# Characterization of Lanthanide Complexes with Bis-1,2,3-triazole-bipyridine Ligands Involved in Actinide/Lanthanide Separation

Julie M. Muller,[†] Shane S. Galley,[‡] Thomas E. Albrecht-Schmitt,[‡] and Kenneth L. Nash*,[†]

[†]Chemistry Department, Washington State University, Pullman, Washington 99164, United States
[‡]Department of Chemistry & Biochemistry, Florida State University, Tallahassee, Florida 32306, United States

S *Supporting Information*

ABSTRACT: The complexation of selected trivalent lanthanide ions with derivatives of the tetranitrogen donor ligands 6,6′-bis-1R,1H-1,2,3-triazol-4-yl-2,2′-bipyridines (BTzBPs, R = alkyl or aryl) was investigated in solid state and in solution. An anhydrous solid $[Ce(Bn-BTzBP)(NO_3)_3]$ (Bn = benzene) complex was synthesized and characterized by single-crystal X-ray diffraction. Eu(III) complexes with the 2-ethyl(hexyl) derivative EH-BTzBP in methanol were studied by time-resolved fluorescence spectroscopy. Earlier studies have identified the EH-BTzBP as a potentially useful solvent extraction reagent for the separation of americium from lanthanide metal ions, a challenging component of advanced nuclear fuel cycles for actinide transmutation. To help identify species formed in the extraction process, the influence of 2-bromohexanoic acid (identified as an essential component of the separation system) on Eu(III) complexes was investigated. Comparison with an organic phase after extraction of Eu(III) by EH-BTzBP and 2-bromohexanoic acid showed that both 1:1 and 1:2 (Eu/EH-BTzBP) complexes are involved in the extraction. UV−visible spectrophotometry was used to compare Eu(III) stability constants with those of other Ln(III) complexes.
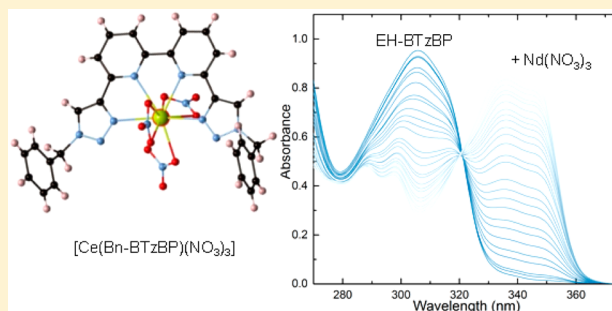
INTRODUCTION

If left untreated, used nuclear fuel remains highly radiotoxic and thermally active for millennia, principally because of the initial presence of uranium activation products, plutonium, and minor actinides (Np, Am, Cm). This time could be reduced to a few hundred years and the effect of long-term heat load/persistent radiotoxicity of power plant wastes on a geologic repository minimized if the transuranium actinides are isolated and subsequently transmuted to shorter-lived or stable nuclides in a fast neutron reactor.[1,2] However, actinides first must be separated from the trivalent lanthanides because the high neutron capture cross sections of some of the lanthanides inhibit efficient transmutation. Solvent extraction is the current preferred technique for the recycling of used nuclear fuel. U, Pu, and Np can be easily removed from the bulk using a modified PUREX process.[3,4] The essential separation of Am and Cm from the lanthanides is challenging because of their similarity in ionic radius, the predominance of the trivalent oxidation state, and the similarity in the nature of their bonding interactions in their coordination complexes. The comparative "softness" of nitrogen donor ligands such as 2,6-bis-1,2,4-triazin-3-yl-pyridines (BTPs) and 6,6′-bis-1,2,4-triazin-3-yl-2,2′-bipyridines (BTBPs) has enabled moderately efficient An/Ln separations.[5−7] However, these reagents have so far failed to fulfill all requirements for a process application because: (1) most of the derivatives synthesized and characterized to date suffer from some degree of instability under highly acidic or radiolytic conditions, (2) solubility in nonpolar diluents is limited, and (3) phase-transfer kinetics is moderately slow.[5−8]
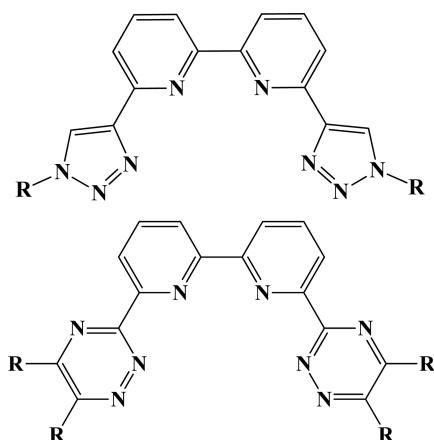
Recently, we synthesized and tested the extraction behavior of a new type of tetradentate nitrogen donor complexant: 6,6′-bis(1-R-1H-1,2,3-triazol-4-yl)-2,2′-bipyridines (R = alkyl or aryl) or BTzBPs (Figure 1).[9] The 2-ethylhexyl derivative, 6,6′-bis(1-(2-ethylhexyl)-1H-1,2,3-triazol-4-yl)-2,2′-bipyridine (EH-BTzBP), exhibited high selectivity for Am over the lanthanides in the presence of the 2-bromohexanoic acid (HA) as lipophilic anion source in toluene, no signs of degradation under highly acidic and oxidative conditions, and rapid phase-transfer kinetics.

The origin of the selectivity of N-donor ligands as well as the need for a lipophilic anion to efficiently extract metal nitrates with some of the ligands is still not fully explained.[10,11] To better understand this observation on a molecular level and to gain information about the structure and speciation of the complexes formed during the extraction process, lanthanide metal complexation was studied by spectroscopic techniques and X-ray crystallography.

In this paper, solid-state cerium nitrate complexes formed with 6,6′-bis(1-benzyl-1H-1,2,3-triazol-4-yl)-2,2′-bipyridine (Bn-BTzBP) were characterized by single-crystal X-ray diffraction and UV−vis−NIR spectroscopy. Crystallography

Figure 1. Schematic representations of BTzBPs (top) and BTBPs (bottom).

Table 1. Selected Crystallographic Information for Ce(Bn-BTzBP)(NO$_3$)$_3$

compound	Ce(C$_{28}$H$_{22}$N$_{11}$O$_9$)
formula mass	1591.35
color and habit	yellow, plate
space group	$P\bar{1}$
a (Å)	9.5464(15)
b (Å)	14.181(2)
c (Å)	7.23.720(4)
α (deg)	103.231(4)
β (deg)	94.598(4)
γ (deg)	96.035(9)
V (Å^3)	3090.4(9)
Z	2
T (K)	273(2)
λ (Å)	0.71073
maximum 2θ (deg)	26.371
ρ_{calc} (g/cm^3)	1.710
μ (Mo Kα) (cm^{-1})	15.46
$R(F)$ for $F_0^2 > 2\sigma(F_0^2)$[a]	0.0559
$R_w(F_0^2)$[b]	0.0827

[a]$R(F) = \sum ||F_o| - |F_c||/\sum |F_o|$. [b]$R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4]^{1/2}$.

studies yield information on the coordination mode and structure of solid metal complexes. Because of the poor solubility of Bn-BTzBP in suitable diluents, Bn-BTzBP metal complexes could not be studied in solution, and EH-BTzBP was used instead. Europium complexes formed with EH-BTzBP in solution were characterized by time-resolved fluorescence spectrometry (TRFS) and UV−vis spectroscopy. The influence of lipophilic anion HA on the europium-BTzBP complexes was studied by TRFS as well.

■ EXPERIMENTAL SECTION

Synthesis of Ce(III)−Bn-BTzBP−Nitrate Crystals. Bn-BTzBP (0.0032 g, 0.0068 mmol) was dissolved in 3 mL of dichloromethane. A 1 mL solution of cerium(III) nitrate (0.086 g, 0.20 mmol) in ethanol was prepared. The ethanol solution was layered on top of the dichloromethane layer. After 3 d of slow diffusion, yellow platelike crystals were obtained that were suitable for single-crystal X-ray diffraction studies.

Crystallographic Studies. A single crystal of Ce(Bn-BTzBP)-(NO$_3$)$_3$ was fixed to a mitogen mount with viscous immersion oil and aligned on a Brüker Quest using a digital camera. Intensity measurements were performed using an IμS X-ray source (Mo Kα, λ = 0.710 73) with high-brilliance and high-performance focusing multilayer optics. Standard Quest software was used for determination of the unit cell and data collection control. Each set had four different φ angles for the crystal, and each exposure covered a range of 0.5° in ω. A total of 1464 frames with an exposure time of 25 seconds per frame was collected. Quest software was used for the integration including Lorentz and polarization corrections. The positions of all hydrogen atoms were calculated, and their refinement parameters were constrained. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques using the program suite SHELX.[12] Solutions were checked using PLATON.[13] Selected crystallographic information is listed in Table 1. Atomic coordinates and additional information are provided in Supporting Information.

Ultraviolet−Visible−Near-Infrared Spectroscopy. UV−vis−NIR absorption data were acquired from a single crystal of Ce(Bn-BTzBP)(NO$_3$)$_3$ using a CRAIC Technologies micro-spectrophotometer. The crystal was placed on a quartz slide under immersion oil, and the data were collected from 250 to 850 nm. The exposure time was automatically optimized by the CRAIC software.

Time-Resolved Fluorescence Spectrometry. Fluorescence emission experiments were performed on a HORIBA FluoroMax-4 Spectrofluorometer attached to a personal computer running the FluorEssence software suite. Europium cations were excited to the $^5L_6$ level by a 150 W ozone-free xenon arc lamp at an excitation wavelength of 393 nm coupled to single-grating Czerny−Turner monochromators for excitation and emission spectral selection. The

detector for emission experiments was a R928P photomultiplier tube with response ranges from 180 to 850 nm. The emission spectra were observed in the range of 525−725 nm using an excitation slit width of 12 nm, emission slit width of 1 nm, increments of 0.1 nm, and an integration time of 0.25 s. To obtain Eu lifetimes, the emission from the $^5D_0 \rightarrow ^7F_2$ (614 nm) transition was measured. Excitation of Eu for lifetime measurements was done by using a pulsed solid-state SpectraLED source at a fixed 394 nm wavelength. Lifetimes were recorded using a time-correlated single-photon counting accessory (FM-2015) for the Fluoromax-4, using an IBH Data Station Hub and analyzed using the DAS 6 decay analysis software package from Horiba Scientific. All samples were prepared by weight and run in screw cap 10 mm quartz fluorimeter cells (five windows). Experimental spectra were fit using the Hypspec software from Protonic Software.[14]

Ultraviolet−Visible Spectrophotometry. Spectro-photometric UV−visible titrations were performed using an HR4000CG-UV-NIR high-resolution spectrometer with a deuterium−halogen DH-2000 light source from Ocean Optics. Optical fibers used to connect the light source to the Ocean Optic device were of VIS grade with a core diameter of ∼400 nm. Quartz cuvettes of 1 cm path length were used. Spectra were recorded on a 250−400 nm wavelength range to follow the $\pi−\pi^*$ absorption band of the EH-BTzBP ligand. A 5 × 10^{-5} M solution of EH-BTzBP in methanol was titrated with Ln(NO$_3$)$_3$ solutions (1 × 10^{-3} to 0.1 M) until the variation in absorbance became negligible. Spectra were fit using Hypspec. All spectroscopic experiments were run in triplicate, and the results were combined in establishing uncertainty limits on the derived parameters.

■ RESULTS AND DISCUSSION

X-ray Crystallography. The structure of Ce(Bn-BTzBP)-(NO$_3$)$_3$ comprises a Ce(III) cation bound by one tetradentate Bn-BTzBP ligand and three chelating bidentate nitrate anions creating a 10-coordinate environment around the metal center. The coordination geometry is best described as sphenocorona, although the coplanarity of the nitrogen atoms from the Bn-BTzBP ligand distorts the environment away from any idealized geometry. A view of Ce(Bn-BTzBP)(NO$_3$)$_3$ is shown in Figure 2. The Ce−O bond distances are diagnostic of the oxidation state of cerium. The Ce−O bond distances range from 2.545(4) to 2.587(4) Å and are indicative of Ce(III). These metrics are important because of the possibility of spontaneous
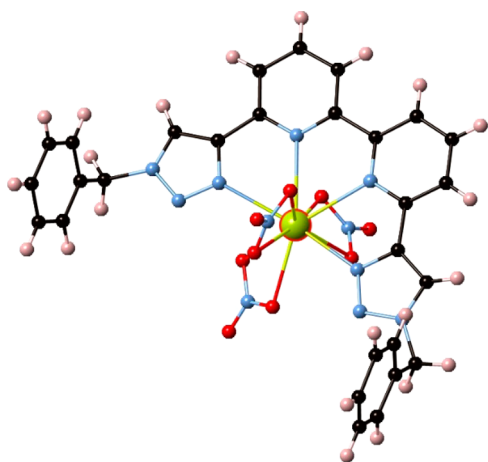
Figure 2. View of the structure of Ce(Bn-BTzBP)(NO$_3$)$_3$ showing the 10-coordinate geometry created by the tetradentate Bn-BTzBP ligand and three chelating nitrate anions.

oxidation of Ce(III) to Ce(IV). These distances, as well as the average Ce−N bond distances of 2.634(5) Å, are far too long for Ce(IV).[15−17] An absorption spectrum of [Ce(Bn-BTzBP)-(NO$_3$)$_3$] was also obtained from a single crystal oriented along [010] to further support the oxidation state assignment (Figure 3). The spectrum shows a moderately broad transition with a peak width at half-height of ∼100 nm and λ_{max} = 332 nm, which is consistent with the 4f−5d transition of Ce(III).[18]
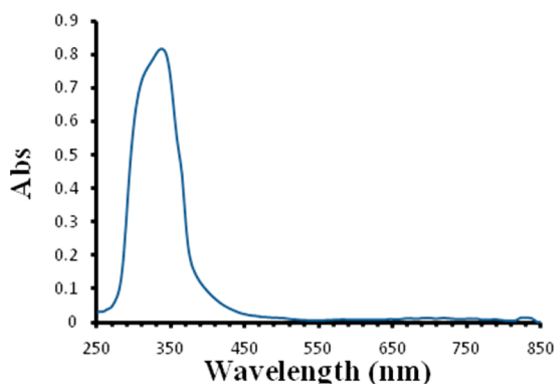
Figure 3. Absorption spectrum of a single crystal of Ce(Bn-BTzBP)(NO$_3$)$_3$ oriented along [010] showing the 4f→5d transition indicative of Ce(III).

The fact that Bn-BTzBP forms a 1:1 complex with cerium in the solid state does not indicate its speciation in solution. Most crystal structures of BTBPs are 1:1 complexes despite the fact that they extract An(III) and Ln(III) as 1:2 complexes.[7] Compared to the structure of [Ce(Bn-BTzBP) (NO$_3$)$_3$], the 6,6′-bis(5,6-diethyl-1,2,4-triazin-3-yl)-2,2′-bipyridine (C2-BTBP) crystal [Ce(C2-BTBP)(NO$_3$)$_3$] has similar Ce−O distances (2.56(2) to 2.584(14) Å) and longer Ce−N bond distances (∼2.68(2) Å).[19]

Spectrofluorimetry. Europium complexes were studied by following the characteristic transition bands $^5D_0{\rightarrow}^7F_0$, $^5D_0{\rightarrow}^7F_1$, and $^5D_0{\rightarrow}^7F_2$ of the Eu(III) fluorescence spectrum. For the $^5D_0{\rightarrow}^7F_0$ transition, a single peak is observed for each distinct Eu(III) species in solution. Its position depends on the Eu(III) coordination number and on the charge of the ligand. The $^5D_0{\rightarrow}^7F_1$ magnetic dipole transition typically shows

splitting patterns in the presence of strong ligand fields. Intensity changes of the hypersensitive $^5D_0{\rightarrow}^7F_2$ electric dipole transition reflects alterations in the ligand field of the first coordination shell of Eu(III). Fluorescence lifetimes of Eu(III) coordination complexes were collected as well. The lifetimes are influenced by nonradiative processes largely coming from OH oscillators of molecules such as water and alcohols present in the first coordination sphere.[20]

Nitrate Medium. Titrations of Eu-containing solutions with EH-BTzBP were first performed in monophasic methanol solutions (with a constant 1% water content) to identify metal/ligand (M/L) complexes in a nitrate medium. The evolution of the Eu(III) fluorescence spectrum in the presence of an increasing amount of EH-BTzBP is shown in Figure 4. The fluorescence emission spectrum of the initial solvated Eu(III) ion (black line on Figure 4) is similar to the spectrum reported in the literature for europium nitrate in methanol containing ∼0.03 M water.[21] The speciation is suggested to be [Eu(NO$_3$)$_2$(MeOH)$_{4.3}$]$^+$ in the inner coordination sphere. The lifetime of 362 ± 10 μs for Eu(III) in this medium is higher than the lifetime of 290 ± 10 μs calculated for Eu(III) in MeOH + 1% H$_2$O (∼0.56 M H$_2$O), suggesting that water might be present in the first coordination sphere of Eu(III) in the latter case.

Upon addition of the ligand, the Eu^{3+} emission spectra exhibit splitting patterns that distinguish different species. For easier visibility of the evolution of the spectra (Figure 4), spectra are arbitrarily divided into two parts with a ligand-to-metal ratio from 0 to ∼1 for part 1 and a ratio higher than 1 for part 2. The $^5D_0{\rightarrow}^7F_0$ transition peak decreases in intensity and simultaneously increases at higher wavelengths (579.6 nm), then decreases again and increases back at lower wavelengths (577.3 nm). The $^5D_0{\rightarrow}^7F_1$ transition band splits into three peaks then reverts to two peaks. The $^5D_0{\rightarrow}^7F_2$ transition band at 616.5 nm decreases in intensity to increase simultaneously at a lower wavelength (613.1 nm) then decreases with a small red shift of the peak, while the intensity at 617.6 nm increases. These spectroscopic changes reflect large changes in the inner coordination sphere of Eu(III) upon addition of the ligand. Both parts of the titration spectra depict several isosbestic points, and three different $^5D_0{\rightarrow}^7F_0$ transition peaks are observed, meaning that three species are involved in the titration experiment: the initial solvated Eu(III) species and two Eu-ligand complexes. Hypspec software[14] was used to model the titration. A good fit was obtained by considering the formation of 1:1 and 1:2 complexes according to the following equilibrium:

$$M^{3+} + xL \rightleftarrows M(L)_x^{3+} \tag{1}$$

Values of log β_1 = 4.8 ± 0.1 and log β_2 = 9.2 ± 0.2 were calculated for Eu(III) by the Hypspec program. Simulated spectra of the two complexes are displayed in Figure 5a, and the fluorescence shifts of each spectrum are included in Table 2.

The emission decay of Eu(III) was recorded upon addition of ligand, and three different lifetimes were assigned to the solvated Eu^{3+} ion, the 1:1 complex (1620 ± 70 μs), and the 1:2 complex (2010 ± 120 μs; Table 3). According to the correlation derived by Horrocks and Sudnick,[22] the recorded lifetimes for the two complexes indicate completely dehydrated metal centers. Complete dehydration of the 1:1 complex suggests full coordination of the tetradentate ligand in addition to two or three inner-sphere nitrate ions coordinated to the metal. The 1:2 complex is likely dehydrated as a result of the
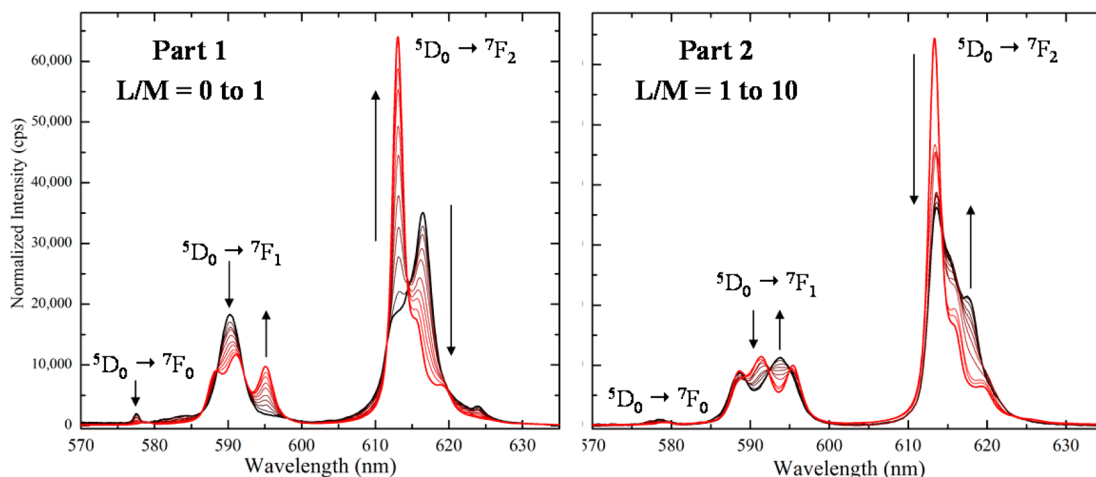
Figure 4. Normalized fluorescence spectra of Eu(III) in methanol/1% water and evolution upon addition of EH-BTzBP.
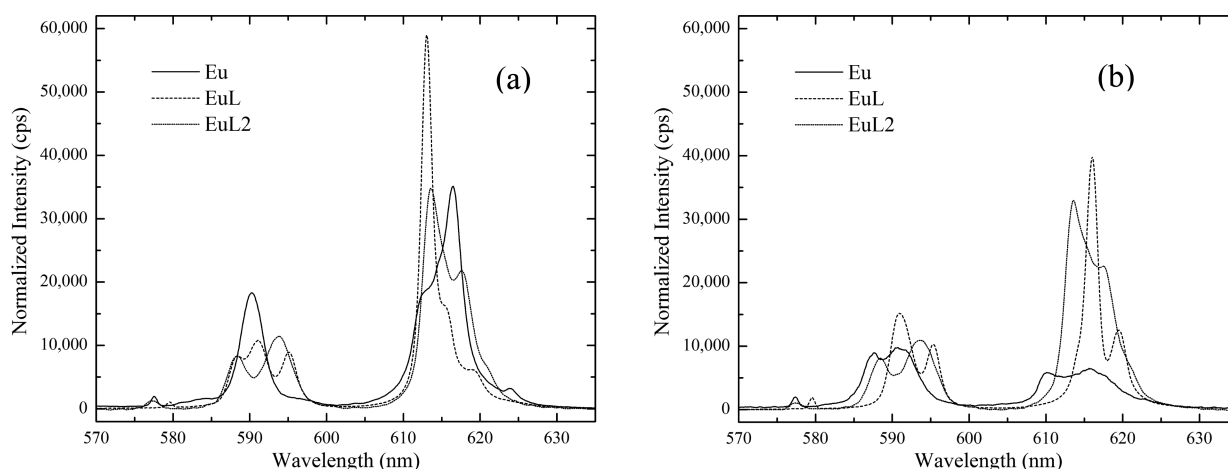

Figure 5. Initial Eu(III) fluorescence spectrum and calculated EuL and EuL$_2$ complexes spectra in the (a) nitrate and (b) perchlorate medium.

Table 2. Wavelengths[a] of the Main Transition Bands (Peaks and Shoulders Maxima) of Each Eu^{3+} Species Fluorescence Spectrum Formed during Eu(III) Titration by EH-BTzBP in Methanol

		without HA		with HA	
		nitrate medium	perchlorate medium	nitrate medium	perchlorate medium
initial spectrum	$^5D_0{\rightarrow}^7F_0$	577.5	577.4	577.9	577.5
	$^5D_0{\rightarrow}^7F_1$	590.3	587.6, 590.7	590.5	589.2, 592.4
	$^5D_0{\rightarrow}^7F_2$	613.0, 616.5, 623.9	610.1, 615.9	613.4, 616.8, 624.6	610.4, 616.5
calculated 1:1 complex spectrum	$^5D_0{\rightarrow}^7F_0$	579.6	579.6	579.8	579.8
	$^5D_0{\rightarrow}^7F_1$	588.4, 591.1, 595.1	591.0, 595.4	589.3, 591.5, 595.6	591.3, 595.7
	$^5D_0{\rightarrow}^7F_2$	613.1, 615.6, 619.5	616.0, 619.5	613.6, 616.1, 619.6	616.3, 619.7
calculated 1:2 complex spectrum	$^5D_0{\rightarrow}^7F_0$	577.3	577.4	579.0	578.9
	$^5D_0{\rightarrow}^7F_1$	588.4, 593.8	588.4, 593.6	588.9, 594.0	588.9, 594.0
	$^5D_0{\rightarrow}^7F_2$	613.6, 617.6	613.6, 617.5	613.7, 617.7	613.8, 617.5

[a]Wavelengths in nanometers.

Table 3. Calculated Fluorescence Lifetimes in Methanol

| medium	initial Eu species	1:1 complex	1:2 complex
nitrate	290 ± 10 μs	1620 ± 70 μs	2010 ± 120 μs
perchlorate	180 ± 10 μs	1410 ± 65 μs	1965 ± 100 μs
nitrate + HA	325 ± 10 μs	1800 ± 90 μs	2200 ± 110 μs
perchlorate + HA	310 ± 10 μs	1750 ± 80 μs	2105 ± 100 μs

coordination of two tetradentate EH-BTzBP ligands enclosing the inner coordination sphere.

Perchlorate Medium. Perchlorate ions have lower affinity for Eu^{3+} than nitrates and are known to be located in the outer coordination sphere of the metal.[23−25] The comparison between nitrate and perchlorate media was used to detect the presence of counterions in the first coordination sphere of Eu^{3+} complexes formed with EH-BTzBP. The previous titration in methanol was repeated using Eu(ClO$_4$)$_3$ in place of Eu(NO$_3$)$_3$.

Spectra were fit using Hypspec with eq 1, and the program converged on a model featuring 1:1 and 1:2 complexes (Eu:EH-BTzBP). Calculated spectra of each species are shown in Figure 5b. The difference between the fluorescence emission spectra of the solvated Eu(III) species in the nitrate medium and in the perchlorate medium in methanol establishes the presence of nitrates in the first coordination sphere of the metal. The fluorescence lifetime for Eu^{3+} in the nitrate medium is longer than in the perchlorate medium (290 μs compared to 180 μs), presumably due to the presence of a smaller number of coordinated methanol or water molecules replaced by nitrates, which are known to have a negligible inhibition effect on fluorescence.[26] The calculated emission spectrum of the 1:1 Eu/EH-BTzBP complex in the perchlorate medium is significantly different from that seen in the nitrate medium (Table 2). This observation confirms that nitrate ions are present in the inner sphere of the 1:1 complex in the nitrate medium. The fluorescence lifetime associated with the 1:1 complex in the perchlorate medium is slightly lower than that in the nitrate medium (1410 μs compared to 1620 μs, respectively), because methanol molecules (whose quenching effect is weaker than that of water) might be filling the rest of the inner coordination shell. The calculated emission spectra for the 1:2 complexes are very similar in both nitrate and perchlorate media, and their fluorescence lifetimes are similar (2010 μs for nitrate and 1965 μs for perchlorate). These results indicate that there are no nitrate ions or water molecules present in the inner coordination sphere of the 1:2 complex.

Presence of 2-Bromohexanoic Acid. Bremer et al.[27] compared the fluorescence spectra of Eu(III) with or without HA in methanol containing 3.3 mol % water and sodium perchlorate. Large changes in the Eu^{3+} spectrum and a significant increase in the fluorescence lifetime (from 182 to 370 μs) in the presence of HA were reported. The authors suggested that more than one 2-bromohexanoate ion is coordinated to the Eu(III) center. In the present work, the influence of HA on the solvated europium nitrate in methanol/1% water was investigated (Figure 6). Despite the presence of a large excess of HA ([HA]/[Eu] = 100), minimal changes are observed in the fluorescence spectrum (Table 2) or the fluorescence lifetime (290 and 325 ± 10 μs). On this basis, it
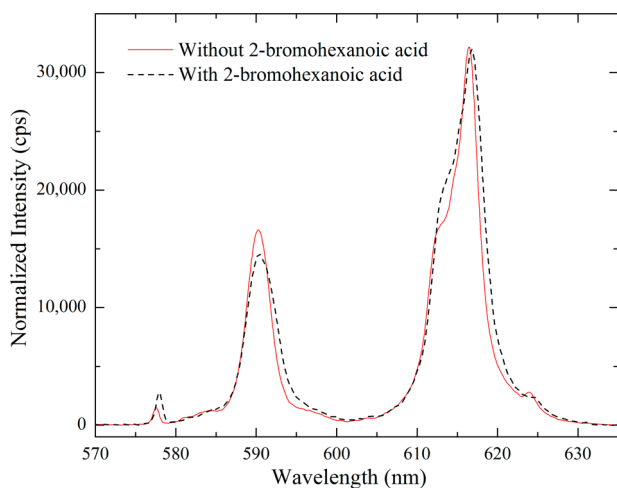
can be argued that the nitrate ion is more strongly complexing than HA in methanol solution.

The same protocol used for the previous titrations of Eu^{3+} by EH-BTzBP was used in the presence of 0.1 M HA. The resulting spectra were fit using the previously described model (eq 1). Initial and calculated spectra for each species are displayed in Figure 7.

In the nitrate medium, the calculated spectra for both complexes (1:1 and 1:2) in the presence of HA are similar to the spectra in the absence of HA (Table 2). This result supports the hypothesis that nitrates more strongly bind Eu(III) than HA in MeOH. In the perchlorate medium, the initial Eu-HA-MeOH species is quite different from the Eu(III) without HA and is identical to the spectrum found in the literature.[27] This is consistent with the presence of HA in the inner sphere of Eu in MeOH. Addition of the ligand leads to 1:1 and 1:2 complex spectra similar to the spectra obtained in the absence of HA, suggesting that all HA molecules are being replaced by the N-donor ligand in the first coordination sphere of Eu(III). However, this is very improbable for the 1:1 complex, since methanol that would be completing the inner coordination sphere is less likely to have a stronger complexation for Eu(III) than HA. The fluorescence lifetimes for the 1:1 complex with and without HA are slightly different as well.
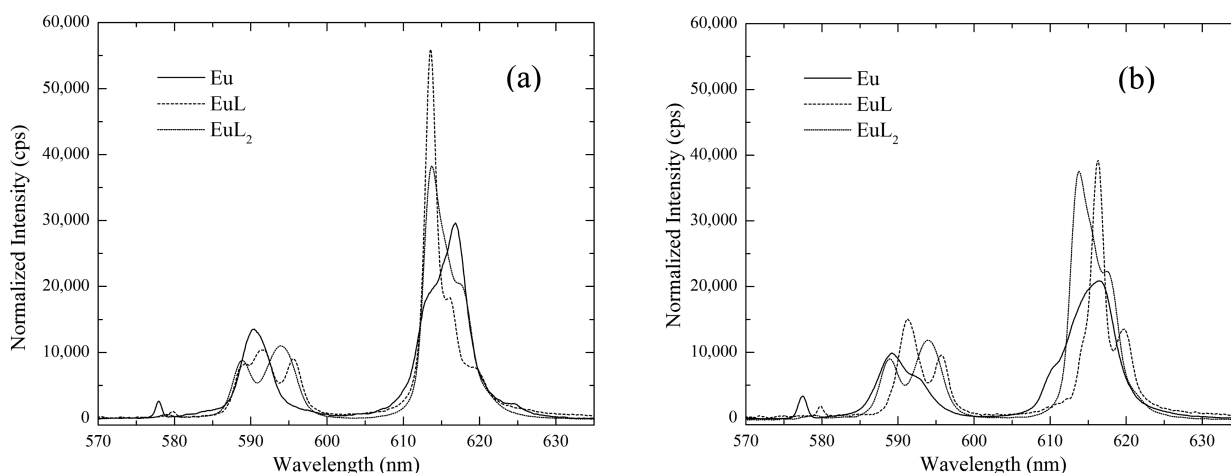
Titration in Toluene. To determine the effect of diluent on coordination, the titration experiment was repeated in toluene. Eu(III) was extracted to the organic phase by HA from a mildly acidic aqueous phase. The Eu-loaded organic phase was then separated, and its fluorescence spectrum and lifetimes were followed upon addition of EH-BTzBP dissolved in toluene and HA. The evolution of the Eu(III) spectrum extracted from the perchlorate medium is shown Figure 8.

The spectrum of Eu^{3+} complexed with HA exhibits single broad fluorescence bands at 577.8, 590.0, and 614.0 nm for the $^5D_0 \rightarrow {^7F_0}$, $^5D_0 \rightarrow {^7F_1}$, and $^5D_0 \rightarrow {^7F_2}$ transitions, respectively. The lifetime associated with this spectrum was calculated to be 250 ± 10 μs. By considering water to be the only fluorescence inhibitor present in the organic phase, the hydration number of Eu^{3+} can be calculated from the following equation:[28]

$$N_{H_2O} = \frac{1.05}{\tau} - 0.44 \tag{2}$$

where τ is the fluorescence lifetime of the Eu species (in ms).

A lifetime of 250 μs corresponds to a hydration number of 3.8 ± 0.5. Depending on their denticity, two or three molecules of HA would be present in the inner coordination sphere of Eu(III). Addition of the N-donor ligand to the toluene solution induces important changes of the Eu(III) spectrum and lifetimes. Unfortunately, the Hypspec software did not generate acceptable fits for equilibrium constants in these experiments. However, the change in the Eu(III) spectrum tends to stabilize for a L/M ratio greater than 200 to give a spectrum that strongly resembles the 1:2 complex spectrum obtained in methanol (peak maxima at 578.7, 588.7, 594.2, 613.5, and 617.1 nm). This result suggests that the 1:2 complex bearing no counterion or HA in its inner coordination sphere is formed in toluene as well. Despite the presence of an isosbestic point, three species were identified by their fluorescence lifetimes: the initial Eu-HA complex, a species with a lifetime of 670 ± 35 μs (N_{H_2O} = 1.1 ± 0.5) assumed to be the 1:1 Eu/EH-BTzBP complex, and the final 1:2 complex with a lifetime of 2035 ± 150 μs. During the titration, a first EH-BTzBP molecule replaces two or three water molecules and one or two

Figure 6. Normalized fluorescence spectra of Eu(III) nitrate in methanol/1% water with or without 0.1 M HA.

Figure 7. Initial Eu(III) fluorescence spectrum and calculated EuL and EuL$_2$ complexes spectra in the (a) nitrate and (b) perchlorate medium.
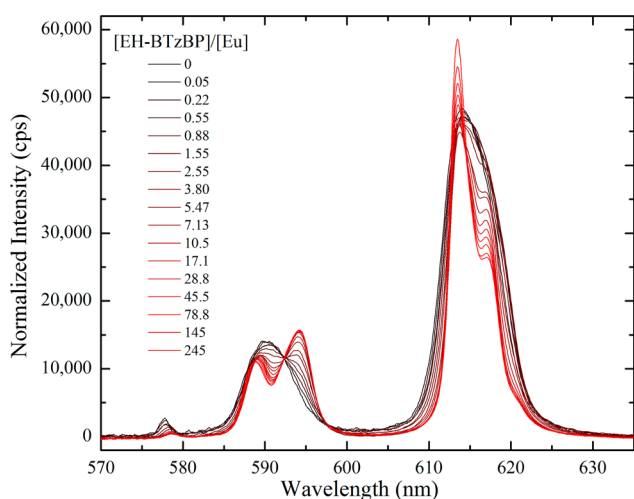
Figure 8. Normalized fluorescence spectra of Eu(III) extracted by 1.0 M HA in toluene from a 0.001 M HClO$_4$ aqueous phase, and addition of aliquots of a EH-BTzBP + 1.0 M HA in toluene to the Eu-loaded organic phase.
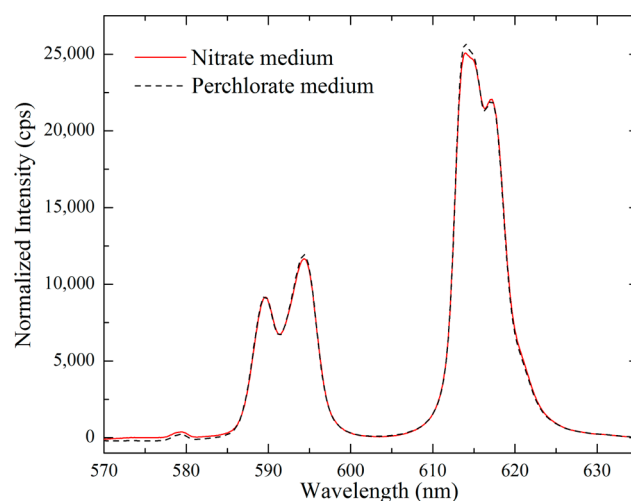
Figure 9. Normalized fluorescence spectra of Eu(III) after extraction to an organic phase of 0.01 M EH-BTzBP + 1 M HA in toluene from an aqueous phase of pH 3 (HNO$_3$ or HClO$_4$).

molecules of HA to form the 1:1 complex. As the titration continues, a second EH-BTzBP molecule replaces the remaining water and HA molecules to obtain the 1:2 complex. Three molecules or dimers of HA would still be present in the outer coordination sphere to achieve electroneutrality of the complex in the organic phase.

Extraction into Toluene. The fluorescence spectrum of Eu(III) complex formed by solvent extraction using the synergistic EH-BTzBP-HA system is shown in Figure 9. The spectrum displays a broad $^5D_0 \rightarrow {}^7F_0$ transition band centered at 579.3 nm, a $^5D_0 \rightarrow {}^7F_1$ transition twofold band with maxima at 589.7 and 594.3 nm and a $^5D_0 \rightarrow {}^7F_2$ transition band that has a maximum intensity at 614 nm with a small shoulder at ∼615 nm and another shoulder with a maximum at 617.2 nm. Modeling of the rate of decrease of fluorescence intensity over time reveals the presence of two different species in the organic phase with lifetimes of 700 ± 50 and 2090 ± 110 μs. Those lifetimes are comparable to the lifetimes of the 1:1 and 1:2 complexes formed in the previous titration in toluene. It is then reasonably assumed that both the 1:1 complex and the 1:2 complex are involved in the extraction. This assumption is consistent with the slope of 1.5 obtained for the extraction of

Eu by the synergistic system with varying concentration of ligand. We have reported previously that Eu(III) is extracted by a mixture of 1:1 and 1:2 complexes.[9]

Ultraviolet Absorption Spectrophotometry. The protonation of the EH-BTzBP ligand by HCl in a MeOH/H$_2$O mixture (75:25) also was investigated using UV absorption detection methods. The UV spectral changes induced in the bipy chromophore by addition of the acid were used to calculate a protonation constant of log $K_1 = 1.5 \pm 0.1$ using the Hypspec software. With such weak hydrogen ion affinity, it is assumed that the organic ligand is unprotonated under the neutral conditions of the following complexation experiments. This avoids competition between protonation and metal complexation and thus enables a more straightforward analysis.

Changes in the EH-BTzBP spectrum in methanol upon addition of lanthanide nitrate (Nd^{3+}, Eu^{3+} and Ho^{3+}) was monitored by UV absorption spectrophotometry (Figure 10). The appearance of isosbestic points on the spectra reveals the presence of at least two species in solution. Hypspec software was used to model the spectra and calculate the associated complexation constants following eq 1. For each of the lanthanides studied, the best fits were obtained with consideration of the formation of two metal complexes: ML
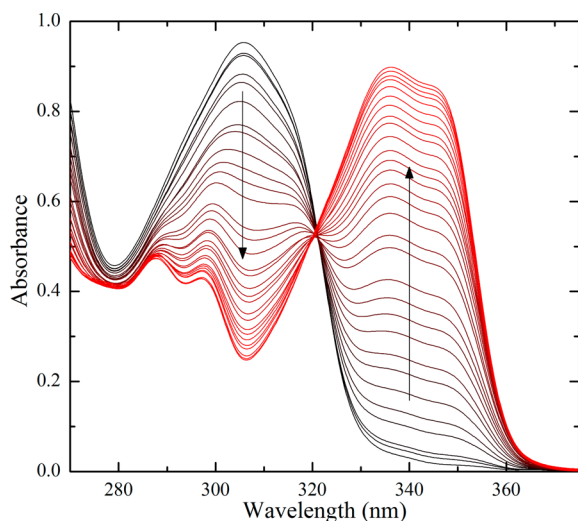
Figure 10. UV spectra of EH-BTzBP (5×10^{-5} M) titrated by $Nd(NO_3)_3$ in methanol (M/L = 0 to 150).

and ML_2. The calculated complexation constants are displayed in Table 4. The constants obtained for Eu(III) by absorption

Table 4. Calculated Stability Constants for Lanthanide Complexes with EH-BTzBP in Methanol

	Nd	Eu	Ho
log β_1	4.2 ± 0.2	4.9 ± 0.2	4.8 ± 0.3
log β_2	9.2 ± 0.4	9.5 ± 0.3	8.9 ± 0.4

spectrophotometry (log $\beta_1 = 4.9 \pm 0.2$ and log $\beta_2 = 9.5 \pm 0.3$) are in good agreement with the constants calculated by spectrofluorimetry (log $\beta_1 = 4.8 \pm 0.1$ and log $\beta_2 = 9.2 \pm 0.2$). The values are lower than the complexation constants reported by Hubscher−Bruder for BTBP ligands (e.g., log $\beta_1 = 5.7 \pm 0.3$ and log $\beta_2 = 11.3 \pm 0.2$ for C5-BTBP-Eu^{3+} complexes in methanol at constant 0.01 M ionic strength[29]), which may explain the lower metal extraction efficiency for EH-BTzBP compared to BTBPs. An increase in the complexation constant value along the lanthanide series would have been expected due to the selectivity of the N-donor ligand for heavier lanthanides. However, the difference between the constants is not significant enough to observe such a trend.

■ **CONCLUSION**

The coordination properties of BTzBP complexants were studied and compared to the similar BTBP ligands. A 1:1 solid-state complex was synthesized and characterized. The crystal showed a trivalent cerium metal center bonded to a tetradentate ligand in a planar configuration and three bidentate nitrates arrayed in the opposite hemisphere. The resolved average Ce−N bond lengths for the Ce-BTBP complex (2.63 Å) are ∼2% shorter than the corresponding bond lengths reported for a similar Ce-BTBP complex, while Ce-nitrate distances are comparable. Complexation studies by spectro-fluorimetry and UV spectrophotometry demonstrated the formation of 1:1 and 1:2 complexes between EH-BTzBP and lanthanides in methanol. These complexes are weaker than the corresponding structurally similar lanthanide BTBP complexes. Further TRFS studies on the Eu-EH-BTzBP complexes demonstrated that the HA is not present in the first coordination sphere in methanol, though the coextractant is

essential for the previously reported phase transfer reaction to occur. Characterization of the complexes formed after extraction into toluene showed that both the 1:1 and 1:2 complexes are involved in the extraction process, consistent with the slope analysis results published previously.

■ **ASSOCIATED CONTENT**

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b02005.

The CIF file corresponding to the Ce(Bn-BTzBP)(NO$_3$)$_3$ crystal (CIF)

■ **AUTHOR INFORMATION**

Corresponding Author
*E-mail: knash@wsu.edu.

Notes
The authors declare no competing financial interest.

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