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solution dynamics and reactivity†

 κ^2 -Coordination of 18-crown-6 to Ce(III) cations:

Haolin Yin, Jerome R. Robinson, Patrick J. Carroll, Patrick J. Walsh and Eric J. Schelter*

The coordination of 18-crown-6 to Ce[N(SiMe₃)Ph^F]₃ (Ph^F = pentafluorophenyl) results in a κ^2 -18-crown-6 complex, a unique coordination mode for an f-block cation. The κ^2 -18-crown-6 complex showed exchange with free 18-crown-6 in solution and facile rearrangement of the crown ligand into a κ^6 -18-crown-6 cerium complex.

The coordination chemistry of f-block cations with macrocyclic polyethers (MCPE) is important historically in f-block chemistry and has drawn attention for the development of new extractants, NMR shift reagents, and model complexes for natural ionophores.¹ As a readily available MCPE prototype, 18-crown-6 exhibits larger stability constants in forming 1:1 lanthanide complexes than its smaller or acyclic counterparts. The log β_1 is 8.75 for La³⁺ with 18-crown-6 in anhydrous propylene carbonate, compared to 6.38 and 5.30 with 15-crown-5 and 18-podand-6, respectively.² The flexibility of the polyether moiety allows 18-crown-6 to bind lanthanide cations throughout the series exclusively in the κ^6 -coordination mode.^{1a,3}

Previous work by Lappert and co-workers on the coordination chemistry of 18-crown-6 with amide- and cyclopentadienidelanthanide complexes demonstrated that diverse coordination chemistry could be achieved by varying the steric bulkiness of the lanthanide supporting ligands, as well as the size of the cations.^{3f,g} Herein, we report a divergent coordination chemistry of 18-crown-6 with Ce[N(SiMe₃)Ph^F]₃ ($-Ph^{F}$ = pentafluorophenyl) (Scheme 1), featuring the first example of an 18-crown-6 moiety κ^{2} -coordinated to an f-block cation. We also show that the κ^{2} -18-crown-6 cerium(m) complex has rich solution behaviour; κ^{2} -coordination of the 18-crown-6 provides a kinetic product, which can be readily converted to κ^{6} -coordination through ligand substitution with choice of solvent.

Previous work by our group⁴ and others⁵ on the coordination chemistry of fluorinated ligands revealed that monometallic



Scheme 1 Synthesis of κ^2 - and κ^6 -coordinated 18-crown-6 complexes 2 and 3, transformation from 2 to 3, and substitution reaction of 2.

species could be achieved through multiple labile $C-F \rightarrow M$ interactions (M = Ln, U), even for ligands with relatively low steric demand. This type of $C-F \rightarrow M$ interaction has been observed crystallographically for electrophilic metal complexes.⁶ The displacement of such weak $C-F \rightarrow M$ interactions leads to unconventional coordination chemistry including the binding of neutral arene molecules in the solid state^{4a} and unusual coordination geometries.⁴ We have also shown that $C-F \rightarrow M$ interactions and substrate binding can be readily identified with solution ¹⁹F and ¹H NMR spectroscopy using paramagnetic Ce(m) (4f¹) cations.^{4a} In the current work, we have reduced the number of labile Ce–F interactions and increased the steric congestion around the metal center to achieve a more crowded coordination sphere at the cerium cation by using {N[(SiMe₃)Ph^F]}⁻ ligands instead of [N(Ph^F)₂]⁻ ligands.^{4,5b}

P. Roy and Diana T. Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104, USA. E-mail: schelter@sas.upenn.edu

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Fig. 1 Thermal ellipsoid plot of **1** at the 30% probability level.

Stirring a concentrated pentane solution of Ce[N(SiMe₃)₂]₃ with HN(SiMe₃)Ph^F for 1 week led to the precipitation of white $Ce[N(SiMe_3)Ph^F]_3$ (1) in 83% yield. An X-ray diffraction study on the colorless crystals obtained from a cold *n*-pentane solution of 1 revealed a monomeric nine-coordinate cerium(III) amide structure with three Ce-N distances averaging 2.397(2) Å, three Ce−F contacts averaging 2.6248(16) Å and three Ce···Me close contacts (Ce-C distances averaging 3.084 Å) (Fig. 1). The compound is isostructural with Sm[N(SiMe₃)Ph^F]₃ reported by Watkin and co-workers.^{5b} Highly shifted proton resonance from the -SiMe₃ group at -9.15 ppm, compared to Ce[N(SiMe₃)₂]₃ at -3.10 ppm in C₆D₆⁷ and broad *ortho*-F resonance at -173.09 ppm, implicated their proximity to the paramagnetic Ce(III) ion in solution. Variable temperature data (Fig. S6 and S7, ESI⁺) collected in toluene- d_8 showed at least eight ¹⁹F resonances below the coalescence temperature, which likely arose from an interplay between multiple $C-F \rightarrow Ce$ interactions^{4,6} and Si- γ -C-H \rightarrow Ce agostic interactions.⁸

Reaction of 1 with 18-crown-6 in *n*-pentane, toluene, or diethyl ether produced its 18-crown-6 adduct 2 as indicated by NMR spectroscopy. A crystallographic study on 2 revealed that the 18-crown-6 moiety was coordinated to the metal cation in a κ^2 -fashion with the associated ethylene moiety folded back into the ring cavity (Fig. 2). The κ^2 -coordination of 18-crown-6 has been documented with small metal cations, 9 for example $MCl_3(H_2O)(\kappa^2$ -18-crown-6) (M = V, Cr), 9a,b $MCl_4(\kappa^2$ -18-crown-6) (M = Ti, Sn), 9c (TiF_4)_2(κ^2 -18-crown-6), 9d [PPh_4][(VCl_4)_2(κ^2 -18-crown-6)], 9b [In(κ^2 -18-crown-6)I_2][InI_4], 9e but not for f-block cations with larger ionic radii and more available binding sites. The Ce³⁺ cation, at 101 pm, is comparable to Na⁺ at 102 pm.¹⁰ This unexpected κ^2 -coordination mode can be attributed to the interplay between steric hindrance of the N[(SiMe_3)Ph^F]^- ligands in 1 and their masking of the Ce^{III} ion by weak C-F \rightarrow Ce interactions.

The solution ¹⁹F spectrum of 2 showed three resonances at room temperature indicating a symmetric environment for the amide ligands on the NMR timescale. Only one broad symmetric proton resonance was observed for the bound 18-crown-6 molecule at -1.30 ppm, implicating a fluxional process at the bound ether moiety. This is in contrast to the observation in



Fig. 2 Thermal ellipsoid plot of 2 at the 30% probability level.

TiCl₄(κ^2 -18-crown-6), where multiple proton resonances are suggestive of tightly coordinated 18-crown-6 to the smaller and more Lewis acidic Ti⁴⁺ cation.^{9f} A variable temperature NMR experiment was performed on **2** in toluene- d_8 from 300–200 K and decoalescence of the coordinated 18-crown-6 proton resonances was observed at 240 K; decoalescence of ¹⁹F resonances due to C–F→Ce interactions was observed at 210 K (Fig. S8 and S9, ESI†).

Storing a C_6D_6 solution of 2 at room temperature led to gradual appearance of two new sets of pentafluorophenyl ring signals as well as two sets of $-SiMe_3$ proton resonances in a 1:2 ratio over several hours by ¹⁹F and ¹H NMR spectroscopies. Facile conversion to the new product was accomplished upon treating 2 with polar solvents, including tetrahydrofuran, dimethoxyethane, pyridine, or DCM (Scheme 1). X-ray analysis of colorless crystals obtained from thf–hexanes layering determined the product 3 to comprise charge separated cations and anions in the form of $\{Ce(\kappa^6-18\text{-crown-6})[N(SiMe_3)Ph^F]_2\}^+$ and $\{Ce[N(SiMe_3)Ph^F]_4\}^-$ (Fig. 3). No C-F \rightarrow Ce interactions were observed in the solid-state structure for the cationic moiety, $Ce(\kappa^6-18\text{-crown-6})[N(SiMe_3)Ph^F]_2^+$. The sharp doublet attributed of the *ortho*-F atom of the cation in its ¹⁹F NMR spectrum also supported the absence of C-F \rightarrow Ce



Fig. 3 Thermal ellipsoid plot of the anionic (left) and cationic (right) fragments of **3** at the 30% probability level (left: $Ce^{III}[N(SiMe_3)Ph^F]_4^-$, right: $Ce^{III}(\kappa^6-18-crown-6)[N(SiMe_3)Ph^F]_2^+)$.

interactions in solution. On the other hand, the {Ce^{III}[N(SiMe₃)Ph^F]₄}⁻ anion exhibits two C-F \rightarrow Ce interactions in the solid state at an average of 2.680(2) Å. These are evident by the broad *ortho*-F resonance in the solution ¹⁹F NMR spectrum (Fig. S11, ESI⁺).

Complex 3 could also be directly prepared by reacting 0.5 equiv. of 18-crown-6 with 1 in THF, DME, pyridine, or DCM in near quantitative yield (Scheme 1). In contrast, 1 reacts with neat DME to form a 1:1 adduct, as judged by ¹H and ¹⁹F spectroscopies, that does not convert to a charge-separated complex. Ce[N(SiMe₃)₂]₃ does not react with 18-crown-6 under the conditions used for the formation of 3, likely due to the relatively larger steric bulk of the [N(SiMe₃)₂]⁻ ligand.

The solution exchange behavior of 2 (κ^{2} -18-crown-6) or 3 (κ^{6} -18-crown-6) with free 18-crown-6 was investigated with ¹H NMR Exchange Spectroscopy (EXSY). Facile exchange between free 18-crown-6 and κ^{2} -18-crown-6 occurred for 2, while no exchange was observed between free 18-crown-6 and κ^{6} -18-crown-6 for 3 (Fig. S18 and S19, ESI†).

The weak coordination of κ^2 -18-crown-6 was also demonstrated by its clean substitution reaction with neutral and anionic donors. Reaction of 2 with 1 equiv. of 4,4'-di-*tert*-butyl-2,2'-bipyridyl (^tBu₂bipy) or KN(SiMe₃)Ph^F resulted in the clean formation of (^tBu₂bipy)Ce[N(SiMe₃)Ph^F]₃ (4) or {Ce[N(SiMe₃)Ph^F]₄}⁻, respectively (Scheme 1). Similar to the coordination sphere in 2, 4 preserved one C-F \rightarrow Ce interaction at 2.673(4) Å (Fig. S4, ESI†). However, no further displacement of the amide ligands to form a charge-separated complex could be achieved by reacting 4 with excess ^tBu₂bipy.

We have demonstrated the presence of C–F→Ce interactions affords unconventional coordination chemistry of Ce[N(SiMe_3)Ph^F]₃ with 18-crown-6, leading to the isolation of κ^{6} - and the first κ^{2} -coordinated crown ether to an f-block cation. The κ^{2} -18-crown-6 showed facile exchange with free 18-crown-6, as indicated by ¹H EXSY experiments as well as its clean substitution reactions with neutral or anionic donors. The transformation of complex 2 to 3 suggested κ^{6} -coordinated complex 3 is the thermodynamically favoured product while the combination of an intermediate, κ^{2} -coordination form. We expect these results will bring more attention to the solution dynamics and solvent effects in molecular f-block chemistry. Further investigations into reversible coordination relevant to C–F→M interactions are currently underway.

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