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Synthesis and characterization of derivatives of heterotrimetallic [Al(III);Sn(II), Ti(IV)]-μ-oxoisopropoxide with β -diketones

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Abstract

Isopropoxy substitution reactions of $[SnO_2TiAl(i\text{-}OPr)_{5-n}L_n]$ with β-diketones in different molar ratios (1:1-1:2) gives compounds of the type $[SnO_2TiAl(i\text{-}OPr)_{5-n}L_n]$ (where n is 1-2 and L = acetylacetonate/ benzoylacetonate anion). The isopropanol librated during the course of reaction is collected azeotropically (isopropanol-benzene) and estimated oxidimetrically to check the progress of the reaction.The derivatives has been characterized by elemental, liberated isopropanol and spectral analysis (IR, ^1H , ^{13}C NMR) and molecular weight measurement.

Keywords: Metal alkoxide, Tin, Titanium,Aluminium, acetylacetonate, benzoylacetonate.

Introduction

Metal alkoxides are nowadays largely employed for preparing ceramic materials, for thin coating films and for supports and catalysts preparation using in the different cases the sol-gel technique or the chemical vapour deposition.[1-2] Applications of metal alkoxides to biology and materials science are very attractive and fast growing research areas. Among the many aspects being studied, the preparation of heteronuclear molecules potential single-source precursors of high technology mixed-metal oxides is one of the most challenging.[3-5]

Alkoxides are considered to be suitable precursors for super or semi-conducting, ferroelectric, dielectric and even biocompatible oxide materials[6,7] 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 uses of heterometallic alkoxides as single-source molecules precursors for synthesis of oxides have seen a rapid growth during the last two decades.The control of particle size and the morphology of the oxide are of crucial importance nowadays both from the fundamental and industrial point of view[8]. The mixed metal oxides prepared from heterometallic-μ-oxoalkoxides[9-12] have been used for absorbing harmful chemicals[13] and gases such as SO_2, CCl_4 and decontaminating chemical warfare agents[14]. The alkaline earth metal titanates like barium titanate, calcium titanate ($CaTiO_3$), strontium titanate ($SrTiO_3$ and $Ba_xSr_{1-x}TiO_3$) due to their exceptional properties expose potential applications in multilayer ceramic capacitors, electro-optic, dielectric and piezoelectric devices[15-18].

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,[19] 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 synthesis derivatives of heterometallic [Al(III);Sn(II);Ti(IV)] -μ-oxoisopropoxide with β-diketones have 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.[20] The general technique and physical measurement were carried out as described elsewhere[21-24]. Heterometallic [Al(III);Sn(II);Ti(IV)]-μ-oxo-*iso*propoxide was prepared by equimolar reaction of tin diacetate and aluminium*iso*propoxide in xylene yields [Sn(OAc)OAl(O-*i*-Pr)$_2$] which on further reaction with titanium *iso*propoxide in 1:1 molar ratio, titanium isopropoxide Ti(i-OPr)$_4$ and aluminium isopropoxide Al((i-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[25]. Tin, titanium and aluminium in the complex and its derivatives with β-diketones were analysed gravimetrically[24].

The Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer over the range of 4000-400 cm^{-1}. The ^{1}H, ^{13}C 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.

Reaction of [SnO$_2$TiAl(O-i-Pr)$_5$]with acetylacetone (Hacac) in 1:1 molar ratio:

The compound [SnO$_2$TiAl(O-*i*-Pr)$_5$] (0.320 g, 0.615 mmol) and acetylacetone (0.061 g, 0.615 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 ^{o}C was fractionated as the binary azeotrope of isopropanol-benzene[26] was collected and checked for completion of the reaction. The excess of the solvent was then removed under reduced pressure (45 ^{o}C /1mm) 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

the reactions of [SnO$_2$TiAl(O-*i*-Pr)$_5$] with β-diketones (HL) in various molar ratios have been performed in refluxing benzene yielded the compounds of the types [SnO$_2$TiAl(O-*i*-Pr)$_4$L] and [SnO$_2$TiAl(O-*i*-Pr)$_3$L$_2$] according to the following reaction scheme:

$$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5] + nHL \xrightarrow[\text{Reflux}]{\text{Benzene}} [SnO_2TiAl(O\text{-}i\text{-}Pr)_{5-n}L_n] + nHO\text{-}i\text{-}Pr$$

(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 [Al(III);Sn(II);Ti(IV)]-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. 16h). This suggest that probably bridging isopropoxy groups could not be replaced.

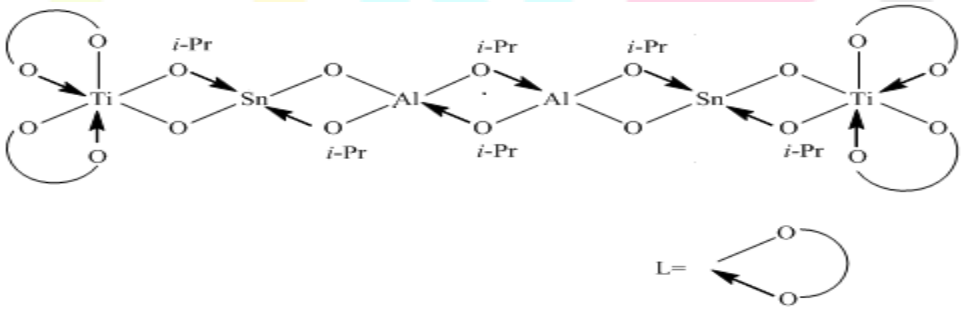
The β-diketone derivatives of [Al(III);Sn(II);Ti(IV)]- μ-oxoisopropoxide are found to be yellow to brownish-yellow colored solids. All β-diketonates show appreciable solubility in common organic solvents (benzene, chloroform, hexane), susceptible to hydrolysis and decompose on heating strongly above ~ 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 [$SnO_2TiAl(O\text{-}i\text{-}Pr)_5$] are assigned to the *gem*-dimethyl[27] 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.[27,28] The IR spectrum of β-diketones[29] display strong bands at ~ 1600–1580 cm^{-1} 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[30]. A number of bands assigned in the region 700–400 cm^{-1} due to M-O stretching vibrations[31] in β-diketonates of -μ-oxoisopropoxide compound.

^{1}H 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 [$SnO_2TiAl(O\text{-}i\text{-}Pr)_5$] are found between δ 7.0-7.6.[32]

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 63.1–64.8[33] 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 δ127.2, 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[34].

On the basis of below analytical studies (Table 1) the following tentative structures have been assigned to 1:2 β-diketone derivative of [$SnO_2TiAl(O\text{-}i\text{-}Pr)_5$] (**Fig.1**)



[$SnO_2TiAl(O\text{-}i\text{-}Pr)_3(acac)_2$]

Fig. 1.

Table- 1 Analytical data

S.No.	Compound g(mmol)	Ligand g(mmol)	Reflux time(hr)	Product g(%)	Anal. Found (calcd.)					
					i –Opr(g)	Sn(%)	Al(%)	Ti(%)	C(%)	H(%)
1	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.320 (0.615)	Hacac 0.061(0.615)	4	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_4(acac)]$ 0.327(94.9)	0.03 (0.03)	21.25 (20.53)	4.82 (3.98)	8.39 (7.95)	36.42 (35.47)	6.25 (6.05)
0..2	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.310 (0.596)	Hacac 0.238(1.05)	6	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_3(acac)_2]$ 0.340(95.1)	0.05 (0.06)	19.83 (18.10)	4.50 (3.96)	7.83 (7.15)	38.00 (37.59)	5.83 (5.17)
3	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.150 (0.288)	Hbzac 0.0466(0.288)	5	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_4(bzac)]$ 0.170(95.0)	0.02 (0.02)	19.13 (17.80)	4.34 (3.75)	7.55 (6.83)	42.44 (41.70)	5.94 (5.26)
4	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.115 (0.221)	Hbzac 0.143(0.442)	7	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_3(bzac)_2]$ 0.150(93.8)	0.03 (0.03)	16.43 (14.75)	3.72 (3.30)	6.49 (5.69)	48.06 (47.73)	5.66 (5.11)

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