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Synthesis, characterisation and hydrolytic reactions of the first pentaisopropoxostannate derivatives of magnesium, zinc and cadmium

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Pentaisopropoxostannate derivatives of the types $[\{M[Sn(OPr^i)_5](\mu\text{–}Cl)\}_2]$ and $[M\{Sn(OPr^i)_5\}_2]$ have been prepared by the reactions of MCl_2 (M = Mg, Zn, and Cd) with $NaSn(OPr^i)_5$ in 1:1 and 1:2 molar ratios, respectively, in benzene. All these derivatives have been characterised by elemental and isopropoxo group analyses, spectroscopic (IR, ^1H and ^{13}C NMR) studies, and molecular weight determinations. Two typical hydrolytic reactions of $[Zn\{Sn(OPr^i)_5\}_2]$ have also been investigated.

Keywords: heterobimetallic isopropoxides, metalalkoxides, pentaisopropoxostannates, main group metal derivatives

The efficacy of alkoxometallate metal ligation in affording complexes with advantageous hydrocarbon solubility, crystallisability, volatility, and resistance to disproportion into component homometal alkoxides is now well-established.[1,2] Furthermore, alkoxometallate ligands have become the focus of intense research, because their metal complexes exhibit an enormous variety of structures as well as interesting physicochemical properties.[1-6] Over the past several years, considerable progress has been made towards the predictability of ordered alkoxometallate ligation on the basis of coordinative metal/ligand bonds. The applications of homo- and heterometallic oxides as advanced inorganic materials[7-9] have further stimulated considerable interest in the rational design of new heterobimetallic alkoxides,[10-11] which could be used to prepare mixed-metal oxides of desired compositional type with high technology applications.[12,13]

In continuation of our earlier studies on heterometallic alkoxides of divalent main group metals containing tin(IV)[14] as a heterometal, we now report the synthesis and characterisation of two new types of derivatives $[M\{Sn(OPr^i)_5\}Cl]$ and $[M\{Sn(OPr^i)_5\}_2]$ (M = Mg, Zn, Cd). Details of these studies are given in Table 1 (analytical and physical data) and Table 2 (spectroscopic data). The noteworthy feature about these studies is the use of the pentaisopropoxostannate anion, $\{Sn(OPr^i)_5\}^-$, as a chelating ligand for the first time. An additional feature about the present study is the stability and solubility of the chloro-derivatives, $[M\{Sn(OPr^i)_5\}Cl]$, which may prove an excellent precursor for the synthesis of novel heterotrimetallic alkoxides, an area of current work.

Results and discussion

This work originated in an attempt to establish whether $\{Sn(OPr^i)_5\}^-$ can form stable coordination complexes. The derivatives were all prepared by the reaction of the appropriate metal chloride with $NaSn(OPr^i)_5$ in desired (1 : 1 and 1 : 2) molar ratios in benzene medium according to the following sequential reactions (eqns (1) and (2)).

The compounds (Table 1) are highly moisture-sensitive, white solids. They are soluble in common organic solvents (*e.g.*, benzene, toluence, *n*-hexane, dichloromethane, etc.) and may be recrystallised from *n*-hexane. The homoleptic derivatives (**4**)–(**6**) are monomeric while the chloro(pentaisopropoxostannate) compounds are dimeric (ebullioscopically) in benzene solutions. It is widely recognised that heterometallic alkoxide molecular precursors are produced by wet chemical approaches, heteromulti-metallic oxide systems having superior properties to those generated by traditional solid-state techniques.[9,12] Keeping this viewpoint in mind, we have carried out reaction of $Zn\{Sn(OPr^i)_5\}_2$ with water (eqn (3)) or $Ba(OH)_2.8H_2O$ (eqn (4)) in isopropyl alcohol, followed by removal of volatiles under reduced pressure and finally heating to ~ 400°C for 2 h to obtain pure mixed-metal oxides.

$$\mathrm{Sn(OPr^i)_4.Pr^iOH + Na} \xrightarrow{\mathrm{C_6H_6/few\ drops\ of\ Pr^iOH}} \mathrm{NaSn(OPr^i)_5} + \tfrac{1}{2}\,\mathrm{H_2} \uparrow \quad (1)$$

$$\mathrm{MCl_2 + nNaSn(OPr^i)_5} \xrightarrow[\text{reflux}]{\mathrm{C_6H_6}} \mathrm{[MCl_{2-n}\{Sn(OPr^i)_5\}_4] + n\ NaCl} \uparrow \quad (2)$$

M = Mg (n = 1) **1**, Zn (n = 1) **2**, Cd (n = 1) **3**,
Mg (n = 2) **4**, Zn (n = 2) **5**, Cd (n = 2) **6**,

$$\mathrm{Zn\{Sn(OPr^i)_5\}_2 + 10\ H_2O} \xrightarrow[\substack{\text{(i) Stir, r.t., 4 h}\\ \text{(ii) Removal of volatiles}}]{\mathrm{PhH/Pr^iOH}} \mathrm{"ZnSn_2(OH)_{10}"} \downarrow + 10\ \mathrm{Pr^iOH} \uparrow$$

$$\downarrow$$

$$\mathrm{ZnSn_2O_5 + 5\ H_2O} \uparrow \quad (3)$$

$$\mathrm{Zn\{Sn(OPr^i)_5\}_2 + 2\ Ba(OH)_2.8H_2O} \xrightarrow[\substack{\text{(i) Stir, r.t., 8 h}\\ \text{(ii) Refluxed 7 h}\\ \text{(iii) Removal of volatiles}\\ \text{(iv) Heating} \sim 400^0\text{C, 2 h}}]{\mathrm{Pr^iOH\ /\ PhH}} \mathrm{Ba_2Sn_2ZnO_7} \downarrow + 10\ \mathrm{Pr^iOH} \uparrow + 11\ \mathrm{H_2O} \uparrow + \mathrm{O_2} \quad (4)$$

The reaction represented by eqn (4) assumes special significance, because water of crystallisation of $Ba(OH)_2.8H_2O$ is believed to be supplied to the alkoxide solution gradually. Thus, inhomogeneous precipitation resulting from rapid hydrolysis was prevented, and it provided an opportunity to incorporate barium into a heterrerobimetallic system.

Spectroscopic studies

IR spectra[14] (Table 2) of the derivatives (**1**) – (**7**) show absorptions in the regions: 1175–1150 and 1130–1110 νOPr^i, 1030–1015 terminal νC–O and 975–945 bridging νC–O, 665–565 νSn–O, and 500–450 cm^{-1} νM–O (M = Mg, Zn, Cd, or Sn(II). These assignments are based on published data concerning metal alkoxides.[1] The chloro-derivatives (**1**)–(**3**) exhibit additional strong to medium intensity bands in the region 340–330 cm^{-1} assignable to νM–Cl (M = Mg, Zn, Cd).

The ^1H NMR spectra of the new derivatives (Table 2) are deceptively simple, exhibiting one doublet due to methyl protons in the δ1.17–1.34 region and a septet at δ4.0–4.30 arising from methine protons. Theoretically two signals for each type, *i.e.* methyl and methine protons are expected. The simpler nature of these spectra may be due to the fluxional behaviour of these derivatives at room temperature, which is a general feature of homo- and heterometallic alkoxides.[1]

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Table 1 Analytical and some physical data for some pentaisopropoxostannate derivatives (**1**)–(**6**)

Compd^a	Analysis (%) Found (Calcd.)M. wt.^{b} Found (Calcd)						
	C	H	Mg/Zn/Cd	Sn	Cl	OPr^i	
[{ Mg[Sn(OPr^i)$_5$](μ–Cl)}$_2$] (1)	38.1 (38.0)	7.5 (7.4)	5.0 (5.1)	25.2 (25.05)	7.5 (7.5)	62.1 (62.3)	940 (474)
[{Zn[Sn(OPr^i)$_5$](μ–Cl)}$_2$] (2)	35.1 (35.0)	6.9 (6.85)	12.7 (12.7)	23.1 (23.05)	7.0 (6.9)	57.4 (57.4)	1035 (515)
[{Cd[Sn(OPr^i)$_5$](μ–Cl)}$_2$] (3)	32.1 (32.1)	6.3 (6.3)	20.1 (20.0)	21.3 (21.1)	6.4 (6.3)	52.5 (52.5)	1125 (562)
[Mg(Sn(OPr^i)$_5$}$_2$] (4)	42.2 (42.3)	8.3 (8.3)	3.0 (2.85)	27.95 (27.85)	–	69.2 (69.3)	862 (853)
[Zn{Sn(OPr^i)$_5$}$_2$] (5)	40.4 (40.3)	7.95 (7.9)	7.5 (7.3)	26.5 (26.6)	–	66.3 (66.1)	907 894)
[Cd{Sn(OPr^i)$_5$}$_2$] (6)	38.4 (38.3)	7.5 (7.50)	12.25 (11.95)	25.3 (25.2)	–	62.7 (62.8)	958 (941)

^{a}All compounds are white solids and do not melt, but decomposed in the temperature range 180–230°C.
^{b}Calculated value for monomer is given in parenthesis.

Table 2 IR(cm^{-1}) and NMR (δ, ppm) data for heterobimetallic isopropoxide complexes (**1** – **6**)

Compd	IR^a	^{1}H^b	^{13}C^b	^{119}Sn^c
1	1030, 945 (νC–O); 1165, 1120 (νOPr^i); 640, 602 (νSn–O); 540 (ν Mg–O); 340, 330 (ν Mg–Cl)	1.22 (d, J = 6 Hz, 30H, CHMe$_2$); 4.02 (m, 5H, CHMe$_2$)	68.5, 67.6 (CHMe$_2$); 28.4, 27.2 (CHMe$_2$)	– 464
2	1025, 953 (νC–O); 1170, 1110 (νOPr^i); 605 (νSn–O); 460 (νZn–O); 340, 330 (νZn–Cl)	1.34 (d, J = 6 Hz, 30H, CHMe$_2$); 4.09 (m, 5H, CHMe$_2$)	66.7, 67.0 (CHMe$_2$); 27.1, 27.0 (CHMe$_2$)	– 462
3	1025, 950 (νC–O), 1175, 1130 (νOPr^i); 595 (νSn–O); 500 (νCd–O); 335, 330 (νCd–Cl)	1.24 (d, J = 6 Hz, 30H, CHMe$_2$); 4.04 (m, 5H, CH Me$_2$)	67.7, 66.7 (CHMe$_2$); 27.4, 26.3 (CHMe$_2$)	– 537
4	1020, 975 (νC–O); 1150, 1120 (νOPr^i); 605, 630 (νSn–O); 485 (ν Mg–O)	1.17 (d, J = 6 Hz, 60H, CHMe$_2$); 4.11 (m, 10H, CHMe$_2$)	75.6, 63.9 (CHMe$_2$); 28.2, 25.4 (CHMe$_2$)	– 442
5	1020, 950 (νC–O); 1165, 1120 (νOPr^i); 665, 565 (νSn–O); 480 (νZn–O)	1.30 (d, J = 6 Hz, 60H, CHMe$_2$); 4.27 (m, 10H, CHMe$_2$)	66.5, 67.0 (CHMe$_2$); 27.6, 26.4 (CHMe$_2$)	– 457
6	1015, 955 (νC–O); 1165, 1120 (νOPr^i); 660, 570 (νSn–O); 470 (νCd–O)	1.20 (d, J = 6 Hz, 60H, CHMe$_2$); 4.08 (m, 10H, CHMe$_2$)	67.3, 65.9 (CHMe$_2$); 27.2, 26.1 (CHMe$_2$)	– 438

^{a}As Nujol mulls.
^{b}Spectra recorded at ambient temperatures in CDCl$_3$ and were referenced to internally using the residual solvent (^{1}H) and solvent (^{13}C) resonances relative to SiMe$_4$(δ = 0).
^{c}Measured in C$_6$H$_6$ and referenced to external SnMe$_4$.

NMR spectrum of dimeric sodium pentaisopropoxotitanate,[15] [NaTi(OPr^i)$_5$]$_2$ exhibits two ^{1}H NMR signals: a doublet (OCH**Me**$_2$) and a broad peak (OC**H**Me$_2$) and two ^{13}C NMR peaks for α- and β-carbons of isopropoxo groups.

^{13}C {^{1}H} NMR signals for (**1**)–(**6**) are observed in the δ 64.0–67.0 and 25.0–28.5 ppm regions due to methine and methyl protons of isoporpoxo groups, respectively.

^{119}Sn NMR signals in derivatives (**1**)–(**6**) appear in the δ –400 to –465 region consistent with five-coordinate[16] tin(IV) derivatives.

In spite of repeated efforts, the structures of these derivatives could not be determined by X-ray crystallography due to various reasons reported earlier also.[5] However, molecular weight data and the ^{1}H as well as ^{119}Sn spectra have been quite helpful in arriving at plausible structural formulation of all the derivatives, as [{M[η^4–Sn(OPr^i)$_5$](μ–Cl)}$_2$] and [M{η^3–Sn(OPr^i)$_5$}$_2$], where M = Mg, Zn, and Cd and η^4 and η^3 represent involvement of four and three isopropoxide groups oxygen atoms in ligating the heterometal atom, respectively. However, for zinc derivatives lower connectivities of {Sn(OPr^i)$_5$}$^-$ ligand may also be possible.

Experimental

All reactions were carried out under a stringently anhydrous atmosphere using special glass apparatus.[14] Reagent grade (BDH) solvents were freshly distilled from appropriate drying agents[17] as required.

Tin tetraisopropoxide isopropanolate Sn(OPr^i)$_4$.Pr^{i}OH was prepared by the literature method.[2] The hydrated metal chlorides: MgCl$_2$.6H$_2$O, ZnCl$_2$.6H$_2$O, and CdCl$_2$.2H$_2$O were made anhydrous by refluxing over excess thionyl chloride,[18] followed by removal of the solid product by filtration, washing with anhydrous CCl$_4$ and final drying under reduced pressure. Finally all of these anhydrous metal chlorides were analysed for their metal and chloride contents, which were found satisfactory.

Chloride was determined by Volhard's method. Tin was estimated as SnO$_2$, which was precipitated on digesting the sample(s) with concentrated nitric acid. Magnesium, barium, zinc, and cadmium contents in the heterobimetallic compounds were determined in the filtrates gravimetrically as MgNH$_4$PO$_4$, BaSO$_4$, ZnNH$_4$PO$_4$, and CdNH$_4$PO$_4$, respectively. For all these determinations literature procedures were followed.[19] Isopropoxy groups in the compounds were determined by the oxidimetric method.[2°]

^{1}H (89.55 MHz), ^{13}C (22.49 MHz), and ^{119}Sn (33.35 MHz) NMR spectra were recorded on a JEOL FX-90 Q spectrometer. ^{1}H NMR spectra (in CDCl$_3$) were referenced with internal TMS (δ = O), while ^{13}C NMR spectra recorded in CCl$_4$ (δ = 96.10) or C$_6$H$_6$ (δ = 128.06) were referenced internally with the solvent peak given in parenthesis. IR spectra (4000–200 cm^{-1}) were recorded in Nujol mulls on a Nicolet Magna 750 spectrophotometer using CsI optics. Molecular weights were determined ebullioscopically in benzene using a Gallenkamp ebulliometer. Microanalytical (C, H) analyses were performed by Regional Sophisticated Instrumentation Centre, Central Drug Research Institute (CDRI), Lucknow.

Preparation of new pentaisopropoxostannate derivatives

Due to similarity in the preparative procedures for the new derivatives, details for only two typical compounds are described.

Preparation of [Zn{Sn(OPr^i)$_5$}Cl] (**2**): To a stirred slurry of ZnCl$_2$ (0.87 g, 6.38 mmol) in benzene (~25 ml) was added NaSn(OPr^i)$_5$ [freshly prepared by the reaction of Na(0.15 g, 6.44 mg atom) with Sn(OPr^i)$_4$.Pr^{i}OH (2.65 g, 6.38 mmol) in benzene (20 ml) containing a small amount of isopropyl alcohol, followed by removal of volatiles under reduced pressure] and the resulting reaction mixture was stirred at room temperature for 4 h, followed by refluxing for 2 h. The precipitated NaCl (0.38 g, 6.50 mmol) was removed by filtration. Volatiles from the filtrate were removed under reduced pressure to obtain a colourless solid (3.13 g, 95%). Recrystallisation from *n*-hexane at –20°C afforded the title compound as a colourless solid (2.70 g, 82%).

Using a procedure similar to that adopted for (**2**). The quantities of the reactants used in each case are given below:
(**1**): MgCl$_2$(0.38 g, 4.0 mmol) and NaSn(OPr^i)$_5$ (1.77 g, 4.0 mmol)
(**3**): CdCl$_2$ (1.12, 6.11 mmol) and NaSn(OPr^i)$_5$ (2.67 g, 6.11 mmol).

Preparation of $Zn\{Sn(OPr^i)_5\}_2$ (**5**): After addition of $NaSn(OPr^i)_5$ [freshly prepared as described above by the reaction of Na (0.10 g, 4.54 mgatom) with $Sn(OPr^i)_4.Pr^iOH$ (1.88 g, 4.53 mmol)] to a slurry of $ZnCl_2$ (0.31 g, 2.27 mmol) in benzene (~15 ml), the reaction mixture was refluxed for 4 h. The precipitated NaCl (0.25 g, 4.27 mmol) was removed by filtration. Removal of the solvent from the filtrate yielded a colourless solid (1.92 g, 97.5%). Analytically pure title compound was obtained by recrystallising from *n*-hexane at –20°C. Yield: 1.68 g (82.8%).

Derivatives (**4**), and (**6**), were also prepared in a manner similar to that described for (**5**). The quantities of the reactants used in each case are given below:

(**4**): $MgCl_2$ (0.19 g, 1.99 mmol) and $NaSn(OPr^i)_5$ (1.74 g, 3.98 mmol).
(**6**): $CdCl_2$ (0.38 g, 2.07 mmol) and $NaSn(OPr^i)_5$ (1.80 g, 4.12 mmol)

Hydrolytic reactions

Reaction of $[Zn\{Sn(OPr^i)_5\}_2]$ *with water*. To a magnetically stirred solution of $[Zn\{Sn(OPr^i)_5\}_2]$ (3.48 g, 3.89 mmol) in benzene (20 ml) was gradually added water (2.1 g) diluted with 40 ml of isopropyl alcohol. The resulting reaction mixture was stirred at room temperature for 4 h. The volatiles were removed under reduced pressure and the resulting hydroxo-product was heated at ~400°C for 2 h to obtain a white solid of composition Sn_2ZnO_5, Anal. calcd. for Sn_2ZnO_5: Sn 62.0, Zn 17.1; found: Sn 62.1, Zn 17.2%.

Reaction of $[Zn\{Sn(OPr^i)_5\}_2]$ *with* $Ba(OH)_2.8H_2O$. To a vigorously stirred suspension of $Ba(OH)_2.8H_2O$ (1.97 g, 6.24 mmol) in isopropyl alcohol (50 ml) was gradually added a solution of $[Zn\{Sn(OPr^i)_5\}_2]$ (2.80 g, 3.13 mmol) in benzene (15 ml). The reaction mixture was stirred vigorously at room temperature for 8 h, and then refluxed for 7 h. The hydrolysed gelatinous product was allowed to cool to room temperature and volatiles removed under reduced pressure to afford a colourless solid, which on heating at ~400°C for 2 h, produced colourless material of composition $Ba_2Sn_2ZnO_7$. Anal.calcd. for $Ba_2Sn_2ZnO_7$: Ba 39.8, Sn 34.4, Zn 9.5; found: Ba 39.9, Sn 34.5, Zn 9.6%.

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