Synthesis and Characterisation of Four Different Types of Heterobimetallic Complexes of Tin(IV)

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ABSTRACT

Four different types of heterobimetallic complexes of tin(IV) $Sn\{M(OPr^i)_n\}_2$-{ $(OCH_2CH_2)_2NR$} (where M = Al, n = 4, R = H (**1**); M = Al, n = 4, R = Me (**2**); M = Al, n = 4, R = C_6H_5 (**3**); M = Nb, n = 6, R = H (**4**); M = Nb, n = 6, R = Me (**5**); M = Nb, n = 6, R = C_6H_5 (**6**)), $Sn\{Al(OR')_4\}_3(OR')$ (where R′ = N=CEtMe (**7**); R′ = $N{=}CMe_2$ (**8**)), $Sn(OCHMeCH_2CMe_2O)_3\{Al(OPr^i)_2\}_2$ (**9**), and $SnAl_2(OCHMeCH_2CMe_2O)_5$ (**10**) have been prepared either by salt-elimination method or by the protonolysis reaction, and characterised by elemental analyses, molecular weight measurements, and spectroscopic studies.

INTRODUCTION

During the last 15 years, heterometallic alkoxides have been used as polymerisation catalyst and molecular precursor for high purity ceramic metal oxide superconductors and other speciality materials /1-8/, and this development has rekindled enthusiasm for fundamental studies of homo- and heterometal alkoxides /3/ an account of which have been presented in a number of excellent review articles /1,2,7,11/.

The first heterometallic alkoxide of tin(IV), $NaSn_2(OEt)_9$ was isolated by Bradley, Caldwell, and Wardlaw /12/ as early as in 1957; however, the exploitation of coordination chemistry of nonaalkoxodistannate ligands $Sn_2(OR)_9^-$ /13/ attracted attention after a hiatus of approximately 38 years.

The renaissance in the study of heterometal alkoxide chemistry of tin(IV) is driven by (i) applications in material science, (ii) the growing availability of new techniques which can probe the structures of these interesting species, (iii) the fact that tin(IV) oxide, and doped tin(IV) oxide, exhibit a variety of interesting physical and chemical properties, most notably transparency and electrical conductivity /9/, and (iv) the fact that complexes of NMR active nuclei (such as ^{119}Sn and ^{27}Al) offer an important probe into the coordination geometry in solution. The above features have synergistically played a major role in the development of interesting heterometallic chemistry of tin(IV) alkoxides and related derivatives/10-11/.

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In continuation of our ongoing programme on novel heterometallic coordination systems based on polyols /11/, we report in this paper four different types of interesting heterobimetallic coordination complexes incorporating tin(IV) and aluminium. The present study assumes a special significance as the chemistry of heterometallic tin(IV) complexes reported in this paper may offer opportunities in the development of higher purity mixed metal oxide films or powder, to control over surface area, porosity or pore volume.

EXPERIMENTAL

All syntheses and manipulations were carried out under strictly anhydrous conditions. All glassware were oven-dried and protected adequately to exclude moisture. Benzene, *n*-hexane, toluene, dichloromethane, and isopropyl alcohol were purified and dried by standard procedures /14/. Isopropoxides of tin/15/, aluminium /16/, and niobium /17/ were prepared by the literature methods. Oximes were prepared by the method described in the literature /18/. Precursor complexes $Sn\{Al(OPr^i)_4\}_2Cl_2$ /19/, $Sn\{Nb(OPr^i)_6\}_2Cl_2$ /20/, and $Sn\{Al(OPr^i)_4\}_2(OPr^i)$ /19/ were prepared by the literature methods. $SnCl_4$ was distilled (110°C/756 mm Hg) prior to use. Diethanolamines $RN(CH_2CH_2OH)_2$ (R = H, Me, Ph) /21-22/, and hexylene glycol /23/ were dried and purified according to the literature methods. Aluminium was determined /24/ as oxinate, while niobium and tin were determined /24/ as their oxides.

IR (4000-400) spectra were recorded on a Nicolet Magna-550 spectrophotometer using CsI optics. The ^1H (89.55 MHz, $CDCl_3$) and ^{13}C(22.49 MHz, C_6H_6) NMR were recorded on JEOL FX 90Q or JEOL FT 300 AL NMR spectrometers using TMS as an internal reference. ^{119}Sn (33.35 MHz) and ^{27}Al (23.79 MHz) NMR spectra were recorded in $CDCl_3$, using tetramethyltin and aqueous solution of aluminium nitrate as external references, respectively. Carbon, hydrogen, and nitrogen analyses were carried out on a Perkin Elmer series II CHNS/O-2400 analyser. Molecular weights were determined cryoscopically/ ebullioscopically in benzene solution.

Preparation of heterobimetallic alkoxide-diethanolaminates

$Sn\{Al(OPr^i)_4\}_2\{(OCH_2CH_2)_2NH\}$ (1)

To a benzene solution (~ 20 ml) of $Sn\{Al(OPr^i)_4\}_2Cl_2$ (2.18 g, 3.04 mmol) was slowly added a suspension of $K_2\{(OCH_2CH_2)_2NH\}$ [prepared by the reaction of K(0.24 g, 6.13 mg atom) with $HN(CH_2CH_2OH)_2$ (0.32 g, 3.04 mmol) in dry isopropyl alcohol (~ 5 ml) and benzene (~ 20 ml), followed by removal of the volatiles] in benzene (~ 15 ml). The resulting reaction mixture was stirred at room temperature for ~ 4 h, followed by refluxing for ~ 1 h. The precipitated KCl (0.45 g) was removed by filtration. The solvent was removed under reduced pressure to yield the title product (**1**) quantitatively (2.04 g, 89%), which was purified by recrystallisation from 2:1 mixture of dichloromethane and *n*-hexane at –20°C. Yield, 1.77 g (78%).

Using a procedure similar to that employed for (**1**), the other derivatives (**2**) - (**6**) were also prepared. The amount of reactants actually used are shown in square brackets against each compound listed below :

(**2**) : $Sn\{Al(OPr^i)_4\}_2Cl_2$ [3.83 g, 5.34 mmol], K [0.42 g, 10.74 mg atom], and $MeN(CH_2CH_2OH)_2$ [0.64 g, 5.37 mmol].

(**3**) : $Sn\{Al(OPr^i)_4\}_2Cl_2$ [4.39 g, 6.12 mmol], K [0.48 g, 12.27 mg atom), and $C_6H_5N(CH_2CH_2OH)_2$ [1.11 g, 6.12 mmol].

(**4**) : $Sn\{Nb(OPr^i)_6]_2Cl_2$ [2.69 g, 2.48 mmol], K[0.20 g, 5.11 mg atom], and $HN(CH_2CH_2OH)_2$ [0.26 g, 2.47 mmol].

(**5**) : $Sn\{Nb(OPr^i)_6)_2Cl_2$ [3.81 g, 3.51 mmol], K[0.27 g, 6.90 mg atom] and $MeN(CH_2CH_2OH)_2$ [0.42 g, 3.52 mmol].

(**6**) : $Sn\{Nb(OPr^i)_6\}_2Cl_2$ [3.32 g, 3.06 mmol], K [0.24 g, 6.13 mg atom], and $C_6H_5N(CH_2CH_2OH)_2$ [0.55 g, 3.03 mmol].

Preparation of heterobimetallic oximates

$Sn\{Al(ON{=}CMeEt)_4\}_3\ (ON{=}CMeEt)$ (7)

To a solution of $Sn\{Al(OPr^i)_4\}_3\ (OPr^i)$ (1.50 g, 1.55 mmol) in benzene (~ 60 ml) was added ethyl methyl ketoxime (1.75 g, 20.10 mmol) and the reaction mixture was allowed to reflux for ~ 18 h, during which the liberated isopropyl alcohol was continuously distilled out and estimated. When the desired amount of isopropyl alcohol (1.22 g, 20.30 mmol) was collected in the azeotrope, the reaction was stopped and allowed to cool to room temperature. The excess solvent was then removed under reduced pressure to afford a yellow solid (1.84 g, 92%) which was recrystallised from *n*-hexane at –20°C in 1.80 g (90%) yield.

A similar procedure was used for the preparation of $Sn\{Al(ON{=}CMe_2)_4\}_3\text{-}(ON{=}CMe_2)$ from $Sn\{Al(OPr^i)_4\}_2(OPr^i)$ (2.49 g, 2.57 mmol) and $Me_2C{=}NOH$ (2.44 g, 33.42 mmol).

Preparation of glycolate complexes

$Sn(OCHMeCH_2CMe_2O)(OCHMeCH_2CMe_2OH)_2$ (A)

To a solution of $Sn(OPr^i)_4.Pr^iOH$ (2.99 g, 7.21 mmol) in benzene (~ 50 ml) was added $HOCHMeCH_2CMe_2OH$ (2.56 g, 21.65 mmol), and the resulting reaction mixture was refluxed for ~ 12 h, during which period the liberated isopropyl alcohol was fractionated out azeotropically with benzene. The isopropyl alcohol in the collected azeotrope was estimated periodically by the oxidimetric method to monitor the progress and completion of the reaction. When the azeotrope showed negligible presence of an oxidisable material, the refluxing was stopped and the reaction mixture was allowed to cool to room temperature. The solvent was then removed under reduced pressure to afford a colourless sticky solid product, which was highly soluble in toluene, *n*-hexane and dichloromethane. Anal. Calc. for (A) (M.wt. = 469) : Sn, 25.30; glycoxy, 74.30. Found (M.wt. = 465) : Sn, 25.50; glycoxy, 74.60. IR (Nujol, cm^{-1}) : 3430 ν(OH), 1160 ν(CMe) skeletal, 1080, 1030 ν(C-O), 610, 525, 485 (Sn-O). ^{1}H NMR ($CDCl_3$, δ, ppm) : 1.23 (d, J = 6Hz, 9H, CHMe); 1.29 (s, 9H, **CMe$_2$**); 1.36 (s, 9H, **CMe$_2$**); 1.46-18.0 (m, 6H, **CH$_2$**); 3.23(br, 2H, **OH**); 4.10-4.47(m, 3H, CHMe). ^{13}C NMR. (C_6H_6, δ, ppm) : 24.6 (**CMe$_2$**), 27.8 (**CMe$_2$**), 32.0(CHMe), 49.9(**CH$_2$**), 65.7 (**CHMe**), 71.2(**CMe$_2$**). ^{119}Sn NMR (C_6H_6, δ, ppm) : – 615.

$\{Al(OPr^i)_2\}_2\{Sn(OCHMeCH_2CMe_2O)_3\}$ (9)

The complex (**A**) (1.46 g, 3.13 mmol) and $Al(OPr^i)_3$ (1.27 g, 6.21 mmol) were mixed in benzene (~ 60 ml) and the resulting reaction mixture was refluxed for ~ 14 h. The liberated isopropyl alcohol (0.37 g, 6.15 mmol) was continuously fractionated out during the above mentioned period in the form of an azeotrope with benzene and estimated. Removal of the volatile components from the solution yielded quantitatively a solid product, which was recrystallised at –20°C from a mixture of toluene and *n*-hexane to obtain analytically pure crystalline solid (2.00 g, 85%).

$Al_2(OCHMeCH_2CMe_2O)_2\,Sn(OCHMeCH_2CMe_2O)_3$ (10)

To a benzene (~ 50 ml) solution of (9) (1.58 g, 2.09 mmol) was added $HOCHMeCH_2CMe_2OH$ (0.50 g, 4.23 mmol), and the reaction mixture was allowed to reflux for ~ 8 h, during which the liberated isopropyl alcohol (0.50 g, 8.32 mmol) was continuously removed and estimated. After completion of reaction (as was indicated by the amount of the liberated isopropyl alcohol collected and absence of alcohol in the azeotrope collected thereafter). The volatiles were removed under reduced pressure to obtain a colourless solid (1.50 g, 97%). The product was recrystallised from *n*-hexane at –20°C as a colourless crystalline solid $Al_2Sn(OCHMeCH_2CMe_2O)_5$ in 1.39 g (90%) yield.

Analytical and some physical data of the new derivatives (1)-(**10**) are summarised in Table I.

Important spectral data of the new complexes (1) – (10) are listed below :

(1) : IR (Nujol, cm^{-1}) : 1140, 1106 ν(OPr^i); 1041, 1008 ν(C-O); 598 ν(Al-O); 549 ν(Sn-O); 451 ν(Sn←N). ^{1}H NMR (δ, ppm) : 1.23 (d, 24H, CH**Me** (terminal)); 1.27 (d, 24H, CH**Me** (bridging)); 3.64 (t, 4H, NCH$_2$); 3.86 (t, 4H, OCH$_2$); 4.08 (m, 4H, **CH**Me (terminal)); 4.21 (m, 4H, **CH**Me (bridging)). ^{119}Sn NMR (δ, ppm) : –606. ^{27}Al NMR (δ, ppm) : 38.

(2) : IR (Nujol, cm^{-1}) : 1133, 1116 ν(OPr^i); 1049, 1000 ν(C-O); 600 ν(Al-O); 533 ν(Sn-O); 433 ν(Sn←N). ^{1}H NMR (δ, ppm) : 1.30 (d, 48H, CH**Me** (terminal+bridging)); 2.68 (s, 3H, N**Me**); 2.80 (t, 4H, NCH$_2$); 2.95 (t, 4H, OCH$_2$); 4.04 (m, 4H, **CH**Me (terminal)); 4.64 (m, 4H, **CH**Me (bridging)). ^{119}Sn NMR (δ, ppm) : –608. ^{27}Al NMR (δ, ppm) : 48.

Table I

Analytical and some physical data for the new derivatives (1)-(10)

Product[a] (% yield, state)	% Analysis Found (Calc.)					M.wt. Found (Calc.)
	Sn	Al/Nb	C	H	N	
$Sn\{Al(OPr^i)_4\}_2\{(OCH_2CH_2)_2NH\}$ (1) (78, solid)	15.15 (15.85)	7.20 (7.21)	44.81 (44.92)	8.53 (8.73)	1.80 (1.87)	762 (749)
$Sn\{Al(OPr^i)_4\}_2\{(OCH_2CH_2)_2NMe\}$ (2) (89, semisolid)	15.23 (15.56)	7.01 (7.08)	45.77 (45.67)	8.67 (8.85)	1.81 (1.83)	778 (763)
$Sn\{Al(OPr^i)_4\}_2\{(OCH_2CH_2)_2NC_6H_5\}$ (3) (80, solid)	14.29 (14.39)	6.51 (6.54)	49.29 (49.51)	8.45 (8.43)	1.60 (1.69)	848 (825)
$Sn\{Nb(OPr^i)_5\}_2\{(OCH_2CH_2)_2NH\}$ (4) (75, sticky solid)	27.06 (27.29)[b]		43.03 (43.01)	8.28 (8.39)	1.21 (1.25)	1148 (1117)
$Sn\{Nb(OPr^i)_6\}_2\{(OCH_2CH_2)_2NMe\}$ (5) (87, waxy solid)	26.33 (26.95)[b]		43.48 (43.54)	8.43 (8.46)	1.21 (1.23)	1143 (1131)
$Sn\{Nb(OPr^i)_6\}_2\{(OCH_2CH_2)_2NC_6H_5\}$ (6) (76, solid)	25.01 (25.54)[b]		46.29 (46.31)	8.16 (8.19)	1.15 (1.17)	1201 (1193)
$Sn\{Al(ON{=}C(Et)Me)_4\}_3(ON{=}C(Et)Me)$ (7) (90, yellowish solid (viscous when freshly prepared))	8.98 (9.00)	6.13 (6.14)	47.33 (47.34)	7.91 (7.95)	13.78 (13.80)	1326 (1318)
$Sn\{Al(ON{=}CMe_2)_4\}_3(ON{=}CMe_2)$ (8) (89, solid)	10.42 (10.44)	7.11 (7.13)	41.10 (41.19)	6.89 (6.92)	16.00 (16.02)	1143 (1136)
$Sn\{OCHMeCH_2CMe_2O\}_3\{Al(OPr^i)_2\}_2$ (9) (85, crystalline solid)	15.80 (15.72)	7.40 (7.10)	47.50 (47.53)	8.48 (8.51)	-	763 (758)
$SnAl_2(OCHMeCH_2CMe_2O)_5$ (10) (90, solid)	15.81 (15.74)	7.13 (7.22)	47.69 (47.78)	7.98 (8.02)	-	759 (754)

[a] All are colourless

[b] mixed oxide

(3) : IR (Nujol, cm^{-1}) : 1133, 1116 ν(OPr^i); 1050, 1000 ν(C-O); 597 ν(Al-O); 533 ν(Sn-O); 450 ν(Sn←N). ^{1}H NMR (δ, ppm) : 1.21 (d, 24H, CH**Me** (terminal)); 1.38 (d, 24H, CH**Me** (bridging)); 3.38 (t, 4H, NC$\mathbf{H_2}$); 3.85 (t, 4H, OC$\mathbf{H_2}$); 4.01 (m, 4H, C**H**Me (terminal)); 4.25 (m, 4H, C**H**Me (bridging)); 6.66(br, 5H, C$_6\mathbf{H_5}$). ^{119}Sn NMR (δ, ppm) : –633. ^{27}Al NMR (δ, ppm) : 49.

(4) : IR (Nujol, cm^{-1}) : 1133, 1116 ν(OPr^i); 1050, 1000 ν(C-O); 582 ν(Al-O); 550 ν(Sn-O); 450 ν(Sn←N). ^{1}H NMR (δ, ppm) : 1.27 (d, 48H, CH**Me** (terminal)); 1.37 (d, 24H, CH**Me** (bridging)); 2.65 (t, 4H, NC$\mathbf{H_2}$); 3.11 (t, 4H, OC$\mathbf{H_2}$); 4.66 (m, 4H, C**H**Me (terminal)); 4.78 (m, 4H, C**H**Me (bridging)). ^{119}Sn NMR (δ, ppm) : –609.

(5) : IR (Nujol, cm^{-1}) : 1149, 1116 ν(OPr^i); 1033, 1000 ν(C-O); 583 ν(Al-O); 549 ν(Sn-O); 433 ν(Sn←N). ^{1}H NMR (δ, ppm) : 1.22 (d, 48H, CH**Me** (terminal)); 1.33(d, 24H, CH**Me** (bridging)); 2.68 (s, 3H, N**Me**); 3.80 (t, 4H, NC$\mathbf{H_2}$); 3.89 (t, 4H, OC$\mathbf{H_2}$); 4.07 (m, 4H, C**H**Me (terminal)); 4.73 (m, 4H, C**H**Me (bridging)). ^{119}Sn NMR (δ, ppm) : –610.

(6) : IR (Nujol, cm^{-1}) : 1155, 1126 ν(OPr^i); 1040, 1008 ν(C-O); 582 ν(Al-O); 549 ν(Sn-O); 451 ν(Sn←N). ^{1}H NMR (δ, ppm) : 1.27 (d, 48H, CH**Me** (terminal)); 1.38 (d, 24H, CH**Me** (bridging)); 3.70 (t, 4H, NC$\mathbf{H_2}$); 4.25 (t, 4H, OC$\mathbf{H_2}$); 4.70 (m, 12H, C**H**Me (terminal + bridging)); 6.22, 7.22 (br, 5H, C$_6\mathbf{H_5}$). ^{119}Sn NMR (δ, ppm) : –635.

(7) : IR (Nujol, cm^{-1}) : 1644, 1617 ν(C=N); 956 ν(N-O); 608, 503 ν(Sn-O); 672, 542 ν(Al-O). ^{1}H NMR (δ, ppm) : 1.49 (t, J = 6 Hz, 39H, N=CMeCH$_2$**Me**); 1.87 (s, 39H, N=C**Me**Et); 2.08-2.37 (q, J=6Hz, 26H, N=CMeC$\mathbf{H_2}$Me). ^{13}C (δ, ppm) : 28.74, 16.80 (N=C**Me**Et); 28.35, 11.32 (N=CMe**C**H$_2$Me); 22.35, 13.42 (N=CMeCH$_2$**Me**), 155.64 (N=**C**MeCH$_2$Me). ^{119}Sn NMR (δ, ppm) :– 667. ^{27}Al NMR : 32.

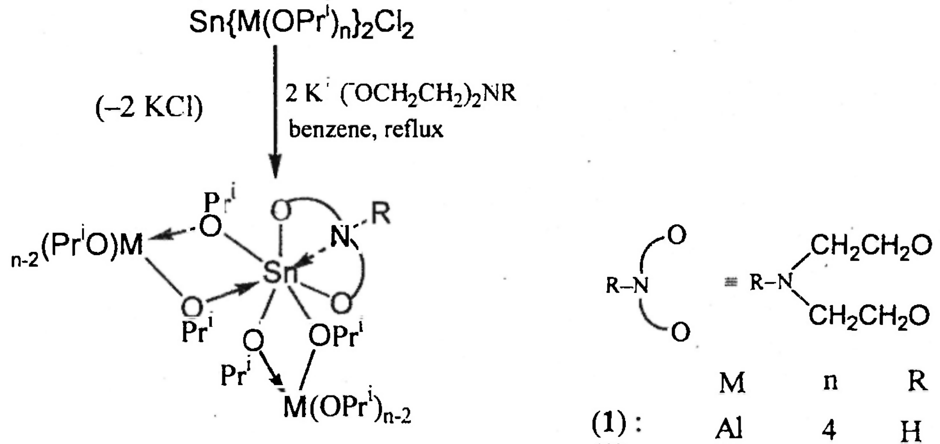
(8) : IR (Nujol, cm^{-1}) : 1636, 1610 ν(C=N); 935 ν(N-O); 610, 550 ν(Sn-O); 656, 540 ν(Al-O). ^{1}H NMR (δ, ppm) : 1.83 (br(s), 78H, N=C$\mathbf{Me_2}$); 1.87 (s, 39H, N=C**Me**Et); 2.08-2.37 (q, J=6Hz, 26H, N=CMeC$\mathbf{H_2}$Me). ^{13}C (δ, ppm) : 21.70, 14.52 (N=C$\mathbf{Me_2}$); 154.56, (N=**C**Me$_2$). ^{119}Sn NMR (δ, ppm) : –668. ^{27}Al NMR : 34.

(9) : IR (Nujol, cm^{-1}) : 1220 ν(CMe) skeletal, 1050 ν(C-O); 1165, 1140 ν(OPr^i); 570, 520 ν(Sn-O); 670, 625 ν(Al-O). ^{1}H NMR (δ, ppm) : 1.16 (d, J = 6Hz, 9H, CH**Me**); 1.23(s, 9H, C$\mathbf{Me_2}$); 1.27 (d, J = 6 Hz, 24H, CH$\mathbf{Me_2}$); 1.30 (s, 9H, C$\mathbf{Me_2}$); 1.49-1.60 (m, 6H, C$\mathbf{H_2}$); 4.20 (septet, J = 6 Hz, 4H, C**H**Me$_2$); 4.47-4.88 (m, 3H, C**H**Me). ^{13}C NMR (δ, ppm) : 25.5 (CH$\mathbf{Me_2}$), 26.8 (C$\mathbf{Me_2}$), 28.3 (C$\mathbf{Me_2}$); 31.2 (CH**Me**), 51.2 (**C**H$_2$), 63.7 (**C**HMe$_2$), 66.5 (**C**HMe), 71.0(**C**Me$_2$). ^{119}Sn NMR (δ, ppm) : –655. ^{27}Al (δ, ppm); 32.

(10) : IR (Nujol, cm^{-1}) : 1170 ν(CMe) skeletal, 1090, 1020 ν(C-O); 545 ν(Sn-O); 680, 645 ν(Al-O). ^{1}H NMR (δ, ppm) : 1.22 (d, J = 6Hz, 15H, CH**Me**); 1.29(s, 15H, C$\mathbf{Me_2}$); 1.34 (s, 15H, C$\mathbf{Me_2}$); 1.43-2.01 (m, 10H, C$\mathbf{H_2}$); 4.02-4.92 (m, 5H, C**H**Me). ^{13}C NMR (δ, ppm) : 27.9 (C$\mathbf{Me_2}$), 28.7 (C$\mathbf{Me_2}$); 32.2 (CH**Me**), 52.9 (**C**H$_2$), 64.9 (**C**HMe), 71.1 (**C**Me$_2$). ^{119}Sn NMR (δ, ppm) : – 660. ^{27}Al (δ, ppm); 32.

RESULTS AND DISCUSSION

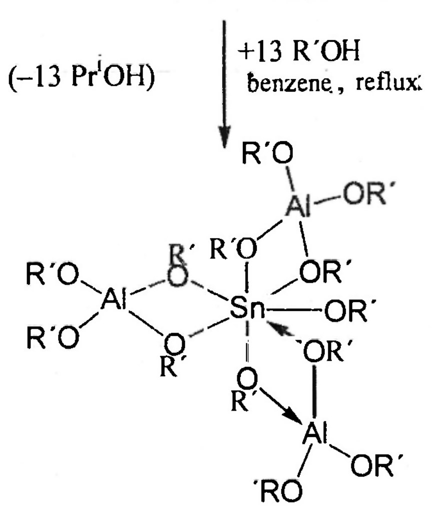
Heterobimetallic coordination complexes of tin(IV) containing isopropoxide and diethanolaminate ligands have been prepared for the first time by the reactions of $Sn\{Al(OPr^i)_4\}_2Cl_2$/$Sn\{Nb(OPr^i)_6\}_2Cl_2$ with potassium salts of diethanolamine and N-substituted diethanolamines (Scheme 1).



	M	n	R
(1) :	Al	4	H
(2) :	Al	4	Me
(3) :	Al	4	C_6H_5
(4) :	Nb	6	H
(5) :	Nb	6	Me
(6) :	Nb	6	C_6H_5

Scheme 1

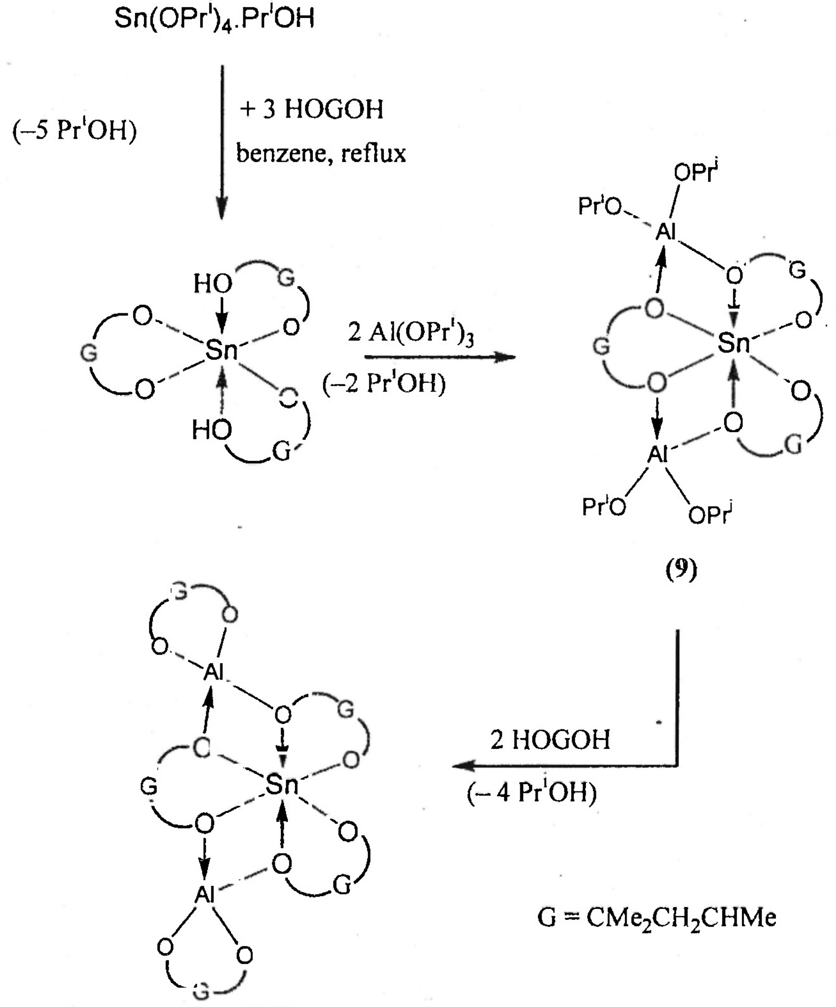
Oximinolysis of $Sn\{Al(OPr^i)_4\}_3(OPr^i)$ with acetoxime or methyl ethyl ketoxime (abbreviated as R′OH) in 1:13 molar ratio yields heterobimetallic oximates of tin(IV) and aluminium (Scheme 2).



(7) R′ = N=C(Et)Me
(8) R′ = N=CMe₂

Scheme 2

Reaction of $Sn(OPr^i)_4.Pr^iOH$ with three equivalents of hexylene glycol (HOGOH) in benzene under refluxing conditions yields the precursor complex $Sn(OGO)(OGOH)_2$ (Scheme 3), which on reaction with two equivalents of $Al(OPr^i)_3$ affords the novel heterobimetallic isopropoxide-glycolate complex (**9**). The latter, on reaction with one equivalent of the glycol, yields the heterobimetallic homoleptic glycolate complex incorporating six-coordinate tin(IV) and four-coordinate aluminium.



(**9**)

(**10**)

Scheme 3

The new derivatives (**1**)-(**10**) are moisture-sensitive, colourless solids or semisolids (Table 1), and soluble in common organic solvents. Determinations of molecular weights by cryoscopic/ebullioscopic methods depict their monomeric nature in benzene solution.

Spectroscopic Studies

IR spectra

Structurally important IR absorptions of the new complexes are summarised in the Experimental Section. Some salient features of infrared studies are (i) the observed shifting in ν(N-H) vibration for (**1**) and (**4**) by ~ 25 cm^{-1} to lower wave number, with respect to that observed in the free diethanolamine (3171 cm^{-1}), which may be ascribed to the coordination of nitrogen to the metal centre, and (ii) the appearance of a new band at 441±9 cm^{-1} assignable to ν(Sn←N) vibration.

^{1}H NMR spectra

The new complexes (**1**)-(**10**) display characteristic signals (see Experimental Section) due to the organic moieties present in the complexes.

A comparison of NH chemical shifts of the complexes (**1**) and (**4**) with that of the diethanolamine $HN(CH_2CH_2OH)_2$ shows ~ 0.20 ± 0.04 ppm downfield shifting, which is consistent with the formation of a transannular Sn←N dative bond /19/.

NMe protons signals in (**2**) and (**5**) exhibit a lowering of about ~ 0.35 ppm with respect to their positions in the parent ligands, supporting coordination of the amino nitrogen to the tin atom.

^{27}Al NMR

The observed ^{27}Al NMR signals (see Experimental Section) are consistent with the presence of tetracoordinate /17/ aluminium in complexes (**1**)-(**3**) and (**7**)-(**10**).

^{119}Sn NMR

The appearance of ^{119}Sn signals for (**1**)-(**6**) in the δ – 606 to – 635 ppm regions is consistent with hexacoordinated tin atom /17/, whereas values at δ –660 to – 668 for complexes (**7**)-(**10**) give support for seven-coordination /18/ of the tin atom.

The observed ^{119}Sn chemical shift data for complexes (**1**)-(**6**) are explainable in terms of (i) the weak interaction between nitrogen and tin(IV) centre and (ii) smaller shielding effect of nitrogen compared to that of oxygen atom.

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