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

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Graphical Abstract

A series of lanthanide complexes containing the fluorinated alkoxide, hexafluoro-*iso*-propoxide (hfip) was synthesized from the amide-alkoxide exchange reaction yielding:

$OH)Sc(H_2O)(hfip)]_2$. The majority of the SOLVO and SPPT products isolated were

identified by PXRD after thermal 650 °C in air, yielded the LnF_3 phase but often this was

mixed with the $Ln(O,F)$ or Ln_2O_3 phases.

Abstract

A series of hydrated hexafluoro-*iso*-propoxide (hfip) 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-hfip. The products were isolated and identified by single crystal X-ray diffraction as: [*cis*-(H₂O)₂(hfip)₂Ln(μ-hfip)]₂ (Ln = **Ce**, **Pr**, **Nd**, **Eu**, **Gd**, **Tb**, **Dy**, **Ho**, **Er**, **Tm**, **Yb**, **Lu**, **Y**), [*trans*-(H₂O)₂(hfip)₂Sc(μ-hfip)]₂ (**Sc**), [(H₂O)₂(hfip)₂La₂(μ-hfip)₃(μ₃-OH)]₂ (**La-OH**), and [(H₂O)(hfip)₂Sc(μ-hfip)(μ-OH)(μ₃-OH)Sc(H₂O)(hfip)]₂ (**Sc-OH**). All species were found to have bound H₂O molecules thought to be present in the hfip. For the non-oxo species, dinuclear species were formed with one bridging and two terminal hfip 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’ hfip and generated tetranuclear species (**La-OH** and **Sc-OH**) that possessed different ligand sets. Initial efforts to determine these compounds utility for LnF₃ nanomaterial production were undertaken using amine solvent in solvothermal (SOLVO) or solution precipitation (SPPT) routes. LnF₃ phases were noted but often this was mixed with the Ln(O,F) or Ln₂O₃ phases.

Keywords. Alkoxide, fluorinated, lanthanides, hexafluoro-*iso*-propoxide, Group 3, Lanthanide

1. Introduction.

Metal alkoxides ($[M(OR)_x]$) 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 $[M(OR)_x]$ 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 $[M(OR)_x]$ 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_x 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_3), has shown some laboratory success as a F^- ion detector.[14, 15] For this work we were interested in exploration of nano- LaF_3 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 $[(\text{H}_2\text{O})_2\text{Ln}(\text{hfip})_3]_n$ derivatives. These hfip 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 $[(\text{H}_2\text{O})_2\text{Ln}(\text{hfip})_3]_n$ species were 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 $\text{H}-\text{OCH}(\text{CF}_3)_2$) in toluene (eq 1). The products were isolated and identified by single crystal X-ray diffraction as $[\text{cis}-(\text{H}_2\text{O})_2(\text{hfip})_2\text{Ln}(\mu\text{-hfip})]_2$ (Ln = **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 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), xylene orange, hexamethylenetetramine (HMTA) buffer, and H-hfip were used as received (Aldrich and Alfa Aesar). 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 LnCl_3 and 3 equivalents of KNR_2 . [19] Complexometric titrations were conducted according to literature reports using EDTA, HMTA, and a xylene 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 ^{19}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 CFCl_3 $\delta = 0$ ppm.

Solution spectra were collected on a Bruker Avance 500 NMR spectrometer under standard experimental conditions: ^1H analysis was performed with a 4-second recycle delay at 16 scans and spectra were referenced to the CDCl_3 peak at 7.24 ppm; ^{13}C analysis was performed with a 10-second recycle delay at a minimum of 64 scans and spectra were referenced to the CDCl_3 peak at 77.0 ppm; The ^{19}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 CFC13 $\delta = 0.0$ 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 $[\text{cis}-(\text{H}_2\text{O})_2(\text{hfip})_2\text{Ln}(\mu\text{-hfip})_2]_2$

2.2.1. 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, 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, 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, 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 H_2O) %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, 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 H_2O) %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, 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 H_2O) %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, 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 H_2O) %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, 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 H_2O) %Dy: Calc. 24.5%. Found: 24.0%.

2.2.8. **Ho.** Used [Ho(NR₂)₃] (1.0 g, 1.5 mmol) in ~ 1.5 mL tol. Added ~6 mL H-hfip. Yield 55% (0.59 g). FTIR (KBr, 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 C₉H₃F₁₈HoO₃ (MW = 666.02, 0 H₂O) %Ho: Calc. 24.8%. Found: 24.7%.

2.2.9. **Er.** Used [Er(NR₂)₃] (0.65 g, 1.0 mmol) in ~ 0.75 mL tol. Added ~3 mL H-hfip. Yield 41% (0.29 g). FTIR (KBr, cm⁻¹) 3405(w), 3314 (w), 2963(w), 2928(w), 2860(w), 1499(m), 1374(m), 1280(m), 1128(s), 1097(s), 886(m), 845(m), 743(m), 687(m), 669(w), 520(m). Complx. Titr. for C₉H₃ErF₁₈O₃ (MW = 668.35, 0 H₂O) %Er: Calc. 25.0%. Found: 24.6%.

2.2.10. **Tm.** Used [Tm(NR₂)₃] (1.0 g, 1.5 mmol) in ~ 1.5 mL tol. Added ~6 mL H-hfip. Yield 57% (0.62 g). FTIR (KBr, cm⁻¹) 3404(w), 3314(w), 2963(w), 2925(w), 2873(w), 1372(m), 1290(m), 1216(m, br), 1178(s), 1128(s), 1094(s), 889(m), 855(m, sh), 846(m), 744(m), 687(m), 657(w), 632 (w). Complx. Titr. for C₉H₃F₁₈O₃Tm (MW = 670.03, 0 H₂O) %Tm: Calc. 25.2%. Found: 25.1%.

2.2.11. **Yb.** Used [Yb(NR₂)₃] (0.50 g, 0.76 mmol) in ~ 0.75 mL tol. Added ~3 mL H-hfip. Yield 98% (0.53 g). FTIR (KBr, cm⁻¹) 3407(w), 3381 (w), 3323(w), 2961(w), 2927(w), 2879(w), 1606(m), 1499(m), 1438(m), 1375(m), 1280(m), 1186(s,br), 1126(s), 1096(s), 886(m), 843(sh), 743(m), 687(m), 650(w), 637 (w), 519(m), 509(m), 496(m). Complx. Titr. for C₉H₃F₁₈O₃Yb (MW = 674.15, 0 H₂O) %Yb: Calc. 25.7%. Found: 25.3%,

2.2.12. **Lu.** Used [Lu(NR₂)₃] (1.0 g, 1.5 mmol) in ~ 1.5 mL tol. Added ~6 mL H-hfip. Yield 41% (0.45 g). FTIR (KBr, cm⁻¹) 3408(w), 3383 (w), 3321(w), 2963(w), 2927(w),

2875(w), 1609(m), 1373(m), 1289(m), 1214(m,sh), 1182(s), 1126(s), 1095(s), 886(m), 845(m, sh), 803(m), 743(m), 687(m), 657(w), 650(w), 636(m), 519(m). Complx. Titr. for $C_9H_3F_{18}LuO_3$ (MW = 676.06, 0 H_2O) %Lu: Calc. 25.9%. Found: 26.2%,

2.2.13. **Y.** Used $[Y(NR_2)_3]$ (0.55 g, 0.96 mmol) in ~ 0.75 mL tol. Added ~3 mL H-hfip. Yield 78% (0.47 g). FTIR (KBr, cm^{-1}) 3406(w), 3312 (w), 2962(w), 2927(w), 2871(w), 2734(w), 2701(w), 1372(m), 1289(m), 1214(m,sh), 1175(s), 1128(s), 1094(s), 889(m), 855(m, sh), 846(m), 743(m), 687(m), 657(m), 535(m), 524(m). Complx. Titr. for $C_9H_3F_{18}O_3Y$ (MW = 590.00, 0 H_2O) %Y: Calc. 15.1%. Found: 15.0%. ^{19}F (H_2O) δ - 75.8.

2.3 *[trans-(H₂O)₂(hfip)₂Sc(μ -hfip)]₂ (Sc).* Used $[Sc(NR_2)_3]$ (1.2 g, 1.9 mmol) in ~ 0.75 mL tol. Added ~3 mL H-hfip. Yield 85% (1.1 g). FTIR (KBr, cm^{-1}) 3414(w), 3317(w), 2963(w), 2928(w), 2859(w), 1373(m), 1284(m), 1259(m,sh), 1228(s), 1183(s), 1118(m), 1092(s), 896(m,sh), 887(m), 862(m, sh), 846(m), 803(m), 744(m), 687(m), 635(w), 536(m), 520(w). Complx. Titr. for $C_9H_3F_{18}O_3Sc$ (MW = 546.05, 0 H_2O) %Sc: Calc. 8.2%, Found: 7.9%. ^{19}F (H_2O) δ -75.8.

2.4 *General X-ray Crystal Structure Information.* Single crystals were mounted onto a MiTeGen microloopTM from a pool of FluorolubeTM and immediately placed in a cold N_2 vapor stream on a Bruker AXS diffractometer employing an incident-beam graphite monochromator, MoK α radiation (λ = 0.71070 Å) and a SMART APEX II CCD detector. Lattice determination and data collection were carried out using SMART Version 5.054 software. Data reduction was performed using the Bruker Apex 3 software package.[23] Structures were solved by direct methods or by using the

PATTERSON method that yielded the heavy atoms, along with a number of the lighter atoms. Subsequent Fourier syntheses yielded the remaining light-atom positions. The hydrogen atoms were fixed in positions of ideal geometry and refined using SHELX[24, 25] or OLEX[26] software. The final refinement of each compound included anisotropic thermal parameters for all non-hydrogen atoms. All final CIF files were checked using the CheckCIF program (<http://www.iucr.org/>). Additional information concerning the data collection and final structural solutions can be found in the supplemental information or by accessing CIF files through the Cambridge Crystallographic Data Base. Tables 1 and 2 list the unit cell parameters, while Table 3 lists select metrical data for **Ce - Sc, La-OH**, and **Sc-OH**. Specific issues that arose with the various crystal structure solutions are discussed below.

Nd - Y (P(-1)) are centro-symmetric dimers with centers of symmetry located between the two Ln cations with two independent molecules in the unit cell. **Ce** and **Pr** (Pca2₁) are also centro-symmetric with a similar center of symmetry but only one unique molecule in the unit cell. For **Ce**, a rotational twin with a BASF of 0.5 was noted, surprisingly with no other disorder observed. The structure solution of **Nd** suffered from disorder on one hfip group, which was modeled using parts and EADP. The CF₃ group on C(8) was extremely disordered and was modeled using parts (a 3 part model was attempted but a third C could not be found); therefore, it was left isotropic. A satisfactory model for the protons on the water O(10) for **Er** could not be determined (i.e., attempts to use PART (two and three part) and SUMP (three individuals like on O9)) but were observed in the electron density maps – peaks exist that would suggest a hydrogen bond between F4 (or F5'). For **Lu**, a disordered toluene on a special position, which displayed

a potential solvent accessible void of 178.6 Å³, was modeled using the program Platon/Squeeze. For **Sc**, the SUMP command was used to model the H atoms, which were split three ways and refined without constraint. The **La-OH** molecule suffered from disorder in the pendant chains of the hfip ligand, which was modeled using rigid models. Cell_now indicated there was a twin (rotated 179.9° from original cell) with a BASF factor of 0.25. The two domains identified by Cell_now were integrated independently, where the final parameters based on refinement on both data sets yielded a minor twin component of 25.0(1)%. The structure solution of the Tm, Tb, and Sc derivatives had partially occupied water molecules coordinated to the respective metal centers.

2.5 Nanomaterials synthesis. Crystalline materials were used for each synthesis. The precursors used were selected based on cation size and structural representation. Solvothermal (SOLVO). ~0.5 g of each sample was weighed out in a glovebox and added to ~40 mL of the selected solvent (pyridine (py) or trioctylamine (TOA)) in a 60 mL ParrTM digestion bomb. The bomb was sealed, transferred to an oven, and heated to 185 °C for 12h. After cooling to room temperature in air, the insoluble material was isolated by centrifugation and washed several times with hexanes. Solution Precipitation (SPPT). ~0.5 g of each sample was weighed out in the glovebox, brought out, and added to 50 mL Schlenk flask with oleylamine (ON, ~25 mL). After the flask was fitted with a reflux condenser, a nitrogen adaptor, and placed under a stream of flowing argon, the sample was heated to ~300 °C for 15-30 min. After cooling to room temperature, the reaction mixture was transferred to a glovebox, was washed several times with hexanes, and the resulting precipitate collected by centrifugation.

2.6 Powder X-ray Diffraction (PXRD). Powder X-ray diffraction (PXRD) was performed on a PANalytical X'Pert Pro diffractometer (10 – 100° two theta) employing Cu K α radiation (1.5406 Å) and a RTMS X'Celerator detector at a scan rate of 3°/sec for the bulk powders or at a scan rate of 0.15°/sec using a zero background holder. The PXRD patterns were analyzed using: JADE 9 software (Materials Data, Inc., Livermore CA) and indexed using The Powder Diffraction File PDF-4+ 2013.

3. Results and Discussion.

Prior to synthesizing this new family of compounds for the production of LnF₃ nanomaterials, a search of structurally characterized Ln-hfip compounds was undertaken to determine if there were any precursors that could be easily implemented for the LnF₃ nanomaterials of interest. While a handful of mixed metal-lanthanide hfip species have been reported,[27] only a few homo-cationic derivatives are available, including: [Ce(hfip)₆](DMAA)[28] (DMAA = N-methyl-N,N,-bis(dimethylaminoethyl)ammonium), [Ce(hfip)₄(L)], [29] (L = DME = dimethoxyethyl ether or TEA = tetramethylethylenediamine, and [(NH₃)₂(hfip)₂Sc(μ-hfip)]₂•tol[11]. Additionally, a set of readily hydrolyzed solvated hfip lanthanide derivatives were recently reported as [(DME)(hfip)₂Ln(μ-hfip)]₂ (Ln = Sm, Yb), [Sm₂(μ-hfip)₃(μ₃-hfip)₂Sm(hfip)₂(THF)_{2.5}(OEt₂)_{0.5}], and [Eu₂(μ-hfip)₃(μ₃-hfip)₂Y(hfip)₂(DME)₂].[12] As can be determined, the number of structurally characterized Ln-hfip derivatives is therefore limited. Based on this void, we undertook the systematic synthesis of Ln-hfip species following the amide-alkoxide exchange of [Ln(NR₂)₃] with H-hfip in toluene (eq

1) to explore the structure types available, determine their properties and their ability to convert to fluoride materials.

The H-hfip ligand was selected from the commercially available fluorinated alcohols (versus tri-fluoroethanol or nona-fluorobutanol) since these derivatives were found to readily generate single crystals. [12] Crystals are necessary in this system due to the limited number of analytical methods available to fully characterize these compounds. This is mainly due to the paramagnetic nature of the Ln cations, the volatility and decomposition properties of the fluorinated ligands. Therefore, we explored FTIR spectroscopic, complexometric titrations, and single crystal analyses of the resulting isolated species to characterize these compounds.

3.1 Synthesis. A variety of synthetic efforts have been reported to generate the Ln-hfip derivatives, including the ammoniolysis of LnCl_3 in the presence of the H-hfip[30] or the alcohols/amide metathesis using $\text{Ln}(\text{NR}_2)_3$ derivatives[11]. Initial attempts in this effort focused on the dissolution of the metal (Ln^0) in H-hfip (or with the addition of a solvent) did not generate any noticeable reaction. This is attributed to the oxide coating that is often associated with Ln^0 ; hence, the surfaces were physically polished and reacted under an argon atmosphere but again no reaction was noted. Attempts at other precursors (i.e., Ln_2O_3 , $\text{LnX}_3 \cdot n\text{H}_2\text{O}$) were not undertaken to avoid oxide or hydrate coordination.

Ultimately, the synthesis of the Ln-hfip precursors was successful following the alcoholysis of the amine,[11] eq 1. Upon addition of the H-hfip to a stirring solution of $[\text{Ln}(\text{NR}_2)_3]$ in toluene, the solution bubbled profusely. This addition was continued until the solution was clear and a pale color of the original $[\text{Ln}(\text{NR}_2)_3]$ solution resulted. X-ray

quality crystals were grown by slow evaporation of the volatile component of the reaction mixture, which typically occurred in less than 12 h. After the mother liquor was decanted away, some crystals were used for single crystal X-ray analysis while the remainder was washed with hexanes, dried *en vacuo*, and used for all subsequent analytical analyses.

3.2 Characterization. *3.2.1 FTIR spectroscopy.* Typically the loss of the HO- stretch for the alcohol is a convenient method for following the completion of an amide-alcohol exchange. In this case, each spectrum displayed a strong HO- stretch around 3000 cm^{-1} . The loss of the amide stretches and ingrowth of the peaks associated with the H-hfip [$\text{H-OCH}(\text{CF}_3)_2$] ligand (KBr: 2962, 2923, 2853, 1384, 1260, 1094, 1020, 905, 798, 673, 663, 550 cm^{-1}) was a strong indication that the reaction had proceeded as written (eq 1). The OH- stretch was originally thought to be retention of H-hfip due to the large excess of the alcohol used in the reaction mixture. Since crystals were easily isolated and single crystal X-ray structure experiments were performed for each sample to assist in identifying the structure of these compounds. As was observed by the single crystal studies, the -OH stretch was determined to be due to bound H_2O .

3.2.2 Single crystal. The syntheses and characterization of the Ln series of hfip-modified compounds (excluding Pm but including **Y** and **Sc**) were investigated with all but **Sm** yielding a successful single crystal X-ray diffraction structural solution. Surprisingly, each solution was found to possess the same general construct (except **La-OH**). Table 1 lists the data collection parameters. Representative of the various structure types noted (**Eu**, **La-OH**, and **Sc**) are shown in Figures 1 - 3, respectively.

For the majority of lanthanides (**Ce** to **Lu** and **Y**), a dinuclear species was observed where each Ln possessed two terminal and two bridging hfip ligands. The **Eu** structure solution is shown in Figure 1, as a representative of this structure type. The octahedral geometry (*OC*-6) around the metal center was finalized by the coordination of two water molecules. These ligands were determined to be water molecules by several aspects of the final molecule: the Ln-O distance is within the range reported in the literature, [27] protons were observed for the crystal structures in several instances and retention of charge neutrality. The water molecules were solved in a *cis* arrangement around the Sc metal, with numerous F---H interactions observed in the final structures.

For the Ln = La synthesis in eq 1, numerous reactions were attempted but crystals always proved difficult to isolate. While we were able to sequester a La crystal that could be successfully used for structural studies, routine isolation of these crystals was never realized. Therefore, the synthesis of the La derivative is not included in the experimental section; however, it is a structure that merits some comments and the structural parameters are reported (see Table 2) to aid in identifying potential products. The compound isolated was **La-OH** (see Figure 2), which proved to be a tetranuclear species, adopting a $[\text{La}_2(\mu_3\text{-OH})]_2$ central core. The protons were located on the hydroxides. The metal atoms of **La-OH** were further bound together by an asymmetric binding of three μ -hfip ligands: two between La(2) and La(1) with only one between La(2) and La(1'). Each of the La possesses a terminal H_2O and H-hfip molecule. This forces the complex to adopt a cube-shared, corner missing arrangement, shown in Figure 2. This results in alternating pseudo octahedral geometry (*OC*-6) and 7-coordinated La metal centers;

however, the F---La bonds pushes the coordination of each metal center one degree higher with 7- and 8-coordination geometries noted for La(2) and La(1), respectively.

The smallest cation in this series, **Sc**, was found to adopt a slightly different structure from the derivatives mentioned above. While the species remained dinuclear with two hfip, two μ -hfip, and two water molecules bound to each metal, the variation in the structure of **Sc** was the *trans* arrangement of the water molecules in the axial position (see Figure 3). A separate larger scale and higher concentration synthesis with the remnants of an H-hfip reagent bottle that had been stored for an extended amount of time ('aged') led to the isolation of **Sc-OH** (Figure 4). For this structure, each of the Sc metal centers adopts a face-shared, corner-missing cube central core which places the metals in a distorted *CN*-6 arrangement. Each of the terminal Sc atoms uses one μ_3 -OH, one μ -OH, one μ -hfip, one terminal H₂O and two terminal hfip ligands to fill their coordination sphere. The two interior Sc metal centers use the same ligand set with only one terminal hfip ligand. The structure is similar to that noted for **La-OH**, but additional OH are present and F---Sc interactions were not observed. This structural change is most likely due to the smaller cation size and higher Lewis acidity of Sc versus La. It is not obvious at this point what led to the -OH formation; therefore, no experimental data is presented besides the single crystal data collection parameters (see Table 2); however, the increased concentration, high temperature, and potentially higher water content of the 'aged' H-hfip may have contributed to the formation of this complex. Repetition of the reaction with 'fresh' H-hfip yielded **Sc**.

The adventitious water present in each of these compounds is thought to be from the H-hfip. Attempts to dehydrate the alcohol by storing it over molecular sieves proved

fruitless as bound water was again located in all structures studied. Interestingly, the H₂O in these samples persists and is not converted to an oxide or hydroxide, except as noted for the smallest cation (**Sc-OH**) and largest cation (**La-OH**) derivatives. This is believed to be due to the H---F interactions and the *pK*_a of the hfip ligand [H-OCH(CH₃)₂ (16.5) > H-OH (15.7) > H-OCH(CF₃)₂ (9.3)]. The H-hfip ligand is a much stronger acid than H₂O, so proton transfer cannot occur as it does in the non-fluorinated complexes.

3.2.3 Metrical data. As mentioned previously, there are few Ln-hfip derivatives[27] that could be used as model compounds, including (solv)Ce(hfip)₄, [Ce(hfip)₆]•2[(CH₃)NH(CH₂CH₂NMe₂)₂][28], and [(NH₃)₂(hfip)₂Sc(μ-hfip)]₂[11]. The Ln-hfip distances of the solvated Ce-monomers (av. 2.14 Å)[28, 29] were found to be shorter than **Ce**. This variation may be due to the change in charge on the metal. The comparison of the distances and angles of **Sc** to the NH₃ adduct [11] were found to be in-line with each other. A search of other fluorinated alkoxide-Ln derivatives yielded [(bis(dimethoxyethyl)ether))Y(hfip)₃],[**31**] [(THF)₃La(hftb)₃] (hftb = hexafluoro-*t*-butoxide),[11] [(NH₃)₂(hftb)₂Ln(μ-hftb)]₂ (Ln = La [11] Pr[32]) and [(THF)₃Eu(ptfb)₃][K]•THF (ptfb = perfluoro-*t*-butoxide)[33]. In addition to the [(DME)(hfip)₂Ln(μ-hfip)]₂ (Ln = Sm, Yb, Tm) species mentioned previously, [(DME)₂Ce(hftb)₂Ce(μ-hftb)]₂, and [(DME)₂Gd(hftb)₃] have also been disseminated and are useful models. [12, 13] It is of note that the authors indicate a number of the DME-hfip-Ln solvates are readily hydrolyzed in air. [12]

For these systems, a direct comparison of the metrical data to the respective metal hfip compounds was made, when possible. For **Y**, the reported distances were slightly

longer than the representative models; whereas, the remainder of the metals appeared to have distances [11, 12, 27-29, 31-33] [12, 13] that were in agreement with the species isolated in this work. The metrical data noted for the DME derivatives proved to be consistent for the Ln-hfip distances; however, Ln-O_{DME} distances were consistently shorter than the Ln-O_{H₂O} distance.[12, 13]

When possible, a comparison of the non-fluorinated OPr^{*i*} derivatives (OCH(CH₃)₂) was also undertaken. The structures of the OPr^{*i*} species tend to be much larger oxo clusters mainly adopting the oft-reported [Ln₅O(OPr^{*i*})₁₃] (Ln = Ce, Nd, Sm, Eu, Gd, Er, Tb, Dy, Ho).[19] The oxo moieties in these compounds are formed through specifically introduced hydrolysis, adventitious water, or ligand decomposition. The only homoleptic species reported is the dinuclear species Ce(IV) complex, [(HOPr^{*i*})(OPr^{*i*})₃Ce(μ-OPr^{*i*})₂].[34, 35] The metrical data for [(HOPr^{*i*})(OPr^{*i*})₃Ce(μ-OPr^{*i*})₂] (Ce-O (OPr^{*i*}) 2.18 Å, Ce-(μ-OPr^{*i*}) 2.31 Å, OPr^{*i*}-Ce-OPr^{*i*} 96.7°, Ce-O-Ce 107.9°) have distances that are slightly shorter and angles more obtuse in comparison to Ce (see Table 3). The change in oxidation state and the change from hfip to OPr^{*i*} should result in both shorter Ce-O bonds and more Ce-O-Ce obtuse angles, as was noted.

For the Ln (including Y and Sc) compounds reported with a “(OR)₃Ln(H₂O)” moiety, the Ln-OH₂ distances ranged from 2.12 to 2.85 Å.[36] All of the distances noted for the Ln-hfip species in this work, fall at the short end of the literature data. In addition, as can be observed in Table 3, the distances systematically decrease as the Ln series is traversed, due to the Ln contraction of the cation sizes. The angles around the Ln metal centers are in agreement with a distorted CN-6 geometry. The strain is due to the μ-hfip ligands. These angles are consistent with similarly constructed [LnO₃]₂

dinuclear moieties found in the literature. The Ln-hfip and Ln-OH₂ distances for both the **Sc-OH** and **La-OH** compounds are in agreement with those noted for the other hfip family members developed in this report. The average distance for compounds that possess the 'La₃(μ₃-OH)' moiety is 2.51 Å, which is comparable to the av 2.47 Å distance observed for **La-OH**. [27, 37-52] The two literature structures reported in the literature with a 'Sc₃(μ₃-OH)' moiety have an av distance of 2.15 Å, which is comparable with the 2.19 Å noted for **Sc-OH**. [53, 54] The angles for these Ln-OH compounds were also found to be in agreement with the literature model compounds. [27, 37-54]

3.2.4 Bulk analysis. Several different analyses were attempted to confirm the bulk powder compositions were consistent with the single crystal structures. The FTIR data previously discussed correlated with the final presence of hfip stretches, bends, and a broad stretch for the bound water at ~3000 cm⁻¹. Therefore, determination of the elemental composition of these compounds was attempted using a Perkin-Elmer CHN/O Elemental Analyzer. [55] Unfortunately, the large percentage of F atoms present (>10% F will cause unreliable results in the H and C data) [56] in these compounds had a negative impact on the generation of any meaningful data and therefore proved to be unreliable in determining the purity of the various compounds. To circumvent the analytical identification issue of the bulk powders, complexometric titrations [22] of the metal content of these compounds were undertaken. The %M found in the samples was found to be consistent with the calculated values of samples with no bound water.

3.2.5 NMR Spectroscopy. As mentioned previously, the use of standard nuclei NMR is limited in probing the solution behavior of the bulk material since the majority of these compounds are paramagnetic; however, the Group 3 cations are accessible. Some representative ^1H , ^{13}C , and ^{19}F NMR data were collected using **Sc** and **Y**. If the structures were retained in solution the terminal and bridging (2:1 ratio) hfip ligands should yield: a ^1H NMR spectrum with two septuplets split by the six F atom nearest neighbors and possibly a singlet for the bound H-OH or H-hfip proton; a $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum with two sets of methine and methyl resonances; a ^{19}F spectrum with two singlets.

A variety of solvents (THF- d_8 , py- d_5 , CDCl_3 , D_2O) were investigated for analysis of the solution behavior of these compounds. The low solubility of these compounds in organic solvents prevented in-depth analyses. CDCl_3 ultimately proved to be the best solvent to yield meaningful spectral data. While a number of nuclei are available, the sensitive ^{19}F (100 % abundant, spin = $\frac{1}{2}$, receptivity relative to ^1H = 0.83, chemical shift range -300 to 400 ppm) proved to be a useful means for studying these compounds. The H-hfip ligand yielded a ^{19}F shift at δ -76.9 ppm; whereas, each of the Ln-hfip species presents a slightly shifted single resonance that is clustered around -75.8 ppm. To further study these compounds, solid-state ^{19}F MAS NMR spectra were collected on the same set of compounds. A single peak was noted at δ -77.1 (**Sc**) and -77.2 (**Y**) for each sample. The difference in the chemical shift of the ^{19}F resonances between the solid state and solution state indicates that the solution state structures are not significantly different from the single crystal X-ray structures. Further, the lack of shift indicates there is little Sc---F interaction as noted in the solid state structure. This implies that the stability of

the structure is due to the $\text{H}_2\text{O} \cdots \text{F}$ interaction, preventing further typical hydrolysis reactivity or dynamic behavior of the ligands.

3.3 Nanomaterials. TGA data were collected on each of the compounds to determine their potential utility for conversion to LnF_3 . Due to the similarity in structure of these compounds, the resulting TGA profiles were expected and found to be very similar. An exothermic event was noted for each sample at $\sim 250^\circ\text{C}$. The size of the event and sharpness of the peak varied with **Lu** being the broadest while **Ce** was the the sharpest. All of the spectra have a small (5-7%) weight loss prior to 125°C , which was associated with loss of the two bound H_2O molecules. Two decomposition steps were noted for the majority of these samples, with a large weight loss before 400°C . The overall weight loss is much too small ($\sim 25 - 50\%$) to confirm complete conversion to either Sc_2O_3 or ScF_3 . However, the temperature observed for the initial weight loss was consistent with successful solution routes to nanoparticle preparation.

Preliminary investigation using amine solvents under both SOLVO and SPPT conditions yielded mixed results in terms of generating LnF_3 (summarized in Table 4). As can be noted, the SOLVO routes led to the oxo containing fluorinated materials. Switching to SPPT efforts, similar mixed anion or phases were noted. It is of note that for each sample, a LnF_3 phase was observed. TEM analyses were not pursued in depth but, the initial survey studies indicated that irregular nanomaterials had been generated. A great deal more work is necessary to determine ideal conditions for each of these compounds in terms of generating phase pure, monodispersed LnF_3 ; however, this does reveal these precursors can generate the desired LnF_3 materials.

4. Conclusions

A new family of lanthanide fluorinated alkoxide derivatives was characterized as the dinuclear species [*cis*-(H₂O)₂(hfip)₂Ln(μ-hfip)]₂ (Ln = **Ce**, **Pr**, **Nd**, **Eu**, **Gd**, **Tb**, **Dy**, **Ho**, **Er**, **Tm**, **Yb**, **Lu**, **Y**). A *trans* arrangement of the H₂O ligands was noted for **Sc**. Two additional tetranuclear structures were observed for the smallest (**Sc-OH**) and largest (**La-OH**) cation that exploited the presence of OH moieties believed to be due to ‘aged’ samples of the H-hfip reagent. The unprecedented structures isolated for this family of compounds are due to the unique properties of the hfip ligand, wherein the H---F interaction and H₂O binding limit the often observed oligomerization noted for the protonated derivatives. Solid and solution state ¹⁹F NMR indicated that crystal structure was in agreement with the solution species. TGA analyses revealed that these compounds would be amenable to nanoparticle synthesis. SOLVO and SPPT methods indicated that LnF₃ could be generated from these compounds; unfortunately, this phase was often mixed with Ln(O,F) or Ln₂O₃. Future work will focus on optimizing the conversion to pure LnF₃ as well as investigating ‘ALn(hfip)₄’ precursors to generate ALnF₄ compounds for scintillator applications.

5. Supporting information.

CCDC 1474628-1474644 contain the supporting crystallographic data for **Ce** – **Sc-OH**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge

Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Table 1. Data collection parameters for **Ce- Sc**.

Table 2. Data collection parameters for **La-OH** and **Sc-OH**.

Table 3. Metrical data for **Ce – Sc**.

Table 4. PXRD identification of resulting nanomaterials from SOLVO and SPPT experiments.

Table 1. Data collection parameters for **Ce – Sc**.

Compound	Ce	Pr	Nd	Eu	Gd
chemical formula	C ₁₈ H ₁₄ Ce ₂ F ₃₆ O ₁₀	C ₁₈ H ₁₄ F ₃₆ O ₁₀ Pr ₂	C ₁₈ H ₁₄ F ₃₆ Nd ₂ O ₁₀	C ₁₈ H ₁₄ Eu ₂ F ₃₆ O ₁₀	C ₁₈ H ₁₄ F ₃₆ Gd ₂ O ₁₀
formula weight	1354.53	1356.11	1362.77	1378.23	1388.79
temp (K)	100.0(2)	100.0(2)	100.0(2)	100.0(2)	100.0(2)
space group	Orthorhombic	Orthorhombic	Triclinic	Triclinic	Triclinic
	Pca2 ₁	Pca2 ₁	P(-1)	P(-1)	P(-1)
<i>a</i> (Å)	16.4521(15)	16.3868(7)	10.2439(10)	10.3651(5)	10.3623(6)
<i>b</i> (Å)	12.1757(11)	12.2136(10)	12.3405(12)	12.3507(6)	12.3298(8)
<i>c</i> (Å)	19.8324(18)	19.7212(12)	16.2956(17)	16.4380(8)	16.4569(10)
□□(deg)	90	90	93.405(4)	93.571(2)	93.688(2)
□ (deg)	90	90	99.087(4)	99.646(2)	99.674(2)
□□(deg)	90	90	108.640(4)	108.610(2)	108.576(2)
<i>V</i> (Å ³)	3972.7(6)	3947.0(4)	1914.1(3)	1950.96(17)	1949.0(2)
<i>Z</i>	4	4	2	2	2
<i>D</i> _{calcd} (Mg/m ³)	2.265	2.282	2.364	2.346	2.366
μ, (Mo, Kα) (mm ⁻¹)	2.476	2.655	2.904	3.403	3.591
<i>R</i> 1 ^a (%) (all data)	2.14(2.38)	2.51(2.68)	5.02(11.34)	2.76(3.13)	5.41 (6.85)
<i>wR</i> 2 ^b (%) (all data)	4.92(5.04)	6.32(6.48)	9.47(11.53)	6.80(7.07)	15.02 (16.47)
Compound	Tb	Dy	Ho	Er	Tm
chemical formula	C ₁₈ H ₁₄ F ₃₆ O ₁₀ Tb ₂	C ₁₈ H ₁₄ Dy ₂ F ₃₆ O ₁₀	C ₁₈ H ₆ F ₃₆ Ho ₂ O ₁₀	C ₃₆ H ₂₆ Er ₄ F ₇₂ O ₂₀	C ₃₆ H _{25.79} F ₇₂ O _{18.89} Tm ₄
formula weight	21392.13	1399.29	1396.09	2815.61	2804.31
temp (K)	100.0(2)	100.0(2)	100.0(2)	100.0(2)	100.0(2)
space group	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
	P(-1)	P(-1)	P(-1)	P(-1)	P(-1)
<i>a</i> (Å)	10.3565(5)	10.3508(5)	10.3413(5)	10.3447(6)	10.3263(15)
<i>b</i> (Å)	12.3041(6)	12.2871(5)	12.2700(6)	12.2525(7)	12.2572(18)
<i>c</i> (Å)	16.4125(8)	16.4262(8)	16.4064(8)	16.3492(9)	16.370(2)

α (deg)	93.538(2)	93.668(2)	93.693(2)	93.685(3)	93.602(4)
$\square$ (deg)	100.103(2)	100.074(3)	100.112(2)	100.937(3)	100.535(4)
γ (deg)	108.192(2)	108.362(2)	108.295(2)	107.106(3)	107.713(4)
V (Å ³)	1940.83(17)	1936.26(16)	1929.87(16)	1928.60(19)	1924.9(5)
Z	2	2	2	1	1
D_{calcd} (Mg/m ³)	2.382	2.400	2.396	2.424	2.419
μ , (Mo, K $\square$) (mm ⁻¹)	3.833	4.049	4.289	4.542	4.798
$R1$ (%) (all data)	2.23(2.94)	4.32 (7.01)	3.89(5.08)	2.16 (2.27)	2.18(2.81)
$wR2$ (%) (all data)	4.75 (5.04)	8.54 (9.47)	9.90(11.18)	4.91 (4.96)	4.62(4.89)
Compound	Yb	Lu	Y	Sc	
chemical formula	C ₁₈ H ₁₄ F ₃₆ O ₁₀ Yb ₂	C ₁₈ H ₁₄ F ₃₆ Lu ₂ O ₁₀	C ₃₆ H ₂₆ F ₇₂ O ₂₀ Y ₄	C ₁₈ H _{12.58} F ₃₆ O _{9.29} Sc ₂	
formula weight	1420.37	1424.23	2502.21	1151.42	
temp (K)	100.0(2)	100.0(2)	100.0(2)	100.0(2)	
space group	Triclinic	Triclinic	Triclinic	Monoclinic	
	P(-1)	P(-1)	P(-1)	P21/n	
a (Å)	10.3255(4)	10.2923(8)	10.3637(8)	9.8264(5)	
b (Å)	12.2523(5)	11.2778(9)	12.2784(10)	14.1552(7)	
c (Å)	16.3105(6)	11.3676(9)	16.3853(12)	14.2465(7)	
$\alpha\square$ (deg)	93.5990(10)	112.727(2)	93.688(3)	90	
β (deg)	101.0720(10)	94.305(2)	100.708(3)	100.087(2)	
γ (deg)	107.3230(10)	110.302(2)	107.554(3)	90	
V (Å ³)	1917.29(13)	1107.58	1937.2(3)	1950.98(17)	
Z	2	1	1	2	
D_{calcd} (Mg/m ³)	2.460	2.135	2.145	1.960	
μ , (Mo, K $\square$) (mm ⁻¹)	5.069	4.622	3.200	0.563	
$R1^a$ (%) (all data)	2.32(2.76)	2.37(2.73)	5.62(8.64)	3.24(3.59)	
$wR2^b$ (%) (all data)	5.20(5.43)	5.12(5.41)	13.42(17.71)	8.62(8.94)	

$$^a R1 = \Sigma \square ||F_o| - |F_c|| / \Sigma |F_o| \times 100$$

$$^b wR2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma (w |F_o|^2)^2]^{1/2} \times 100$$

Table 2. Data collection parameters for **La-OH** and **Sc-OH**.

Compound	La-OH	Sc-OH
chemical formula	C ₃₀ H ₁₆ F ₆₀ La ₄ O ₁₆	C ₂₄ H ₂₀ F ₄₈ O ₁₆ Sc ₄
formula weight	2328.07	1656.24
temp (K)	100.0(2)	100(2)
space group	Triclinic P(-1)	Triclinic P(-1)
<i>a</i> (Å)	11.088(2)	11.3087(12)
<i>b</i> (Å)	12.836(3)	12.0028(12)
<i>c</i> (Å)	13.310(3)	12.1588(13)
α (deg)	112.89(3)	86.457(5)
β (deg)	105.40(3)	63.130(5)
γ (deg)	94.90(3)	63.866(5)
<i>V</i> (Å ³)	1644.1(7)	1302.1(2)
<i>Z</i>	1	1
<i>D</i> _{calcd} (Mg/m ³)	2.351	2.112
μ , (Mo, K α) (mm ⁻¹)	2.771	0.731
<i>R</i> 1 ^a (%) (all data)	4.91(7.72)	5.75(7.87)
<i>wR</i> 2 ^b (%) (all data)	11.38(13.09)	14.62(16.48)

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o| \times 100$$

$$^b wR2 = [\sum w (F_o^2 - F_c^2)^2 / \sum (w |F_o|^2)^{1/2}] \times 100$$

Table 3. Select average metrical data (bond distances (Å) and angles (deg) for **Ce-Sc**, **La-OH**, and **Sc-OH**.

Comp'd	Distances (Å)				Angles (deg)		
	Ln-hfip (av)	Ln-(μ-hfip) (av)	Ln-OH ₂ (av)	H ₂ O---F (shortest)	O _{H2O} -Ln-O _{H2O}	hfip-Ln-hfip	Ln-(μ-hfip)-Ln
Ce	2.21	2.44	2.68	2.21	83.6	98.4	109.8
Pr	2.20	2.43	2.66	2.30	83.5	98.7	109.4
Nd	2.17	2.38	2.61	2.27	86.9	102.8	108.0
Eu	2.15	2.35	2.57	2.36	86.4	104.1	106.6
Gd	2.14	2.35	2.55	2.31	85.9	104.1	106.4
Tb	2.13	2.33	2.53	2.31	85.8	105.2	106.1
Dy	2.11	2.32	2.51	2.44	85.3	104.3	105.7
Ho	2.11	2.30	2.50	2.58	85.5	104.0	105.5
Er	2.10	2.29	2.48	2.45	85.5	103.8	105.5
Tm	2.09	2.28	2.46	2.33	84.5	103.9	105.9
Yb	2.07	2.29	2.45	2.38	84.7	103.2	105.1
Lu	2.07	2.27	2.42	2.39	83.0	99.4	104.8
Y	2.10	2.30	2.49	2.52	84.6	104.0	105.8
Sc	1.95	2.16	2.31	2.41	177.5	94.8	106.2
La-OH	2.21	2.48	2.67	2.52	----	----	103.4
Sc-OH	1.95	2.19	2.29	2.48	----	103.8	103.1

Table 4. PXRD identification of resulting nanomaterials from SOLVO and SPPT experiments.

Process-solvent	sample	450 °C post	
SOLVO - py	Dy	<i>DyOF</i>	PDF 00-033-0524
	Y	<i>YOF</i> <i>YF₃</i>	PDF 00-006-0347 PDF 00-032-1431
SOLVO - TOA	Ce	<i>CeO₂</i> <i>CeF₃</i>	PDF: 00-049-1415 PDF: 99-000-0623
	Dy	<i>DyO</i>	PDF 00-033-0524
	Lu	<i>LuF₃</i>	PDF 00-032-0612
SOLVO-ON	Y	<i>YF₃</i>	PDF 00-032-1431
	sample	650 °C post	
SPPT - ON	Ce	<i>CeF₃</i>	PDF: 99-000-0623
	Tb	<i>TbF₃</i>	PDF 01-084-1479
	Dy	<i>DyOF</i>	PDF 00-033-0524
	Yb	<i>Yb(O,F)_{1.93}</i> <i>YbF₂</i>	PDF 00-052-0778 PDF 00-036-0819
	Y	<i>YOF</i> <i>Y₅O₄F₇</i> <i>YF₃</i>	PDF 04-009-6515 PDF 04-011-5071 PDF 00-032-1431
	Sc	<i>Sc₂O₃</i> <i>ScF₃</i>	PDF 00-042-1463 PDF 00-046-1243

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Figure 3. Structure plot using **Sc**. Thermal ellipsoids of heavy atoms drawn at 30%. Carbon, fluorine (dotted) and hydrogen atoms drawn as ball and stick for clarity.

Figure 4. Structure plot using **Sc-OH**. Thermal ellipsoids of heavy atoms drawn at 30%. Carbon, fluorine and hydrogen atoms drawn as ball and stick for clarity.

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(a)

(b)

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