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Synthesis of new heterobimetallic [Al(III)-Ti(IV)]-μ-oxomixedisopropoxy acetates and their spectral & thermal studies

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Abstract

A new heterobimetallic [Al(III)-Ti(IV)]-μ-oxoisopropoxy acetate $[(OAc)_2TiO_2Al_2(OPr^i)_4]$ has been synthesized by the thermal condensation of aluminium isopropoxide and titanium(IV) acetate and characterized by liberated isopropanol, elemental, spectral (IR, ^1H , ^{13}C, NMR and mass), thermal analysis, molecular weight data. Many isopropoxy substitution reactions of [Al(III)-Ti(IV)]-μ-oxoisopropoxy acetate compound with different cycloalkanols in different molar ratios (1:1-1:2) yielded the mono to bi derivatives $[(OAc)_2TiO_2Al_2(OPr^i)_{4-n}(CA)_n\}$ (where n is 1-2 and CA = cyclopentanol/cyclohexanol/cycloheptanol anion)] respectively of the parent compound and have been characterized by elemental, liberated isopropanol and spectral analysis (IR, ^1H , ^{13}C and ^{27}Al NMR).The above studies revealed interesting facets in support of plausible structures of parent compound and its cycloalkanol derivatives.

Keywords: heterometallic-μ-oxoisopropoxy acetate, Aluminium, Titanium, β-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.[1] 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.[2] The mixed metal oxides prepared from heterometallic-μ-oxoalkoxides[3-6] have been used for absorbing harmful chemicals[7] and gases such as SO_2, CCl_4, and decontaminating chemical warfare agents.[8] The $MgAl_2O_4$ prepared from $[MgO_2Al_2(OPr^i)_4]_2$ has been used to destructively adsorb paraxon [diethyl-4-nitrophenol phosphate (DNPP)].[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 ~ 21800 at 8 GHz) and proper dielectric constant (ε_r ~ 17.0-17.5).[10] Recently, $MgTiO_3$ ceramic is widely applied in capacitors, resonators, filters, antennas, radar, direct broadcasting satellite and global positioning system operating at microwave frequencies.[11,12] Magnesium titanates ($MgTiO_3$, Mg_2TiO_4, $MgTi_2O_5$), silicates[13] ($MgSiO_3$, $MgSiO_4$) and aluminate[14] ($MgAl_2O_4$) are commercially produced as low dielectric components. Furthermore, aluminum titanate (Al_2TiO_5, 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.[15,16] Apart from their role as precursors for mixed metal oxides, the bimetallic-μ-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.[17,18] Recently, 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 polydisperties.[19] Volatile organometallic alkoxides, 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, the cycloalkanol derivatives of heterobimetallic [Al(III)-Ti(IV)]-μ-oxoisopropoxy acetate are prepared from the condensation of [Al(III)-Ti(IV)]-μ-oxoisopropoxy acetate and cycloalkanols in different molar ratio, the reaction proceeds with stepwise formation of pure bimetallic [Al(III)-Ti(IV)]-μ-oxomixedisopropoxy 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 their molecular weight determination and different spectral study have been made.

2. Results and Discussion

2.1. Spectral Analysis of cycloalkanol derivatives of $[(OAc)_2TiO_2Al_2(OPr^i)_4]$

2.1.1. IR spectra

The strong bands observed at 1615 cm^{-1} and 1430 cm^{-1} due to asym $C\cdots O$ and sym $C\cdots O$ stretch in the IR spectrum of titanium acetate are found present in the spectra of cyclic alcohol derivatives of $[(OAc)_2TiO_2Al_2(OPr^i)_4]$ indicates the presence of acetate groups. The IR spectra cyclic alcohol derivatives of $[(OAc)_2TiO_2Al_2(OPr^i)_4]$ show absorption bands in the region 1360-1340 cm^{-1} which are the characterstics of *gem*-dimethyl portion of isopropoxy group. A number of bands are observed in the range of 1165-1150 cm^{-1} and 1135-1115 due to combination bands ν(C-O+OPr^i) of the terminal and bridging isopropoxy group 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 isopropoxy group. A band appeared at approximately 950-925 cm^{-1} is due to ν(C-O) stretching of bridging isopropoxy group. 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 specta of μ-oxomixedisopropoxy acetate indicates the deprotonation of cyclic alcohols. A number of vibrations are observed in the region 700-400 cm^{-1} are due to M-O stretching in μ-oxo compound and its cycloalcoholates.[22,23]

2.1.2. NMR spectra of cyclic alcohol derivatives of $[(OAc)_2TiO_2Al_2(OPr^i)_4]$

In the ^{1}H NMR spectra of the cycloalkanol derivatives of [Al(III)-Ti(IV)]-μ-oxoisopropoxy acetate, a broad overlapping multiplet centered between δ 0.8–1.2 ppm in all derivatives at room temperature 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. All cyclic alcohol derivatives of μ-oxoisopropoxy acetate compound show singlet at δ 2.1-2.3 ppm due to methyl protons of the acetate group.[24] The ^{13}C NMR spectra of 1:1 cyclic alcohol derivatives of μ-oxoisopropoxy acetate show two prominent peaks between δ 27.1–27.7 ppm and δ 28.1–29 ppm assignable to the methyl carbon of terminal and bridging isopropoxy groups. The two peaks observed at δ 62.2–62.7 ppm and δ 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 δ 28.1-28.9 and 63.2-63.9 ppm in 1:2 derivatives confirms the substitution of terminal group.[25]

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

To further gain an insight into the structure, effect on the solubility and stability of $(OAc)_2TiO_2Al_2(OPr^i)_4$, many reactions of $(OAc)_2TiO_2Al_2(OPr^i)_4$ with cycloalkanols (HCA) were carried out in different molar ratios in refluxing benzene. The reactions yielded compounds of the type $(OAc)_2TiO_2Al_2(OPr^i)_3(CA)$ and $(OAc)_2TiO_2Al_2(OPr^i)_2(CA)_2$, according to the following reaction ***scheme 2***:

$$(OAc)_2TiO_2Al_2(OPr^i)_4 + nHCA \xrightarrow{\text{refluxing benzene}} [(OAc)_2TiO_2Al_2(OPr^i)_{4-n}(CA)_n] + nPr^iOH$$

(n= 1-2, HCA = cyclopentanol/ cyclohexanol/cycloheptanol)

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)]-μ-oxoisopropoxy acetate could be replaced by cycloalkanol. Futher replacement of isopropoxy groups could not be achieved even with an excess of ligand (cycloalkanol) and

prolonged refluxing time (18 h). This indicates the non-replacement of bridging isopropoxy groups and that only terminal isopropoxy groups are substituted by cycloalkanols.

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

The molecular weight measurement carried out in dry benzene using cryoscopic method suggests monomeric nature of cycloalcoholates.

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.[28-31] Aluminium isopropoxide [$Al(OPr^i)_3$] and titanium acetate [$Ti(OAc)_4$] were purchased from Aldrich and used as received. Cycloalkanols were dried prior to use. The isopropoxy groups in the μ-oxoisopropoxide and liberated isopropanol formed in preparation of β-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.[32] Titanium was estimated as TiO_2 via the formation of titanium-phenazone complex.[29] Perkin-Elmer 1710 FTIR spectrometer over the range 4000-400 cm^{-1} used to record the Infrared spectra. The ^1H, ^{13}C NMR spectra were recorded in $CDCl_3$ 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 $[(OAc)_2TiO_2Al_2(OPr^i)_4]$

The [Al(III)-Ti(IV)]-μ-oxoisopropoxy acetate was synthesized by thermal condensation between $Al(OPr^i)_3$ (2.421 g, 11.867 mmol) and $Ti(OAc)_4$ (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/l 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. > 370°C). [Yield: 96%; For $[(OAc)_2TiO_2Al_2(OPr^i)_4]$ Analysis: Found(%): OPr^i, 46.9; Al, 10.8; Ti, 9.1 Calcd(%): OPr^i, 48.4; Al, 11.1 Ti, 9.6].

3.3. *Reaction of $[(OAc)_2TiO_2Al_2(OPr^i)_4]$ with cyclopentanol (HCA) in 1:1 molar ratio:*

The $[(OAc)_2TiO_2Al_2(OPr^i)_4]$ (0.425 g, 0.873 mmol) and cyclopentanol (0.075 g, 0.873 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 isoproponol-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 cycloalcoholates 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 $[(OAc)_2TiO_2Al_2(OPr^i)_4]$ and its cycloalkanol derivatives of the type $[(OAc)_2TiO_2Al_2(OPr^i)_3(CA)]$ and $[(OAc)_2TiO_2Al_2(OPr^i)_2(CA)_2]$. It is observed the cycloalcoholates are found more stable and less prone to hydrolysis as compared to parent

compound. The proposed structures of cycloalkanol derivatives of $[(OAc)_2TiO_2Al_2(OPr^i)_4]$ of the type $[(OAc)_2TiO_2Al_2(OPr^i)_3(CA)]$ and $[(OAc)_2TiO_2Al_2(OPr^i)_2(CA)_2]$ are shown by Figure 1.

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TABLE 1 – Analytical and physical data of the studied compounds

S.No.	Comp. g (mmol)	Ligand g(mmol)	Molar ratio	Refluxing time (hrs)	Product (%)	Anal. Found (Calc.) HOPr^i (%)	Al (%)	Ti (%)
1.	$[(OAc)_2TiO_2Al_2(OPr^i)_4]$ 0.425 (0.873)	HCA^1 0.075 (0.873)	1:1	6	$[(OAc)_2TiO_2Al_2(OPr^i)_3(CA^1)]$ (85.6)	11.98 (12.32)	09.87 (10.50)	08.87 (09.14)
2.	$[(OAc)_2TiO_2Al_2(OPr^i)_4]$ 0.387 (0.794)	HCA^1 0.136 (1.588)	1:2	8½	$[(OAc)_2TiO_2Al_2(OPr^i)_2(CA^1)_2]$ (84.8)	23.55 (24.64)	09.23 (09.98)	08.34 (08.68)
3.	$[(OAc)_2TiO_2Al_2(OPr^i)_4]$ 0.403 (0.827)	HCA^2 0.082 (0.827)	1:1	6½	$[(OAc)_2TiO_2Al_2(OPr^i)_3(CA^2)]$ (82.6)	11.87 (12.32)	09.32 (10.26)	08.56 (08.93)
4.	$[(OAc)_2TiO_2Al_2(OPr^i)_4]$ 0.389 (0.798)	HCA^2 0.159 (1.597)	1:2	9	$[(OAc)_2TiO_2Al_2(OPr^i)_2(CA^2)_2]$ (83.5)	23.12 (24.64)	09.21 (09.52)	08.01 (08.28)
5.	$[(OAc)_2TiO_2Al_2(OPr^i)_4]$ 0.354 (0.726)	HCA^3 0.083 (0.726)	1:1	9	$[(OAc)_2TiO_2Al_2(OPr^i)_2(CA^3)_2]$ (83.5)	11.93 (12.12)	09.82 (10.01)	08.32 (08.71)
6.	$[(OAc)_2TiO_2Al_2(OPr^i)_4]$ 0.335 (0.687)	HCA^3 0.157 (1.375)	1:2	9	$[(OAc)_2TiO_2Al_2(OPr^i)_2(CA^3)_2]$ (83.5)	23.92 (24.24)	09.14 (09.12)	07.74 (07.93)

TABLE 2 – Analytical and physical data of the studied compounds

S.No.	Compound	Empirical formula	Formula weight	Anal. Found (Calcd) % C	H	O
1.	$[(OAc)_2TiO_2Al_2(OPr^i)_4]$	$C_{16}H_{34}Al_2TiO_{10}$	487	38.54 (39.42)	6.45 (6.98)	31.69 (32.79)
2.	$[(OAc)_2TiO_2Al_2(OPr^i)_3(CA^1)]$	$C_{18}H_{36}Al_2TiO_{10}$	514	41.23 (42.02)	6.87 (7.00)	31.57 (31.12)
3.	$[(OAc)_2TiO_2Al_2(OPr^i)_2(CA^1)_2]$	$C_{20}H_{38}Al_2TiO_{10}$	541	43.21 (44.36)	6.67 (7.02)	28.65 (29.57)
4.	$[(OAc)_2TiO_2Al_2(OPr^i)_3(CA^2)]$	$C_{19}H_{38}Al_2TiO_{10}$	526	46.15 (46.78)	5.69 (6.1)	29.11 (29.83)
5.	$[(OAc)_2TiO_2Al_2(OPr^i)_2(CA^2)_2]$	$C_{22}H_{42}Al_2TiO_{10}$	567	43.19 (43.35)	4.98 (5.20)	27.53 (27.75)
6.	$[(OAc)_2TiO_2Al_2(OPr^i)_2(CA^3)_1]$	$C_{20}H_{40}Al_2TiO_{10}$	539	43.29	7.13	28.53

			(44.52)	(7.42)	(29.68)
7.	$[(OAc)_2TiO_2Al_2(OPr^i)_2(CA^3)_2]$	$C_{24}H_{46}Al_2TiO_{10}$	592	46.79	7.58	27.44
				(48.64)	(7.77)	(27.02)

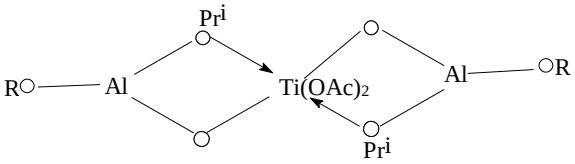

Figure 1: Suggested structure of $[(OAc)_2Al_2O_2Ti(OPr^i)_2(OR)_2]$ Where OR=Cycloalkanol anion