



## Synthesis, X-ray structures, and characterization of hexafluoro-*iso*-propoxide group 3 and lanthanide precursors



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### ARTICLE INFO

#### Article history:

Received 4 June 2016

Accepted 22 July 2016

Available online 29 July 2016

#### Keywords:

Alkoxide

Fluorinated

Lanthanides

Hexafluoro-*iso*-propoxide

Lanthanide

### ABSTRACT

A series of hydrated hexafluoro-*iso*-propoxide (hfp) lanthanide complexes was synthesized from the amide-alkoxide exchange reaction of the lanthanide *bis*-trimethylsilyl amide dissolved in toluene and an excess amount of H-hfp. The products were isolated and identified by single crystal X-ray diffraction as: [*cis*-(H<sub>2</sub>O)<sub>2</sub>(hfp)<sub>2</sub>Ln(μ-hfp)]<sub>2</sub> (Ln = Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y), [*trans*-(H<sub>2</sub>O)<sub>2</sub>(hfp)<sub>2</sub>Sc(μ-hfp)]<sub>2</sub> (**Sc**), [(H<sub>2</sub>O)<sub>2</sub>(hfp)<sub>2</sub>La<sub>2</sub>(μ-hfp)<sub>3</sub>(μ<sub>3</sub>-OH)]<sub>2</sub> (**La-OH**), and [(H<sub>2</sub>O)(hfp)<sub>2</sub>Sc(μ-hfp)(μ-OH)(μ<sub>3</sub>-OH)Sc(H<sub>2</sub>O)(hfp)]<sub>2</sub> (**Sc-OH**). All species were found to have bound H<sub>2</sub>O molecules thought to be present in the hfp. For the non-oxo species, dinuclear species were formed with one bridging and two terminal hfp ligands. The waters were *cis*-oriented for all samples but the smallest derivative, **Sc**, where they were located in *trans* arrangement. Oxo species were formed by 'aged' hfp and generated tetranuclear species (**La-OH** and **Sc-OH**) that possessed different ligand sets. Initial efforts to determine these compounds utility for LnF<sub>3</sub> nanomaterial production were undertaken using amine solvent in solvothermal (SOLVO) or solution precipitation (SPPT) routes. LnF<sub>3</sub> phases were noted but often this was mixed with the Ln(O,F) or Ln<sub>2</sub>O<sub>3</sub> phases.

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### 1. Introduction

Metal alkoxides ([M(OR)<sub>x</sub>]) have found widespread utility as precursors to metal oxide ceramic materials. This is usually due to their high solubility, high volatility, and ability to cross-link forming extended networks upon exposure to ambient water. Several efforts have clearly shown the connection between the structure of the [M(OR)<sub>x</sub>] precursor and the final properties obtained [1–7]. Unfortunately, the large radii to small charge of the OR ligand, the high donor activity of the oxygen atom, and low steric hindrance of the pendant carbon chain results in structures of [M(OR)<sub>x</sub>] that are often different than *a priori* predicted [5–9]. Typically, these characteristics result in larger structures with higher vapor pressures and lower solubility. Fluorinated alkoxide ligands can overcome some of these issues, since they yield decreased M–O interaction through the electron withdrawing nature of the pendant CF<sub>x</sub> groups and M–F interactions that can occur, which leads to lower nuclearity compounds

with higher volatility and increased stability to hydrolysis [6,10–13]. Unfortunately for ceramic oxide production, upon conversion, fluoride retention is often observed; however, this 'detrimental' F-retention has been successfully exploited for the production of fluoride based materials [10].

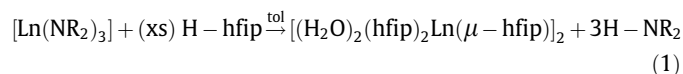
In particular, lanthanum fluoride (LaF<sub>3</sub>), has shown some laboratory success as a F<sup>−</sup> ion detector [14,15]. For this work we were interested in exploration of nano-LaF<sub>3</sub> as a sensor for tracers in 'hot rock' sub-stratus, water injected, geothermal power (GTP) applications [16–18]. While numerous F-ligated species have been successfully exploited (i.e., alkoxides, carboxylates, β-diketonates, etc) for the production of F-containing materials [10], this report details on the synthesis and characterization of a series of previously unreported species, hydrated lanthanide hexafluoro *iso*-propoxide ([ (H<sub>2</sub>O)<sub>2</sub>Ln(hfp)<sub>3</sub>]<sub>n</sub>) derivatives. These hfp ligated species are of interest due to the increased flexibility of chemistry, structures, and modifications available with these monodentate ligands compared to the polydentate fluorinated carboxylate, β-diketonates, etc. ligands that have been previously exploited [10].

After numerous attempts using a variety of Ln-based precursors under a variety of conditions, the [(H<sub>2</sub>O)<sub>2</sub>Ln(hfp)<sub>3</sub>]<sub>n</sub> species were

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synthesized from the reaction of lanthanide bis-trimethylsilyl amide  $[\text{Ln}(\text{NR}_2)_3]_n$  where  $\text{R} = \text{Si}(\text{CH}_3)_3$  with excess H-hfip (or H-OCH(CF<sub>3</sub>)<sub>2</sub>) in toluene (Eq. (1)). The products were isolated and identified by single crystal X-ray diffraction as  $[\text{cis}-(\text{H}_2\text{O})_2(\text{hfip})_2\text{Ln}(\mu\text{-hfip})_2]$  ( $\text{Ln} = \text{Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y}$ ),  $[\text{trans}-(\text{H}_2\text{O})_2(\text{hfip})_2\text{Sc}(\mu\text{-hfip})_2]$  (**Sc**),  $[(\text{H}_2\text{O})_2(\text{hfip})_2\text{La}_2(\mu\text{-hfip})_3(\mu_3\text{-OH})_2]$  (**La-OH**), and  $[(\text{H}_2\text{O})(\text{hfip})_2\text{Sc}(\mu\text{-hfip})(\mu\text{-OH})(\mu_3\text{-OH})\text{Sc}(\text{H}_2\text{O})(\text{hfip})_2]$  (**Sc-OH**). In our hands, the **Sm** derivative could not be isolated. Select species from this novel family of compounds were used to characterize and survey the utility of these compounds as precursors to  $\text{LnF}_3$  nanomaterials under solvothermal (SOLVO) and solution precipitation (SPPT) conditions.



## 2. Material and methods

All compounds described below were handled with rigorous exclusion of air and water using standard Schlenk line and glove box techniques, unless otherwise noted. Analytical data were collected on freshly dried crystalline samples. All anhydrous solvents, ammonium chloride  $[(\text{NH}_4)\text{Cl}]$ , potassium bis-trimethylsilylamide  $[\text{KNR}_2]$ , ethylenediamine, tetra-acetic acid disodium salt di-hydrate (EDTA), xylenol orange, hexamethylenetetramine (HMTA) buffer, and H-hfip were used as received (Aldrich and Alfa Aesar).  $\text{LnCl}_3$  were either purchased (Aldrich and Alfa Aesar) or synthesized directly from the metal [19,20] with (aq)HCl, followed by dehydration using  $(\text{NH}_4)\text{Cl}$  [21].  $[\text{Ln}(\text{NR}_2)_3]$  were synthesized according to literature reports from the reaction of  $\text{LnCl}_3$  and 3 equivalents of  $\text{KNR}_2$  [19]. Complexometric titrations were conducted according to literature reports using EDTA, HMTA, and a xylenol orange indicator [22].

Crystalline materials were used for all analytical analyses. FTIR data were collected on samples in pressed KBR pellets using a Nicolet 6700 FTIR spectrometer under a flowing atmosphere of nitrogen. The solid-state <sup>19</sup>F magic angle spinning (MAS) NMR spectra were obtained on a Bruker Avance-I 400 NMR spectrometer at an observed frequency 376.48 MHz using a 2.5 mm rotor spinning at 20 kHz. The 1D MAS spectra were obtained using a rotor-synchronized Hahn Echo with the chemical shift referenced to the secondary external standard PTFE ( $\delta = -122$  ppm) with respect to  $\text{CFCl}_3$   $\delta = 0$  ppm.

Solution spectra were collected on a Bruker Avance 500 NMR spectrometer under standard experimental conditions: <sup>1</sup>H analysis was performed with a 4-s recycle delay at 16 scans and spectra were referenced to the  $\text{CDCl}_3$  peak at 7.24 ppm; <sup>13</sup>C analysis was performed with a 10-s recycle delay at a minimum of 64 scans and spectra were referenced to the  $\text{CDCl}_3$  peak at 77.0 ppm; The <sup>19</sup>F NMR spectra were obtained using a 5 s recycle delay, a sweep width of 400 ppm, with the chemical shift referenced to the external secondary standard  $\text{CFCl}_3$   $\delta = 0.0$  ppm.

### 2.1. General Synthesis

In an argon filled glovebox,  $[\text{Ln}(\text{NR}_2)_3]$  was dissolved in toluene and an excess amount of H-hfip was added via pipette, until the reaction mixture stopped effervescing and became clear. After this time, the reaction was set aside with the cap loose until crystals formed, typically within a 12 h period. Yields reported are for the first batch isolated and were not optimized.

### 2.2. $[\text{cis}-(\text{H}_2\text{O})_2(\text{hfip})_2\text{Ln}(\mu\text{-hfip})_2]$

#### 2.2.1. Ce

Used  $[\text{Ce}(\text{NR}_2)_3]$  (0.50 g, 0.80 mmol) in ~0.75 mL tol. Added ~3 mL H-hfip. Yield 50% (0.27 g). FTIR (KBr,  $\text{cm}^{-1}$ ) 3405(w), 3318(w), 2964(w), 2923(w), 2896(w), 1372(m), 1283(m), 1228(s), 1181(s), 1092(s), 889(m), 846(m), 743(m), 687(m), 652(w), 520(m). Complx. Titr. for  $\text{C}_9\text{H}_3\text{CeF}_{18}\text{O}_3$  (MW = 641.21)%Ce: Calc. 21.8%. Found 21.5%.

#### 2.2.2. Pr

Used  $[\text{Pr}(\text{NR}_2)_3]$  (0.50 g, 0.96 mmol) in ~0.75 mL tol. Added ~3 mL H-hfip. Yield 55% (0.29 g). FTIR (KBr,  $\text{cm}^{-1}$ ) 3406(w), 3314(w), 2963(w), 2927(w), 2865(w), 1373(m), 1285(m), 1213(s), 1179(s), 1089(s), 888(m), 846(m), 742(m), 687(m), 648(w), 520(m). Complx. Titr. for  $\text{C}_9\text{H}_3\text{F}_{18}\text{O}_3\text{Pr}$  (MW = 646.03)%Pr: Calc. 22.0%. Found 22.0%.

#### 2.2.3. Nd

Used  $[\text{Nd}(\text{NR}_2)_3]$  (0.50 g, 0.80 mmol) in ~0.75 mL tol. Added ~3 mL H-hfip. Yield 24% (0.13 g). FTIR (KBr,  $\text{cm}^{-1}$ ) 3404(w), 3317(w), 2962(w), 2926(w), 2860(w), 2723(w), 2686(w), 1374(m), 1286(m), 1260(s), 1216(s), 1174(s), 1129(s), 1088(s), 885(m), 845(m), 742(m), 686(m), 655(w), 643(w), 520(m). Complx. Titr. for  $\text{C}_9\text{H}_3\text{F}_{18}\text{NdO}_3$  (MW = 645.33, 0  $\text{H}_2\text{O}$ )%Nd: Calc. 22.4%. Found 22.2%.

#### 2.2.4. Eu

Used  $[\text{Eu}(\text{NR}_2)_3]$  (0.55 g, 0.87 mmol) in ~0.75 mL tol. Added 3 mL H-hfip. Yield 42% (0.25 g). FTIR (KBr,  $\text{cm}^{-1}$ ) 3407(w), 2962(w), 2926(w), 2858(w), 1374(m), 1284(m), 1257(s,sh), 1213(s), 1177(s), 1090(s), 887(m), 845(m), 800(m), 742(m), 687(m), 615(w). Complx. Titr. for  $\text{C}_9\text{H}_3\text{EuF}_{18}\text{O}_3$  (MW = 653.06, 0  $\text{H}_2\text{O}$ )%Eu: Calc. 23.3%. Found: 23.5%.

#### 2.2.5. Gd

Used  $[\text{Gd}(\text{NR}_2)_3]$  (1.0 g, 1.6 mmol) in ~1.5 mL tol. Added ~6 mL H-hfip. Yield 62% (0.67 g). FTIR (KBr,  $\text{cm}^{-1}$ ) 3405(w), 3314(w), 2963(w), 2927(w), 2869(w), 1373(m), 1288(m), 1210(s), 1177(s), 1128(s), 1094(s), 889(m), 855(sh), 845(m), 743(m), 687(m), 653(w), 631(w), 522(m). Complx. Titr. for  $\text{C}_9\text{H}_3\text{F}_{18}\text{GdO}_3$  (MW = 658.34, 0  $\text{H}_2\text{O}$ )%Gd: Calc. 23.9%. Found: 23.9%.

#### 2.2.6. Tb

Used  $[\text{Tb}(\text{NR}_2)_3]$  (1.0 g, 1.6 mmol) in ~1.5 mL tol. Added ~6 mL H-hfip. Yield 32% (0.35 g). FTIR (KBr,  $\text{cm}^{-1}$ ) 3405(w), 3313(w), 3181(w), 2870(w), 2732(w), 2687(w), 1379(m), 1301(s), 1177(s), 1247(s), 1209(s), 1158(s), 1105(s), 889(m), 855(sh), 845(m), 743(m), 687(m), 654(w), 631(w), 525(m). Complx. Titr. for  $\text{C}_9\text{H}_3\text{F}_{18}\text{O}_3\text{-Tb}$  (MW = 660.02, 0  $\text{H}_2\text{O}$ )%Tb: Calc. 24.1%. Found: 24.4%.

#### 2.2.7. Dy

Used  $[\text{Dy}(\text{NR}_2)_3]$  (0.50 g, 0.77 mmol) in ~0.75 mL tol. Added ~3 mL H-hfip. Yield 57% (0.31 g). FTIR (KBr,  $\text{cm}^{-1}$ ) 3293(w), 2962(w), 2927(w), 2873(w), 2858(w,sh), 1375(m), 1286(m), 1257(m,sh), 1206(s), 1180(s), 1124(s), 1903(s), 891(m), 855(sh), 845(m), 743(m), 687(m), 669(w), 519(w), 472(m). Complx. Titr. for  $\text{C}_9\text{H}_3\text{-DyF}_{18}\text{O}_3$  (MW = 658.34, 0  $\text{H}_2\text{O}$ )%Dy: Calc. 24.5%. Found: 24.0%.

#### 2.2.8. Ho

Used  $[\text{Ho}(\text{NR}_2)_3]$  (1.0 g, 1.5 mmol) in ~1.5 mL tol. Added ~6 mL H-hfip. Yield 55% (0.59 g). FTIR (KBr,  $\text{cm}^{-1}$ ) 3406(w), 3313(w), 2963(w), 2927(w), 2872(w), 1373(m), 1288(m), 1211(s), 1177(s), 1125(s), 1126(s), 1093(s), 889(m), 855(sh), 845(m), 743(m), 687(m), 655(w), 632(w), 521(m). Complx. Titr. for  $\text{C}_9\text{H}_3\text{F}_{18}\text{HoO}_3$  (MW = 666.02, 0  $\text{H}_2\text{O}$ )%Ho: Calc. 24.8%. Found: 24.7%.

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