Synthesis of organoheterobimetallic [Bu$_2$Sn(IV)-Ti(IV)]-µ-oxoisopropoxide and its β-diketonates

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A new organoheterobimetallic-µ-oxoisopropoxide of the type [Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$] has been synthesized by the thermal condensation of dibutyltin diacetate and titanium isopropoxide in 1:2 molar ratio in refluxing xylene. The isopropoxy substitution reactions of this µ-oxoisopropoxide compound with β-diketones in different molar ratios (1:1-1:4) gives compounds of the type [Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_{6-n}$L$_n$] (where n is 1-4 and L = acetylacetonate/benzoylacetonate anion) respectively. The µ-oxoisopropoxide compound has been characterized by elemental, spectral analysis (IR, ^{1}H , ^{13}C, ^{119}Sn NMR and mass) and molecular weight data. The β-diketonates of [Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$] have been characterized by elemental, liberated isopropanol and spectral analysis (IR, ^{1}H , ^{13}C NMR).

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Metal-oxygen clusters are of great importance for the development of new multi-component materials and catalysts based on metal oxides[1].The development of novel single-source precursors which allow the synthesis of size- and shaped selected, homo- and hetero-metal[2] oxide particles is a major challenge in materials science. Volatile organometallic alkoxides are among the best precursors for the synthesis of mixed metal oxides because they can be used in metal-organic-chemical-vapor-deposition (MOCVD), in sol-gel synthesis or in solid synthesis.[2] Recently, synthesis of homogenously dispersed bimetallic oxides in nano crystalline or amorphous form has been reported by Klabunde *et al.*[3] Apart from their role as precursors for mixed metal oxides the bimetallic-µ-oxoalkoxides of transition metals have been found to rank among the best catalysts for the polymerization of heterocyclic monomers like lactones, oxiranes, thiiranes and epoxides.[4,5] Molybdenum and tungsten alkoxides in their middle oxidation state have been used as a model for reductive cleavage of carbon monoxide to carbides

and oxides via the Fisher-Tropsch reaction.[6] Owing to the ever-growing importance of hetero metallic alkoxides and oxoalkoxides it was considered worthwhile to synthesize [Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$]. To further gain an insight into its structure, its reactions have been carried out in different stoichiometric ratios with β-diketones.

Experimental

All manipulations have been carried out under anhydrous conditions[7] and the solvents and reagents used were purified and dried by standard methods[7]. The general technique and physical measurement were carried out as described elsewhere.[8-10] Dibutyltin diacetate [Bu$_2$Sn(OAc)$_2$] and titanium isopropoxide [Ti(OPr^i)$_4$] (Aldrich) were used as received. Acetyl acetone was dried prior to use and benzoylacetone (Hi-media) was used as received. The isopropoxy groups in the µ-oxoisopropoxide compound and liberated isopropanol formed in preparation of β-diketonates were estimated oxidimetrically.[11] Tin and titanium were estimated gravimetrically.[10] The complex [Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$] and its β-diketonates were decomposed in conc. HCl and extracted in dil. HCl, tin was precipitated as sulphide (*p*H 5-6), filtered and estimated as SnO$_2$[10]. The H$_2$S was boiled off completely from the filtrate and titanium was estimated as TiO$_2$ via the formation of titanium-phenazone complex.[10]

The Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer over the range 4000-400 cm^{-1}. The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded in CDCl$_3$ on Bruker Avance II 400 NMR spectrometer. The mass spectrum was recorded on a Waters QTOF2 mass spectrometer equipped with Quadrupole and time of flight (TOF) analyzers.

Synthesis of [Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$]

The µ-oxoisopropoxide compound was synthesized by thermal condensation between Bu$_2$Sn(OAc)$_2$ (1.823 g, 5.193 mmol) and Ti(OPr^i)$_4$ (2.938 g, 10.386 mmol) in xylene. The contents were refluxed for about 8 h on a fractionating column and the isopropyl acetate formed during the reaction was distilled off continuously from 78°C to boiling point of xylene[8, 12] (139°C). The solvent xylene was completely removed
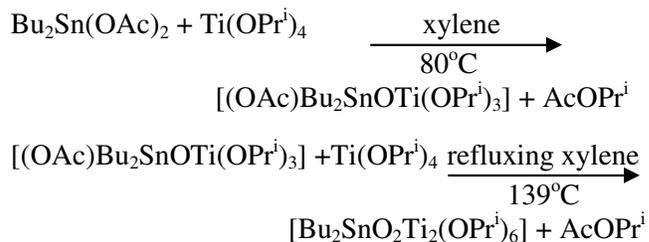
at (~70 °C /1mm) yielding a highly viscous brownish-yellow transparent liquid. [Yield: 95%; Anal.: Found: OPr^i, 49.5; Sn, 16.6; Ti, 13.4. For [Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$] Calc: OPr^i, 49.9; Sn, 16.9; Ti, 13.9].

Reaction of [Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$] with acetylacetone (Hacac) in 1:1 molar ratio

The compound [Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$] (0.350 g, 0.489 mmol) and acetylacetone (0.049 g, 0.490 mmol) were refluxed in ~ 50 ml benzene in a flask connected to a 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 isoproponol-benzene[12]. The azeotrope was collected and checked for completion of the reaction. The excess of the solvent was then removed under reduced pressure (45 °C /1mm) yielding a yellowish brown highly viscous product. The preparations of other β-diketonates of [Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$] in different molar ratios were carried out by similar procedure and the analytical results have been summarized in Table 1.

Results and discussion

The preparation of the organoheterobimetallic-μ-oxoisopropoxide [Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$] follows the following reaction scheme:

$$Bu_2Sn(OAc)_2 + Ti(OPr^i)_4 \xrightarrow[\text{80°C}]{\text{xylene}}$$

$$[(OAc)Bu_2SnOTi(OPr^i)_3] + AcOPr^i$$

$$[(OAc)Bu_2SnOTi(OPr^i)_3] + Ti(OPr^i)_4 \xrightarrow[\text{139°C}]{\text{refluxing xylene}}$$

$$[Bu_2SnO_2Ti_2(OPr^i)_6] + AcOPr^i$$

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

The strong bands observed at 1610 cm^{-1} and 1435 cm^{-1} due to asyn$C \cdots O$ and syn$C \cdots O$ stretch respectively in the IR spectrum of dibutyltin diacetate are absent in the spectrum of dibutyl Sn(IV)-Ti(IV)-μ-oxoisopropoxide indicating the complete removal of acetate groups in μ-oxo compound[13]. The spectrum of the μ-oxoisopropoxide shows absorption bands at ~1360 cm^{-1} and ~1165 cm^{-1} are the characteristics of *gem*-dimethyl porti on and combination band ν(C-O+OPr^i) of the terminal and bridging isopropoxy group respectively[14]. A band appearing at approximately 950 cm^{-1} is assigned to ν(C-O) stretching of bridging isopropoxy group[14,15]. A number of vibrations are observed in the region

Table 1—Analytical data of the studied compounds

S. No.	Comp g (mmol)	Ligand g(mmol)	Molar ratio	Refluxing time	Product g (%)	Found (Calc.) OPr^i (g)	Sn (%)	Ti (%)
1.	[Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$] 0.350 (0.490)	Hacac 0.049(0.490)	1:1	4	[Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_5$(acac)] 0.253(68.5)	0.03 (0.03)	15.81 (15.76)	12.90 (12.70)
2.	[Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$] 0.345 (.480)	Hacac 0.096 (.960)	1:2	6	[Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_4$(acac)$_2$] 0.26 (69)	0.06 (0.06)	15.00 (14.97)	12.60 (12.00)
3.	[Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$] 0.325 (.455)	Hacac 0.136 (1.364)	1:3	8	[Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_3$(acac$_3$)] 0.26 (68.6)	0.08 (0.08)	14.46 (14.25)	11.90 (11.50)
4.	[Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$] 0.315 (0.440)	Hacac 0.176 (1.763)	1:4	9	[Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_2$(acac)$_4$] 0.26 (68.5)	0.10 (0.11)	13.74 (13.60)	11.20 (10.90)
5.	[Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$] 0.374 (0.523)	Hbzac 0.085 (.523)	1:1	4	[Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_5$(bzac)] 0.348 (81.1)	0.03 (0.03	14.62 (14.57)	11.34 (11.72)
6.	[Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$] 0.377 (0.527)	Hbzac 0.171 (1.06)	1:2	7	[Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_4$(bzac)$_2$] 0.383 (78.9)	0.06 (0.06)	12.82 (12.95)	10.53 (10.42)
7.	[Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$] 0.368 (0.515)	Hbzac 0.251(1.544)	1:3	8	[Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_3$(bzac)$_3$] 0.437 (83.0)	0.09 (0.09)	11.53 (11.65)	8.92 (9.36)
8.	[Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$] 0.397 (0.530)	Hbzac 0.344 (2.12)	1:4	9	[Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_2$(bzac)$_4$] 0.482 (80.87)	0.12 (0.13)	10.32 (10.59)	8.70 (8.52)

700-400 cm^{-1} due to M-O stretching vibrations[16] in μ-oxo compound.

A sharp singlet observed at δ 2.1 ppm in the ^{1}H NMR spectrum of dibutyltin diacetate is absent in the spectrum of [Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$], which confirms the complete removal of acetate groups. ^{1}H NMR spectrum of dibutyl Sn(IV)-Ti(IV)-μ-oxoisopropoxide shows a number of peaks centered between δ 0.8 - 1.2 ppm due to the intermixing of methyl protons of terminal and bridging isopropoxy groups along with butyl groups on tin[17]. A multiplet centered at δ 4.4 ppm is observed due to the methine proton of isopropoxy group in the μ-oxo compound.

The ^{13}C NMR spectrum of dibutyl Sn(IV)-Ti(IV)-μ-oxoisopropoxide shows two prominent peaks at ~ δ 27.4 and ~ δ 27.9 ppm assignable to the methyl carbon of terminal and bridging isopropoxy groups and the other two peaks observed at δ 62.6 ppm and δ 62.8 ppm in the ^{13}C NMR spectrum are due to terminal and bridging methine carbon of the isopropoxy groups[18]. The other peaks at δ 25.4, 25.3, 24.1 and 13.4 ppm are assignable to C-1, C-2, C-3 and C-4 respectively of the butyl groups[19].

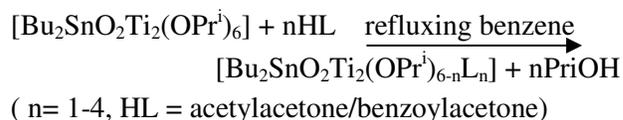A sharp signal at δ −192.4 ppm in the ^{119}Sn NMR spectrum of dibutyl Sn(IV)-Ti(IV)-μ-oxoisopropoxide is attributed to the hexacoordination about Sn atom in the compound.[20]

The positive ion mass spectrum of Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$ was carried in dry toluene containing 17% isopropanol by volume. The significant mass peaks observed at (*m/z*) 711.2, 596.6, 544.4, 371.3, 331.2, 274.3 and 246.2 (Fig. 1) in the spectrum can be assigned to the fragments Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6^+$, SnO$_2$Ti$_2$(OPr^i)$_6^+$, SnO$_2$Ti$_2$(OPr^i)$_5^+$, SnO$_2$Ti$_2$(OPr^i)$_2^+$, Bu$_2$Sn$^+$, SnO$_2$(OPr^i)$_2^+$ and Ti$_2$O$_2$(OPr^i)$_2^+$ respectively[21].

Mass spectrum and the molecular weight measurement carried out in dry benzene using cryoscopic method suggests monomeric nature of the compound.

To further gain an insight into the structure of [Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$], the reactions of this compound with β-diketones (HL) in various molar ratios in refluxing benzene was carried out. The reaction yielded compounds of the type [Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_5$L], [Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_4$L$_2$], [Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_3$L$_3$] and [Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_2$L$_4$] according to the following reaction scheme:

$$[Bu_2SnO_2Ti_2(OPr^i)_6] + nHL \xrightarrow{\text{refluxing benzene}} [Bu_2SnO_2Ti_2(OPr^i)_{6-n}L_n] + nPriOH$$

(n= 1-4, HL = acetylacetone/benzoylacetone)

The isopropanol liberated during the course of the reaction was collected azeotropically (isopropanol-benzene) and estimated oxidimetrically to check the progress of the reaction. It was observed that only four out of the six of isopropoxy groups of dibutyl Sn(IV)-Ti(IV)-μ-oxoisopropoxide could be replaced by β-diketones. Futher replacement of isopropoxy groups could not be achieved even with an excess of

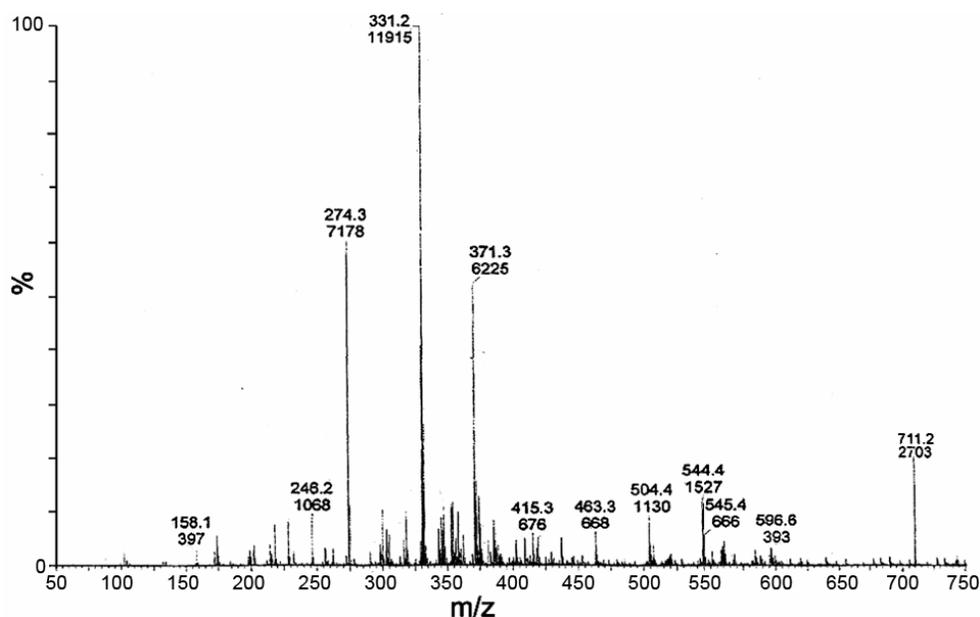Fig. 1—Mass spectrum of Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$.

ligand (β-diketones) and prolonged refluxing time (approx. 12 h). This indicates the presence of both terminal and bridging isopropoxy groups and that only terminal isopropoxy groups are substituted.

The β-diketone derivatives of dibutyl Sn(IV)-Ti(IV)-μ-oxoisopropoxide are found to be brownish-yellow colored highly viscous to semi-solids. All β-diketonates show appreciable solubility in common organic solvents (benzene, chloroform, hexane), susceptible to hydrolysis and decompose on heating strongly.

The IR spectra of 1:1 to 1:3 β-diketone derivatives of μ-oxoisopropoxide show absorption bands in the region 1360–1340 cm^{-1} and 1165–1150 cm^{-1}, which are characterstics of *gem*-dimethyl group and combination band $v(C-O+OPr^i)$ of the terminal and bridging isopropoxy groups respectively. Absence of band at ~ 1165 cm^{-1} in the spectrum of 1:4 β-diketonates indicates the absence of terminal isopropoxy group. A band appearing at ~ 950 cm^{-1} is due to $v(C-O)$ stretching of bridging isopropoxy group[14,15] . The IR spectrum of β-diketones[22] display strong bands at ~ 1600–1580 cm^{-1} and ~1520–1500 cm^{-1} due to $v_{sym}(C=O)$ and $v_{asym}(C=C)$ respectively along with a broad band at ~ 3100–2700 cm^{-1} due to enolic $v(O-H)$. The non-shifting of $v(C=O)$ frequency and the disappearence of broad band appearing in the region 3100–2700 cm^{-1} in β-diketones suggests that bonding takes place through both the oxygens of CO groups in the derivatives. A number of vibrations are observed in the region 700–400 cm^{-1} due to M-O stretching vibrations[16] in β-diketonates of μ-oxoisopropoxide compound.

^{1}H NMR spectra of all the β-diketone derivatives of dibutyl Sn(IV)-Ti(IV)-μ-oxoisopropoxide show broad multiplet centered between δ, 0.8–1.2 ppm due to the intermixing of methyl protons of isopropoxy groups along with butyl groups on tin. A broad multiplet centered at δ, 4.1 ppm is due to the methine proton of isopropoxy groups in the spectra of all derivatives. All the β-diketone derivatives of μ-oxoisopropoxide compound show singlet at δ, 2.1 ppm and ~δ, 5.8 ppm due to methyl and methine proton of the ligand moiety respectively. Further, the peaks observed in the region δ, 7.0–7.7 ppm in benzoylacetone derivative of dibutyl Sn(IV)-Ti(IV)-μ-oxoisopropoxide are due to the phenyl ring protons.

The ^{13}C NMR spectra of 1:1 to 1:3 β-diketone derivatives of μ-oxoisopropoxide compound show two prominent peaks between δ 27.4–27.7 ppm and δ 27.9–28.4 ppm assignable to the methyl carbon of terminal and bridging isopropoxy groups. The two peaks observed at δ 62.6–62.8 ppm and δ 62.8–63.1 ppm are assignable to the methine carbons of isopropoxy groups[18] in the derivatives. However, only one peak is observed at about δ 63 ppm in 1:4 derivatives. The other peaks due to butyl group are found at their usual positions as seen in the μ-oxo compound[19]. Two peaks observed in the range δ 191.8–183.0 ppm and δ 100.42–93.4 ppm are due to carbonyl carbon and methine carbon of ligand moiety in all the β-diketone derivatives of μ-oxoisopropoxide compound. The peaks observed at δ, 127.2, 126.7, 125.6 and 136.4 ppm are due to *ortho, meta, para* and substituted carbon of the phenyl ring respectively in the spectra of benzoylacetone derivative of μ-oxoisopropoxide compound.[19]

On the basis of above studies the following tentative structures (**I** and **II**) have been assigned to the [Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$] and β-diketone derivatives of μ-oxo compound (1:4) .
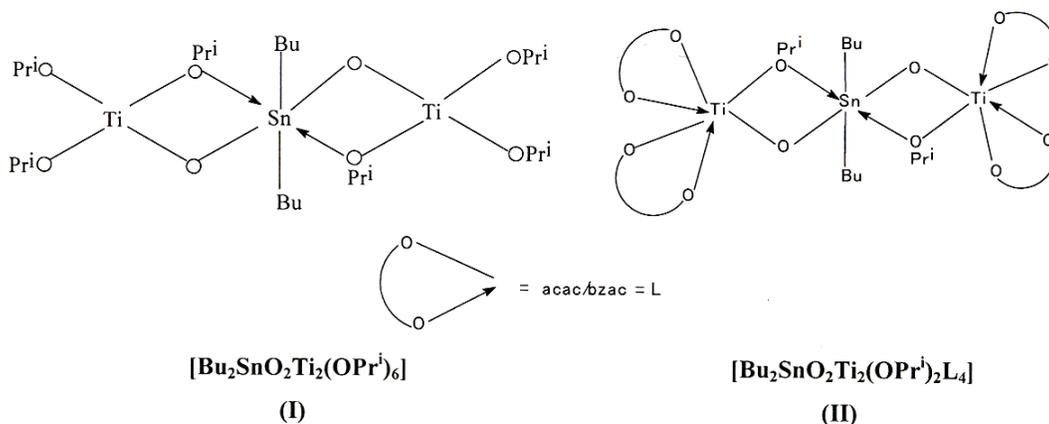
[Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_6$]

(I)

[Bu$_2$SnO$_2$Ti$_2$(OPr^i)$_2$L$_4$]

(II)

Acknowledgement

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