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Synthesis of heterotrimetallic [Al(III);Sn(II);Ti(IV)]-μ-oxo-*iso*propoxide and heterotrimetallic [Al(III);Sn(II);Ti(IV)]- μ- oxo-mixedalkoxides

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Abstract

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 affords heterometallic [Al(III);Sn(II);Ti(IV)]-μ-oxo-*iso*propoxide with continuous libration of isopropyl acetate. The isopropoxy substitution reaction of μ-oxo compound with cyclic alcohols such as cyclohexanol (HCA^1) and Cycloheptanol (HCA^2) in stoichiometric ratios 1:1 and 1:2 in refluxing benzene gives compound of the type [$SnO_2TiAl(O\text{-}i\text{-}Pr)_{5-n}(CA^1)_n$] and [$SnO_2TiAl(O\text{-}i\text{-}Pr)_{5-n}(CA^2)_n$]. The μ-oxo compound has been characterized by elemental, spectral analysis (IR, ^{1}H , ^{13}C,^{119}Sn and^{13}Al NMR) and molecular weight measurement. The derivatives has been characterized by elemental, liberated isopropanol and spectral analysis (IR, ^{1}H , ^{13}C NMR).

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].

The above features underline the importance and utility of μ-oxo compounds, it was therefore considered worthwhile to synthesize heterotrimetallic [Al(III);Sn(II);Ti(IV)]-μ-oxo-*iso*propoxide and heterotrimetallic [Al(III);Sn(II);Ti(IV)]- μ- oxo-mixedalkoxides

Experimental methodology

Synthesis of heterotrimetallic [Al(III);Sn(II); Ti(IV)]- μ- oxo-isopropoxide

The [Sn(OAc)OAl(O-*i*-Pr)$_2$)] compound was synthesized by refluxing the Sn(OAc)$_2$ and Al(O-*i*-Pr)$_3$ in 1:1 molar ratio in xylene. The compound [Al(III);Sn(II)]–μ-oxo-*iso*propoxyacetate (3.169g, 9.356 mmol) and titanium *iso*propoxide (2.656g, 9.356 mmol) were refluxed in 1:1 molar ratio in xylene to obtain heterotrimetallic [Al(III);Sn(II);Ti(IV)]-μ-oxo-*iso*propoxide. The reaction takes place in two steps and can be represented as shown below:

$$Sn(OAc)_2 + Al(O\text{-}i\text{-}Pr)_3 \xrightarrow[139\ ^0C]{\text{Reflux, Xylene}} [Sn(OAc)OAl(O\text{-}i\text{-}Pr)_2] + Ac(O\text{-}i\text{-}Pr)$$

$$[Sn(OAc)OAl(O\text{-}i\text{-}Pr)_2] + Ti(O\text{-}i\text{-}Pr)_4 \xrightarrow[139\ ^0C]{\text{Reflux, Xylene}} [SnO_2TiAl(O\text{-}i\text{-}Pr)_5] + Ac(O\text{-}i\text{-}Pr)$$

The *iso*propyl acetate formed during the reaction was distilled off continuously from 78 °C to boiling point of xylene (139 °C) for about 8 hrs on a fractionating column. The excess of the solvent was removed under reduced pressure resulting in deep yellow highly viscous transparent solid product, highly susceptible to hydrolysis and soluble in common organic solvents such as benzene, toluene, chloroform and carbon tetrachloride etc. [Yield: 96 %].

Analysis found (calcd) : O-*i*-Pr : 0.621g (0.60g); Sn 22.28 (22.80); Ti : 8.62 (8.12); Al : 5.18 (4.95).

Molecular weight measurements carried out in dry benzene using cryoscopic method suggests dimeric nature of the compound. The µ-oxo compound and benzene were taken in 1:10 ratio. A depression in freezing point of 1.66 was observed and the corresponding molecular weight of the µ-oxo compound was found 1035.12.

Synthesis of 1:1 heterotrimetallic [Al(III);Sn(II);Ti(IV)]-µ-oxo-mixedalkoxides

To the compound $[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ (0.352 g, 0.676 mmol)) is added cyclohexanol (0.0492 g, 0.492 mmol) in 50 ml benzene in a flask connected to short distillation column and refluxed for 4 hrs at ~ 100 °C. The reaction can be represented as:

$$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5] + nHCA^1 \xrightarrow[\text{Reflux}]{\text{Benzene}} [SnO_2TiAl(O\text{-}i\text{-}Pr)_{5-n}(CA^1)_n] + nHO\text{-}i\text{-}Pr$$

n =1, HCA^1= cyclohexanol

The *iso*propanol liberated during the reaction was distilled off azeotropically and its amount was estimated oxidimetrically in order to check the progress of reaction. After the completion of reaction the excess of the solvent was removed under reduced pressure to get viscous yellowish red product dried at 45 °C/1mm. All the derivatives were found to be reddish yellow viscous liquid, soluble in common organic solvents and susceptible to hydrolysis and decompounds on heating above 200 ^{0}C.

Similar procedure was adopted for the reactions of $[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ with cyclohexanol and cycloheptanol in different molar ratios. The details are given in tables **(Table-1)** along with analytical data.

Table-1: Analytical data

S.No	Compound g(mmol)	Ligand g(mmol)	Molar Ratio	Refluxing time	Product g(%)	Anal. Calcd. (found)			
						HO-*i*-Pr g	Sn (%)	Ti (%)	Al (%)
1	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.352 (0.676)	HCA^1 0.0492 (0.492)	1:1	4	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_4(CA^1)]$ 0.304 (80.3)	0.041 (0.04)	21.17 (20.82)	8.54 (8.05)	4.83 (4.50)
2	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.349 (0.670)	HCA^1 0.097 (0.97)	1:2	5	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_3(CA^1)_2]$ 0.333 (82.7)	0.08 (0.078)	19.74 (19.56)	7.97 (7.65)	4.50 (4.10)
3	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.358 (0.688)	HCA^2 0.057 (0.50)	1:1	4	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_4(CA^2)]$ 0.320 (81.2)	0.041 (0.04)	20.66 (20.10)	8.33 (7.98)	4.71 (4.25)
4	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.363 (0.697)	HCA^2 0.115 (1.015)	1:2	5	$[SnO_2TiAl(O\text{-}i\text{-}Pr)_3(CA^2)_2]$ 0.365 (83.4)	0.083 (0.080)	18.88 (18.35)	7.62 (7.31)	4.30 (3.92)

Result and discussions:

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 affords heterometallic [Al(III);Sn(II);Ti(IV)]-μ-oxo-*iso*propoxide. The *iso*propyl acetate formed during the course of reaction was continuously removed in the temperature range 78-139 °C (i.e. up to the boiling point of xylene). The reaction takes place in two steps and can be depicted as shown below:

$$Sn(OAc)_2 + Al(O\text{-}i\text{-}Pr)_3 \xrightarrow[139\ ^0C]{\text{Reflux, Xylene}} [Sn(OAc)OAl(O\text{-}i\text{-}Pr)_2] + Ac(O\text{-}i\text{-}Pr)$$

$$[Sn(OAc)OAl(O\text{-}i\text{-}Pr)_2] + Ti(O\text{-}i\text{-}Pr)_4 \xrightarrow[139\ ^0C]{\text{Reflux, Xylene}} [SnO_2TiAl(O\text{-}i\text{-}Pr)_5] + Ac(O\text{-}i\text{-}Pr)$$

The above reactions involve the substitution of both the acetyl groups is confirmed by oxidimetrically estimating the *iso*propoxy groups in the μ-oxo compound. The μ-oxo compound is a deep yellow viscous transparent product, highly susceptible to hydrolysis and soluble in common organic solvents such as benzene, toluene, chloroform and carbon tetrachloride etc.

In order to get the information regarding the nature and structure of $[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$, [Al(III);Sn(II);Ti(IV)]-μ-oxo-mixedalkoxides have been prepared by the reaction of [Al(III);Sn(II);Ti(IV)]-μ-oxo-*iso*propoxide with cyclic alcohols such as cyclohexanol (HCA^1) and Cycloheptanol (HCA^2) in stoichiometric ratios 1:1 and 1:2 in refluxing benzene.

The products of the type $[SnO_2TiAl(O\text{-}i\text{-}Pr)_{5-n}(CA^1)_n]$ and $[SnO_2TiAl(O\text{-}i\text{-}Pr)_{5-n}(CA^2)_n]$ are obtained as a result of the reactions of μ-oxo-*iso*propoxide compound with cyclohexanol and cycloheptanol respectively. The reactions of μ-oxo-*iso*propoxide compound with cyclohexanol can be represented as follows:

$$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5] + nHCA^1 \xrightarrow[\text{Reflux}]{\text{Benzene}} [SnO_2TiAl(O\text{-}i\text{-}Pr)_{5-n}(CA^1)_n] + nHO\text{-}i\text{-}Pr$$

n =1-2, HCA^1= cyclohexanol

Similar procedure was adopted for the reactions of $[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ with cyclohexanol and cycloheptanol in different molar ratios. The *iso*propanol liberated during the course of reaction was collected azeotropically (*iso*propanol-benzene) and estimated oxidimetrically[19] to check the progress of reaction. It has been found that only two out of five *iso*propoxy groups of the compound $[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ could be replaced. The three *iso*propoxy groups could not be replaced even on refluxing an excess of cyclic alcohols with $[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ for a long time (38 hrs). All the derivatives were found to be redish yellow viscous liquid, soluble in common organic solvents and susceptible to hydrolysis and decompounds on heating above 200 ^{0}C.

Infrared Spectral Studies

A strong band observed at 1630 cm^{-1} due to C=O stretch in the IR spectrum of tin acetate is absent in the spectrum of [Al(III);Sn(II);Ti(IV)]-μ-oxo-*iso*propoxide indicates the complete removal of acetate groups in the μ-oxo compound.[20]

The spectrum of μ-oxo-*iso*propoxide shows absorption bands in the region ~1365-1350 cm^{-1}, ~1170 cm^{-1} and 1125-1020 cm^{-1} are the characteristics of *gem*-dimethyl[21] portion and combination band *ν*(C-O + O-*i*-Pr) of the terminal and bridging *iso*propoxy groups respectively. A band appearing at approx. 950 cm^{-1} is assigned to *ν*(C-O) stretching of bridging *iso*propoxy groups.[21,22] Bands observed below 700 cm^{-1} are due to M-O stretching in μ-oxo compound.

The IR spectra of cyclic alcohol derivatives of $[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ shows absorption bands in the region 1360-1340 cm^{-1} which are the characteristics of *gem*-dimethyl portion of *iso*propoxy group. A number of bands are observed in the range 1165-1150 cm^{-1} and 1135-1115 cm^{-1} due to combination band *ν*(C-O + O-*i*-Pr) of the terminal and bridging *iso*propoxy groups respectively. No peak is observed at ~1165 cm^{-1} in the

spectrum of 1:2 derivative of μ-oxo compound indicates the absence of terminal *iso*propoxy group. A band appeared at approx. 950-925 cm^{-1} is due to *ν*(C-O) stretching of bridging *iso*propoxy group.[21,22] A broad band observed at ~3350 cm^{-1} in the spectra of cyclic alcohols due to *ν*(O-H) stretch is found absent in the spectra of μ-oxo-mixedalkoxides indicates the deprotonation of cyclic alcohols. A number of vibrations are observed around 670 cm^{-1} are due to M-O stretching in μ-oxo compound and its cycloalcoholates.

NMR Spectral Studies

^{1}H NMR Spectra

A peak at δ 2.1 ppm in tin diacetate due to methyl protons of the acetate groups was absent in the μ-oxo compound [$SnO_2TiAl(O$-*i*-$Pr)_5$] confirms the replacement of the acetyl groups. The ^{1}H NMR spectra of the compound [$SnO_2TiAl(O$-*i*-$Pr)_5$] shows a numbers of peaks between 0.8-1.7 due to the intermixing of terminal and bridging methyl protons of *iso*propoxy groups.[23] A multiplet centered at δ 4.4 ppm is observed in the spectra of μ-oxo-*iso*propoxide due to the methine protons of *iso*propoxy groups.[24]

^{1}H NMR spectra of cycloalcoholates derivatives of [$SnO_2TiAl(O$-*i*-$Pr)_5$] -μ-oxo-*iso*propoxide show a number of peaks centered at δ 1.2 ppm due to the intermixing of terminal and bridging methyl protons of *iso*propoxy groups. A broad multiplet centered at δ 4.2-4.5 is due to methine proton of *iso*propoxy groups.[25] In the 1:2 derivatives the multiplet was not as broad as in 1:1 derivatives indicates the presence of only bridging *iso*prppoxy groups.

^{13}C NMR Spectra

The ^{13}C NMR Spectra of compound [$SnO_2TiAl(O$-*i*-$Pr)_5$] display two prominent peaks between δ 27.7 ppm and δ 28.4 ppm assignable to the methyl carbon of terminal and bridging *iso*propoxy groups. Two peaks are observed at δ 64.4 ppm and δ 64.7 ppm due to methine carbons of two different *iso*propoxy groups.[26]

The ^{13}C NMR spectra of 1:1 cyclic alcohol derivatives of μ-oxo-*iso*propoxide compound show two prominent peaks between δ 25.3- 26.1 ppm and δ 26.4-28.8 ppm assignable to methyl carbon of terminal and bridging *iso*propoxy groups. The two peaks observed at δ 64.1 ppm and δ 64.5 ppm assignable to methine carbon of *iso*propoxy groups in the derivative. The spectra of 1:2 cycloalcholates exhibit a single peak at δ 69.2 ppm in place of two signals observed at δ 64.1 ppm and δ 64.5 ppm in 1:1 derivative[25] suggest the presence of only bridging *iso*propoxy groups. Moreover, the two signals are observed at ~ δ 36.1 ppm and ~ δ 82.2 ppm due to the methylene and methine carbon of the cycloalkoxy group in all the derivatives.

^{119}Sn NMR Spectrum

The ^{119}Sn NMR spectrum of [Al(III);Sn(II);Ti(IV)]-μ-oxo-*iso*propoxide exhibits a sharp signal at δ 74.52 assignable to the tetra coordination about Sn(II).[27]

^{27}Al NMR Spectra

The ^{27}Al NMR Spectra of [$SnO_2TiAl(O\text{-}i\text{-}Pr)_5$] and cycloalcoholate derivatives shows a singlet at δ 70.16 ppm indicating at tetrahedral environment about the Al atom and is surrounded by four oxygen atoms.[28]

Molecular Weight Determination

Molecular weight measurements carried out in dry benzene using cryoscopic method suggests dimeric nature of the compound

On the basis of above studies the following tentative structures can be assigned to [Al(III);Sn(II);Ti(IV)]-μ-oxo-*iso*propoxide and [$SnO_2TiAl(O\text{-}i\text{-}Pr)_3(OR)_2$] -μ-oxo-mixedalkoxide (**Fig 1 and 2**), in which the lone pair oxygen atom forming μ-oxo bridges probably play important role in fulfilling the vacant coordination sites on the central tin atom.

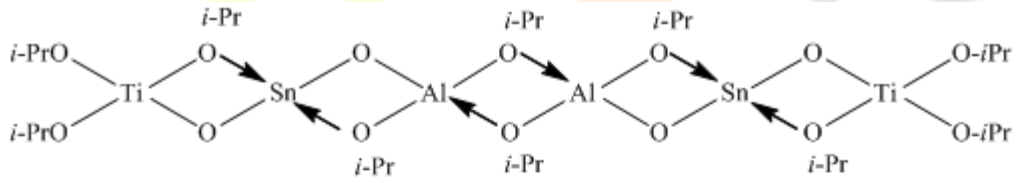
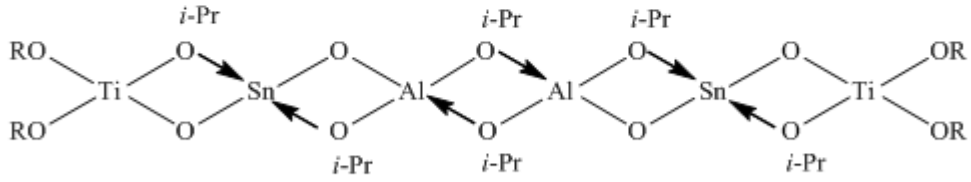


Fig. 1: [$SnO_2TiAl(O\text{-}i\text{-}Pr)_5$]



$RO^{\ominus}$ = cyclohexanol anion

Fig. 2: [$SnO_2TiAl(O\text{-}i\text{-}Pr)_3(OR)_2$]

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