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Synthesis, spectral and thermal studies on salicylate derivatives of heterobimetallic [Ca(II)-Ti(IV)]-μ-oxoisopropoxide

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ABSTRACT

The methyl, ethyl and phenyl Salicylate derivatives of heterobimetallic-μ-oxoisopropoxide [$CaO_2Ti_2(OPr^i)_6$] have been prepared as a result of many reactions of μ-oxoisopropoxide with methyl Salicylate ($HRSAL^1$), ethyl Salicylate ($HRSAL^2$), and phenyl Salicylate ($HRSAL^3$) in different molar ratios (1:1-1:4). The Salicylate derivatives of the type [$CaO_2Ti_2(OPr^i)_{6-n}(RSAL)_n$] (where n is 1-4 and RSAL = Salicylate anion) were obtained. The Salicylate derivatives have been characterized by elemental, spectral (IR, ^1H, ^{13}C NMR), thermal and molecular weight measurement. Hydrothermally assisted sol-gel process gives the hydrolyzed product and thermal study of these products favors the formation of multicomponent oxides. The studies reveal that Salicylate derivatives are monomeric in nature and low susceptible to hydrolysis as compared to parent compound and may prove excellent precursors for the mixed metal oxides.

KEYWORDS

Heterobimetallic-μ-oxoisopropoxide;
Calcium;
Titanium;
Salicylate;
Thermoanalysis.

INTRODUCTION

The investigation and the use of heterometallic alkoxides as single-source molecules precursors for synthesis of oxides have seen a rapid growth during the last more than one and half decade. The bimetallic oxo complexes, the 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[1]. Nano-structured oxide, the new type of materials shows properties different from materials with μm-scale microstructures are gaining more and more interests during the past few years. A variety of chemical routes have been developed to prepare ceramic nano-structures, because the traditional solid-state method could not meet particle size requirements and versatility of synthesis process. Some chemical methods offer possibly a preparation at lower temperatures, a homogenous primary structure and limited higher order aggregation and a small distribution of particle sizes. 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[2]. The mixed metal oxides prepared

from heterometallic-μ-oxoalkoxides[3-6] have been used for absorbing harmful chemicals[7] and decontaminating chemical warfare agents[8]. The alkaline earth metal titanates like barium titanate, calcium titanate ($CaTiO_3$), strontium titanate ($SrTiO_3$ and $Ba_xSr_{1-x}TiO_3$) due to their exceptional properties expose potential applications in multilayer ceramic capacitors, electro-optic, dielectric and piezoelectric devices[9-12]. The perovskite $CaTiO_3$ with its unique structure, higher stability and biocompatibility, finds potential application in the fields of communication, electronics and in biotechnology[13-15]. The ability of immobilizing the rare earths of $CaTiO_3$ by forming solid solutions with highly radioactive wastes makes the $CaTiO_3$ useful for disposal of highly radioactive wastes[16-17]. Recently, calcium titanate has also been used as a competent anticorrosion pigment for paints[18]. 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[19-20].

In the present investigation, the derivatives of heterobimetallic [Ca (II)-Ti (IV)]-μ-oxoisopropoxide are prepared from the condensation of $[CaO_2Ti_2(OPr^i)_6]$ with different Salicylates in molar ratios (1:1-1:4) , and the reaction proceeds with stepwise formation of Salicylate derivatives of bimetallic [Ca (II)-Ti (IV)]-μ-oxoisopropoxide, which are the molecular species that can be purified by distillation, allowing the isolation of pure molecular precursors.

EXPERIMENTAL

Instrumentation, reagents and general techniques

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[21-26]. Hydrated calcium acetate (Aldrich) was made anhydrous with acetic anhydride and titanium isopropoxide $[Ti(OPr^i)_4]$ (Aldrich) used without further purification. The methyl salicylate ($HRSAL^1$), ethyl salicylate ($HRSAL^2$), and phenyl salicylate ($HRSAL^3$) were prepared in laboratory and purified before use. The isopropoxy groups in the μ-oxoisopropoxide and liberated isopropanol formed in preparation of Salicylate derivatives were estimated oxidimetrically. Calcium was determined complexometrically and gravimetric estimation has been done for titanium[25]. Titanium was estimated as TiO_2 via the formation of titanium-phenazone complex [25]. 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. TG study has been made on Diamond TG/DTA PerkinElmer instrument. Elemental analyses were carried out by PerkinElmer 2400 II series CHNS/O Analyzer.

Synthesis of derivatives of $[CaO_2Ti_2(OPr^i)_6]$ with salicylates

The [Ca (II)-Ti (IV)]-μ-oxoisopropoxide was synthesized by reported methods on thermal condensation of $Ca(OAc)_2$ and $Ti(OPr^i)_4$ in mixture of xylene and decalin in 1:2 molar ratio[21-24].

Reaction of μ-oxo compound with methyl salicylate in 1:1 molar ratio

The $[CaO_2Ti_2(OPr^i)_6]$ (0.666 g, 1.282 mmol) and methyl salicylate (0.195g, 1.282 mmol) were refluxed in benzene were refluxed in ~ 50 ml 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 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 Salicylate derivatives were carried out by similar procedure and the analytical results have been summarized in TABLE 1.

The hydrolyzed product of Salicylates of μ-oxo compound obtained by hydrothermally assisted sol-gel processing. For the hydrothermally assisted sol-gel processing, Salicylate derivatives were diluted 20 times by weight with isopropanol, the mixture was loaded into a glass container and transferred into a 300 ml stainless steel autoclave. Dilution of Salicylate derivatives and their transfer into autoclave was per-

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formed in moisture-free atmosphere to prevent their hydrolysis before introducing into a hydrothermal chamber. The gap between glass container and chamber was filled with 40 ml of distilled water and then the autoclave was tightly closed. The chamber was heated 120°C for five hours, the autoclave was cooled and the product was filtered off and dried overnight at 100°C.

TABLE 1 : Analytical and physical data of studied compounds

S.No.	Compound g(mmol)	Ligand g(mmol)	Refluxing time(h)	Product (%)	Anal. Found (calcd.)					
					OPr^i(g)	Ca(%)	Ti(%)	C(%)	H(%)	O(%)
1	$[CaO_2Ti_2(OPr^i)_6]$ 0.666 (1.282)	$HRSAL^1$ 0.195(1.282)	7	$[CaO_2Ti_2(OPr^i)_5(RSAL^1)]$78.9	0.03 (0.03)	6.65 (6.53)	14.99 (15.35)	45.12 (45.09)	6.81 (6.86)	19.98 (20.91)
2	$[CaO_2Ti_2(OPr^i)_6]$ 0.439 (0.845)	$HRSAL^1$ 0.257(1.690)	8½	$[CaO_2Ti_2(OPr^i)_4(RSAL^1)_2]$ 75.3	0.06 (0.06)	5.31 (5.68)	13.22 (13.35)	47.54 (47.72)	5.97 (5.96)	22.65 (22.72)
3	$[CaO_2Ti_2(OPr^i)_6]$ 0.419 (0.807)	$HRSAL^1$ 0.368(2.241)	9	$[CaO_2Ti_2(OPr^i)_3(RSAL^1)_3]$80.5	0.09 (0.09)	4.86 (5.02)	11.69 (11.80)	49.65 (49.74)	5.12 (5.27)	24.05 (24.12)
4	$[CaO_2Ti_2(OPr^i)_6]$ 0.359 (0.692)	$HRSAL^1$ 0.421(2.769)	12	$[CaO_2Ti_2(OPr^i)_2(RSAL^1)_4]$79.3	0.11 (0.12)	4.29 (4.5)	10.35 (10.58)	50.98 (51.35)	5.5 (4.72)	23.97 (25.22)
5	$[CaO_2Ti_2(OPr^i)_6]$ 0.601 (1.157)	$HRSAL^2$ 0.191(1.157)	7	$[CaO_2Ti_2(OPr^i)_5(RSAL^2)]$81.6	0.03 (0.03)	6.29 (6.4)	14.86 (15.04)	45.79 (46.08)	6.94 (7.04)	20.14 (20.48)
6	$[CaO_2Ti_2(OPr^i)_6]$ 0.430 (0.827)	$HRSAL^2$ 0.273(1.654)	9	$[CaO_2Ti_2(OPr^i)_4(RSAL^2)_2]$80.5	0.06 (0.06)	5.37 (5.47)	12.38 (12.87)	49.19 (49.31)	6.24 (6.30)	21.78 (21.91)
7	$[CaO_2Ti_2(OPr^i)_6]$ 0.374 (0.719)	$HRSAL^2$ 0.356(2.157)	10½	$[CaO_2Ti_2(OPr^i)_3(RSAL^2)_3]$78.6	0.09 (0.09)	4.67 (4.79)	11.19 (11.25)	51.32 (51.73)	5.72 (5.74)	21.68 (22.99)
8	$[CaO_2Ti_2(OPr^i)_6]$ 0.365 (0.703)	$HRSAL^2$ 0.464(2.812)	12	$[CaO_2Ti_2(OPr^i)_4(RSAL^2)_4]$80.4	0.11 (0.12)	4.33 (4.25)	9.36 (10.0)	53.39 (53.61)	5.32 (5.31)	23.21 (23.82)
9	$[CaO_2Ti_2(OPr^i)_6]$ 0.410 (0.789)	$HRSAL^3$ 0.169(0.789)	7	$[CaO_2Ti_2(OPr^i)_5(RSAL^3)]$81.3	0.03 (0.03)	5.89 (5.93)	13.75 (13.94)	49.32 (49.85)	6.42 (6.52)	18.28 (18.99)
10	$[CaO_2Ti_2(OPr^i)_6]$ 0.348 (0.670)	$HRSAL^3$ 0.287(1.341)	8½	$[CaO_2Ti_2(OPr^i)_4(RSAL^3)_2]$81.9	0.06 (0.06)	4.60 (4.83)	10.97 (11.35)	54.64 (55.07)	5.54 (5.55)	19.14 (19.32)
11	$[CaO_2Ti_2(OPr^i)_6]$ 0.320 (0.616)	$HRSAL^3$ 0.396(1.850)	10½	$[CaO_2Ti_2(OPr^i)_3(RSAL^3)_3]$81.5	0.08 (0.09)	3.98 (4.07)	9.34 (9.57)	58.66 (58.65)	4.66 (4.88)	18.85 (19.55)
12	$[CaO_2Ti_2(OPr^i)_6]$ 0.289 (0.556)	$HRSAL^3$ 0.476(2.224)	12	$[CaO_2Ti_2(OPr^i)_2(RSAL^3)_4]$78.9	0.11 (0.12)	3.45 (3.52)	8.09 (8.27)	61.01 (61.26)	4.25 (4.40)	19.47 (19.78)

RESULTS AND DISCUSSION

To overcome the phase segregation problem and provide a excellent precursors for bi-component oxides, many reactions of [Ca (II)-Ti (IV)]-μ-oxoisopropoxide with bidentate Salicylates (HRSAL) i.e. methyl salicylate ($HRSAL^1$), ethyl salicylate ($HRSAL^2$), phenyl salicylate ($HRSAL^3$) are performed in different molar ratios in refluxing benzene, yielding the products of type $[CaO_2Ti_2(OPr^i)_5(RSAL)]$, $[CaO_2Ti_2(OPr^i)_4(RSAL)_2]$, $[CaO_2Ti_2(OPr^i)_3(RSAL)_3]$ and $[CaO_2Ti_2(OPr^i)_2(RSAL)_4]$. The preparation of the Salicylate derivatives of $[CaO_2Ti_2(OPr^i)_6]$ follows the following reaction scheme 1:

The $[CaO_2Ti_2(OPr^i)_6]$ and its salicylate derivatives are susceptible to hydrolysis and soluble in common organic solvents such as benzene, chloroform and carbon tetrachloride etc. 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 isopropoxy groups of [Ca (II)-Ti (IV)]-μ-oxoisopropoxide could be replaced by Salicylates. Futher replacement of isopropoxy groups could not be achieved even with an excess of ligand (salicylates) and prolonged refluxing time (26 h). This indicates the non-replacement of bridging isopropoxy groups and that only terminal isopropoxy groups are substituted by salicylates.

$$[CaO_2Ti_2(OPr^i)_6] + nHRSAL \xrightarrow{\text{refluxing benzene}} [CaO_2Ti_2(OPr^i)_{6-n}(RSAL)_n] + nPr^iOH$$

(n= 1-4, HRSAL = methyl/ethyl/phenyl Salicylate)

Scheme 1

Spectral analysis of salicylate derivatives of $[CaO_2Ti_2(OPr^i)_6]$

IR spectra

The IR spectra of salicylates show a broad band in the region 3000-2700 cm^{-1}due to (O-H), the absence of this band in the derivatives of μ-oxocompounds indicates the deprotonation of these ligands. The ν(C-O) band appearing at ~1645 cm^{-1} in salicylates shows a downward shift of 15-25 cm^{-1} in the derivatives, indicating the coordination of the carbonyl oxygen of the salicylates to the metal atom. A strong band observed at ~1240cm^{-1} in salicylates due to phenolic ν(C-O) vibrations is shifted 10-20cm^{-1} higher in the derivatives indicating bond formation of phenolic oxygen of salicylate to the metal atom. All the derivatives show an absorption band in the region 1360-1340 cm^{-1} is characteristic of *gem*-dimethyl of the isopropoxy group. The bands observed at about 1160 and 1120 cm^{-1} in 1:3 salicylate derivatives of $[CaO_2Ti_2(OPr^i)_6]$ have been assigned to combination bands ν(C-O+OPr^i) non-bridging and ν(C-O+OPr^i) bridging of the isopropoxy groups respectively[27]. However, the band at~1160 cm^{-1} due to ν(C-O+OPr^i) terminal is absent in 1:4 salicylate derivatives suggests the presence of bridging isopropoxy groups only. The vibration occurring at ~940 cm^{-1} in all the derivatives has been assigned to (C-O) of the bridging isopropoxy group. A number of bands appearing in the region 700-400 $cm^{-1}$are due to M-O stretching vibrations in these derivatives[28-29]. The bands related to phenyl groups in the salicylate derivatives are observed at their usual positions in the IR spectra as observed in the ligands[29]. The IR spectra of the derivatives indicate that salicylates behave as monobasic bidentate ligands.

NMR spectra

^{1}H NMR spectra of all the Salicylate derivatives of $[CaO_2Ti_2(OPr^i)_6]$ show broad multiplet centered between δ 0.8–1.2 ppm due to the intermixing of methyl protons of isopropoxy groups. A broad multiplet centered at δ 4.1 is due to the methine proton of isopropoxy groups in the spectra of all derivatives. Very similar spectra obtained for compounds formed by reactions of 1:5 and 1:6 molar ratios of μ-oxo compound and Salicylates as of 1:4 Salicylate derivatives of μ-oxoisopropoxide. This confirms the non-replacement of bridging isopropoxy groups by Salicylates.

The ^{1}H NMR spectra of salicylates show a broad singlet at ~δ12.9 ppm due to phenolic O-H proton, the absence this peak in the derivatives confirms their deprotonation. The peak at ~δ 3.9 ppm due to methyl protons of methyl salicylate and methene proton of the ethyl salicylate is found to overlap with the multiplet centered at δ 4.2 ppm due to methine protons of the isopropoxy group in the derivatives of $[CaO_2Ti_2(OPr^i)_6]$. A broad doublet centered at ~δ1.2 ppm is observed in mono to tri derivatives is due to the methyl protons of different types of isopropoxy groups (terminal and intramolecularly bridged). However, a fairly sharp doublet at δ1.1ppm is observed in methyl and phenyl salicylate tetra derivatives indicate the presence of only one type of isopropoxy group/s (probably bridging). In case of ethyl salicylate derivatives the methyl protons are mixed with the methyl protons of the isopropoxy group resulting in a broad peak centered at δ1.1ppm. The signals due to phenyl ring protons of salicylate moiety are observed at their usual positions (δ6.4 – δ7.6 ppm) in all the derivatives.

The ^{13}C NMR spectra mono derivatives of $[CaO_2Ti_2(OPr^i)_6]$ shows two prominent peaks at δ ~26.3 and δ ~28.2 ppm assignable to the methyl carbon of terminal and interamolecularly bridged isopropoxy moiety and two different type of methine carbons of isopropoxy group is confirmed by the two signals observed at δ ~62.6 ppm and δ ~63.7 ppm[30]. The spectra of 1:4 Salicylate derivatives of μ-oxoisopropoxide show the absence of terminal isopropoxy group. Very similar spectra obtained for compounds formed by reactions of 1:5 and 1:6 molar ratios of μ-oxo compound and Salicylates as of 1:4 Salicylate derivatives of μ-oxoisopropoxide. This confirms the non-replacement of bridging isopropoxy groups by Salicylates.

The peaks observed in the region δ122-145 ppm are due to carbon atoms on benzene ring, however, the peak observed at about δ165-169 ppm is due to ring carbon linked to the ester group and a peak observed at about δ186-189ppm is due to carbon of the ester group (-COOR)[30].

Thermal studies

The thermal decomposition of Salicylate derivatives of $[CaO_2Ti\ (OPr^i)_4]$ have been examined by thermogravimetric analysis under a flow of dry nitrogen, up to 800°C at a heating rate of 10°C/min. The

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minor weight loss (1.65-1.89 %) starts at 56.5-59.8ºC and completed at 185-187ºC with a weight loss of due to presence of moisture and fraction of solvent present, if any. The second and major one starts at 180-185ºC and is completed at 359-363ºC, resulting in a residue amounting to 11.589-12.957% of the initial weight, probably due to the decomposition of partially hydrolyzed μ-oxo Salicylate into metal/mixed metal oxides suggesting the volatile nature of compound[31].

TABLE 2 : Study of thermograms of hydrolyzed product of various salicylate derivatives of $[CaO_2Ti(OPr^i)_4]$

Sr. No.	Compound	Temperature range (ºC)	Weight loss (%)
1.	$[CaO_2Ti_2(OPr^i)_5(RSAL^1)]$	(a) 55-220 (b) 220-345 (c) >345	(a) 6 (b) 41.22 (c) No significant loss
2.	$[CaO_2Ti_2(OPr^i)_4(RSAL^1)_2]$	(a) 54-222 (b) 222-349 (c) >349	(a) 6 (b) 53.83 (c) No significant loss
3.	$[CaO_2Ti_2(OPr^i)_3(RSAL^2)_3]$	(a) 58-219 (b) 219-352 (c) >352	(a) 4 (b) 61.85 (c) No Significant loss
4.	$[CaO_2Ti_2(OPr^i)_2(RSAL^2)_4]$	(a) 56-221 (b) 221-355 (c) >355	(a) 5 (b) 66.94 (c) No significant loss
5.	$[CaO_2Ti_2(OPr^i)_5(RSAL^3)]$	(a) 57-220 (b) 220-348 (c) >348	(a) 4 (b) 42.39 (c) No significant loss
6.	$[CaO_2Ti_2(OPr^i)_4(RSAL^3)_2]$	(a) 59-225 (b) 225-355 (c) >355	(a) 6 (b)54.23 (c) No significant loss
7.	$[CaO_2Ti_2(OPr^i)_3(RSAL^4)_3]$	(a) 56-224 (b) 224-350 (c) >350	(a) 5 (b) 64.59 (c) No significant loss
8.	$[CaO_2Ti_2(OPr^i)_2(RSAL^4)_4]$	(a) 61-230 (b) 230-355 (c) >355	(a) 4 (b) 71.37 (c) No significant loss
9.	$[CaO_2Ti_2(OPr^i)_5(RSAL^1)]$	(a) 53-224 (b) 224-348 (c) >348	(a) 5 (b) 47.31 (c) No significant loss
10.	$[CaO_2Ti_2(OPr^i)_4(RSAL^1)_2]$	(a) 54-223 (b) 223-351 (c) >351	(a) 6 (b) 60.0 (c) No significant loss
11.	$[CaO_2Ti_2(OPr^i)_3(RSAL^2)_3]$	(a) 58-221 (b) 221-356 c) >356	(a) 5 (b) 68.99 (c) No significant loss
12.	$[CaO_2Ti_2(OPr^i)_4(RSAL^2)_2]$	(a) 57-224 (b) 224-359 (c) >359	(a) 4 (b) 72.24 (c) No significant loss

The thermogravimetric analysis of various hydrolyzed product of different Salicylate derivatives have been performed up to 800ºC at 10ºC/min. Thermograms of various hydrolysed Salicylate derivatives studied as, the weight loss in stage (a) observed due to the traces of water and solvent present in hydrolyzed product of μ-oxo compound. The major weight loss in stage (b) occurs probably due to the elimination of hydroxy groups and organic moieties present in the hydrolyzed product which is directly followed by last stage (c) ranging from 345-359º C to 800ºC, leaving a residue that is less than the calculated for mixed metal oxide and metal oxides ($CaTiO_3$ and TiO_2). The detailed study of thermograms of hydrolyzed product of various Salicylate derivatives is summarized in TABLE 2.

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

CONCLUSION

The aforementioned studies reveals the suggestive structures of Salicylate derivatives of oxo complex of the type $[CaO_2Ti_2(OPr^i)_5(RSAL)]$, $[CaO_2Ti_2(OPr^i)_4(RSAL)_2]$, $[CaO_2Ti_2(OPr^i)_3(RSAL)_3]$ and $[CaO_2Ti_2(OPr^i)_2(RSAL)_4]$. TGA study reveals the volatile nature of derivatives and their hydrolysed product may fabricate the mixed metal oxides. The proposed structures double and terta derivatives are given in Figure 1 and Figure 2 respectively.

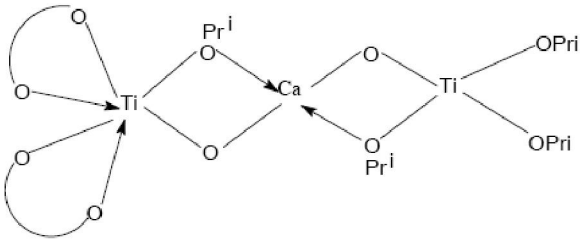

Figure 1: Suggested structure of $[CaO_2Ti_2(OPr^i)_4(RSAL)_2]$

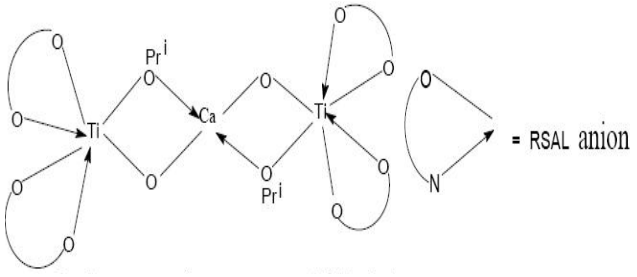

Figure 2: Suggested structure of $[CaO_2Ti_2(OPr^i)_2(RSAL)_4]$

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