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RESEARCH ARTICLE

Synthesis, Characterisation and Thermal Behaviour of Salicylates of Heterobimetallic [Ca(II)-Sn(IV)]-μ-Oxoisopropoxide

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Abstract: The heterobimetallic-μ-oxoisopropoxide $[CaO_2Sn_2(OPr^i)_6]$ provides different salicylate derivatives of the type $[CaO_2Sn_2(OPr^i)_{6-n}(RSAL)_n]$ (where n is 1-4 and RSAL = Salicylate anion) with methyl salicylate ($HRSAL^1$), ethyl salicylate ($HRSAL^2$) and phenyl salicylate ($HRSAL^3$). The derivatives have been characterized by elemental, spectral (IR, ^1H, ^{13}C NMR), thermal and molecular weight measurement. The hydrolyzed product of these salicylate derivatives obtained by hydrothermally assisted sol-gel process favors the formation of multicomponent oxides subject to their thermal study. The studies reveal that salicylate derivatives are monomeric in nature and low susceptible to hydrolysis in comparison to parent compound and may prove excellent precursors for the mixed metal oxides.

Keywords: Heterobimetallic-μ-oxoisopropoxide, Calcium, Tin, Salicylates, Thermal analysis

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]. 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 multicomponent oxides synthesised as a result of 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]. 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 $CaSnO_3$ cubes exhibit high sensitivity, selectivity and reversibility to ethanol sensing due to a good combination of high specific surface areas, multi-composition and well-defined geometrics leading to selective surface activities of cubic shape $CaSnO_3$ crystals[10]. Alkaline earth stannates have gained considerable attraction in recent years because of thermal stability in air and strong physical and chemical interaction with absorbed species. The materials have a variety of applications in ceramic dielectrics[11,12], gas-sensing materials[13] and battery electrode bodie[s14]. The absorbed oxygen atom on the surface of the metal oxide, influences its electrical properties by producing an electron-depleted space-charge layer in the space-charge region of the species and makes the study more interested. Among the metal oxides, SnO_2 acts as an important base material for gas sensing devices. Similarly, Calcium stannate in a pure and in doped form has been shown a gas sensing materials[15-17]. There are many articles about properties and behaviour of these type of materials, but no thoroughly and reliable studies are available on synthesis and thermodynamic stability of them in the SnO_2, $CaSnO_3$ and Ca_2SnO_4 configurations. 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.

In the present investigation, the derivatives of heterobimetallic [Ca(II)-Sn(IV)]-μ-oxoisopropoxide are prepared from the condensation of $[CaO_2Sn_2(OPr^i)_6]$ with different salicylates in molar ratios (1:1-1:4) and the reaction proceeds with stepwise formation of salicylate derivatives of bimetallic [Ca(II)-Sn(IV)]-μ-oxoisopropoxide, which are the molecular species that can be purified by distillation, allowing the isolation of pure molecular precursors.

Experimental

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[18-23]. Hydrated calcium acetate (Aldrich) was made anhydrous with acetic anhydride and titanium isopropoxide $[Sn(OPr^i)_4]$ (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[22]. Titanium was estimated as TiO_2 via the formation of titanium-phenazone complex[22]. 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 $[CaO_2Sn_2(OPr^i)_6]$ with salicylates

The [Ca(II)-Sn(IV)]-μ-oxoisopropoxide was synthesized by reported methods on thermal condensation of $Ca(OAc)_2$ and $Sn(OPr^i)_4$ in mixture of xylene and decalin in 1:2 molar ratio[18-21].

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

The $[CaO_2Sn_2(OPr^i)_6]$ (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 ^oC 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.

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 %	Sn%	C%	H%	O%
1	$[CaO_2Sn_2(OPr^i)_6]$ 0.860 (1.296)	$HRSAL^1$ 0.197 (1.296)	8	$[CaO_2Sn_2(OPr^i)_5(RSAL^1)]$ 80.1	0.05 (0.06)	5.21 (5.29)	31.44 (31.48)	37.95 (38.09)	5.51 (5.55)	19.01 (19.04)
2	$[CaO_2Sn_2(OPr^i)_6]$ 0.565 (0.852)	$HRSAL^1$ 0.259 (1.704)	10	$[CaO_2Sn_2(OPr^i)_4(RSAL^1)_2]$ 77.5	0.08 (0.09)	4.78 (4.71)	28.14 (28.06)	42.42 (42.45)	4.93 (4.95)	22.65 (22.64)
3	$[CaO_2Sn_2(OPr^i)_6]$ 0.563 (0.848)	$HRSAL^1$ 0.387 (2.546)	12	$[CaO_2Sn_2(OPr^i)_3(RSAL^1)_3]$ 79.1	0.09 (0.11)	4.22 (4.25)	25.22 (25.31)	45.87 (45.95)	5.47 (4.46)	25.32 (25.53)
4	$[CaO_2Sn_2(OPr^i)_6]$ 0.493 (0.743)	$HRSAL^1$ 0.452(2.973)	14	$[CaO_2Sn_2(OPr^i)_2(RSAL^1)_4]$ 79.3	0.13 (0.15)	3.71 (3.87)	23.19 (23.06)	48.89 (48.83)	4.07 (4.07)	27.78 (27.9)
5	$[CaO_2Sn_2(OPr^i)_6]$ 0.760 (1.145)	$HRSAL^2$ 0.189 (1.145)	8	$[CaO_2Sn_2(OPr^i)_5(RSAL^2)]$ 80.8	0.08 (0.09)	5.14 (5.2)	30.87 (30.94)	39.12 (39.01)	5.75 (5.72)	18.85 (18.72)
6	$[CaO_2Sn_2(OPr^i)_6]$ 0.573 (0.863)	$HRSAL^2$ 0.285 (1.727)	10	$[CaO_2Sn_2(OPr^i)_4(RSAL^2)_2]$ 80.2	0.06 (0.06)	4.44 (4.57)	27.21 (27.23)	43.91 (43.93)	5.22 (5.26)	21.98 (21.96)
7	$[CaO_2Sn_2(OPr^i)_6]$ 0.528 (0.795)	$HRSAL^2$ 0.394 (2.387)	12½	$[CaO_2Sn_2(OPr^i)_3(RSAL^2)_3]$ 78.8	0.09 (0.10)	4.01 (4.08)	24.26 (24.31)	47.79 (47.80)	4.84 (4.9)	24.52 (24.51)
8	$[CaO_2Sn_2(OPr^i)_6]$ 0.480 (0.724)	$HRSAL^2$ 0.478 (2.896)	14	$[CaO_2Sn_2(OPr^i)_4(RSAL^2)_4]$ 79.4	0.13 (0.14)	3.74 (3.69)	21.88 (21.95)	50.99 (50.92)	4.69 (4.61)	26.54 (26.56)
9	$[CaO_2Sn_2(OPr^i)_6]$ 0.580 (0.873)	$HRSAL^3$ 0.187 (0.873)	8	$[CaO_2Sn_2(OPr^i)_5(RSAL^3)]$ 81.5	0.03 (0.04)	4.77 (4.89)	29.79 (29.89)	42.59 (42.54)	5.38 (5.37)	17.57 (17.6)

Contd…

10	$[CaO_2Sn_2(OPr^i)_6]$ 0.442 (0.666)	$HRSAL^3$ 0.285 (1.331)	10½	$[CaO_2Sn_2(OPr^i)_4(RSAL^3)_2]$ 80.5	0.06 (0.07)	4.16 (4.11)	24.39 (24.48)	49.27 (49.38)	4.68 (4.73)	19.78 (19.75)
11	$[CaO_2Sn_2(OPr^i)_6]$ 0.426 (0.641)	$HRSAL^3$ 0.412 (1.925)	12½	$[CaO_2Sn_2(OPr^i)_3(RSAL^3)_3]$ 80.2	0.08 (0.10)	3.52 (3.55)	21.08 (21.13)	54.55 (54.59)	4.22 (4.26)	21.35 (21.31)
12	$[CaO_2Sn_2(OPr^i)_6]$ 0.401 (0.604)	$HRSAL^3$ 0.517 (2.416)	14	$[CaO_2Sn_2(OPr^i)_2(RSAL^3)_4]$ 78.4	0.12 (0.13)	3.09 (3.12)	18.55 (18.59)	58.17 (58.12)	3.88 (3.9)	22.41 (22.5)

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 performed 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.

Results and Discussion

Many reactions of [Ca(II)-Sn(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 $[CaO_2Sn_2(OPr^i)_5(RSAL)]$, $[CaO_2Sn_2(OPr^i)_4(RSAL)_2]$, $[CaO_2Sn_2(OPr^i)_3(RSAL)_3]$ and $[CaO_2Sn_2(OPr^i)_2(RSAL)_4]$. The preparation of the salicylate derivatives of $[CaO_2Sn_2(OPr^i)_6]$ follows the following reaction scheme 1:

$$[CaO_2Sn_2(OPr^i)_6] + nHRSAL \xrightarrow{\text{refluxing benzene}} [CaO_2Sn_2(OPr^i)_{6-n}(RSAL)_n] + nPr^iOH$$

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

Scheme 1

The 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)-Sn(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.

Spectral Analysis of salicylate derivatives of $[CaO_2Sn_2(OPr^i)_6]$

IR spectra

The complete disappearance of a broad band in the region 3000-2700 cm^{-1} due to ν(O-H), in all μ-oxo salicylate deivatives indicates the deprotonation of these ligands. The downward shift of 15-25 cm^{-1} in ν(C-O) band appearing at ~1645 cm^{-1} in salicylate derivatives are indicating

the coordination of the carbonyl oxygen of the salicylates to the metal atom. A strong band observed at ~1240 cm^{-1} in salicylates due to phenolic ν(C-O) vibrations is shifted 10-20 cm^{-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 $[CaO_2Sn_2(OPr^i)_6]$ 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[24]. 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 ν(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[25-26]. 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[26]. 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 $[CaO_2Sn_2(Opr^i)_6]$ 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 4.1-4.4 observed due to the ethane 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 ethane proton of the ethyl salicylate is found to overlap with the multiplet centered at δ 4.2 ppm due to ethane protons of the isopropoxy group in the derivatives of $[CaO_2Sn_2(Opr^i)_6]$. 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 δ1.1 ppm. 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 $[CaO_2Sn_2(Opr^i)_6]$ shows two prominent peaks at δ 26.3-26.7 and δ 28.1.28.9 ppm assignable to the methyl carbon of terminal and interamolecularly bridged isopropoxy moiety and two different type of ethane carbons of isopropoxy group is confirmed by the two signals observed at δ 62.6-62.9 ppm and δ ~63.4-64.2 ppm[27]. The spectra of 1:4 salicylate derivatives of *μ*-oxoisopropoxide show the absence of terminal isopropoxy group. All signals of $[CaO_2Sn_2(Opr^i)_2(RSAL)_4]$ are experiential in the spectra taken for compounds formed by reactions of 1:5 and 1:6 molar ratios of μ-oxo compound and salicylates confirms the non-replacement of bridging isopropoxy groups by salicylates. The peaks observed in the region δ128.8-141.3 ppm are due to carbon atoms on benzene ring, however, the peak observed at about δ163.8-169.9 ppm is due to ring carbon linked to the ester group and a peak observed at δ175.3-182.7 ppm is due to carbon of the ester group (-COOR)[27].

Thermal studies

The thermal decomposition of salicylate derivatives of $[CaO_2Sn(OPr^i)_4]$ have been examined by thermogravimetric analysis under a flow of dry nitrogen, up to 800 ^oC at a heating rate of 10 ºC/min. The minor weight loss (1.77-2.12%) starts at 55.5-59.8 ºC and completed at 184.8-188.5 ºC with a weight loss of due to presence of moisture and fraction of solvent present, if any. The second and major one starts at 1884.8-188.5 ºC and is completed at 359-363 ºC, resulting in a residue amounting to 12.247-13.857% 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[28].

The thermogravimetric analysis of various hydrolyzed product of different salicylate derivatives have been performed up to 800 ^oC at 10 ^oC/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 345-359 ºC to 800 ºC, leaving a residue that is less than the calculated for mixed metal oxide and metal oxides ($CaSnO_3$ and SnO_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.

Table 2. Study of thermograms of hydrolyzed product of various salicylate derivatives of $[CaO_2Sn(OPr^i)_4]$

S. No.	Compound	Temperature range, ºC	Weight loss, %
1.	$[CaO_2Sn_2(OPr^i)_5(RSAL^1)]$	(a) 54-215, (b) 215-350 (c) >350	(a) 6, (b) 47.84 (c) No significant loss
2.	$[CaO_2Sn_2(OPr^i)_4(RSAL^1)_2]$	(a) 54-218, (b) 218-354 (c) >354	(a) 5, (b) 54.17 (c) No significant loss
3.	$[CaO_2Sn_2(OPr^i)_3(RSAL^2)_3]$	(a) 56-220, (b) 220-356 (c) >356	(a) 5, (b) 58.36 (c) No Significant loss
4.	$[CaO_2Sn_2(OPr^i)_2(RSAL^2)_4]$	(a) 55-225, (b) 225-358 (c) >358	(a) 4, (b) 62.51 (c) No significant loss
5.	$[CaO_2Sn_2(OPr^i)_5(RSAL^3)]$	(a) 59-228, (b) 228-356 (c) >349	(a) 5, (b) 49.85 (c) No significant loss
6.	$[CaO_2Sn_2(OPr^i)_4(RSAL^3)_2]$	(a) 58-225, (b) 225-352 (c) >352	(a) 6, (b)54.84 (c) No significant loss
7.	$[CaO_2Sn_2(OPr^i)_3(RSAL^4)_3]$	(a) 53-227, (b) 227-355 (c) >355	(a) 4, (b) 61.25 (c) No significant loss
8.	$[CaO_2Sn_2(OPr^i)_2(RSAL^4)_4]$	(a) 61-230, (b) 230-358 (c) >358	(a) 5, (b) 62.41 (c) No significant loss
9.	$[CaO_2Sn_2(OPr^i)_5(RSAL^1)]$	(a) 53-222, (b) 222-350 (c) >350	(a) 5, (b) 53.08 (c) No significant loss
10.	$[CaO_2Sn_2(OPr^i)_4(RSAL^1)_2]$	(a) 58-227, (b) 227-355 (c) >355	(a) 6, (b) 58.48 (c) No significant loss
11.	$[CaO_2Sn_2(OPr^i)_3(RSAL^2)_3]$	(a) 58-228, (b) 228-356 (c) >356	(a) 4, (b) 65.42 (c) No Significant loss
12.	$[CaO_2Sn_2(OPr^i)_4(RSAL^2)_2]$	(a) 61-239, (b) 239-345 (c) >345	(a) 5, (b) 68.22 (c) No significant loss

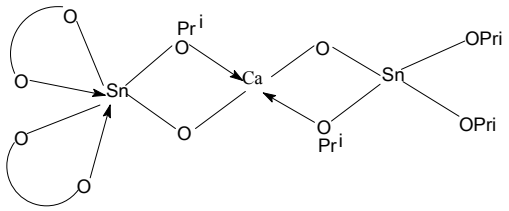


Figure 1. Suggested structure of $[CaO_2Sn_2(OPr^i)_4(RSAL)_2]$

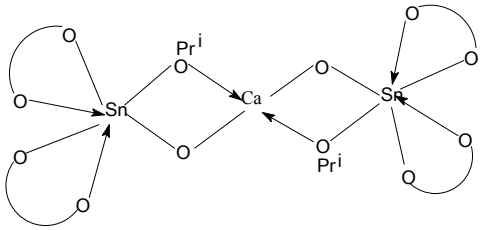
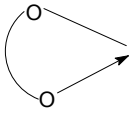


Figure 2. Suggested structure of $[CaO_2Sn_2(OPr^i)_2(RSAL)_4]$



= RSAL anion

Conclusion

The aforementioned studies reveals the suggestive structures of salicylate derivatives of oxo complex of the type $[CaO_2Sn_2(OPr^i)_5(RSAL)]$, $[CaO_2Sn_2(OPr^i)_4(RSAL)_2]$, $[CaO_2Sn_2(OPr^i)_3(RSAL)_3]$ and $[CaO_2Sn_2(OPr^i)_2(RSAL)_4]$. 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.

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