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SYNTHESIS AND CHARACTERIZATION OF NONAISOPROPOXODISTANNATO COMPLEXES OF MAGNESIUM(II), BARIUM(II), ZINC(II) AND CADMIUM(II)*

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Abstract—Novel heterobimetallic isopropoxides of the types $[MSn_2Cl(OPr^i)_9]_2$(**A**) and $[MSn_4(OPr^i)_{18}]$(**B**) (M = Mg, Zn or Cd) have been synthesized by the reactions of MCl_2 (M = Mg, Zn or Cd) with $KSn_2(OPr^i)_9$ in 1 : 1 and 1 : 2 molar ratios respectively. Derivatives $[MSn_2(OPr^i)_{10}]_2$(**C**) (M = Cd) and $[MAlSn_2(OPr^i)_{13}]$(**D**), where M = Zn, Cd or Mg have also been prepared by the equimolar reactions of **A** with $KOPr^i$ or $KAl(OPr^i)_4$ respectively. Further, the derivatives, $[BaSn_2(OPr^i)_{10}]_2$ and $[BaSn_4(OPr^i)_{18}]$ have been obtained by the reactions of barium with isopropyl alcohol in the presence of required molar ratios of $Sn(OPr^i)_4 \cdot Pr^iOH$.

In view of the main group bivalent metals being components of many useful dielectric materials based on mixed metal oxides such as $BaTiO_3$,[1] $Ba_{0.6}K_{0.4}BiO_3$,[2] $BaMg_{1/3}Ta_{2/3}O_3$,[3] $MgAl_2O_4$,[4] and Cd_2SnO_4,[5] as well as the high T_c superconductors like $YBa_2Cu_3O_{7-x}$,[6] the synthesis of soluble alkoxy precursors[7–11] of these metals for the sol–gel process assumed special significance. Although alkoxides of bivalent metals $M(OR)_2$ appear to have limited solubility in organic solvents including the parent alcohols,[12] a number of volatile and soluble heterometallic alkoxides, e.g. (i) $M\{Al(OPr^i)_4\}_2$ [M = Be,[13] Mg,[14] Ca,[14] Sr,[14] Ba,[14] Zn,[13] Cd[13]], (ii) $M\{Zr_2(OPr^i)_9\}_2$ (M = Mg,[15] Ca,[15] Sr,[15] Ba,[15] Zn,[16] Cd[16]) and (iii) $M\{Nb(OPr^i)_6\}_2$ (M = Mg,[17] Ca,[17] Sr,[17] Ba,[17] Zn,[16] Cd[16]) have already been reported from our laboratories.

During the present studies, tin was chosen as the second component of the heterometal alkoxides in view of scanty knowledge about tin(IV) heterometal alkoxide derivatives such as $[Cd_4Sn_4(\mu_4\text{-}O)_2(OAc)_{10}(OCH_2Bu^t)_{10}]$,[18] $[ZnSn(OEt)_6]$[19] and $Sn\{Al(OPr^i)_4\}_4$.[20] In spite of the importance of tin oxides in view of their optical and electrical[21] properties, the sol–gel route for their preparation has not been exploited due to inherent difficulties in the preparation of simple tin alkoxides themselves. Mehrotra[22] has recently suggested the use of more conveniently synthesizable soluble sodium nonaisopropoxodistannate, $NaSn_2(OPr^i)_9$, as a precursor for tin oxide ceramic materials.

In view of the above, hetero(bi- and tri-)metallic isopropoxides of Mg^{II}, Ba^{II}, Zn^{II} and Cd^{II} with Sn^{IV} are described in this paper.

EXPERIMENTAL

All experimental work was performed under strictly moisture free atmospheres. Chemicals and solvents were purified and dried by literature methods.[23]

The metal chlorides MCl_2 (M = Zn or Cd) were made anhydrous by refluxing with thionyl chloride.[24] Magnesium chloride was made anhydrous by heating a mixture of $MgCl_2 \cdot 6H_2O$ (B.D.H.) and NH_4Cl, in a current of dry HCl gas. The purity of the anhydrous metal chlorides ($ZnCl_2$, $CdCl_2$, $MgCl_2$) was tested by analyses of the metal

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* Dedicated to the outstanding chemist and our friend Professor Heinz Noth on the occasion of his 65th birthday.

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as well as chloride contents and these were in all cases found to be within the $\pm0.5\%$ error of the expected values. Barium metal granules (B.D.H.) were used as received.

$K\{Sn_2(OPr^i)_9\}$ was prepared[25] by the reaction of freshly distilled $SnCl_4$(2 mol) with $KOPr^i$ (9 mol) initially at 0°C followed by refluxing in benzene–isopropyl alcohol for 3 h. $Sn(OPr^i)_4 \cdot Pr^iOH$ was prepared by the literature method.[26]

In heterobimetallic isopropoxides, tin was separated as hydrated tin dioxide[27] and estimated as SnO_2. After removal of the tin, zinc, cadmium and magnesium were estimated in the filtrate as $ZnNH_4PO_4$, $CdNH_4PO_4 \cdot H_2O$ and $MgNH_4PO_4 \cdot 6H_2O$[27] respectively and barium was estimated as $BaSO_4$.[27] Isopropoxy groups were estimated by an oxidimetric method.[28] Chloride was estimated by Volhard's method.[27]

IR spectra (4000–200 cm^{-1}) were recorded on a Perkin–Elmer 577 spectrometer as Nujol mulls using CsI optics. NMR spectra were recorded on a JEOL FX-90Q spectrometer (^1H, 89.55 MHz; ^{13}C, 22.49 MHz; ^{27}Al, 23.29 MHz; and ^{119}Sn, 33.35 MHz). The chemical shift references were as follows: ^1H and ^{13}C, $SiMe_4$ (internal); ^{119}Sn, $SnMe_4$ (external) and ^{27}Al, 1 M $\{Al(H_2O)_6\}^{3+}$ (external). Molecular weights were determined ebullioscopically in benzene with a Gallenkamp ebulliometer using a thermister sensing device.

Preparation of nonaisopropoxodistannatometal (Mg, Ba, Zn or Cd) complexes

Synthesis of $[ClZn\{Sn_2(OPr^i)_9\}]_2$ (**4B**). $SnCl_4$ (3.46 g, 13.28 mmol) and $KOPr^i$ [prepared by the reaction of potassium (2.34 g, 59.84 mmol) with isopropyl alcohol (~15 cm^3) in benzene (~20 cm^3)] in 2 : 9 molar ratio were mixed at 0°C, followed by refluxing for about 3 h, to ensure completion of the reaction. The excess solvent from the reaction mixture was removed under reduced pressure (0.5 mm at 30°C) to afford the solid $KSn_2(OPr^i)_9$, which was dissolved in dry benzene (~25 cm^3) and added dropwise to a pre-stirred suspension of $ZnCl_2$ (0.90 g, 6.60 mmol) in benzene (~20 cm^3). The reaction mixture was stirred at ~65°C for ~5 h. The precipitated KCl (0.49 g, 6.57 mmol) was removed by filtration. The volatiles were removed from the filtrate under reduced pressure (1 mm Hg) at room temperature to afford $ClZn\{Sn_2(OPr^i)_9\}$ (5.70 g, 99%) as a white solid. The product was purified by recrystallization at −15°C from a (3 : 1) mixture of *n*-hexane–toluene in 65% yield.

Adopting a similar procedure, reactions of $K\{Sn_2(OPr^i)_9\}$ with MCl_2 (M = Mg, Zn or Cd) in appropriate molar ratios afforded the derivatives, $[ClMg\{Sn_2(OPr^i)_9\}]_2$ (**6B**), $Mg\{Sn_2(OPr^i)_9\}_2$ (**3A**), $Zn\{Sn_2(OPr^i)_9\}_2$ (**1A**), $[ClCd\{Sn_2(OPr^i)_9\}]_2$ (**5B**) and $Cd\{Sn_2(OPr^i)_9\}_2$ (**2A**) in quantitative yields. All these could be purified by recrystallization at −15°C from (3 : 1) *n*-hexane–toluene in 50–65% yields; preparative and analytical details are listed in Table 1.

Synthesis of $[Ba\{Sn_2(OPr^i)_9\}_2]$ (**12A**). The mixture containing barium granules (0.22 g, 1.60 mmol), $Sn(OPr^i)_4 \cdot Pr^iOH$ (2.60 g, 6.41 mmol), and a few crystals of iodine in minimum amounts of isopropyl alcohol (~3 cm^3) and benzene (~25 cm^3) was refluxed for ~12 h, during which the barium metal reacted, giving rise to a reaction mixture containing a suspension of tiny particles. After removal of the volatiles *in vacuo* the resulting solid was dissolved in benzene and filtered to remove suspended particles. From the filtrate, volatiles were removed under reduced pressure to afford $Ba\{Sn_2(OPr^i)_9\}_2$ (2.59, 96%) as a pale yellow solid which was purified by recrystallization at −10°C from a (2 : 3) CCl_4–*n*-hexane mixture in 50% yield.

Adopting a similar procedure, a 1 : 2 reaction of Ba granules with $Sn(OPr^i)_4 \cdot Pr^iOH$ in C_6H_6–Pr^iOH affords $[BaSn_2(OPr^i)_{10}]_2$ (**11C**) as a pale yellow solid, which was purified by recrystallization from (2 : 3) CCl_4–*n*-hexane in 55% yield.

Synthesis of $[\{Al(OPr^i)_4\}Zn\{Sn_2(OPr^i)_9\}]$ (**8D**). A benzene (~25 cm^3) suspension of $K\{Al(OPr^i)_4\}$ {freshly prepared by refluxing potassium (0.08 g, 2.12 mmol), $Al(OPr^i)_3$ (0.45 g, 2.20 mmol) and isopropyl alcohol (2 cm^3) in benzene (20 cm^3), followed by removal of the volatiles} was slowly added to the benzene solution (25 cm^3) of $ClZn(Sn_2(OPr^i)_9\}$ (1.85 g, 2.12 mmol). The reaction mixture was then stirred at room temperature for 8 h, followed by heating at ~70°C for ~4 h. The precipitated KCl (0.16 g, 2.14 mmol) was separated by filtration. Solvents from the filtrate were removed under reduced pressure (1 mm Hg at 27°C) to afford $[ZnAlSn_2(OPr^i)_{13}]$ (**8D**) (2.30 g; 99%) as a colourless viscous material, which was dissolved in *n*-hexane and filtered to remove suspended parties and finally dried *in vacuo* to yield (95%) a white viscous product.

A similar reaction of $KAl(OPr^i)_4$ with $[ClCd\{Sn_2(OPr^i)_9\}_2$ (**5B**) or $[ClMg\{Sn_2(OPr^i)_9\}]_2$ (**6B**) in 2 : 1 molar ratio in C_6H_6 affords $[CdAlSn_2(OPr^i)_{13}]$ (**9D**) or $[MgAlSn_2(OPr^i)_{13}]$ (**10D**) in quantitative yield.

RESULTS AND DISCUSSION

The reactions employed in the syntheses of heterometallic isopropoxides described in this

Table 1. Synthetic and analytical data for nonaisopropoxodistannato derivatives of Zn^{II}, Cd^{II}, Mg^{II} and Ba^{II}

S. No.	Reactants[a] (g; mmol)	Product[b] (Yield %)[c]	Analysis[d] (%)					Mol.wt.[d]
			Mg/Ba Zn/Cd	Sn	Pr^iO	Cl	Mixed oxide	
1	$ZnCl_2+K\{Sn_2(OPr^i)_9\}[K(2.34; 59.84)+SnCl_4(3.46; 13.28)]$ (0.90; 6.0)	$ClZn\{Sn_2(OPr^i)_9\}$ (**1A**) (65)	7.5 (7.5)	27.3 (27.3)	61.1 (61.1)	4.1 (4.1)	—	1900 (870)
2	$ZnCl_2+2K\{Sn_2(OPr^i)_9\}[K(0.52; 13.30)+SnCl_4(0.77; 2.96)]$ (0.20; 1.47)	$Zn\{Sn_2(OPr^i)_9\}_2$ (**4B**) (60)	4.0 (4.1)	30.0 (29.6)	66.2 (66.3)	—	—	1550 (1603)
3	$CdCl_2+K\{Sn_2(OPr^i)_9\}[K(0.89; 22.76)]+SnCl_4(1.32; 5.07)$ (0.46; 2.51)	$ClCd\{Sn_2(OPr^i)_9\}$ (**2A**) (70)	12.2 (12.3)	25.8 (25.9)	57.9 (58.0)	3.8 (3.9)	—	—
4	$CdCl_2+2K\{Sn_2(OPr^i)_9\}[K(0.86; 22.0)+SnCl_4(1.26; 4.84)]$ (0.22; 1.20)	$Cd\{Sn_2(OPr^i)_9\}_2$ (**5B**) (60)	6.8 (6.8)	28.8 (28.8)	64.4 (64.4)	—	—	1570 (1649)
5	$MgCl_2+K\{Sn_2(OPr^i)_9\}[K(0.81; 20.72)+SnCl_4(1.20; 4.60)]$ (0.22; 2.31)	$ClMg\{Sn_2(OPr^i)_9\}$ (**3A**) (60)	2.9 (2.9)	28.8 (28.6)	64.0 (64.1)	4.2 (4.2)	—	1650 (829)
6	$MgCl_2+2K\{Sn_2(OPr^i)_9\}[K(1.55; 39.64)+SnCl_4(2.30; 8.83)]$ (0.21; 2.20)	$Mg\{Sn_2(OPr^i)_9\}_2$ (**6B**) (55)	1.5 (1.6)	30.6 (30.4)	68.0 (68.0)	—	—	1550 (1562)
7	$ClCd\{Sn_2(OPr^i)_9\}+KOPr^i[K(0.10; 2.55)+Pr^iOH$ (5 ml)] (2.44; 2.66)	$(Pr^iO)Cd\{Sn_2(OPr^i)_6\}$ (7C) (50)	11.9 (11.9)	25.3 (25.2)	62.7 (62.7)	—	—	1750 (941)
8	$Ba+2Sn(OPr^i)_4\cdot Pr^iOH(2.72; 6.55)$ (0.45; 3.28)	$(Pr^iO)Ba\{Sn_2(OPr^i)_9\}$ (**11C**) (55)	14.2 (14.21)	24.6 (24.6)	61.1 (61.1)	—	—	1900 (966)
9	$Ba+4Sn(OPr^i)_4\cdot Pr^iOH(2.60; 6.41)$ (0.22; 1.60)	$Ba\{Sn_2(OPr^i)_9\}_2$ (**12A**) (50)	8.1 (8.2)	28.4 (28.3)	63.4 (63.5)	—	—	1650 (1676)
10	$ClZn\{Sn_2(OPr^i)_9\}+K\{Al(OPr^i)_4\}[K(0.08; 2.12)+Al(OPr^i)_3(0.45; 2.20)]$ (1.85; 2.12)	$\{Al(OPr^i)_4\}Zn\{Sn_2(OPr^i)_9\}$ (**8D**) (95)[e]	—	—	69.9 (70.0)	—	40.9 (41.0)	1050 (1097)
11	$ClCd\{Sn_2(OPr^i)_9\}+K\{Al(OPr^i)_4\}[K(0.08; 2.17)+Al(OPr^i)_3(0.44; 2.15)]$ (2.0; 2.18)	$\{Al(OPr^i)_4\}Cd\{Sn_2(OPr^i)_9$ (**9D**) (96)[e]	—	—	67.0 (67.1)	—	44.0 (44.4)	1100 (1144)
12	$ClMg\{Sn_2(OPr^i)_9\}+K\{Al(OPr^i)_4\}[K(0.10; 2.5)+Al(OPr^i)_3(0.54; 2.6)]$ (2.21; 2.67)	$[\{Al(OPr^i)_4\}Mg\{Sn_2(OPr^i)_9\}]$ (**10D**) (97)[e]	—	—	72.6 (72.7)	—	39.0 (38.7)	—

[a] In benzene.

[b] The derivatives **8D, 9D** and **10D** are viscous in nature while others are colourless solids.

[c] Crude products were obtained in 99% yields but noted yields refer to the crystallized products, unless otherwise indicated.

[d] Determined ebullioscopically in benzene and calculated values are given in parentheses.

[e] Refer to the yield obtained after extraction with *n*-hexane and evaporation of the volatiles under reduced pressure.

paper can be represented by the following six equations:

$$MCl_2 + 2KSn_2(OPr^i)_9 \longrightarrow [MSn_4(OPr^i)_{18}] + 2KCl\downarrow \tag{1}$$

A

1A : M = Zn; **2A** : M = Cd; **3A** : M = Mg

$$2MCl_2 + 2KSn_2(OPr^i)_9 \longrightarrow [MSn_2(OPr^i)_9Cl]_2 + 2KCl\downarrow \tag{2}$$

B

4B : M = Zn; **5B** : M = Cd; **6B** : M = Mg

$$[MSn_2(OPr^i)_9Cl]_2 + 2KOPr^i \longrightarrow [MSn_2(OPr^i)_{10}]_2 + 2KCl\downarrow \tag{3}$$

C

7C : M = Cd

$$[MSn_2(OPr^i)_9Cl]_2 + 2KAl(OPr^i)_4 \longrightarrow 2[MAlSn_2(OPr^i)_{13}] + 2KCl\downarrow \tag{4}$$

D

8D : M = Zn; **9D** : M = Cd; **10D** : M = Mg

$$2Ba + 4Sn(OPr^i)_4 \cdot Pr^iOH \longrightarrow [BaSn_2(OPr^i)_{10}]_2 + 2H_2\uparrow \tag{5}$$

11C

$$Ba + 4Sn(OPr^i)_4 \cdot Pr^iOH \xrightarrow{C_6H_6/Pr^iOH} [BaSn_4(OPr^i)_{18}] + 2Pr^iOH + H_2\uparrow. \tag{6}$$

12A

All these derivatives can be obtained in an analytically pure state by recrystallization at −10 to −15°C from *n*-hexane–toluene or *n*-hexane. Attempts to volatilize (200–260°C/0.01 mm Hg) these complexes resulted in decomposition with darkening in colour. These new derivatives (Table 1) are highly moisture-sensitive solids or viscous materials, soluble in common organic solvents (such as C_6H_6, $C_6H_5CH_3$, CH_2Cl_2, CCl_4 and *n*-C_6H_{14}). The derivatives **4B, 5B, 5C, 7C** and **11C** tend to exhibit dimeric behaviour, while the derivatives **1A, 2A, 3A, 8D, 9D** and **10D** are monomeric in boiling benzene.

IR spectra of the derivatives show absorptions[12] in the regions: 1120–1180 υ(OCHMe$_2$), 1030–930 υ(C—O), 500–580 υ(Sn—O), 600–740 υ(Al—O) and 400–475 υ(M—O) (M = Mg^{II}, Zn^{II} or Cd^{II}). The metal chloride frequencies[16] in **4B, 5B** and **6B** were observed in the region 290–340 cm^{-1}.

The ^{1}H NMR spectra (Table 2) of nonaisopropoxodistannato complexes of Mg^{II} and Ba^{II} (i.e. **3A, 6B, 11C** and **12A**) exhibit three types of doublets centred in the region δ1.24–1.48 ppm and two separate septets in the region δ4.02–4.47 ppm, due to β- and α-protons respectively.

Interestingly the room temperature ^{1}H NMR (Table 2) spectra (in CDCl$_3$) of nonaisopropoxodistannatozinc(II) and -cadmium(II) complexes depict more resolved methyl signals compared to those of analogous nonaisopropoxodizirconato Zn(II) and -Cd(II) complexes.[16] For example, in derivatives **4B** and **5B** two distinct doublets due to terminal and bridging (see Table 2) OCHMe$_2$ groups were observed in the regions 1.25–1.27 and 1.43–1.44 ppm roughly in the ratio of 5 : 4 which could be interpreted in terms of the structure shown in Fig. 1(a), in which the bridging chlorine atoms are located symmetrically above and below the plane containing four tin atoms. This type of structure is supported by the X-ray structures of [{Ba[Zr$_2$(OPr^i)$_9$](μ-OPr^i)}$_2$][29] and [{Cd[Zr$_2$(OPr^i)$_9$](μ-Cl)}$_2$].[30] However, ^{1}H and ^{13}C NMR spectra (at room temperature) of these derivatives exhibit only two distinguishable doublets due to isopropoxy groups, instead of four different possible environments for isopropoxy groups of Sn$_2$(OPr^i)$_9$ units involved in tetradentate ligation in [M{Sn$_2$(OPr^i)$_9$}(μ-Cl)]$_2$ [M = Zn (**4B**) or Cd (**5B**)].

Further, in view of the known X-ray structure of [Ba{Zr$_2$(OPr^i)$_9$}$_2$],[29] the bis-derivative [Ba{Sn$_2$(OPr^i)$_9$}$_2$] might be anticipated to adopt a similar structure (Fig. 1b), wherein both the Sn$_2$(OPr^i)$_9$ units are tetradentedly bonded to the barium atom, and the two comparable Sn$_2$(OPr^i)$_9$ ligands have a staggered ("bow-tie or spiro") conformation about barium.

In the derivatives **1A, 2A** and **3A** it is very likely that Sn$_2$(OPr^i)$_9$ units might be bonded tridentedly with Zn^{II}, Cd^{II} and Mg^{II} centres, with the further possibility of ligation of some appropriately situated isopropoxo groups, particularly in the case of the larger Cd^{II}. The Zn^{II}, Cd^{II} and Mg^{II} centres in **8D, 9D** and **10D** may involve tetradentate and bidentate ligation of Sn$_2$(OPr^i)$_9$ and Al(OPr^i)$_4$ units respectively (Fig. 1c). The isopropoxo ligands bridging M to Al may be symmetrically located above and below the MSn$_2$ plane.

The ^{13}C NMR spectra (Table 2) of all the derivatives exhibit (i) two peaks, one in each the regions δ26.1–26.7 and 27.4–27.6 ppm, due to β-carbon atoms of bridging and terminal isopropoxy groups, and (ii) two peaks, one in each of the regions δ66.4–66.7 and 67.8–68.09 ppm, due to α-carbon atoms of bridging and terminal isopropoxy groups. In spite of the utility of ^2J(^{119}Sn—O—^{13}C) coupling, con-

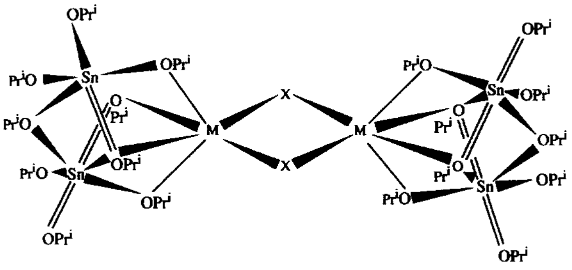
Table 2. ^{1}H, ^{13}C{^{1}H} and ^{119}Sn NMR spectral data (chemical shift, ppm) at 20°C for nonaisopropoxodistannato derivatives of Sn^{II}, Cd^{II}, Mg^{II} and Ba^{II}

Compound	^{1}H^a	^{13}C^b OCH—(CH$_3$)$_2$	^{119}Sn^c
1A	1.27 [d(J = 6 Hz), 48H, OCH*Me*$_2$(t)], 1.44 [d(J = 6 Hz), 60H, OCH*Me*$_2$(b)], 4.44 [Sept(J = 6 Hz), 18H, OC*H*Me$_2$(b+t)]	26.60 [β-*C*(t)], 27.52 [β-*C*(b)], 66.53 [α-*C*(t)], 67.93 [α-*C*(b)]	−595.8
4B	1.27 [d(J = 6.2 Hz), 60H, OCH*Me*$_2$(t)], 1.46 [d(J = 6.2 Hz), 48H, OCH*Me*$_2$(b)], 4.42 [Sept(J = 6.2 Hz), 18H, OC*H*Me$_2$(b+t)]	26.88 [β-*C*(t)], 27.51 [β-*C*(b)], 66.71 [α-*C*(t)], 67.98 [α-*C*(b)]	−595.7
2A	1.25 [d(J = 6.5 Hz), 48H, OCHMe$_2$(t)], 1.43 [d(J = 6.5 Hz), 60H, OCH*Me*$_2$(b)], 4.40 [Sept(J = 6.5 Hz), 18H, OC*H*Me$_2$(b+t)]	26.20 [β-*C*(t)], 27.55 [β-*C*(b)], 66.40 [α-*C*(t), 67.90 [α-*C*(b)]	−596.6
5B	1.23 [d(J = 6 Hz), 60H, OCH*Me*$_2$(t)], 1.45 [d(J = 6 Hz), 48H, OCH*Me*$_2$(b)], 4.46 [Sept(J = 6 Hz), 18H, OC*H*Me$_2$(b+t)]	26.22 [β-*C*(t)], 27.53 [β-*C*(b)], 66.47 [α-*C*(t)], 67.98 [α-*C*(b)]	−595.7
3A	1.24 [d(J = 6.5 Hz), 48H, OCH*Me*$_2$(t)], 1.31 [d(J = 6.5 Hz), 36H, OCH*Me*$_2$(μ_2-b)], 1.44 [d(J = 6.5 Hz), 24H, OCH*Me*$_2$(μ_3-b)], 4.33 [m, 18H, OC*H*Me$_2$(b+t)]	—	−597.0
6B	1.22 [d(J = 6 Hz), 60H, OCH*Me*$_2$(t)], 1.29 [d(J = 6 Hz), 24H, OCH*Me*$_2$(μ_2-b)], 1.45 [d(J = 6 Hz), 24H, OCH*Me*$_2$(μ_3-b)], 4.26 [m, 18H, OCH*H*Me$_2$(b+t)]	—	−595.7
7C	1.27 [d(J = 6.5 Hz), 48H, OCH*Me*$_2$(t)], 1.44 [d(J = 6.5 Hz), 72H, OCH*Me*$_2$(b)], 4.45 [Sept(J = 6.5 Hz), 20H, OC*H*Me$_2$(b+t)]	26.16 [β-*C*(t)], 27.46 [β-*C*(b)], 66.45 [α-*C*(t)], 67.93 [α-*C*(b)]	−595.5
11C	1.26 [d(J = 6 Hz), 48H, OCH*Me*$_2$(t)], 1.30 [d(J = 6 Hz), 48H, OCH*Me*$_2$(μ_2-b)], 1.48 [d(J = 6 Hz), 24H, OCH*Me*$_2$(μ_3-b)], 4.02 [Sept(J = 6 Hz), 8H, OC*H*Me$_2$(t)], 4.46 [Sept(J = 6 Hz), 12H, OC*H*Me$_2$(b)]	—	−597.0
12A	1.24 [d(J = 6.4 Hz), 48H, OCH*Me*$_2$(t)], 1.27 [d(J = 6.4 Hz), 36H, OCH*Me*$_2$(μ_2-b)], 1.46 [J = 6.4 Hz), 24H, OCH*Me*$_2$(μ_3-b)], 4.11 [Sept(J = 6.4 Hz), 8H, OC*H*Me$_2$(t)], 4.47 [Sept(J = 6.4 Hz), 10H, OC*H*Me$_2$(b)]	—	−596.5
8D	1.27 [d(J = 6 Hz), 36H, OCH*Me*$_2$(t)], 1.44 [d(J = 6 Hz), 42H, OCH*Me*$_2$(b)], 4.45 [Sept(J = 6 Hz), 13H, OC*H*Me$_2$(b+t)]	26.16 [β-*C*(t)], 27.46 [β-*C*(b)], 66.45 [α-*C*(t)], 67.93 [α-*C*(b)]	−595.5
10D	1.27 [d(J = 6 Hz), 36H, OCH*Me*$_2$(t)], 1.44 [d(J = 6 Hz), 42H, OCH*Me*$_2$(b)], 4.31 [Sept(J = 6 Hz), 13H, OC*H*Me$_2$(b+t)]	26.22 [β-*C*(t)], 27.52 [β-*C*(b)], 66.53 [α-*C*(t)], 67.99 [α-*C*(b)]	−596.5
9D	1.25 [d(J = 6.5 Hz), 36H, OCH*Me*$_2$(t)], 1.43 [d(J = 6.5 Hz), 42H, OCH*Me*$_2$(b)], 4.26 [Sept(J = 6.5 Hz), 13H, OC*H*Me$_2$(b+t)]	26.20 [β-*C*(t)], 27.50 [β-*C*(b)], 66.50 [α-*C*(t)], 67.90 [α-*C*(b)]	−595.45

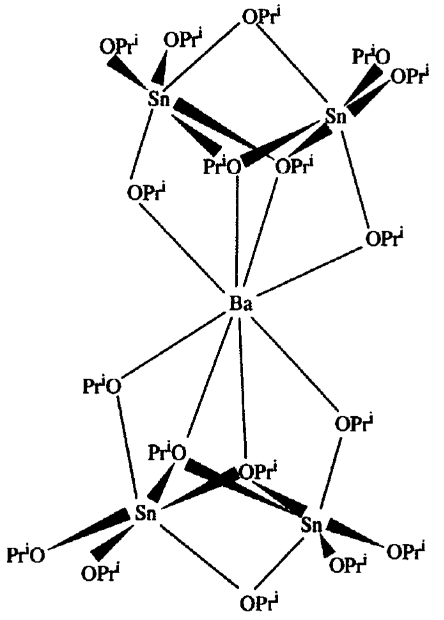
[a] Measured in CDCl$_3$, chemical shifts are positive to low frequency of SiMe$_4$ and given as chemical shift (δ), [multiplicity (J in Hz), relative intensity, and assignment; where t = terminal, b = bridging, and sept = septet].

[b] Measured in CDCl$_3$, chemical shifts are positive to low frequency of SiMe$_4$.

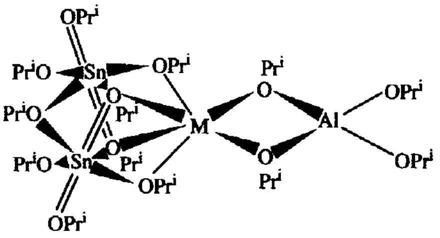
[c] Measured in C$_6$H$_6$, chemical shifts are negative to high frequency of SnMe$_4$. ^{119}Sn—O—^{117}Sn coupling constants are approximately 112 Hz.



(a) (M = Ba, X = OPr^i; M = Cd, X = Cl or OPr^i)



(b)



(c) (M = Ba, Mg, Zn, Cd)

Fig. 1.

stant values in distinguishing terminal versus doubly bridging alkoxide ligands in derivatives of the type $[\mathrm{Sn(OBu}^i)_4\cdot\mathrm{Bu}^i\mathrm{OH}]_2$,[31] unequivocal evaluation of $^2J(^{119}\mathrm{Sn—O—}^{13}\mathrm{C})$ coupling constant values in the ^{13}C NMR spectra of the newly synthesized derivatives (Table 2) could not be possible due to (i) the ill-resolved nature of the spectra, particularly at the bottom of the peak, and smaller magnitude of the coupling contants, and (ii) intramolecular fast exchange.

The ^{119}Sn NMR spectra (Table 2) at room temperature of all these derivatives show a sharp signal at δ -596.2 ± 0.8 ppm characteristic of an octahedral environment around tin. Observation of $^2J(^{119}\mathrm{Sn—O—}^{117}\mathrm{Sn})$ nuclear spin–spin coupling constant values 112 Hz in all these spectra shows that the $[\mathrm{Sn}_2]$ core remains intact even in solution. Furthermore, we note that the ^{119}Sn NMR chemical shifts are lower (by 45 ppm) than the value observed for the six-coordinate tin(IV) in $\mathrm{KSn_2(OPr}^i)_9$ (δ -640.19 ppm), which may be the result of significant covalent interaction between metal M (M = $\mathrm{Mg^{II}}$, $\mathrm{Ba^{II}}$, $\mathrm{Zn^{II}}$ or $\mathrm{Cd^{II}}$) and $\mathrm{Sn_2(OPr}^i)_9$ unit(s).

These observations tend to support the proposed structures shown in Fig. 1. However, in the absence of single crystal X-ray diffraction studies for which our attempts have not been successful so far, the above structural conclusions are rather speculative.

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