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New Schiff bases derivatives of [Ca(II)-Sn(IV)]-μ-oxoisopropoxide: Synthesis, spectral and thermal studies

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ABSTRACT

New Schiff base derivatives of heterobimetallic-μ-oxoisopropoxide $[CaO_2Sn_2(OPr^i)_6]$ have been synthesized between the thermal condensation of μ-oxoisopropoxide with Salicylidene-aniline (HSB^1), Salicylidene-o-toluidene (HSB^2), and Salicylidene-p-chloroaniline (HSB^3) in different molar ratios (1:1-1:4) yielding the compounds of the type $[CaO_2Sn_2(OPr^i)_{6-n}(SB)_n]$ (where n is 1-4 and SB = Schiff base anion) respectively. The Schiff base derivatives have been characterized by elemental, spectral (IR, ^1H, ^{13}C NMR), thermal and molecular weight measurement. The hydrolyzed products obtained using the hydrothermally assisted sol-gel process was carried to thermal studies which favors the formation of multicomponent oxides. The Schiff base derivatives are found monomeric in nature and less prone to hydrolysis in comparison to parent compound and may prove dazzling precursors for the mixed metal oxides.

KEYWORDS

Heterobimetallic-μ-oxoisopropoxide;
Calcium;
Tin;
Schiff bases;
Thermoanalysis.

INTRODUCTION

In recent years, alkaline earth stannates have gained considerable attraction because of thermal stability in air, and strong physical and chemical interaction with absorbed species. Due to this fact that oxygen atoms absorbed on the surface of the metal oxide, particle influences its electrical properties by producing an electron-depleted space-charge layer in the space-charge region of the species[1,2]. The materials have a diversity of applications in ceramic dielectrics, gas-sensing materials and battery electrode bodies[3,4]. The heterometallic oxoalkoxides as single-source molecules precursors for synthesis of oxides have seen a rapid growth during the last more than one and half decade. The M-O-M' bridges in bimetallic oxo complexes provide homogeneity of the newly formed oxide phases at the molecular level. The above measured inclination 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[5]. 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. Due to the incongruity of traditional solid-state method to meet particle size requirements and versatility of synthesis process, a number of chemical methods have been developed to prepare ceramic nano-structures. 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 mixed metal oxides prepared from heterometallic-μ-oxoalkoxides[6-9] have been used for absorbing harmful chemicals[10] and decontaminating chemical warfare agents[11]. 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[12-15]. The perovskite $CaTiO_3$ with its unique structure, higher stability and biocompatibility, finds potential application in the fields of communication, electronics and in biotechnology[16-18]. 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[19,20]. Recently, calcium titanate has also been used as a competent anticorrosion pigment for paints[21].

In this finding, the Schiff base derivatives of heterobimetallic [Ca(II)-Sn(IV)]-μ-oxoisopropoxide are prepared from the condensation of $[CaO_2Sn_2(OPr^i)_6]$ with different Schiff bases in molar ratios (1:1-1:4), and the reaction proceeds with stepwise formation of Schiff base 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

Instrumentation, reagents and general techniques

All manipulations were conceded out in dry nitrogen atmosphere to exclude the moisture throughout the present investigations. The standard methods were employed for physical measurement and to purify and dry the solvents and reagents used[22-27]. Hydrated calcium acetate (Aldrich) was made anhydrous with acetic anhydride and tin isopropoxide $[Sn\ (OPr^i)_4]$ (Alfa) used without further purification. The Salicylidene-aniline (HSB^1), Salicylidene-o-toluidene (HSB^2), and Salicylidene-p-chloroaniline (HSB^3) were prepared in laboratory and purified before use. The isopropoxy groups in the μ-oxoisopropoxide and liberated isopropanol formed in preparation of Schiff base derivatives were estimated oxidimetrically. Calcium was determined complexometrically and gravimetric estimation has been done for titanium[26]. Tin was estimated as SnO_2 via the formation of titanium-phenazone complex[26]. 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 Schiff base derivatives of $[CaO_2Sn_2(OPr^i)_6]$

The [Ca(II)-Sn(IV)]-ì-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[22-25].

Reaction of μ-oxo compound with Salicylidene-aniline in 1:1 molar ratio

The $[CaO_2Sn_2(OPr^i)_6]$ (0.724 g, 1.091 mmol) and Salicylidene-aniline (0.214 g, 1.091 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 8 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 solvent was then removed under reduced pressure yielding a yellowish semi-solid product. The other schiff base derivatives were synthesised by similar procedure and the analytical results have been summarized in TABLE 1.

The hydrolyzed product of Schiff bases of μ-oxo compound obtained by hydrothermally assisted sol-gel processing. For the hydrothermally assisted sol-gel processing, Schiff base 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 Schiff base 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.

TABLE 1 : Analytical and physical data of studied compounds

S.No.	Compoundg (mmol)	Ligandg (mmol)	Refluxing time(h)	Product (%)	Anal. Found (calcd.)					
					$HOPr^i$(g)	Ca(%)	Sn(%)	C(%)	H(%)	N(%)
1	$[CaO_2Sn_2(OPr^i)_6]$ 0.724 (1.091)	HSB^1 0.214(1.091)	8	$[CaO_2Sn_2(OPr^i)_5(SB^1)]$ 81.4	0.05 (0.06)	4.91 (4.99)	29.63 (29.71)	41.92 (41.94)	5.60 (5.61)	1.71 (1.74)
2	$[CaO_2Sn_2(OPr^i)_6]$ 0.502(0.757)	HSB^1 0.297(1.515)	10	$[CaO_2Sn_2(OPr^i)_4(SB^1)_2]$ 78.8	0.08 (0.09)	4.25 (4.26)	25.11 (25.37)	48.57 (48.61)	5.08 (5.11)	2.87 (2.98)
3	$[CaO_2Sn_2(OPr^i)_6]$ 0.422 (0.663)	HSB^1 0.374(1.908)	11½	$[CaO_2Sn_2(OPr^i)_3(SB^1)_3]$ 80.5	0.09 (0.11)	3.58 (3.72)	22.01 (22.13)	53.87 (53.81)	4.75 (4.74)	3.91 (3.90)
4	$[CaO_2Sn_2(OPr^i)_6]$ 0.418 (0.629)	HSB^1 0.493(2.515)	13	$[CaO_2Sn_2(OPr^i)_2(SB^1)_4]$ 82.1	0.13 (0.15)	3.24 (3.3)	19.54 (19.63)	57.35 (57.42)	4.39 (4.45)	4.58 (4.62)
5	$[CaO_2Sn_2(OPr^i)_6]$ 0.507 (0.765)	HSB^2 0.173(0.765)	8	$[CaO_2Sn_2(OPr^i)_5(SB^2)]$ 81.0	0.08 (0.09)	4.71 (4.81)	28.59 (28.64)	41.88 (41.87)	5.62 (5.65)	1.67 (1.68)
6	$[CaO_2Sn_2(OPr^i)_6]$ 0.345 (0.520)	HSB^2 0.235(1.04)	9½	$[CaO_2Sn_2(OPr^i)_4(SB^2)_2]$ 80.5	0.06 (0.06)	4.11 (4.0)	23.68 (23.84)	48.12 (48.09)	5.24 (5.21)	2.84 (2.80)
7	$[CaO_2Sn_2(OPr^i)_6]$ 0.390 (0.588)	HSB^2 0.397(1.756)	11½	$[CaO_2Sn_2(OPr^i)_3(SB^2)_3]$ 79.7	0.09 (0.10)	3.49 (3.43)	20.33 (20.42)	52.45 (52.53)	4.87 (4.89)	3.55 (3.60)
8	$[CaO_2Sn_2(OPr^i)_6]$ 0.382 (0.575)	HSB^2 0.498(2.303)	13	$[CaO_2Sn_2(OPr^i)_4(SB^2)_4]$ 80.8	0.13 (0.14)	2.99 (3.0)	17.69 (17.86)	55.71 (55.85)	4.58 (4.65)	4.21 (4.20)
9	$[CaO_2Sn_2(OPr^i)_6]$ 0.494 (0.744)	HSB^3 0.172(0.744)	8	$[CaO_2Sn_2(OPr^i)_5(SB^3)]$ 82.0	0.03 (0.04)	4.72 (4.78)	28.42 (28.46)	40.11 (40.19)	5.30 (5.26)	1.61 (1.67)
10	$[CaO_2Sn_2(OPr^i)_6]$ 0.420 (0.634)	HSB^3 0.293(1.268)	9	$[CaO_2Sn_2(OPr^i)_4(SB^3)_2]$ 82.4	0.06 (0.07)	3.87 (3.97)	23.54 (23.61)	45.19 (45.23)	4.48 (4.56)	2.77 (2.78)
11	$[CaO_2Sn_2(OPr^i)_6]$ 0.381 (0.574)	HSB^3 0.398(1.722)	11½	$[CaO_2Sn_2(OPr^i)_3(SB^3)_3]$ 81.5	0.08 (0.10)	3.32 (3.39)	20.14 (20.16)	48.76 (48.81)	4.11 (4.06)	3.55 (3.55)
12	$[CaO_2Sn_2(OPr^i)_6]$ 0.375 (0.566)	HSB^3 0.523(2.264)	12½	$[CaO_2Sn_2(OPr^i)_2(SB^3)_4]$ 80.7	0.12 (0.13)	2.97 (2.96)	17.66 (17.60)	51.45 (51.47)	3.64 (3.70)	4.17 (4.14)

RESULTS AND DISCUSSION

To overcome the phase segregation problem and provide a excellent precursors for bi-component oxides, many reactions of [Ca(II)-Sn(IV)]-μ-oxoisopropoxide with bidentate schiff bases (HSB) i.e. salicylidene aniline (HSB^1), salicylidene-o-toluidene (HSB^2), salicylidene p-chloroaniline (HSB^3) are performed in different molar ratios in refluxing benzene, yielding the products of type $[CaO_2Sn_2(OPr^i)_5(SB)]$, $[CaO_2Sn_2(OPr^i)_4(SB)_2]$, $[CaO_2Sn_2(OPr^i)_3(SB)_3]$ and $[CaO_2Sn_2(OPr^i)_2(SB)_4]$. The preparation of the Schiff base derivatives of $[CaO_2Sn_2(OPr^i)_6]$ follows the following reaction scheme 1:

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

(n= 1-4, HSB = Schiff bases)

Scheme 1

The $[CaO_2Sn_2(OPr^i)_6]$ and its Schiff base derivatives are found soluble in common organic solvents such as benzene, chloroform and carbon tetrachloride etc and prone to hydrolysis. The isopropanol liberated during the course of the reaction was collected azeotropically (isopropanol-benzene) and estimated oxidimetrically to check the progress of the reaction. The hydrolysis rate decreases with increase in coordination number of metal ion. The studies reveal that only four out of the six isopropoxy groups of [Ca(II)-Sn(IV)]-μ-oxoisopropoxide are substituted by Schiff bases. The substitution of fifth and sixth isopropoxy groups could not be achieved even with an excess of ligand (Schiff bases) and prolonged refluxing time (28 h). This indicates the non-replacement of bridging isopropoxy groups and that only terminal isopropoxy groups are substituted by Schiff bases.

Spectral analysis of Schiff base derivatives of $[CaO_2Sn_2(OPr^i)_6]$

IR spectra

The absorption bands appeared in the region 1365-1345 cm^{-1} and 1165-1140 cm^{-1} in spectra of mono to tri Schiff base derivatives are the characterstics of *gem-*

dimethyl portion and combination band ν (C-O+OPr^i) of the terminal and bridging isopropoxy group respectively[28]. The disappearance of peak at 1165 cm^{-1} in spectra tetra Schiff base derivatives indicates the complete substitution of terminal isopropoxy group. A band appeared at approximately 950 cm^{-1} is due to ν (C-O) stretching of bridging isopropoxy group. Similar spectra obtained for compounds formed by reactions of 1:5 and 1:6 molar ratios of μ-oxo compound and Schiff bases as of 1:4 Schiff base derivatives of μ-oxoisopropoxide. This reavels the non-replacement of bridging isopropoxy groups by Schiff bases.

The ν(O-H) band occurring in the region ~3400-3100 cm^{-1} in spectra of Schiff bases is found absent in all Schiff base derivatives, indicating the deprotonation of these ligands. Schiff bases show The strong bands observed at ~1565 cm^{-1} and ~1260 cm^{-1} due to ν(C=N) and ν(C-O) vibrations of azomethine and phenolic groups respectively in Schiff base spectra are shifted downward in ν (C=N) stretch by ~15-25 cm^{-1} indicating the coordination of azomethine nitrogen of the ligand to the metal atom and upward shift in ν (C-O) by ~ 20-30 cm^{-1} suggesting the bond formation of phenolic oxygen of the Schiff base to the metal in the derivatives[28]. In the region 700-400 cm^{-1}, numbers of bands are observed in spectra of all derivatives due to M-O and M-N stretching vibrations[29,30].

NMR spectra

^{1}H NMR

A broad multiplet centered between δ 0.8–1.2 ppm was observed in spectra of Schiff base derivatives of $[CaO_2Sn_2(OPr^i)_6]$ due to the intermixing of methyl protons of isopropoxy groups. A multiplet centered at δ 4.1 is due to the methine proton of isopropoxy groups in the spectra of all derivatives. Same spectra were observed for the complexes formed by reactions of 1:5 and 1:6 molar ratios of μ-oxo compound and Schiff bases as of 1:4 Schiff base derivatives of μ-oxoisopropoxide. This confirms the non-replacement of bridging isopropoxy groups by Schiff bases. The signals observed at δ 6.8-7.8 ppm are due to phenyl ring protons. The phenolic (O-H) protons peak at δ 11-11.5 ppm in Schiff bases is found absent in their derivatives of $[CaO_2Sn_2(OPr^i)_6]$ indicates the deprotonation of phenolic group. In the case of salicylidene-o-toluidene derivatives an additional signal at δ 2.3-2.5 ppm has been observed due to methyl protons substituted on the benzene ring.

^{13}C NMR

The spectra of mono to tri Schiff base derivatives of $[CaO_2Sn_2(OPr^i)_6]$ shows two prominent peaks at δ ~26.1-26.5 and δ ~28.2-28.7 ppm assignable to the methyl carbon of terminal and interamolecularly bridged isopropoxy moiety and two different type of methine carbons of isopropoxy group are confirmed by the two signals observed at δ ~62.2-8 ppm and δ ~63.2-7 ppm[31]. The spectra of 1:4 Schiff base 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 Schiff bases as of 1:4 Schiff base derivatives of μ-oxoisopropoxide. This confirms the non-replacement of bridging isopropoxy groups by Schiff bases.

Two signals observed in the range δ 160.1-164.7 ppm and δ 150.8-147.3 ppm are due to carbonyl carbon and methine carbon attached to nitrogen of ligand moiety in all the Schiff derivatives of μ-oxoisopropoxide compound. Moreover, a number of signals are observed between δ 135.5 – 118.2 ppm due to the different carbons of two phenyl rings[31].

Thermal studies

The thermogravimetric analysis of Schiff base derivatives of $[CaO_2Sn\ (OPr^i)_6]$ have been examined by under a flow of dry nitrogen, up to 800°C at a heating rate of 10°C/min. The minor weight loss (1.50-1.89 %) starts at 56.5-59.3°C and completed at 184.6-189.3°C with a weight loss of due to presence of moisture and fraction of solvent present, if any. The second and major one starts at 178.7-188.4°C and is completed at 359-363°C, resulting in a residue amounting to 12.362-12.905% of the initial weight, probably due to the decomposition of partially hydrolyzed μ-oxo Schiff base into metal/mixed metal oxides suggesting the volatile nature of compound[32].

The thermogravimetric analysis of various hydrolyzed product of different Schiff base derivatives have been performed up to 800°C at 10°C/min. Thermograms of various hydrolysed Schiff base 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 ($CaSnO_3$ and SnO_2). The detailed study of thermograms of hydrolyzed product of various Schiff base derivatives is summarized in TABLE 2.

TABLE 2 : Study of thermograms of hydrolyzed product of various salicylate derivatives of $[CaO_2Sn_2(OPr^i)_6]$

Sr. No.	Compound	Temperature range (ºC)	Weight loss (%)
1.	$[CaO_2Sn_2(OPr^i)_5(SB^1)]$	(a) 52-222 (b) 222-350 (c) > 350	(a) 6 (b) 39.88 (c) No significant loss
2.	$[CaO_2Sn_2(OPr^i)_4(SB^1)_2]$	(a) 53-225 (b) 225-357 (c) > 357	(a) 5 (b) 52.70 (c) No significant loss
3.	$[CaO_2Sn_2(OPr^i)_3(SB^2)_3]$	(a) 58-227 (b) 227-355 (c) > 355	(a) 5 (b) 59.58 (c) No Significant loss
4.	$[CaO_2Sn_2(OPr^i)_2(SB^2)_4]$	(a) 54-229 (b) 229-355 (c) > 355	(a) 6 (b) 63.79 (c) No significant loss
5.	$[CaO_2Sn_2(OPr^i)_5(SB^3)]$	(a) 57-228 (b) 228-358 (c) > 358	(a) 5 (b) 43.99 (c) No significant loss
6.	$[CaO_2Sn_2(OPr^i)_4(SB^3)_2]$	(a) 56-224 (b) 224-357 (c) > 357	(a) 4 (b)55.87 (c) No significant loss
7.	$[CaO_2Sn_2(OPr^i)_3(SB^4)_3]$	(a) 51-229 (b) 229-356 (c) > 356	(a) 5 (b) 63.07 (c) No significant loss
8.	$[CaO_2Sn_2(OPr^i)_2(SB^4)_4]$	(a) 53-235 (b) 235-365 (c) > 365	(a) 6 (b) 66.11 (c) No significant loss
9.	$[CaO_2Sn_2(OPr^i)_5(SB^1)]$	(a) 54-228 (b) 228-358 (c) > 358	(a) 5 (b) 43.54 (c) No significant loss
10.	$[CaO_2Sn_2(OPr^i)_4(SB^1)_2]$	(a) 54-227 (b) 227-356 (c) > 356	(a) 5 (b) 55.47 (c) No significant loss
11.	$[CaO_2Sn_2(OPr^i)_3(SB^2)_3]$	(a) 53-231 (b) 231-359 (c) > 359	(a) 6 (b) 61.87 (c) No Significant loss
12.	$[CaO_2Sn_2(OPr^i)_4(SB^2)_2]$	(a) 55-229 (b) 229-363 (c) > 363	(a) 5 (b) 68.36 (c) No significant loss

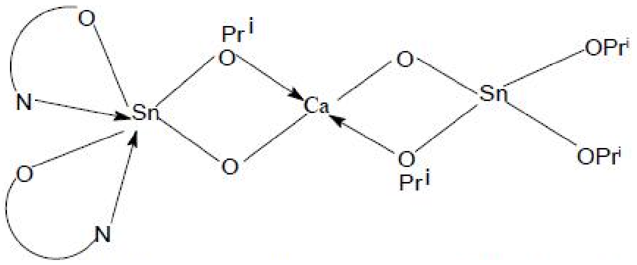


Figure 1 : Suggested structure of $[CaO_2Sn_2(OPr^i)_4(SB)_2]$

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

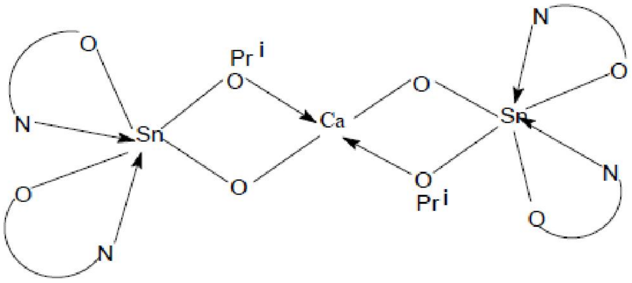
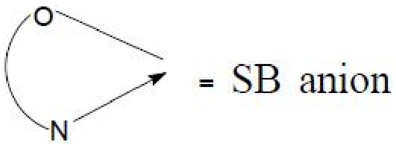


Figure 2 : Suggested structure of $[CaO_2Sn_2(OPr^i)_2(SB)_4]$



CONCLUSION

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