

# A novel route to synthesis the excellent precursors for nanocrystalline mixed oxide particles of Aluminium and Titanium

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## Abstract

A new heterobimetallic [Al(III)-Ti(IV)]- $\mu$ -oxoisopropoxy acetate [(OAc)<sub>2</sub>TiO<sub>2</sub>Al<sub>2</sub>(OPr<sup>i</sup>)<sub>4</sub>] has been synthesized by the thermal condensation of aluminium isopropoxide and titanium(IV) acetate and characterized by liberated isopropanol, elemental, spectral (IR, <sup>1</sup>H, <sup>13</sup>C, NMR and mass), thermal analysis, molecular weight data. Many isopropoxy substitution reactions of [Al(III)-Ti(IV)]- $\mu$ -oxoisopropoxy acetate compound with  $\beta$ -diketones in different molar ratios (1:1-1:2) yielded the mono to bi derivatives [(OAc)<sub>2</sub>TiO<sub>2</sub>Al<sub>2</sub>(OPr<sup>i</sup>)<sub>4-n</sub>L<sub>n</sub>] (where n is 1-2 and L = acetylacetonate/benzoylacetonate anion) respectively of the parent compound and have been characterized by elemental, liberated isopropanol and spectral analysis (IR, <sup>1</sup>H, <sup>13</sup>C and <sup>27</sup>Al NMR). The above studies revealed interesting facets in support of plausible structures of parent compound and its  $\beta$ -diketonates.

**Keywords:** heterometallic- $\mu$ -oxoisopropoxy acetate, Aluminium, Titanium,  $\beta$ -diketones, thermoanalysis

## 1. Introduction

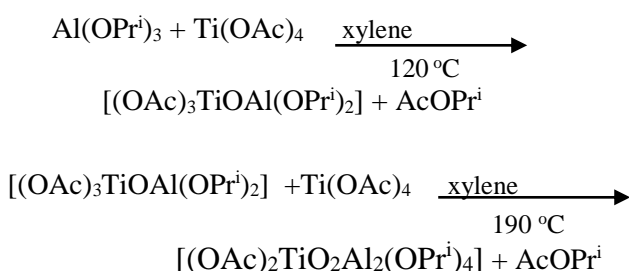
The uses of heterometallic alkoxides as single-source molecule precursors for the preparation of oxides have seen a rapid growth during the last one and half decades. The control of particle size and the morphology of the oxide are of crucial importance nowadays both from the fundamental and industrial point of view.<sup>1</sup> These true precursors play a significant role in the phase formation of complex oxides. The M-O-M bridges in bimetallic oxo complexes provide homogeneity of the newly formed oxide phases at the molecular level. The

above-considered peculiarity in the composition, stoichiometry, solubility and reactivity of ortho- and oxoalkoxides are widely used in the sol-gel synthesis of a series of very important composites.<sup>2</sup> The mixed metal oxides prepared from heterometallic- $\mu$ -oxoalkoxides<sup>3-6</sup> have been used for absorbing harmful chemicals<sup>7</sup> and gases such as SO<sub>2</sub>, CCl<sub>4</sub>, and decontaminating chemical warfare agents.<sup>8</sup> The MgAl<sub>2</sub>O<sub>4</sub> prepared from [MgO<sub>2</sub>Al<sub>2</sub>(OPr<sup>i</sup>)<sub>4</sub>]<sub>2</sub> has been used to destructively adsorb paraxon [diethyl-4-nitrophenol phosphate (DNPP)].<sup>9</sup> Magnesium titanate (MgTiO<sub>3</sub>) ceramic has been proved to be an excellent dielectric material since it has low dielectric loss (high quality factor  $Q \sim 21800$  at 8 GHz) and proper dielectric constant ( $\epsilon_r \sim 17.0-17.5$ ).<sup>10</sup> Recently, MgTiO<sub>3</sub> ceramic is widely applied in capacitors, resonators, filters, antennas, radar, direct broadcasting satellite and global positioning system operating at microwave frequencies.<sup>11,12</sup> Magnesium titanates (MgTiO<sub>3</sub>, Mg<sub>2</sub>TiO<sub>4</sub>, MgTi<sub>2</sub>O<sub>5</sub>), silicates<sup>13</sup> (MgSiO<sub>3</sub>, MgSiO<sub>4</sub>) and aluminate<sup>14</sup> (MgAl<sub>2</sub>O<sub>4</sub>) are commercially produced as low dielectric components. Furthermore, aluminum titanate (Al<sub>2</sub>TiO<sub>5</sub>, AT) is a promised high-temperature ceramic material characterized by outstanding thermal shock resistance, high corrosion resistance, and low coefficient of thermal expansion. Hence, it has been considered as a successful candidate in various severe thermal environments, such as thermal processing technology, thermal insulation, refractory, metallurgy, glass and automotive industry, and engine components.<sup>15,16</sup> Apart from their role as precursors for mixed metal oxides, the bimetallic- $\mu$ -oxoalkoxides of transition metals have been found to rank among the excellent catalysts for the polymerization of heterocyclic monomers like lactones, oxiranes, thiiranes and epoxides.<sup>17,18</sup> Recently,  $\beta$ -diketiminato derivative of zinc alkoxide exhibits the highest rate of polymerization with better stereoselectivity in the formation of polylactic from the rac-lactide with aggregation and narrow polydisperties.<sup>19</sup> Volatile organometallic alkoxides, the preminent precursors for the synthesis of mixed metal oxides because of their use in metal-organic-chemical-vapor-deposition (MOCVD), in sol-gel synthesis or in solid synthesis.<sup>20,21</sup>

In the present investigation, heterobimetallic [Al(III)-Ti(IV)]- $\mu$ -oxoisopropoxy acetate is prepared from the condensation of two moles of aluminium isopropoxide and one moles of titanium(IV) acetate, and the reaction proceeds with stepwise formation of pure bimetallic [Al(III)-Ti(IV)]- $\mu$ -oxoisopropoxy acetate, which is a molecular species that can be purified by distillation, allowing the isolation of pure molecular precursors and to gain an insight in to its structure and prevent the phase secretion problem due to its strong tendency to hydrolysis, its  $\beta$ -diketonates are synthesized.

## 2. Results and Discussion

The preparation of the heterometallic- $\mu$ -oxoisopropoxy acetate [(OAc)<sub>2</sub>TiO<sub>2</sub>Al<sub>2</sub>(OPr<sup>i</sup>)<sub>4</sub>] follows the following reaction *scheme 1*:



### *Scheme 1.*

The [(OAc)<sub>2</sub>TiO<sub>2</sub>Al<sub>2</sub>(OPr<sup>i</sup>)<sub>4</sub>] obtained is a pale yellow semi-solid, susceptible to hydrolysis and soluble in common organic solvents such as benzene, chloroform and carbon tetrachloride etc.

## 2.1. Spectral Analysis of [(OAc)<sub>2</sub>TiO<sub>2</sub>Al<sub>2</sub>(OPr<sup>i</sup>)<sub>4</sub>]

### 2.1.1. IR spectra

The strong bands observed at 1610 cm<sup>-1</sup> and 1435 cm<sup>-1</sup> due to asym C=O and sym C=O stretch respectively in the IR spectrum spectrum of [Al(III)-Ti(IV)]- $\mu$ -oxoisopropoxy acetate indicating the presence of acetate groups. The spectrum of the  $\mu$ -oxoisopropoxy acetate shows absorption bands at ~1360 cm<sup>-1</sup> and ~1165 cm<sup>-1</sup> are the characteristics of *gem*-dimethyl portion and combination band  $\nu(\text{C-O+OPr}^i)$  of the terminal and bridging isopropoxy group respectively. A band appearing at approximately 950 cm<sup>-1</sup> is assigned to  $\nu(\text{C-}$

O) stretching of bridging isopropoxy group.<sup>22</sup> A number of vibrations are observed in the region 700-400 cm<sup>-1</sup> due to M-O stretching vibrations in  $\mu$ -oxo compound.<sup>23</sup>

### 2.1.2. NMR spectra

A sharp singlet observed at  $\delta$  2.1 ppm in the <sup>1</sup>H NMR spectrum of [Al(III)-Ti(IV)]- $\mu$ -oxoisopropoxy acetate confirms the presence of acetate groups in  $\mu$ -oxo compound. <sup>1</sup>H NMR spectrum of [Al(III)-Ti(IV)]- $\mu$ -oxoisopropoxy acetate shows a number of peaks centered between  $\delta$  0.8 - 1.2 ppm due to the intermixing of methyl protons of terminal and bridging isopropoxy groups.<sup>24</sup> A multiplet centered at  $\delta$  4.2 ppm is observed due to the methine proton of isopropoxy group in the  $\mu$ -oxo compound. The <sup>13</sup>C NMR spectrum of [Al(III)-Ti(IV)]- $\mu$ -oxoisopropoxy acetate shows two prominent peaks at  $\sim \delta$  26.9 and  $\sim \delta$  27.2 ppm assignable to the methyl carbon of terminal and bridging isopropoxy groups and the other two peaks observed at  $\delta$  62.9 ppm and  $\delta$  64.1 ppm in the <sup>13</sup>C NMR spectrum are due to terminal and bridging methine carbon of the isopropoxy groups.<sup>25</sup>

### 2.1.3. Mass spectra

The positive ion mass spectrum of [(OAc)<sub>2</sub>TiO<sub>2</sub>Al<sub>2</sub>(OPr<sup>i</sup>)<sub>4</sub>] was carried in dry toluene containing 17% isopropanol by volume. The significant mass peaks observed at (m/z) 487.6, 426.8, 367.7, 254.3, 197.2, 164.6, 105.1, 88.7, 46.5 and 24.1 in the spectrum can be assigned to the fragments (OAc)<sub>2</sub>TiO<sub>2</sub>Al<sub>2</sub>(OPr<sup>i</sup>)<sub>4</sub><sup>+</sup>, (OAc)<sub>2</sub>TiO<sub>2</sub>Al<sub>2</sub>(OPr<sup>i</sup>)<sub>3</sub><sup>+</sup>, (OAc)<sub>2</sub>TiO<sub>2</sub>Al<sub>2</sub>(OPr<sup>i</sup>)<sub>2</sub><sup>+</sup>, TiO<sub>2</sub>Al<sub>2</sub>(OPr<sup>i</sup>)<sub>2</sub><sup>+</sup>, TiO<sub>2</sub>(OAc)<sub>2</sub><sup>+</sup>, Ti(OAc)<sub>2</sub><sup>+</sup>, TiOAl<sup>+</sup>, Ti<sup>+</sup> and Al<sup>+</sup> respectively.<sup>26</sup>

## 2.2. Thermal Analysis of (OAc)<sub>2</sub>TiO<sub>2</sub>Al<sub>2</sub>(OPr<sup>i</sup>)<sub>4</sub>

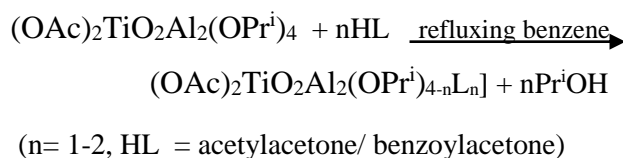
TGA of (OAc)<sub>2</sub>TiO<sub>2</sub>Al<sub>2</sub>(OPr<sup>i</sup>)<sub>4</sub> has been performed up to 800 °C at 10°C/min. The total weight loss of 82.24 % was observed from 68.5 to 560°C. A small weight loss between 68.5 to 185°C is probably due to the presence of moisture and traces of solvent in compound. A rapid weight loss was observed between  $\sim$  185 to

480°C indicates the volatile nature of  $\mu$ -oxo compound. Further, the remaining weight 10.260 % observed is due to the decomposition of partially hydrolysed  $\mu$ -oxo compound in to mixed metal oxide.

The TGA of hydrolyzed product of  $(\text{OAc})_2\text{TiO}_2\text{Al}_2(\text{OPr}^i)_4$  have been performed up to 800°C at 10°C/min. The weight loss of about 3-4 % in hydrolyzed product of parent compound is due to the traces of water present. The weight loss of 42.56 % observed from 220°C to 487°C is probably due to the elimination of hydroxy groups and organic moieties<sup>27</sup> present in the hydrolyzed product  $(\text{OAc})_2\text{TiO}_2\text{Al}_2(\text{OH})_4$  resulting from the hydrolysis of  $(\text{OAc})_2\text{TiO}_2\text{Al}_2(\text{OPr}^i)_4$ . The final product remaining is probably the mixed metal oxide  $\text{Al}_2\text{TiO}_5$ . The TG analysis is consistent with the formulation of the compound as  $(\text{OAc})_2\text{TiO}_2\text{Al}_2(\text{OPr}^i)_4$ .

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

To further gain an insight into the structure, effect on the solubility and stability, many reactions of  $(\text{OAc})_2\text{TiO}_2\text{Al}_2(\text{OPr}^i)_4$  with  $\beta$ -diketones ( HL) were carried out in different molar ratios in refluxing benzene. The reactions yielded compounds of the type  $(\text{OAc})_2\text{TiO}_2\text{Al}_2(\text{OPr}^i)_3\text{L}$  and  $(\text{OAc})_2\text{TiO}_2\text{Al}_2(\text{OPr}^i)_2\text{L}_2$ , according to the following reaction *scheme 2*:



### *Scheme 2*

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 two out of the four isopropoxy groups of [Al(III)-Ti(IV)]- $\mu$ -oxoisopropoxy acetate could be replaced by  $\beta$ -diketones. Further replacement of isopropoxy groups could not be achieved even with an excess of ligand ( $\beta$ -diketones) and prolonged refluxing time (18 h). This indicates the non-replacement of bridging isopropoxy groups and that only terminal isopropoxy groups are substituted by  $\beta$ -diketones.

The  $\beta$ -diketone derivatives of [Al(III)-Ti(IV)]- $\mu$ -oxoisopropoxy acetate are found to be yellow colored semi-solids to solids. All  $\beta$ -diketonates show appreciable solubility in common organic solvents (benzene, chloroform, hexane), susceptible to hydrolysis and decompose on heating strongly.

### 2.3. Spectral Analysis of $\beta$ -diketone derivatives of [(OAc)<sub>2</sub>TiO<sub>2</sub>Al<sub>2</sub>(OPr<sup>i</sup>)<sub>4</sub>]

#### 2.3.1. IR spectra

The IR spectrum of 1:1  $\beta$ -diketonates show absorption bands in the region 1365–1340 cm<sup>-1</sup> and 1165–1150 cm<sup>-1</sup> which are characteristics of *gem*-dimethyl group and combination band  $\nu(\text{C-O+OPr}^i)$  of the terminal and bridging isopropoxy groups respectively. Absence of band at 1360–1340 cm<sup>-1</sup> in the spectrum of 1:2  $\beta$ -diketonates indicates the absence of terminal isopropoxy group. A band is appearing at ~950 cm<sup>-1</sup> due to  $\nu(\text{C-O})$  stretching of bridging isopropoxy group. The IR spectrum of  $\beta$ -diketones display strong bands at ~1600–1580 cm<sup>-1</sup> and ~1520–1500 cm<sup>-1</sup> due to  $\nu_{\text{sym}}(\text{C=O})$  and  $\nu_{\text{asym}}(\text{C=C})$  respectively along with a broad band at ~3100–2700 cm<sup>-1</sup> due to enolic  $\nu(\text{O-H})$ . The non shifting of  $\nu(\text{C=O})$  frequency and the disappearance of broad band appearing in the region 3200–2700 cm<sup>-1</sup> in  $\beta$ -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<sup>-1</sup> due to M-O stretching vibrations in  $\beta$ -diketonates.

#### 2.3.2. NMR spectra

In the <sup>1</sup>H NMR spectra of the  $\beta$ -diketonates, the enolic peak at  $\delta$  13 ppm in  $\beta$ -diketones is found absent and a broad overlapping multiplet centered between  $\delta$  0.8–1.2 ppm in all derivatives at room temperature is due to intermixing of the methyl protons of the bridging and isobranched vibrations of isopropoxy groups. A broad multiplet centered at  $\delta$  4.0–4.6 ppm is due to the methine proton of isopropoxy groups in all spectra. All  $\beta$ -diketonates of  $\mu$ -oxoisopropoxy acetate compound show singlet at  $\delta$  2.1–2.3 ppm and  $\delta$  5.5–5.9 ppm due to methyl and methine proton of the ligand moiety respectively. Further, the peaks observed in the region  $\delta$  7.0–

7.7 ppm in benzoyl acetone derivative of [Al(III)-Ti(IV)]- $\mu$ -oxoisopropoxide are due to the phenyl ring protons.

The  $^{13}\text{C}$  NMR spectra of 1:1 to 1:3  $\beta$ -diketone derivatives of  $\mu$ -oxoisopropoxide compound show two prominent peaks between  $\delta$  27.1–27.7 ppm and  $\delta$  28.1–29 ppm assignable to the methyl carbon of terminal and bridging isopropoxy groups. The two peaks observed at  $\delta$  62.2–62.7 ppm and  $\delta$  63.2–63.9 ppm are assignable to the methine carbons of terminal and bridging isopropoxy groups in the derivatives. Single peak is observed at  $\delta$  28.1–28.9 and 63.2–63.9 ppm in 1:2 derivatives confirms the substitution of terminal group. Two peaks observed in the range  $\delta$  182.8–193.2 ppm and  $\delta$  100.42–93.4 ppm are due to carbonyl carbon and methine carbon of ligand moiety in all  $\beta$ -diketonates. The peaks observed at  $\delta$  127.8, 126.7, 124.5 and 135.9 ppm are due to *ortho*, *meta*, *para* and substituted carbon of the phenyl ring respectively in the spectra of benzoylacetone derivative of parent compound.

The molecular weight measurement carried out in dry benzene using cryoscopic method suggests monomeric nature of  $\beta$ -diketonates.

### 3. Experimental

#### 3.1. General procedure, materials and analytical measurements

All the operations were carried out in dry nitrogen atmosphere using a vacuum line. Hydrocarbon solvents and reagents used were purified and dried by standard methods. The general technique and physical measurement were carried out as described elsewhere.<sup>28-31</sup> Aluminium isopropoxide [Al(OPr<sup>i</sup>)<sub>3</sub>] and titanium acetate [Ti(OAc)<sub>4</sub>] were purchased from Aldrich and used as received. Acetyl acetone was dried prior to use and benzoyl acetone (Hi-media) was used without drying prior to use. The isopropoxy groups in the  $\mu$ -oxoisopropoxide and liberated isopropanol formed in preparation of  $\beta$ -diketonates were estimated oxidimetrically. Aluminium was extracted with N-p-tolyl-2-theno hydroxamic acid (PTTHA) determined spectrophotometrically and gravimetric estimation has been done for titanium.<sup>32</sup> Titanium was estimated as

TiO<sub>2</sub> via the formation of titanium-phenazone complex.<sup>29</sup> Perkin-Elmer 1710 FTIR spectrometer over the range 4000-400 cm<sup>-1</sup> used to record the Infrared spectra. The <sup>1</sup>H, <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on Bruker Avance II 400 NMR spectrometer. The mass spectrum recorded on a Waters QTOF2 mass spectrometer equipped with Quadrupole and time of flight (TOF) analyzers. TG study has been made on Diamond TG/DTA Perkin Elmer instrument. Elemental analyses were carried out by Perkin Elmer 2400 II series CHNS/O Analyzer. Absorbance measurements were made with a Shimadzo (Japan) UV-Visible, model UV 160 spectrophotometer.

### 3.2. Synthesis of [(OAc)<sub>2</sub>TiO<sub>2</sub>Al<sub>2</sub>(OPr<sup>i</sup>)<sub>4</sub>]

The [Al(III)-Ti(IV)]-μ-oxoisopropoxy acetate was synthesized by thermal condensation between Al(OPr<sup>i</sup>)<sub>3</sub> (2.421 g, 11.867 mmol) and Ti(OAc)<sub>4</sub> (1.697 g, 5.930 mmol) in xylene. The contents refluxed for about 8h on a fractionating column and the isopropyl acetate formed in the reaction was removed continuously from 80°C until the temperature rose to the boiling point of xylene (139°C). The reaction was then continued at this temperature for 2 h to ensure its completion. The excess of xylene was distilled at 35-40°C/1 mm, leaving behind a yellow semi-solid product which was dissolved in benzene. Slow evaporation of benzene gave a pale yellow glassy solid which get decomposed on heating strongly (dec. > 340°C). [Yield: 96%; For [(OAc)<sub>2</sub>TiO<sub>2</sub>Al<sub>2</sub>(OPr<sup>i</sup>)<sub>4</sub>] Analysis: Found(%): OPr<sup>i</sup>, 46.9; Al, 10.8; Ti, 9.1 Calcd(%): OPr<sup>i</sup>, 48.4; Al, 11.1 Ti, 9.6].

### 3.3. Reaction of [(OAc)<sub>2</sub>TiO<sub>2</sub>Al<sub>2</sub>(OPr<sup>i</sup>)<sub>4</sub>] with acetylacetone (Hacac) in 1:1 molar ratio:

The [(OAc)<sub>2</sub>TiO<sub>2</sub>Al<sub>2</sub>(OPr<sup>i</sup>)<sub>4</sub>] (0.482 g, 0.988 mmol) and acetylacetone (0.099 g, 0.988 mmol) were refluxed in ~ 50 ml benzene in a flask connected to a short distillation column on an oil bath for about 6 h. The isopropanol liberated at 72-78°C was fractionated as the binary azeotrope of isopropanol-benzene. The azeotrope was collected and checked for completion of the reaction. The excess of the solvent was then



removed under reduced pressure yielding a yellowish semi-solid product. The syntheses of other  $\beta$ -diketonates were carried out by similar procedure and the analytical results have been summarized in Table 1 and Table 2.

#### 4. Conclusion

The aforementioned studies reveals the suggestive structures of the  $[(\text{OAc})_2\text{TiO}_2\text{Al}_2(\text{OPr}^i)_4]$  and its  $\beta$ -diketonate of the type  $[(\text{OAc})_2\text{TiO}_2\text{Al}_2(\text{OPr}^i)_3(\text{L})]$  and  $[(\text{OAc})_2\text{TiO}_2\text{Al}_2(\text{OPr}^i)_2(\text{L})_2]$ . TGA study reveals the volatile nature of parent compound and its hydrolysed product may fabricate the mixed metal oxides. It is observed the  $\beta$ -diketonate are found more stable and less prone to hydrolysis as compared to parent compound. The proposed structures of parent compound and its bi derivatives are shown in Figure 1 and Figure 2 respectively.

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TABLE 1 – Analytical and physical data of the studied compounds

S.No. Comp.	Ligand	Molar	Refluxing	Product	Anal. Found (Calc.)		
					HOPr <sup>i</sup>	Al	Ti
g (mmol)	g (mmol)	ratio	time (hrs)	(%)	(%)	(%)	
1. [(OAc) <sub>2</sub> TiO <sub>2</sub> Al <sub>2</sub> (OPr <sup>i</sup> ) <sub>4</sub> ] (0.482 g, 0.988 mmol)	Hacac 0.099 (0.988)	1:1	6	[(OAc) <sub>2</sub> TiO <sub>2</sub> Al <sub>2</sub> (OPr <sup>i</sup> ) <sub>3</sub> (acac)] (85.6)	11.10 (11.36)	09.87 (10.22)	07.88 (08.90)
2. [(OAc) <sub>2</sub> TiO <sub>2</sub> Al <sub>2</sub> (OPr <sup>i</sup> ) <sub>4</sub> ] 0.382 (0.782)	Hacac 0.156 (1.565)	1:2	8½	[(OAc) <sub>2</sub> TiO <sub>2</sub> Al <sub>2</sub> (OPr <sup>i</sup> ) <sub>2</sub> (acac) <sub>2</sub> ] (84.8)	19.85 (21.12)	08.57 (09.51)	08.14 (08.27)
3. [(OAc) <sub>2</sub> TiO <sub>2</sub> Al <sub>2</sub> (OPr <sup>i</sup> ) <sub>4</sub> ] 0.459 (0.941)	Hbzac 0.152 (0.941)	1:1	6½	[(OAc) <sub>2</sub> TiO <sub>2</sub> Al <sub>2</sub> (OPr <sup>i</sup> ) <sub>3</sub> (bzac)] (82.6)	09.58 (10.17)	09 (09.15)	07.23 (07.97)
4. [(OAc) <sub>2</sub> TiO <sub>2</sub> Al <sub>2</sub> (OPr <sup>i</sup> ) <sub>4</sub> ] 0.369 (0.756)	Hbzac 0.245 (1.512)	1:2	9	[(OAc) <sub>2</sub> TiO <sub>2</sub> Al <sub>2</sub> (OPr <sup>i</sup> ) <sub>2</sub> (bzac) <sub>2</sub> ] (83.5)	16.15 (17.34)	07.17 (07.80)	06.38 (06.79)

TABLE 2 – Analytical and physical data of the studied compounds

S.No.	Compound	Empirical formula	Formula weight	Anal. Found (Calcd) %		
				C	H	O
1.	[(OAc) <sub>2</sub> TiO <sub>2</sub> Al <sub>2</sub> (OPr <sup>i</sup> ) <sub>4</sub> ]	C <sub>16</sub> H <sub>34</sub> Al <sub>2</sub> TiO <sub>10</sub>	488	38.23 (39.34)	6.18 (6.97)	21.68 (32.79)
2.	[(OAc) <sub>2</sub> TiO <sub>2</sub> Al <sub>2</sub> (OPr <sup>i</sup> ) <sub>3</sub> (acac)]	C <sub>18</sub> H <sub>34</sub> Al <sub>2</sub> TiO <sub>11</sub>	528	39.32 (40.90)	6.07 (6.44)	32.57 (33.33)
3.	[(OAc) <sub>2</sub> TiO <sub>2</sub> Al <sub>2</sub> (OPr <sup>i</sup> ) <sub>2</sub> (acac) <sub>2</sub> ]	C <sub>20</sub> H <sub>34</sub> Al <sub>2</sub> TiO <sub>12</sub>	568	41.13 (42.25)	6.12 (6.34)	32.17 (33.80)
4.	[(OAc) <sub>2</sub> TiO <sub>2</sub> Al <sub>2</sub> (OPr <sup>i</sup> ) <sub>3</sub> (bzac)]	C <sub>23</sub> H <sub>36</sub> AlTi <sub>2</sub> O <sub>11</sub>	590	46.15 (46.78)	5.63 (6.1)	27.76 (29.83)
5.	[(OAc) <sub>2</sub> TiO <sub>2</sub> Al <sub>2</sub> (OPr <sup>i</sup> ) <sub>2</sub> (bzac) <sub>2</sub> ]	C <sub>25</sub> H <sub>36</sub> AlTi <sub>2</sub> O <sub>12</sub>	692	42.19 (43.35)	4.86 (5.20)	27.53 (27.75)

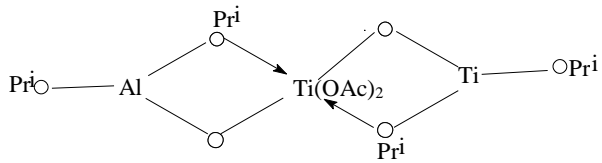


Figure 1: Suggested structure of  $[AlO_2Ti_2(OPr)_6]$

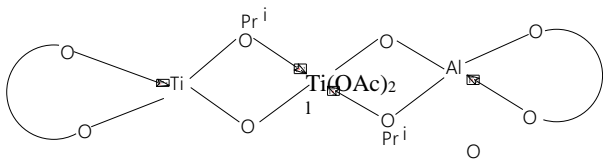


Figure 2: Suggested structure of  $[AlO_2Ti_2(OPr)_2(L)_4]$

