

# SYNTHESIS AND STRUCTURAL ANALYSIS OF SCHIFF BASE DERIVATIVES OF NEW HETEROMETALLIC [AL<sup>III</sup>-BU<sub>2</sub>SN<sup>IV</sup>-B<sup>III</sup>]-M- OXOISOPROPOXIDE

*Rajesh Kumar\* and Porob Roshan Atma Ram†*

*Department of chemistry, Haryana Institute of Engineering & Technology,  
Kaithal – 136027, Haryana, India*

*†Department of Chemistry, CMJ University, Shillong*

## ABSTRACT

*New Schiff base derivatives of heterometallic- $\mu$ -oxoisopropoxide [Bu<sub>2</sub>SnO<sub>2</sub>AlB(OPri)<sub>4</sub>] have been synthesized by the thermal condensation  $\mu$ -oxoisopropoxide compound with Schiff bases in different molar ratios (1:1-1:2) yielded the compounds of the type [Bu<sub>2</sub>SnO<sub>2</sub>AlB(OPri)<sub>4</sub>-n(SB)<sub>n</sub>] (where n is 1-2 and SB = Schiff base anion) respectively. The  $\mu$ -oxoisopropoxide derivatives have been characterized by elemental, spectral (IR, <sup>1</sup>H, <sup>13</sup>C, <sup>27</sup>Al, <sup>119</sup>Sn and <sup>11</sup>B NMR), and molecular weight measurement. The studies reveal that the derivative compounds show dimeric nature. Further these are found low susceptible to hydrolysis as compared to parent compound and may prove excellent precursors for the mixed metal oxides.*

**Keywords:** *Heterometallic-  $\mu$ -oxoalkoxides, Aluminium, Tin, Boron, Schiff bases*

## 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 control of particle size and the morphology of the oxide are of crucial importance nowadays both from the fundamental and industrial point of view<sup>1</sup>. Heterometallic- $\mu$ -oxoalkoxides are often associated with more accessible precursors such as carboxylates, Schiff bases and  $\beta$ -diketonates in chemical routes to complex mixed metal oxides. The mixed metal oxides of the type MAl<sub>2</sub>O<sub>4</sub> (M=Ca, Mg, Mn, Co, Fe, Ni, Zn) obtained from heterometallic- $\mu$ -oxoalkoxides precursors<sup>2-5</sup> have found use to new ceramics<sup>6,7</sup> and medicinally important such as for absorbing harmful chemicals<sup>8</sup> and gases such as SO<sub>2</sub>, CCl<sub>4</sub>, and decontaminating chemical warfare agents.<sup>9</sup> Interestingly MgAl<sub>2</sub>O<sub>4</sub> prepared from [MgO<sub>2</sub>Al<sub>2</sub>(OPri)<sub>4</sub>]<sub>2</sub> have been used to destructively adsorb paraxon [diethyl-4-nitrophenol phosphate (DNPP)]<sup>10</sup> 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.<sup>11-15</sup> Core/shell bimetallic mixtures, such as MgO coated with V<sub>2</sub>O<sub>3</sub>, possess their own unique sorption and catalytic properties.<sup>16</sup> In view of the solubility of metal alkoxides<sup>17,18</sup> and oxoalkoxides<sup>19,20</sup> in organic solvents, these materials are strongly preferred as precursors in sol-gel processes. In heterometallic- $\mu$ -

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 hydrolyzability. 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.

Owing to the importance and utility of  $\mu$ -oxo compounds and to overcome the phase segregation problem, it was considered of interest to provide modified precursors as the Schiff base derivatives of  $[\text{Bu}_2\text{SnO}_2\text{AlB}(\text{OPr}^i)_4]$ .

## EXPERIMENTAL

### Instrumentation

The general technique and physical measurement were carried out as described elsewhere.<sup>21-22</sup> The Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer over the range of 4000-400  $\text{cm}^{-1}$ . The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  NMR spectra were recorded in  $\text{CDCl}_3$  on Bruker Avance II 400 NMR spectrometer. The molecular weight data was determined by the cryoscopic method using a Beckman thermometer.

### Reagents

All reagents used were of analytical grade. All manipulations have been carried out under anhydrous conditions, solvents and reagents used were purified and dried by standard methods<sup>23</sup>. dibutyltin diacetate  $[\text{Bu}_2\text{Sn}(\text{OAc})_2]$  (Aldrich) and aluminium isopropoxide  $[\text{Al}(\text{OPr}^i)_3]$  (Aldrich) and triisopropyl borate  $\text{B}(\text{OPr}^i)_3$  (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.

### Procedure

$[\text{SnO}_2\text{AlB}(\text{OPr}^i)_4]$  and Schiff bases were prepared in laboratory by reported methods.<sup>24-26</sup> The isopropoxy groups in the  $\mu$ -oxoisopropoxide compound and liberated isopropanol formed in preparation of Schiff base derivatives were estimated oxidimetrically.<sup>27</sup> Tin and aluminium were analyzed gravimetrically and boron was estimated volumetrically<sup>22</sup>. 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  $\mu$ -oxo compounds. The Schiff base derivatives of  $\mu$ -oxo compound  $[\text{Bu}_2\text{SnO}_2\text{AlB}(\text{OPr}^i)_4]$  were decomposed in conc. in order to elucidate the structure of  $\mu$ -oxo compounds. The Schiff base derivatives of  $\mu$ -oxo compound  $[\text{Bu}_2\text{SnO}_2\text{AlB}(\text{OPr}^i)_4]$  were decomposed in conc.

HCl and extracted in dilute HCl, tin was precipitated as sulphide (pH 5-6), filtered and estimated as  $\text{SnO}_2$ .<sup>22</sup> the  $\text{H}_2\text{S}$  was boiled off completely from the filtrate and aluminium was estimated as aluminium oxinate<sup>22</sup>.

## Synthesis of derivatives of $[\text{Bu}_2\text{SnO}_2\text{AlB}(\text{OPri})_4]$ with Schiff bases

### *Synthesis of 1:1 salicylidene-aniline derivative of $\mu$ -oxo compound*

The compound  $[\text{Bu}_2\text{SnO}_2\text{AlB}(\text{OPri})_4]$  (0.447g, 0.856 mmol) and salicylidene-aniline (0.169g, 0.856 mmol) were refluxed in benzene (~50 ml) for 4 hrs 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 isopropanol-benzene.<sup>20</sup> 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 / 1mm Hg) yielding a yellowish brown solid product.

Similar procedure was adopted for the preparation of other derivatives of  $[\text{Bu}_2\text{SnO}_2\text{AlB}(\text{OPri})_4]$  with schiff bases (HSB) i.e. Salicylidene-aniline (HSB<sup>1</sup>), Salicylidene-o-toluidene (HSB<sup>2</sup>), Salicylidene-p-toluidene (HSB<sup>3</sup>) and Salicylidene-p-chloroaniline (HSB<sup>4</sup>) in stoichiometric ratio of 1:1 and 1:2 molar ratios.

The details are given in (Table-1) along with analytical data.

## RESULTS AND DISCUSSION

Many reactions of  $[\text{Bu}_2\text{SnO}_2\text{AlB}(\text{OPri})_4]$  with bidentate schiff bases (HSB) i.e. salicylidene-aniline (HSB<sup>1</sup>), salicylidene-o-toluidene (HSB<sup>2</sup>), salicylidene-p-toluidene (HSB<sup>3</sup>), salicylidene-p-chloroaniline (HSB<sup>4</sup>) are performed in different molar ratios in refluxing benzene, in which the products of type  $[\text{Bu}_2\text{SnO}_2\text{AlB}(\text{OPri})_3(\text{SB})]$ ,  $[\text{Bu}_2\text{SnO}_2\text{Ti}_2(\text{OPri})_2(\text{SB})_2]$  are obtained. The general reaction can be given as follows.



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  $[\text{Bu}_2\text{SnO}_2\text{AlB}(\text{OPri})_4]$  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 yellowish brown solid product, soluble in common organic solvents such as benzene, chloroform and hexane, low susceptible to hydrolysis and decomposed on heating (~150°C).

## IR Spectra

The IR spectra of the 1:1 Schiff base derivatives of  $[\text{Bu}_2\text{SnO}_2\text{AIB}(\text{OPr}^i)_4]$  show absorption bands in the region  $1360\text{-}1340\text{ cm}^{-1}$  and  $1165\text{-}1150\text{ cm}^{-1}$  are the characteristics of *gem*-dimethyl portion and combination band  $\nu(\text{C-O}+\text{OPr}^i)$  of the terminal and bridging isopropoxy group respectively.<sup>20</sup> No peak is observed at  $1165\text{ cm}^{-1}$  in the spectrum of 1:2 Schiff base derivatives indicates the absence of terminal isopropoxy group. A band appeared at approximately  $950\text{ cm}^{-1}$  is due to  $\nu(\text{C-O})$  stretching of bridging isopropoxy group. However all these bands are also observed in 1:3 and 1:4 Schiff base derivatives as that found in 1:2 Schiff base derivatives of  $\mu$ -oxoisopropoxide compound reveals the presence of bridging isopropoxy group even in the 1:4 Schiff base derivatives.

The  $\nu(\text{O-H})$  band occurring in the region  $\sim 3400\text{-}3100\text{ cm}^{-1}$  in the Schiff bases disappears completely in the derivatives, indicating the deprotonation of these ligands. Schiff bases show intense bands at  $\sim 1565\text{ cm}^{-1}$  and  $\sim 1260\text{ cm}^{-1}$  due to  $\nu(\text{C=N})$  and  $\nu(\text{C-O})$  vibrations of azomethine and phenolic groups respectively. The downward shift in  $\nu(\text{C=N})$  stretch by  $\sim 15\text{-}25\text{ cm}^{-1}$  indicating the coordination of azomethine nitrogen of the ligand to the metal atom and upward shift in  $\nu(\text{C-O})$  by  $\sim 20\text{-}30\text{ cm}^{-1}$  suggesting the bond formation of phenolic oxygen of the Schiff base to the metal in the derivatives.<sup>27</sup> A number of peaks are observed in the region  $700\text{-}400\text{ cm}^{-1}$  due to M-O and M-N stretching vibrations in  $\mu$ -oxo compounds which is difficult to assign exactly due to the overlapping of bands in this region.<sup>28</sup>

## NMR Spectral Studies

### $^1\text{H}$ NMR

$^1\text{H}$  NMR spectra of all the Schiff base derivatives of  $[\text{Bu}_2\text{SnO}_2\text{AIB}(\text{OPr}^i)_4]$  show broad multiplet centered between  $\delta 0.8\text{-}1.2$  ppm due to the intermixing of methyl protons of isopropoxy groups.<sup>26</sup> A broad multiplet centered at  $\delta 4.1$  is due to the methine proton of isopropoxy groups in the spectra of all derivatives. These signals are also observed in 1:3 and 1:4 Schiff base derivatives indicate the presence of bridging isopropoxy group.

In the  $^1\text{H}$  NMR spectra of all derivatives, the signals observed at  $\delta 6.8\text{-}7.8$  ppm are due to phenyl ring protons. Disappearance of peak at  $\delta 11.2$  ppm due to phenolic (O-H) protons of Schiff base in their derivatives of  $[\text{Bu}_2\text{SnO}_2\text{AIB}(\text{OPr}^i)_4]$  indicates the deprotonation of phenolic group. In the case of salicylidene-*o*-toluidene and salicylidene-*p*-toluidene derivatives an additional signal at  $\delta 2.3\text{-}2.5$  ppm has been observed due to methyl protons substituted on the benzene ring.

### $^{13}\text{C}$ NMR

The  $^{13}\text{C}$  NMR spectra of 1:1 Schiff base derivatives of  $[\text{Bu}_2\text{SnO}_2\text{AIB}(\text{OPr}^i)_4]$  shows two prominent peaks at  $\delta \sim 27.4$  and  $\delta \sim 27.9$  ppm assignable to the methyl carbon of terminal and intermolecularly bridged isopropoxy moiety and two different type of methine carbons of isopropoxy group is confirmed by the two signals observed at  $\delta \sim 62.6$  ppm and  $\delta \sim 62.8$  ppm.<sup>29</sup>

Further the spectra of 1:2 schiff base derivatives of  $\mu$ -oxoisopropoxide show the absence of terminal isopropoxy group. All signals of 1:2 spectra are observed in the spectra of 1:3 and 1:4 schiff base derivatives of  $\mu$ -oxo compound indicating non-removal of the bridging isopropoxy group. Two signals observed in the range  $\delta$  160.3-164.0 ppm and  $\delta$  150-147 ppm are due to carbonyl carbon and methine carbon attached to nitrogen of ligand moiety in all the Schiff derivatives of  $\mu$ -oxoisopropoxide compound. Moreover, a number of signals are observed between  $\delta$  133 - 117 ppm due to the different carbons of two phenyl rings.<sup>29</sup>

#### <sup>27</sup>Al NMR

The <sup>27</sup>Al NMR spectra of all Schiff base derivatives of [Bu<sub>2</sub>SnO<sub>2</sub>AlB(OPr<sup>i</sup>)<sub>4</sub>] show a singlet in the range  $\delta$  62-69 ppm indicating tetrahedral environment about the Al atom and is surrounded by four oxygen atoms.<sup>30</sup>

#### <sup>119</sup>Sn NMR

The <sup>119</sup>Sn NMR spectra of all Schiff base derivatives of [SnO<sub>2</sub>AlB(OPr<sup>i</sup>)<sub>4</sub>] exhibit a sharp signal in the range  $\delta$  489-467 ppm assignable to the tetracoordination about Sn(II) attributed to the dimeric nature of  $\mu$ -oxo compound.<sup>31</sup>

#### <sup>11</sup>B NMR

The <sup>11</sup>B NMR spectra of all Schiff base derivatives of [SnO<sub>2</sub>AlB(OPr<sup>i</sup>)<sub>4</sub>] display a broad signal in the range  $\delta$  -3.23 to  $\delta$  -3.87 ppm indicating a tetra-coordinated environment about B atom which is surrounded by four oxygen atoms.<sup>25</sup>

### Molecular weight measurements

The molecular weight measurement carried out in dry benzene using cryoscopic method suggests the polymeric nature of all  $\mu$ -oxo compounds.

### CONCLUSION

The aforesaid analytical study suggest the following proposed structures of Schiff base derivatives of the type [Bu<sub>2</sub>SnO<sub>2</sub>AlB(OPr<sup>i</sup>)<sub>3</sub>(SB)], [Bu<sub>2</sub>SnO<sub>2</sub>AlB(OPr<sup>i</sup>)<sub>2</sub>(SB)<sub>2</sub>] as shown in **Figure 1**.

### REFERENCES

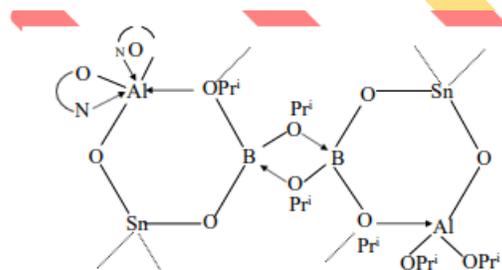
1. Vayssieres L, Hagfeldt A, Lindquist S E, *Pure Appl Chem*, 2000, **72**, 47.
2. Kapoor P N, Bhagi A K, Mulukutla R S, Klabunde K, 'Dekker Encyclopedia of Nanoscience and Nanotechnology', Marcel Dekker, Inc, New York, 2004, 2007.
3. Kapoor P N, Sharma H K, Bhagi A K, Sharma M, *J Ind Chem Soc*, 2004, **81**, 273.
4. Kapoor P N, Heroux D, Mulukutla R S, Zaikovskii V, Klabunde K J, *J Mater Chem*, 2003, **13**, 410.
5. Sharma H K, Kumar R, *Indian J chem*, 2008, **47A**, 854.

6. *Manzer L E, Kourtakis K, WO Pat Appl, 99-US18962, 1999, 19990819.*
7. *Osgan M, Teyssie P, J Polym Sci Polym Lett Ed, 1967, 5, 789.*
8. *Carnes C L, Kapoor P N, Klabunde K J, Bonevich J, Chem Mater, 2002, 14, 2922.*
9. *Wagner G W, Procell L R, O'Connor R J, Munavalli S, Carnes C L, Kapoor P N, Klabunde K J, J Am Chem Soc, 2001, 123, 1636.*
10. *Medine G M, Zaikovskii V, Klabunde K J, J Mater Chem, 2004, 14, 757.*
11. *Klabunde K J, Stark J V, Koper O, Mohs C, Park D G, Decker S, Jiang Y, Lagadic I, Zhang D, J Phys Chem, 1996, 100, 12 142.*
12. *Stark J V, Park D G, Lagadic I, Klabunde K J, Chem Mater, 1996, 8, 1904.*
13. *Koper O, Lagadic I and Klabunde K J, Chem Mater, 1997, 9, 838.*
14. *Klabunde K J, US Pat, 1999, 5 990 373.*
15. *Koper O, Klabunde K J, US Pat, 2000, 6 057 488.*
16. *Jiang Y, Decker S, Mohs C, Klabunde K J, J Catal, 1998, 180, 24.*
17. *Bhagat M, Singh A, Mehrotra R C; Synth React Inorg Metal-org Chem, 1998, 28, 997.*
18. *Mehrotra R C, Singh A, Bhagat M, Godhwani J, J Sol-gel Sci&Tech, 1998, 13, 45.*
19. *Sharma H K, Kapoor P N, Indian J chem, 2004, 43A, 556.*
20. *Sharma M, Bhagi A K, Priti, Kansal R, Kumar R, Kapoor P N, Indian J Chem, 2005, 44A, 1*
21. *Sharma H K, Kapoor, P N, Polyhedron, 1988, 7, 1389.*
22. *Vogel A I, A Text Book of Quantitative analysis, Eds, Longman, London, 1989.*
23. *Perrin D D, Armarego W L F, Perrin D R, Purification of Laboratory Chemicals, 2<sup>nd</sup> Edn, Pergamon Press, New York, 1980.*
24. *Osipov O A, Minkin Dsh. Verknovodova V I, Knyazhanskii M I, Zh Neorg Khim, 1967, 12, 1549.*
25. *Mayadeo M S, J Ind Chem Soc 1967, 11, 502.*
26. *Kumar R, Sharma H K, Inorganic Chemistry An Indian Journal, 2008, 3(3), 218*
27. *Bradley D C, Halim F M A, Wardlaw W, J Chem Soc, 1950, 3450.*
28. *Nakamoto K, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Eds.: John Wiley and Sons, New York, 1986.*

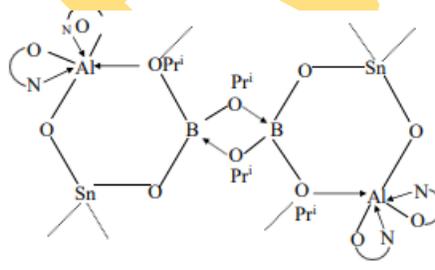
29. *Brcitmair E, Voelter W, <sup>13</sup>C NMR spectroscopy (High Resolution Methods and Application in Organic Chemistry and Biochemistry), VCH, New York, 1990*
30. *Mueller D, Hoebbel, Gessner W, Chem Phys Lett, 1981, 84, 2.*
31. *Nguyen TT, Ogwuru N, Eng G, App Org Chem, 2000, 14, 345.*

**Table -1: Analytical data of studied compounds**

S.No. Compound g (mmol)	Ligand g (mmol)	Molar ratio	Refluxing time hrs	Product g (%)	Anal. Calcd.(found)			
					HOPr <sup>i</sup> g (%)	Sn (%)	Al (%)	B (%)
1. [Bu <sub>2</sub> SnO <sub>2</sub> AlB(OPr <sup>i</sup> ) <sub>4</sub> ] 0.280(0.536)	HSB <sup>1</sup> 0.106 (0.536)	1:1	4	[Bu <sub>2</sub> SnO <sub>2</sub> AlB(OPr <sup>i</sup> ) <sub>3</sub> (SB <sup>1</sup> )] 0.301 (84.6)	0.07 (0.07)	19.83 (19.73)	4.50 (4.22)	1.83 (1.87)
2. [Bu <sub>2</sub> SnO <sub>2</sub> AlB(OPr <sup>i</sup> ) <sub>4</sub> ] 0.297 (0.545)	HSB <sup>1</sup> 0.215 (1.09)	1:2	6	[Bu <sub>2</sub> SnO <sub>2</sub> AlB(OPr <sup>i</sup> ) <sub>2</sub> (SB <sup>1</sup> ) <sub>2</sub> ] 0.382 (84.7)	0.121 (0.119)	18.03 (17.87)	3.74 (3.77)	1.76 (1.77)
3. [Bu <sub>2</sub> SnO <sub>2</sub> AlB(OPr <sup>i</sup> ) <sub>4</sub> ] 0.279 (0.534)	HSB <sup>2</sup> 0.113 (0.534)	1:1	4	[Bu <sub>2</sub> SnO <sub>2</sub> AlB(OPr <sup>i</sup> ) <sub>3</sub> (SB <sup>2</sup> )] 0.302 (83.1)	0.069 (0.068)	19.74 (19.72)	4.46 (4.42)	1.81 (1.86)
4. [Bu <sub>2</sub> SnO <sub>2</sub> AlB(OPr <sup>i</sup> ) <sub>4</sub> ] 0.293 (0.541)	HSB <sup>2</sup> 0.228 (1.082)	1:2	7	[Bu <sub>2</sub> SnO <sub>2</sub> AlB(OPr <sup>i</sup> ) <sub>2</sub> (SB <sup>2</sup> ) <sub>2</sub> ] 0.383 (84.1)	0.118 (0.103)	17.70 (17.56)	3.63 (3.65)	1.72 (1.77)
5. [Bu <sub>2</sub> SnO <sub>2</sub> AlB(OPr <sup>i</sup> ) <sub>4</sub> ] 0.270(0.506)	HSB <sup>3</sup> 0.117 (0.506)	1:1	4	[Bu <sub>2</sub> SnO <sub>2</sub> AlB(OPr <sup>i</sup> ) <sub>3</sub> (SB <sup>3</sup> )] 0.287 (79.7)	0.067 (0.065)	19.42 (19.36)	4.32 (4.73)	1.76 (1.88)
6. [Bu <sub>2</sub> SnO <sub>2</sub> AlB(OPr <sup>i</sup> ) <sub>4</sub> ] 0.274 (0.518)	HSB <sup>3</sup> 0.240 (1.036)	1:2	7	[Bu <sub>2</sub> SnO <sub>2</sub> AlB(OPr <sup>i</sup> ) <sub>2</sub> (SB <sup>3</sup> ) <sub>2</sub> ] 0.385 (84.2)	0.113 (0.107)	17.25 (17.28)	3.55 (3.43)	1.69 (1.67)



Proposed structure of  
[SnO<sub>2</sub>AlB(OPr<sup>i</sup>)<sub>3</sub>(SB)]



Proposed structure of  
[SnO<sub>2</sub>AlB(OPr<sup>i</sup>)<sub>2</sub>(SB)<sub>2</sub>]

**Figure 1**

