrate, acetate, monodispersed metal hydrous oxides, mainly due to the ease of their purification, solubility in organic solvents, volatility and their extremely facile hydrolizability.

The facile hydrolytic susceptibility of metal and hetero metallic alkoxides has been increasingly utilized in the sol-gel technique: the conversion of a metal alkoxide dissolved in an organic solvent (generally the parent alcohol) into a hydroxo-oxo-alkoxide 'sol,' followed by gelation and sintering to gives the desired ceramic material. This development has led to much interest in the mechanism of the hydrolysis process and also in the actual composition of the hydroxo- or oxo-alkoxide derivatives formed[9-11].

To overcome the problem of very fast rate of hydrolysis of metal alkoxides attempts are being made to provide modified precursor the alkoxy groups have been substituted by other ligands for example such as acetylacetone, benzoylacetone which may undergo hydrolysis at slower rate[12], and to get information about structural features, solubilities and effect of chelating group on the stability of μ-oxo compounds, their β-diketones have been synthesized.

The above features underline the importance and utility of μ-oxo compounds, it was therefore considered worthwhile to synthesize new ternary heterometallic dibutyl [Sn(IV), Ti(IV), Al(III)]-μ-oxoisopropoxide and in order to get insight into its structure its β-diketonates have also been synthesized and characterized.

EXPERIMENTAL

All manipulations have been carried out under anhydrous conditions and solvents and the reagents used were of analytical grade and purified by recommended method[13]. The general technique and physical measurement were carried out as described elsewhere[14-16]. Dibutyltin diacetate $Bu_2Sn(OAc)_2$, titanium isopropoxide $Ti(i\text{-}OPr)_4$ and aluminium isopropoxide $Al((i\text{-}OPr)_3$ (Aldrich) were used as received. Acetyl acetone was dried prior to use and benzoyl acetone (Hi-media) was used as received. The estimation of isopropoxy groups in the μ-oxoisopropoxide and isopropyl alcohol liberated in synthesis of β-diketonates were carried out oxidimetrically[17]. Tin, titanium and aluminium in the complex and its derivatives with β-diketones were analyzed gravimetrically[16].

Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer over the range of 4000-400 cm^{-1}. The ^1H, ^{13}C, ^{119}Sn and ^{27}Al NMR spectra were recorded in $CDCl_3$ on Bruker Avance II 400 NMR spectrometer. Elemental analysis was carried on Perkin Elmer 2400 CHN Elemental Analyser.

Synthesis of $[Bu_2SnO_2TiAl(i\text{-}OPr)_5]$: The μ-oxoisopropoxide compound was synthesized by thermal condensation between $[Bu_2Sn(OAc)OAl(i\text{-}OPr)_2]$ (1.223 g, 2.700 mmol) and $Ti(i\text{-}OPr)_4$ (2.938 g, 10.336 mmol) in refluxing xylene for about 8 h on a fractionating column and the isopropyl acetate formed during the reaction was distilled off continuously from 78 °C to the boiling point of xylene[14,18] (139 °C). The solvent xylene was completely removed under reduced pressure (70 °C/1 mm) yielding a yellowish solid. [Yield: 95 %]. Found: i-OPr, 58.69; Sn, 19.71; Ti, 15.81; Al, 4.15; C, 34.05; H, 6.80 for $[Bu_2SnO_2TiAl(i\text{-}OPr)_5]$ Calcd: i-OPr, 58.95; Sn, 19.77; Ti, 15.94; Al,4.24 C, 35.97; H, 6.99.

Reaction of $Bu_2SnO_2TiAl(i\text{-}OPr)_5]$ with acetylacetone (Hacac) in 1:1 molar ratio: The compound $[Bu_2SnO_2TiAl(i\text{-}OPr)_5]$ (0.320 g, 0.532 mmol) and acetylacetone (0.053 g, 0.530 mmol) were refluxed in 50 mL benzene in a flask connected to short distillation column on an oil bath for about 4 h. The isopropanol liberated at 72-78 °C was fractionated as the binary azeotrope of isopropanol-benzene[18] was collected and checked for completion of the reaction. The excess of the solvent was then removed under reduced pressure (45 °C/1 mm) yielding a yellowish brown solid. The 1:2 derivatives were prepared by similar procedure and the analytical results have been summarized in Table-1.

RESULTS AND DISCUSSION

Preparation of the organoheterotrimetallic-μ-oxoisopropoxide $[Bu_2SnO_2TiAl(i\text{-}OPr)_5$ follows the following reactions scheme:

$$Bu_2Sn(OAc)_2 + Al(i\text{-}OPr)_3 \xrightarrow[139\ °C,\ 8h]{Xylene,\ Reflux} Bu_2Sn(OAc)\,OAl(i\text{-}OPr)_2 + Ac\ (i\text{-}OPr)$$

$$Bu_2Sn(OAc)\,OAl(i\text{-}OPr)_2 + Ti(i\text{-}OPr)_4 \xrightarrow[139\ °C,\ 8h]{Xylene,\ Reflux} Bu_2SnO_2\ TiAl(i\text{-}OPr)_5\ +\ Ac\ (i\text{-}OPr)$$

The μ-oxoisopropoxide compound obtained is a yellow solid, susceptible to hydrolysis and soluble in common organic solvents such as benzene, chloroform, carbon tetrachloride, *etc*.

An important feature in the IR spectrum of the compound $[Bu_2SnO_2TiAl(i\text{-}OPr)_5]$ is that the strong bands observed at 1610 and 1435 cm^{-1} due to $\nu_{asym}(C{=}O)$ and $\nu_{sym}(C{=}O)$, respectively in dibutyltin diacetate have been found to be absent indicating the complete removal of acetate groups[19]. Also appearance of new band in the region 1370-1340 cm^{-1} has been assigned to *gem*-dimethyls[20] of isopropoxy groups. Similarly the bands observed in the region 1180-1160 and 1130-1110 cm^{-1} have been assigned to the combination bands $\nu(C\text{-}O + i\text{-}OPr)$ terminal and bridging groups respectively and a band at 950 cm^{-1} is assigned to $\nu(C\text{-}O)$ stretching vibration suggest bridging isopropoxy groups in the compound[20,21]. A number of bands observed in the region 700-400 cm^{-1} is due to M-O stretching vibrations[22] in μ-oxo compound.

In the ^1H NMR spectrum of dibutyltin diacetate a sharp singlet observed at δ 2.1 is found to be absent in the spectrum of $[Bu_2SnO_2TiAl(i\text{-}OPr)_5]$ their by confirming the complete removal of acetate groups. ^1H NMR spectrum of dibutyl [Sn(IV), Ti(IV), Al(III)]-μ-oxoisopropoxide exhibits overlapping doublets between δ 0.9-δ 1.2 due to methyl protons of terminal and bridging isopropoxy groups[22]. A multiplet centered at δ 4.0 is observed due to the methine proton of isopropoxy groups in the μ-oxo compound[22].

^{13}C NMR spectrum of dibutyl [Sn(IV), Ti(IV), Al(III)]-μ-oxoisopropoxide shows prominent peaks at δ 27.6 and δ 28.1 assignable to the methyl carbon of terminal and bridging isopropoxy groups, respectively. The peaks at δ 64.1 and δ 66.7 in the ^{13}C NMR spectrum are due to terminal and bridging methine carbon of the isopropoxy groups[23], respectively. The other peaks at δ 27.2, δ 25.4, δ 14.8 and δ 13.6 are assignable to C-1, C-2, C-3 and C-4, respectively of the butyl group[24].

The ^{119}Sn NMR spectrum of dibutyl [Sn(IV), Ti(IV), Al(III)]-μ-oxoisopropoxide exhibits a sharp signal at -192.4 assignable to the hexacoordination about Sn(IV)[25].

^{27}Al NMR: ^{27}Al NMR spectrum of the compound $[Bu_2SnO_2TiAl(i\text{-}OPr)_5]$ display a signal at δ 67.7 ppm indicating a tetra-coordinated environment about Al atom which is surrounded by four oxygen atoms[26].

TABLE- 1
ANALYTICAL DATA

S.No.	Compound g (mmol)	Ligand g (mmol)	Reflux time (h)	Product g (%)	Anal. Found (calcd.)					
					i-r (g) H (%)	Sn (%)	Al (%)	Ti (%)	C (%)	H (%)
1	$[Bu_2SnO_2TiAl(i\text{-}OPr)_5]$ 0.320 (0.532)	Hacac 0.053(0.53)	4	$[Bu_2SnO_2TiAl(i\text{-}OPr)_4$ (acac)] 0.323(94.9)	0.03 (0.03)	18.45 (18.53)	3.90 (3.98)	14.82 (14.95)	37.26 (37.47)	6.05 (6.55)
2	$[Bu_2SnO_2TiAl(i\text{-}OPr)_5]$ 0.315 (0.524)	Hacac 0.105(1.05)	6	$[Bu_2SnO_2TiAl(iOPr)_3$ $(acac)_2]$ 0.337(94.4)	0.05 (0.06)	17.35 (17.44)	3.72 (3.76)	13.95 (14.07)	38.52 (38.79)	5.75 (6.17)
3	$[Bu_2SnO_2TiAl(i\text{-}OPr)_5]$ 0.160 (0.267)	Hbzac 0.0433(0.267)	5	$[Bu_2SnO_2TiAl(i\text{-}OPr)_4$ (bzac)] 0.178(95.0)	0.02 (0.02)	16.85 (16.90)	3.61 (3.65)	13.58 (13.63)	42.65 (42.70)	5.98 (6.26)
4	$[Bu_2SnO_2TiAl(i\text{-}OPr)_5]$ 0.130 (217)	Hbzac 0.0703(0.434)	7	$[Bu_2SnO_2TiAl(i\text{-}OPr)_3$ $(bzac)_2]$ 0.163(93.6)	0.03 (0.03)	14.64 (14.75)	3.17 (3.20)	11.79 (11.90)	47.57 (47.73)	5.20 (5.71)

The molecular weight measurement carried out in dry benzene by cryoscopic method suggests dimeric nature of the compound.

In order to get an insight into the structure of [$Bu_2SnO_2TiAl(i\text{-}OPr)_5$] its reactions with β-diketones (HL) in various molar ratios have been performed in refluxing benzene yielded the compounds of the types [$Bu_2SnO_2TiAl(i\text{-}OPr)_4L$] and [$Bu_2SnO_2TiAl(i\text{-}OPr)_3L_2$] according to the following reaction scheme:

$$Bu_2SnO_2TiAl(i-OPr)_5 + nHL \xrightarrow{\text{Refluxing benzene}}$$

$$Bu_2SnO_2TiAl(i-OPr)_{5-n}L_n + n i\text{PrOH}$$

(n = 1-2, HL = acetylacetone/benzoylacetone)

The isopropanol liberated during the reaction collected azeotropically (isopropanol-benzene) and estimated oxidimetrically to check the progress of the reaction. It was observed that only two out of the five of isopropoxy groups of dibutyl [Sn(IV), Ti(IV), Al(III)] -μ-oxoisopropoxide could be replaced by β-diketones. Futher replacement of isopropoxy groups could not be achieved even with an excess of ligand (β-diketones) and prolonged refluxing time in benzene (approx. 16 h). This suggest that probably bridging isopropoxy groups could not be replaced.

The β-diketone derivatives of dibutyl [Sn(IV), Ti(IV), Al(III)]-μ-oxoisopropoxide are found to be yellow to brownish-yellow coloured solids. All β-diketonates show appreciable solubility in common organic solvents (benzene, chloroform, hexane), susceptible to hydrolysis and decompose on heating strongly above 180 °C.

The absorption bands in the region 1360-1340, 1165-1150 and 1010-900 cm^{-1} in the IR spectra of 1:1 and 1:2 β-diketone derivatives of [$Bu_2SnO_2TiAl(i\text{-}OPr)_5$] are assigned to the *gem*-dimethyl[20] portion and combination band ν(CO + *i*-OPr) of the terminal and bridging isopropoxy groups, respectively. A band appearing at 950 cm^{-1} is due to ν(C-O) stretching of bridging isopropoxy group[20,21]. The IR spectrum of β-diketones[27] display strong bands at 1600-1580 and 1520-1500 cm^{-1} due to ν_{sym}(C=O) and ν_{asym}(C=C), respectively along with a broad band at 3100-2700 cm^{-1} due to enolic ν(O-H). The non shifting of ν(C=O) frequency and the disappearence of broad band in the region 3100-2700 cm^{-1} in β-diketonates suggest the metal-ligand bonding takes place through the oxygens of both CO groups in the derivatives[28]. A number of bands assigned in the region 700-400 cm^{-1} due to M-O stretching vibrations[22] in β-diketonates of -μ-oxoisopropoxide compound.

^1H NMR spectra of 1:1 and 1:2 β-diketonates display overlapping doublets between δ 1.1 and δ 1.3 are due to methyl protons and a multiplet centered at δ 4.1 due to the methine proton of terminal and bridging isopropoxy groups respectively. All the derivatives exhibit singlet at δ 2.1 and δ 5.8 due to methyl and methine proton of the ligand moiety respectively. The peaks due to the phenyl ring protons in benzoylacetone derivative of [$Bu_2SnO_2TiAl(i\text{-}OPr)_5$] are found between δ 7.0-7.6 .

The ^{13}C NMR spectra of 1:1 and 1:2 β-diketonates show two prominent peaks between δ 25.6-26.0 and δ 28.0-28.8 assignable to the methyl carbons and two peaks at δ 62.6-62.8 and δ 63.1-64.823 assigning methine carbons of terminal and bridging isopropoxy groups respectively in the derivatives. Two peaks exhibited in the range δ 191.8-183.0 and δ 100.42-93.4 are due to carbonyl carbon and methine carbon of ligand moiety in all the β-diketonates. The peaks observed at δ 127.2, δ 126.7, δ 125.6 and δ 136.4 are due to *ortho*, *meta* and *para* substituted carbon of the phenyl ring, respectively in the spectra of benzoylacetone derivatives[24].

Thermal analysis: Thermogravimetric analysis of hydrolyzed product of [$Bu_2SnO_2TiAl(i\text{-}OPr)_5$] have been performed up to 800 °C. The loss about 3-4 % is due to the traces of water present in hydrolyzed product of μ-oxo compound. The weight loss of 36.189 % observed from 220 °C to 340 °C[29] is probably due to the elimination of hydroxy groups and organic moieties present in the hydrolysed product [$Bu_2SnO_2TiAl(OH)_5$] resulting from the hydrolysis of [$Bu_2SnO_2TiAl(i\text{-}OPr)_5$]. The final product remaining is probably the $SnTiAlO_5$ mixed metal oxide. The TG analysis is consistent with the formulation of the compound as [$Bu_2SnO_2TiAl(i\text{-}OPr)_5$].

DTA plot of the hydrolysed product of [$Bu_2SnO_2TiAl(i\text{-}OPr)_5$] shows an broad exothermic peak corresponding to the combustion of organic moities while a sharper exothermic suggesting crystallisation is observed at temperature below 554.3 °C[29].

On the basis of below analytical studies (Table-1) the following tentative structures have been assigned to the [$Bu_2SnO_2TiAl(i\text{-}OPr)_5$] and β-diketone derivatives of μ-oxo compound (1:2) (Fig. 1 and 2)

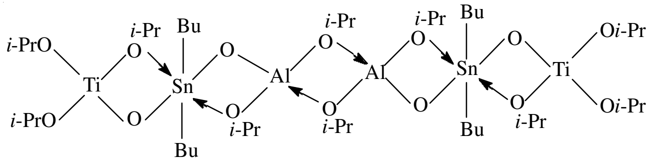

Fig. 1. Structure of [$Bu_2SnO_2TiAl(i\text{-}OPr)_5$]

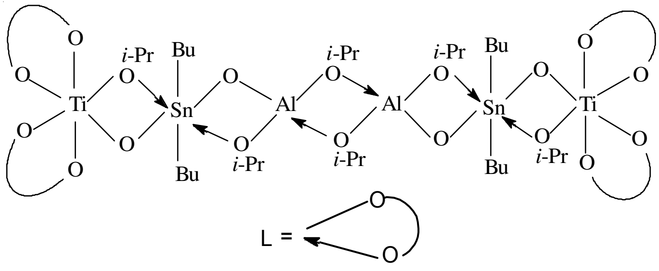

Fig. 2. Structure of [$Bu_2SnO_2TiAl(i\text{-}OPr)_3(acac)_2$]

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