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SYNTHESIS AND CHARACTERIZATION OF NOVEL HOMO- AND HETEROLEPTIC NONAISOPROPOXODIZIRCONATOSAMARIUM(III) COMPLEXES

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Abstract—Heterobimetallic isopropoxide derivatives of samarium(III) of the types $[Cl_{3-n}Sm\{Zr_2(OPr^i)_9\}_n]$ ($n = 1$, 2 or 3) have been prepared by the interaction of $SmCl_3 \cdot 3Pr^iOH$ with $K\{Zr_2(OPr^i)_9\}$ in the desired molar (1 : 1, 1 : 2 or 1 : 3) ratios in benzene. Chloride-isopropoxo (or tetraisopropoxoaluminato) exchange reactions have led to the formation of interesting hetero-(bi- or tri-) metal isopropoxides of samarium(III), $L_{3-n}Sm\{Zr_2(OPr^i)_9\}_n$ [$L = OPr^i$, $n = 1$ or 2; $L = Al(OPr^i)_4$, $n = 1$]. All these products have been characterized by elemental analyses and spectroscopic (IR, NMR) studies.

During the last few years there has been an unprecedented spurt of interest in the alkoxide chemistry of yttrium and lanthanum, due to various reasons such as (1) the formation of alkoxide derivatives of unusual compositions and structural patterns,[1–7] (2) the presence of yttrium and lanthanum in high temperature oxide superconductors,[8] (3) heterometal alkoxide derivatives proving to be useful precursors for ceramic materials via the sol–gel process,[9–12] (4) the possibility of utilization of volatile heterometal alkoxides as convenient precursors for oxide films by MOCVD techniques,[13,14] and (5) the high technological applications of samarium based magnets such as Sm_5Co.

Although samarium diiodide has recently proved to be a versatile stoichiometric reagent in various organic transformations,[15,16] the chemistry of metal-organic derivatives of samarium is mainly restricted to organometallics[15,16] except for derivatives like $[Sm\{N(SiMe_3)_2\}_3]$,[17] $[Sm\{Al(OPr^i)_4\}_3]$,[18] and $Li_5Sm(OBu^t)_8$[19] and $Sm[TeC_6Me_3\text{-}2,3,6]_2(THF)_2$.[20]

Further, although organometallic[15,16] derivatives of samarium are now well known in both tri- and bivalent states, the alkoxide and amide chemistry of samarium is so far limited to the trivalent state.[17,21,22]

In view of the above we report herein the synthesis and characterization of homo- and heteroleptic alkoxo-zirconates of samarium(III), with the intuition that derivatives of the types $[ClSm\{Zr_2(OPr^r)_9\}_2]$ and $[Cl_2Sm\{Zr_2(OPr^i)_9\}]$ may prove useful as precursors for the synthesis of heterometallic alkoxide systems, and that these chloro-precursors would make accessible the hetero-bimetallic alkoxides of samarium(II).

EXPERIMENTAL

In view of the highly moisture-sensitive nature of the heterometal isopropoxide systems, stringent precautions were taken to exclude moisture during all of the experimentation.

All solvents were dried by refluxing and distilling over the appropriate agent (in parentheses): benzene, toluene and n-hexane (Na/benzophenone), isopropanol [Na; $Al(OPr^i)_3$] prior to use. Finally, traces of moisture from benzene and isopropanol were removed by azeotropic distillation after adding 1–2 cm^3 of dry isopropanol or benzene, respectively.

Anhydrous samarium trichloride was prepared by heating a mixture of hydrated samarium trichloride and ammonium chloride (in excess) in a current of dry chlorine and hydrogen chloride

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gases; the heating temperature was carefully regulated to avoid the formation of fusible oxychloride [SmOCl]. The anhydrous chloride was finaly converted into $SmCl_3 \cdot 3Pr^iOH$, by dissolving and crystallizing using isopropyl alcohol as a solvent. Zirconium isopropoxide isopropanolate was prepared by the literature procedure.[23]

Zirconium was estimated as ZrO_2 after precipitation as mandelate and ignition to the oxide. After removal of zirconium as mandelate the samarium content in the filtrate was precipitated as oxalate and estimated as Sm_2O_3.

Isopropoxy contents in the new derivatives were estimated by the oxidimetric method[24] using N—$K_2Cr_2O_7$ solution in 12.5% H_2SO_4. Chlorine was estimated by Volhard's method.[25]

IR spectra [4000–200 cm^{-1}] were recorded on Nujol mulls on Perkin–Elmer 557 and Carl–Zeiss M80 spectrophotometers using CsI optics. ^1H (89.55 MHz) and ^{13}C (22.49 MHz) NMR were recorded on a JEOL FX 90Q FT NMR spectrometer in $CDCl_3$ or C_6H_6, respectively. Chemical shifts were referenced internally to protio solvent impurities (δ 7.25/$CDCl_3$) and solvent ^{13}C references (δ 128.5, C_6H_6) and have been reported in ppm downfield of tetramethylsilane (TMS).

Synthesis of $Cl_2Sm\{Zr_2(OPr^i)_9\}$

A benzene (*ca* 25 cm^3) solution of $K\{Zr_2(OPr^i)_9\}$ [freshly prepared by the interaction of potassium (0.114 g, 2.91 mmol) in isopropyl alcohol (*ca* 5 cm^3) and refluxing with $Zr(OPr^i)_4 \cdot Pr^iOH$ (2.25 g, 5.80 mmol) in (*ca* 20 cm^3) benzene, followed by removal of volatiles under reduced pressure] was added dropwise to a benzene suspension (*ca* 20 cm^3) of $SmCl_3 \cdot 3Pr^iOH$. The reaction mixture was stirred for *ca* 12 h, during which time the colour of the reaction mixture was changed from light yellow to dirty white. Precipitated KCl (0.21 g, 2.82 mmol) was separated by filtration and the excess solvent from the filtrate was removed under reduced pressure to afford a crystalline solid product of the composition $Cl_2Sm\{Zr_2(OPr^i)_9\}$ (2.71 g, 99%), which was recrystallized from n-hexane in 60% yield. Found: Sm, 15.9; Zr, 20.5; Cl, 7.5; OPr^i, 56.7. Calc. for $Cl_2Sm\{Zr_2(OPr^i)_9\}$: Sm, 16.1; Zr, 19.5; Cl, 7.5; OPr^i, 56.9%.

Preparation of $[ClSm\{Zr_2(OPr^i)_9\}_2]$

A benzene (*ca* 20 cm^3) solution of $K\{Zr_2(OPr^i)_9\}$ [freshly prepared by dissolving potassium (0.4 g, 6.13 mmol) in isopropyl alcohol (*ca* 5 cm^3) and benzene (*ca* 10 cm^3) and then interacting under refluxing conditions with $Zr(OPr^i)_4 \cdot Pr^iOH$ (4.85 g, 12.50 mmol), followed by stripping off the volatiles under reduced pressure] was slowly added to a continuously stirred suspension of $SmCl_3 \cdot 3Pr^iOH$ (1.36 g, 3.11 mmol) in benzene (*ca* 20 cm^3). After stirring the reaction mixture at room temperature for 12 h the precipitated KCl (0.53 g, 7.11 mmol) was separated by filtration. Volatiles were removed from the filtrate under reduced pressure to afford a dirty white solid product of the composition $[ClSm\{Zr_2(OPr^i)_9\}_2]$ (4.69 g, 93%). The compound was purified by distillation at (145°C/0.5 mm) in 60% yield. Found: Sm, 9.1; Zr, 22.8; Cl, 2.2; OPr^i, 65.3. Calc. for $[ClSm\{Zr_2(OPr^i)_9\}_2]$: Sm, 9.3; Zr, 22.6; Cl, 2.2; OPr^i, 65.9%.

Preparation of $[Sm\{Zr_2(OPr^i)_9\}_3]$

A solution of $K\{Zr_2(OPr^i)_9\}$ [freshly prepared by dissolving potassium (0.31 g, 7.92 mmol) in the presence of dry isopropyl alcohol (*ca* 5 cm^3) and benzene (*ca* 20 cm^3) followed by refluxing and removal of volatiles under reduced pressure] in benzene (*ca* 20 cm^3) was added slowly to a suspension of $SmCl_3 \cdot 3Pr^iOH$ (1.15 g, 2.63 mmol) in benzene (*ca* 15 cm^3). The reaction mixture was refluxed for 3 h. The precipitated KCl (0.59 g, 7.92 mmol) was filtered off. After the removal of volatiles from the filtrate under reduced pressure an off-white sticky solid product of the composition $[Sm\{Zr_2(OPr^i)_9\}_3]$ (5.72, 95%) was obtained. The compound was purified by sublimation at 182°/0.5 mm in 80% yield. Found: Sm, 6.4; Zr, 24.2; OPr^i, 69.3. Calc. for $[Sm\{Zr_2(OPr^i)_9\}_3]$: Sm, 6.5; Zr, 23.8; OPr^i, 69.5%.

Reaction of $[ClSm\{Zr_2(OPr^i)_9\}_2]$ *with* $K(OPr^i)$

A benzene (*ca* 20 cm^3) suspension of $KOPr^i$ [prepared by the interaction of potassium with isopropyl alcohol (*ca* 20 cm^3), followed by the removal of volatiles] was added dropwise to a solution of $[ClSm\{Zr_2(OPr^i)_9\}_2]$ (3.05 g, 1.88 mol) in benzene (*ca* 15 cm^3). The reaction mixture was stirred at room temperature for *ca* 8 h. The precipitated KCl (0.18 g, 2.14 mmol) was removed by filtration. After removal of the volatiles from the filtrate under reduced pressure a dirty white sticky solid of the composition $[(OPr^i)Sm\{Zr_2(OPr^i)_9\}_2]$ (3.03 g, 97%) was obtained, which was distilled at 174°C/0.5 mm in 50% yield. Found: Sm, 9.4; Zr, 22.5; OPr^i, 68.5. Calc. for $[(OPr^i)Sm\{Zr_2(OPr^i)_9\}_2]$: Sm, 9.2; Zr, 22.3; OPr^i, 68.5%.

A similar procedure was adopted to prepare the off-white solid product of the composition $[(OPr^i)_2Sm\{Zr_2(OPr^i)_9\}]$ (1.29 g, 99%) by the interaction of $KOPr^i$ and $Cl_2Sm\{Zr_2(OPr^i)_9\}$ in a 2:1 molar ratio. The compound was recrystallized from an n-hexane and toluene mixture. Found: Sm, 15.2; Zr, 19.6; OPr^i, 66.0. Calc. for $[(OPr^i)_2Sm\{Zr_2(OPr^i)_9\}]$: Sm, 15.2; Zr, 18.5; OPr^i, 66.1%.

Reaction of $[Cl_2Sm\{Zr_2(OPr^i)_9\}]$ *with* $K\{Al(OPr^i)_4\}$ *in a* 1 : 2 *molar ratio*

A benzene (*ca* 20 cm^3) suspension of $K\{Al(OPr^i)_4\}$ [freshly prepared from potassium (0.24 g, 6.13 mmol) and $Al(OPr^i)_3$ (1.25 g, 6.11 mmol) in isopropyl alcohol (*ca* 15 cm^3) and benzene (*ca* 15 cm^3) followed by the removal of the volatiles] was slowly added to a benzene solution (*ca* 20 cm^3) of $[Cl_2Sm\{Zr_2(OPr^i)_9\}]$ (2.87 g, 3.06 mmol). The reaction mixture was stirred at room temperature for 12 h and the precipitated KCl (0.50 g, 6.71 mmol) was separated by filtration. Removal of volatiles from the filtrate under reduced pressure afforded a pale white sticky mass of the composition $\{Al(OPr^i)_4\}_2Sm\{Zr_2(OPr^i)_9\}$ (3.54 g, 83%), which was distilled at 235°C/0.05 mm in 50% yield. Found: Sm, 10.2; Zr, 14.4; OPr^i, 72.0. Calc. for $\{Al(OPr^i)_4\}_2Sm\{Zr_2(OPr^i)_9\}$: Sm, 10.8; Zr, 13.1; OPr^i, 72.2%.

RESULTS AND DISCUSSION

Interaction of $SmCl_3 \cdot 3Pr^iOH$ and $K\{Zr_2(OPr^i)_9\}$ in different molar ratios (1 : 1, 1 : 2 and 1 : 3) in benzene results in the formation of hetero- and homoleptic nonaisopropoxodizirconatosamarium(III) complexes, according to the following reactions:

$$SmCl_3 \cdot 3Pr^iOH + nK\{Zr_2(OPr^i)_9\} \longrightarrow [Cl_{3-n}Sm\{Zr_2(OPr^i)_9\}_n] + nKCl\downarrow + 3Pr^iOH$$

Ia: $n = 1$; **Ib**: $n = 2$; **Ic**: $n = 3$.

Replacement of chloride in the derivatives **Ia** and **Ib** with alkoxo and/or alkoxometallato groups produced derivatives according to the reaction shown below:

$$[Cl_{3-n}Sm\{Zr_2(OPr^i)_9\}_n] + (3-n)KL \xrightarrow{(3-n)KCl} [(L)_{3-n}Sm\{Zr_2(OPr^i)_9\}_n]$$

IIa: $L = OPr^i, n = 1$;
IIb: $L = OPr^i, n = 2$;
IIc: $L = Al(OPr^i)_4, n = 2$.

All of these new hetero-(bi- or tri-)metallic isopropoxo derivatives are off-white coloured solids (in some cases sticky in nature), highly moisture-sensitive, soluble in common organic solvents and generally volatile.

IR spectral studies

The IR spectra of hetero-(bi- or tri-)metallic isopropoxides[26–29] of samarium(III) exhibit characteristic absorptions in the region (cm^{-1}): 1160–1190 (Me_2C skeleton vibrations), 950–1070, ν(C—O terminal), 920–950, ν(C—O bridging); 670–699, ν(Al—O); 540–570, ν(Zr—O); and 400–470, ν(Sm—O). Samarium–chlorine stretching absorptions[30,31] have been observed in **Ia** and **Ib** in the range 210–380 cm^{-1}.

NMR (^1H *and* ^{13}C) *spectral studies*

The ^1H NMR spectra of the new derivatives (in $CDCl_3$ at room temperature) exhibit doublets ($J = 6$ Hz) for gem-dimethyl protons at δ 1.24 (**IB**), 1.36 (**IIa**), 1.21 (**IIb**) and 1.26 (**IIc**), while methine protons of these complexes are observed as averaged septets ($J = 6$ Hz) at δ 4.39, 4.48, 4.04 and 4.31 ppm, respectively. However, the derivative **Ic** exhibits two doublets ($J = 6$ Hz) of gem-dimethyl protons at δ 1.24 and 1.35, but the methine protons appear as a broad peak centred at δ 4.28 ppm. Similarly, ^{13}C NMR spectra of the two typical derivatives **Ib** and **IIc** display only two types of resonances (**Ib**, 69.67, 26.49; **IIc**, 66.30, 26.50 ppm), characteristic of α- and β-carbons of the isopropoxy groups, respectively. The ^1H NMR signals of the above derivatives could not be resolved further, even at −65°C, to throw any light on their structural features.

Interestingly, the spectrum of **Ia** exhibits the following chemical shifts for gem-dimethyl protons, which could be grouped in the intensity ratio 5 : 2 : 2, respectively: (a) two overlapping doublets ($J = 6$ Hz) at δ 1.55 and 1.63 (terminal OPr^i); (b) a doublet ($J = 6$ Hz) at δ 2.35 (μ_2-OPr^i); and (c) a doublet ($J = 6$ Hz) at δ 9.22 (μ_3–OPr^i) ppm. A broad peak centred at δ 4.89 ppm may be ascribed to the methine protons of the terminal and μ_2-OPr^i groups, whereas the methine proton resonances of μ_3-OPr^i could not be distinguished in the range −50 to +55 ppm. Although any conjectures may be rather speculative in the absence of a single-crystal X-ray structure so far, these data appear to conform essentially to three types of isopropoxy groups, as observed in the ^1H NMR spectrum of $[\{Cd\{Zr_2(OPr^i)_9\}(\mu\text{-}Cl)\}_2]$,[32] the X-ray structure[33] of which showed a tetradentate ligation mode of $\{Zr_2(OPr^i)_9\}^-$ units.

The above results, coupled with (1) the tendency of samarium(III) (ionic radii = 1.10 Å) to achieve higher coordination states,[34,35] (2) the ability of $\{Zr_2(OPr^i)_9\}^-$ to function in a bi-,[36] tri-[36] or tetradentate[32,37] fashion, and (3) the observed molecular complexities in benzene tend to favour tetradentate ligation of $\{Zr_2(OPr^i)_9\}^-$ in **Ia** and **IIa**, tridentate bonding in **Ib** and **IIb** and bidentate ligation in **Ic** and **IIc**. Furthermore, in derivatives **Ib**, **IIb**, **Ic** and **IIc** the possibility of ligation of a more suitably situated isopropoxy group(s) to increase the coordination state of the samarium(III) ion cannot be ruled out.

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