

Synthesis and characterization of volatile cerium(IV) hexafluoroisopropoxide complexes. Structure of $[\text{Hpmdien}]_2[\text{Ce}\{\text{OCH}(\text{CF}_3)_2\}_6]$

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The reaction between the cerium isopropoxide $[\text{Ce}_2(\text{OPr}^i)_8(\text{Pr}^i\text{OH})_2]$ and hexafluoroisopropyl alcohol (Hhfp) in THF at room temperature resulted in the formation of $[\text{Ce}(\text{hfp})_4(\text{THF})_2(\text{Pr}^i\text{OH})_x]$. More stable compounds namely $[\text{Ce}(\text{hfp})_4(\text{diglyme})]$, $[\text{Ce}(\text{hfp})_4(\text{bipy})_2]$ and $[\text{Ce}(\text{hfp})_4(\text{tmen})]$ were obtained if the alcoholysis was achieved in the presence of a Lewis base (diglyme = 2,5,8-trioxanonane, bipy = 2,2'-bipyridine, tmen = *N,N,N',N'*-tetramethylethane-1,2-diamine). The use of *N,N,N',N'',N''*-pentamethyldiethylenetriamine (pmdien) afforded $[\text{Hpmdien}]_2[\text{Ce}(\text{hfp})_6]$ and $[\text{Ce}(\text{hfp})_3(\text{OPr}^i)(\text{pmdien})]$. All compounds were volatile and characterized by elemental analyses, FT-IR, ¹H and ¹⁹F NMR. The pmdien salt was also characterized by X-ray diffraction. The cerium atom is six-co-ordinated [Ce–O 2.183(5)–2.208(5) Å] with the CF₃ groups forming nearly a crown (Ce···F 4.06–4.32 Å). The metallic anion $[\text{Ce}(\text{hfp})_6]^{2-}$ and the $[\text{Hpmdien}]^+$ cations are associated by a short F···C contact (3.15 Å). The interactions are retained in solution as evidenced by ¹H and ¹⁹F NMR.

Cerium oxide is an interesting candidate for several areas of technological applications due to its high chemical stability,¹ interesting optical properties² and low lattice mismatch to high *T_c* superconductors and silicon, and thus its potential value for buffer layers.³ Fluoride on the other hand is involved in the formulation of γ scintillations.⁴ Different methods have been used for the deposition of ceria thin films. Chemical routes, namely sol-gel processing and metal-organic chemical vapour phase deposition (MOCVD) are flexible and quite cheap with respect to physical methods.⁵ However, they rely on the availability of appropriate precursors. The MOCVD processes have a great potential for CeO₂ layers having the quality required for microelectronic applications but only a few volatile cerium derivatives have been reported. Although some volatile cerium(III) alkoxides or aryl oxides are known,^{5a} β -diketonates mostly have been used for the growth of CeO₂ layers. These precursors are essentially $[\text{Ce}(\text{thd})_4]$ (thd = 2,2,6,6-tetramethylheptane-3,5-dionate)^{6,7} and the fluorinated derivatives $[\text{Ce}(\text{fdh})_4]$ (fdh = 1,1,1-trifluoro-5,5-dimethylhexane-2,4-dionate).⁸ Some stable cerium(III) fluorinated β -diketonate adducts namely $[\text{Ce}(\text{fdh})_3(\text{phen})]$,⁸ $[\text{Ce}_2(\text{fod})_6(\text{tetraglyme})]$ ⁹ (fod = heptafluoro-2,2-dimethyloctane-3,5-dionate, tetraglyme = 2,5,8,11,14-pentaoxapentadecane) and more recently $[\text{Ce}_2(\text{etbd})_6(\text{tetraglyme})]$ and $[\text{NH}_4][\text{Ce}(\text{etbd})_4]$ (etbd = 1-ethoxy-4,4,4-trifluorobutane-1,3-dionate) have been reported.¹⁰ A volatile cerium(IV) methylpivaloylmethanate has also been obtained in our group.^{5b} Fluorinated alkoxides have been shown to give access to volatile homo- and hetero-metallic derivatives for yttrium¹¹ and trivalent lanthanides,¹² and transition metals such as zirconium.¹³

We report here our investigations on the synthesis and characterization of the cerium(IV) hexafluoroisopropoxide $[\text{Ce}(\text{hfp})_4(\text{THF})_2]$. More stable and volatile adducts namely $[\text{Ce}(\text{hfp})_4(\text{diglyme})]$, $[\text{Ce}(\text{hfp})_4(\text{bipy})_2]$ and $[\text{Ce}(\text{hfp})_4(\text{tmen})]$

were obtained with polydentate Lewis bases (diglyme = 2,5,8-trioxanonane, bipy = 2,2'-bipyridine, tmen = *N,N,N',N'*-tetramethylethane-1,2-diamine). The use of *N,N,N',N'',N''*-pentamethyldiethylenetriamine (pmdien) afforded $[\text{Hpmdien}]_2[\text{Ce}(\text{hfp})_6]$ and $[\text{Ce}(\text{hfp})_3(\text{OPr}^i)(\text{pmdien})]$. All compounds were volatile and characterized by elemental analyses, FT-IR, ¹H and ¹⁹F NMR. The salt $[\text{Hpmdien}]_2[\text{Ce}(\text{hfp})_6]$ was also characterized by X-ray diffraction and shown to comprise ion pairs associated by F···C interactions.

Experimental

All manipulations were routinely performed under a nitrogen atmosphere using Schlenk tubes and vacuum line techniques with dried and distilled solvents. Hexafluoroisopropyl alcohol (Hhfp) (Aldrich) was stored over molecular sieves and used as received. The compound $[\text{Ce}_2(\text{OPr}^i)_8(\text{Pr}^i\text{OH})_2]$ was prepared according to the literature.¹⁴ Proton, ¹³C and ¹⁹F NMR spectra were recorded on solutions on a Bruker AC-200 spectrometer. The fluorine chemical shifts are reported with respect to CFCl₃, positive to low field. Infrared spectra were registered with a Perkin-Elmer FT-IR Paragon 500 spectrometer as Nujol mulls between KBr plates. Analytical data were obtained from the Centre de Microanalyses du CNRS.

Syntheses

$[\text{Ce}(\text{hfp})_4(\text{THF})_2]$ 3. A solution of ammonium cerium(IV) nitrate (0.72 g, 1.32 mmol) in 10 ml of THF was added dropwise to sodium hexafluoroisopropoxide (1.5 g, 7.96 mmol) in 10 ml of THF. Evolution of ammonia and formation of a white precipitate was observed. After stirring for 3 h, filtration followed by evaporation of the filtrate to dryness left 1 g of a beige powder analysing as $[\text{Ce}(\text{hfp})_4(\text{THF})_2(\text{H}_2\text{O})_{0.5}]$ (IR and ¹H NMR evidence). Sublimation at 120 °C under 10⁻³ mmHg gave compound **3**. IR (cm⁻¹): 1288s, 1265s, 1214s, 1184s, 1151s, 1100s [$\nu(\text{C}-\text{F})$, $\nu(\text{C}-\text{O})$]; 1015m, 892m, 846m, 742m, 687m, 656m; 530 (sh), 515m, 377m [$\nu(\text{Ce}-\text{OR})$]. ¹H NMR (CDCl₃):

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δ 4.95 (m, 4 H, CH), 4.05 (t, 8 H, α -CH₂, $J = 5.4$) and 1.95 (q, 8 H, β -CH₂, $J = 5.4$ Hz). ¹³C-¹H NMR (CDCl₃): δ 129 (CH), 123, 117 (CF₃); 70 (α -CH₂) and 24 (β -CH₂). ¹⁹F NMR (CDCl₃): δ 76.8 (d, $J = 5.5$ Hz).

An alternative synthesis was the alcohol exchange between [Ce₂(OPrⁱ)₈(PrⁱOH)₂] and hexafluoroisopropyl alcohol (8 equivalents) in THF at room temperature. After 5 h the solution was stripped to dryness. Recrystallization in hexane–THF (1:1) gave yellow crystals (89%) analysing as [Ce(hfip)₄(THF)₂(PrⁱOH)_{0.35}]. Sublimation at 100 °C (10⁻³ mmHg) gave **3**. This compound is soluble in common organic solvents excluding aliphatic hydrocarbons.

[Ce(hfip)₄(diglyme)] 4. Hexafluoroisopropyl alcohol (0.98 ml, 9.3 mmol) diluted in 15 ml of THF was added to a solution of [Ce₂(OPrⁱ)₈(PrⁱOH)₂] (1.01 g, 1.16 mmol) in 15 ml of THF. Diglyme (0.33 ml, 2.32 mmol) was added after 2 h. Stirring was maintained for 1 h more and the reaction medium was stripped to dryness. The crude product was recrystallized in hexane–THF (1:1). Yellow crystals (1.6 g, 73%) of compound **4** were obtained. Sublimation was observed at 70 °C under 10⁻⁴ mmHg, mp 234 °C, decomp. 250 °C (Found: C, 22.87; H, 1.92. Calc. for C₁₈H₁₈CeF₂₄O₇: C, 22.92; H, 1.91%). IR (cm⁻¹): 1285s, 1262s, 1216s, 1175s, 1153s, 1101s [ν (C–O), ν (C–F)]; 1055s, 1009m, 957s, 889m, 877m, 844m, 742s, 688s, 658m; 533m, 513m, 372m [ν (Ce–OR)]. ¹H NMR (CDCl₃): δ 5.15 (spt, 4 H, CH, $J = 5.5$ Hz), 3.95 (s, 8 H, CH₂) and 3.85 (s, 6 H, Me). ¹⁹F NMR (CDCl₃): δ -76.52 (d, $J = 5.9$ Hz).

[Ce(hfip)₄(bipy)₂] 5. Same procedure but with addition of bipyridine (4 equivalents). After 3 h the reaction medium was evaporated to dryness. The yellow powder was washed several times with hexane (90%). Sublimation was achieved at 120 °C (10⁻⁴ mmHg), mp 200 °C, decomp. 230 °C (Found: C, 33.76; H, 1.77; N, 4.94. Calc. for C₃₂H₂₀CeF₂₄N₄O₄: C, 34.28; H, 1.78; N, 4.99%). IR (cm⁻¹): 1601m [ν (C=C)], 1577m [ν (C=N)], 1291s, 1262s, 1216s, 1170s, 1142s, 1095s [ν (C–O), ν (C–F)]; 1009m, 889m, 846m, 762m, 741m, 688m, 649m, 642m, 624m; 521m, 510s, 418m [ν (Ce–OR)]. ¹H NMR (CDCl₃): δ 9.68 (m, 4 H, CH), 8.25 (d, 4 H, CH, $J = 7$), 8.05 (t, 4 H, CH, $J = 7$ Hz), 7.50 (t, 4 H, CH, $J = 7$ Hz) and 4.09 (m, 4 H, CH). ¹⁹F NMR (CDCl₃): δ -76.35 (d, $J = 6.0$ Hz).

[Ce(hfip)₄(tmen)] 6. The compound tmen (4 equivalents; 1.45 ml, 9.6 mmol) was added to a solution of [Ce₂(OPrⁱ)₈(PrⁱOH)₂] (2.1 g, 2.4 mmol) and hexafluoroisopropyl alcohol (2.03 ml, 9.6 mmol) in toluene (30 ml). After crystallization, 3 g (67%) of yellow crystals of **6** were obtained, sublimation at 74 °C (10⁻⁴ mmHg), mp 155 °C, decomp. 200 °C, soluble in diethyl ether, THF, DME and insoluble in hexane and PrⁱOH (Found: C, 23.80; H, 2.45; N, 3.20. Calc. for C₁₈H₂₀CeF₂₄N₂O₄: C, 23.38, H, 2.18; N, 3.03%). IR (cm⁻¹): 1291s, 1268s, 1211s, 1183s, 1148s, 1103s [ν (C–O), ν (C–F)], 1018m, 977w, 972w, 949m, 893s, 845s, 790m, 741s, 688s, 653m, 614w; 585w, 534 (sh), 521m, 516m, 465w, 437 [ν (Ce–OR)]. ¹H NMR (CDCl₃): δ 5.13 (spt, 4 H, CH, $J = 6$ Hz), 2.98 (s, 4 H, CH₂) and 2.75 (s, 12 H, CH₃). ¹⁹F NMR (CDCl₃): δ -76.10 (d, $J = 5.0$ Hz). ¹³C-¹H NMR (CDCl₃): δ 80.19, 79.53 (OCH); 57.37 (CH₂); 47.20, 45.72 (Me). Soluble in diethyl ether, toluene, THF, DME, insoluble in hexane and PrⁱOH.

[Hpmdien]₂[Ce(hfip)₆] 7 and [Ce(hfip)₃(OPrⁱ)(pmdien)] 8. The compound Hhfp (0.525 ml, 5 mmol) in 10 ml of THF was added to a solution of [Ce₂(OPrⁱ)₈(PrⁱOH)₂] (0.545 g, 0.62 mmol) in 10 ml of THF. Pentamethyldiethylenetriamine (0.521 ml, 2.49 mmol) was added. Yellow crystals of **7** (0.74 g, 40%) (soluble in THF and alcohols but insoluble in hexane) and orange crystals of **8** (0.16 g, 15%) were obtained by recrystallization of the crude product in toluene.

Compound **7** (mp 113 °C, decomp. 182 °C), sublimed

at 70 °C at 10⁻⁴ mmHg, in 85% yield if the preceding reaction was achieved with an excess of hexafluoroisopropyl alcohol (Found: C, 28.37; H, 3.68; N, 5.65. Calc. for C₃₆H₅₄CeF₃₆N₆O₆: C, 28.97; H, 3.62; N, 5.63%) IR (cm⁻¹): 3453w [ν (N–H)], 1285s, 1211s, 1164s, 1160s, 1091s [ν (C–O), ν (C–F)]; 1028m, 1000vs, 972m, 881m, 841s, 779m, 767m, 739m, 682s, 648m; 546m, 532m, 516m, 506m [ν (Ce–OR)]. ¹H NMR (CDCl₃): δ 8.76 (s, 2 H, NH), 5.34 (m, 2 H, CH), 4.50 (m, 4 H, CH), 2.65 (m, 6 H, Me), 2.51 (s, 16 H, CH₂), 2.31 (s, 12 H, Me) and 2.29 (s, 12 H, Me). ¹⁹F NMR (CDCl₃): δ -74.78 (d, $J = 5.0$) and -76.19 (d, $J = 5.1$ Hz).

Compound **8**, soluble in the usual organic solvents (toluene, THF, CHCl₃) (Found: C, 25.30; H, 3.53; N, 4.93. Calc. for C₂₁H₃₃CeF₁₈N₃O₄: C, 28.84; H, 3.77; N, 4.80%). IR (cm⁻¹): 1286s, 1262s, 1211s, 1168s, 1090s [ν (C–O), ν (C–F)]; 964s, 886m, 843s, 801m, 740s, 686s, 648m; 568m, 533m, 520m, 509m [ν (Ce–OR)]. ¹H NMR (CDCl₃): δ 5.29 (m, br, 3H, CH), 5.20 [spt, 1 H, CH(Prⁱ), $J = 6$], 3.25 (m, 4 H, CH₂), 2.66 (s, 12 H, Me), 2.55 (s, 3 H, Me), 2.38 (m, 4 H, CH₂) and 1.13 (d, 6 H, Me, $J = 6$ Hz). ¹⁹F NMR (CDCl₃): δ -75.53 (d, $J = 5.0$ Hz).

Crystallography

Suitable crystals of compound **7** were obtained directly from the reaction medium. Accurate cell dimensions and orientation matrices were obtained by least-squares refinements of 25 accurately centered reflections. No significant variations were observed in the intensities of three checked reflections during data collection. Complete crystallographic data and collection parameters are listed in Table 1. The data were corrected for Lorentz-polarization effects. Computations were performed by using the PC version of CRYSTALS.¹⁵ Scattering factors and corrections for anomalous absorption were taken from ref. 16. The structure was solved by Patterson techniques and refined by full-matrix least squares with anisotropic thermal parameters for all atoms. Hydrogen atoms on carbon atoms were introduced in calculated positions.

CCDC reference number 186/1135.

See <http://www.rsc.org/suppdata/dt/1998/3437/> for crystallographic files in .cif format.

Results and discussion

Synthesis and characterization

The alcohol exchange reaction between the cerium isopropoxide [Ce₂(OPrⁱ)₈(PrⁱOH)₂] and hexafluoroisopropyl alcohol [Hhfp = OHCH(CF₃)₂] (1:8 stoichiometry) in THF at room temperature afforded a cerium hexafluoropropoxide adduct **1**. Proton NMR and FT-IR data indicate the presence of THF as well as PrⁱOH ligands, the overall formula being [Ce(hfip)₄(THF)₂(PrⁱOH)_x] ($x \approx 0.35$). An analogous adduct [Ce(hfip)₄(THF)₂(H₂O)_{0.5}]**2** was obtained by treating ammonium cerium(IV) nitrate [(NH₄)₂Ce(NO₃)₆] and sodium hexafluoroisopropoxide (1:6) in THF. The presence of residual PrⁱOH or water probably retained by hydrogen bonding, as observed for other fluoroalkoxides,^{12,13} was evidenced by absorption bands between 3370 and 3170 cm⁻¹ in the infrared spectra. Sublimation of either **1** or **2** proceeded with elimination of the hydroxyl type ligands PrⁱOH or water giving the [Ce(hfip)₄(THF)₂] adduct **3**. This was however extremely moisture sensitive giving hydrates [ν (OH) 3300, 3195, γ (OH) 1700, 1623 cm⁻¹] and no satisfactory analytical data could thus be obtained. Anhydrous **3** was recovered after sublimation. The facility of substituting all OR groups on cerium isopropoxide contrasts with the observations on [Zr₂(OPrⁱ)₈(PrⁱOH)₂]¹³ or Ti(OPrⁱ)₄¹⁷ which failed to give [M(hfip)₄] (M = Ti or Zr) by alcoholysis even by refluxing in toluene.

Stabilization of cerium hexakis(hexafluoroisopropoxide) was achieved by complexation with various multidentate O- or N-donors. Such ligands have been largely used as a means

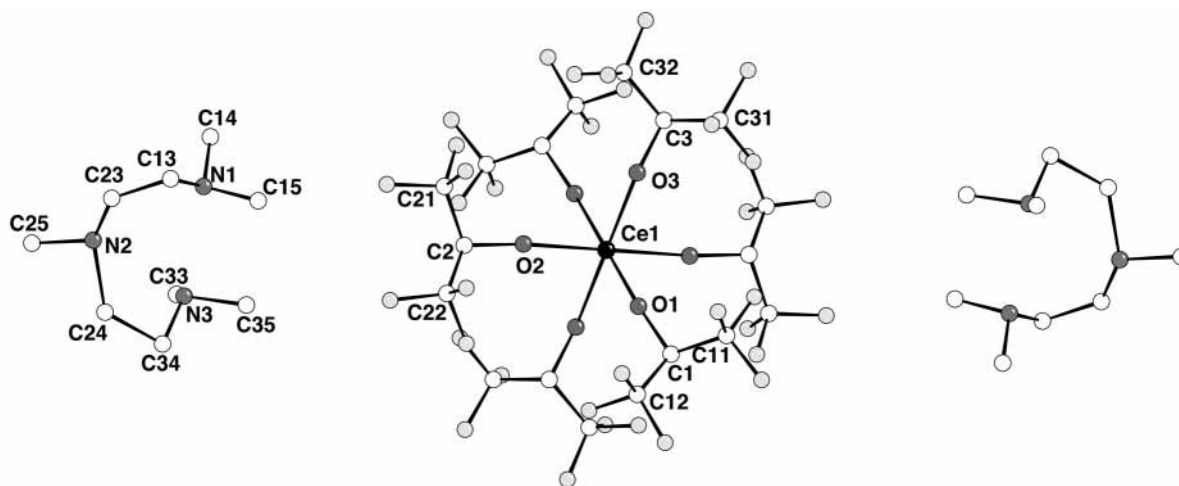
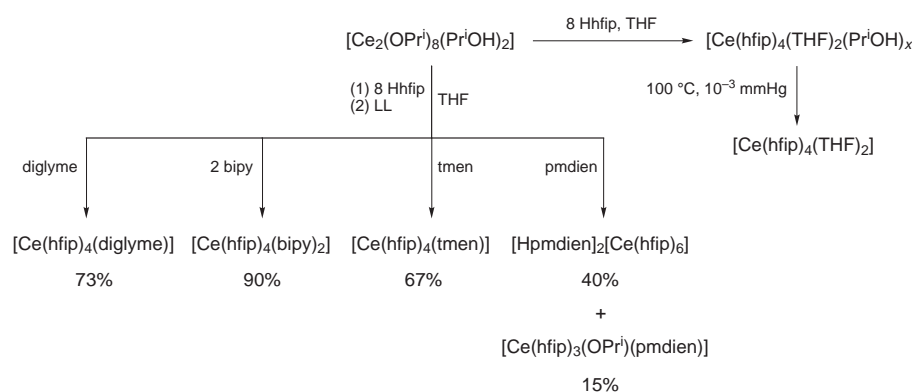


Fig. 1 Ball and stick drawing of $[\text{Hpmdien}]_2[\text{Ce}(\text{hfip})_6]$.



Scheme 1

to improve the stability of barium derivatives.^{5,18} These, namely diglyme, bipy and tmen were added to the reaction medium after alcoholysis of $[\text{Ce}_2(\text{OPr})_8(\text{Pr}^i\text{OH})_2]$ in THF. The $[\text{Ce}(\text{hfip})_4(\text{diglyme})]$ **4**, $[\text{Ce}(\text{hfip})_4(\text{bipy})_2]$ **5** and $[\text{Ce}(\text{hfip})_4(\text{tmen})]$ **6** complexes were isolated in high yields as slightly yellow solids. The reaction achieved in the presence of pmdien was more complicated and two compounds namely $[\text{Hpmdien}]_2[\text{Ce}(\text{hfip})_6]$ **7** and $[\text{Ce}(\text{hfip})_3(\text{OPr})(\text{pmdien})]$ **8** were isolated under similar conditions (in 40 and 15% yield respectively). The formation of the heteroleptic species **8** was disfavored if the alcoholysis of $[\text{Ce}_2(\text{OPr})_8(\text{Pr}^i\text{OH})_2]$ was achieved in hexane with a large excess of hexafluoroisopropyl alcohol (1 : 12) and **7** was then isolated in 85% yield. The various synthetic routes are collected in Scheme 1. The compounds were characterized by elemental analysis, FT-IR, ^1H and ^{19}F NMR and by single crystal X-ray analysis for **7**.

The FT-IR spectra are characterized by very intense broad bands around $1290\text{--}1100\text{ cm}^{-1}$ corresponding to the C–F vibrations. Additional sharp bands due to the co-ordinated Lewis base are present but are shifted with respect to the free base [$\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ at 1601 and 1577 cm^{-1} for **5** by comparison to 1583 and 1561 cm^{-1} for unco-ordinated bipyridine for instance]. Sharp absorption bands of the Ce–OR bonds are also observed below 600 cm^{-1} .

The solubility of all compounds allowed their characterization by NMR. The integration ratio between the multiplet of hfip and the peaks due to the neutral base confirm the analytical formulation. The spectra of the $\text{Ce}(\text{hfip})_4$ adducts **4**, **5** and **6** display an unique multiplet for the CH groups in the proton spectra and a single doublet around $\delta -76$ in the ^{19}F NMR spectra. These data suggest that the hexafluoroisopropoxide ligands are magnetically equivalent or that the species are dynamic on the NMR time scale. By contrast, two types of hexafluoroisopropoxide ligands are observed for **7**, either by ^1H

or ^{19}F NMR. Complexes **4** and **6** are characterized in the ^1H NMR by multiplets around $\delta 5.15$. The resonances of the neutral ligands diglyme and tmen are shifted to low field on coordination. The diglyme ligand appears as two singlets at $\delta 3.95$ and 3.85 for the CH_2 and methyl groups respectively thus suggesting a tridentate co-ordination mode. The tmen ligand resonates at $\delta 2.75$ and 2.98 . The $[\text{Ce}(\text{hfip})_4(\text{bipy})_2]$ adduct is characterized by a CH multiplet at much higher field, $\delta 4.09$. One set of signals (multiplets at $\delta 9.68$, 8.25 , 8.05 and 7.50) is observed for the two bipyridine ligands. Beside the signals of two types of hexafluoroisopropoxide ligands, the ^1H NMR spectra of compound **7** show the peaks corresponding to the CH_2 , NMe and NMe_2 groups of the triamine ligand as well as a broad singlet at $\delta 8.76$ suggesting its protonation. The spectra of $[\text{Ce}(\text{hfip})_3(\text{OPr})(\text{pmdien})]$ **8** are characterized by two types of CH protons attributed to the two types of alkoxide ligands in contrast to **7**, no signal is detected at lower field.

The formulation of compounds **3**, **4** and **6** suggests that the metal is six-co-ordinated. The volatility and spectroscopic data of **5** suggest that both bipyridine molecules are linked to the metal which should thus be eight-co-ordinated. Such a co-ordination number has been observed for $[\text{Ce}(\text{thd})_4]$ or $\text{Na}[\text{Ce}(\text{fdh})_4]$,⁷ or $[\text{Ce}_2(\text{etbd})_6(\text{tetraglyme})]$.¹⁰ Cerium is probably seven-co-ordinated in $[\text{Ce}(\text{hfip})_4(\text{diglyme})]$ or $[\text{Ce}(\text{hfip})_3(\text{OPr})(\text{pmdien})]$; this co-ordination number was observed for $[\text{Ce}_4\text{O}(\text{OPr})_{14}]$.¹⁹ The same co-ordination number would be observed for a neutral $[\text{Ce}(\text{hfip})_4(\text{pmdien})]$ species with a tridentate behaviour for the amine. The ionic species $[\text{Hpmdien}]_2[\text{Ce}(\text{hfip})_6]$ is apparently more stable probably as a result of the formation of a very symmetrical anion. The ability of cerium to achieve co-ordination numbers higher than six as well as the high Lewis acidity of fluoroalkoxides might explain the poor stability of the $[\text{Ce}(\text{hfip})_4(\text{THF})_2]$ adduct with respect to hydration.

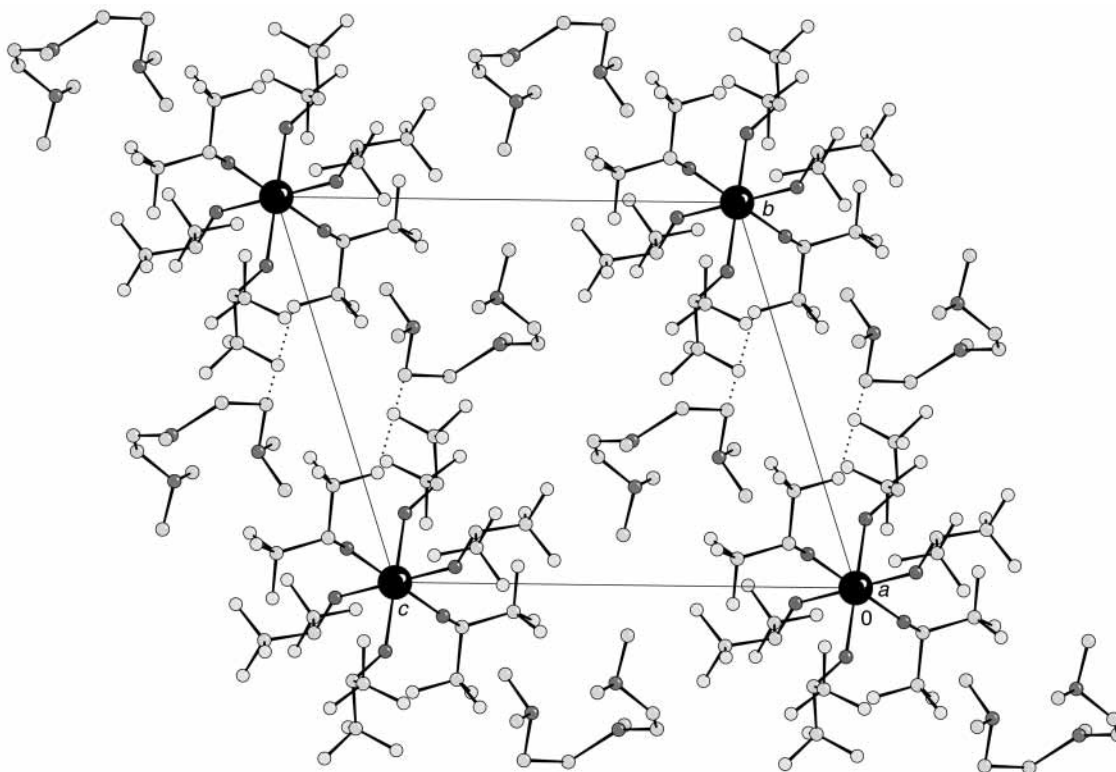


Fig. 2 Packing of $[\text{Hpmdien}]_2[\text{Ce}(\text{hfp})_6]$ (projection on the bc plane).

Table 1 Crystal data for $[\text{Hpmdien}]_2[\text{Ce}(\text{hfp})_6]$

Formula	$\text{C}_{36}\text{H}_{54}\text{CeF}_{36}\text{N}_6\text{O}_6$
M	1491
$a/\text{\AA}$	10.421(4)
$b/\text{\AA}$	11.709(3)
$c/\text{\AA}$	13.101(7)
α°	71.34(3)
β°	83.98(4)
γ°	77.03(3)
$V/\text{\AA}^3$	1475(1)
Z	1
Crystal system	Triclinic
Space group	$P\bar{1}$
μ/cm^{-1}	9.36
T/K	225
Number of data collected	5496
Number of unique data	5183
Number of unique data used for refinement	3009 $[(F_o)^2 > 3\sigma(F_o)^2]$
$R(\text{int})$	0.0356
R	0.0511
R'	0.0597

Molecular structure of compound 7

Compound 7 was fully characterized by X-ray diffraction. The structure is depicted in Figs. 1 and 2, selected bond lengths and angles in Table 2. The structure is based on a centrosymmetrical $[\text{Ce}(\text{hfp})_6]^{2-}$ anion associated to two $[\text{Hpmdien}]^+$ cations (since the H atoms on the nitrogen were not located, the NH bonds of the cations result essentially from the FT-IR, NMR and considerations of charge balance). The surrounding of the six-co-ordinated cerium atom is quite regular [Ce–O distances 2.183(5)–2.208(5) Å] with O–Ce–O angles close to 90° and the hexafluoroisopropoxide ligands form nearly a crown around the metal. The shortest cerium–fluorine distance corresponds to $\text{Ce}\cdots\text{F}(113)$ with a value of 4.06 Å. Its symmetrical bond and ten other Ce \cdots F–C distances are found in the range 4.18–4.32 Å which means that each hfp ligand provides two fluorine atoms for a weak interaction with the metal. Activation of

Table 2 Selected interatomic distances (Å) and angles ($^\circ$) for compound 7

Ce(1)–O(1)	2.208(5)	Ce(1)–O(3)	2.203(5)
Ce(1)–O(2)	2.183(5)		
O(1)–Ce(1)–O(2)	88.9(2)	O(1)–Ce(1)–O(2')	91.1(2)
O(1)–Ce(1)–O(3)	90.1(2)	O(1)–Ce(1)–O(3')	89.9(2)
O(2)–Ce(1)–O(3)	89.9(2)	O(2)–Ce(1)–O(3')	90.1(2)
Ce(1)–O(1)–C(1)	144.7(5)	Ce(1)–O(2)–C(2)	156.5(5)
Ce(1)–O(3)–C(3)	143.3(5)		

carbon–fluorine bonds by metallic species has been observed in a number of complexes giving short $\text{M}\cdots\text{F}\cdots\text{C}$ interactions.²⁰ These distances are however much longer than the Ce–O bond lengths or the sum of the van der Waals radii (≈ 3.20 Å) and than the interactions found for barium derivatives (usually 3–3.20 Å).¹¹

The Ce–O bond distances are longer than those observed for non-fluorinated terminal Ce–OR {2.088 Å av. for $[\text{Ce}_2(\text{OPr}^i)_8(\text{Pr}^i\text{OH})_2]$ } and comparable to the Ce–HOPrⁱ coordination bonds.¹⁴ The Ce–O–C angles associated to the hexafluoroisopropoxide ligands are also smaller than those observed for usual OR ligands which are more prone to π bonding. These data are consistent with the observations on other metallic fluoroalkoxides.^{11,13} However the Ce–O(2)–C(2) angle is significantly larger (156.5°) than that of the other fluoroalkoxide groups (average 144.0°). Examination of the interactions between the anion and the cation shows a short $\text{F}\cdots\text{C}$ contact (3.15 Å), whereas the shortest $\text{N}\cdots\text{F}$ distances, between N(3) and F(111) and N(3) and F(122), have values of 3.917 and 4.050 Å respectively. The $\text{N}\cdots\text{F}$ distances are relatively long but the $\text{F}\cdots\text{H}\cdots\text{C}$ are shorter than those observed for $[\text{Htmn}]_2[\text{Sr}(\text{tfpd})_4]$ (tfpd = 1,1,1-trifluoropentane-2,4-dionate) [3.342(5)–3.499(5) Å].²¹ The opening of the Ce–O(2)–C(2) angle is thus probably related to the short $\text{F}(222)\cdots\text{C}(34)$ contact of 3.15 Å (C–H 1.20 Å, $\text{H}\cdots\text{F}$ distance smaller than the sum of the van der Waals radii). These interactions are apparently retained in the CDCl_3 solutions used for NMR thus giving rise

to two types of signals in a 2:4 ratio and **7** can be considered as tight cation-anion pairs. The protonated amine cations observed in complex **7** result probably because of proton transfer from free Pr^+OH to the amine ligand in solution as observed for $[\text{Htmen}]_2[\text{Sr}(\text{tfpd})_4]$ and $[\text{Hpmdien}]_2[\text{M}(\text{tfpd})_4]$ ($\text{M} = \text{Sr}$ or Ba).²¹ The ion $[\text{Ce}(\text{hfip})_6]^{2-}$ expands the range of non- or weakly co-ordinating anions based on metals and fluorinated alkoxide ligands.^{22,23}

Physical properties

The ligand exchange reactions between $[\text{Ce}(\text{hfip})_4(\text{THF})_2]$ and chelating ligands afforded more air stable derivatives, the order of stability being $[\text{Ce}(\text{hfip})_4(\text{tmen})] < [\text{Ce}(\text{hfip})_4(\text{diglyme})] \ll [\text{Ce}(\text{hfip})_4(\text{bipy})_2]$. All these compounds are volatile and sublime unchanged (no loss of the Lewis base occurs during volatilization). We notice that although THF is labile and could be exchanged in solution by multidentate ligands, the compound is thermally stable. Most adducts display melting points around 200 °C while sublimation was observed in the range 70–120 °C (under 10^{-4} mmHg), depending on the molecular weight thus providing a temperature window for practical use.

At first glance the volatility of compound **7** was surprising. Volatility has however also been reported for a number of trivalent lanthanide fluoro- β -diketonates involving anions. These are associated with various cations such as alkali metals as observed for $\text{Cs}[\text{Y}(\text{hfac})_4]^{24}$ or $\text{Na}[\text{Ce}(\text{fdh})_4]^{25}$ or protonated amines such as $[\text{Et}_2\text{NH}_2][\text{Er}(\text{hfac})_4]^{26}$ whereas the recently reported $[\text{Y}(\text{hfac})_2(\text{triglyme})]^+[\text{Y}(\text{hfac})_4]^-$ ²⁷ provides another example of a cationic counter ion (Hhfac = 1,1,1,3,3,3-hexafluoropentane-2,4-dione). Related species were found for alkaline earth metals namely $[(\text{H}_2\text{en})_{1.5}[\text{Ba}(\text{hfac})_5] \cdot \text{EtOH}]^{28}$ and $[\text{Htmen}]_2[\text{Sr}(\text{tfpd})_4]$. The latter is however only volatile under mass spectrometry conditions.²¹ Hydrogen bonding between the protonated amines and the fluorinated β -diketonate appears as a general feature for these compounds. Hydrocarbon soluble alkoxides based on ion pairs are not unprecedented. Representative examples are $\{[\text{Me}_2\text{NH}_2][\text{Pb}(\text{hfip})_3]\}_2^{29}$ and $[\text{Me}_2\text{NH}_2]^+[\text{Al}(\text{OSiMe}_3)_4]^-$; they were obtained by alcoholysis of the metallic amide. Ion pairs associated by hydrogen bonding between oxygen atoms on the siloxides and hydrogen atoms of the dimethylammonium cations are found in the solid for the aluminum species. It sublimes under dynamic vacuum but with some decomposition to $\text{Al}_2(\text{OSiMe}_3)_6$.³⁰ No volatility data were reported for the lead species.

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