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FULL PAPER

Reactivity of the europium hexafluoroacetylacetonate (hfac) complex, Eu(hfac)$_3$(diglyme), and related analogs with potassium: formation of the fluoride hfac "ate" complexes, [LnF(hfac)$_3$K(diglyme)]$_2$

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The europium hexafluoroacetylacetonate complex Eu(hfac)$_3$(diglyme) was synthesized to examine its fluorescence and conversion to a Eu(II) analog. Reaction of Eu(hfac)$_3$(diglyme) with potassium produced the unexpected trivalent product [EuF(hfac)$_3$K(diglyme)]$_2$. This reduction system was studied further by synthesizing other Ln(hfac)$_3$(diglyme) analogs and examining their reactivity with potassium. The Nd, Sm, and Gd analogs of Ln(hfac)$_3$(diglyme) also react with potassium to form [LnF(hfac)$_3$K(diglyme)]$_2$ as observed for europium. Reactions of the Eu(II) precursors, EuI$_2$(thf)$_4$ and {[Zr$_2$(O^{i}Pr)$_9$]Eu(μ-I)}$_2$ with K(hfac) also form trivalent products, namely Eu(hfac)$_3$(diglyme) and [Zr$_2$(O^{i}Pr)$_9$]Eu(hfac)$_2$.

Introduction

The facile synthesis and stability to air and moisture of the hexafluoroacetylacetonate (hfac) complexes La(hfac)$_3$(diglyme)[1] and Gd(hfac)$_3$(diglyme)[2] reported by Fragalà and coworkers make this class of compounds attractive when soluble, stable, monometallic lanthanide complexes are needed which are convenient to obtain and handle. As part of our studies in poly- and heteropoly-metallic europium chemistry,[3–7] we were interested, for comparative purposes, in some monometallic Eu(III) and Eu(II) complexes which would be convenient references for fluorescence studies of polymetallic species. The Ln(hfac)$_3$(diglyme) compounds seemed ideal and the synthesis of both trivalent and divalent hfac europium complexes was examined.

We report here the synthesis of the europium analog, Eu(hfac)$_3$(diglyme),[8] and its surprising reactivity with potassium. The unexpected formation of a trivalent europium complex from the reaction with potassium engendered a broader examination of Ln(hfac)$_3$(diglyme) complexes and their reactivity with potassium. This led to a series of potassium salts of the formula [LnF(hfac)$_3$K(diglyme)]$_2$. Reactions of divalent europium precursors with hfac reagents are also reported along with their trivalent products.

Results

Synthesis of Ln(hfac)$_3$(diglyme) complexes

The Nd, Sm and Eu[4] analogs of La(hfac)$_3$(diglyme)[1] and Gd(hfac)$_3$(diglyme)[2] were readily prepared following the literature procedure of reacting the appropriate lanthanide oxide, 1,1,1,5,5,5-hexafluoroacetylacetone (Hhfac), and diglyme in toluene, in a single reaction flask, eqn. (1).

$$\mathrm{Ln_2O_3 + 6\,CF_3COCH_2COCF_3 + 2\,CH_3OCH_2CH_2OCH_2CH_2OCH_3 \longrightarrow 2\,Ln(hfac)_3(diglyme) + 3\,H_2O} \quad (1)$$
$$\mathrm{Ln = Nd,\ \mathbf{2};\ Sm,\ \mathbf{3},\ Eu,\ \mathbf{4}}$$

A slight excess of lanthanide oxide and diglyme favors the convenient isolation of the product since all the hexafluoroacetylacetone is totally reacted and the excess oxide is separated during sublimation. The measured yields for Nd(hfac)$_3$(diglyme), **2**, (89%), Sm(hfac)$_3$(diglyme), **3**, (92%), and Eu(hfac)$_3$(diglyme), **4**, (86%), were similar to the high yields found for La (90%) and Gd (88%).

The commercially available cerium oxide, CeO$_2$, did not readily form an isolable complex with 1,1,1,5,5,5-hexafluoroacetylacetone and diglyme in toluene. Only the ligand hydrolysis product, CF$_3$C(OH)$_2$CH$_2$C(OH)$_2$CF$_3$, was isolated in pure form. This compound was identified by ^{1}H NMR spectroscopy and X-ray crystallography.[9]

To obtain Ce(hfac)$_3$(diglyme), commercially available Ce(acac)$_3$, (acac = acetylacetonate) was used as a precursor as shown in eqn. (2). Tb(hfac)$_3$(diglyme) was made in an analogous manner. A slight excess of Hhfac and diglyme was used to aid in the isolation of the product, since this allows all of the Ln(acac)$_3$ to be consumed.

$$\mathrm{Ln(CH_3COCHCOCH_3)_3 + 3\,Hhfac + diglyme \longrightarrow Ln(hfac)_3(diglyme) + 3\,CH_3COCH_2COCH_3} \quad (2)$$
$$\mathrm{Ln = Ce,\ \mathbf{1},\ (90\%),\ Tb,\ \mathbf{5},\ (94\%)}$$

Complexometric titrations performed on **1**–**5** were consistent with the Ln(hfac)$_3$(diglyme) formulae and the IR spectra of these species were nearly identical to those of the La[1] and Gd[2] analogs. **1**–**5** are volatile and are readily purified by sublimation. The fact that **1**–**5** do not co-crystallize with any water in the solid state is consistent with the results obtained for both La and Gd. Since the metals in **1**–**5** are paramagnetic, the ^{1}H and ^{13}C NMR spectra of these compounds were not definitive and X-ray data were obtained to unambiguously confirm their identities.

The molecular structures of all of the Ln(hfac)$_3$(diglyme) systems examined so far are similar, Fig. 1, but the complexes have been found to crystallize in three different space groups. The La complex[1] crystallizes in $P2_1/c$, Ce, Nd, Eu, Sm, and Gd[2] crystallize in $P2_1/n$, and Tb crystallizes in $Pna2_1$. A comparison

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Table 1 X-Ray data collection parameters[a] for Sm(hfac)$_3$(diglyme), **3**, Eu(hfac)$_3$(diglyme), **4**, Tb(hfac)$_3$(diglyme), **5**, [EuF(hfac)$_3$K(diglyme)]$_2$, **6**, [SmF(hfac)$_3$K(diglyme)]$_2$, **7**, [NdF(hfac)$_3$K(diglyme)]$_2$, **9**, and [Zr$_2$(O^{i}Pr)$_9$]Eu(hfac)$_2$, **10**

Empirical formula	$C_{21}H_{17}F_{18}O_9$-Sm **3**	$C_{21}H_{17}F_{18}O_9$-Eu **4**	$C_{21}H_{17}F_{18}O_9$-Tb **5**	$C_{49}H_{42}O_{18}F_{38}K_2$-Eu$_2$ **6**	$C_{42}H_{34}O_{18}F_{38}K_2$-Sm$_2$ **7**	$C_{42}H_{34}O_{18}F_{38}K_2$-Nd$_2$ **9**	$C_{37}H_{65}O_{13}F_{12}Zr_2$-Eu **10**
Formula weight	905.70	907.31	914.27	2022.95	1927.59	2007.51	1372.42
Temperature/K	158(2)	158(2)	163(2)	158(2)	163(2)	158(2)	158(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$Pna2_1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a/Å	10.1210(6)	9.7264(5)	22.378(1)	13.1218(6)	12.0241(6)	13.1362(9)	16.6625(9)
b/Å	15.674(1)	15.5649(7)	11.1908(6)	13.2706(6)	12.4246(6)	13.3292(9)	21.312(1)
c/Å	19.301(1)	20.547(1)	12.3993(6)	22.126(1)	13.5664(7)	22.182(1)	16.4412(8)
α/°	90	90	90	91.171(1)	92.292(1)	90.727(1)	90
β/°	97.248(10)	103.519(10)	90	91.827(1)	114.633(1)	91.957(1)	100.911(1)
γ/°	90	90	90	111.005(1)	113.686(1)	110.714(1)	90
Volume/Å^3	3037.5(3)	3024.4(3)	3105.1(3)	3592.9(3)	1633.9(1)	3629.4(4)	5732.8(5)
Z	4	4	4	2	1	2	4
ρ_{calc}/Mg m^{-3}	1.981	1.993	1.956	1.870	1.959	1.837	1.590
μ/mm^{-1}	2.090	2.231	2.431	2.006	2.078	1.688	1.530
$R1$[b] (all data)	0.0220	0.0211	0.0240	0.1037	0.0269	0.0660	0.0553
$wR2$[c] (all data)	0.0497	0.0454	0.0500	0.1572	0.0628	0.1283	0.1398

[a] Radiation: Mo-Kα (μ = 0.71073 Å). Monochromator: highly oriented graphite. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_c|$. [c] $wR2 = [\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma [w(F_o^2)^2]]^{1/2}$.

Table 2 Comparison of bond distances (Å) in the Ln(hfac)$_3$(diglyme) complexes of Ln = La,[1] Sm, **3**, Eu, **4**, Gd[2] and Tb, **5**

Bond	La	Sm	Eu	Gd	Tb
Ln–O(1)(hfac)	2.527(5)	2.401(1)	2.425(1)	2.403(7)	2.432(3)
Ln–O(2)(hfac)	2.489(6)	2.437(1)	2.418(1)	2.354(7)	2.368(2)
Ln–O(3)(hfac)	2.471(6)	2.386(1)	2.364(1)	2.412(7)	2.362(2)
Ln–O(4)(hfac)	2.485(6)	2.419(1)	2.397(1)	2.399(6)	2.354(3)
Ln–O(5)(hfac)	2.530(6)	2.437(1)	2.439(1)	2.381(7)	2.355(2)
Ln–O(6)(hfac)	2.473(6)	2.406(1)	2.399(1)	2.417(7)	2.399(2)
Ln–O(7)(diglyme)	2.638(6)	2.579(1)	2.563(1)	2.528(7)	2.519(2)
Ln–O(8)(diglyme)	2.634(6)	2.555(1)	2.531(1)	2.527(7)	2.534(2)
Ln–O(9)(diglyme)	2.645(6)	2.545(1)	2.553(1)	2.578(8)	2.516(2)
Ln–O (av. hfac)	2.50(2)	2.41(2)	2.41(2)	2.39(2)	2.38(2)
Ln–O (av. diglyme)	2.639(4)	2.56(1)	2.55(1)	2.54(2)	2.53(1)

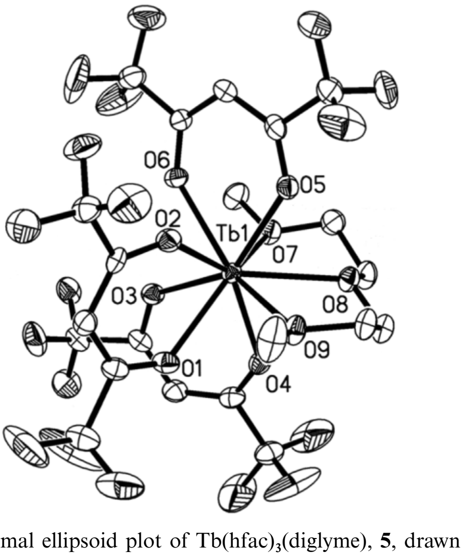

Fig. 1 Thermal ellipsoid plot of Tb(hfac)$_3$(diglyme), **5**, drawn at the 50% probability level with hydrogen atoms omitted for clarity.

of the unit cell parameters is given in Table 1. Unit cell data only were collected for Ln = Ce, Nd.

The detailed structural information obtained on Eu(hfac)$_3$(diglyme),[4] Sm(hfac)$_3$(diglyme), and Tb(hfac)$_3$(diglyme) is not unusual compared to the data on La(hfac)$_3$(diglyme) and Gd(hfac)$_3$(diglyme). As shown in Table 2, the bond lengths vary as expected when differences in ionic radii are considered.

Luminescence of Eu(hfac)$_3$(diglyme), 4

The luminescence spectrum of **4** was dominated by the intense $^5D_0 \longrightarrow {}^7F_2$ transition at 610 nm in the red region of the visible spectrum. Luminescence lifetime measurements of the emission were consistent with a single exponential decay of luminescence *vs.* time, and gave a lifetime of 0.70 ms. This value, which is longer than the typical 0.1 ms lifetime of aqueous Eu(III)[10] and of several Eu(III) cryptates (0.27–0.41 ms),[11] is consistent with the anhydrous nature of **4**.

Reactivity of the Ln(hfac)$_3$(diglyme) complexes with potassium. The europium system

In an attempt to obtain a divalent europium hexafluoroacetylacetonate complex from Eu(hfac)$_3$(diglyme), **4**, reduction with potassium in toluene was examined. A color change from light yellow to brown occurred within a matter of hours and generated a suspension that could be separated by centrifugation to leave a yellow solution. The soluble material crystallized from the toluene supernatant and was found to have a similar, although not equivalent, infrared spectrum to that of **4**. An X-ray diffraction study of the crystals revealed a tetrametallic species of the formula [EuF(hfac)$_3$K(diglyme)]$_2$, **6**, Fig. 2. The composition, magnetic moment, and bond lengths in **6** are all consistent with a trivalent, rather than a divalent europium product. The monomeric unit in **6** is formally composed of **4** and one equivalent of KF, which is likely to have formed from the decomposition of a hexafluoroacetylacetonate ligand.[12] Luminescence spectra of the solution obtained from the potassium reaction did not contain any transitions associated with divalent europium and were similar to those found for **4**.

Nd, Sm, and Gd analogs

Although it is not surprising to find KF in a product of a

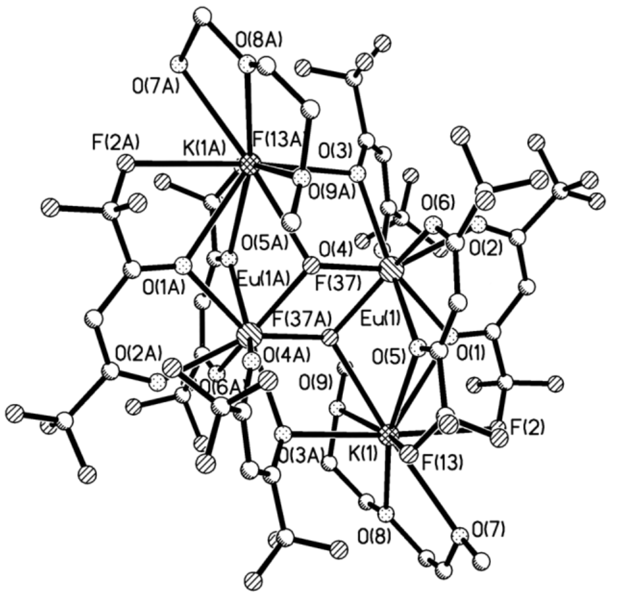

Fig. 2 Ball and stick diagram of one of the crystallographically independent molecules in $[EuF(hfac)_3K(diglyme)]_2$, **6**, with hydrogen atoms omitted for clarity.

potassium reduction reaction involving fluorinated ligands, it is conceivable that potassium reduced Eu(III) to Eu(II) and the fluoride abstraction occurred *via* Eu(II). To examine this possibility, the potassium reduction chemistry of related Nd, Sm, and Gd analogs of $Eu(hfac)_3(diglyme)$ was studied. This series was chosen since there was variation in both radial size and access to divalent states, two factors which are most likely to be important in this system.

In the case of Sm, which also has an accessible divalent state (Eu(III)/Eu(II) = −0.35 V; Sm(III)/Sm(II) = −1.55 V *vs.* NHE),[13] an analogous fluoride-containing product, $[SmF(hfac)_3K(diglyme)]_2$, **7**, was obtained in a yield similar (70%) to that of the Eu reaction. **7** was identified by X-ray crystallography and is similar in structure to **6**. For Gd and Nd, which do not have easily accessible divalent states (Gd(III)/Gd(II) = −3.9 V; Nd(III)/Nd(II) = −2.6 V), products, **8** and **9**, analogous to those found for Eu and Sm were also obtained. Each of these products, **7**–**9**, was characterized by complexometric titration and IR spectroscopy and identified by X-ray crystallography. Since the structures of **6**–**9** are quite similar only the structure of **6** will be described in detail.

Structure of $[EuF(hfac)_3K(diglyme)]_2$, 6

Complex **6** has two independent molecules in the unit cell, each of which is located about an inversion center. The two molecules are similar except that one has two long K ··· F interactions {involving K(1)} and the other has three {involving K(2)}. The metal and donor atom structure of the first of these is shown schematically in Fig. 3. The four metal centers in **6** have a planar rectangular geometry which is very common in the alkoxide chemistry of heterometallic complexes of composition $M_2M'_2$. This structural motif, shown in Chart 1, has been thoroughly described in a review.[14] Complex **6** is more complicated in that it contains bridging bidentate hfac ligands and tridentate diglyme ligands instead of simple OR groups.

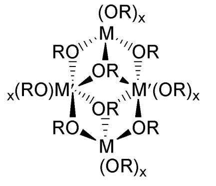

Chart 1 Generalized structure of $M_2M'_2$ mixed metal alkoxide complexes.

Table 3 Bond distances (Å) in $[LnF(hfac)_3K(diglyme)]_2$ [Ln = Eu, **6** (molecule 1); Sm, **7**;[b] Nd, **9** (molecule 1)]

Bond	Eu	Nd	Sm
Ln(1)–O(1) (hfac bridging)	2.433(5)	2.461(4)	2.514(2)
Ln(1)–O(2) (hfac terminal)	2.408(6)	2.438(4)	2.417(2)
Ln(1)–O(3) (hfac bridging)	2.414(5)	2.433(4)	2.433(2)
Ln(1)–O(4) (hfac terminal)	2.415(6)	2.474(3)	2.435(2)
Ln(1)–O(5) (hfac bridging)	2.434(6)	2.473(4)	2.436(2)
Ln(1)–O(6) (hfac terminal)	2.394(6)	2.431(4)	2.449(2)
Ln(1)–F(37)	2.271(5)	2.326(3)	2.309(2)
Ln(1)–F(37A)	2.292(4)	2.307(3)	2.290(2)
K(1)–O(1) (hfac bridging)	2.839(6)	2.908(4)	2.944(2)
K(1)–O(5) (hfac bridging)	3.018(7)	3.325(6)	3.023(2)
K(1)–O(5A) (hfac bridging)	2.901(6)	2.933(4)	2.970(2)
K(1)–O(7) (diglyme)	2.900(12)	2.814(6)	2.780(2)
K(1)–O(8) (diglyme)	2.648(15)	2.801(7)	2.765(2)
K(1)–O(9) (diglyme)	2.893(9)	2.774(6)	2.800(2)
K(1)–F(37A)	2.711(5)	2.647(3)	2.744(2)
K(1)–F(2) (hfac)	2.988(7)	3.015(4)	2.848(2)
K(1)–F(13) (hfac)	3.284(10)	3.394(4)	2.906(2)
K(1)–F(16A) (hfac) only for Sm			3.170(2)

[b] Atom numbering is for **6** and **9** only.

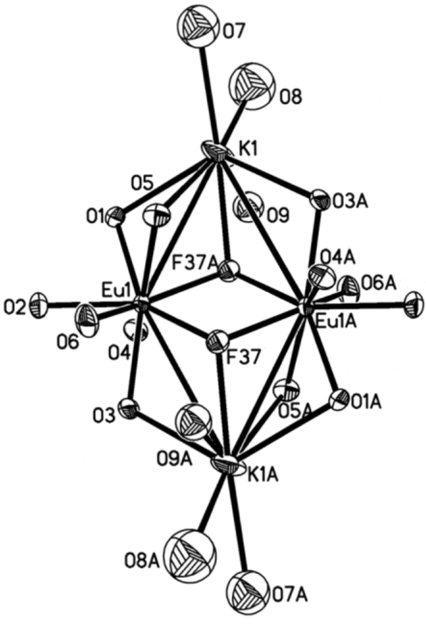

Fig. 3 Ball and stick diagram of the metal oxygen skeleton of one of the crystallographically independent molecules of $[EuF(hfac)_3K(diglyme)]_2$, **6**.

Complex **6** is comprised of two Eu_2K triangles which share the common Eu ··· Eu edge. The three metals in each triangle are connected by (a) one triply bridging fluoride ligand, F(37), (b) oxygen atoms from two bridging hfac ligands on one edge, O(1) and O(5), and (c) an oxygen from another bridging hfac ligand on the other edge, O(5A). Each potassium is coordinated by a bridging fluoride, the three bridging hfac oxygen atoms, and three oxygens from a terminal tridentate diglyme ligand, O(7), O(8), and O(9). In addition, in the molecule shown in Figs. 2 and 3 there are two fluorides from hfac ligands, F(2) and F(13), which are oriented towards the potassium. Each europium is coordinated to both bridging fluorides, the three bridging hfac oxygens, and three additional non-bridging hfac oxygen atoms O(2), O(4), and O(6) for a total coordination number of eight.

The 2.394(6)–2.434(6) Å range of Eu–O(hfac) distances (see Table 3) is similar to the 2.364(1)–2.425(1) Å span of distances in **4**. In all of the [LnF(hfac)$_3$K(diglyme)]$_2$ complexes, the Ln–O(hfac) distances do not follow the regular pattern that terminal distances are shorter than bridging distances, usually observed for monodentate ligands. The variations in these distances may be due to constraints of the bidentate ligand and the requirements of packing the ligands around the Eu$_2$K core. The 2.271(5) and 2.292(4) Å Eu–(μ-F) distances are in the range of those in the four Eu(III)–F complexes in the Cambridge Crystallographic Data Base, 2.247–2.341 Å for Eu–(μ-F) bonds and 2.193–2.197 Å for Eu–F(terminal) bonds. The 2.711(5) Å K–F(37A) distance is just that expected from adding the difference in ionic radii between eight coordinate potassium and europium, 0.44 Å, to the Eu–F bond length.

In one molecule of **6**, two hfac fluoride atoms are located around the potassium at distances of 2.988(7) and 3.284(10) Å. In the other molecule in the unit cell, there are three such distances: 2.989(7), 3.042(7), and 3.112(6) Å. These distances are comparable to the long range K ··· FCF$_2$ distances, 2.810(6)–3.325(5) Å, found in {H$_2$B[3,5-(CF$_3$)$_2$Pz]$_2$}K.[15] The difference in the two molecules in the same unit cell may be due to packing forces and how they affect the rotation around the C–CF$_3$. These variations are also seen in the other structures. Complex **9** is isomorphous with **6**, but **7**, which is not, is similar to the second molecule in **6** and **9** in that it has three long range K ··· F distances.

Reactions of Eu(II) complexes with Khfac

In efforts to make a Eu(II) hfac complex by an alternative route, reactions of divalent europium precursors with hfac reagents were examined. The reaction of EuI$_2$(thf)$_2$[34] with Khfac was examined, but gave the Eu(III) product, Eu(hfac)$_3$(diglyme), **4**, as the main isolated species. A Eu(II) di-zirconium-nona-isopropoxide (dzni) complex, {[Zr$_2$(O^{i}Pr)$_9$]Eu(μ-I)}$_2$, which is synthesized from EuI$_2$(thf)$_4$ and K[Zr$_2$(O^{i}Pr)$_9$],[16] was also reacted with Khfac. Again, a Eu(III) product was surprisingly formed, [Zr$_2$(O^{i}Pr)$_9$]Eu(hfac)$_2$,**10**, Fig. 4. This complex was characterized by IR spectroscopy, elemental analysis, and X-ray crystallography.

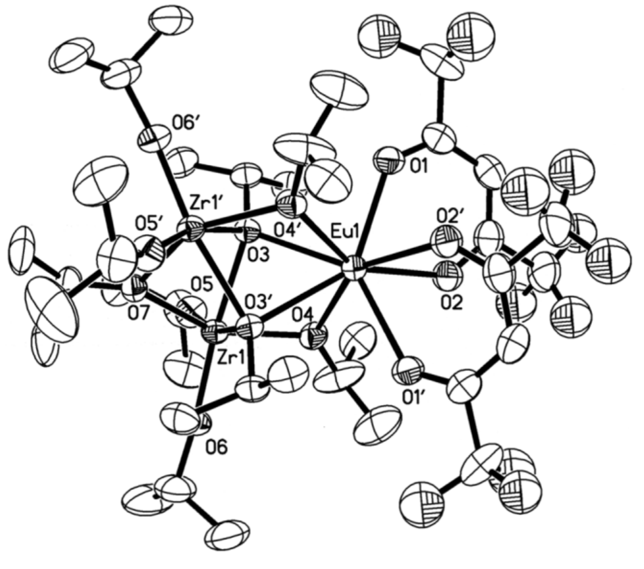

Fig. 4 Thermal ellipsoid plot of [Zr$_2$(O^{i}Pr)$_9$]Eu(hfac)$_2$, **10**, drawn at the 30% probability level with hydrogen atoms omitted for clarity.

Structure of [Zr$_2$(O^{i}Pr)$_9$]Eu(hfac)$_2$, 10

Complex **10** contains an eight coordinate Eu(III) ion ligated by four oxygens of the di-zirconium-nona-isopropoxide (dzni) ligand and four oxygens of two hfac ligands. The eight oxygens define a square antiprism. O(1), O(2), O(3), and O(4) are coplanar to within 0.037 Å, as are O(1′), O(2′), O(3′), and O(4′) and the sets have a 5.5° dihedral angle between their planes. The 2.390(3) Å Eu–O(1) and 2.400(3) Å Eu–O(2) bond distances (see Table 4) are in the 2.364(1)–2.439(1) Å range of analogous distances in Eu(hfac)$_3$(diglyme), **4**. The similarities of these distances indicate that the dzni ligand in **10** takes the place of an hfac ligand and the diglyme in **4**. This is reasonable considering that the dzni ligand has previously been found to replace a (C$_5$Me$_5$)(thf)$_2$ ligand set in [(C$_5$Me$_5$)(thf)$_2$Eu(μ-I)]$_2$.[4] The 2.487(3) Å Eu–O(3) bond arising from a triply bridging isopropoxide is longer than the 2.399(3) Å Eu–O(4) analog arising from a doubly bridging isopropoxide as expected. These Eu–O(dzni) distances are shorter than the 2.541(5) and 2.600(5) Å triply bridging and 2.506(5) and 2.525(5) Å doubly bridging analogs in the divalent europium dzni complex, {[Zr$_2$(O^{i}Pr)$_9$]-Eu(μ-I)}$_2$,[8] as expected for Eu(III) *vs.* Eu(II) radii,[17,18] The bond lengths within the dzni unit are similar to those of other dzni complexes.[4]

Table 4 Bond distances (Å) in [Zr$_2$(O^{i}Pr)$_9$]Eu(hfac)$_2$, **10**

Bond	**10**
Eu–O(1)	2.390(3)
Eu–O(2)	2.400(3)
Eu–O(3)	2.487(3)
Eu–O(4)	2.399(3)

Discussion

The synthetic method of Fragalà and coworkers to convert La and Gd oxides and hexafluoroacetylacetone into Ln(hfac)$_3$-(diglyme) complexes can be readily extended to Nd, Sm, and Eu with yields typically >90%. The Ln(hfac)$_3$(diglyme) complexes can also be conveniently made from Ln(acac)$_3$ precursors as demonstrated for Ln = Ce and Tb. These readily sublimable Ln(hfac)$_3$(diglyme) compounds can be handled in air without decomposition and constitute a valuable series of easily manipulated monometallic lanthanide complexes.

Attempts to form Eu(II) complexes of the hfac ligand have been much more challenging. The formation of the trivalent [EuF(hfac)$_3$K(diglyme)]$_2$, **6**, from the reaction of potassium with Eu(hfac)$_3$(diglyme), **4**, is complicated by the fact that fluoride abstraction apparently occurs. The abstraction of a fluoride from an hfac ligand has previously been observed in the mass spectra of La(hfac)$_3$(diglyme)[1] and La(hfac)$_3$(triglyme)[1] which contain a variety of [(hfac)$_a$MF$_b$]$^+$ ions including [LaF$_2$]$^+$. In addition, there is evidence of fluorine transfer processes in the spectra of the analogous alkaline-earth[19–21] and gadolinium adducts.[2] Metal hfac complexes are also known to form metal fluorides when they are used as MOCVD precursors.[20,22,23] The mass spectrum of Khfac was also examined in this regard and found to contain only two fluoride-containing fragments, [(hfac)$_2$K$_3$F]$^+$ at m/z = 589 and [(hfac)$_3$K$_5$F]$^+$ at m/z = 835, although they were not the more prevalent ions.

The potassium/Eu(hfac)$_3$(diglyme) conversion to trivalent [EuF(hfac)$_3$K(diglyme)]$_2$ could involve Eu(II), since potassium can easily accomplish this reduction. Although Eu(II) is not a very strong reductant, it has been shown to perform fluoride abstraction with the proper substrates. For example, (C$_5$Me$_5$)$_2$-Eu(OEt$_2$) reacts with allylic organic fluorides to make (C$_5$Me$_5$)$_2$EuF(OEt$_2$).[11] The formation of the Sm analogue, could be explained similarly, but formation of the analogous product with Gd suggests that fluoride abstractions do not require an easily accessible divalent state. Recently a considerable amount of unusual lanthanide chemistry has been reported in the presence of potassium metal and this system may be another such case.[24–29]

In the reactions of both divalent precursors, EuI$_2$(thf)$_2$ and [(dzni)Eu(μ-I)]$_2$, with Khfac, Eu(II) is necessarily involved in the reaction. In each case, and despite the different ligands, the main product is a Eu(III) complex. These results suggest that there may be several routes by which trivalent Eu/hfac complexes can form.

Experimental

The Ln(hfac)$_3$(diglyme) complexes **1**–**5** (Ln = Ce, **1**; Nd, **2**; Sm, **3**; Eu, **4**; Tb, **5**) were synthesized and handled in air. The [LnF(hfac)$_3$K(diglyme)]$_2$complexes **6**–**9** (Ln = Eu, **6**; Sm, **7**; Gd, **8**; Nd, **9**) and [Zr$_2$(O^{i}Pr)$_9$]Eu(hfac)$_2$, **10**, were handled under nitrogen using Schlenk, vacuum line, and glove box techniques. ^{1}H NMR spectra were obtained using Omega 500 MHz and Bruker DX-400 MHz NMR spectrometers at 25 °C. ^{19}F NMR spectra were obtained using a Bruker DX-400 MHz NMR spectrometer at 25 °C. Magnetic moments were measured by the method of Evans[30,31] on a Omega 500 MHz NMR spectrometer. Infrared spectra were recorded as thin films[32] on a ASI ReactIR 1000 spectrometer or as KBr pellets on a Perkin Elmer series 1600 FTIR. Mass spectrometric data were obtained using a Micromass, model LCT electrospray Time of Flight mass spectrometer. Complexometric analyses were performed as previously described.[33] Commercial Ln$_2$O$_3$(Ln = La, Nd, Eu, Sm, Gd), (Molycorp), Ce(acac)$_3$ and Tb(acac)$_3$ (Alfa) were used without further purification (acac = acetylacetonate). 1,1,5,5,5-Hexafluoroacetylacetone (Hhfac), toluene, and diglyme were purchased from Aldrich and used without further purification. The hexanes and toluene used in the glove box were refluxed over potassium or sodium metal and distilled. Potassium and sodium metal were stored under mineral oil, freshly cut, and washed with hexanes before use. EuI$_2$(thf)$_2$[34] and {[Zr$_2$(O^{i}Pr)$_9$]Eu(μ-I)}$_2$[4] were prepared according to the literature.

Syntheses

Ce(hfac)$_3$(diglyme), 1. Diglyme (0.675 g, 5.03 mmol) was added *via* syringe to a suspension of Ce(acac)$_3$ (2.00 g, 4.57 mmol) in toluene (40 cm^3). Hhfac (2.76 g, 13.3 mmol) was added to the vigorously stirred suspension. After the mixture was stirred for 10 h at room temperature, toluene was removed under vacuum. The yellow solid was transferred to a sublimation tube and sublimed at 86 °C and 2 × 10^{-5} Torr, (3.67 g, 90%). Mp 75 °C. X-Ray quality crystals were grown from a toluene solution at −31 °C. Anal. calc. for $C_{21}H_{17}F_{18}O_9Ce$: Ce, 15.7. Found: 15.5%. ^{19}F NMR (CDCl$_3$, 20 °C) δ −74.2 (s). IR (KBr) 1649 m, 1608 s, 1558 s, 1531 s, 1496 s, 1256 m, 1202 m, 1138 m, 1091 s, 1049 s, 1010 s, 947 s, 872 s, 802 s, 660 s, 584 s cm^{-1}. Crystallographic data: $P2_1/n$, $a = 9.85(4)$, $b = 15.67(4)$, $c = 20.48(4)$ Å, $\alpha = 90.00$, $\beta = 103.85(1)$, $\gamma = 90.00°$, $V = 3067.8(4)$ Å^3.

Nd(hfac)$_3$(diglyme), 2. The preparation of **2**–**4** followed the literature procedure for the La and Gd analogs[1,2] with some modifications. Diglyme (0.703 g, 5.24 mmol) was added *via* syringe to a suspension of Nd$_2$O$_3$ (0.923 g, 2.74 mmol) in toluene (30 cm^3). Hhfac (3.11 g, 14.96 mmol) was added to the vigorously stirred suspension and the mixture was heated at reflux for 4 h. Toluene was then removed under vacuum and the solids were transferred to a sublimation tube and sublimed at 90 °C and 2 × 10^{-5} Torr to yield a purple solid (3.99 g, 89%). Mp 105 °C. X-Ray quality crystals were grown from a toluene solution at −31 °C. Anal. calc. for $C_{21}H_{17}F_{18}O_9Nd$: Nd, 16.0. Found: 16.1%. IR (KBr) 1648 m, 1602 s, 1561 s, 1548 s, 1496 m, 1485 s, 1385 s, 1259 m, 1196 m, 1139 m, 1101 m, 1048 s, 1010 s, 948 s, 872 s, 802 s, 660 s, 585 s cm^{-1}. Crystallographic data: $P2_1/n$, $a = 9.76(4)$, $b = 15.61(4)$, $c = 20.50(4)$ Å, $\alpha = 90.00$, $\beta = 103.48(1)$, $\gamma = 90.00°$, $V = 3037.5(4)$ Å^3.

Sm(hfac)$_3$(diglyme), 3. Complex **3** (9.5 g, 92%) was prepared as described for **2** from Sm$_2$O$_3$ (2.19 g, 6.28 mmol), Hhfac (7.13 g, 34.30 mmol), and diglyme (1.61 g, 12.00 mmol). It sublimes at 86 °C and 2 × 10^{-5} Torr to yield a yellow solid. Mp 116 °C. X-Ray quality crystals were grown from a solution of toluene at −31 °C. Anal. calc. for $C_{21}H_{17}F_{18}O_9Sm$: Sm, 16.6. Found: 16.8%. ^{1}H NMR (CDCl$_3$, 20 °C) δ 8.11 (s, 3H, CH), 3.28 (m), 0.29 (s), 0.22 (m, 8H, CH$_2$CH$_2$), −2.18 (s, 6H, OCH$_3$). ^{19}F NMR (CDCl$_3$, 20 °C) δ −76.5 (s). IR (KBr) 1648 m, 1602 s, 1561 s, 1448 s, 1496 m, 1485 s, 1278 m, 1215 m, 1158 m, 1078 s, 980 s, 871 s, 799 s, 660 s, 584 s, 544 s, 464 s cm^{-1}.

Eu(hfac)$_3$(diglyme), 4[4]**.** Complex **4** (6.66 g, 86%) was prepared as described for **2** from Eu$_2$O$_3$ (1.508 g, 4.285 mmol), Hhfac (5.348 g, 25.70 mmol) and diglyme (1.436 g, 10.83 mmol). It sublimes at 90 °C and 2 × 10^{-5} Torr to yield a light yellow solid. Mp 114 °C. Anal. calc. for $C_{21}H_{17}F_{18}O_9Eu$: Eu, 16.7. Found: Eu, 16.8%. ^{1}H NMR (CDCl$_3$, 20 °C) δ −1.1 (s, $\Delta\nu_{1/2}$ = 27 Hz), −0.15 (s, $\Delta\nu_{1/2}$ = 24 Hz), 0.85 (s, $\Delta\nu_{1/2}$ = 27 Hz), 0.95 (s, $\Delta\nu_{1/2}$ = 12 Hz), 1.21 (s, $\Delta\nu_{1/2}$ = 12 Hz), 1.62 (s, $\Delta\nu_{1/2}$ = 12 Hz), 2.11 (s, $\Delta\nu_{1/2}$ = 6 Hz), 4.06 (s, $\Delta\nu_{1/2}$ = 15 Hz), 10.13 (s, $\Delta\nu_{1/2}$ = 15 Hz). Magnetic susceptibility: $\chi_G^{298\ K} = 7.0 \times 10^{-6}$, $\mu_{eff}^{298\ K} = 3.9\ \mu_B$. ^{19}F NMR (CDCl$_3$, 20 °C) δ −81.9 (s). IR (KBr): 3145 w, 2957 m, 1651 s, 1601 w, 1558 m, 1531 m, 1495 s, 1464 m, 1346 m 1261 s, 1211 s, 1135 s, 1097 w, 1074 m, 1041 m, 1013 w, 976 m, 868 s, 830 w, 797 s, 764 m, 736 m, 656 s, 581 s, 530 m, 464 m cm^{-1}.

Tb(hfac)$_3$(diglyme), 5. Complex **5** was prepared following the procedure for **1** from Tb(acac)$_3$ (0.983 g, 2.15 mmol), diglyme (0.290 g, 2.16 mmol), and Hhfac (1.39 g, 6.68 mmol) in 20 cm^3 of toluene. The mixture was stirred for 12 hours at room temperature. **5** sublimed at 95 °C and 2 × 10^{-5} Torr to yield a colorless solid (1.86 g, 94%). X-Ray quality crystals of **5** precipitated when a toluene solution was undergoing rotary evaporation. Mp 85 °C. Anal. calc. for $C_{21}H_{17}F_{18}O_9Tb$: Tb, 17.4; Found: Tb, 17.1%. IR (thin film): 2949 m, 1656 s, 1559 w, 1556 m, 1529 m, 1505 m, 1486 s, 1467 m, 1251 s, 1204 s, 1150 s, 1098 w, 1054 m, 1007 m, 950 m, 876 s, 838 w, 799 s, 706 s, 660 s cm^{-1}.

[EuF(hfac)$_3$K(diglyme)]$_2$, 6. Eu(hfac)$_3$(diglyme) (0.275 g, 0.30 mmol) and potassium metal (0.120 g, 3.10 mmol) were combined in 5 mL of toluene. The color changed from light yellow to orange/brown as the reaction was stirred overnight. A fine brown solid was removed by centrifugation and the orange solution was decanted. The solution was concentrated to 1 mL by rotary evaporation and 1mL of hexane was added. Colorless crystals of **6** formed overnight from the mother liquor (0.201 g, 69 %). Anal. calc. for $C_{49}H_{42}O_{18}F_{38}K_2Eu_2$: Eu, 15.0. Found: Eu, 15.8%. Magnetic susceptibility: $\chi_G^{298\ K} = 5.9 \times 10^{-6}$, $\mu_{eff}^{298\ K} = 3.7\ \mu_B$. IR (KBr): 2925 m, 2840 m, 1731 w, 1651 s, 1599 w, 1557 m, 1534 m, 1510 m, 1468 m, 1355 w, 1257 s, 1210 s, 1146 s, 1097 m, 1046 w, 1013 w, 975 w, 942 w, 867 m, 797 m, 759 w, 637 w, 661 s, 581 m, 525 w cm^{-1}.

[SmF(hfac)$_3$K(diglyme)]$_2$, 7. Complex **7** (0.115 g, 70%) was prepared as described for **6** from crystals of **3** (0.155 g, 0.171 mmol) and potassium metal (0.067 g, 1.71 mmol) in toluene. Yellow X-ray quality crystals of **7** precipitated out of solution during rotary evaporation of toluene. Anal. calc. for $C_{49}H_{42}O_{18}F_{38}K_2Sm_2$: Sm, 15.6. Found: 16.4%. IR (thin film) 1718 m, 1664 s, 1594 s, 1494 m, 1444 m, 1254 s, 1208 s, 1150 s, 803 m cm^{-1}.

[GdF(hfac)$_3$K(diglyme)]$_2$, 8. Complex **8** (0.170 g, 84%) was prepared as described for **6** from crystals of Gd(hfac)$_3$(diglyme) (0.190 g, 0.0978 mmol) and K (0.081 g, 0.978 mmol) in toluene. Yellow X-ray quality crystals of **8** precipitated out of solution during rotary evaporation. Anal. calc. for $C_{49}H_{42}O_{18}F_{38}K_2Gd_2$: Gd, 15.5. Found: Gd, 16.0%. IR (thin film) 1718 m, 1664 s, 1594 s, 1494 m, 1444 m, 1254 s, 1208 s, 1150 s, 803 m cm^{-1}. Crystallographic data: $P\bar{1}$, $a = 12.001(3)$, $b = 12.379(3)$, $c = 13.540(3)$ Å, $\alpha = 92.888(1)$, $\beta = 114.511(1)$, $\gamma = 113.935(1)°$, $V = 1619.2(3)$ Å^3.

[NdF(hfac)$_3$K(diglyme)]$_2$, 9. Complex **9** (0.320 g, 72%) was prepared as described for **6** from crystals of **2** (0.210 g, 0.233 mmol) and K (0.091 g, 2.330 mmol). Light brown X-ray quality crystals of **9** grew overnight in a concentrated solution at −31 °C. Anal. calc. for $C_{49}H_{42}O_{18}F_{38}K_2Nd_2$: Nd, 14.4. Found: Nd, 15.0%. IR (thin film) 1718 m, 1664 s, 1594 s, 1494 m, 1444 m, 1254 s, 1208 s, 1150 s, 803 m cm^{-1}.

[Zr$_2$(O^{i}Pr)$_9$]Eu(hfac)$_2$, 10. Addition of {[Zr$_2$(O^{i}Pr)$_9$]Eu(μ-I)}$_2$ (0.370 g, 0.37 mmol) to Khfac (0.183 g, 0.75 mmol) in 5 cm^3 of thf formed a red-brown solution. Khfac was obtained from the reaction of Hhfac and potassium in toluene. After 12 h the solution was centrifuged to remove a gray precipitate. Removal of solvent from the red solution by rotary evaporation left a red-brown oil. Repeated trituration with hexanes did not give a solid product, but recrystallization from toluene at −30 °C yielded **10** as red crystals suitable for X-ray crystallography (0.247 g, 53%). Anal. calc. for $C_{37}H_{65}O_{13}F_{12}Zr_2Eu$: Eu, 11.9. Found: Eu, 10.9%. IR (thin film): 3030 w, 2968 s, 2930 m, 2864 m, 2625 w, 1660 s, 1606 m, 1494 s, 1463 m, 1363 m, 1336 w, 1254 s, 1177 s, 1150 s, 1007 s, 957 m, 833 m, 799 w, 725 m, 694 s cm^{-1}.

Formation of Eu(hfac)$_3$(diglyme) from EuI$_2$ and Khfac. Addition of diglyme (0.068 g, 0.504 mmol) and Khfac (0.248 g, 1.08 mmol) in a 5 cm^3 thf solution of EuI$_2$(thf)$_2$ (0.277 g, 0.504 mmol) formed a red-brown solution. After 14 h the solution was centrifuged to remove a gray precipitate. Removal of solvent from the red solution by rotary evaporation left a red-brown solid. Recrystallization from toluene at −31 °C yielded **4** as yellow crystals suitable for X-ray crystallography (0.30 g, 0.33 mmol).

X-Ray data collection, structure determination, and refinement for 3–7, 9, and 10. All crystals were coated with Paratone oil, mounted on glass fibers and transferred to the Bruker CCD platform diffractometer under a cold stream. The SMART[35] program package was used to determine the unit-cell parameters and for data collection. The raw frame data were processed using SAINT[36] and SADABS[37] to yield the reflection data files. Subsequent calculations were carried out using the SHELXTL[38] program. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques.

Hydrogen atoms were included using a riding model. Disorder in the CF$_3$ groups was modeled by assigning partial occupancy to the disordered components. Experimental parameters for the data collection and structure refinement of **3**–**7** and **9**–**10** are given in Table 1. Important bond distances for **3**–**7**, and **9**–**10** are given in Tables 2–4.

Sm(hfac)$_3$(diglyme), 3 and Eu(hfac)$_3$(diglyme), 4. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$ which was later determined to be correct. The fluorine atoms were disordered and included using partial site-occupancy factors (0.50 for all atom pairs). For **3** at convergence, $wR2 = 0.0497$ and GOF = 1.029 for 605 variables refined against 7313 unique data (As a comparison for refinement on F, $R1 = 0.0190$ for those 6668 data with $I > 2.0\sigma(I)$). For **4** at convergence, $wR2 = 0.0454$ and GOF = 1.097 for 591 variables refined against 7178 unique data (As a comparison for refinement on F, $R1 = 0.0193$ for those 19148 data with $I > 2.0\sigma(I)$).

Tb(hfac)$_3$(diglyme), 5. The diffraction symmetry was mmm and the systematic absences were consistent with the orthorhombic space groups $Pnma$ and $Pna2_1$. It was later determined that the noncentrosymmetric space group $Pna2_1$ was correct. At convergence, $wR2 = 0.0500$ and GOF = 1.033 for 510 variables refined against 7544 data (As a comparison for refinement on F, $R1 = 0.0202$ for those 6852 data with $I > 2.0\sigma(I)$). The absolute structure was assigned by refinement of the Flack parameter.[39]

[EuF(hfac)$_3$K(diglyme)]$_2$, 6, [SmF(hfac)$_3$K(diglyme)]$_2$, 7, and [NdF(hfac)$_3$K(diglyme)]$_2$, 9. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. Two independent molecules of the formula unit are present. Each molecule was located about an inversion center. For **6** at convergence, $wR2 = 0.1572$ and GOF = 1.064 for 855 variables refined against 16562 unique data (As a comparison for refinement on F, $R1 = 0.656$ for those 11396 data with $I > 2.0\sigma(I)$). For **7** fluorine atoms F(17), F(18) and F(19) were disordered. These atoms were included using two components with partial site-occupancy-factors (0.60/0.40). For **7** at convergence, $wR2 = 0.0628$ and GOF = 1.026 for 487 variables refined against 7666 unique data (As a comparison for refinement on F, $R1 = 0.0247$ for those 7216 data with $I > 2.0\sigma(I)$). For **9** there was one molecule of toluene solvent present per formula unit. At convergence, $wR2 = 0.1283$ and GOF = 1.030 for 977 variables refined against 17150 data (As a comparison for refinement on F, $R1 = 0.0492$ for those 13659 data with $I > 2.0\sigma(I)$).

[Zr$_2$(O^{i}Pr)$_9$]Eu(hfac)$_2$, 10. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space groups Cc and $C2/c$. It was later determined that the centrosymmetric space group $C2/c$ was correct. The molecule was located on a two-fold rotation axis. All fluorine atoms and C(18) were disordered and included using multiple components with partial site-occupancy-factors. There was one molecule of toluene solvent present per formula unit. The solvent molecule was also located on a two-fold axis and was disordered. Hydrogens associated with disordered carbon atoms and with the solvent molecule were not included in the refinement. At convergence, $wR2 = 0.1398$ and GOF = 1.098 for 315 variables refined against 6764 unique data (As a comparison for refinement on F, $R1 = 0.0505$ for those 6083 data with $I > 2.0\sigma(I)$).

CCDC reference numbers 171876–171881 and 177170.

See http://www.rsc.org/suppdata/dt/b1/b104095m/ for crystallographic data in CIF or other electronic format.

Conclusion

The stable class of monometallic hfac lanthanide complexes of the type Ln(hfac)$_3$(diglyme) (Ln = La, Gd) has been extended to Ce, Nd, Sm, Eu, and Tb. The reaction of potassium with these complexes can be used to generate a new class of heterometallic trivalent lanthanide hexafluoroacetylacetonate complexes namely the potassium salts [LnF(hfac)$_3$K(diglyme)]$_2$ (Ln = Eu, Sm, Gd, and Nd). In these studies the hfac ligand has demonstrated a tendency to stabilize the higher oxidation state of europium, since the trivalent Eu(III) hfac complexes, Eu(hfac)$_3$(diglyme) and [Zr$_2$(O^{i}Pr)$_9$]Eu(hfac)$_2$, are also the main products isolated from Eu(II) precursors and Khfac.

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