SYNTHESIS, CHARACTERIZATION AND REACTIONS OF SOME ALKOXOALUMINATES OF TIN(IV)

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Abstract—Novel heterometal alkoxides of tin(IV) with the compositions $[Cl_{4-n}Sn{Al}(OPr^i)_4]_n]$ (where n = 1-3) and $[Cl_2Sn{Al}(OBu^i)_4]_2]$ have been synthesized by the reactions of SnCl₄ with the appropriate potassium alkoxoaluminate in the requisite molar ratio. Replacement of chloride in these derivatives has yielded heterometal (bi- or tri-) derivatives of the types $[(OR)_{4-n}Sn{Al}(OPr^i)_4]_n]$ (R = Prⁱ, Buⁱ; n = 2 or 3) and $[{Zr_2(OPr)_9}]$ Sn{Al}(OPrⁱ)_4]_3]. The new heterometal alkoxides have been characterized by elemental analyses, molecular weight measurements, IR and multinuclear (¹H, ¹³C, ²⁷Al and ¹¹⁹Sn) NMR spectral studies.

Metal alkoxides have in recent years emerged as highly attractive precursors^{1,2} for ceramic materials by the sol-gel process. In view of the difficulties³⁻⁵ in the synthesis of simple tin(IV) alkoxides, $Sn(OR)_4$, by the conventional methods, their applications in these directions continue to be rather limited.

The use of heterometal alkoxides, e.g. Mg{Al $(OPr^{i})_{4}_{2}$, as molecular precursors⁶ for oxide ceramics like MgAl₂O₄ has been depicted to have some distinct advantages.⁷ In view of the comparative ease with which a bimetallic alkoxide, e.g. NaSn₂ $(OR)_{9}$, can be synthesized, its use as a more convenient precursor has been recently suggested.^{8,9} It is relevant to mention that a few bimetallic alkoxides of tin(II)^{10,11} have already been described from our laboratories.

The synthesis of a number of interesting chloride bimetallic alkoxides of tin(IV) are described in this paper and the use of such chloro derivatives for stable novel trimetallic derivatives has been demonstrated for the first time.

EXPERIMENTAL

Stringent precautions were taken to exclude moisture throughout the experimental procedure.

All reactions were carried out in glass apparatus, which was initially cleaned, rinsed with ethyl alcohol and oven dried (140–150°C) followed by cooling in a moisture-free atmosphere prior to use.

Tin tetrachloride (Aldrich) was distilled $(114^{\circ}/760 \text{ mm})$ before use.

Aluminium alkoxides^{12,13} were prepared by the procedures reported in the literature.

Tin was determined by precipitation as cupferrate¹⁴ followed by estimation as SnO_2 after ignition. Aluminium in the filtrate was determined gravimetrically as oxinate.¹⁴

Isopropoxy contents were estimated by an oxidimetric¹² method using N-K₂Cr₂O₇ solution in 12.5% H₂SO₄. Chloride was estimated volumetrically by Volhard's method.¹⁴

IR (4000–200 cm⁻¹) spectra were recorded in Nujol mulls on a CARL ZEISS JENA specord M-80 spectrophotometer. Multinuclear NMR studies were performed on a JEOL FX 90Q spectrometer. 27 Al and 119 Sn NMR chemical shifts were measured using Al(NO₃)₃ · x H₂O and SnMe₄ as external references, respectively.

Molecular weights were determined ebullioscopically in benzene.

Preparation of $[Cl_2Sn{Al(OPr^i)_4}_2]$

A solution of $K{Al(OPr^i)_4}$ freshly prepared by the reaction of potassium (2.96 g, 75.88 mmol) in a mixture of isopropanol (~5 cm³) and benzene

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 $(\sim 10 \text{ cm}^3)$ followed by interaction with Al(OPrⁱ)₃ (15.49 g, 75.84 mmol) in benzene (~15 cm³) was added slowly to a clear solution of SnCl₄ (9.85 g, 37.78 mmol) in benzene (~20 cm³). After complete addition, the reaction mixture was stirred for ~3 h at room temperature.

During the above addition some heat was evolved; the reaction mixture was stirred at ambient temperature to ensure completion. The precipitated KCl (5.45 g, 73.05 mmol) was filtered off. Removal of volatiles from the filtrate under reduced pressure (1.0 mm) yielded a viscous product of the composition $[Cl_2Sn{Al(OPr^i)_4}_2]$ (24.35 g, 90%). The product could be volatilized unchanged at 140°/ 0.1 mm in 60% yield.

Similarly, the reaction of $SnCl_4$ and K{Al(OPr')_4} in 1:3 molar ratio in benzene at room temperature afforded [ClSn{Al(OPr')_4}_3] (b.p. 128°/0.1, 80%).

Reaction of $[Cl_2Sn{Al(OPr^i)_4]_2}]$ with KOPrⁱ

To a benzene solution (~25 cm³) of the chloro complex [Cl₂Sn{Al(OPrⁱ)₄}₂] (3.78 g, 5.27 mmol) was added slowly a suspension of KOPrⁱ [prepared from potassium (0.41 g, 10.58 mmol) and isopropanol (~5 cm³)] followed by stirring at room temperature for ~12 h. The reaction mixture was then refluxed for ~1 h. The precipitated KCl (0.78 g, 10.45 mmol) was removed by filtration. The solvent was stripped off from the filtrate under reduced pressure (1.0 mm) to yield a viscous mass of the title product in 94% yield, which was purified by distillation (b.p. 133°/0.1 mm, 70%).

In a similar procedure, reaction of $[Cl_2Sn{Al} (OPr^i)_4]_2$ with KOBu^t in 1:2 molar ratio afforded a viscous mass of the composition $[(OBu^t)_2Sn{Al}(OPr^i)_4]_2$ (b.p. 138°/0.1 mm, 65%).

Preparation of $[{Zr_2(OPr')_9}Sn{Al(OPr')_4}_3]$

To a clear solution of $[ClSn{Al(OPr^i)_4}_3]$ (3.83 g, 4.05 mmol) in benzene (~20 cm³) was added dropwise a solution of K $\{Zr_2(OPr^i)_9\}$ [freshly prepared by the interaction of KOPrⁱ (potassium (0.08 g, 2.04 mmol) in ~5 cm³ isopropanol) with Zr(O Prⁱ)_4 · PrⁱOH (3.15 g, 4.06 mmol) in benzene (~15 cm³)]. The reaction mixture was stirred for ~1 h at 70°C, followed by stirring at room temperature for ~12 h. The precipitated KCl (0.29 g, 3.88 mmol) was then filtered off. Removal of volatiles from the filtrate yielded the desired product (6.38 g, 96%) as a viscous mass which could be volatilized unchanged at 180°/0.1 mm in 70% yield.

Further preparative, analytical and physical data are listed in Table 1.

RESULTS AND DISCUSSION

Interactions of SnCl₄ with potassium tetraalkoxy aluminates, K{Al(OR)₄} ($\mathbf{R} = \mathbf{Pr}^i$, Buⁱ), in different molar ratios in benzene have yielded novel chloride bimetallic alkoxides which can be represented by the following equation :

$$SnCl_4 + n K \{Al(OR)_4\} \longrightarrow$$

$$[Cl_{4-n}Sn \{Al(OR)_4\}_n] + n KCl \downarrow$$

$$Ia: R = Pr^i, n = 1; Ib: R = Pr^i, n = 2;$$

$$Ic: R = Bu^i, n = 2; Id: R = Pr^i, n = 3.$$

Out of the above, Ia is a viscous liquid, thermally labile and tending to liberate $SnCl_4$ at $80^{\circ}C$ under reduced pressure.

Replacement of chloride from mono- and dichloro derivatives (**Id** and **Ib**) with alkoxo groups afforded alkoxide isopropoxymetallates of the types $[(OR)_{4-n}Sn{Al(OPr^i)_4}_n]$ according to the following equation :

$$[Cl_{4-n}Sn{Al(OPr^{i})_{4}_{n}] + (4-n) KOR \longrightarrow$$

$$[(OR)_{4-n}Sn{Al(OPr^{i})_{4}_{n}] + (4-n) KCl \downarrow$$

$$Ie: R = Pr^{i}, n = 2; If: R = Bu^{t}, n = 2;$$

$$Ig: R = Pr^{i}, n = 3; Ih: R = Bu^{t}, n = 3.$$

All these new heterometal derivatives (Table 1) are initially colourless viscous products, highly soluble in common organic solvents. They are extremely susceptible to moisture and develop a yellow tinge on storage. These (except Ic, which decomposes on heating under reduced pressure into volatile Al(OBu¹)₃ and non-volatile [Cl₂Sn(OBu¹)₂]) could be volatilized unchanged under reduced pressure, thus corroborating their identity as stable coordination complexes. The chloro complexes [Cl_{4-n}Sn {Al(OPrⁱ)₄}_n] (n = 2, 3) have shown a monomeric behaviour in solution which is depicted by their observed molecular complexities in boiling benzene and single peaks in ¹¹⁹Sn NMR spectra.

Interaction of Id with $K\{Zr_2(OPr^i)_9\}$ in a 1:1 molar ratio in benzene led to the formation of a novel ter-metallic alkoxide of tin(IV) of the type $[\{Zr_2(OPr^i)_9\}Sn\{Al(OPr^i)_4\}_3]$ (IIIa):

$$[ClSn{Al(OPr^{i})_{4}}_{3}] + K{Zr_{2}(OPr^{i})_{9}} \longrightarrow$$
IIIa + KCl ↓

The ¹H NMR spectrum of **IIIa** exhibits two upfield doublets (δ 1.03, 1.11; 1.16, 1.23 ppm) assignable to terminal isopropoxy protons whereas a downfield doublet (δ 1.29, 1.36 ppm) centred at δ 1.32 ppm is probably due to bridging isopropoxy protons. These data are corroborated by ¹³C NMR

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S.			Yield	Volatility	7	Analysis (%), Foun	d (Calc.)		Mol.
No.	Reactants	Product	%	°C/mm	Sn	Al	Zr	OR	ច	wt
-	SnCl ₄ +K{Al(OPr ¹) ₄ }	[Cl ₃ Sn{Al(OPr [*]) ₄ }]	60	D,	24.2	5.7		48.2	21.5	
	2				(24.3)	(5.9)		(48.4)	(21.7)	(488)
6	SnCl ₄ +2K{Al(OPr ⁱ) ₄ }	[Cl ₂ Sn{Al(OPr ¹) ₄ } ₂]	80	140/0.1	16.4	6.7		65.7	9.5	680
					(16.6)	(7.5)		(0.99)	(6:6)	(116)
ąĘ	SnCl ₄ +2K{Al(OBu ^t) ₄ }	[Cl ₂ Sn{Al(OBu ¹) ₄ } ₂]	95	D	14.6	7.5	and the second se	1	3.2	856
					(14.3)	(1.3)			(3.2)	(828)
4	SnCl ₄ +3K{Al(OPr ⁾ } ₄ }	[CISn{Al(OPr ^j) ₄] ₃]	80	128/0.1	12.5	8.7		74.0	3.5	1036
					(12.6)	(8.6)		(15.0)	(3.7)	(944)
S	[Cl ₂ Sn{Al(OPr ¹) ₄ } ₂]+2KOPr ¹	$[(OPr')_2Sn{Al(OPr')_4}_2]$	70	133/0.1	15.5	7.1		77.1	1	1194
					(15.5)	(7.1)		(17.4)		(763)
9	[Cl,Sn{Al(OPr'),},]+2KOBu ^t	[(OBu ^t),Sn{Al(OPr [†]),}	65	138/0.1	14.8	6.9		59.1	1	835
					(15.0)	(6.8)		(59.7)		(162)
٢	[CISn{Al(OPr ⁱ) ₄ } ₃]+KOPr ⁱ	[(OPr ⁱ)Sn{Al(OPr ⁱ),}]	09	130/0.1	12.2	8.4		79.2	1	1035
					(12.3)	(8.4)		(19.4)		(968)
œ	[CISn{Al(OPr') ₄ } ₄]+KOBu ^t	[(OBu')Sn{Al(OPr') ₄ } ₃]	50	141/0.2	12.1	8.3	-	72.0		1016
				·	(12.1)	(8.2)		(72.2)		(982)
6	[CISn{Al(OPr)}]	[{Zr,(OPr') ₀ }Sn{Al(OPr') ₄ },]	02	180/0.1	7.3		10.8	75.9		1635
	+K{Zr ₂ (OPr),}				(7.3)		(10.7)	(76.5)		(1623)
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^aD: Decomposes on heating under reduced pressure; yield indicated in such cases is of crude product. ^b Soft solid: all other products viscous liquids.

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observations: δ 72.80, 71.02, 70.58, 67.98, 66.52, 63.54 (α -carbons); 28.33, 27.46, 26.76, 26.27, 25.84, 25.51 ppm (β -carbons). The ¹¹⁹Sn NMR spectrum showed a single peak at -695.4 ppm.

IR spectra (4000–200 cm⁻¹) of these complexes exhibit absorption bands characteristic of metalalkoxy groups. ¹⁵⁻¹⁸ These new derivatives (Table 1) display absorptions in the range 1200–700 cm⁻¹ characteristic of alkoxy group vibrations: 1170, 1130, 1090*, 960* (ν OPrⁱ); 1200–1155, 1040–1000*, 900–820, 770–720* (ν OBu¹). Some of these vibrations (marked by asterisk) appear to arise from the C—O stretching vibrations while the others may be due to skeletal vibrations. The metal–oxygen stretching vibrations have been observed in the range 705–535 cm⁻¹.

The chloro complexes of the type $[Cl_{4-n}Sn{Al} (OR)_{4}_{n}]$ (R = Prⁱ, Buⁱ, when n = 2; R = Prⁱ when n = 3) exhibit additional absorptions in the range 335–305 cm⁻¹ due to Sn—Cl¹⁹ stretching frequencies. The C—O stretching vibrations have been observed in the range 1180–930 cm⁻¹ and as expected these are found to be sensitive to the structure of the alkoxy group.

The room temperature ¹H NMR spectrum (in $CDCl_3$) of freshly distilled $[Cl_2Sn{Al(OPr^i)_4}_2]$ exhibits a complex pattern displaying three doublets each in regions assignable to bridging (δ 1.36, 1.42, 1.40, 1.47, 1.53 ppm) and terminal (δ 1.05, 1.12, 1.14, 1.21, 1.17, 1.24 ppm) gem-dimethyl protons. The methine protons are obtained as two distinct septets centred at δ 4.71 and 4.14 ppm. The nature of these ¹H NMR peaks in the spectrum could be explained on the basis of (i) non-interchangeability and magnetic non-equivalence of the bridging and terminal isopropoxy groups, and (ii) the possibility of cis-trans isomerism²¹ existing in solution. These tentative suggestions receive further support by the observed nature of the ¹³C NMR spectrum [δ 70.20, 69.31, 68.87, 67.98, 63.63 (α-carbons); 26.15, 24.81, 23.48, 23.03, 22.59, 21.70 ppm (β -carbons)]. The appearance of a sharp ¹¹⁹Sn NMR signal at -602.75 ppm is indicative of a hexacoordinate environment around the central tin atom.²⁰

The proton NMR spectrum of [ClSn{Al $(OPr^i)_4$ }] exhibits three sets of overlapping doublets in both the regions of bridging and terminal isopropoxy groups. The observation of such a complex spectrum is interpretable in terms of the magnetically inequivalent nature of both bridging and terminal isopropoxy groups and the possibility of the existence of isomeric forms in solution arising from a pentagonal bipyramidal geometry around tin. A similar pattern observed for the ¹³C NMR spectrum [δ 70.96, 70.37, 69.72, 67.71, 66.63, 63.76 (α -carbons); 27.89, 27.68, 27.08, 26.76, 26.00, 25.62

ppm (β -carbons)] could be explained on the basis of the above assumptions. The shift in the ¹¹⁹Sn NMR signal observed at -602.75 ppm in the octahedral [Cl₂Sn{Al(OPrⁱ)₄}₂] to -627.61 ppm for [ClSn{Al(OPrⁱ)₄}₃] appears to indicate²⁰ a higher coordination state (probably 7) for tin in the latter complex.

The derivative [(OPr¹)Sn{Al(OPr¹)₄}₃] displays a highfield triplet (δ 1.10, 1.14, 1.23 ppm) arising from two overlapping doublets due to terminal isopropoxy groups. The doublet (δ 1.40, 1.34 ppm) centred at 1.37 ppm is assignable to bridging isopropoxy groups. These observations are corroborated by the ¹³C NMR spectrum [δ 70.15, 68.63, 66.47, 65.55, 64.19, 63.60 (α -carbons); 28.11, 27.57, 27.03, 26.70, 26.11, 25.51 ppm (β -carbons)]. The ¹¹⁹Sn NMR spectrum shows a single peak at -646.27 ppm indicative of a seven-coordinate geometry around the tin atom.

The ¹H NMR spectrum of [(OBu^t)Sn{Al (OPrⁱ)₄}₃] exhibits a doublet (δ 1.29, 1.38 ppm) centred at δ 1.33 ppm due to the *gem*-dimethyl protons of the bridging isopropoxy groups, two doublets (δ 1.23, 1.18; 1.14, 1.07 ppm) centred at 1.20 ppm and 1.10 ppm are ascribable to *gem*-dimethyl protons of terminal isopropoxy groups. The peak observed at δ 1.25 ppm is due to methyl protons of tert-butoxy groups which is corroborated by ¹³C NMR observations δ 66.52 (α -carbon); 34.07 ppm (β -carbons). The ¹¹⁹Sn NMR chemical shift is observed as a single peak at - 669.40 ppm suggesting a pentagonal bipyramidal geometry of the complex.

An interesting feature of the ¹H NMR spectrum of the complex $[(OPr^i)_2Sn{Al(OPr^i)_4}_2]$ (Ie) is its simpler pattern as compared to that of its precursor chloro complex (Ib). The spectrum shows four peaks in the high-field region appearing as three overlapping doublets and ascribable to terminal gem-dimethyl protons, whereas the bridged isopropoxy groups appear as an averaged doublet centred at δ 1.37 ppm. The derivative exhibits some oligomerization in boiling benzene with a molecular complexity of 1.6 suggesting the existence of an equilibrium between monomeric octahedral and dimeric pentagonal bipyramidal species. These conclusions are supported by the ¹¹⁹Sn NMR spectrum which showed two resonances at -595.58 and - 669.69 ppm, characteristic of six- and seven-coordinated tin(IV) species. The nature of the above spectrum remained unaltered even when examined as a neat liquid.

Interestingly, the substitution of two OPrⁱ groups in Ie by bulkier OBuⁱ groups tends to make the product, $[(OBuⁱ)_2Sn{Al(OPrⁱ)_4}_2]$, monomeric as depicted by its observed molecular weight in

S. No.	Complex	Solvent	¹¹⁹ Sn shift (ppm) (reference SnMe₄)	²⁷ Al shift (ppm) (reference Al(NO ₃) ₃ · x H ₂ O)
1	$[Cl_2Sn{Al(OPr^i)_4}_2]$	Benzene	-602.75	67.12
2	$[Cl_2Sn{Al(OBu^t)_4}_2]$	Benzene	- 565.02	58.24
3	$[ClSn{Al(OPr')_4]_3}]$	Benzene	-602.75	65.10
4	$[(OPr^{i})_{2}Sn\{Al(OPr^{i})_{4}\}_{2}]$	Benzene	- 595.58, -669.69	
5	$[(OBu^{t})_{2}Sn\{Al(OPr^{t})_{4}\}_{2}]$	Benzene	-625.46	60.44
6	$[(OPr^{i})Sn{Al(OPr^{i})_{4}}]$	Benzene	646.27	66.25
7	$[(OBut)Sn{Al(OPri)_4}_3]$	Benzene	-669.40	66.76
8	$[{Zr_2(OPr')_9}Sn{Al(OPr')_4}_3]$	Benzene	- 695.40	61.00

Table 2. ¹¹⁹Sn and ²⁷Al chemical shifts for heterometal alkoxides of tin(IV)

benzene. The ¹H NMR spectrum exhibits an averaged doublet due to bridging isopropoxy groups centred at δ 1.35 ppm and a triplet (δ 1.23, 1.16, 1.10 ppm) due to two overlapping doublets arising from terminal isopropoxy groups. The signal due to the *tert*-butoxy groups appears to merge in the peak at δ 1.23 ppm. These observations tend to indicate a predominantly *cis*-octahedral geometry²¹ for the molecule.

The ²⁷Al NMR spectra of the complexes displayed broad resonances (Table 2) in the range characteristic of the tetrahedral aluminium²² moiety, and thus supporting the conclusions derived from ¹H, ¹³C and ¹¹⁹Sn NMR studies, wherein tetra-alkoxo aluminates exhibit bidentate ligating behaviour:



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