Chem Sci Trans., 2012, **1(2),** 387-395
DOI:10.7598/cst2012.144

Chemical Science Transactions
ISSN/E-ISSN: 2278-3458/2278-3318

RESEARCH ARTICLE

Synthesis and Pyrolytic Studies of Schiff Base Derivatives of Heterotrinucleic[Al^{III}-Sn^{II}-B^{III}]-μ-oxoisopropoxide

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Received 9 May 2012 / Accepted 28 May 2012

Abstract: New Schiff base derivatives of heteronucleic-μ-oxoisopropoxide[$SnO_2AlB(OPr^i)_4$] have been synthesized by thermal condensation of μ-oxoisopropoxide with salicylidene-aniline (HSB^1), salicylidene-*o*-toluidene (HSB^2), salicylidene-*p*-toluidene (HSB^3) and salicylidene-*p*-chloroaniline (HSB^4) in different molar ratios (1:1-1:2) yielded the compounds of the type [$SnO_2AlB(OPr^i)_{4-n}(SB)_n$] (where n is 1-2 and SB = Schiff base anion). The Schiff base derivatives have been characterized by elemental, spectral (IR, ^1H, ^{13}C, ^{27}Al, ^{119}Sn and ^{11}B 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 multi-component oxides. The studies reveal that Schiff base derivatives are polymeric in nature and low susceptible to hydrolysis as compared to parent compound and may prove excellent precursors for the mixed metal oxides.

Keywords: Heteronucleic-μ-oxoalkoxides, Aluminium, Tin, Boron, Schiff bases, TG analysis

Introduction

In the preparation of multi-component metal oxide material, some important factors should be concentrating on, related to the structure, properties and performance of the final material. These aspects are essential to control the stoichiometry, homogeneity, phase and cyrstallinity, which are directly related to the structure and reactivity of the metal-organic precursors in homogeneous solutions. The performance of “advanced” mixed metal oxide materials such as optoelectronic ceramics is greatly affected by control of these properties. The stoichiometry and homogeneity depends on the structure and reactivity of the precursor solutions. Addition of two different metal-organic reagents, AC. (closed spheres) and BO, (open spheres), in equimolar ratios to a solvent can give different possible results (assuming they dissolve): (i) they may not react, (ii) they may react, especially with the addition of water, to give a single molecular species like ABCpOq (shaded spheres), or (iii) a mixture of molecular species with different metal atom stoichiometries may be formed. The molecular level homogeneity is same for (i) and (ii) but there is a possibility of regional in homogeneity for (iii), although the overall stoichiometry is correct. Whatever the result, It seems reasonable that the control over homogeneity and stoichiometry at molecular level would be useful. However, the preparation of a specific precursor resulting in a specific oxide is difficult, especially if bi- or multi-metallic ceramic oxides are targeted[1]. 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 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]. Heterometallic-μ-oxoalkoxides are often associated with more accessible precursors such as carboxylates, Schiff bases and β-diketonates in chemical routes to intricate mixed metal oxides. The mixed metal oxides of the type MAl_2O_4 (M=Ca, Mg, Mn, Co, Fe, Ni, Zn) obtained from heterometallic-μ-oxoalkoxides precursors[2-5] have found use to new ceramics[6,7] and medicinally important such as for absorbing harmful chemicals[8] and gases such as SO_2, CCl_4 and decontaminating chemical warfare agents[9]. Interestingly $MgAl_2O_4$ prepared from $[MgO_2Al_2(OPr^i)_4]_2$ have been used to destructively adsorb paraxon [diethyl-4-nitrophenol phosphate (DNPP)][10]. Nanocrystalline metal oxides of magnesium, calcium, aluminium and transition metals have proven to be exceptional adsorbents and catalysts due to their smaller size and high surface area[11-15]. Core/shell bimetallic mixtures, such as MgO coated with V_2O_3, possess their own unique sorption and catalytic properties[16]. In view of the solubility of metal alkoxides[17,18] and oxoalkoxides[19,20] in organic solvents, these materials are strongly preferred as precursors in sol- gel processes. In heterometallic-μ-oxoalkoxides M-O-M' linkage is present, which makes the M-O-M' bond strong and stable as compared to other precursors. Non-cleavage of the M-O-M' bond even upon hydrolysis followed by dehydration, makes homogenous oxides of high surface area mixed metal oxides nanoparticles. Therefore, these compounds are considered as especially suitable precursors over other precursors such as metal nitrate, acetate, monodispersed metal hydrous oxides, mainly due to the ease of their purification, solubility in organic solvents, volatility and their extremely facile hydrolizability. The hydrolysis rates of metal alkoxides (especially in the case of heterometallic alkoxides) are very high due to electrophilic nature of metal and its ability to expand its coordination number which complicates the problem by causing phase segregation. Therefore, careful handling and controlled hydrolysis are required to avoid phase segregation problem during hydrolysis of such compounds.

Many metal alkoxides thermally decompose in the range ~100-300 °C. Depending on process conditions, this thermolysis can afford nanosized powders of oxide or metallic phases. When certain specifications such as homogeneity, high purity, narrow particle-size distribution, fabrication of functional materials intended for aircraft, space, electronic fields, and chemical industry: individual oxides, their solid solutions, complex oxides, powders of metals and alloys active towards sintering, the sol-gel process is probably the best approach[21]. Hence, hydrothermally assisted sol-gel method was used for the preparation of hydrolyzed product. This method is simple, low temperature process and cost effective route for the preparation of crystalline oxides; sol-gel is expensive route for the preparation of ceramics. Due to high sensitivity of metal alkoxides to the moisture and inhomogeneous precipitation hydothermal assisted sol-gel method is preferred over conventional sol-gel processing[10-13]. The aim of this work was to prepare suitable precursors for mixed metal oxide powders from their metal alkoxides by hydrothermally assisted sol-gel process.

Experimental

The Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer over the range of 4000-400 cm^{-1}. The ^{1}H, ^{13}C, ^{27}Al, ^{11}B and ^{19}Sn 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. The molecular weight data was determined by the cryoscopic method using a Beckman thermometer.

Reagents

Tin diacetate [$Sn(OAc)_2$] (Aldrich) and aluminium isopropoxide [$Al(OPr^i)_3$] (Aldrich) and triisopropyl borate $B(OPr^i)_3$ (Aldrich) were used as received. Benzene was purchased from Ranbaxy, kept in presence of sodium wire for two days and distilled twice before use to ensure the complete removal of moisture. Salicylidene-aniline (HSB^1), salicylidene-*o*-toluidene (HSB^2), salicylidene-*p*-toluidene (HSB^3) and salicylidene-*p*-chloroaniline (HSB^4) were purchased from Aldrich and used as received.

Procedure

All reagents used were of analytical grade. All manipulations have been carried out under dry nitrogen to exclude the moisture throughout the present investigations. Solvents and reagents used were purified and dried by standard methods[22-26]. [$SnO_2AlB(OPr^i)_4$] was prepared in laboratory by reported methods[27-29]. The isopropoxy groups in the μ-oxoisopropoxide compound and liberated isopropanol formed in preparation of Schiff base derivatives were estimated oxidimetrically[30]. Tin and aluminium were analyzed gravimetrically and boron was estimated volumetrically[25]. Further, spectral study of tin, aluminium and boron has also been carried out to find out their respective coordination number in order to elucidate the structure of μ-oxo compounds. The Schiff base derivatives of μ-oxo compound [$SnO_2AlB(OPr^i)_4$] were decomposed in conc. HCl and extracted in dilute HCl, tin was precipitated as sulphide (pH 5-6), filtered and estimated as SnO_2[25]. The H_2S was boiled off completely from the filtrate and aluminium was estimated as aluminium oxinate[25].

Synthesis of derivatives of [$SnO_2AlB(OPr^i)_4$] with Schiff bases

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

The compound [$SnO_2AlB(OPr^i)_4$] (0.364 g, 0.856 mmol) and salicylidene-aniline (0.169 g, 0.856 mmol) were refluxed in benzene (~50 mL) for 6 h at ~100 °C in a flask connected to short distillation column. The liberated isopropanol was collected continuously at 72-78 °C as a binary azeotrope of isoproponol-benzene[23]. The isopropanol in azeotrope was estimated oxidimetrically to check the completion of the reaction. The excess of the solvent was then removed at reduced pressure (45 °C/1 mm Hg) yielding a yellow coloured solid product.

Similar procedure was adopted for the preparation of other derivatives of [$SnO_2AlB(OPr^i)_4$] with Schiff bases (HSB) *i.e.* salicylidene-aniline (HSB^1), salicylidene-o-toluidene (HSB^2), salicylidene-*p*-toluidene (HSB^3) and salicylidene-*p*-chloroaniline (HSB^4) in stoichiometric ratio of 1:1 and 1:2 molar ratios. The details along with analytical data are given 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.	Compound g, mmol	Ligand g, mmol	Reflux time, h	Product g, %	Anal. Found (calcd.)					
					OPr^i, g	Sn, %	Al, %	B, %	C, %	H, %
1	$[SnO_2AlB(OPr^i)_4]$ 0.364 (0.856)	HSB^1 0.169(0.856)	6	$[SnO_2AlB(OPr^i)_3(SB^1)]$ 0.416(86.3)	0.05 (0.05)	21.03 (21.13)	4.56 (4.79)	1.84 (1.95)	53.15 (53.28)	5.44 (5.50)
2	$[SnO_2AlB(OPr^i)_4]$ 0.342 (0.804)	HSB^1 0.318(1.608)	11½	$[SnO_2AlB(OPr^i)_2(SB^1)_2]$ 0.512(90.7)	0.10 (0.10)	16.87 (16.97)	3.66 (3.85)	1.42 (1.45)	57.96 (58.20)	4.64 (4.85)
3	$[SnO_2AlB(OPr^i)_4]$ 0.348 (0.818)	HSB^2 0.173(0.818)	6½	$[SnO_2AlB(OPr^i)_3(SB^2)]$ 0.422(89.4)	0.04 (0.05)	20.49 (20.64)	4.57 (4.68)	1.88 (1.90)	54.01 (54.16)	5.64 (5.72)
4	$[SnO_2AlB(OPr^i)_4]$ 0.329 (0.774)	HSB^2 0.327(1.548)	12½	$[SnO_2AlB(OPr^i)_2(SB^2)_2]$ 0.503(89.3)	0.09 (0.09)	16.19 (16.34)	3.55 (3.70)	1.47 (1.51)	59.21 (59.34)	5.17 (5.21)
5	$[SnO_2AlB(OPr^i)_4]$ 0.362 (0.851)	HSB^3 0.179(0.851)	5½	$[SnO_2AlB(OPr^i)_3(SB^3)]$ 0.436(88.7)	0.04 (0.05)	20.47 (20.64)	4.58 (4.68)	1.87 (1.90)	53.97 (54.16)	5.63 (5.72)
6	$[SnO_2AlB(OPr^i)_4]$ 0.317 (0.745)	HSB^3 0.315(1.49)	11	$[SnO_2AlB(OPr^i)_2(SB^3)_2]$ 0.474(90.8)	0.03 (0.09)	16.25 (16.34)	3.65 (3.70)	1.49 (1.51)	59.18 (59.34)	5.13 (5.21)
7	$[SnO_2AlB(OPr^i)_4]$ 0.372 (0.875)	HSB^4 0.202(0.875)	6	$[SnO_2AlB(OPr^i)_3(SB^4)]$ 0.534(87.8)	0.04 (0.05)	19.77 (19.96)	4.49 (4.53)	1.78 (1.88)	53.22 (53.28)	4.96 (5.03)
8	$[SnO_2AlB(OPr^i)_4]$ 0.337 (0.792)	HSB^4 0.365(1.584)	12	$[SnO_2AlB(OPr^i)_2(SB^4)_2]$ 0.680(89.2)	0.09 (0.10)	15.34 (15.51)	3.43 (3.52)	1.35 (1.43)	57.89 (58.20)	4.08 (4.17)

Results and Discussion

Many reactions of $[SnO_2AlB(OPr^i)_4]$ with Schiff bases (HSB) *i.e.* salicylidene-aniline (HSB^1), salicylidene-*o*-toluidene (HSB^2), salicylidene-*p*-toluidene (HSB^3) and salicylidene-*p*-chloroaniline (HSB^4) are performed in different molar ratios in refluxing benzene, in which the products of type $[SnO_2AlB(OPr^i)_3(SB)]$, $[Bu_2SnO_2Ti_2(OPr^i)_2(SB)_2]$ are obtained. The general reaction can be given as follows.

$$[SnO_2AlB(OPr^i)_4] \quad + \ nHSB \xrightarrow{\text{refluxing benzene}} [SnO_2AlB(OPr^i)_{4-n}(SB)_n] + nPr^iOH$$

Where n = 1-2 and HSB = Schiff bases

The isopropanol liberated during the course of reaction is collected azeotropically (isopropanol-benzene) and estimated oxidimetrically to check the progress of the reaction and it has been observed that only two out of four of isopropoxy groups of $[SnO_2AlB(OPr^i)_4]$ could be replaced with Schiff base. Further replacement of third and fourth isopropoxy groups could not be achieved even with an excess of ligand (Schiff base) and prolonged refluxing time (approx. 20 hours).

All derivatives are found to be yellow coloured solid product, soluble in common organic solvents such as benzene, chloroform and hexane, low susceptible to hydrolysis and decomposed on heating (~180 °C).

IR spectra

The IR spectra of the 1:1 Schiff base derivatives of $[SnO_2AlB(OPr^i)_4]$ show absorption bands in the region 1360-1340 cm^{-1} and 1165-1150 cm^{-1} are the characterstics of *gem*-dimethyl portion and combination band ν(C-O+OPr^i) of the terminal and bridging isopropoxy group respectively[30]. No peak is observed at 1165 cm^{-1} in the spectrum of 1:2 Schiff base derivatives indicates the absence 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 1:3 and 1:4 molar ratios of μ-oxo compound and Schiff bases as of 1:2 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 the schiff bases disappears completely in the derivatives, indicating the deprotonation of these ligands. Schiff bases show intense bands at ~1565 cm^{-1} and ~1260 cm^{-1} due to ν(C=N) and ν(C-O) vibrations of azomethine and phenolic groups respectively. The downward shift 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[27]. A number of peaks are observed in the region 700-400 cm^{-1} due to M-O and M-N stretching vibrations in μ-oxo compounds which is difficult to assign exactly due to the overlapping of bands in this region[30]. A number of peaks are observed in the region 700-400 cm^{-1} due to M-O and M-N stretching vibrations in μ-oxo compounds which is difficult to assign exactly due to the overlapping of bands in this region[31].

NMR spectral studies

^1H NMR

^1H NMR spectra of all the Schiff base derivatives of $[SnO_2AlB(OPr^i)_4]$ show broad multiplet centered between δ 0.8–1.2 ppm due to the intermixing of methyl protons of isopropoxy groups[24]. 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 1:3 and 1:4 molar ratios of μ-oxo compound and Schiff bases as of 1:2 Schiff base derivatives of μ-oxoisopropoxide. This confirms the non-replacement of bridging isopropoxy groups by Schiff bases.

In the ^{1}H NMR spectra of all derivatives, the signals observed at δ 6.8-7.8 ppm are due to phenyl ring protons. Disappearance of peak at δ 11.2 ppm due to phenolic (O-H) protons of Schiff base in their derivatives of $[SnO_2AlB(OPr^i)_4]$ indicates the deprotonation of phenolic group. In the case of salicylidene-*o*-toluidene and salicylidene-*p*-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 ^{13}C NMR spectra mono derivatives of $[SnO_2AlB(OPr^i)_4]$ shows two prominent peaks at δ ~27.4 and δ ~27.9 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 ~62.8 ppm[32]. The spectra of 1:2 Schiff base derivatives of μ-oxoisopropoxide show the absence of terminal isopropoxy group. Very similar spectra obtained for compounds formed by reactions of 1:3 and 1:4 molar ratios of μ-oxo compound and Schiff bases as of 1:2 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 164-160.3 ppm and δ 150-147 ppm are due to carbonyl carbon and methine carbon attached to nitrogen of ligand moiety in all the Schiff derivatives of μ-oxoisopropoxide compound. Morever, a number of signals are observed between δ 133-117 ppm due to the different carbons of two phenyl rings[32].

^{27}Al NMR

The ^{27}Al NMR spectra of all Schiff base derivatives of $[SnO_2AlB(OPr^i)_4]$ show a singlet at ~δ1 ppm indicating octahedral environment about the Al atom and is surrounded by six oxygen atoms[33].

^{119}Sn NMR

The ^{119}Sn NMR spectra of all Schiff base derivatives of $[SnO_2AlB(OPr^i)_4]$ exhibit a sharp signal in the range δ 489-467 ppm assignable to the tetra-coordination about Sn(II) attributed to the polymeric nature of μ-oxo compound[34].

^{11}B NMR

The ^{11}B NMR spectra of all Schiff base derivatives of $[SnO_2AlB(OPr^i)_4]$ display a broad signal in the range δ –3.23 to δ –3.87 ppm indicating a tetra-coordinated environment about B atom which is surrounded by four oxygen atoms[28].

Thermal studies

The thermal decomposition of Schiff base derivatives of $[SnO_2AlB(OPr^i)_4]$ have been examined by thermogravimetric analysis under a flow of dry nitrogen, up to 800 °C at a heating rate of 20 ºC/min. The TGA curve shows two stages of weight loss. The first and small step starts at 59.3 ºC and completed at 198 ºC with a weight loss of 2.07% due to presence of moisture and fraction of solvent present, if any. The second and major one starts at 198 ºC and is completed at 364 ºC, resulting in a residue amounting to 10.55% 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[35]. Similar thermograms observed for other Schiff base derivatives of $[SnO_2AlB(OPr^i)_4]$.

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 to 800 ºC, leaving a residue that is less than the calculated for mixed metal oxide and metal oxides ($SnAl_2O_4$, SnO and B_2O_3). The detailed study of thermograms of hydrolyzed product of various Schiff base derivatives is summarized in Table 2. The molecular weight measurement carried out in dry benzene using cryoscopic method suggest the polymeric nature of all Schiff base derivatives.

Table 2. Study of thermograms of hydrolyzed product of various Schiff base derivatives of $[SnO_2AlB(OPr^i)_4]$

S. No.	Compound	Temperature range, ºC	Weight loss, %
1.	$[SnO_2AlB(OPr^i)_3(SB^1)]$	(a) 54-215, (b) 215-340 (c) >340	(a) 5, (b) 57.65 (c) No significant loss
2.	$[SnO_2AlB(OPr^i)_2(SB^1)_2]$	(a) 52-221, (b) 221-345 (c) >345	(a) 6, (b) 64.52 (c) No significant loss
3.	$[SnO_2AlB(OPr^i)_3(SB^2)]$	(a) 58-227, (b) 227-353 (c) >353	(a) 5, (b) 58.62 (c) No Significant loss
4.	$[SnO_2AlB(OPr^i)_2(SB^2)_2]$	(a) 53-225, (b) 225-354 (c) >354	(a) 4, (b) 67.35 (c) No significant loss
5.	$[SnO_2AlB(OPr^i)_3(SB^3)]$	(a) 57-229, (b) 229-353 (c) >353	(a) 4, (b) 59.74 (c) No significant loss
6.	$[SnO_2AlB(OPr^i)_2(SB^3)_2]$	(a) 55-226, (b) 226-358 (c) >358	(a) 5, (b) 66.68 (c) No significant loss
7.	$[SnO_2AlB(OPr^i)_3(SB^4)]$	(a) 56-224, (b) 224-340 (c) >340	(a) 5, (b) 59.91 (c) No significant loss
8.	$[SnO_2AlB(OPr^i)_2(SB^4)_2]$	(a) 61-227, (b) 227-349 (c) >349	(a) 4, (b) 68.85 (c) No significant loss

Conclusion

The aforesaid analytical study suggest the following proposed structures of Schiff base derivatives of the type $[SnO_2AlB(OPr^i)_3(SB)]$ and $[SnO_2AlB(OPr^i)_2(SB)_2]$ Figure 1 and Figure 2. Thermal study favors the formation of multicomponent oxides from the hydrolyzed product of Schiff base derivatives.

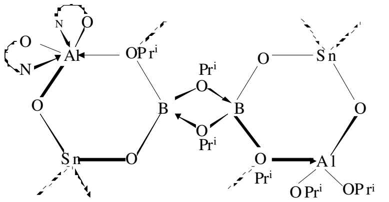


Figure 1. Plausible structure of $[SnO_2AlB(OPr^i)_3(SB)]$

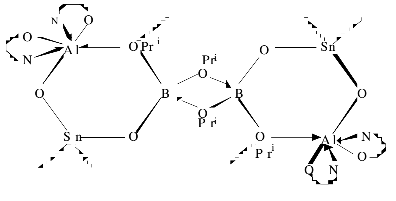
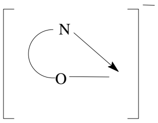


Figure 2. Plausible structure of $[SnO_2AlB(OPr^i)_2(SB)_2]$



= anion of Schiff base [SB]

Acknowledgement

The author expresses gratitude to the Haryana Institute of Engineering& Technology, Kaithal for the necessary facilities to accomplish this work.

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