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Synthesis, Bonding, and Reactivity of a Cerium(IV) Fluoride Complex

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Ⓢ *Supporting Information*

ABSTRACT: Oxidation of Ce[N(SiMe$_3$)$_2$]$_3$ in the presence of PF$_6^-$ or BF$_4^-$ afforded isolation of CeF[N(SiMe$_3$)$_2$]$_3$. Structural and electrochemical characterization shows that this compound is in its tetravalent oxidation state and contains a terminal fluoride ligand. Spectroscopy and density functional theory have been used to characterize the Ce−F bond as ionic, which is reinforced by an initial reactivity study that demonstrates the nucleophilicity of the fluoride ligand.

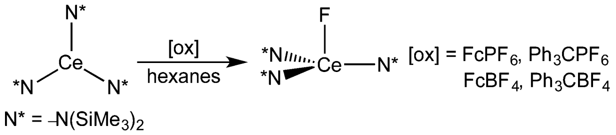
Owing to the utility of fluorinated compounds in pharmaceutical and industrial chemistry, the area of synthetic fluorine chemistry is a rapidly developing field.[1] While many examples of metal fluoride coordination compounds have been reported in transition-metal chemistry,[2] main-group chemistry,[3] and actinide chemistry,[4] few examples are known in lanthanide chemistry.[5] The highly electropositive nature of the lanthanides promotes strong bonding with hard fluoride ions, stabilizing divalent, trivalent, and tetravalent lanthanide fluoride materials.[6] To date, several examples of terminal trivalent lanthanide fluorides have been reported in molecular chemistry.[7] In tetravalent lanthanide chemistry, an interesting solvate of CeF$_4$, [CeF$_4$(NH$_3$)$_4$]·NH$_3$, has been characterized and contains CeF$_4$(NH$_3$)$_4$ units interconnected in an extended lattice by F---H−N hydrogen-bonding interactions (Figure S1 in the Supporting Information, SI).[8] We reasoned that a coordination complex containing a terminal fluoride ligand bound to a cerium(IV) ion would maximize the ionicity of the metal−ligand bond and could therefore serve as a novel source of nucleophilic fluoride.

Although the tetravalent oxidation state of cerium has been shown to be accessible in nonaqueous coordination chemistry,[9] isolation of cerium(IV) coordination complexes by one-electron oxidation reactions is quite sensitive to conditions.[4b,9a,10] Of particular interest to this work, cerium(IV) halide complexes supported by tripodal amine (tren) and bis(trimethylsilyl)amido ligand frameworks have been reported from oxidation of cerium(III) precursors.[4b,10a,c,d] However, previous efforts to synthesize a cerium(IV) fluoride complex in the bis(trimethylsilyl)amido framework using CoF$_3$ or AgBF$_4$ did not lead to an isolable product.[10d]

As part of a general interest in the effect of ligand environments on the stability of high-valent cerium,[9a,11] we have used the bis(trimethylsilyl)amido ligand scaffold to synthesize the first molecular cerium(IV) fluoride compound. Electrochemical, spectroscopic, and computational characterization of this compound were used to describe its electronic structure and potential as a source of nucleophilic fluoride.

Noting that trityl chloride was used successfully by Arnold and co-workers in the oxidation of Ce[N(SiMe$_3$)$_2$]$_3$,[4b] we reacted Ce[N(SiMe$_3$)$_2$]$_3$ with the fluoride-containing oxidants Ph$_3$CBF$_4$ and Ph$_3$CPF$_6$ in hexanes (Scheme 1). ^{1}H NMR analysis in C$_6$D$_6$ showed conversion to a single product, evidenced by a sharp singlet at +0.39 ppm. The ^{13}C NMR spectrum of the reaction mixture revealed a resonance at +4.75 ppm, while ^{19}F NMR showed a singlet at +312.3 ppm. On the basis of these data, we assigned the reaction product as CeF[N(SiMe$_3$)$_2$]$_3$ (**1**), which we isolated in 50% yield. Ferrocenium reagents also proved to be viable oxidants for Ce[N(SiMe$_3$)$_2$]$_3$. Reactions of Ce[N(SiMe$_3$)$_2$]$_3$ with FcBF$_4$ or FcPF$_6$ similarly led to the formation of **1**. These reactions likely proceeded by oxidation of the cerium(III) cation followed by fluoride abstraction from the weakly coordinating anions BF$_4^-$ or PF$_6^-$. Reaction conditions that included a tetrahydrofuran (THF) solvent and a PF$_6^-$-containing oxidant led to THF polymerization over the course of several hours, providing evidence for formation of the PF$_5$ byproduct.[12] With compound **1** in hand, we turned to its characterization and bonding analysis.

Scheme 1. Synthesis of 1



Compound **1** crystallizes with two molecules in its asymmetric unit (Figures 1 and S2 in the SI). Both molecules show approximate C_3 symmetry about the Ce−F bond axis. As expected, the terminal Ce−F bond distances in **1** of 2.065(6) and 2.065(7) Å are shorter than the reported terminal cerium(III) fluoride bonds in CeF(DippForm)$_2$(THF) and CeFCp′$_2$ [2.1217(15) and 2.165(2) Å, respectively][7c,13] and the reported terminal cerium(IV) fluoride bonds that are present in crystallographically characterized extended lattices [2.182(2) and 2.184(7) Å].[14] The Ce−N bond distances in **1** range from 2.201(10) to 2.254(9) Å, which are shorter than the Ce−N bond distance in the trivalent compound Ce[N(SiMe$_3$)$_2$]$_3$ [2.320(3) Å][15] and slightly longer than the Ce−N bond distances in the tetravalent compounds CeCl[N(SiMe$_3$)$_2$]$_3$ and CeBr[N-

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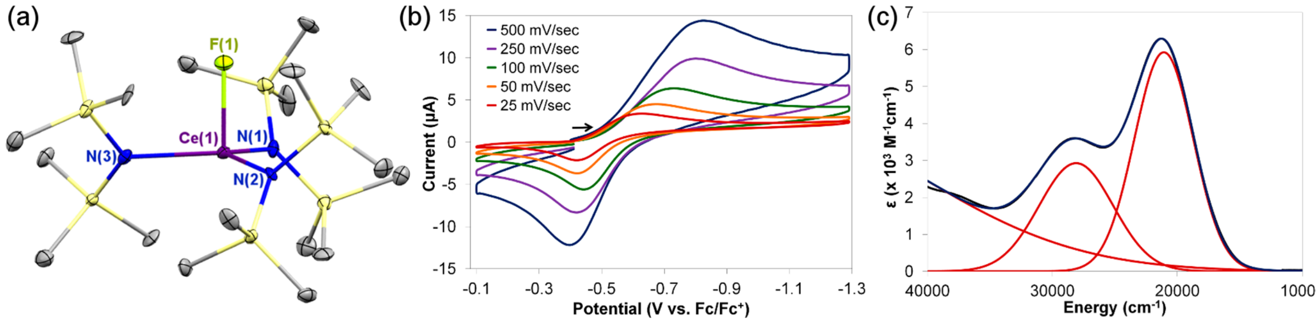

Figure 1. (a) 30% probability thermal ellipsoid plot of one molecule in the asymmetric unit of **1**. Hydrogen atoms have been removed for clarity. Selected bond distances (Å): Ce(1)−F(1) 2.065(7); Ce(1)−N(1) 2.229(9); Ce(1)−N(2) 2.241(9); Ce(1)−N(3) 2.254(9). (b) Isolated cerium(III/IV) redox couple in the cyclic voltammogram of **1** centered at −0.56 V versus Fc/Fc$^+$ in THF with 0.1 M [^{n}Pr$_4$N][BAr$^F{}_4$]; [**1**] = ca. 1 mM. (c) Electronic absorption spectrum of **1** (blue), component fits used for spectral deconvolution (red), and sum of the component fits (black).

(SiMe$_3$)$_2$]$_3$ [2.217(3) and 2.219(7) Å, respectively].[10c,d] Structural characterization of the previously reported compound UF[N(SiMe$_3$)$_2$]$_3$ (**2**)[16] was completed for comparison to the bonding metrics in **1**. Compound **2** os isostructural but not isomorphous with compound **1** and shows similar metal−ligand bond distances, as expected based on the similarity of the ionic radii of the cerium(IV) and uranium(IV) ions.[17] The crystal structure of **2** has a U−F bond distance of 2.0649(12) Å and U−N bond distances that range from 2.2498(16) to 2.2533(16) Å (Figure S3 in the SI).

In the context of isolating and characterizing **1**, we revisited the solution electrochemistry of its parent complex, Ce[N(SiMe$_3$)$_2$]$_3$. Electrochemical analysis of Ce[N(SiMe$_3$)$_2$]$_3$ in THF with 0.1 M [^{n}Pr$_4$N][BAr$^F{}_4$] showed a quasi-reversible feature at $E_{1/2}$ = +0.35 V versus Fc/Fc$^+$ (Figure S5 in the SI). Given the oxidation potentials of the trityl and ferrocenium cations at −0.11 and 0.00 V, respectively,[18] electrochemical analysis of Ce[N(SiMe$_3$)$_2$]$_3$ suggested that chemical oxidations employed in the synthesis of **1** would not be thermodynamically accessible. We hypothesized that precoordination of fluorinated anions to the cerium ion make chemical oxidations more accessible by increasing the electron density at the cerium cation. Electrochemical analysis of **1** performed using THF solutions of [^{n}Pr$_4$N][BAr$^F{}_4$] exhibited a quasi-reversible redox feature with $E_{1/2}$ = −0.56 V versus Fc/Fc$^+$ and a wave separation of 0.26 V (Figure 1). This feature is shifted 0.91 V to more reducing potentials compared to the cerium(III/IV) couple for Ce[N(SiMe$_3$)$_2$]$_3$ because of the more electron-rich ligand environment in compound **1**.

The electronic absorption spectrum of a solution of **1** collected in THF (Figure 1) revealed several broad features in the UV/visible region centered at 476, 357, and 217 nm with molar absorptivities of 5590, 2860, and 2620 M^{-1} cm^{-1}, respectively. These features were assigned to ligand-to-metal charge-transfer bands, which have been observed in the visible region for cerium(IV) complexes.[11a,19] IR spectroscopy performed on **1** revealed a band at 493 cm^{-1} that was assigned to the Ce−F stretching mode on the basis of a comparison to reported Ln−F bond vibrations that range from 470 to 585 cm^{-1} and the U−F stretching mode of 509 cm^{-1} in **2**.[16,20]

Electronic structure calculations of compound **1** were performed in order to describe the nature of the Ce−F bond. The geometry-optimized gas-phase structure of **1** and the calculated IR spectrum were found to be in excellent agreement with the experimental results (Table S4 and Figure S6 in the SI). The highest occupied molecular orbitals (HOMOs) in compound **1** are largely composed of the bis(trimethylsilyl)amido ligand atomic orbitals, and the calculated lowest unoccupied molecular orbital (LUMO)−LUMO+6 in compound **1** are primarily of Ce 4f character.

A negative natural charge of the fluorine atom was expected given the results of previously calculated cerium(IV) fluoride bonds.[4b,21] The natural charge of the fluorine atom in **1** of −0.540 and the calculated Mayer bond order of the Ce−F bond of 0.853 indicated ionic bonding with electron density polarized toward the fluoride ligand. The Ce−F bonding interaction in **1** is described by several calculated natural bond orbitals, each of which is composed of >95% fluorine atomic orbitals. In contrast, electronic structure calculations of isostructural uranium-containing compound **2** show a slightly larger Mayer bond order of 0.912 for the U−F bond, demonstrating a more covalent metal halide interaction in **2** compared to **1**. Evidence of increased covalency of uranium ligand bonding compared to cerium ligand bonding has been previously observed.[4b,22]

AOMix calculations were used to identify the molecular orbitals that contain significant contributions from the fluorine atomic orbitals. The 2s and 2p atomic orbitals on the fluoride ligand are strongly localized in low-lying filled molecular orbitals, which show minimal contributions from p, d, and f atomic orbitals on cerium. The molecular orbitals with significant contributions from 2p atomic orbitals on fluorine are shown in Figures 2 and S9 in the SI. In total, bonding analysis of **1** implies the expected predominantly ionic interaction between the cerium and fluoride ions in **1**.

The implication of the ionic nature of the Ce−F bonding interaction in **1** was explored in a preliminary reactivity study. The reaction of **1** with Me$_3$Si−Cl in THF at room temperature showed 90% conversion to Me$_3$Si−F over 15 h, with CeCl[N(SiMe$_3$)$_2$]$_3$ as the cerium-containing product.[10c] This reaction

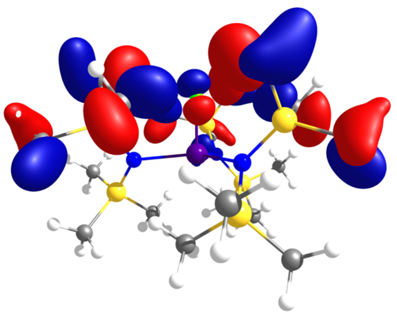

Figure 2. Calculated HOMO−23. Atomic orbital contributions (%): Ce p, 3.06; Ce d, 7.12; Ce f, 2.31; F p, 78.76.

shows attack by fluoride at the electrophilic component of the substrate, demonstrating that the Ce−F bond in **1** is nucleophilic and reactive.

We have demonstrated isolation of the first molecular species containing a terminal fluoride ligand bound to high-valent cerium, which was characterized by X-ray diffraction, spectroscopy, electrochemistry, and density functional theory. Our results support the expected ionicity of the cerium(IV) fluoride bond. On the basis of its ionic bonding, the terminal fluoride was determined to be nucleophilic in a halogen exchange reaction. We expect that reactions to further functionalize **1** will be fruitful toward the aim of describing new ligand environments for cerium(IV) compounds as well as the potential for **1** to act as a nucleophilic fluorinating agent for organic substrates.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data (CIFs), full experimental details, cyclic voltammograms, NMR data, and DFT results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Furuya, T.; Kamlet, A. S.; Ritter, T. *Nature* **2011**, *473*, 470−477.

(2) (a) Doherty, N. M.; Hoffman, N. W. *Chem. Rev.* **1991**, *91*, 553−573. (b) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373−431. (c) Mezzetti, A.; Claus, B. *Helv. Chim. Acta* **2002**, *85*, 2686−2703. (d) Murphy, E. F.; Ramaswamy, M.; Roesky, H. W. *Chem. Rev.* **1997**, *97*, 3425−3468.

(3) (a) Roesky, H. W. *Inorg. Chem.* **1999**, *38*, 5934−5943. (b) Nagendran, S.; Roesky, H. W. *Organometallics* **2008**, *27*, 457−492. (c) Pinkas, J.; Roesky, H. W. *J. Fluorine Chem.* **2003**, *122*, 125−150.

(4) (a) Thomson, R. K.; Graves, C. R.; Scott, B. L.; Kiplinger, J. L. *Dalton Trans.* **2010**, *39*, 6826−6831 and references cited therein. (b) Arnold, P. L.; Turner, Z. R.; Kaltsoyannis, N.; Pelekanaki, P.; Bellabarba, R. M.; Tooze, R. P. *Chem.—Eur. J.* **2010**, *16*, 9623−9629. (c) Lewis, A. J.; Nakamaru-Ogiso, E.; Kikkawa, J. M.; Carroll, P. J.; Schelter, E. J. *Chem. Commun.* **2012**, *48*, 4977−4979. (d) Kosog, B.; La Pierre, H. S.; Heinemann, F. W.; Liddle, S. T.; Meyer, K. *J. Am. Chem. Soc.* **2012**, *134*, 5284−5289.

(5) Dorn, H.; Murphy, E. F.; Shah, S. A. A.; Roesky, H. W. *J. Fluorine Chem.* **1997**, *86*, 121−125.

(6) (a) Greis, O.; Haschke, J. M. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Eyring, L., Eds.; Elsevier: New York, 1982; Vol. 5, pp 387−460. (b) Rogers, E.; Dorenbos, P.; van der Kolk, E. *New J. Phys.* **2011**, *13*, 093038/1−093038/32.

(7) (a) Cole, M. L.; Deacon, G. B.; Junk, P. C.; Konstas, K. *Chem. Commun.* **2005**, 1581−1583. (b) Cole, M. L.; Junk, P. C. *Chem. Commun.* **2005**, 2695−2697. (c) Cole, M. L.; Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Konstas, K.; Wang, J. *Chem.—Eur. J.* **2007**, *13*, 8092−8110. (d) Watson, P. L.; Tulip, T. H.; Williams, I. *Organometallics* **1990**, *9*, 1999−2009. (e) Hillier, A. C.; Zhang, X.; Maunder, G. H.; Liu, S. Y.; Eberspacher, T. A.; Metz, M. V.; McDonald, R.; Domingos, A.; Marques, N.; Day, V. W.; Sella, A.; Takats, J. *Inorg. Chem.* **2001**, *40*, 5106−5116.

(8) Kraus, F.; Baer, S. A. *Z. Naturforsch. B* **2011**, *66*, 868−870.

(9) (a) Robinson, J. R.; Carroll, P. J.; Walsh, P. J.; Schelter, E. J. *Angew. Chem., Int. Ed.* **2012**, *51*, 10159−10163. (b) Broderick, E. M.; Thuy-Boun, P. S.; Guo, N.; Vogel, C. S.; Sutter, J. R.; Miller, J. T.; Meyer, K.; Diaconescu, P. L. *Inorg. Chem.* **2011**, *50*, 2870−2877. (c) Binnemans, K. In *Handbook on the Physics and Chemistry of the Rare Earths*; Elsevier: New York, 2006; pp 281−392. (d) Yu, P.; O'Keefe, T. J. *J. Electrochem. Soc.* **2006**, *153*, C80−C85. (e) Bian, Y.; Jiang, J.; Tao, Y.; Choi, M. T. M.; Li, R.; Ng, A. C. H.; Zhu, P.; Pan, N.; Sun, X.; Arnold, D. P.; Zhou, Z.-Y.; Li, H.-W.; Mak, T. C. W.; Ng, D. K. P. *J. Am. Chem. Soc.* **2003**, *125*, 12257−12267. (f) Wester, D. W.; Palenik, G. J.; Palenik, R. C. *Inorg. Chem.* **1985**, *24*, 4435−4437. (g) Streitwieser, A.; Kinsley, S. A.; Jenson, C. H.; Rigsbee, J. T. *Organometallics* **2004**, *23*, 5169−5175.

(10) (a) Dröse, P.; Crozier, A. R.; Lashkari, S.; Gottfriedsen, J.; Blaurock, S.; Hrib, C. G.; Maichle-Mössmer, C.; Schädle, C.; Anwander, R.; Edelmann, F. T. *J. Am. Chem. Soc.* **2010**, *132*, 14046−14047. (b) Morton, C.; Alcock, N. W.; Lees, M. R.; Munslow, I. J.; Sanders, C. J.; Scott, P. *J. Am. Chem. Soc.* **1999**, *121*, 11255−11256. (c) Eisenstein, O.; Hitchcock, P. B.; Hulkes, A. G.; Lappert, M. F.; Maron, L. *Chem. Commun.* **2001**, 1560−1561. (d) Hitchcock, P. B.; Hulkes, A. G.; Lappert, M. F. *Inorg. Chem.* **2004**, *43*, 1031−1038. (e) Hitchcock, P. B.; Hulkes, A. G.; Lappert, M. F.; Li, Z. *Dalton Trans.* **2004**, 129−136. (f) Crozier, A. R.; Bienfait, A. M.; Maichle-Mossmer, C.; Tornroos, K. W.; Anwander, R. *Chem. Commun.* **2013**, *49*, 87−89.

(11) (a) Mahoney, B. D.; Piro, N. A.; Carroll, P. J.; Schelter, E. J. *Inorg. Chem.* **2013**, *52*, 5970−5977. (b) Williams, U. J.; Mahoney, B. D.; Lewis, A. J.; DeGregorio, P. T.; Carroll, P. J.; Schelter, E. J. *Inorg. Chem.* **2013**, *52*, 4142−4144. (c) Robinson, J. R.; Booth, C. H.; Carroll, P. J.; Walsh, P. J.; Schelter, E. J. *Chem.—Eur. J.* **2013**, *19*, 5996−6004.

(12) Sims, I. D. *J. Chem. Soc.* **1964**, 864−865.

(13) Maron, L.; Werkema, E. L.; Perrin, L.; Eisenstein, O.; Andersen, R. A. *J. Am. Chem. Soc.* **2004**, *127*, 279−292.

(14) (a) Sykora, R. E.; Albrecht-Schmitt, T. E. *Chem. Mater.* **2001**, *13*, 4399−4401. (b) Yu, R.; Wang, D.; Ishiwata, S.; Saito, T.; Azuma, M.; Takano, M.; Chen, Y.; Li, J. *Chem. Lett.* **2004**, *33*, 458−459.

(15) Rees, W. S.; Just, O.; Van Derveer, D. S. *J. Mater. Chem.* **1999**, *9*, 249−252.

(16) Stewart, J. L. *Tris[bis(trimethylsilyl)amido]uranium: Compounds with Tri-, Tetra-, and Pentavalent Uranium*; Lawrence Berkeley Laboratory: Berkeley, CA, 1988.

(17) Shannon, R. *Acta Crystallogr., Sect. A* **1976**, *32*, 751−767.

(18) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877−910.

(19) Vogler, A.; Kunkely, H. *Inorg. Chim. Acta* **2006**, *359*, 4130−4138.

(20) Chen, M.; Dixon, D. A.; Wang, X.; Cho, H.-G.; Andrews, L. *J. Phys. Chem. A* **2011**, *115*, 5609−5624.

(21) Clark, D. L.; Gordon, J. C.; Hay, P. J.; Poli, R. *Organometallics* **2005**, *24*, 5747−5758.

(22) Jones, M. B.; Gaunt, A. J.; Gordon, J. C.; Kaltsoyannis, N.; Neu, M. P.; Scott, B. L. *Chem. Sci.* **2013**, *4*, 1189−1203.