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Facile Encapsulation of Ln(II) Ions into Cryptate Complexes from $LnI_2(THF)_2$ Precursors (Ln = Sm, Eu, Yb)

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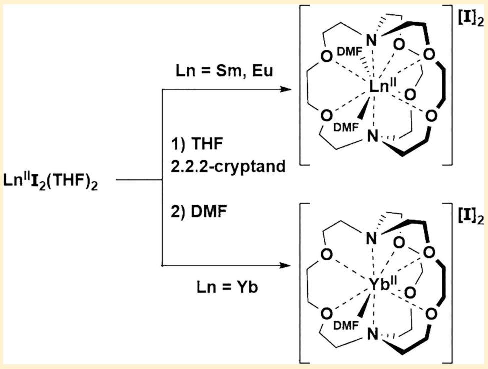
Supporting Information

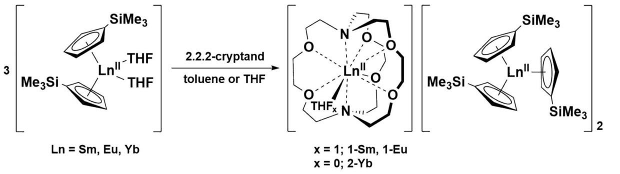
ABSTRACT: The reactivity of $LnI_2(THF)_2$ (Ln = Sm, Eu, Yb; THF = tetrahydrofuran) with 2.2.2-cryptand (crypt) was explored to see if these readily accessible precursors could provide new examples of lanthanide-in-crypt complexes. The crystallographically characterized Ln(II)-in-crypt complexes $[Ln(crypt)(DMF)_2][I]_2$ (Ln = Sm, Eu) and $[Yb(crypt)(DMF)][I]_2$ (DMF = dimethylformamide) were synthesized by reacting $LnI_2(THF)_2$ (Ln = Sm, Eu, Yb) with crypt in THF and recrystallizing from DMF. Crystallographic data were also obtained on the Ln(II)-in-crypt (Ln = Sm, Eu) complexes $[Ln(crypt)(DMF)_2][BPh_4]_2$, which were synthesized by addition of 2 equiv of $NaBPh_4$ to $[Ln(crypt)(DMF)_2][I]_2$.



INTRODUCTION

Although the 2.2.2-cryptand (crypt) ligand has been known since 1973[1,2] and lanthanide-encapsulated crypt complexes were reported in 1979,[3] Ln-in-crypt complexes were not heavily studied in subsequent decades. Most of the examples involved lanthanides in the +3 oxidation state.[4−7] However, Allen and co-workers recently reported new examples of Eu(II)-in-crypt[8−10] complexes as well as related Eu(II)-in-azacrypt[11,12] complexes. Since the crypt ligand has been found to stabilize low oxidation states for rare-earth metals,[6,8] Ln(II)-in-crypt complexes could be attractive precursors to expand the limits of redox chemistry of rare-earth metals.[13]

Encapsulation of rare-earth ions using crypt first captured our attention with the discovery that Sm(II), Eu(II), and Yb(II) can be readily incorporated into crypt from the metallocene precursors, $Cp'_2Ln(THF)_2$ ($Cp' = C_5H_4SiMe_3$; THF = tetrahydrofuran).[14] The trimetallic Ln(II) complexes $[Ln(crypt)(THF)][Cp'_3Ln]_2$, **1-Ln** (Ln = Sm, Eu), and $[Yb(crypt)][Cp'_3Yb]_2$, **2-Yb**, are formed according to eq 1.[14]



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Following this result, we sought to synthesize Ln(II)-in-crypt examples with a single type of Ln(II) coordination environment to better examine the Ln(II)-in-crypt moiety. We were also interested in synthesizing Ln(II)-in-crypt complexes from common Ln(II) starting materials such as the diiodides, $LnI_2(THF)_2$, that are precursors to the metallocenes of eq 1. Recently, we found that U(III)-in-crypt and La(III)-in crypt complexes can be synthesized directly from the metal trihalides.[15] We report here that Sm(II), Eu(II), and Yb(II) ions can be encapsulated by crypt starting from $LnI_2(THF)_2$ precursors.

EXPERIMENTAL SECTION

All syntheses and manipulations described below were conducted under argon with rigorous exclusion of air and water using glovebox, Schlenk-line, and high-vacuum-line techniques. All $LnI_2(THF)_2$ (Ln = Sm, Eu, Yb)[16,17] materials were prepared according to previously published literature. 2.2.2-Cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, Aldrich) was placed under vacuum (1×10^{-3} Torr) for 12 h before use. $NaBPh_4$ was purchased from Aldrich and recrystallized from acetone/hexanes. Solvents were sparged with ultrahigh purity (UHP) Ar and dried over columns containing Q-5 and molecular sieves. Deuterated dimethylformamide (DMF-d_7) was dried with 3 Å molecular sieves and degassed by three freeze−pump−thaw cycles. ^1H NMR spectra were recorded on Bruker CRYO500 MHz or GN500 MHz spectrometer and referenced internally to residual protio-solvent resonances. IR samples were prepared as KBr pellets on a Varian 1000 FT-IR or a Jasco FT/IR-4700 spectrometer. Elemental analyses were performed on a PerkinElmer series II 2400 CHNS analyzer.

$[Sm(2.2.2\text{-cryptand})(DMF)_2][I]_2$, 3-Sm. In an argon-filled glovebox, a blue THF (3 mL) solution of $SmI_2(THF)_2$ (100 mg, 0.18 mmol) was added to a colorless THF (1 mL) solution of 2.2.2-cryptand (69 mg, 0.18 mmol) dropwise while the solution was stirred. A green precipitate immediately formed. After 1 h of stirring, THF was removed in vacuo, and 1 mL of dimethylformamide (DMF) was added to dissolve the green solid to form a purple solution. This solution was layered into Et_2O and placed in a −35 °C freezer. After 1

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d, purple crystals suitable for X-ray crystallography were obtained (133 mg, 79%). ^{1}H NMR (DMF-d_7): δ 4.03 [12H, OCH_2CH_2O], 3.94 [12H, NCH$_2$CH_2O], 2.42 [12H, NCH_2]. IR: 2913m, 2877m, 2849w, 2827w, 2797w, 1653w, 1484m, 1462m, 1380w, 1354s, 1320m, 1281m, 1271m, 1246m, 1174w, 1128m, 1116m, 1094s, 1074s, 1064s, 1025m, 954s, 936s, 902m, 872w, 842m, 826m, 814m, 754m, 677w. Anal. Calcd for desolvated [Sm(crypt)]I$_2$, $C_{18}H_{36}N_2O_6I_2Sm$: C, 27.69; H, 4.65; N, 3.59. Found: C, 27.85; H, 4.59; N, 3.69%.

[Eu(2.2.2-cryptand)(DMF)$_2$][I]$_2$, 3-Eu. As described for **3-Sm**, a light green THF solution of EuI$_2$(THF)$_2$ (100 mg, 0.18 mmol) was added to a solution of 2.2.2-cryptand (68 mg, 0.18 mmol) dropwise while the solution was stirred. A colorless precipitate immediately formed. DMF was added to dissolve the colorless solid to form a colorless solution. This solution was layered into Et$_2$O and placed in a −35 °C freezer. After 1 d, colorless crystals suitable for X-ray crystallography were obtained (148 mg, 88%). IR: 2913m, 2876m, 2857w, 2825w, 2799w, 1653w, 1481m, 1460m, 1422w, 1372m, 1353s, 1320m, 1280m, 1273m, 1246m, 1174w, 1128m, 1117s, 1094s, 1073s, 1062s, 1025m, 953, 937s, 902m, 873w, 843m, 826m, 816m, 754m. Anal. Calcd for desolvated [Eu(crypt)]I$_2$, $C_{18}H_{36}N_2O_6I_2Eu$: C, 27.64; H, 4.64; N, 3.58. Found: C, 27.98; H, 4.39; N, 3.56%.

[Yb(2.2.2-cryptand)(DMF)][I]$_2$, 4-Yb. As described for **3-Sm**, a yellow THF solution of YbI$_2$(THF)$_2$ (100 mg, 0.18 mmol) was added to a THF solution of 2.2.2-cryptand (66 mg, 0.18 mmol) forming a colorless precipitate. After removal of THF, addition of DMF to the colorless solid formed a light yellow solution. This was layered in Et$_2$O and placed in a −35 °C freezer, and after 1 d, pale yellow crystals suitable for X-ray crystallography were isolated (113 mg, 74%). ^{1}H NMR (DMF-d_7): δ 3.93 [12H, OCH_2CH_2O], 3.90 [12H, NCH$_2$CH_2O], 2.83 [12H, NCH_2]. IR: 2912m, 2876m, 2840m, 2803w, 1641s, 1492w, 1470w, 1462m, 1456m, 1435m, 1417m, 1379m, 1352s, 1291m, 1273m, 1257w, 1248w, 1240m, 1170w, 1112m, 1079s, 1066s, 1059m, 1046m, 1026w, 948m, 935m, 899w, 835w, 819m, 752m, 681m, 664m. Anal. Calcd for [Yb(crypt)(DMF)]I$_2$, $C_{21}H_{43}N_3O_7I_2Yb$: C, 28.78; H, 4.95; N, 4.79. Found: C, 27.94; H, 4.75; N, 4.69%.

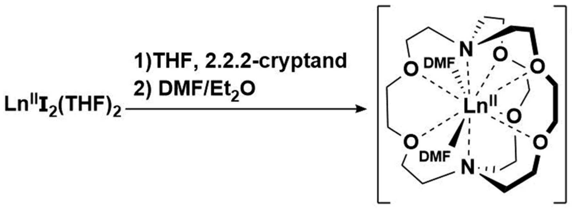
[Sm(2.2.2-cryptand)(DMF)$_2$][BPh$_4$]$_2$, 5-Sm. In an argon-filled glovebox, a colorless DMF (1 mL) solution of NaBPh$_4$ (37 mg, 0.11 mmol) was added dropwise to a stirred purple DMF (3 mL) solution of [Sm(crypt)(DMF)$_2$][I]$_2$, **3-Sm**, (50 mg, 0.054 mmol). After the solution was stirred overnight, a white precipitate formed, presumably NaI, and it was removed via filtration. The purple DMF solution was layered into Et$_2$O and placed in a −35 °C freezer. After 1 d, purple crystals suitable for X-ray crystallography were isolated (51 mg, 71%).

[Yb(DMF)$_6$][BPh$_4$]$_2$, 6-Yb. In an argon-filled glovebox, YbI$_2$(THF)$_2$ (100 mg, 0.18 mmol), 2.2.2-cryptand (66 mg, 0.18 mmol), and NaBPh$_4$ (120 mg, 0.35 mmol) were stirred in DMF overnight. The solution became orange without sign of precipitate. The solution was layered into Et$_2$O overnight, and orange crystals suitable for X-ray crystallography were isolated.

X-ray Data Collection, Structure Determination, Refinement, UV−Visible Spectroscopy, and NMR Spectroscopy. Crystallographic details on complexes **3-Sm**, **3-Eu**, **4-Yb**, **5-Sm**, **5-Eu**, and **6-Yb** are summarized in the Supporting Information. UV−Visible and NMR spectra of **3-Sm**, **3-Eu**, and **4-Yb** are also summarized in the Supporting Information.

RESULTS AND DISCUSSION

Encapsulation of Sm(II), Eu(II), and Yb(II). Addition of THF solutions of LnI$_2$(THF)$_2$ (Ln = Sm, Eu) to a THF solution of 2.2.2-cryptand (crypt) generates precipitates that dissolve in DMF. Crystallization of these solutions yields the Ln(II)-in-crypt complexes, [Ln(crypt)(DMF)$_2$][I]$_2$, **3-Ln**, identified by X-ray diffraction, eq 2, Figure 1.



(2)

Ln = Sm, Eu

3-Ln

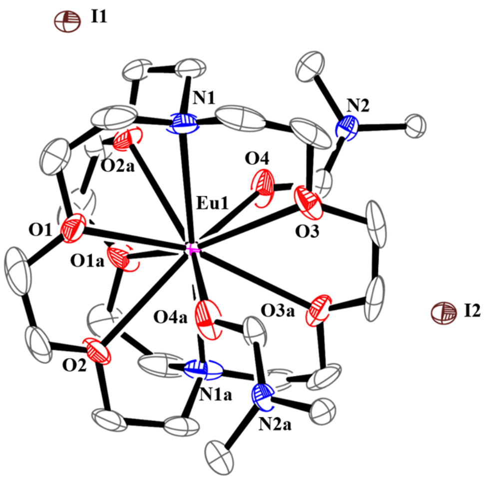


Figure 1. ORTEP representation of [Eu(crypt)(DMF)$_2$][I]$_2$, **3-Eu**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. **3-Sm** is isomorphous with **3-Eu**.

The crystal data show that each metal in **3-Ln** is encapsulated by the crypt ligand and is also coordinated to two molecules of DMF. Both iodides in **3-Ln** are outer-sphere counteranions. The 10-coordinate geometry of the Ln(II) ion can be described as a tetra-capped trigonal prism with crypt nitrogen donor atoms capping the triangular faces and DMF oxygen atoms capping two of the rectangular faces. Similar structures were previously described for the Ln(III) complexes [La(crypt)(OH$_2$)Cl]Cl$_2$,[7] [La(crypt)(DMF)(OTf)][OTf]$_2$,[7] [La(crypt)Cl$_2$]Cl,[15] and [U(crypt)I$_2$]I.[15]

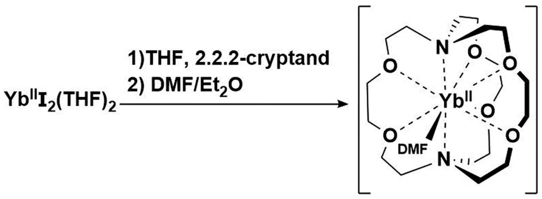
Table 1 presents metrical data on all the new Ln(II)-in-crypt complexes in this paper as well as comparisons with [Eu(crypt)(THF)][Cp′$_3$Eu]$_2$, **1-Eu**, [Yb(crypt)][Cp′$_3$Yb]$_2$, **2-Yb**, and [Eu(crypt)Cl][Cl]. Since the crystal structure of [Sm(crypt)(THF)][Cp′$_3$Sm]$_2$, **1-Sm**, was of insufficient quality to provide metrical data, it is not included. The table shows that, in the **3-Ln** complexes, the 2.740(1) to 2.793(1) Å

Table 1. Ln(II)−O(crypt) and Ln(II)−N(crypt) Bond Distance Ranges (Å)

	Ln(II)−O(crypt)	Ln(II)−N(crypt)	C.N.	reference
5-Sm	2.737(1)−2.783(1)	2.934(2)−2.942(2)	10	this study
3-Sm	2.740(1)−2.793(1)	2.876(2)	10	this study
5-Eu	2.731(2)−2.782(2)	2.937(2)−2.945(2)	10	this study
3-Eu	2.731(2)−2.767(3)	2.871(3)	10	this study
1-Eu	2.620(3)−2.681(4)	2.849(5)−2.871(5)	9	ref 14
[Eu(crypt)Cl][Cl]	2.659(3)−2.707(4)	2.838(3)−2.859(3)	9	ref 9
4-Yb	2.513(2)−2.717(2)	2.783(3)−2.790(3)	9	this study
2-Yb	2.444(7)−2.539(5)	2.649(6)−2.740(10)	8	ref 14

Sm(II)−O(crypt) and 2.731(2) to 2.767(3) Å Eu(II)−O(crypt) bond distances are shorter than the 2.876(2) Å Sm(II)−N(crypt) and 2.871(3) Å Eu(II)−N(crypt) distances as is typical in Ln-in-crypt complexes. The Eu(II)−O(crypt) bond distances in 10-coordinate **3-Eu** are longer than the 2.620(3) to 2.681(4) Å distances in the 9-coordinate **1-Eu**,[14] as expected for a higher coordinate complex. However, the Eu(II)−N(crypt) distance in **3-Eu** is in the range of those in **1-Eu**. The 2.546(3) Å Eu(II)−O(DMF) bond distance in **3-Eu** is significantly shorter than the Eu(II)−O(crypt) distances, but it is similar to the 2.558(3) Å Eu(II)−O(THF) distance in **1-Eu**.

A Yb(II)-in-crypt complex, $[Yb(crypt)(DMF)][I]_2$, **4-Yb**, was synthesized in a similar manner to eq 2. However, in the case of this smaller metal, the product contains only one coordinated DMF, eq 3, Figure 2. This difference in solvation is similar to the difference between $[Ln(crypt)(THF)][Cp'_3Ln]_2$, **1-Ln** (Ln = Sm, Eu), and $[Yb(crypt)][Cp'_3Yb]_2$, **2-Yb**, eq 1, in that the Yb complex has one less coordinated solvent molecule.[14] The 2.513(2) to 2.717(2) Å Yb(II)−O(crypt) distances in **4-Yb** span a wide range that is not so useful for comparison with the 2.444(7) to 2.539(5) Å distances in **2-Yb**. Although the 2.783(3) and 2.790(3) Å Yb−N(crypt) distances in **4-Yb** are similar, the analogues in **2-Yb** span a wide range, 2.649(6) to 2.740(10) Å. The Yb−N(crypt) distances in **4-Yb** are 0.090 and 0.085 Å less than those in **3-Sm** and **3-Eu**, respectively. In contrast, the data available in the Shannon radii compilation[18] show a 0.18 and 0.16 Å difference between the 8-coordinate Yb(II) and 9-coordinate Sm(II) and Eu(II), respectively. However, the 2.389(2) Å Yb(II)−O(DMF) distance in **4-Yb** is 0.168 and 0.157 Å less than the Sm−O(DMF) and Eu−O(DMF) distances in **3-Sm** and **3-Eu**, which is in the range predicted by the Shannon data. Overall, the metrical data suggest that the crypt ligand is quite flexible in its coordination behavior depending on the specific metal and additional ligands present.



(3)

4-Yb

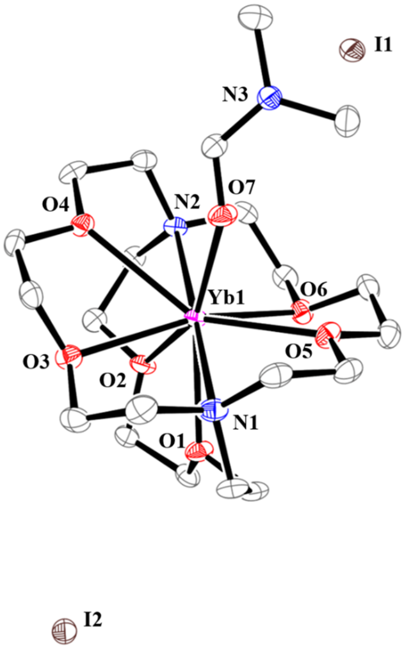
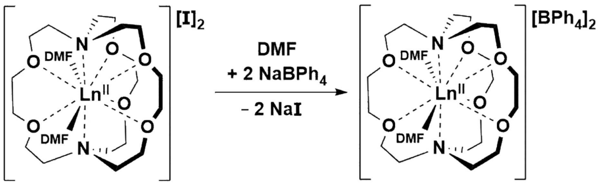


Figure 2. ORTEP representation of $[Yb(crypt)(DMF)][I]_2$, **4-Yb**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

Ionic Metathesis with Sm and Eu. Addition of 2 equiv of $NaBPh_4$ to a DMF solution of $[Ln(crypt)(DMF)_2][I]_2$, **3-Ln** for Ln = Sm, Eu, in DMF generated tetraphenylborate analogues of **3-Ln**, namely, the isomorphous Sm and Eu complexes, $[Ln(crypt)(DMF)_2][BPh_4]_2$, **5-Ln**, eq 4, Figure 3.



(4)

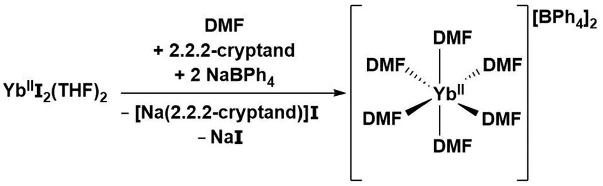
3-Ln **5-Ln**

Ln = Sm, Eu

The Sm−O(crypt) and Eu−O(crypt) metrical parameters in **5-Ln** are similar to those in **3-Ln**, but the Sm−N(crypt) is 0.062 Å longer, and the Eu−N(crypt) is 0.070 Å longer, Table 1. This is another example of the flexibility of the crypt ligand and could be related to the position of the $[BPh_4]^{1-}$ anions as described below.

In all the new structures above, the formyl hydrogen atoms of the DMF molecules have short distances to the nearest crypt oxygen atoms (see Supporting Information for full details). In **5-Sm**, these are H22···O5, 2.75(2) Å, and H19···O2, 3.07(2) Å. Hydrogen bonding from an outer-sphere DMF oxygen to an inner-sphere formyl hydrogen is also observed: H19···O9 is 2.55(2) Å, Figure 3. Additionally, hydrogen atoms of the crypt ligand and the methyl group of the DMF molecules have short distances to the phenyl ring hydrogen atoms in $[BPh_4]^{1-}$ ranging from 2.27 to 2.41 Å, which is in the range consistent with dispersion forces.[19−21] It is unknown if these distances and the position of the two $[BPh_4]^{1-}$ anions are related to the difference in Sm−N(crypt) distances in **3-Sm** and **5-Sm** (see above). Isomorphous **5-Eu** has similar close contacts.

Ionic Metathesis with Yb. Attempts to make **5-Yb** according to eq 4 by stepwise addition of $NaBPh_4$ to isolated **3-Yb** and by direct reaction of $NaBPh_4$ with YbI_2 and crypt, eq 5, were not successful. Instead, encapsulation of Na(I) was confirmed by X-ray crystallography by comparing the unit cell of the product of eq 5 with the known $[Na(crypt)][I]$.[22] The Yb(II) ion in this reaction was isolated as an orange DMF solvate, $[Yb(DMF)_6][BPh_4]_2$, **6-Yb**, eq 5. Solvated Ln(II)



(5)

6-Yb

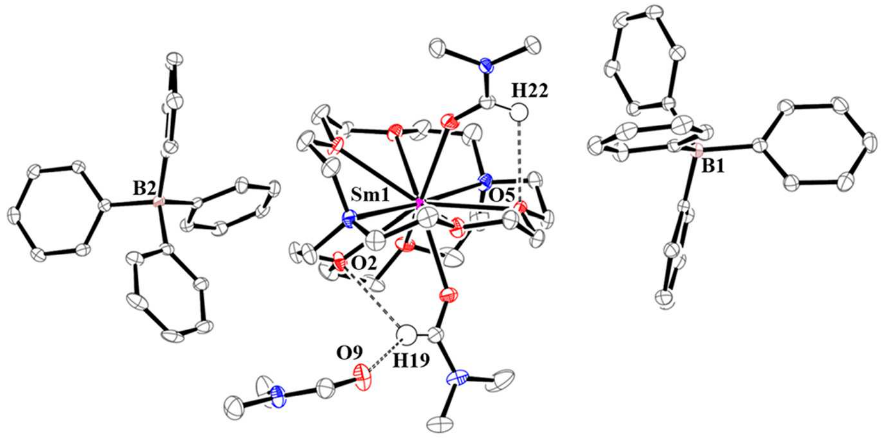


Figure 3. ORTEP representation of $[Sm(crypt)(DMF)_2][BPh_4]_2$, **5-Sm**, with thermal ellipsoids drawn at the 50% probability level, and dashed lines represent hydrogen bonding. Hydrogen atoms, except for H19 and H22, were omitted for clarity.

complexes have been isolated as $[BPh_4]^{1-}$ salts in the past from a variety of reactions, including $(C_9H_7)_2Sm(THF)_3$ + $[Et_3NH][BPh_4]$ to form $[Sm(THF)_7][BPh_4]_2$, $(C_5Me_5)Sm[N(SiMe_3)_2](THF)_2$ + $[Et_3NH][BPh_4]$ to form $[Sm(THF)_7][BPh_4]_2$, $[(C_5Me_5)Yb(THF)]_2(C_8H_8)$ + $AgBPh_4$ to form $[Yb(THF)_6][BPh_4]_2$, $[(C_5Me_5)Yb[N(SiMe_3)_2](THF)_2$ + $[Et_3NH][BPh_4]$ to form $[Yb(THF)_6][BPh_4]_2$, and $[Yb[N(SiMe_3)_2]_2(THF)_2$ + $[Et_3NH][BPh_4]$ to form $[Yb(MeCN)_8][BPh_4]_2$.[23]

The Yb−O(DMF) distances range from 2.311(2) to 2.403(2) Å in **6-Yb**, similar to the Yb−O(DMF)distance in **4-Yb**. There are several H···H distances between 2.33 and 2.44 Å in this structure involving $DMF/(BPh_4)^{1-}$ and $crypt/(BPh_4)^{1-}$ combinations. The 6-coordinate Shannon radii of Na(I) and Yb(II) are essentially identical with a radius of 1.02 Å.[18] The preferential formation of the $[Yb(DMF)_6]^{2+}$ cation over the encapsulated $[Yb(crypt)]^{2+}$ cation can be rationalized by Pauling electroneutrality. Since the DMF molecule can adopt an iminolate resonance structure, $^{-}O-C(H){=}N^{+}Me_2$, where the oxygen has a partial negative charge and the nitrogen has a partial positive charge, DMF would preferentially coordinate to the higher charged Yb(II) ion, leaving the neutral oxygen donor atoms in crypt to coordinate the lower charged Na(I) ion.

■ CONCLUSION

In summary, the complexes $[Ln(crypt)(DMF)_2][I]_2$, **3-Sm** and **3-Eu**, and $[Yb(crypt)(DMF)][I]_2$, **4-Yb**, provide new examples of Ln(II)-in-crypt complexes for Sm(II), Eu(II), and Yb(II) and demonstrate that simple starting materials, namely, $LnI_2(THF)_2$, can be used to synthesize them directly. The tetraphenylborate salts $[Ln(crypt)(DMF)_2][BPh_4]_2$, **5-Sm** and **5-Eu**, can be obtained by ionic metathesis. However, attempts to make the tetraphenylborate analogue of Yb gave the sodium crypt complex [Na(crypt)]I and $[Yb(DMF)_6][BPh_4]_2$, **6-Yb**, rather than a Yb crypt product. Previous studies have shown that trivalent $LaCl_3$ can also undergo facile encapsulation by crypt in DMF to form $[La(crypt)Cl_2]Cl$,[15] but in that case, two of the halide ligands are retained on the metal. In **3-Ln**, **4-Yb**, and **5-Ln**, the Ln(II) ions are free of any anionic coordinating ligands. This may facilitate further reduction of the metal.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b01049.

> NMR and UV−vis spectra, crystallographic details including crystal data and structure refinement, selected bond distances and angles, and ball-and-stick representations (PDF)

Accession Codes

CCDC 1909429−1909433 and 1935279 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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