Pergamon

Polyhedron Vol. 14, No. 17-18, pp. 2461-2465, 1995
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0277-5387/95 $9.50+0.00

0277-57387(95)00057-7

THE FIRST NONAISOPROPOXODISTANNATE DERIVATIVES OF LANTHANIDES AND YTTRIUM*

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(*Received* 21 *November* 1994; *accepted* 17 *January* 1995)

Abstract—Novel heterometallic isopropoxides of the lanthanides(III) and yttrium(III) with the formula $[LnCl_{3-x}\{Sn_2(OPr^i)_9\}_x]$ (Ln = La, Pr, Nd, Lu and Y; $x = 2$ or 3) have been synthesized by the reactions of $LnCl_3 \cdot 3Pr^iOH$ with $KSn_2(OPr^i)_9$ in 1:2 and 1:3 molar ratio in benzene. These complexes have been characterized by elemental analyses, isopropoxy group estimations and molecular weight measurements. Their spectral [IR, electronic, multinuclear (^1H, ^{13}C, ^{119}Sn) NMR] properties have been studied and discussed.

In spite of the current resurgence of interest in homo- and hetero-metallic alkoxide chemistry[1–7] in the context of a search for useful precursors for the formation of novel heteropolymetallic alkoxides[8–13] and mixed metal oxide-based ceramics,[1–3,14–16] there has been little recent development in tin(IV) alkoxide chemistry[7,17] since the work of Bradley *et al.*,[18] Maire[19] and Mehrotra and Gupta.[20] Recently described heterometallic alkoxides containing tin(IV) include $\{KSn(OBu^t)_5\}$,[21] $[\{(COD)Rh\}_2Sn(OEt)_6]$,[22] $[Tl_2Sn(OEt)_6]$,[23] $[Cd_4Sn_4(\mu_4\text{-}O)_2(O_2CCH_3)(OCH_2Bu^t)_{10}]$,[24] $[ZnSn(OEt)_6]$,[25] $[Sn\{Al(OPr^i)_4\}_4]$,[26] $NaSn_2(OR)_9$[18] and $[Sn\{Al(OPr^i)_4\}_nCl_{4-n}]$[27] ($n$ = 1, 2 or 3). Investigations on the alkoxide chemistry of yttrium and the lanthanides have aroused considerable interest[4] due to the flexibility in structural and reactivity patterns of such complexes coupled with the discovery of superconducting properties of yttrium/lanthanide[28] based mixed metal oxides.

During the past 15 years the $[Zr_2(OPr^i)_9]^-$ ligand[4,8–12] has played a significant role in the development of heterometal alkoxide chemistry, but analogous derivatives with $[Sn_2(OPr^i)_9]^-$ have not been investigated[17] so far. In view of the comparative ease with which $NaSn_2(OR)_9$ can be synthesized,[18] its use as a convenient and versatile precursor has recently been suggested.[29]

Additionally, tin(IV) oxide and mixed metal oxides doped with tin(IV) oxide exhibit notable optical transparency and electrical conductivity,[30] leading to applications as transparent electrodes in optoelectronic devices, thin film resistors, gas sensors and wear-resistant coating. Thus, the investigations of heterometal alkoxide chemistry involving tin(IV) may offer opportunities in the development of novel classes of heterometallic alkoxides, as well as advanced ceramic materials.

In view of the well-known difficulties in X-ray crystal structure elucidation of alkoxide derivatives,[1b] the utility of ^{119}Sn nuclei as NMR probes may provide structurally useful information which could be of considerable value in the structural elucidation of metal derivatives containing the $[Sn_2(OPr^i)_9]^-$ fragment. We therefore report here the synthesis and characterization of the title compounds.

EXPERIMENTAL

Experimental, analytical and instrumentation procedures were similar to those described in some

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* Dedicated by A.S. and R.C.M., with all best wishes to their good friend Professor M. F. Lappert, F.R.S., a distinguished Inorganic and Organometallic Chemist, on the occasion of his 40 years of Chemical Research. In addition, Anirudh Singh would like to express his gratitude for the pivotal role that Mike played in introducing him to the *f*-element chemistry during his post-doctoral research at Sussex University.

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of our earlier publications.[4,13] Potassium nonaisopropoxodistannate, $KSn_2(OPr^i)_9$, was prepared following the literature method.[18]

Synthesis of nonaisopropoxodistannatometal complexes

$[LaCl\{Sn_2(OPr^i)_9\}_2]$ (**2a**). A benzene (~20 cm^3) solution of freshly prepared $KSn_2(OPr^i)_9$ (2.63 g, 3.26 mmol) was slowly added to a pre-stirred suspension of $LaCl_3 \cdot 3Pr^iOH$ (0.69 g, 1.62 mmol) in benzene (~15 cm^3). The reaction mixture was initially stirred at ~70°C for 10 h and at room temperature for 10 h, during which time $LaCl_3 \cdot 3Pr^iOH$ dissolved completely and KCl was precipitated out. Removal of KCl (0.23 g, 3.08 mmol) by filtration and stripping out the volatiles from the filtrate under reduced pressure yielded the complex as a white foamy solid. The title complex, **2a**, was recrystallized in 60% yield from n-hexane–dichloromethane mixture at −20°C.

Other complexes prepared according to the same procedure include: $[Ln\{Sn_2(OPr^i)_9\}_2Cl]$ [Ln = Y (**1a**), Pr (**3a**), Nd (**4a**) and Lu (**5a**)]. Physical and analytical data for these complexes are listed in Table 1.

$[Nd\{Sn_2(OPr^i)_9\}_3]$ (**4b**). To a pre-stirred suspension of $NdCl_3 \cdot 3Pr^iOH$ (0.48 g, 1.11 mmol) in benzene (~15 cm^3), a freshly prepared solution of $KSn_2(OPr^i)_9$ (2.70 g, 3.34 mmol) in benzene (~20 cm^3) was added slowly. After complete addition of $KSn_2(OPr^i)_9$, the mixture was refluxed for 3 h. The precipitated KCl (0.23 g, 3.08 mmol) was removed by filtration. From the filtrate a white foamy solid of composition $[Nd\{Sn_2(OPr^i)_9\}_3]$ (2.70 g, 90%) was obtained by removing the volatiles under reduced pressure at room temperature. Complex **4b** was recrystallized from n-hexane at −20°C in 50% yield.

Adopting similar procedures, derivatives of composition $[Ln\{Sn_2(OPr^i)_9\}_3]$ [Ln = Y (**1b**), La (**2b**), Pr (**3b**) and Lu (**5b**)] have also been synthesized. Further details of all the complexes are summarized in Table 1.

RESULTS AND DISCUSSION

Reactions of $LnCl_3 \cdot 3Pr^iOH$ with $KSn_2(OPr^i)_9$ in different (1:2 and 1:3) molar ratios in benzene afforded novel heterobimetallic isopropoxides according to the following general reaction:

$$LnCl_3 \cdot 3Pr^iOH + xKSn_2(OPr^i)_9 \xrightarrow{C_6H_6} [LnCl_{3-x}\{Sn_2(OPr^i)_9\}_x] + xKCl\uparrow \quad (1)$$

1a Ln = Y, $x = 2$; **1b** Ln = Y, $x = 3$
2a Ln = La, $x = 2$; **2b** Ln = La, $x = 3$
3a Ln = Pr, $x = 2$; **3b** Ln = Pr, $x = 3$
4a Ln = Nd, $x = 2$; **4b** Ln = Nd, $x = 3$
5a Ln = Lu, $x = 2$; **5b** Ln = Lu, $x = 3$

These novel heterometallic isopropoxides (Table 1) are highly moisture-sensitive white (**1a**, **1b**, **2a**, **2b**, **5a**, **5b**), green (**3a**, **3b**) or blue (**4a**, **4b**) solids, soluble in common organic solvents; they exhibit monomeric nature ebullioscopically in benzene. The identity of the products has been confirmed by their recrystallization from n-hexane–dichloromethane at −20°C in ~60% yield with unchanged stoichiometry.

Table 1. Analytical[a] and physical data for new heterometallic isopropoxides of lanthanide(III) and yttrium(III)[b]

			Analysis (%)			
Complex (Ln)	Colour	Yield[c]	Ln	Sn	Cl	OPr^i
1a (Y)	Colourless	68	5.3 (5.4)	28.5 (28.6)	2.1 (2.1)	63.6 (63.9)
2a (La)	Colourless	60	8.0 (8.1)	27.5 (27.7)	2.0 (2.1)	62.0 (62.1)
3a (Pr)	Pale green	65	8.1 (8.2)	27.6 (27.8)	2.1 (2.07)	61.8 (62.0)
4a (Nd)	Blue	60	8.3 (8.4)	27.6 (27.6)	2.0 (2.1)	61.2 (61.8)
5a (Lu)	Colourless	67	9.9 (10.0)	27.0 (27.2)	1.9 (2.0)	60.5 (60.8)
1b (Y)	Colourless	64	3.6 (3.7)	29.8 (29.7)	—	66.1 (66.5)
2b (La)	Colourless	65	5.7 (5.7)	29.0 (29.1)	—	64.8 (65.2)
3b (Pr)	Green	62	5.8 (5.7)	29.1 (29.1)	—	64.9 (65.1)
4b (Nd)	Blue	50	5.7 (5.9)	29.0 (29.1)	—	64.7 (65.0)
5b (Lu)	Colourless	64	7.0 (7.1)	28.8 (28.7)	—	63.9 (64.2)

[a] Calculated values in parentheses.

[b] These are monomeric (ebullioscopically) in benzene solution.

[c] Yields refer to crystallized derivatives from initial products which are obtained almost in calculated amounts.

The IR spectra (4000–200 cm^{-1}) of these complexes exhibit absorption bands characteristic of metal–isopropoxy groups[31] [e.g. skeletal vibrations of the isoproxy groups in the region 1150–1105 cm^{-1}; ν (C—O) absorptions in the region 1085–930 cm^{-1}; medium to strong intensity broad ν(M—O) (where M = Zr, Al or Sn) absorptions at 560–525 cm^{-1} and those at 460–400 cm^{-1} due to ν (Ln—O), where Ln = Y, La, Pr, Nd or Lu]. The chloro derivatives (**1a**, **2a**, **3a**, **4a**, **5a**) exhibit additional absorption bands in the region 290–220 cm^{-1} due to Ln—Cl stretching frequencies.[32]

Attempts to elucidate the structure of any of the derivatives **1a**–**5a** by X-ray crystallography have so far not been successful. The following ^{1}H and ^{13}C NMR evidence, although not quite conclusive, indicates a structure $[Ln\{\eta^3\text{-}[Sn_2(\mu\text{-}OPr^i)_3(OPr^i)_6]\}_2Cl]$ similar to that of $[LaCl\{Zr_2(OPr^i)_9\}_2]$[4b] (see Fig. B of ref. 4b), involving the tridentate ligational mode of nonaisopropoxodistannate, $[(Pr^iO)_3Sn(\mu\text{-}OPr^i)_3Sn(OPr^i)_3]^-$ and is briefly mentioned below.

The ^{1}H NMR spectra (in $CDCl_3$ at room temperature) of **1a**–**5a** exhibit two pairs of doublets in the integrated intensity ratio 1.25 : 1 centred at δ1.23 and 1.43, due to *gem*-dimethyl protons respectively at terminal and bridging sites (Table 2). In these derivatives, of the three isopropoxy groups in the $Sn(\mu\text{-}OPr^i)_3Sn$ unit only two and one of six terminal $Sn—OPr^i$ groups of each $[Sn_2(OPr^i)_9]^-$ fragment appear to be involved in ligating lanthanide(III) ions. The methine protons appear as a broad multiplet (arising due to overlapping of septets) centred at δ4.35. The ^{13}C NMR spectra (Table 2) of these complexes also showed two peaks for the α- and β-carbon atoms of the isopropoxy groups. The distinction between doubly ($\mu_2\text{-}OPr^i$) and triply ($\mu_3\text{-}OPr^i$) bridging isopropoxy groups was not possible, even on lowering the temperature to -40°C. ^{119}Sn NMR signals observed at $\sim\delta -597$ (Table 2) are indicative of a hexa-coordinate environment around the tin atom.[33]

As expected, complexes **1b**–**5b** also exhibited a similar ^{1}H NMR spectral pattern: two doublets at δ1.25 (terminal $Sn—OPr^i$) and 1.44 [bridging, $Sn(\mu\text{-}OPr^i)_3Sn$] (intensity ratio 2 : 1) due to methyl protons. The methine protons appeared as broad multiplets centred at δ4.36. ^{13}C NMR spectra (Table 2) of these complexes also indicate the presence of isopropoxy groups, preferably in two different environments. The retention of a hexa-

Table 2. ^{1}H, ^{13}C and ^{119}Sn NMR data[a] for the new complexes

Complex (Ln)	^{1}H[b]	^{13}C[c]	^{119}Sn
1a (Y)	1.22 [d, J = 6.1 Hz, 60H, Me(t)],1.44 [d, J = 6.1 Hz, 48H, Me(b)], 4.37 [m, 18H, CH(t+b)]	26.98, 27.52 (Me); 66.53, 67.98 (CH)	−597
1b (Y)	1.27 [d, J = 6.2 Hz, 108H, Me(t)],1.44 [d, J = 6.2 Hz, 54H, Me(b)], 4.31 [m, 27H, CH (t+b)]	26.16, 27.46 (Me); 66.47, 67.93 (CH)	−597
2a (La)	1.2 [d, J = 6.2 Hz, 60H, Me(t)], 1.45 [d, J = 6.2 Hz, 48H, Me(b)], 4.33 [m, 18H, CH(t+b)]	26.16, 27.46(Me); 66.48, 67.96 (CH)	−596
2b (La)	1.26 [d, J = 6.2 Hz, 108H, Me(t)], 1.43 [d, J = 6.2 Hz, 54H, Me(b)], 4.35 [m, 27H, CH(t+b)]	26.49, 27.46 (Me); 66.47, 67.93 (CH)	−596
3a (Pr)	1.26 [d, J = 6.0 Hz, 60H, Me(t)], 1.43 [d, J = 6.0 Hz, 48H, Me(b)], 4.40 [m, 18H, CH(t+b)]	24.64, 25.94 (Me); 65.10, 66.48 (CH)	−598
3b (Pr)	1.25 [d, J = 6.0 Hz, 108H, Me(t)], 1.44 [d, J = 6.0 Hz, 54H, Me(b)], 4.42 [m, 27H, CH(t+b)]	24.70, 26.00 (Me); 65.01, 66.47 (CH)	−598
4a (Nd)	1.24 [d, J = 6.2 Hz, 60H, Me(t)], 1.42 [d, J = 6.2 Hz, 48H, Me(b)], 4.38 [br, 18H,CH(t+b)]	27.14, 27.53 (Me); 63.53, 67.98 (CH)	−597
4b (Nd)	1.22 [d, J = 6.2 Hz, 108H, Me(t)], 1.44 [d, J = 6.2 Hz, 54H, Me(b)], 4.33 [br, 27H, CH(t+b)]	23.56, 24.86 (Me); 63.87, 65.87 (CH)	−598
5a (La)	1.27 [d, J = 6.0 Hz, 60H, Me(t)], 1.44 [d, J = 6.0 Hz, 48H, Me(b)], 4.43[m, 18H, CH(t+b)]	26.92, 27.48 (Me); 66.48, 67.92 (CH)	−597
5b (Lu)	1.25 [d, J = 6.0 Hz, 108H, Me(t)], 1.43 [d, J = 6.0 Hz, 54H, Me(b)], 4.32 [m, 27H, CH(t+b)]	26.24,27.38 (Me); 66.52, 67.86 (CH)	−597

[a] Given as chemical shift (δ), multiplicity J in Hz, relative intensity, assignment. Abbreviations: t = terminal, b = bridging, br = broad, m = multiplet.

[b] Recorded in $CDCl_3$.

[c] Recorded in benzene.

Table 3. Hypersensitive electronic absorption, oscillator strength (P), nephelauxetic ratio ($\bar{\beta}$), covalency parameter (δ) and bonding parameter ($b^{1/2}$) for the new complexes[a] **3b**, **4a** and **4b**

Complex	λ_{max}, in nm (ε_{max}, in $dm^3\ mol^{-1}\ cm^{-1}$)	Transition	$P \times 10^6$	$\bar{\beta}$	δ	$b^{1/2}$
3b (Pr)	446 (6.96) [446 (6.53)]	$^3H_4 \rightarrow {}^3P_2$	30.21 [9.73]	0.9916	0.850	0.045
	5.88 (4.90) [588 (2.42)]	$^3H_4 \rightarrow {}^2D_2$	22.31 [8.01]			
4a (Nd)	588 (11.42) [572 (5.82)]	$^4I_{9/2} \rightarrow {}^2G_{7/2}, {}^4G_{5/2}$	56.63 [13.49]	0.9805	1.990	0.069
4b (Nd)	584 (14.70) [572 (5.82)]	$^4I_{9/2} \rightarrow {}^2G_{7/2}, {}^4G_{5/2}$	79.11 [13.49]	0.9883	1.183	0.052

[a] The corresponding values for aquo ions are given in square brackets.

coordinate environment around the tin atom in these derivatives is supported by the appearance of a single ^{119}Sn NMR peak in each case in the range $\delta - 596$ to -598. These data are in favour of the structural formulation $[Ln\{\eta^2\text{-}[Sn_2(\mu\text{-}OPr^i)_3(OPr^i)_6]\}_3]$ (see below, analogous to that in $[La\{Zr_2(OPr^i)_9\}_3]$, Fig. C of ref. 4b), in which only two doubly bridged isopropoxy groups of $[(Pr^iO)_3Sn(\mu\text{-}OPr^i)_3Sn(OPr^i)_3]^-$ are involved in ligating lanthanide(III) ions.

The appearance of a sharp, single ^{119}Sn NMR peak at about $\delta - 600$ for all the new complexes is indicative of a single species, with the tin atom in a hexa-coordinate environment. Furthermore, the observed ^{119}Sn NMR chemical shifts (Table 2) are lower than those observed (at $\delta - 640.0$) for six-coordinate tin in $KSn_2(OPr^i)_9$; this may be the result of comparatively covalent interactions between $[Sn_2(OPr^i)_9]^-$ units and the lanthanide(III) ions.

In order to probe the coordination environment[34–38] around the lanthanide(III) ions in heterobimetallic isopropoxides reported in this paper, the electronic spectra of a few typical derivatives of Pr^{III} and Nd^{III} (Table 3) have been examined. The pseudo-nephelauxetic ($\bar{\beta}$), bonding ($b^{1/2}$) and convalency (δ) parameters for **3b**, **4a** and **4b** are listed in Table 3. The $b^{1/2}$ values indicate the extent of 4*f* orbital participation in complexation. The positive values of δ and $b^{1/2}$ and $\bar{\beta}$ values less than unity for these three complexes point towards the apparent covalent nature[34,36] of the metal (Ln)–ligand $[Sn_2(OPr^i)_9]^-$ bonds in these derivatives.

Furthermore, comparing the shape and intensity of the absorption of the hypersensitive bands (Table 3) with the reported spectra[37] of six-, seven- and eight-coordinated species, it appears that Pr^{III} in **3b** and Nd^{III} in **4b** are in a six-coordinate environment, whereas Nd^{III} in **4a** is more likely to be seven-coordinated.

Acknowledgements—Financial support by the CSIR and DST, New Delhi, is gratefully acknowledged. The authors are also indebted to Mr Suman K. Gupta for recording the NMR spectra.

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