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A TRLFS Study on the Complexation of Cm^{III} and Eu^{III} with 2,6-Bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine in Water/Methanol Mixture

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The complexation of Cm^{III} and Eu^{III} with 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (*n*Pr-BTP) in water/methanol solution is studied. 1:3 complexes [M(*n*Pr-BTP)$_3$]$^{3+}$ form from the solvated metal ions upon addition of ligand. The conditional stability constants are $\log K_{\mathrm{Cm^{III}}} = 14.4$ and $\log K_{\mathrm{Eu^{III}}} = 11.9$. For both metal ions the complexation reaction is both enthalpy and entropy driven. $\Delta H_{\mathrm{Cm^{III}}}$ is 10.1 kJ/mol more negative than $\Delta H_{\mathrm{Eu^{III}}}$, whereas the entropy difference is small. The difference in ΔG between the formation of the Cm^{III} and Eu^{III} complexes is in good agreement with *n*Pr-BTP's selectivity in liquid-liquid extraction.

Introduction

The partitioning and transmutation (P&T) strategy aims at reducing the long-term radiotoxicity of spent nuclear fuels by separating long-lived actinides (Np, Pu, Am and Cm) and transmuting them into shorter-lived or stable nuclides by neutron irradiation.[1,2] The separation of trivalent actinides (An^{III}) from the chemically similar lanthanides (Ln^{III}) in the so-called SANEX process is a key element of this strategy. This separation is required as some of the Ln^{III} have large neutron cross sections, thus compromising transmutation efficiency.

It has been demonstrated[3–5] that this separation is achievable by selective liquid-liquid extraction using soft donor extracting agents such as heterocyclic N-donor ligands. Of these, hydrophobic bis(triazinyl)pyridines (BTP)[6] and bis(triazinyl)bipyridines (BTBP)[7–9] are the most promising candidates. However, none of them fulfil all criteria for application in an industrial process, hence requiring optimisation. Such optimisation implies good understanding of the driving force behind their selectivity for An^{III} over Ln^{III}.

It was shown that BTPs act as tridentate ligands,[10] forming 1:3 complexes with An^{III} and Ln^{III} in the solid state[10–12] and in organic solution.[6,13–19,36,37] Titrations in organic phase[16,17] demonstrate these 1:3 complexes' preferential formation with An^{III} compared to Ln^{III}. However, there are only subtle structural differences between the An^{III}-BTP and Ln^{III}-BTP complexes in organic solution which do not explain An^{III}/Ln^{III} selectivity.[16,17,19]

We perform a comparative study on the complexation of Cm^{III} and Eu^{III} with *n*Pr-BTP [2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine] (Figure 1) in water/methanol, 1:1. The formation of the respective BTP complexes is followed by time resolved laser-induced fluorescence spectroscopy (TRLFS). An aqueous solvent is used since long chain alcohols such as 1-octanol (which are commonly used to dissolve BTPs[4,6]) solubilise significant quantities of water.[20] Our studies are performed in water/methanol mixture since *n*Pr-BTP is only sparely soluble in pure water. Furthermore, we are interested in whether BTP's selectivity is confined to the organic phase (where an extracting agent works). This question is of relevance for the development of innovative separations processes based on selective aqueous complexation of actinides,[21] a concept dating back to the earlier days of actinide separations.[22] A similar study on BTBP proved that BTBP's selectivity is not confined to the organic phase only.[23]

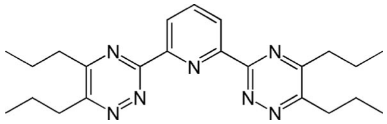

Figure 1. *n*Pr-BTP [2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine].

Results and Discussion

Cm^{III} Fluorescence Spectra

The evolution of the Cm^{III} fluorescence spectra in water/methanol, 1:1 resulting from the $^6D'_{7/2} \rightarrow {}^8S'_{7/2}$ transition in the presence of an increasing concentration of *n*Pr-BTP is shown in Figure 2. At [*n*Pr-BTP] = 0 the solvated metal

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ion $[Cm(solv.)]^{3+}$ is present, displaying a broad emission band at 594.3 nm. Except for a small bathochromic shift, the fluorescence spectrum is comparable to that of the aquo ion (with 9 H_2O in the inner coordination sphere), exhibiting a fluorescence maximum at 593.7 nm.[25] Differences in the inner coordination sphere are also expressed in a slightly longer fluorescence lifetime of 71 µs (compared to 65 µs of the aquo complex[25]) and are due to the coordination of methanol instead of water.[26] Inner sphere nitrate coordination is not expected under these conditions.[27]

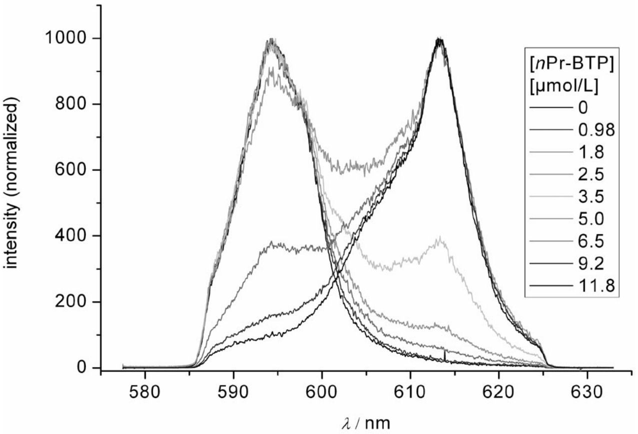

Figure 2. Normalised fluorescence spectra of Cm^{III} in water/methanol, 1:1 at increasing *n*Pr-BTP concentration. $[Cm^{III}]_{ini}$ = 1.82×10^{-7} mol/L.

In the presence of increasing *n*Pr-BTP concentration two Cm-BTP complex species are formed simultaneously, displaying emission maxima at 602.0 nm and 613.2 nm, respectively (species 1 and 2). Both exhibit bathochromic shifts compared to the solvated metal ion, indicating a larger ligand field splittings caused by stronger complexation of the metal ion.

Upon further addition of ligand, the concentrations of both species 1 and 2 increase. Only minor amounts of species 1 are formed (maximum: 9.1% at 3.53×10^{-6} mol/L), while the amount of species 2 increases steadily until it becomes the only complex species present in solution at ligand concentrations above 6×10^{-5} mol/L. Each spectrum is analysed by peak deconvolution, using the fluorescence spectra of the three single components. Species 2 exhibits a significantly higher fluorescence intensity compared to the solvated metal ion (FI species 2/$[Cm(solv.)]^{3+}$ = 17) and above BTP concentrations of 11.8 µmol/L the emission spectra are dominated by the intense fluorescence of species 2. The resulting speciation diagram is shown in Figure 3.

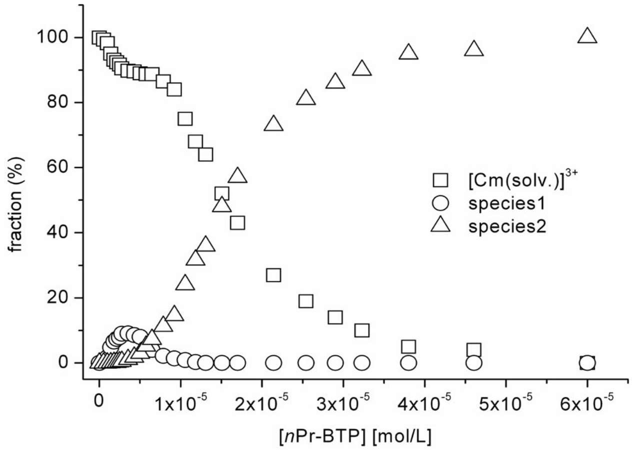

Figure 3. Distribution of Cm^{III} complex species in water/methanol, 1:1 as a function of the *n*Pr-BTP concentration. $[Cm^{III}]_{ini}$ = 1.82×10^{-7} mol/L.

Eu^{III} Fluorescence Spectra

The Eu^{III} fluorescence spectra resulting from the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions as a function of the *n*Pr-BTP concentration are shown in Figure 4. In contrast to Cm^{III}, changes in the Eu^{III} coordination sphere cause only small shifts of the fluorescence band. The $^5D_0 \rightarrow {}^7F_2$ transition on the other hand is hypersensitive and reflects changes in the ligand field of Eu^{III} by changes of the transition ratio ($^7F_1/^7F_2$).

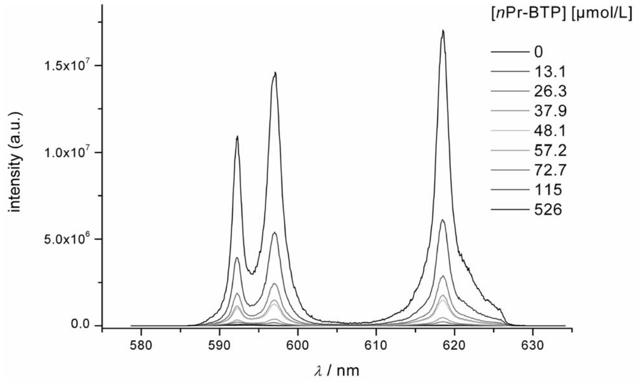

Figure 4. Fluorescence spectra of Eu^{III} in water/methanol, 1:1 at increasing *n*Pr-BTP concentration. $[Eu^{III}]_{ini}$ = 2.14×10^{-5} mol/L.

The emission spectrum of the solvated Eu^{III} species ($[Eu(solv.)]^{3+}$) in water/methanol, 1:1 shows one broad emission band with an emission maximum at 593.4 nm resulting from the $^5D_0 \rightarrow {}^7F_1$ transition. The broad emission band resulting from the $^5D_0 \rightarrow {}^7F_2$ transition is centered at 617.4 nm. The transition ratio $^7F_1/^7F_2$ of the solvated species is 2.88 and thus lower than 3.74 for the aquo ion (having 9 H_2O molecules in the first coordination sphere), indicating a decrease in symmetry. Since inner sphere coordination of nitrate is not expected under the given conditions,[28] the differences must be due to the coordination of methanol. This is also reflected in a longer fluorescence lifetime (118 µs) compared to the aquo ion (110 µs).[29]

A new species forms upon addition of ligand, showing a distinct splitting of the $^5D_0 \rightarrow {}^7F_1$ emission band with maxima at 592.3 nm and 597.1 nm and a narrow $^5D_0 \rightarrow {}^7F_2$ transition band at 618.5 nm (species 3). The $^7F_1/^7F_2$ transition ratio for this species is 0.86.

The fluorescence intensity of $[Eu(solv.)]^{3+}$ is significantly lower than that of species 3 (FI species 3/$[Eu(solv.)]^{3+}$ = 80).

Hence, in the presence of even small amounts of species 3 the emission spectrum is dominated by the strong fluorescence of this species, rendering analysis of the spectra by peak deconvolution impossible. As the overall fluorescence intensity increases linearly with the concentration of species 3, the concentration of species 3 is determined from the total fluorescence intensity, and the concentration of $[Eu(solv.)]^{3+}$ is calculated from the difference between the total Eu^{III} concentration and the concentration of species 3. The resulting speciation diagram is shown in Figure 5. For *n*Pr-BTP concentrations larger than 5.2×10^{-4} mol/L species 3 is the only species present in solution.

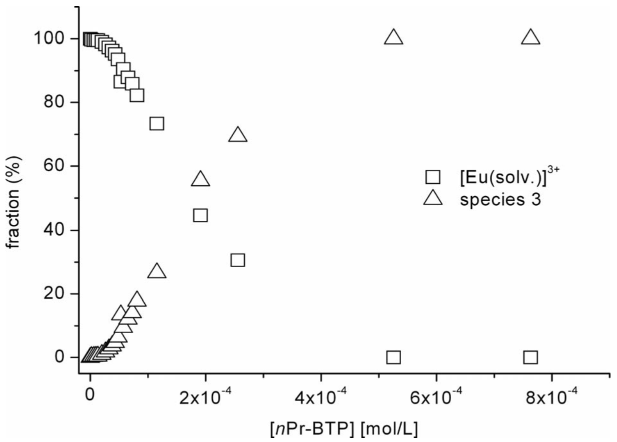

Figure 5. Distribution of Eu^{III} complex species in water/methanol, 1:1 as a function of the *n*Pr-BTP concentration. $[Eu^{III}]_{ini} = 2.14 \times 10^{-5}$ mol/L.

Identification of the Complexed Species

The emission spectra of both species 2 and 3 are known from previous TRLFS studies and their composition has been determined to be $[M(nPr\text{-}BTP)_3]^{3+}$.[15–17] To confirm the formation of a metal ion:ligand 1:3 species upon addition of *n*Pr-BTP to the solvated metal ions ($[M(solv.)]^{3+}$), slope analysis of the obtained titration results is performed using the following Equation (1):

$$[M(solv.)]^{3+} + n\ nPr\text{-}BTP \rightleftharpoons [M(nPr\text{-}BTP)_n]^{3+} \quad (1)$$

It follows Equation (2):

$$\log\left(\frac{\left[\left[M\left(nPr\text{-}BTP\right)_n\right]^{3+}\right]}{\left[\left[M\left(solv.\right)\right]^{3+}\right]}\right) = \log K + n\ \log\left[nPr\text{-}BTP\right] \quad (2)$$

According to this, a linear correlation between the logarithm of the concentration ratio $[[M(nPr\text{-}BTP)_n]^{3+}]/[[M(solv.)]^{3+}]$ and the logarithm of the free *n*Pr-BTP concentration with a slope of *n* exists. Figure 6 shows the double logarithmic plot of the spectroscopically determined concentration ratios of the different species in solution at various ligand concentrations. Slopes of 2.99 and 3.06, respectively, are obtained by linear regression, confirming the formation of 1:3 complexes for both, Cm^{III} and Eu^{III}.

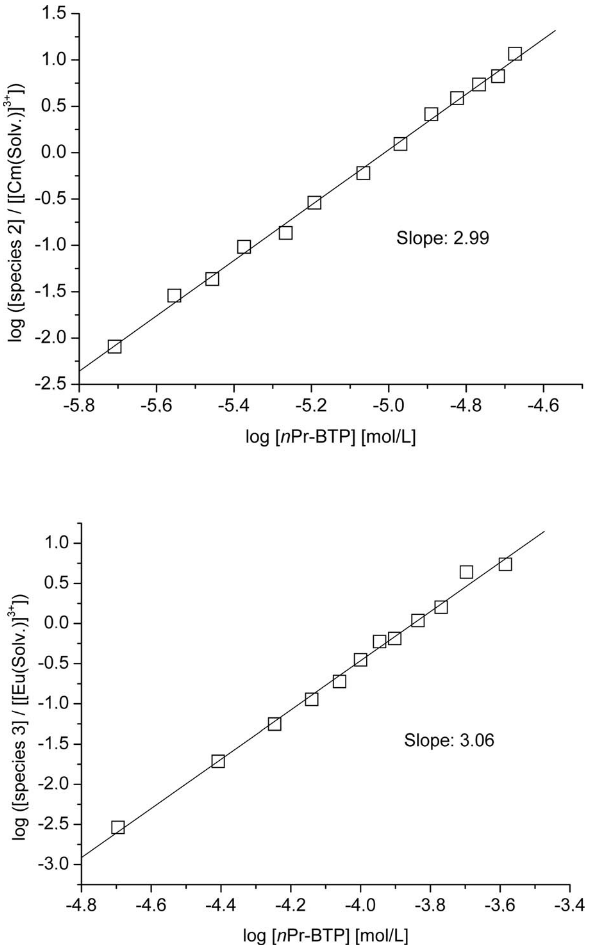

Figure 6. Double logarithmic plot of $[[M(nPr\text{-}BTP)_3]^{3+}]/[[M(solv.)]^{3+}]$ concentration ratio vs. free *n*Pr-BTP concentration for Cm^{III} (top) and Eu^{III} (bottom).

The fluorescence spectra of both 1:3 complex species are identical to the spectra of the $[M(nPr\text{-}BTP)_3]^{3+}$ complexes which form in 1-octanol.[16,17] However, the present study is performed in a mixture of water and methanol so that inner sphere hydration has to be considered. To demonstrate the absence of solvent molecules in the first coordination sphere the fluorescence lifetimes of both 1:3 complexes is determined. The fluorescence lifetime increases with decreasing number of quenching molecules in the first coordination sphere. Both coordinated water[30,31] and alcohol[32] molecules cause fluorescence quenching, mainly by energy transfer via excitation of vibrational modes of OH functions. A linear correlation between the Eu^{III} fluorescence lifetime and the number of water molecules in the first coordination sphere [Equation (3)] allows to calculate the number of water ligands from the fluorescence lifetime.[30] A similar correlation for the fluorescence lifetime of Cm^{III} is shown in Equation (4).[31]

$$Eu^{III}\text{: } n(H_2O) = 1.07\ k_{obs} - 0.62 \quad (3)$$

$$Cm^{III}\text{: } n(H_2O) = 0.65\ k_{obs} - 0.88 \quad (4)$$

The fluorescence lifetime τ of the Eu^{III} 1:3 complex species in water/methanol, 1:1 is determined to be 1727 µs (see Figure 7). According to Equation (3) this proves the absence of quenching molecules (water, alcohol) in the inner coordination sphere. Thus we conclude the complex to be of the same composition as the complex which forms in 1-octanol.[16,17]

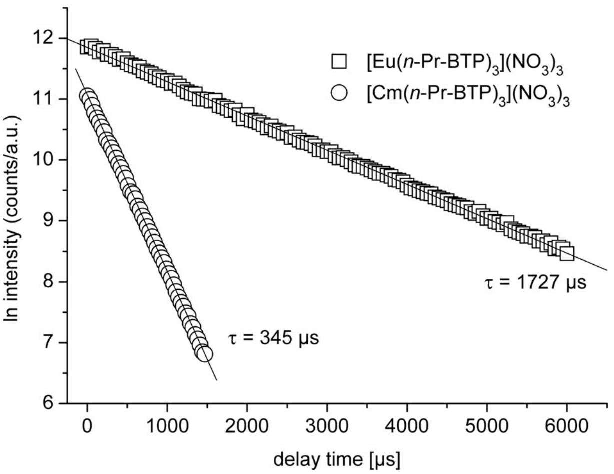

Figure 7. Decay of the fluorescence intensity of [M(nPr-BTP)]$^{3+}$ in H$_2$O/MeOH, 1:1.

As was shown for BTBP ligands,[23] the number of coordinated quenching molecules for Cm^{III} cannot be calculated according to Equation (4) since additional quenching processes by intramolecular energy transfer between the Cm^{III} ion and the organic ligand occur. The same applies to the BTP ligands. However, the fluorescence lifetime is in good agreement with that of the [Cm(nPr-BTP)$_3$]$^{3+}$ complex in 1-octanol.[17]

Species 1 cannot be characterised in detail due to its low concentration. However, from a previous work[17] it is deduced from the position and shape of its emission spectrum to represent a 1:1 species.

Stability Constants

Conditional stability constants of the Cm^{III} and Eu^{III} [M(nPr-BTP)$_3$]$^{3+}$ complexes are calculated from the species distributions obtained spectroscopically according to Equation (5) (see Table 1).

$$K = \frac{\left[\left[\mathrm{M}(n\text{Pr-BTP})_3\right]^{3+}\right]}{\left[\left[\mathrm{M}(\text{Solv.})\right]^{3+}\right] \times [n\text{Pr-BTP}]^3} \tag{5}$$

Furthermore, TRLFS titrations at varied metal ion or nitrate concentrations are performed to validate Equation (5). As shown in Table 1 and Figure 8, neither metal ion nor nitrate concentration affect the stability constants, proving that Equation (5) is applicable to calculate the stability constants.

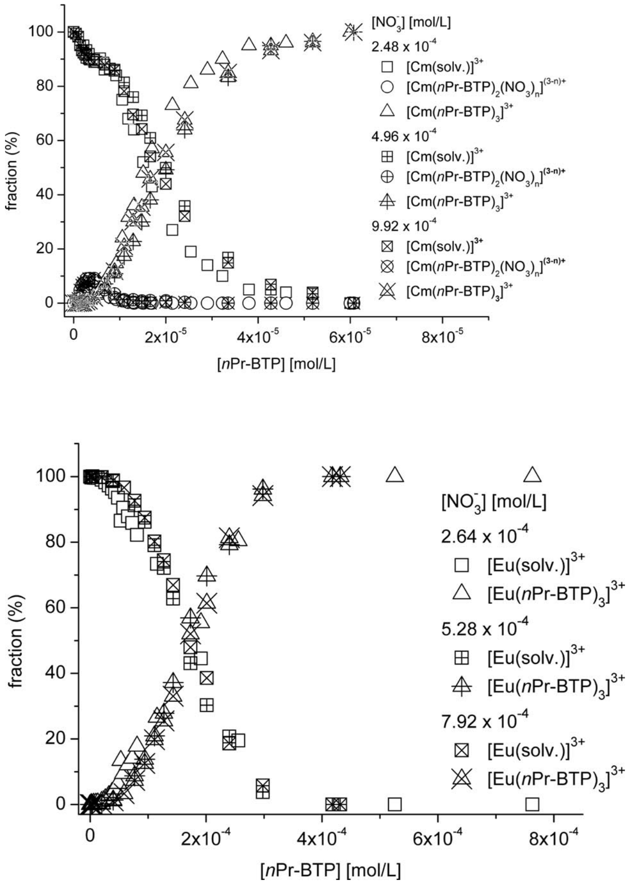

Figure 8. Species distribution of Cm^{III} (top) and Eu^{III} (bottom) with nPr-BTP at various nitrate concentrations.

An average $\log K_{\mathrm{Cm^{III}}} = 14.4 \pm 0.1$ and $\log K_{\mathrm{Eu^{III}}} = 11.9 \pm 0.1$ for the complexation of Cm^{III} and Eu^{III} with nPr-BTP are determined, respectively. The value found for $K_{\mathrm{Eu^{III}}}$ is in excellent agreement with $\log K_{\mathrm{Eu^{III}}} = 12.0$ found

Table 1. Stability constants of the Cm^{III} and Eu^{III} [M(nPr-BTP)$_3$]$^{3+}$ complexes at various metal ion and nitrate concentrations.

[Cm^{III}]$_{\text{ini}}$ [10^{-7} mol/L]	[NO$_3^-$]$_{\text{ini}}$ [10^{-4} mol/L]	$\log K_{\mathrm{Cm^{III}}}$ [L^3/mol^3]	[Eu^{III}]$_{\text{ini}}$ [10^{-5} mol/L]	[NO$_3^-$]$_{\text{ini}}$ [10^{-4} mol/L]	$\log K_{\mathrm{Eu^{III}}}$ [L^3/mol^3]
1.82	2.48	14.5 ± 0.2	1.50	1.85	11.9 ± 0.1
3.64	4.96	14.3 ± 0.2	2.14	2.64	12.0 ± 0.1
7.28	9.92	14.4 ± 0.2	4.28	5.28	12.1 ± 0.1
1.82	9.92	14.4 ± 0.2	2.14	5.28	11.9 ± 0.1
1.82	17.36	14.3 ± 0.2	2.14	7.92	11.8 ± 0.1
Average $\log K_{\mathrm{Cm^{III}}}$	14.4 ± 0.1		average $\log K_{\mathrm{Eu^{III}}}$	11.9 ± 0.1	

in previous studies.[13] The stability constant of the Cm^{III} complex is 320 times higher than the stability constant of the respective Eu^{III} complex. This difference in the stability constants corresponds to $\Delta\Delta G$ (20 °C) = $-RT\ln[K_{Cm^{III}}/K_{Eu^{III}}]$ = –14.0 kJ/mol.

Temperature Dependence of the Stability Constants

To determine the enthalpic and entropic data of the complex formation, the temperature dependences of the stability constants are determined in the range of 10 to 50 °C. The resulting stability constants of the $[M(n\text{Pr-BTP})_3]^{3+}$ complexes as a function of the reciprocal temperature are shown in Figure 9. The thermodynamic data are determined by linear fitting of the spectroscopically obtained stability constants according to the van 't Hoff equation [Equation (6)]. The results are summarised in Table 2.

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{6}$$

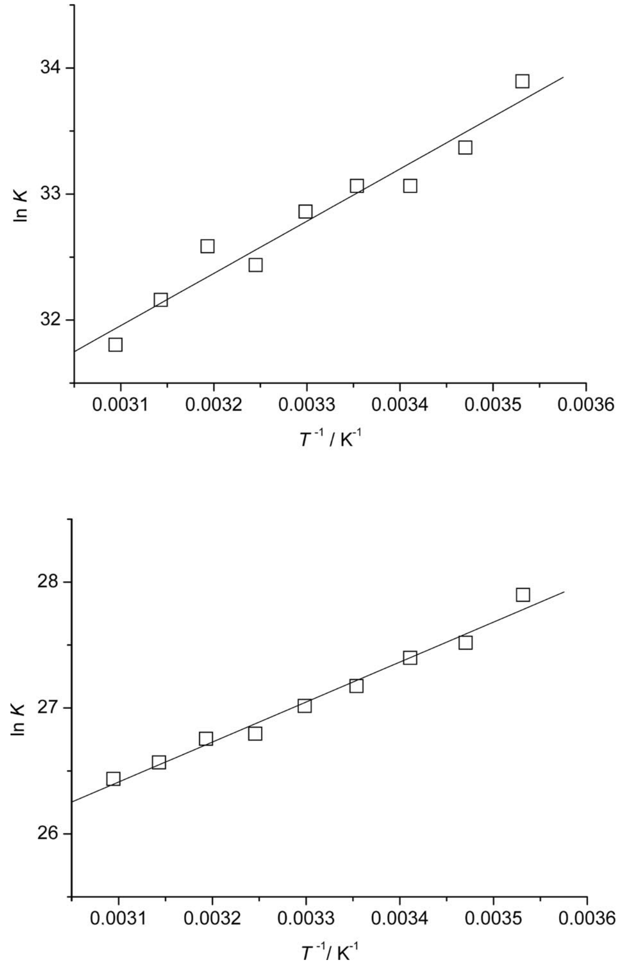

Figure 9. Temperature dependency of the stability constants of the complexation of Cm^{III} (top) and Eu^{III} (bottom) with *n*Pr-BTP. 1.79×10^{-7} mol/L Cm^{III} and 1.7×10^{-5} mol/L *n*Pr-BTP; 1.53×10^{-5} mol/L Eu^{III} and 3.1×10^{-4} mol/L *n*Pr-BTP.

Table 2. Thermodynamic data for the complexation of Cm^{III} and Eu^{III} with *n*Pr-BTP in water/methanol, 1:1.

	ΔH [kJ/mol]	ΔS [J/(mol K)]	ΔG (20 °C) [kJ/mol]
Cm^{III}	–36.5 ± 4.7	148 ± 17	–79.9 ± 7.5
Eu^{III}	–26.4 ± 1.8	138 ± 7	–66.8 ± 2.8
Δ	–10.1	–10	–13.1

Due to the negative enthalpy changes the complexations of both metal ions is exothermic [$\Delta H_{Cm^{III}}$ = –36.5 kJ/mol, $\Delta H_{Eu^{III}}$ = –26.4 kJ/mol]. However, ΔH is 10.1 kJ/mol more negative for the complexation of Cm^{III} than for Eu^{III}.

The entropy change is found to be $\Delta S_{Cm^{III}}$ = 148 J/(mol K) and $\Delta S_{Eu^{III}}$ = 138 J/(mol K), resulting in a difference $\Delta\Delta S$ = –10 J/(mol K), which is within the error range. Thus comparable complexation mechanisms for both metal ions can be concluded.

The difference in ΔG (20 °C) of –13.1 kJ/mol results mainly from the difference in ΔH and is in good agreement with $\Delta\Delta G = -RT\ln[K_{Cm^{III}}/K_{Eu^{III}}]$ = 14.0 kJ/mol from the titration studies.

From the titrations a separation factor $SF_{Cm^{III}/Eu^{III}} = K_{Cm^{III}}/K_{Eu^{III}}$ = 320 is calculated. This value is in good agreement with $SF_{Cm^{III}/Eu^{III}}$ = 220 from extraction experiments.[33]

Conclusions

In this study we present the first comparative thermodynamic investigation on the complexation of An^{III} and Ln^{III} with BTP ligands.

By addition of *n*Pr-BTP to Cm^{III} or Eu^{III} in water/methanol, 1:3 complexes $[M(n\text{Pr-BTP})_3]^{3+}$ form from the solvated metal ions. The stability constant of the Cm^{III} complex is 320 L^3/mol^3 higher than that of the Eu^{III} complex. This difference is due to a more negative change of enthalpy for the complexation of Cm^{III}. Entropic differences are negligible.

The difference in ΔG (20 °C) determined from the Gibbs–Helmholtz equation is $\Delta\Delta G$ (20 °C) = –13.1 kJ/mol. This is in good agreement with $\Delta\Delta G$ (20 °C) = $-RT\ln[K_{Cm^{III}}/K_{Eu^{III}}]$ = –14.0 kJ/mol derived from the titration experiments, which underlines the accuracy of the obtained data. Furthermore, the difference in stability constants is in good agreement with results from liquid-liquid extraction studies.

In analogy to an earlier study on the complexation of BTBP ligands,[23] we identified enthalpy changes of complexation as the molecular driving force of selectivity. This finding is crucial for the design of future SANEX ligand generations and provides the fundament for quantum chemical calculations.

BTPs are highly selective extraction agents. The present study confirms that their selectivity is maintained in both organic and aqueous monophasic conditions, which is a very important aspect concerning the development of innovative SANEX processes.

Experimental Section

Chemicals: $Eu(NO_3)_3$ was from Alfa–Aesar, methanol and ammonium nitrate were purchased from Merck. All chemicals were used as received. The isotopic mass distribution of the $Cm(NO_3)_3$ solution is 97.1 % ^{248}Cm, 2.8 % ^{245}Cm, < 1 % ^{243}Cm, ^{244}Cm, and ^{246}Cm. *n*Pr-BTP was synthesized as described earlier.[6]

Sample Preparation: As *n*Pr-BTP is insufficiently soluble in water, the studies are performed in a 1:1 mixture of water and methanol. The *n*Pr-BTP solution is prepared by dissolving 4.04 mg (10 µmol) *n*Pr-BTP in 5 mL of methanol and subsequent dilution with 5 mL of distilled water, resulting in a 10^{-3} mol/L stock solution of *n*Pr-BTP in water/methanol, 1:1. For Cm^{III} studies two different *n*Pr-BTP solutions (10^{-4} and 10^{-5} mol/L) are prepared by dilution of the stock solution, for Eu^{III} studies 10^{-4} mol/L or 10^{-3} mol/L solutions are used. The stock solutions are prepared freshly every three days since decomposition of *n*Pr-BTP by hydrolysis and/or photolysis was found to occur after a few days.

Titrations are performed by successive addition of the corresponding amount of *n*Pr-BTP solution to a solution of $Cm(NO_3)_3$, or $Eu(NO_3)_3$, prepared as described elsewhere.[23] The resulting solution is allowed to equilibrate for 15 min before measurement, which was shown in preliminary studies to be sufficient to reach equilibrium.

The $Cm(NO_3)_3$ solutions are prepared by diluting 30/60/120 µL of a 6.05×10^{-6} mol/L aqueous stock solution of $Cm(NO_3)_3$ in 0.01 mol/L HNO_3 with a, 1:1 mixture of water and methanol to 1 mL, resulting in $1.82/3.64/7.28 \times 10^{-7}$ mol/L solution of Cm^{III}. The $Eu(NO_3)_3$ solutions are prepared similarly, using 20/40/80 µL of a 1.07×10^{-3} mol/L aqueous stock solution of $Eu(NO_3)_3$ in 0.01 mol/L HNO_3, resulting in a $2.14/4.28/8.56 \times 10^{-5}$ mol/L solution of Eu^{III} in water/methanol.

$Cm(NO_3)_3$ (1.82×10^{-7} mol/L) and $Eu(NO_3)_3$ (2.14×10^{-5} mol/L) solutions with varied nitrate concentrations ($[NO_3^-] = 9.92 \times 10^{-4}$ mol/L and 17.36×10^{-4} mol/L for Cm^{III}, $[NO_3^-] = 5.28 \times 10^{-4}$ mol/L and 7.92×10^{-4} mol/L for Eu^{III}) are prepared by adding NH_4NO_3.

Due to dilution pH varies in a narrow range between 2.5 and 2.8 throughout titration. However, hydrolysis of Cm^{III}[34] or Eu^{III}[35] is not expected in this pH range.

TRLFS Measurements: TRLFS measurements are performed using an excimer-pumped dye laser system (Lambda Physics 201 and FL 3002). A wavelength of 396.6 nm for Cm^{III} and 394 nm for Eu^{III} is used for excitation. Emission spectra are recorded from 580 to 620 nm after a delay time of 1.2 µs to discriminate short-lived fluorescence of the organic ligand. The fluorescence emission is detected by an optical multichannel analyser consisting of a polychromator (Jobin Yvon, HR 320) with a 1200 lines/mm grating and an intensified photodiode array (Spectroscopic Intruments, ST 180, IRY 700G). Details on the experimental setup are given elsewhere.[24] The cuvette is placed in a temperature-controlled copper holder. All measurements are performed at $T = 20$ °C, if not stated otherwise.

TRLFS measurements are performed as described in ref.[23]

Acknowledgments

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