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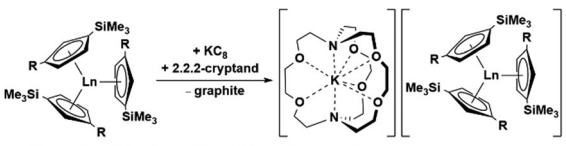
Synthesis of rare-earth-metal-in-cryptand dications, $[Ln(2.2.2\text{-cryptand})]^{2+}$, from Sm^{2+}, Eu^{2+}, and Yb^{2+} silyl metallocenes $(C_5H_4SiMe_3)_2Ln(THF)_2$†

Daniel N. Huh, [a] Christopher M. Kotyk, [a] Milan Gembicky, [b] Arnold L. Rheingold, [b] Joseph W. Ziller [a] and William J. Evans *[a]

$Cp'_2Ln(THF)_2$ metallocenes ($Cp' = C_5H_4SiMe_3$) react with 2.2.2-cryptand (crypt) to form Ln^{2+}-in-crypt complexes, $[Ln(crypt)(THF)][Cp'_3Ln]_2$ (Ln = Sm, Eu) and $[Yb(crypt)][Cp'_3Yb]_2$, that contain Ln^{2+} ions surrounded only by neutral ligands. A bimetallic, mixed-ligand metallocene/opened-crypt complex of Sm^{2+}, $[Sm(C_{16}H_{32}N_2O_6\text{-}\kappa^2O{:}\kappa^2O')SmCp''_2]$, was obtained by KC_8 reduction of $Cp''_2Sm(THF)$ $[Cp'' = C_5H_3(SiMe_3)_2]$ in the presence of crypt.

Recent studies of reductive rare-earth metal chemistry have shown that the +2 oxidation state is available for all of the rare-earth metals (except Pm, which was not studied due to its radioactivity) as soluble molecular complexes, $[K(crypt)][Cp'_3Ln]$ ($Cp' = C_5H_4SiMe_3$).[1–4] Previously, only Eu, Yb, Sm, Tm, Dy, and Nd were thought to be capable of forming isolable +2 complexes based on the calculated redox potentials for the reduction of $4f^n$ Ln^{3+} ions to $4f^{n+1}$ Ln^{2+} species.[5,6] The new Ln^{2+} ions were obtained according to eqn (1) in tris(cyclopentadienyl) ligand environments that had low lying d_{z^2} orbitals such that $4f^n5d^1$ ground states became available *via* reduction of a $4f^n$ Ln^{3+} ion with potassium.[1–6]



R = H, Ln = Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, and Lu
R = $SiMe_3$, Ln = La and Ce

(1)

A natural extension of the discovery of new +2 oxidation states is the pursuit of molecular complexes of lanthanide metals ions in the +1 oxidation state. Ln^{1+} ions are known in the gas phase for all lanthanides,[7] molecular complexes of Sc^{1+} ions have been isolated and crystallographically characterized,[8,9] and spectroscopic evidence for Sm^{1+} in the solid state has been reported.[10] In addition, $Ln(C_6H_3{}^tBu_3\text{-}1,3,5)_2$ complexes have been isolated for Ln = Nd, Tb, Dy, Ho, Er, and Lu that have the formal oxidation state of zero.[11] Sm^{1+} is an attractive target since it could have a half-filled shell $4f^7$ electron configuration. In attempts to isolate Ln^{1+} ions, silylcyclopentadienyl ligands were chosen since they are known to stabilize low oxidation state Ln^{2+} ions.[1,3–6,12]

We report here that reduction of $Cp''_2Sm(THF)$[13] $[Cp'' = C_5H_3(SiMe_3)_2]$ in the presence of crypt following the procedures of eqn (1) produced an unusual lanthanide-in-cryptand product, $[Sm(C_{16}H_{32}N_2O_6\text{-}\kappa^2O{:}\kappa^2O')SmCp''_2]$ arising from cleavage of crypt C–O bonds. Many reports of C–O bond cleavage under reducing conditions are in the literature.[14–20] Reactions of crypt alone with Ln^{2+} metallocenes were examined to obtain background information on the samarium reaction. Crystallographic data were obtainable with $Cp'_2Ln(THF)_2$ (Ln = Sm, Eu, Yb) that provided a general synthesis of Ln^{2+}-in-crypt dications with ligand redistribution counteranions, $[Cp'_3Ln]^{1-}$.

The reduction of dark green $Cp''_2Sm(THF)$ with KC_8 in the presence of crypt immediately formed a dark brown product that was characterized by X-ray crystallography as the bimetallic, mixed-ligand, metallocene/opened-crypt Sm^{2+} complex, $[Sm(C_{16}H_{32}N_2O_6\text{-}\kappa^2O{:}\kappa^2O')SmCp''_2]$, **1-Sm**, Fig. 1, eqn (2). The product is highly unusual in that one Sm^{2+} ion has lost both cyclopentadienyl ligands and resides inside a modified cryptand ligand that has lost a "CH_2CH_2" bridge. The resulting crypt fragment is formally a dianion, $(C_{16}H_{32}N_2O_6)^{2-}$ containing two anionic alkoxide functionalities. These coordinate to a $SmCp''_2$ moiety, which effectively replaces the CH_2CH_2 bridge to complete the cryptand structure. Unfortunately, the X-ray data on **1-Sm** were sufficient for a connectivity-only structure and detailed bond distance analysis is not possible.

To investigate the unusual result in eqn (2), the reactivity of Ln^{2+} silyl metallocenes with the crypt ligand alone was studied as a control reaction. Since reactions of crypt with $Cp''_2Sm(THF)$[13]

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† Electronic supplementary information (ESI) available. CCDC 1551235–1551238. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7cc04396a

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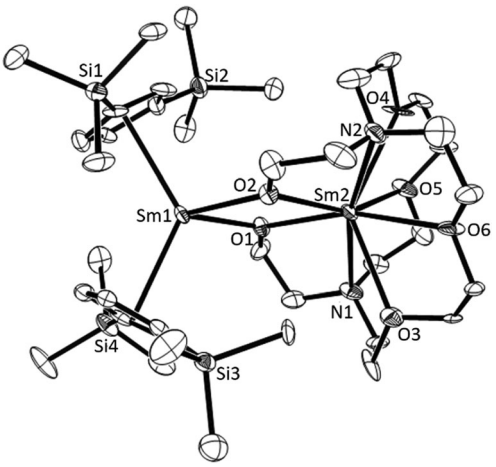


Fig. 1 ORTEP representation of [Sm($C_{16}H_{32}N_2O_6$-κ^2O:κ^2O′)SmCp′′$_2$], **1-Sm**, with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

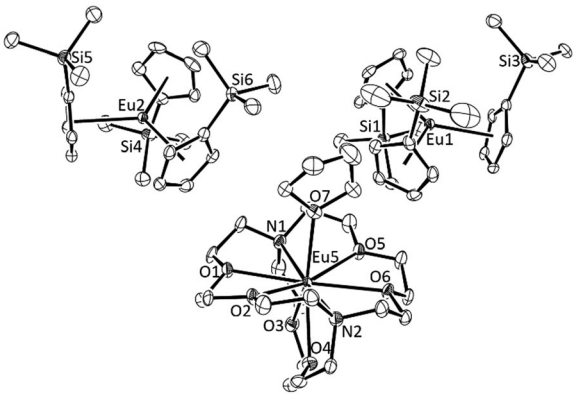
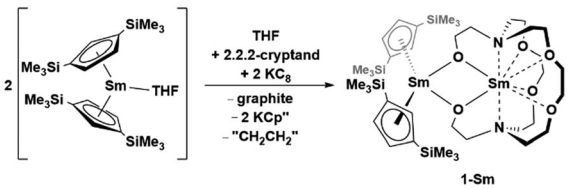


Fig. 2 ORTEP representation of [Eu(crypt)(THF)][Cp′$_3$Eu]$_2$, **2-Eu**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Distances in Å: Eu5–O1 2.656(4), Eu5–O2 2.657(4), Eu5–O3 2.632(4), Eu5–O4 2.620(3), Eu5–O5 2.657(4), Eu5–O6 2.682(4), Eu5–O7 2.567(3), Eu5–N1 2.855(5), Eu5–N2 2.871(5), average Eu–Cp′ centroid 2.62.

did not give tractable products, the reactivity of the less soluble Cp′ analog was studied.

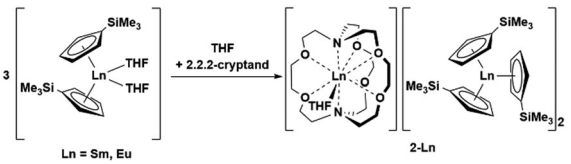


(2)

The Cp′$_2$Ln(THF)$_2$ complexes (Ln = Sm,[4] Eu[15]) react in THF with crypt in the absence of a reductant within two minutes to form new examples of dark purple Sm^{2+}-in-crypt and dark red Eu^{2+}-in-crypt complexes, [Ln(crypt)(THF)][Cp′$_3$Ln]$_2$, **2-Ln**, isolated in 50% (Sm) and 67% (Eu) yields. As shown in eqn (3), a ligand rearrangement occurs that generates two $[Cp'_3Ln]^{1-}$ anions and a $[Ln(crypt)(THF)]^{2+}$ countercation in the complexes [Ln(crypt)(THF)][Cp′$_3$Ln]$_2$, **2-Ln**, Fig. 2. This reaction is reminiscent of the ligand rearrangement reported by Lappert and coworkers in which unsolvated Cp′′$_2$Sm reacts with 18-crown-6 (18-c-6) in benzene to form a monocyclopentadienyl crown cation complex of a tris(cyclopentadienyl) anion, [Sm(18-c-6)Cp′′][Cp′′$_3$Sm].[21]

The $[Ln(crypt)(THF)]^{2+}$ dication in **2-Ln** is unusual in two respects: it is a rare case of a Ln^{2+} ion in a crypt and a rare case of any lanthanide ion in a crypt without an additional anionic ligand. Several examples of Ln^{3+} ions in crypt have been reported including the X-ray crystal structures of $[Ln(NO_3)_5(OH_2)]$-$[Ln(crypt)(NO_3)]$ (Ln = Nd, Sm, Eu),[22–24] $[La(crypt)(OH_2)Cl](Cl)_2$,[25] $[La(crypt)(OTf)(DMF)](OTf)_2$,[25] and $[Eu(crypt)(ClO_4)](ClO_4)_2$.[26] In each of these cases, there is an anionic ligand binding the lanthanide in addition to crypt. Ln^{2+} ions have not been reported in crypt, to our knowledge, but the structure of Eu^{2+} in a fluorobenzocryptand, [5,6-(4-fluorobenzo)-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacos-5-ene], [Eu(fluorobenzocrypt)Cl]Cl, is known.[27] As in all other cases, there is one anionic ligand bound to the metal in addition to this cryptand.

The metrical parameters in [Eu(crypt)(THF)][Cp′$_3$Eu]$_2$, **2-Eu**, will be discussed in detail, since the crystallographic data on **2-Sm** were sufficient for connectivity only. The bond distances and angles in the $[Cp'_3Eu]^{1-}$ counteranions in **2-Eu** are the same as those of $[K(crypt)][Cp'_3Eu]^3$ within the error limits. The nine-coordinate encapsulated Eu^{2+} ion has an irregular geometry that can be roughly described as a hexagonal pyramid that has the THF oxygen, O7, in the axial position and O3 and O4 below the "plane" of O1, O2, O5, O6, N1 and N2 donor atoms. The latter six atoms and Eu5 are only co-planar to within 0.19 Å. The 174° N–Eu–N angle in the cation of **2-Eu** is within the range of angles of 169.26 to 178.72° observed in the five Ln^{3+} crypt structures listed earlier. The 2.568(3) Å Eu–O_{THF} distance in **2-Eu** is consistent with that in $[(C_5Me_5)Eu(THF)]_2[C_8H_4(Si^iPr_3)_2]$, 2.555(5) Å.[13,28] The Eu–O_{crypt} distances in **2-Eu** range from 2.620(3) to 2.681(4) Å and the Eu–N_{crypt} lengths vary from 2.849(5) to 2.870(5) Å. Previously isolated Eu^{3+} cryptates were reported to have shorter bond distances as expected for the smaller +3 ion:[29] $[Eu(crypt)(ClO_4)]$-$(ClO_4)_2$, Eu–O_{crypt} 2.44(4) to 2.52(3) Å and Eu–N_{crypt} 2.64(3) to 2.70(5) Å; $[Eu(NO_3)_5(OH_2)][Eu(crypt)(NO_3)]$, Eu–$O_{crypt}$ 2.440(3) to 2.563(4) Å and Eu–N_{crypt} 2.747(5) to 2.776(6) Å.[23,26]



(3)

In the case of the smaller metal, ytterbium, a Ln^{2+}-in-crypt dication was obtained that has no coordinated THF. Purple Cp′$_2$Yb(THF)$_2$ reacts with crypt in toluene to form green [Yb(crypt)][Cp′$_3$Yb] in 18% yield, Fig. 3, eqn (4). To our knowledge, **3-Yb** is the first example of ytterbium in a cryptand. As in the anion of **2-Eu**, the $[Cp'_3Yb]^{1-}$ anion bond distances in **3-Yb** are equivalent to those of the previously reported [K(crypt)][Cp′$_3$Yb].[3] The coordination geometry of the encapsulated Yb^{2+} is also irregular, but it can be approximated by a bicapped distorted octahedron with the nitrogen atoms in capping vertices. The Yb–O_{crypt} and Yb–N_{crypt} average distances are 0.15 to 0.16 Å

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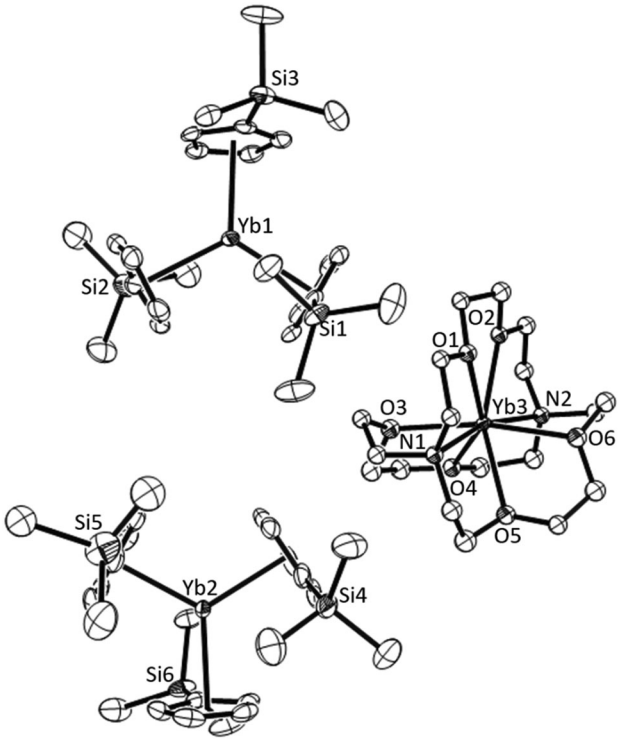
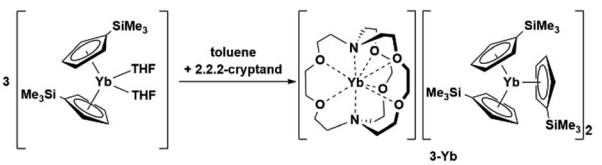


Fig. 3 ORTEP representation of [Yb(crypt)][Cp′$_3$Yb]$_2$, **3-Yb**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Distances in Å: Yb3–O1 2.508(8), Yb3–O2 2.496(6), Yb3–O3 2.444(7), Yb3–O4 2.539(5), Yb3–O5 2.506(6), Yb3–O6 2.493(6), Yb3–N1 2.634(15), Yb3–N2 2.613(10), average Yb–Cp′ centroid 2.50.

shorter than those in **2-Eu**, which is similar to the difference in ionic radii of 0.16 Å for nine-coordinate Eu^{2+} and eight-coordinate Yb^{2+} ions.[29]



(4)

The facile ligand distribution in eqn (3) and (4) was not expected. It was thought that Ln^{2+} ions would prefer anionic cyclopentadienyl ligands to the neutral ligand environment of the $[Ln(crypt)(THF)]^{2+}$ or $[Ln(crypt)]^{2+}$ dications. Formation of the $[Cp'_3Ln]^{1-}$ counteranions is also unusual since $(Cp')^{1-}$ loss from these anions appears to be facile in some cases.[2] The transformation in eqn (2) is even more unusual. It is not known if this involves a Sm^{1+} intermediate or if traditional Sm^{2+} reaction pathways can lead to such species. The Ln^{2+} cryptate cations are interesting in reduction chemistry since Allen and coworkers have found that Eu^{2+} is stabilized with respect to oxidation when encapsulated in cryptates.[30] Hence, these complexes may be good precursors to Ln^{1+} species.

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