

Synthesis and characterization of new heterobimetallic $[\text{Sn}^{\text{II}}\text{-Ti}^{\text{IV}}]\text{-}\mu\text{-oxoisopropoxide}$ and its $\beta\text{-diketonates}$

H. K. Sharma^{a*}, Jashmer Singh^a, Rajesh Kumar^b and Amardeep^a

^aDepartment of Chemistry, Kurukshetra University, Kurukshetra-136 119, Haryana, India

E-mail : hks1chem@yahoo.co.in, jasmerdav70@gmail.com

^bHaryana Institute of Engineering and Technology, Kaithal-136 027, Haryana, India

Manuscript received 17 October 2011, revised 17 May 2012, accepted 11 July 2012

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

Keywords : Metal alkoxide, tin, titanium, acetylacetonate, benzoylacetonate.

Introduction

The chemistry of metal alkoxide and oxoalkoxide has been ever gaining much attention due to amazing properties possessed^{1,2} by these alkoxides. A large number of synthetic routes have been developed for the synthesis of these alkoxides^{1,3,4}. Much of this work has coincided with an interest in designing better precursors for the deposition of metal oxide by methods such as the sol-gel route^{5,6}, MOCVD^{7,8} and co-precipitation⁹.

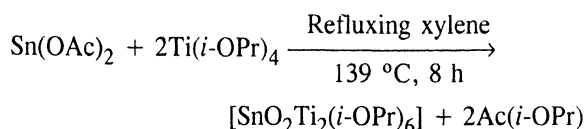
A large number of bimetallic- $\mu\text{-oxoalkoxide}$ of general formula $(\text{OR})_2\text{-Al-O-M-O-Al}(\text{OR})_2$ where M is a bivalent transition metal (Cr^{II} , Mn^{II} , Fe^{II} , Co^{II} , Ni^{II} , Zn^{II} or Mo^{II}) or main group metals^{10,4} (Mg, Ca, Sn and Pb) and R = an alkyl group usually propyl or butyl, have been synthesized¹¹. It has been reported that these bimetallic- $\mu\text{-oxoalkoxide}$ are among the best catalyst for polymerization of heterocyclic monomers such as lactones, oxiranes, thiiranes and epoxides^{12,13}. The $\mu\text{-oxoalkoxide}$ with central atoms (Cr, Mo and Fe) have been found to bind molecular oxygen rapidly at room temperature^{14,15}. The bimetallic- $\mu\text{-oxoalkoxide}$ have amazingly high solubility in common organic solvents which makes them excellent precursors for the synthesis of mixed metal oxides by sol-gel processes⁵. Due to high solubility of metal

and bimetallic alkoxide in organic solvents they could also used as model for exploring the frontiers between heterogeneous and homogeneous catalysts¹³.

It was considered worthwhile to synthesize a new heterobimetallic $\text{Sn}^{\text{II}}\text{-Ti}^{\text{IV}}\text{-}\mu\text{-oxoisopropoxide}$ and in order to get an insight into its structure its $\beta\text{-diketonates}$ have also been synthesized and characterized.

Results and discussion

The preparation of the heterobimetallic- $\mu\text{-oxoisopropoxide}$ $[\text{SnO}_2\text{Ti}_2(i\text{-OPr})_6]$ follows the following reaction scheme :



The $\mu\text{-oxoisopropoxide}$ compound obtained is a deep yellow highly viscous transparent liquid, susceptible to hydrolysis, decomposes on heating above 170 °C and soluble in common organic solvents such as benzene, chloroform, carbon tetrachloride etc.

A sharp band observed at $\sim 1630\text{ cm}^{-1}$ due to $\text{C}=\text{O}$ in IR spectrum of tin diacetate is absent in that of $[\text{SnO}_2\text{Ti}_2(i\text{-OPr})_6]$ indicating the complete removal of

acetate groups in μ -oxo compound¹⁶. Instead, a band exhibited in the region ~ 1370 – 1340 cm^{-1} is assigned to *gem*-dimethyls¹⁷ of isopropoxy group. Similarly the bands observed in the region 1180 – 1160 and 1130 – 1110 cm^{-1} have been assigned to the combination bands $\nu(\text{C-O} + i\text{-OPr})$ of bridging isopropoxy group respectively. A band appearing at approximately 950 cm^{-1} is assigned to $\nu(\text{C-O})$ stretching of the bridging isopropoxy group^{17,18}. A number of bands observed in the region 700 – 400 cm^{-1} due to M–O stretching vibrations¹⁹ in μ -oxo compound.

In the ^1H NMR spectrum of tin diacetate a sharp singlet observed at $\delta 2.1$ is found to be absent in the spectrum of $[\text{SnO}_2\text{Ti}_2(i\text{-OPr})_6]$ their by confirming the complete removal of acetate groups. ^1H NMR spectrum (Fig. 1) of $\text{Sn}^{\text{II}}\text{-Ti}^{\text{IV}}\text{-}\mu\text{-oxoisopropoxide}$ exhibits overlapping doublets between $\delta 1.0$ – 1.1 due to methyl protons of terminal and bridging isopropoxy groups^{20,21}. A multiplet centered at $\delta 4.4$ is observed due to the methine proton of isopropoxy groups in the μ -oxo compound²¹.

The ^{13}C NMR spectrum (Fig. 2) of $\text{Sn}^{\text{II}}\text{-Ti}^{\text{IV}}\text{-}\mu\text{-oxoisopropoxide}$ shows prominent peaks at $\delta 25.6$ and 28.4 assignable to the methyl carbon of terminal and bridging isopropoxy groups respectively. The peaks at $\delta 62.6$ and 64.7 in the ^{13}C NMR spectrum are due to terminal and bridging methine carbon of the isopropoxy groups²² respectively.

The ^{119}Sn NMR spectrum (Fig. 3) of $\text{Sn}^{\text{II}}\text{-Ti}^{\text{IV}}\text{-}\mu\text{-oxoisopropoxide}$ exhibits a sharp signal at $\delta 75.11$ assignable to the tetracoordination about Sn^{II} ²³.

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

The positive ion mass spectrum (Fig. 4) of $[\text{SnO}_2\text{Ti}_2(i\text{-OPr})_6]$ was carried in dry toluene containing 17% isopropanol by volume. The significant mass peaks observed at (m/z) 602.2 , 544.4 , 369.3 , 331.2 , 274.3 and 246.2 in the spectrum can be assigned to the fragments $\text{SnO}_2\text{Ti}_2(i\text{-OPr})_6^+$, $\text{SnO}_2\text{Ti}_2(i\text{-OPr})_5^+$, $\text{SnO}_2\text{Ti}_2(i\text{-OPr})_4^+$, $\text{Ti}_2(i\text{-OPr})_4^+$, $\text{SnO}_2(i\text{-OPr})_2^+$ and $\text{Ti}_2\text{O}_2(i\text{-OPr})_2^+$ respectively²⁴. The mass spectrum analysis further confirms the monomeric nature of the compound.

In order to get an insight into the structure of $[\text{SnO}_2\text{Ti}_2(i\text{-OPr})_6]$ its reactions with β -diketones (HL) in various molar ratios have been performed in refluxing benzene yielded the compounds of the types $[\text{SnO}_2\text{Ti}_2(i\text{-OPr})_5\text{L}]$, $[\text{SnO}_2\text{Ti}_2(i\text{-OPr})_4\text{L}_2]$, $[\text{SnO}_2\text{Ti}_2(i\text{-OPr})_3\text{L}_3]$ and $[\text{SnO}_2\text{Ti}_2(i\text{-OPr})_2\text{L}_4]$ according to the following reaction scheme :

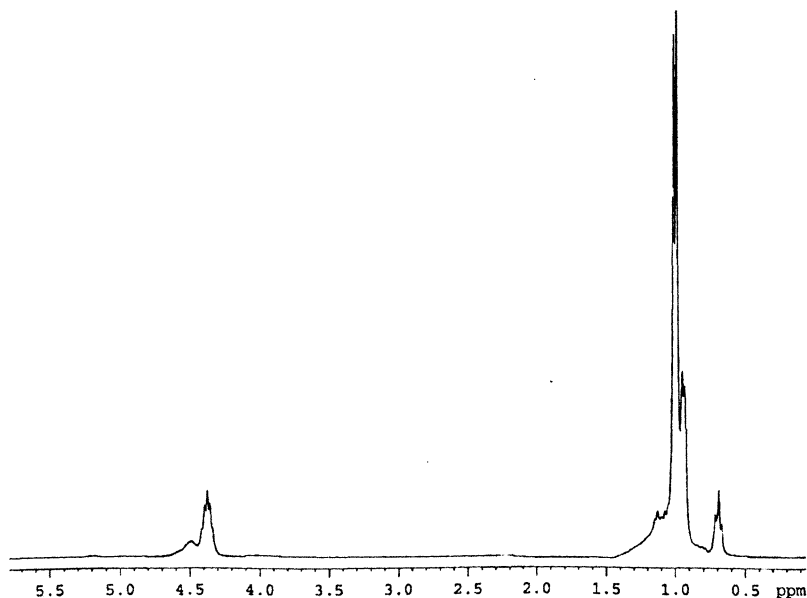
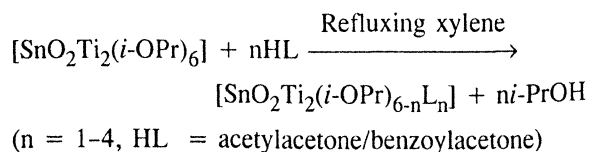


Fig. 1

Note

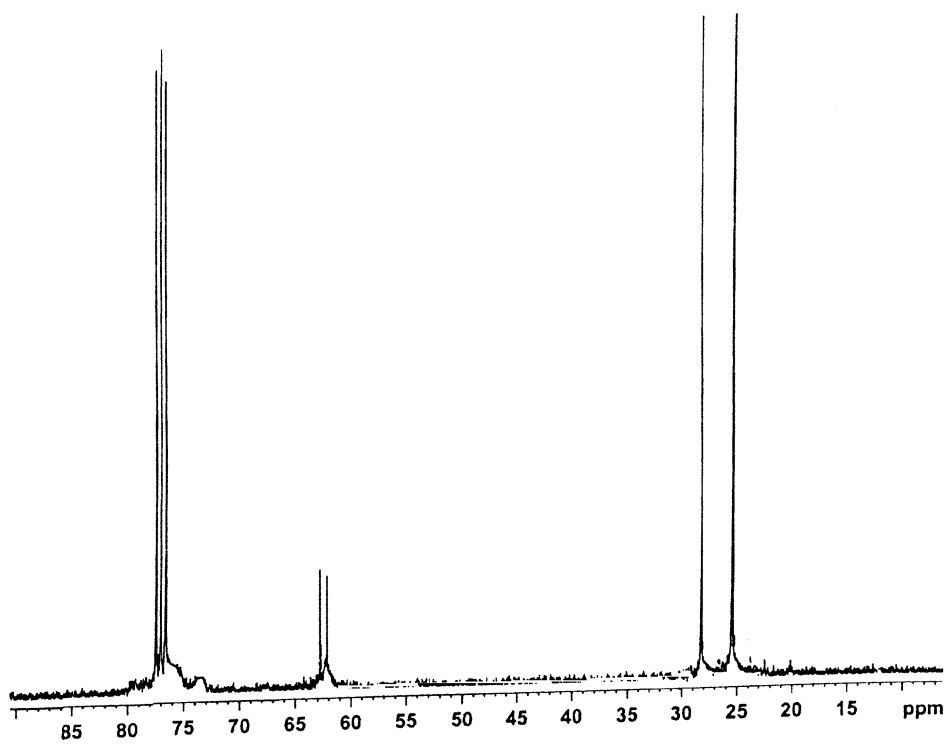


Fig. 2

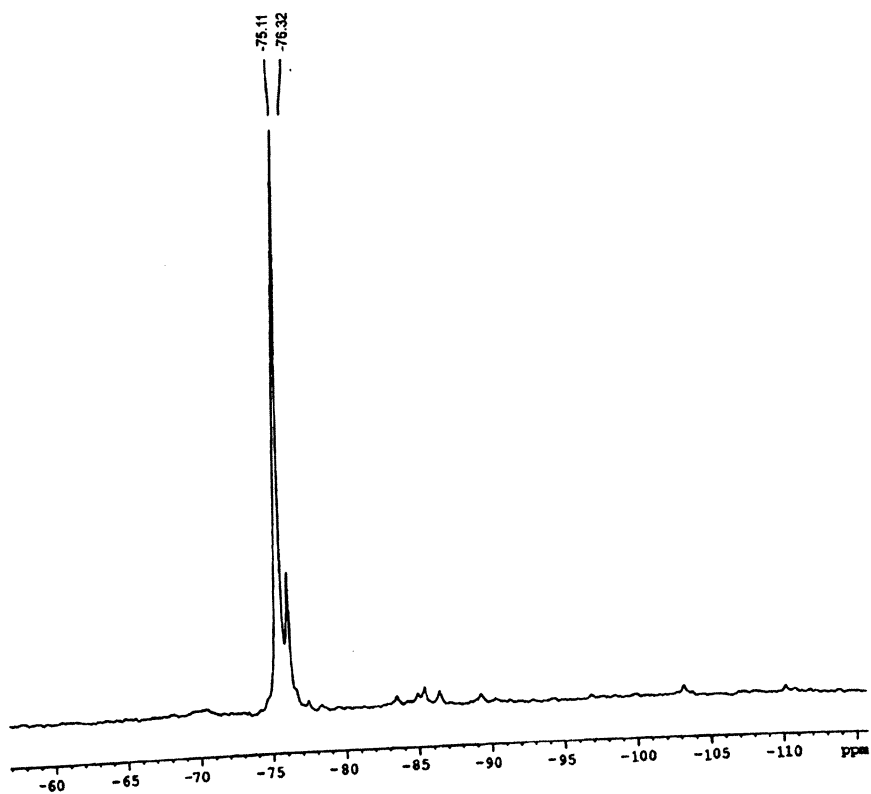


Fig. 3

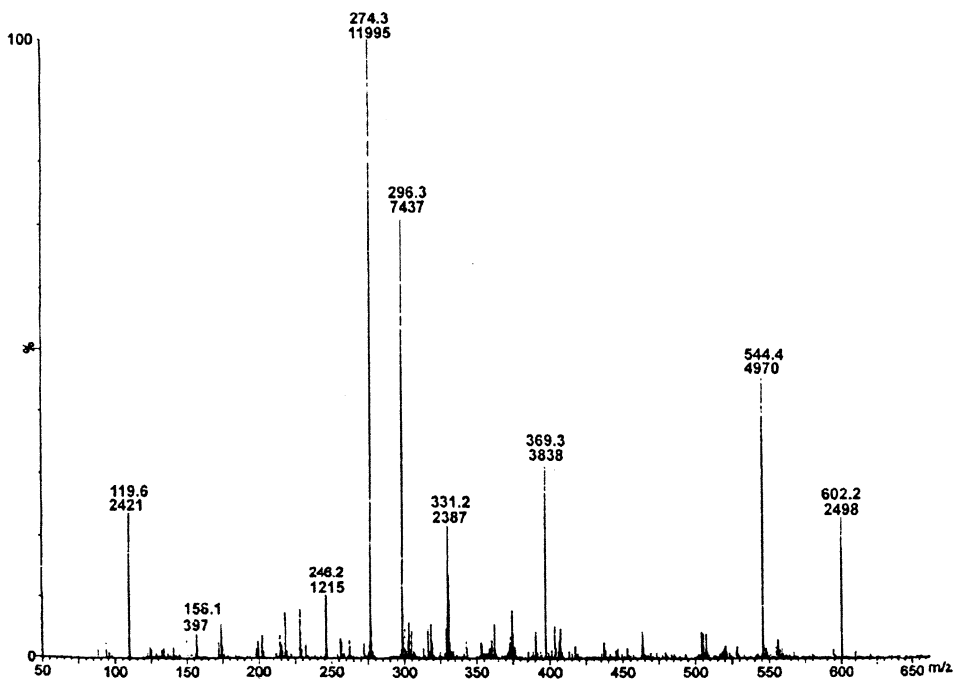


Fig. 4

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 four out of the six of isopropoxy groups of $\text{Sn}^{\text{II}}\text{-Ti}^{\text{IV}}\text{-}\mu\text{-oxoisopropoxide}$ could be replaced by β -diketones. Further 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 suggests that probably bridging isopropoxy groups could not be replaced.

The β -diketone derivatives of $\text{Sn}^{\text{II}}\text{-Ti}^{\text{IV}}\text{-}\mu\text{-oxoisopropoxide}$ are found to be yellow to brownish-yellow colored viscous liquid/semi-solids. All β -diketonates show appreciable solubility in common organic solvents (benzene, chloroform, hexane), susceptible to hydrolysis and decompose on heating strongly above $\sim 180^\circ\text{C}$.

The absorption bands in the region $1360\text{--}1340$, $1165\text{--}1150$ and $1010\text{--}900\text{ cm}^{-1}$ in the IR spectra of 1 : 1 to 1 : 3 β -diketone derivatives of $[\text{SnO}_2\text{Ti}_2(i\text{-OPr})_6]$ are assigned to the *gem*-dimethyl¹⁷ portion and combination band $\nu(\text{CO} + i\text{-OPr})$ of the terminal and bridging isopropoxy groups respectively. The absence of band at $\sim 1165\text{--}1150\text{ cm}^{-1}$ in the 1 : 4 β -diketonates spectra indicates the complete substitution of terminal isopropoxy groups by chelating

ligands. A band appearing at $\sim 950\text{ cm}^{-1}$ is due to $\nu(\text{C}\text{--}\text{O})$ stretching of bridging isopropoxy group^{17,18}. The IR spectrum of β -diketonates²⁵ display strong bands at $\sim 1600\text{--}1580\text{ cm}^{-1}$ and $\sim 1520\text{--}1500\text{ cm}^{-1}$ due to $\nu_{\text{sym}}(\text{C}=\text{O})$ and $\nu_{\text{asym}}(\text{C}=\text{C})$ respectively along with a broad band at $\sim 3100\text{--}2700\text{ cm}^{-1}$ due to enolic $\nu(\text{O}\text{--}\text{H})$. The non shifting of $\nu(\text{C}=\text{O})$ frequency and the disappearance of broad band in the region $3100\text{--}2700\text{ cm}^{-1}$ in β -diketonates suggest the metal-ligand bonding takes place through the oxygens of both CO groups in the derivatives. A number of vibrations assigned in the region $700\text{--}400\text{ cm}^{-1}$ due to M-O stretching vibrations¹⁸ in β -diketonates of $\mu\text{-oxoisopropoxide}$ compound.

^1H NMR spectra of 1 : 1 to 1 : 3 β -diketonates display overlapping doublets between $\delta \sim 1.1$ and ~ 1.3 are due to methyl protons and a broad multiplet centered at $\delta \sim 4.1$ due to the methine proton of terminal and bridging isopropoxy groups respectively. A fairly sharp doublet at $\delta \sim 1 : 2$ and a multiplet centered at $\delta \sim 4.2$ in the 1 : 4 β -diketonates spectra are assigned to methyl and methine protons of bridging isopropoxy groups. This indicates complete substitution of terminal isopropoxy group by chelating ligands. Moreover, all the derivatives exhibit singlet at $\delta 2.1$ and ~ 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 $[\text{SnO}_2\text{Ti}_2(i\text{-OPr})_6]$ are found between δ 7.0–7.6 .

The ^{13}C NMR spectra of 1 : 1 to 1 : 3 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 63.1–64.8²¹ assigning methine carbons of terminal and bridging isopropoxy groups respectively in the derivatives. Two peaks observed at δ ~28.0 and ~64.0 in the 1 : 4 β -diketonates spectra further confirm the complete substitution of terminal isopropoxy group by chelating ligands²². Moreover, 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 derivatives²².

Thermal analysis :

The thermogravimetric analysis (Fig. 5) of hydrolyzed product of $[\text{SnO}_2\text{Ti}_2(i\text{-OPr})_6]$ 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 15.189% observed from 220 °C to

340 °C²⁶ is due to the elimination of hydroxy groups present in the hydrolysed product $[\text{SnO}_2\text{Ti}_2(\text{OH})_6]$ resulting from the hydrolysis of $[\text{SnO}_2\text{Ti}_2(i\text{-OPr})_6]$. The final product remaining is probably the SnTi_2O_5 mixed metal oxide. The TG analysis is consistent with the formulation of the compound as $[\text{SnO}_2\text{Ti}_2(i\text{-OPr})_6]$.

The DTA plot (Fig. 6) of the hydrolysed product of $[\text{SnO}_2\text{Ti}_2(i\text{-OPr})_6]$ shows an endothermic peak at temperature below ~200 °C indicating loss of water present in the hydrolysed product. Above 200 °C there is an exothermic loss of water from the hydroxy group to yield oxide as the final product.

On the basis of below analytical studies (Table 1) the following tentative structures have been assigned to the $[\text{SnO}_2\text{Ti}_2(i\text{-OPr})_6]$ and β -diketone derivatives of μ -oxo compound (1 : 4) (Figs. 7 and 8).

Experimental

All manipulations have been carried out under anhydrous conditions and the solvents and reagents used were purified and dried by standard methods²⁷. The general technique and physical measurement were carried out as described elsewhere^{28–30}. Tin diacetate $\text{Sn}(\text{OAc})_2$ and titanium isopropoxide $\text{Ti}(i\text{-OPr})_4$ (Aldrich) were used as

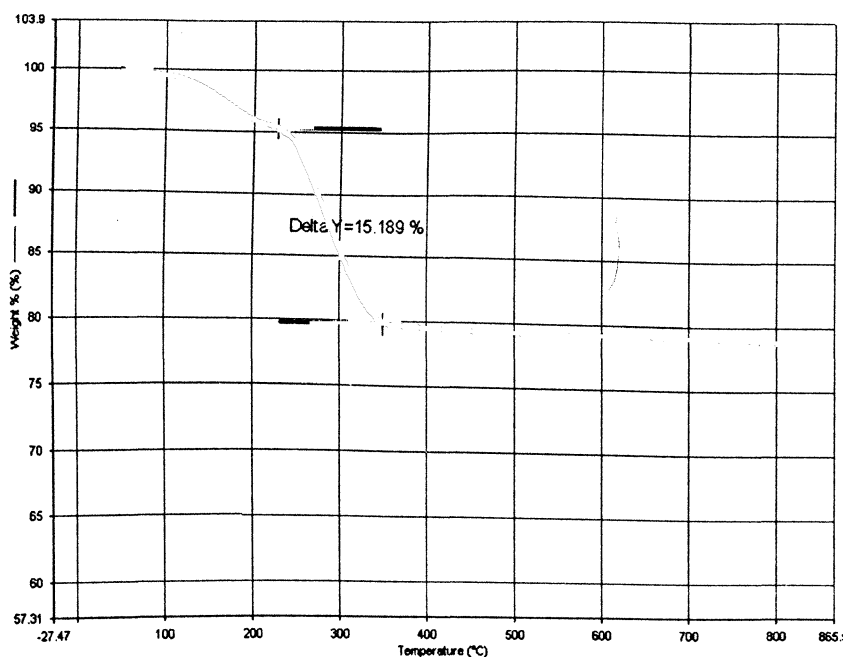


Fig. 5

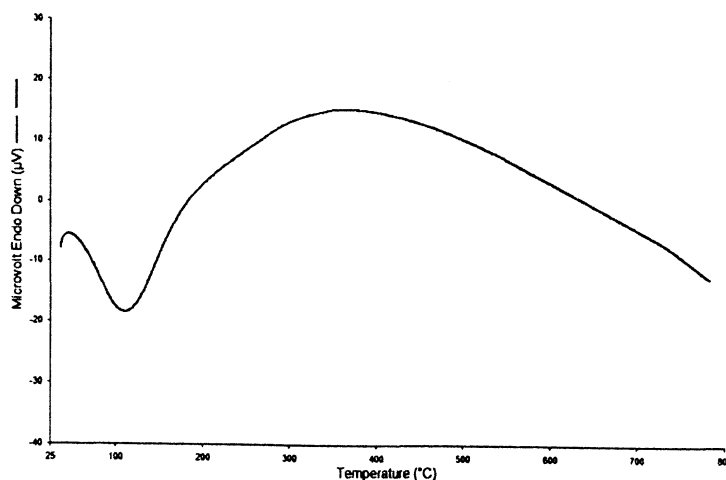


Fig. 6

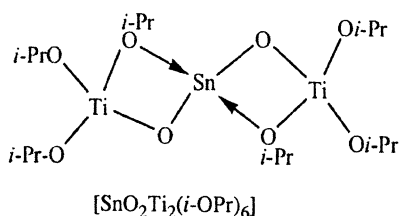


Fig. 7

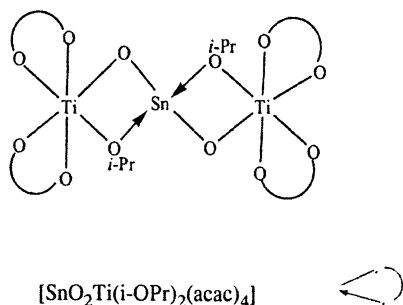


Fig. 8

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 oxidimetrically³¹. Tin and titanium in the complex and its derivatives with β -diketonates were analysed colorimetrically^{32,33} using 4-chloro-1,2-dimercaptobenzene and *N*-acetylsalicyloyl-*N*-phenylhydroxylamine as a colour developing reagent respectively.

The infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer over the range of 4000–400 cm^{-1} . The ^1H , ^{13}C and ^{119}Sn NMR spectra were recorded in

CDCl_3 on Bruker Avance II 400 NMR spectrometer. The mass spectrum was performed on a Waters QTOF2 mass spectrometer equipped with Quadrupole and time of flight (TOF) analyzers. Elemental analysis was carried on Perkin-Elmer 2400 CHN Elemental Analyser.

Synthesis of $[\text{SnO}_2\text{Ti}_2(\text{i-OPr})_6]$:

The μ -oxoisopropoxide compound was synthesized by thermal condensation between $\text{Sn}(\text{OAc})_2$ (1.223 g, 5.168 mmol) and $\text{Ti}(\text{i-OPr})_4$ (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 boiling point of xylene^{28,4} (139 °C). The solvent xylene was completely removed under reduced pressure (~ 70 °C/1 mm) yielding a deep yellow highly viscous transparent liquid. yield : 95% (Found : *i*-OPr, 58.69; Sn, 19.71; Ti, 15.81; C, 35.40; H, 6.35. $[\text{SnO}_2\text{Ti}_2(\text{i-OPr})_6]$ calcd. for : *i*-OPr, 58.95; Sn, 19.77; Ti, 15.94; C, 35.97; H, 6.99%).

Reaction of $[\text{SnO}_2\text{Ti}_2(\text{i-OPr})_6]$ with acetylacetone (*Hacac*) in 1 : 1 molar ratio :

The compound $[\text{SnO}_2\text{Ti}_2(\text{i-OPr})_6]$ (0.320 g, 0.532 mmol) and acetylacetone (0.053 g, 0.53 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-benzene⁴ 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 viscous liquid

Table 1. Analytical data

Sl. no.	Compound (g, mmol)	Ligand (g mmol)	Reflux time (h)	Product g (%)	Analysis : Found (Calcd.)				
					<i>i</i> -Opr (g)	Sn (%)	Ti (%)	C (%)	H (%)
1.	[SnO ₂ Ti ₂ (<i>i</i> -OPr) ₆] 0.320 (0.532)	Hacac 0.053 (0.53)	4	[SnO ₂ Ti ₂ (<i>i</i> -OPr) ₅ (acac)] 0.320 (94.9)	0.03 (0.03)	18.45 (18.53)	14.82 (14.95)	37.26 (37.47)	6.05 (6.55)
2.	[SnO ₂ Ti ₂ (<i>i</i> -OPr) ₆] 0.315 (0.524)	Hacac 0.105 (1.05)	6	[SnO ₂ Ti ₂ (<i>i</i> -OPr) ₄ (acac) ₂] 0.337 (94.4)	0.05 (0.06)	17.35 (17.44)	13.95 (14.07)	38.52 (38.79)	5.75 (6.17)
3.	[SnO ₂ Ti ₂ (<i>i</i> -OPr) ₆] 0.298 (0.496)	Hacac 0.148 (1.48)	8	[SnO ₂ Ti ₂ (<i>i</i> -OPr) ₃ (acac) ₃] 0.339 (95.0)	0.08 (0.09)	16.38 (16.44)	13.21 (13.30)	39.75 (39.97)	5.35 (5.82)
4.	[SnO ₂ Ti ₂ (<i>i</i> -OPr) ₆] 0.298 (0.496)	Hacac 0.197 (1.97)	10	[SnO ₂ Ti ₂ (<i>i</i> -OPr) ₂ (acac) ₄] 0.356 (94.5)	0.11 (0.12)	15.51 (15.60)	12.60 (12.60)	41.01 (41.02)	5.17 (5.52)
5.	[SnO ₂ Ti ₂ (<i>i</i> -OPr) ₆] 0.160 (0.267)	Hbzac 0.0433 (0.267)	5	[SnO ₂ Ti ₂ (<i>i</i> -OPr) ₅ (bzac)] 0.178 (95.0)	0.02 (0.02)	16.85 (16.90)	13.58 (13.63)	42.65 (42.70)	5.98 (6.26)
6.	[SnO ₂ Ti ₂ (<i>i</i> -OPr) ₆] 0.130 (0.217)	Hbzac 0.0703 (0.434)	7	[SnO ₂ Ti ₂ (<i>i</i> -OPr) ₄ (bzac) ₂] 0.163 (93.6)	0.03 (0.03)	14.64 (14.75)	11.79 (11.90)	47.57 (47.73)	5.20 (5.71)
7.	[SnO ₂ Ti ₂ (<i>i</i> -OPr) ₆] 0.140 (0.233)	Hbzac 0.151 (0.935)	10	[SnO ₂ Ti ₂ (<i>i</i> -OPr) ₃ (bzac) ₃] 0.200 (94.7)	0.04 (0.04)	13.04 (13.10)	10.42 (10.56)	51.42 (51.63)	4.95 (5.29)
8.	[SnO ₂ Ti ₂ (<i>i</i> -OPr) ₆] 0.150 (0.250)	Hbzac 0.162 (1.001)	12	[SnO ₂ Ti ₂ (<i>i</i> -OPr) ₂ (bzac) ₄] 0.239 (95.1)	0.05 (0.06)	11.64 (11.76)	9.42 (9.50)	54.45 (54.73)	4.65 (4.95)

product. The other β -diketonates were prepared by similar procedure and the analytical results have been summarized in Table 1.

Acknowledgement

Our sincere thanks are due to Kurukshetra University, Kurukshetra for providing the necessary facilities, SAIF, Punjab University, for spectral and elemental analysis and CSIR, New Delhi for providing JRF to Jashmer Singh.

References

1. D. C. Bradley, R. C. Mehrotra, I. P. Rothwell and A. Singh, "Alkoxo and Aryloxo Derivatives of Metals", Academic Press, London, New York, 2001.
2. M. H. Chisholm, *J. Organomet. Chem.*, 1987, **334**, 77.
3. H. K. Sharma, Rajesh Kumar and R. K. Baweja, *J. Indian Chem. Soc.*, 2006, **83**, 1.
4. M. Sharma, A. K. Bhagi, Priti, R. Kansal, R. Kumar and P. N. Kapoor, *Indian J. Chem., Sect. A*, 2005, **44**, 1.
5. P. N. Kapoor, H. K. Sharma, Ajay K. Bhagi and M. Sharma, *J. Indian Chem. Soc.*, 2004, **81**, 273.
6. W. G. Menezes, P. H. C. Camargo, M. M. Oliveira, D. J. Evans, J. F. Soares and A. J. G. Zarbin, *J. Colloid Interface Sci.*, 2006, **299**, 291.
7. J. M. Gaskell, A. C. Jones, H. C. Aspinall, S. Przybylak, P. R. Chalker, K. Black, H. O. Davies, P. Taechakumput, S. Taylor and G. W. Critchlow, *J. Mater. Chem.*, 2006, **16**, 3854.
8. Y. Cao, W. Yang, W. Zhang, G. Liu and P. Yue, *New. J. Chem.*, 2004, **28**, 218.
9. Moises A. Carreon, Vadim V. Gulians, Li Yuan, Andrew R. Hughett, Alan Dozier, Gulaim A. Seisenbaeva and Vadim G. Kessler, *Eur. J. Chem.*, 2006, **2006**, 4983.
10. H. K. Sharma and P. N. Kapoor, *Indian J. Chem., Sect. A*, 2004, **43**, 556.
11. M. Osgan and Ph. Teyssie, *J. Polym. Sci. Polym. Lett.*, 1967, **5**, 789.
12. K. J. Kalabunde, J. V. Stark, O. Koper, C. Mohs, D. G. Park, S. Decker, Y. Jiang, I. Lagadic and D. Zhang, *J. Phys. Chem.*, 1996, **100**, 12142.
13. O. Koper, I. Lagadic and K. J. Kalabunde, *Chem. Mater.*, 1997, **9**, 838.
14. Ph. Teyssie, J. P. Bioul, L. Hocks and T. Ouhadi, *CHEMTECH*, 1977, 192.
15. L. Hocks, J. P. Bioul, A. Hamitou, J. L. Merbeht, T. Ouhadi, Ch. Stevens and Ph. Teyssie, *J. Mol. Catal.*, 1977, **3**, 135.
16. A. K. Sawyer, "Organotin Compounds", Vol. I, Marcel Dekker, Inc, New York, 1971.
17. C. T. Lynch, K. S. Masdiyanni, J. S. Smith and W. J. Grawford, *Anal. Chem.*, 1964, **36**, 2332.
18. V. A. Koznov, N. I. Kuzlova, N. Ya. Turova and Yu. S. Nekrasov, *Zh. Neorg. Khim.*, 1979, **24**, 1526.
19. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", John Wiley and Sons, New York, 1986.
20. Sonika, A. K. Narula, O. P. Vermani and H. K. Sharma, *J. Organomet. Chem.*, 1994, **470**, 67.

21. T. Ouhadi, A. Hamitou, R. Jerome and Ph. Teyssie, *Macromolecules*, 1976, **2**(6), 927.
22. E. Breitmaier and W. Voelter, "¹³C NMR spectroscopy (High Resolution Methods and Application in Organic Chemistry and Biochemistry)", VCH, New York, 1990.
23. J. Holecek, M. Nadvornik, K. Handir and A. Lycka, *J. Organomet. Chem.*, 1986, **315**, 25.
24. L. Thomas, W. Henderson, G. A. Bowmaker, J. M. Seakins and R. P. Cooney, *J. Mater. Chem.*, 1997, **7**(8), 1553.
25. R. Kansal, PhD Thesis, Department of Chemistry, Delhi University, Delhi, 1991.
26. L. G. Hubert-Pfalzgraf, D. Stephane, Repipernik, M. Marie-Cecile, S. Bernard, V. Jacqueline and D. Jean-Claude, *J. Mater. Chem.*, 1997, **7**, 53.
27. D. D. Perrin, W. L. F. Armarego and D. R. Perrin. "Purification of Laboratory Chemicals", 2nd ed., Pergamon Press, New York, 1980.
28. H. K. Sharma and Rajesh Kumar, *Indian J. Chem., Sect. A*, 2008, **47**, 854.
29. R. Ramchandran, B. Singh, A. K. Narula, P. K. Gupta and R. N. Kapoor, *Polyhedron*, 1985, **4**, 1007.
30. A. I. Vogel, "A Text Book of Quantitative Analysis", Longman, London, 1989.
31. D. C. Bradley, F. M. A. Halim and W. Wardlaw, *J. Chem. Soc.*, 1950, 3450.
32. H. K. Sharma, Ramesh Kataria and J. R. Mehta, *J. Indian Chem. Soc.*, 2007, **84**, 693.
33. R. L. Nunez, M. C. Mochon and A. G. Perez, *Talanta*, 1986, **33**(7), 587.