Synthesis, spectral, and thermoanalytical studies on the new heterobimetallic [Mg(II)-Ti(IV)]-μ-oxoisopropoxide and its β-diketonates

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Abstract: The new heterobimetallic [Mg(II)-Ti(IV)]-μ-oxoisopropoxide was synthesized on treatment of magnesium acetate with titanium(IV) isopropoxide in refluxing decalin in 1:2 molar ratio and characterized by liberated isopropanol, elemental, spectral (IR, ^{1}H and ^{13}C NMR, and mass), thermal analysis, and molecular weight data. The reactions of [Mg(II)-Ti(IV)]-μ-oxoisopropoxide compound with β-diketones in different molar ratios (1:1–1:4) yielded mono to tetra derivatives [{MgO$_2$Ti$_2$(OPr^i)$_{6-n}$L$_n$}] (where n is 1–4 and L = acetylacetonate/benzoylacetonate anion)] of the μ-oxo complex and were characterized by elemental, liberated isopropanol, and spectral analysis (IR and ^{1}H and ^{13}C NMR). These studies revealed interesting facets in support of plausible structures of the parent compound and its β-diketonates.

Key words: Heterometallic-μ-oxoisopropoxide, magnesium, titanium, β-diketones, thermoanalysis

1. Introduction

Bimetallic oxo complexes, 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 peculiarities 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.[1] The use of heterometallic alkoxides as single-source molecule precursors for synthesis of oxides has seen rapid growth over the last 15 years. The control of particle size and the morphology of the oxide are of crucial importance nowadays both from the fundamental and industrial points of view.[2] The multicomponent oxides synthesized as a result of the sol-gel technique on heterometallic-μ-oxoalkoxides[3−6] are found efficient to reduce the effect of harmful chemicals[7] and decontaminating chemical warfare agents.[8,9] Magnesium titanate (MgTiO$_3$) ceramic has been proved to be an excellent dielectric material since it has low dielectric loss (high quality factor $Q \sim 21{,}800$ at 8 GHz) and a suitable dielectric constant ($\varepsilon_r \sim 17.0$–17.5).[10] Recently, MgTiO$_3$ ceramic has been widely applied in capacitors, resonators, filters, antennas, radar, direct broadcasting satellites, and global positioning systems operating at microwave frequencies.[11,12] Magnesium titanates (MgTiO$_3$, Mg$_2$TiO$_4$, MgTi$_2$O$_5$), silicates[13] (MgSiO$_3$, MgSiO$_4$), and aluminate[14] (MgAl$_2$O$_4$) are commercially produced as low dielectric components. Magnesium titanate thin films had a very smooth and densely packed surface morphology and showed excellent properties as the reaction barrier layer between Pt and Si.[15] The porous SrTiO$_3$ spheres exhibited enhanced photocatalytic activity, which could achieve 100% degradation of Rhodamine B with a UV irradiation for
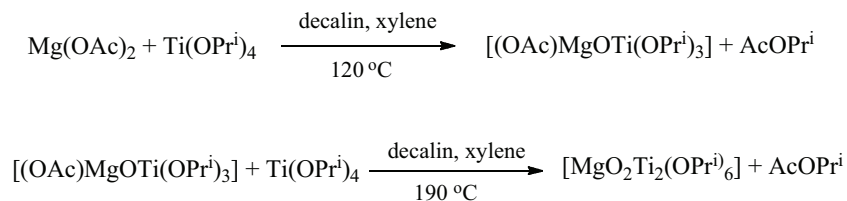
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20 min.[16] The bimetallic-μ-oxoalkoxides of transition metals have also been proved to be exceptional catalysts for the polymerization of heterocyclic monomers like lactones, oxiranes, thiiranes, and epoxides.[17,18] The β-diketiminate derivative 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 polydispersities.[19] Volatile organometallic alkoxides are the preeminent 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.[20,21]

In the present investigation, heterobimetallic [Mg(II)-Ti(IV)]-μ-oxoisopropoxide is prepared from the condensation of 1 mole of magnesium acetate and 2 moles of titanium isopropoxide, and the reaction proceeds with stepwise formation of pure bimetallic [Mg(II)-Ti(IV)]-μ-oxoisopropoxide, which is a molecular species that can be purified by distillation, allowing the isolation of pure molecular precursors, and to gain an insight into its structure and prevent the phase secretion problem due to its strong tendency to hydrolysis, its β-diketonates are synthesized.

2. Results and discussion

The common reactions that take place during the formation of bimetallic-μ-oxoisopropoxide $[\mathrm{MgO_2Ti_2(OPr^{\it i})_6}]$ are shown in Scheme 1:

$$\mathrm{Mg(OAc)_2 + Ti(OPr^i)_4 \xrightarrow[120\,^oC]{decalin,\ xylene} [(OAc)MgOTi(OPr^i)_3] + AcOPr^i}$$

$$\mathrm{[(OAc)MgOTi(OPr^i)_3] + Ti(OPr^i)_4 \xrightarrow[190\,^oC]{decalin,\ xylene} [MgO_2Ti_2(OPr^i)_6] + AcOPr^i}$$

Scheme 1.

The $[\mathrm{MgO_2Ti_2(OPr^{\it i})_6}]$ obtained is a pale yellow semisolid, susceptible to hydrolysis, and soluble in common organic solvents such as benzene, chloroform, and carbon tetrachloride.

2.1. Spectral analysis of $[\mathbf{MgO_2Ti_2(OPr^{\it i})_6}]$

2.1.1. IR spectra

The IR spectrum of [Mg(II)-Ti(IV)]-μ-oxoisopropoxide showing the absence of strong bands at $\sim$1610 cm^{-1} and $\sim$1435 cm^{-1} due to asym C$=$C and sym C$=$C stretch, respectively, indicates the complete removal of acetate groups. The absorption bands at $\sim$1360 cm^{-1} and $\sim$1165 cm^{-1} are characteristic of the *gem*-dimethyl portion and combination band ν(C-O+OPr$^{\it i}$) of the terminal and bridging isopropoxy group, respectively. A band appearing at $\sim$950 cm^{-1} is assignable to ν(C-O) stretching of the bridging isopropoxy group.[22] A number of vibrations are observed in the region 700–400 cm^{-1} due to M-O stretching vibrations in μ-oxo compound.[23]

2.1.2. NMR spectra

The sharp singlet observed at δ 2.1 ppm in the ^{1}H NMR spectrum of magnesium acetate is absent in the spectrum of $[\mathrm{MgO_2Ti_2(OPr^{\it i})_6}]$, which confirms the complete removal of acetate groups. The ^{1}H NMR spectrum of [Mg(II)-Ti(IV)]-μ-oxoisopropoxide shows a number of peaks centered between δ 0.8 and 1.2 ppm due to the intermixing of methyl protons of terminal and bridging isopropoxy groups.[24] The presence of the

methine proton of the isopropoxy group is indicated by the multiplet centered at δ 4.2 ppm in the spectrum. The ^{1}H NMR spectrum of $[MgO_2Ti_2(OPr^i)_6]$ is presented in Figure 1.
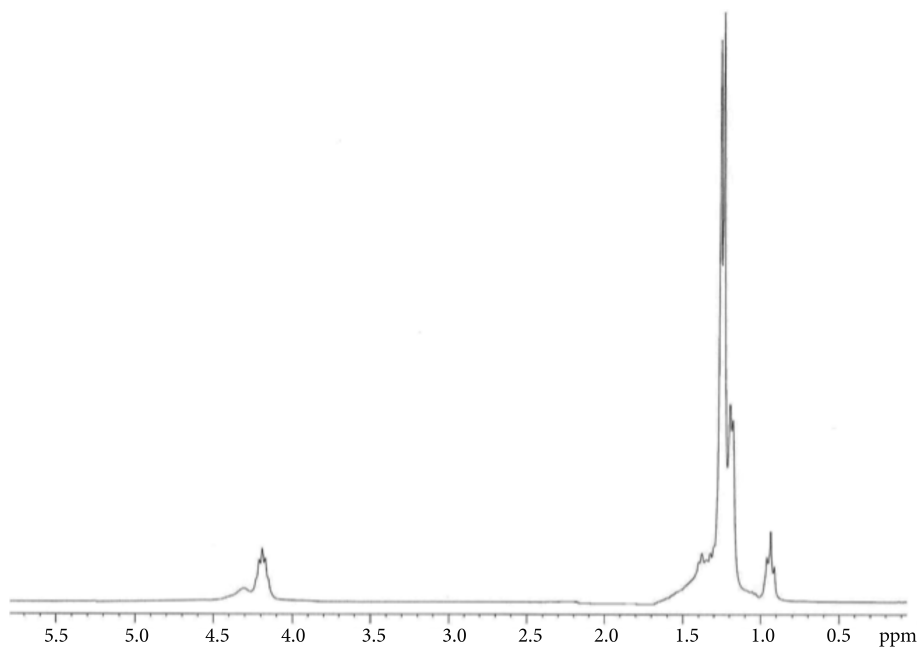

Figure 1. ^{1}H NMR spectrum of $[MgO_2Ti_2(OPr^i)_6]$.

The ^{13}C NMR spectrum of $[Mg(II)-Ti(IV)]-\mu$-oxoisopropoxide shows 2 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 2 peaks observed at δ 62.9 ppm and δ 64.1 ppm in the ^{13}C NMR spectrum are due to the terminal and bridging methine carbon of the isopropoxy groups.[25] The ^{13}C NMR spectrum of $[MgO_2Ti_2(OPr^i)_6]$ is shown in Figure 2.

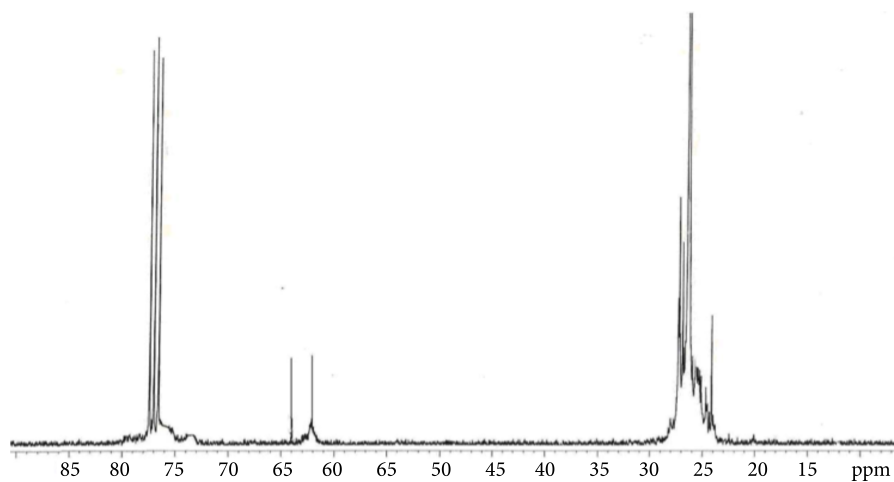**Figure 2.** ^{13}C NMR spectrum of $[MgO_2Ti_2(OPr^i)_6]$.

2.1.3. Mass spectra

The positive ion mass spectrum was obtained in dry toluene with 17% isopropanol by volume. The significant mass peaks observed at (m/z) 503.7, 446.6, 384.7, 267.9, 264.2, 225.8, 172.8, 134.2, 46.7, and 24.2 in the spectrum can be assigned to the fragments $MgO_2Ti_2(OPr^i)_6^+$, $MgO_2Ti_2(OPr^i)_5^+$, $MgO_2Ti_2(OPr^i)_4^+$, $MgO_2Ti_2(OPr^i)_2^+$, $MgO_2Ti(OPr^i)_3^+$, $Ti(OPr^i)_3^+$, $MgO_2(OPr^i)_2^+$, $MgOTi^+$, Ti^+, and Mg^+, respectively.[26] The mass spectrum of $MgO_2Ti_2(OPr^i)_6$ is shown in Figure 3.
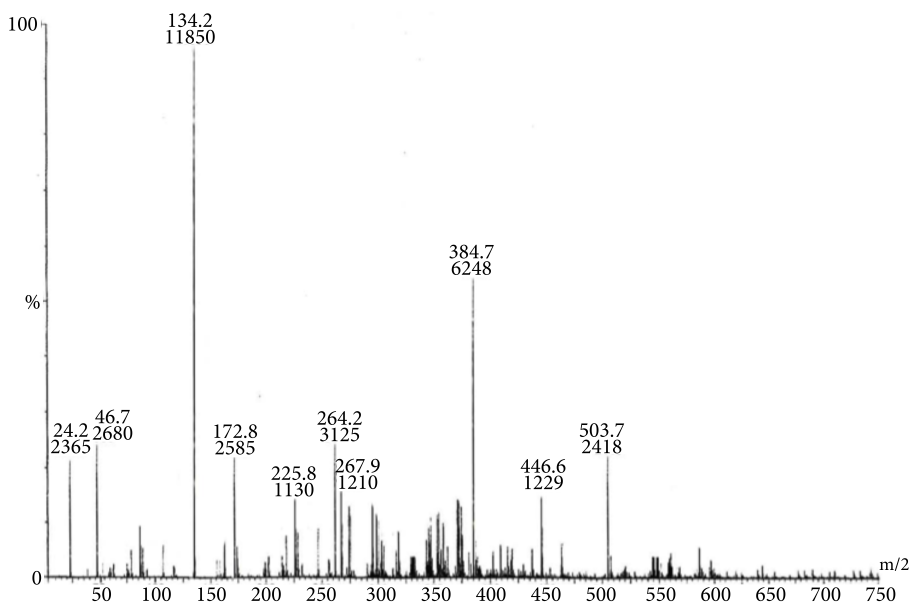
Figure 3. Mass spectrum of $MgO_2Ti_2(OPr^i)_6$.

2.2. Thermal analysis of $[MgO_2Ti_2(OPr^i)_6]$

The thermogram of $[MgO_2Ti_2(OPr^i)_6]$ was obtained with a linear rise in temperature up to 700 °C at 10 °C/min. A total weight loss of 89.740% was observed from 58.9 to 340 °C. The small weight loss between 58.9 and 180 °C is probably due to the presence of moisture and traces of solvent in the compound. A rapid weight loss was observed between $\sim$180 and 350 °C, indicating the volatile nature of the μ-oxo compound. Further, the remaining weight 10.260% observed is due to the decomposition of partially hydrolyzed μ-oxo compound into mixed metal oxide.

The TGA of the hydrolyzed product of $[MgO_2Ti_2(OPr^i)_6]$ was performed up to 800 °C at 10 °C/min. The hydrolyzed product showing weight loss of about 3%–4% may be due to the traces of water present. The weight loss of 19.273% observed from 220 °C to 340 °C is probably due to the elimination of hydroxy groups and organic moieties[27] present in the hydrolyzed product of $[MgO_2Ti_2(OPr^i)_6]$. The final product remaining is probably the mixed metal oxide. The TGA is consistent with the formulation of the compound as $[MgO_2Ti_2(OPr^i)_6]$. The thermogram of the hydrolyzed product of $[MgO_2Ti_2(OPr^i)_6]$ is given in Figure 4.

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

To further gain an insight into the structure, and effect on the solubility and stability, many reactions of $[MgO_2Ti_2(OPr^i)_6]$ with β-diketones (HL) were carried out in different molar ratios in refluxing benzene

yielding oxo complexes of the type $[MgO_2Ti_2(OPr^i)_5L]$, $[MgO_2Ti_2(OPr^i)_4L_2]$, $[MgO_2Ti_2(OPr^i)_3L_3]$, and $[MgO_2Ti_2(OPr^i)_2L_4]$ according to the following reaction (Scheme 2):
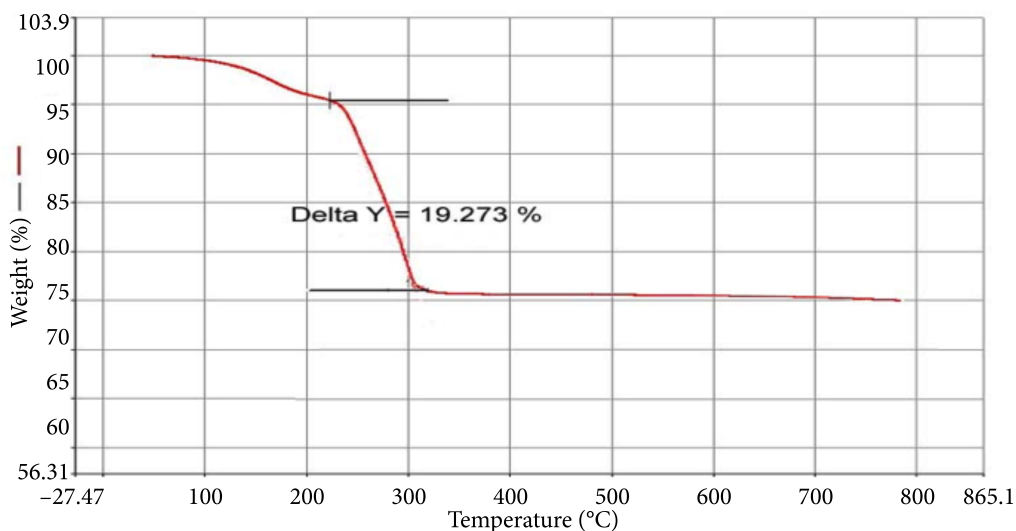
Figure 4. TGA of hydrolyzed product of $[MgO_2Ti_2(OPr^i)_6]$.

$$[MgO_2Ti_2(OPr^i)_6] + nHL \xrightarrow{\text{refluxing benzene}} [MgO_2Ti_2(OPr^i)_{6-n}L_n] + nPr^iOH$$

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

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 4 out of the 6 isopropoxy groups of [Mg(II)-Ti(IV)]-μ-oxoisopropoxide could be replaced by β-diketones. The replacement of bridged isopropoxy groups could not be achieved even with an excess of ligand (β-diketones) and refluxing the contents for about 28 h.

The β-diketone derivatives of [Mg(II)-Ti(IV)]-μ-oxoisopropoxide are found to be yellow colored semisolids to solids. All β-diketonates show appreciable solubility in common organic solvents (benzene, chloroform, hexane), are susceptible to hydrolysis, and decompose on heating strongly.

2.3. Spectral analysis of β-diketone derivatives of $[MgO_2Ti_2(OPr^i)_6]$

2.3.1. IR spectra

The absorption bands in the regions 1365–1340 cm^{-1} and 1165–1150 cm^{-1}, which are characteristic of the *gem*-dimethyl group and combination band ν(C-O+OPr^i) of the terminal and bridging isopropoxy groups, respectively, are shown in mono to tri β-diketonates, but the absence of a band at 1360–1340 cm^{-1} in the spectrum of 1:4 β-diketonates indicates the removal of the terminal isopropoxy group. All derivatives show a band at 930–950 cm^{-1}, which indicates ν(C-O) stretching of the bridging isopropoxy group. The spectra of β-diketones display strong bands at $\sim$1600–1580 cm^{-1} and $\sim$1520–1500 cm^{-1} due to ν_{sym}(C=O) and ν_{asym}(C=C), respectively, along with a broad band at $\sim$3100–2700 cm^{-1} due to enolic ν(O-H). The nonshifting

of ν(C=O) frequency and the disappearance of the broad band appearing in the region 3200–2700 cm^{-1} in β-diketones suggest 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 in β-diketonates.

2.3.2. NMR spectra

In the ^{1}H NMR spectra of the β-diketonates, the absence of an enolic peak at δ 12–13 ppm indicates the deprotonation of ligand, and the broad overlapping multiplet centered between δ 0.8 and 1.2 ppm is due to intermixing of the methyl protons of the bridging and isobranching vibrations of isopropoxy groups. A broad multiplet centered at δ 4.0–4.6 ppm is due to the methine proton of isopropoxy groups in all spectra. The β-diketonates of μ-oxoisopropoxide compound show singlets at δ 2.1–2.3 ppm and δ 5.5–5.9 ppm due to methyl and methine protons of the ligand moiety, respectively. Further, the peaks observed in the region δ 7.0–7.7 ppm in the benzoyl acetone derivative of [Mg(II)-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 2 prominent peaks at δ 27.1–27.7 ppm and δ 28.1–29 ppm assignable to the methyl carbon of terminal and bridging isopropoxy groups. The peaks observed at δ 62.2–62.7 ppm and δ 63.2–63.9 ppm are revealed to be the methine carbons of terminal and bridging isopropoxy groups in the derivatives. The single peaks observed at δ 28.1–28.9 and 63.2–63.9 ppms in tetra derivatives show the absence of methine of the terminal isopropoxy group. The peaks observed in the range δ 182.8–193.2 ppm and δ 100.42–93.4 ppm are due to carbonyl carbon and methine carbon of ligand moiety in all β-diketonates. The peaks observed at δ 127.8, 126.7, 124.5, and 135.9 ppm are due to *ortho*, *meta*, *para*, and substituted carbon, respectively, of the phenyl ring.

The molecular weight measurement carried out in dry benzene using cryoscopy suggests a monomeric nature of β-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. The hydrocarbon solvents and reagents used were purified and dried by standard methods. The general technique and physical measurements were carried out as described elsewhere.[28−31] Hydrated magnesium acetate (Aldrich) was made anhydrous with acetic anhydride and titanium isopropoxide [Ti(OPr^i)$_4$] (Aldrich) was used without further purification. Acetyl acetone was dried prior to use and benzoyl acetone (Hi-media) was used as received. The isopropoxy groups in the μ-oxoisopropoxide and liberated isopropanol formed during the preparation of β-diketonates were estimated oxidimetrically. Magnesium was extracted with N-p-tolyl-2-theno hydroxamic acid (PTTHA) determined spectrophotometrically and gravimetric estimation was performed for titanium.[32] Titanium was estimated as TiO$_2$ via the formation of titanium-phenazone complex.[29] A PerkinElmer 1710 FTIR spectrometer over the range 4000–400 cm^{-1} was used to record the infrared spectra. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance II 400 NMR spectrometer using CDCl$_3$ as reference solvent. A Waters QTOF2 mass spectrometer equipped with quadrupole and time of flight (TOF) analyzers was used to record the mass spectrum. Thermogravimetric studies were conducted on a Diamond TG/DTA PerkinElmer instrument. Elemental analyses were carried out using a PerkinElmer 2400 II series CHNS/O analyzer. Absorbance measurements were recorded on a Shimadzu (Japan) UV-Visible, model UV 160 spectrophotometer.

3.2. Synthesis of $[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_6]$

The [Mg(II)-Ti(IV)]-μ-oxoisopropoxide was synthesized by thermal condensation between Mg(OAc)_2 (1.224 g, 8.619 mmol) and $\text{Ti(OPr}^i)_4$ (4.878 g, 17.238 mmol) in a mixture of xylene and decalin. The contents were refluxed for about 15 h on a fractionating column and the isopropyl acetate formed in the reaction was removed continuously from 80 °C to the boiling point of decalin (190 °C). Further, the reaction was carried out for 2 h to ensure the completion of the reaction. The excess of decalin was distilled at 40–50 °C/1 mm, leaving behind a yellow semisolid product, which was dissolved in benzene, and slow evaporation of the benzene furnished a pale yellow amorphous solid that was decomposed on heating strongly (dec. > 350 °C). [Yield: 96%; For $[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_6]$ Anal.: Found(%): OPr^i, 54.9; Mg, 3.5; Ti, 36.8 Calcd(%): OPr^i, 54.6; Mg, 3.7 Ti, 36.7].

3.3. Reaction of $[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_6]$ with acetylacetone (Hacac) in 1:1 molar ratio

The $[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_6]$ (0.352 g, 0.7 mmol) and acetylacetone (0.07 g, 0.7 mmol) were refluxed in $\sim$50 mL of benzene in a flask connected to a short distillation column on an oil bath for about 7 h. The isopropanol liberated at 72–78 °C was fractionated, collected, and checked for completion of the reaction. The excess solvent was then removed under reduced pressure, yielding a yellowish semisolid product. The syntheses of other β-diketonates were carried out by a similar procedure and the analytical results are summarized in Tables 1 and 2.

Table 1. Analytical and physical data of the studied compounds.

S.No.	Comp. g (mmol)	Ligand g (mmol)	Molar ratio	Refluxing time (h)	Product (%)	Anal. Found (Calc.)		
						HOPr^i g	Mg (%)	Ti (%)
1.	$[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_6]$ (0.352 g, 0.7 mmol)	Hacac 0.07 (0.7)	1:1	7	$[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_5(\text{acac})]$ (80.5)	0.03 (0.03)	4.49 (4.41)	17.52 (17.28)
2.	$[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_6]$ 0.277 (0.55)	Hacac 0.110 (1.1)	1:2	8½	$[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_4(\text{acac})_2]$ (79.8)	0.06 (0.07)	4.28 (4.11)	17.32 (16.09)
3.	$[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_6]$ 0.271 (0.539)	Hacac 0.167 (1.67)	1:3	11½	$[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_3(\text{acac})_3]$ (77.9)	0.08 (0.09)	4.17 (3.85)	16.23 (15.06)
4.	$[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_6]$ 0.274 (0.545)	Hacac 0.218 (2.18)	1:4	14	$[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_2(\text{acac})_4]$ (81.5)	0.12 (0.12)	3.87 (3.61)	15.56 (14.16)
5.	$[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_6]$ 0.242 (0.481)	Hbzac 0.078 (0.481)	1:1	7	$[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_5(\text{bzac})]$ (80.8)	0.03 (0.04)	3.98 (3.96)	15.65 (15.51)
6.	$[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_6]$ 0.283 (0.561)	Hbzac 0.182 (1.123)	1:2	8	$[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_4(\text{bzac})_2]$ (83.5)	0.07 (0.07)	3.35 (3.38)	13.45 (13.28)
7.	$[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_6]$ 0.294 (0.584)	Hbzac 0.284 (1.753)	1:3	12½	$[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_3(\text{bzac})_3]$ (81.9)	0.09 (0.10)	2.92 (2.96)	11.7 (11.6)
8.	$[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_6]$ 0.308 (0.612)	Hbzac 0.397 (2.45)	1:4	14½	$[\text{MgO}_2\text{Ti}_2(\text{OPr}^i)_2(\text{bzac})_4]$ (81.2)	0.12 (0.13)	2.58 (2.63)	10.28 (10.31)

Table 2. Analytical and physical data of the studied compounds.

S. No.	Compound	Empirical formula	Formula weight	Anal. Found (Calcd) %		
				C	H	O
1.	$[MgO_2Ti_2(OPr^i)_6]$	$C_{18}H_{42}MgTi_2O_8$	504	41.89 (42.85)	8.14 (8.33)	24.28 (25.39)
2.	$[MgO_2Ti_2(OPr^i)_5(acac)]$	$C_{20}H_{42}MgTi_2O_9$	544	42.98 (44.12)	7.16 (7.72)	25.78 (26.47)
3.	$[MgO_2Ti_2(OPr^i)_4(acac)_2]$	$C_{22}H_{42}MgTi_2O_{10}$	584	46.13 (45.20)	6.69 (7.19)	26.38 (27.39)
4.	$[MgO_2Ti_2(OPr^i)_3(acac)_3]$	$C_{24}H_{42}MgTi_2O_{11}$	624	46.12 (46.15)	6.34 (6.73)	27.76 (28.20)
5.	$[MgO_2Ti_2(OPr^i)_2(acac)_4]$	$C_{26}H_{42}MgTi_2O_{12}$	664	46.34 (46.98)	6.19 (6.32)	27.53 (28.91)
6.	$[MgO_2Ti_2(OPr^i)_5(bzac)]$	$C_{25}H_{44}MgTi_2O_9$	606	48.43 (49.50)	7.88 (7.26)	21.65 (23.76)
7.	$[MgO_2Ti_2(OPr^i)_4(bzac)_2]$	$C_{32}H_{46}MgTi_2O_{10}$	708	53.57 (54.23)	6.60 (6.49)	21.45 (22.59)
8.	$[MgO_2Ti_2(OPr^i)_3(bzac)_e]$	$C_{39}H_{48}MgTi_2O_{11}$	810	55.95 (57.77)	5.37 (5.92)	20.47 (21.72)
9.	$[MgO_2Ti_2(OPr^i)_2(bzac)_4]$	$C_{46}H_{50}MgTi_2O_{12}$	912	59.16 (60.52)	5.13 (5.48)	22.09 (21.05)

4. Conclusion

The aforementioned studies reveal the suggested structures of the $[MgO_2Ti_2(OPr^i)_6]$ and its β-diketonate of the type $[MgO_2Ti_2(OPr^i)_5(L)]$, $[MgO_2Ti_2(OPr^i)_4(L)_2]$, $[MgO_2Ti_2(OPr^i)_3(L)_3]$, and $[MgO_2Ti_2(OPr^i)_2(L)_4]$. TGA reveals the volatile nature of the parent compound and its hydrolyzed product may fabricate mixed metal oxides. It is observed the β-diketonates are more stable and less prone to hydrolysis as compared to the parent compound. The proposed structures of the parent compound and its tetra derivatives are shown in Figures 5 and 6, respectively.
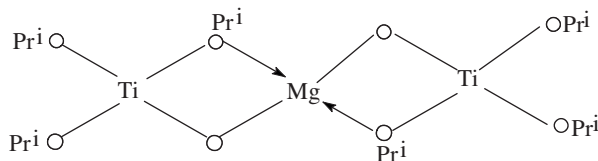

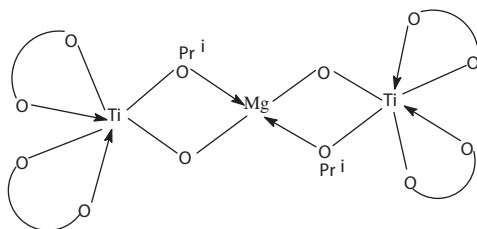**Figure 5.** Suggested structure of $[MgO_2Ti_2(OPr^i)_6]$.

Figure 6. Suggested structure of $[MgO_2Ti_2(OPr^i)_2(L)_4]$.

Acknowledgment

References

1. Turova, N. Ya. *Russian Chem. Rev.* **2004**, *73*, 1041–1064.
2. Vayssieres, L.; Hagfeldt, A.; Lindquist, S. E. *Pure Appl. Chem.* **2000**, *72*, 47–52.
3. Kapoor, P. N.; Bhagi, A. K.; Mulukutla, R. S.; Klabunde, K. J. *Dekker Encyclopedia of Nanoscience and Nanotechnology*; Marcel Dekker: New York, 2004, 2007.
4. Kapoor, P. N.; Sharma, H. K.; Bhagi, A. K.; Sharma, M. *J. Ind. Chem. Soc.* **2004**, *81*, 273–281.
5. Mohammadnezhad, G.; Amini, M. M.; Khavasi, H. R. *Dalton Trans.* **2010**, *39*, 10830–10832.
6. Hubert-Pfalzgraf, L. G.; Daniele, S. *C. R. Chimie* **2004**, *7*, 521–527.
7. Carnes, C. L.; Kapoor, P. N.; Klabunde, K. J.; Bonevich, J. *Chem. Mater.* **2002**, *14*, 2922–2929.
8. Wagner, G. W.; Procell, L. R.; O'Connor, R. J.; Munavalli, S.; Carnes, C. L.; Kapoor, P. N.; Klabunde, K. J. *J. Am. Chem. Soc.* **2001**, *123*, 1636–1644.
9. Medine, G. M.; Zaikovskii, V.; Klabunde, K. J. *J. Mater. Chem.* **2004**, *14*, 757–763.
10. Haurt, L. G. J.; Vries, A. J.; Blasse, G. *Mater. Res. Bull.* **1984**, *19*, 817–824.
11. Li, D. D.; Wang, L. Q.; Xue, D. F. *J. Alloy. Compd.* **2010**, *492*, 564–569.
12. Huang, C. L.; Chen, Y. B. *Surf. Coat. Technol.* **2006**, *200*, 3319–3325.
13. Herbert, J. M. *Ceramic Dielectrics and Capacitors*; Philadelphia, PA, USA: Gorden and Breach Science Publishers, 1985.
14. Kapoor, P. N.; Heroux, D.; Mulukutla, R. S.; Zaikovskii, V.; Klabunde, K. J. *J. Mater. Chem.* **2003**, *13*, 410–414.
15. Lee, C. H.; Kim, S. *Integr. Ferroelectr.* **2003**, *57*, 1265–1270.
16. Dong, W.; Li, X.; Yu, J.; Guo, W.; Li, B.; Tan, L.; Li, C.; Shi, J.; Wang, G. *Mater. Lett.* **2012**, *67*, 131–134.
17. Koper, O.; Lagadic, I.; Klabunde, K. J. *Chem. Mater.* **1997**, *9*, 838–848.
18. Klabunde, K. J.; Stark, J. V.; Koper, O.; Mohs, C.; Park, D. G.; Decker, S.; Jiang, Y.; Lagadic, I.; Zhang, D. *J. Phy. Chem.* **1996**, *100*, 12142–12153.
19. Athar, T.; Hakeem, A.; Topnani, N. *J. Chil. Chem. Soc.* **2011**, *56*, 887–890.
20. Sharma, H. K.; Kapoor, P. N.; Bhagi, A. K.; Sharma, M. *J. Indian Chem. Soc.* **2004**, *81*, 273–281.
21. Hench, L. L.; West, J. K. *Chem. Rev.* **1990**, *90*, 33–72.
22. Lynch, C. T.; Masdiyanni, K. S.; Smith, J. S.; Crawford, W. J. *Anal. Chem.* **1964**, *36*, 2332–2337.
23. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds;* John Wiley: New York, NY, USA, 1986.
24. Sonika, Narula, A. K.; Vermani, O. P.; Sharma, H. K. *J. Organomet. Chem.* **1994**, *470*, 67–72.
25. Brcitmair, E.; Voelter, W. ^{13}C *NMR Spectroscopy*; VCH: New York, NY, USA, 1990.
26. Lever, T.; Henderson, W.; Bowmaker, G. A.; Seakins, J. M.; Cooney, R. P. *J. Mater. Chem.* **1997**, *7*, 1553–1558.
27. Hubert-Pfalzgraf, L. G.; Daniele, S.; Papiernik, R; Massiani, M. C.; Septe, B.; Vaissermann, J.; Daran, J. C. *J. Mater. Chem.* **1997**, *7*, 753–762.
28. Sharma, H. K.; Kapoor, P. N. *Polyhedron* **1988**, *7*, 1389–1391.
29. Vogel, A. I. *A Text Book of Quantitative Analysis*; Longman: London, UK, 1989.
30. Sharma, H. K.; Kumar, R. *Indian J. Chem.* **2008**, *47A*, 854–858.
31. Kumar, R. *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry* (In Press).
32. Dallali, Nasser, Agrawal, Y. K. *Iran. J. Chem. & Chem. Eng.* **2004**, *23*, 65–71.