Unique Eu\textsuperscript{II} Coordination Environments with a Janus Cryptand

Guo-Xia Jin,\textsuperscript{†,‡,§} Matthew D. Bailey,\textsuperscript{‡,§} and Matthew J. Allen*\textsuperscript{‡}

\textsuperscript{†}College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Functionalized Probes for Chemical Imaging, Key Laboratory of Molecular and Nano Probes, Ministry of Education, Shandong Normal University, Jinan 250014, P. R. China
\textsuperscript{‡}Department of Chemistry, Wayne State University, Detroit, Michigan 48202, United States

ABSTRACT: Two new Eu\textsuperscript{II}-containing cryptates were prepared with a new nitrogenous cryptand functionalized with three benzo groups. The introduction of three aromatic rings into the ligand backbone imparts lopsided geometrical features on the resulting Eu\textsuperscript{II} coordination environments. In both complexes, the interactions between Eu and the amines on the aromatic side of the molecule are weaker than those on the nonaromatic side, resulting in one discrete unit with two distinct faces. One of the new complexes is, to the best of our knowledge, the first direct observation of a bis-aquo Eu\textsuperscript{II}-containing cryptate with two nonadjacent inner-sphere water molecules. In addition to solid-phase structure, the electronic UV−visible and emission spectra of the new complexes were studied in acetonitrile. Experimental results show that the decreased Lewis basicity of the aromatic face hypsochromically shifts absorbances and emissions from a structurally related compound without the benzo groups.

INTRODUCTION

Europium in the divalent state has potential uses in a variety of applications including molecular catalysis,\textsuperscript{1} medical imaging,\textsuperscript{2} and as components of luminescent devices,\textsuperscript{3} magnetic devices,\textsuperscript{4} and other functional materials.\textsuperscript{5} Consequently, there is interest in exploring new ligands as a means of varying the physicochemical features of Eu\textsuperscript{II}-containing complexes. Here, we describe a new cryptand, 3 (Figure 1), designed to combine the features of ligand 1, which encapsulates divalent europium,\textsuperscript{6} and ligand 2, whose derivatives have garnered interest in augmenting electronic properties of d-block metals.\textsuperscript{7} By incorporating the benzo groups of ligand 2 into a cryptand that is of a proper size for Eu\textsuperscript{II}, we expected a plane of asymmetry to divide Eu\textsuperscript{II} between the two tertiary amines, resulting in one discrete unit with two distinct faces.\textsuperscript{8} Given that asymmetry often has interesting effects on the properties of molecules, we thought that ligand 3 would impart changes to both the solid-state and solution-phase properties of the resulting cryptates. Here, we report the syntheses and solid- and solution-phase characterization of two Eu\textsuperscript{II}-containing cryptates based on new benzo-containing cryptand 3, Eu3Cl\textsubscript{2} and Eu3I\textsubscript{2}, including crystal structures and absorption, excitation, and emission spectroscopy.

RESULTS AND DISCUSSION

The new cryptand was prepared in three steps from a known compound (Scheme 1). Briefly, acylation of N(\textit{o}-PhNH\textsubscript{2})\textsubscript{3} (2) with chloroacetyl chloride yielded tris(2-chloroacetamide)-amine 4. Reaction of 4 with tris(2-aminoethyl)amine afforded amide 5, and reduction of 5 with BH\textsubscript{3}·tetrahydrofuran (BH\textsubscript{3}·THF) gave tribenzo-aza222 cryptand 3 as an off-white solid. Metalation of cryptand 3 with EuCl\textsubscript{2} in anhydrous methanol followed by filtration and slow evaporation produced yellow, blocklike crystals of [Eu3Cl\textsubscript{2}]Cl (6). Because of the low solubility of Eu3I\textsubscript{2} in methanol, other solvents were pursued for metalation with EuI\textsubscript{2}. Ultimately, metalation of cryptand 3 with EuI\textsubscript{2} was performed in THF followed by filtration and diffusion with hexanes to produce cryptate Eu3I\textsubscript{2}·THF as a yellow powder. This powder was dissolved in wet acetone, and the resulting solution was slowly evaporated to produce yellow, blocklike crystals of cryptate [Eu3(\textit{H}_2\textsubscript{O})\textsubscript{2}]I\textsubscript{2} (7).

Figure 1. Ligands 1, 2, and 3.
3.189(2) and 3.294(10) Å for 6 and 7, respectively, are longer than the longest Eu−N bond of which we are aware (3.11(1) Å).9 These long interactions make the assignment of coordination numbers for both complexes ambiguous because of the unclear extent to which N1 contributes to the overall ligation. However, because of the pyramidalization of N1 indicating the accompanying lone pair faces toward the europium ion, and for convenience, we will refer to the Eu−N1 interactions of 6 and 7 as bonds.

Cryptate 6 crystallizes in space group P21/c, and the unit cell contains a cationic cryptate with one inner-sphere chloride, as well as one outer-sphere chloride and two molecules of methanol. The structure of 6 shows that EuII is coordinated to all eight nitrogens of the ligand and to one chloride ion in a distorted staggered hula-hoop geometry (Figure 2).10 The presence of two different types of coordinating nitrogens, aromatic and aliphatic, causes the europium ion to sit lopsided in the cryptand. This lopsided ligation is seen quantitatively in the longer bond distances between EuII and the amines on the

Figure 2. (a) (top) Cryptate 6, (middle) crystal structure of 6, and (bottom) view of the hula-hoop geometry of 6; (b) (top) cryptate 7, (middle) crystal structure of 7, and (bottom) view of the tetracapped trigonal prism in 7. Thermal ellipsoids are drawn at the 50% probability. H atoms, noncoordinated counterions, and noncoordinated solvent molecules were omitted for clarity.
Table 1. Selected Bond Distances (Å) of 6, 7, and Eu1Cl2

<table>
<thead>
<tr>
<th></th>
<th>6</th>
<th>7</th>
<th>Eu1Cl2 a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu–Ntertiary, Ar</td>
<td>3.189(2)</td>
<td>3.294(10)</td>
<td>NA</td>
</tr>
<tr>
<td>Eu–Ntertiary, alk</td>
<td>2.792(3)</td>
<td>2.893(10)</td>
<td>2.845(14)–2.921(10)</td>
</tr>
<tr>
<td>Eu–Nsecondary, Ar</td>
<td>2.824(2)–2.860(2)</td>
<td>2.878(10)–2.950(10)</td>
<td>NA</td>
</tr>
<tr>
<td>Eu–Nsecondary, alk</td>
<td>2.673(5)–2.740(2)</td>
<td>2.656(11)–2.743(10)</td>
<td>2.675(10)–2.958(15)</td>
</tr>
</tbody>
</table>

aNA = not applicable.

The aromatic face of the molecule (tertiary: N1; secondary: N3, N5, and N7) relative to the nonaromatic face (tertiary: N2; secondary: N4, N6, and N8; Table 1). The distances between EuII and the aromatic secondary amines are an average of 0.127 Å longer than the distances between EuII and the aliphatic secondary amines, and the aryl Eu1–N1 distance is 0.397 Å longer than the alkyl Eu1–N2 distance. These differences likely arise from the decreased Lewis basicity of the amines on the aromatic face of the cryptand, relative to the aliphatic face, due to the electron-withdrawing nature of the benzo groups.

Crypsis 7 crystallizes in the space group P1, and the unit cell contains one cationic cryptate with two inner-sphere water molecules, as well as two outer-sphere chlorides, two outer-sphere water molecules, and one outer-sphere molecule of acetone. The structure of 7 shows that EuII adopts an uncommon 10-coordinate distorted C2v tetracapped trigonal prismatic geometry (Figure 2). The arrangement of the caps is unique in that both triangular faces are capped as well as two of the rectangular faces of the trigonal prism. Although multiple examples of tetracapped trigonal prisms have been reported,12 these previous reports describe C3v symmetric molecules with three of the rectangular faces and one triangular face capped. The C2v, tetracapped trigonal prism in 7 is, to the best of our knowledge, the first report of the geometry for a diverval lanthanide.13

Despite the geometrical differences between 6 and 7, EuII in 7 coordinates to the alkyl amines more closely than the aromatic amines similar to complex 6. The distances between EuII and the secondary amines on the aromatic face of 7 (N3, N5, and N7) are an average of 0.210 Å longer than the distances between EuII and the amines on the aliphatic face (N4, N6, and N8). Furthermore, the aryl Eu1–N1 distance of 7 is 0.401 Å longer than the Eu1–N2 distance on the aliphatic side.

In addition to the difference between the aromatic and aliphatic sides of 6 and 7, differences in bond distances are also apparent in comparison of complexes 6 and 7 with the all-aliphatic Eu1Cl2. The distances between EuII and the aromatic secondary amines in 6 and 7 are 0.043 and 0.119 Å longer, respectively, than the average EuII secondary amine distance in Eu1Cl2. Conversely, the distances between EuII and the aliphatic secondary amines in 6 and 7 are 0.084 and 0.100 Å shorter, respectively, than the average EuII secondary amine distance Eu1Cl2. This trend holds for the EuII aromatic tertiary amine distances in 6 and 7 that are 0.268 and 0.373 Å longer, respectively, than the longest EuII tertiary amine distance in Eu1Cl2. Interestingly, while the EuII aliphatic tertiary amine distance in 6 is 0.53 Å shorter than the shortest EuII tertiary amine distance in Eu1Cl2, the EuII aliphatic tertiary amine distance in 7 is 0.048 Å longer. These differences highlight the influence that the two distinct sides of cryptand 3 have on the positioning of EuII within cryptates.

Beyond comparisons of EuII-containing cryptates, the literature describing complexes formed with derivatives of ligand 2 enables analogies to be drawn between 6 and 7 and d-block complexes. A series of crystallographically characterized complexes has been reported of both hexamethylated ligand 2 (2(CH3)6) and its ethylene-bridged analogue (hexamethylated tris(2-aminoethyl)amine, Tren(CH3)6) with CuII, FeII, CoII, and NiII.14 Although 2(CH3)6 and Tren(CH3)6 contain benzo groups or ethylene diamines that influence the electronic properties of the resulting complexes, they do not influence the structure of d-block metals like we observed for EuII. Specifically, there is no statistically significant lengthening of central M–N bonds (p > 0.01) in the d-block complexes of 2(CH3)6 relative to corresponding complexes of Tren(CH3)6 except in the case of NiII.15 The lengthening of the NiII–N bond represents a 1% increase in bond length. In comparison, the lengthening of 6 and 7 versus Eu1Cl2 represents 9 and 13% increases in bond length, respectively (p > 0.0001).15

This discrepancy with the influence of the benzo groups on bond length likely arises from the primarily electrostatic binding of EuII. Among the eight nitrogen donors in ligand 3, EuII favors the more potent electron donors on the aliphatic half of the ligand. This favoring of aliphatic over aromatic is not the case of the aforementioned complexes of CuII, FeII, CoII, and NiII that do not have an option for choosing between aliphatic or aromatic amines. In this respect, by tethering two sets of four nitrogen donors with different Lewis basicity together in ligand 3, we facilitated the observed lopsided binding.

In addition to ligand 3 imparting interesting geometric features to EuII-containing complexes, an important feature of cryptate 7 is that it has two coordinated water molecules. The water molecules likely come from either the nonanhydrous solvent used in the crystallization or from the atmosphere of the wet glovebox. To the best of our knowledge, only one other, noncryptate, EuII-containing complex has been reported to have two nonadjacent inner-sphere water molecules;16 making the crystal structure of 7 the first direct observation of a bis-aquo EuII-containing cryptate with two nonadjacent inner-sphere water molecules. The Eu–Owater distances are 2.714(5) and 2.793(5) Å. Experimental verification of the ability of EuII-containing cryptates to interact with two water molecules has implications in the design of EuII-based contrast agents for magnetic resonance imaging and is consistent with our previous observations.2,17

Electronic Absorption and Emission Spectroscopy. To explore if the decreased Lewis basicity of the aromatic face impacted solution-phase properties, in addition to solid-phase structure, we studied the UV–visible spectra of Eu3Cl3, Eu3I3, and Eu1Cl3 in acetonitrile (Figure 3A and Table 2). Previous studies of Eu1Cl3 were performed in aqueous media; however, complexes Eu3Cl3 and Eu3I3 are not soluble in water, so a parallel study could not be performed. Therefore, acetonitrile was used for solution-phase studies because all three complexes are soluble in that solvent. Solutions of Eu1Cl3 and Eu3Cl3 were generated by dissolving crystalline material in acetonitrile,
to the bathochromic shift of 42 nm between the absorption of \([\text{Cu}^{2+}(\text{CH}_3_2\text{CN})_4\text{Cl}_2]\) compared to \([\text{CuTren}(\text{CH}_3_2\text{CN})_6\text{Cl}_2]\). In the \(\text{Cu}^{II}\) containing complexes, the absorptions were assigned as arising from d–d transitions. This discrepancy between \(\text{Cu}^{II}\) and \(\text{Eu}^{II}\) could be accounted for with a 4f–5d transition. The 4f orbitals would be expected to be relatively unchanged by the ligand; therefore, if the addition of benzo groups raised the energy of the 5d orbitals relative to \(\text{Eu}^{II}\), then the absorption would be hypsochromically shifted. Conversely, in the case of \(\text{Cu}^{III}\), both orbitals involved in the absorbance are susceptible to the changes in the ligand field. If all of the d orbitals energies are raised, similar to the proposed energy shift of the d orbitals in \(\text{Eu}^{II}\) and \(\text{Eu}^{III}\), it is possible that relative energetic shifts could lead to a d–d transition that is bathochromically shifted. Regardless of the mechanism, ligand 3 imparts a unique influence on the optical absorption of \(\text{Eu}^{III}\), and this observation led us to explore the influence of 3 on the solution-phase emission of \(\text{Eu}^{III}\).

To characterize the luminescence properties of \(\text{Eu}^{II}\)-containing complexes of 3 in solution, we acquired excitation and emission spectra of \(\text{Eu}^{III}\)-containing complexes (Figure 3). The excitation maximum of \(\text{Eu}^{III}\)-containing complexes occurred at 354 nm, resulting in a broad purple-blue emission (370–600 nm, \(\lambda_{\text{em}}\) max = 424 nm) that is hypsochromically shifted compared to the emission of \(\text{Eu}^{III}\) in acetonitrile (450–650 nm, \(\lambda_{\text{em}}\) max = 511 nm, excited at 400 nm). Similarly, \(\text{Eu}^{III}\)-containing complexes showed an excitation maximum at 345 nm resulting in a broad emission (360–610, \(\lambda_{\text{em}}\) max = 419 nm) that is hypsochromically shifted compared to the emissions of both \(\text{Eu}^{III}\)-containing complexes. The Stokes shifts for \(\text{Eu}^{III}\)-containing complexes are all between 3000 and 7000 cm

### Table 2. Selected Spectral Features of 3, \(\text{Eu}^{III}\)-containing complexes, \(\text{Eu}^{III}\)-containing complexes, and \(\text{Eu}^{III}\)-containing complexes, the absorptions were assigned as arising from \(\text{d}–\text{d} \) transitions. This discrepancy between \(\text{Cu}^{II}\) and \(\text{Eu}^{II}\) could be accounted for with a 4f–5d transition. The 4f orbitals would be expected to be relatively unchanged by the ligand; therefore, if the addition of benzo groups raised the energy of the 5d orbitals relative to \(\text{Eu}^{II}\), then the absorption would be hypsochromically shifted. Conversely, in the case of \(\text{Cu}^{III}\), both orbitals involved in the absorbance are susceptible to the changes in the ligand field. If all of the d orbitals energies are raised, similar to the proposed energy shift of the d orbitals in \(\text{Eu}^{II}\) and \(\text{Eu}^{III}\), it is possible that relative energetic shifts could lead to a d–d transition that is bathochromically shifted. Regardless of the mechanism, ligand 3 imparts a unique influence on the optical absorption of \(\text{Eu}^{III}\), and this observation led us to explore the influence of 3 on the solution-phase emission of \(\text{Eu}^{III}\).

To characterize the luminescence properties of \(\text{Eu}^{II}\)-containing complexes of 3 in solution, we acquired excitation and emission spectra of \(\text{Eu}^{III}\)-containing complexes (Figure 3). The excitation maximum of \(\text{Eu}^{III}\)-containing complexes occurred at 354 nm, resulting in a broad purple-blue emission (370–600 nm, \(\lambda_{\text{em}}\) max = 424 nm) that is hypsochromically shifted compared to the emission of \(\text{Eu}^{III}\) in acetonitrile (450–650 nm, \(\lambda_{\text{em}}\) max = 511 nm, excited at 400 nm). Similarly, \(\text{Eu}^{III}\)-containing complexes showed an excitation maximum at 345 nm resulting in a broad emission (360–610, \(\lambda_{\text{em}}\) max = 419 nm) that is hypsochromically shifted compared to the emissions of both \(\text{Eu}^{III}\)-containing complexes. The Stokes shifts for \(\text{Eu}^{III}\)-containing complexes are all between 3000 and 7000 cm

### CONCLUSIONS

Two new \(\text{Eu}^{II}\)-containing cryptates were synthesized using new tribenzo-aza222 cryptand 3. The introduction of three aromatic rings into one side of the ligand has a dramatic effect on the resulting \(\text{Eu}^{II}\) coordination environments and absorption and emission properties. The coordination polyhedron in 7 is an unusual \(\text{C}_7\) tetracapped trigonal prism, and 7 is the first example of a bis-aquo \(\text{Eu}^{II}\)-containing cryptate characterized in the solid state. Beyond \(\text{Eu}^{II}\), we expect this new ligand will be of interest for use with many other metals.

### EXPERIMENTAL DETAILS

**General.** Flash chromatography was performed using silica gel 60, 230–400 mesh (EMD Chemicals), or neutral activated aluminum oxide Brockmann 1 (Sigma-Aldrich). Preparative layer chromatography (PLC) was performed on PLC plates precoated with neutral \(\text{Al}_2\text{O}_3\) 60 F254 (1.5 mm thickness, EMD Millipore Corporation). Analytical thin-layer chromatography (TLC) was performed on ASTM TLC plates precoated with silica gel 60 F254 (250 μm thickness), or on neutral \(\text{Al}_2\text{O}_3\) 150 F254 TLC plates (EMD Chemicals). Commercially available chemicals were of reagent-grade purity or better and were used and solutions of \(\text{Eu}^{III}\) were generated by dissolving \(\text{Eu}^{III}\)-THF powder in acetonitrile. The UV–visible spectrum of \(\text{Eu}^{III}\) showed two absorptions centered at 224 and 289 nm (\(\varepsilon = 3.4 \times 10^3 \) and \(1.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}\), respectively), and \(\text{Eu}^{III}\) showed two absorptions centered at 244 and 282 nm (\(\varepsilon = 4.3 \times 10^3 \) and \(1.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}\), respectively). These absorptions are hypsochromically shifted from both the \(\pi–\pi^*\) transition in the spectrum of 3 (308 nm, \(\varepsilon = 9.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}\)) and the two absorption bands of \(\text{Eu}^{III}\) (270 and 378 nm, \(\varepsilon = 2.1 \times 10^3 \) and \(4.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}\), respectively). These 89 and 96 nm hypsochromic shifts of the lower-energy envelopes of \(\text{Eu}^{III}\) and \(\text{Eu}^{III}\), respectively, compared to \(\text{Eu}^{III}\) are the opposite
without further purification unless otherwise noted. Tris(2-aminophenyl)amine (2) was prepared by following a published procedure.74

1H NMR spectra were obtained using a Mercury 400 (400 MHz) or Varian 500 (500 MHz) spectrometer, and 13C NMR spectra were obtained using a Mercury 400 (101 MHz) or Varian 500 (126 MHz) spectrometer. Chemical shifts are reported relative to residual solvent signals (CDCl3, δ: 1H: δ 7.27, 13C: δ 77.23). NMR data are assumed to be first-order, and the apparent multiplicity is reported as “s” = singlet, “d” = doublet, “q” = quartet, “t” = triplet, “m” = multiplet, or “brs” = broad singlet. Italicized elements are those that are responsible for the shifts. Correlation spectroscopy (COSY), distortionless enhancement by polarization transfer (DEPT), and heteronuclear multiple quantum coherence (HMQC) spectra were used to assign spectral peaks. High-resolution electrospray ionization mass spectra (HRESIMS) were obtained on a Waters LCT premier time-of-flight high-resolution mass spectrometer. Elemental analysis (C, H, and N) determinations were performed by Midwest Microlab (Indianapolis).

UV-visible absorbance was measured using a Shimadzu UVmini-1240 spectrophotometer. Excitations and emissions were recorded using a Horiba Jobin Yvon Fluoromax-4 spectrophotometer. Excitation spectra were collected at 1 nm resolution with an emission slit width of 10 nm and an excitation slit width of 1 nm. Emission spectra were collected at 1 nm resolution with an excitation slit width of 10 nm and an emission slit width of 1 nm. Infrared spectra were obtained on Shimadzu FTIR Tracer-100 spectrometer using an ATR cell. Infrared samples were prepared in inert atmosphere glove boxes under parafilm oil. Inductively coupled plasma mass spectrometric (ICP−MS) measurements were acquired on an Agilent Technologies 7700 series ICP−MS instrument at the Lumigen Instrument Center in the Department of Chemistry at Wayne State University. All dilutions were performed with aqueous 2% HNO3, which was also used for blank samples during calibration. The calibration curve was created using the 153Eu isotope ion count for a 0−100 ppb concentration range (diluted from Fluka ICP standard solution, Eu2O3 in aqueous 2% HNO3, 1000 mg Eu/L). All samples were diluted to fall within this range.

N,N’,N”-(Nitrilotris(benzene-2,1-diyl))tris(2-chloroacetamide) 4. 2-Chloroacetyl chloride (2.96 g, 2.08 mL, 26.2 mmol) was added dropwise to a mixture of tris(2-aminophenyl)amine (2; 0.766 g, 2.62 mmol) and K2CO3 (3.62 g, 26.2 mmol) in acetone (30 mL) at ambient temperature. The resulting mixture was stirred at ambient temperature. After 24 h, the reaction mixture was poured into ice water (20 mL) and extracted with ethyl acetate (3 × 20 mL). The organic extract was dried over MgSO4. Purification by silica gel chromatography (ethyl acetate/petroleum ether 1:1) produced 2 as a white solid (1.10 g, 80%). 1H NMR (400 MHz, CDCl3, δ): 8.53 (s, 3H, H-meta), 7.73 (d, J = 8.0 Hz, 3H, H-para), 7.24−7.10 (m, 6H, H-meta), 6.88 (d, J = 8.0 Hz, 3H, H-para), 3.80 (s, 6H, CH2); 13C NMR (101 MHz, CDCl3, δ): 164.7−138.3, 130.0, 127.3 (CH2), 126.1 (CH), 125.6 (CH2), 124.4 (CH), 42.5 (CH2); TLC: Rf = 0.50 (1:1 ethyl acetate/petroleum ether); HRESIMS (m/z): [M + H]+ calcd for C30H42EuI2N8O3, 1034.1886; found, 1034.1886.

Amide 5. To a solution of tris(2-aminophenyl)amine (173 mg, 1.18 mmol) in EtOH (30 mL) was added a solution of 4 (616 mg, 1.18 mmol) in EtOH (30 mL) and Et3N (1.0 mL). The mixture was heated at reflux under Ar for 36 h. After completion of the reaction, the solvent was removed under reduced pressure. The residue was purified using a neutral Al2O3 column (ethyl acetate/hexanes 1:1 followed by CH2Cl2/MeOH 20:1) to yield 370 mg (56%) of 5 as a white solid. 1H NMR (400 MHz, CDCl3, δ): 9.53 (s, 3H, H-meta), 7.69 (d, J = 8.0 Hz, 3H, H-para), 7.17 (t, J = 8.0 Hz, 3H, H-para), 7.06 (t, J = 8.0 Hz, 3H, H-para), 6.80 (d, J = 8.0 Hz, 3H, H-para), 3.25−1.98 (m, 21H, CH2 + NH); 13C NMR (101 MHz, CDCl3, δ): 169.7, 138.8, 130.9, 126.3 (CH2), 125.5 (CH), 124.1 (CH), 56.3 (CH2), 52.2 (CH2), 48.2 (CH2); TLC: Rf = 0.50 (20:1 CH2Cl2/MeOH); HRESIMS (m/z): [M + H]+ calcd for C30H42N8O5, 579.2989; found, 579.2984.

Ligand 3. Amide 5 (0.40 g, 0.72 mmol, 1 equiv) was dissolved in anhydrous THF under Ar and cooled to 0°C. Then, BH3·THF (1.0 M in THF, 8.6 mL, 8.6 mmol, 12 equiv) was added. After the addition, the resulting solution was heated at 65°C for 24 h. The reaction mixture was cooled to ambient temperature and quenched with methanol (2 mL). The solvent was removed under reduced pressure. Methanol (40 mL) was added, and the mixture was heated at reflux for 12 h under Ar. Solvent was removed under reduced pressure, and the resulting residue was purified with neutral Al2O3 PLC (CH2Cl2/MeOH 30:1) to yield 200 mg (54%) of 3 as an off-white solid. 1H NMR (500 MHz, CDCl3, δ): 7.06 (t, 3H, J = 8 Hz, H-meta), 6.88 (d, 3H, J = 8 Hz, H-para), 6.75 (d, 3H, J = 8 Hz, H-para), 6.62 (t, 3H, J = 8 Hz, H-para), 3.72 (d, 3H, J = 8 Hz, NH), 3.43 (q, 3H, J = 8 Hz, CH2), 2.88−2.81 (m, 3H, CH3), 2.80−2.74 (m, 3H, CH3), 2.72−2.53 (m, 15H, CH2), 2.05 (brs, 3H, NH); 13C NMR (126 MHz, CDCl3, δ): 143.7, 132.8, 126.1 (CH), 125.3 (CH), 117.6, 112.2 (CH), 56.8 (CH2), 49.7 (CH3), 48.0 (CH2), 44.4 (CH2); TLC: Rf = 0.50 (30:1 CH2Cl2/MeOH); HRESIMS (m/z): [M + H]+ calcd for C30H43N8, 515.3611; found, 515.3624.

Preparation of Complexes. Complex 6. Crystals of 6 were prepared in a dry (no water and no molecular oxygen) glovebox under an Ar atmosphere. X-ray quality crystals of 6 were prepared by dissolving EuCl3 (6.5 mg, 0.029 mmol, 1 equiv) and 3 (15 mg, 0.029 mmol, 1 equiv) in methanol (0.25 mL) under an atmosphere of Ar. The resulting solution was stirred for 1 h and filtered through a 0.2 μm hydrophilic filter to produce a clear, pale yellow filtrate. Solvent was slowly evaporated to afford yellow, blocklike crystals (10 mg, 45%). C30H42Cl2EuN8CH2OH: Anal. Calc. C 43.82, H 6.02, N 14.56; found C 43.82, H 6.04, N 14.57%. IR (paraffin oil, cm−1) 2762 (w), 3265 (w), 3209 (m, br), 1596 (m), 1583 (w), 1495 (s), 1458 (s), 1366 (m), 1310 (m), 1259 (w), 1232 (m), 1175 (w).

Complex 7. Crystals of 7 were prepared in a wet (water allowed but no molecular oxygen) glovebox under an N2 atmosphere. Complex 7 was prepared by dissolving Eu3I2 (12 mg, 0.029 mmol, 1 equiv) and 3 (15 mg, 0.029 mmol, 1 equiv) in THF (0.50 mL) under an atmosphere of N2. The resulting solution was stirred for 1 h and filtered through a 0.2 μm hydrophilic filter to produce a yellow filtrate. Yellow powder was precipitated by diffusion of hexane into the THF solution, collected, and dried under vacuum (21 mg, 73%). C30H42EuI2N8C16H20: calc C 41.14, H 5.08, N 11.29; found C 40.90, H 4.83, N 10.79. IR (paraffin oil, cm−1) 3272 (w), 3162 (m, br), 1651 (m), 1597 (m), 1590 (s), 1492 (s), 1351 (w), 1339 (w), 1311 (w), 1295 (w), 1253 (m), 1231 (m), 1206 (w), 1170 (m). This powder was dissolved in acetone (0.65 mL), and slow solvent evaporation afforded yellow, blocklike crystals suitable for X-ray single-crystal diffraction.
The authors thank L. A. Ekanger for helpful discussions and C. Winter for use of the IR spectrometer. The authors acknowledge Shandong Provincial Education Association for International Exchanges for support. M. J. A. gratefully acknowledges a Schaap Faculty Scholar Award, and this material is supported by the National Science Foundation under Grant No. CHE-1564755.

The authors declare no competing financial interest.