Spectroscopic Study on the Complexation of trivalent Actinide and Lanthanide ions with TEDGA in Solution

Thomas Sittel,*[b] Maximilian Meißner,[a] Max Keller,[a] Andreas Geist,[b] and Petra J. Panak[a, b]

NMR spectroscopy studies on the complexation of La(III), Sm(III), Lu(III), Y(III) and Am(III) with N,N,N′,N′-tetraethyldiglycolamide (TEDGA) have been performed. Initial studies concerning the stoichiometry of the complexes prove the formation of [M-(TEDGA)$_3$]$^{3+}$ in D$_2$O and [M(TEDGA)$_{1-3}$]$^{3+}$ in CD$_3$CN. Decreasing the solvent polarity translates to an increase of the complex stability as shown by complementary TRLFS studies with Cm(III). Due to delocalization of the lone electron pair of the amide nitrogen atom, the M(III)–O interaction has been studied indirectly by collecting ^{13}C and ^{15}N NMR data. The observed chemical shifts prove that the interaction of the trivalent ions, An(III) and Ln(III), and TEDGA is almost identical.
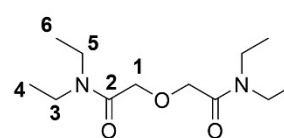
Introduction

The interaction between organic ligands and trivalent lanthanide or actinide ions is primarily dictated by electrostatic forces. In some instances, however, the interaction may exhibit a pronounced partial covalent character, as evidenced by NMR studies of Am(III) complexes with N-donor ligands such as 2,6-bis(1,2,4-triazin-3-yl)pyridine (BTP). [Am(nPr-BTP)$_3$](NO$_3$)$_3$ shows a notable shift in the coordinated nitrogen atoms of the ligand, approximately 300 ppm when compared to similar weakly paramagnetic or diamagnetic lanthanide ions.[1] This significant distinction is further validated through the investigation of ^{15}N shifts in similar complexes involving iPr-BTP, 2,6-Bis(1H-pyrazol)-3-yl-pyridine (BPP) and 2,6-bis(1H-1,2,3-triazol-4-yl)pyridine (PTEH).[2]

To gain a deeper understanding of the interaction mechanisms in trivalent lanthanide and actinide complexes, further studies employing structurally divers hard and soft donor ligands are of significant interest. Tridentate O-donor ligands such as N,N,N′,N′-tetraoctyldiglycolamide (TODGA)[3] or N,N,N′,N′-tetraethyldiglycolamide (TEDGA)[4] have been widely studied due to their potential applications in actinide recycling strategies.[5] Most spectroscopic studies involving actinide complexes with these ligands have primarily focused on the determination of stability constants and complex speciation.[3a,5c,6]

Probing the Ln(III)-O or An(III)-O interaction through NMR is challenging, as the NMR active nucleus, ^{17}O (I = 5/2), possesses a low natural abundance of 0.04%. Hence, detecting ^{17}O accurately necessitates either labeling or the use of substantial quantities of the substances, which is often impractical. However, the structure of diglycolamides offers an indirect approach to investigate bonding properties. The lone pair of electrons of the amide nitrogen atom is delocalized into the π-system of the carbonyl group, thus forming a conjugated system. As a result, the amide bond can be described as a resonance between two alternative structures (see Figure 1).[7] Thus, by examining the chemical shifts of the nitrogen and carbon atoms within the amide group in diglycolamide complexes, valuable insights into the bonding properties of the Ln(III)-O and An(III)-O bonds can be obtained.

In this study, we offer a comprehensive NMR spectroscopic examination of the interaction between TEDGA and Ln(III) (La, Sm, Lu), Y(III), and Am(III). Our analysis involves ^{13}C and ^{1}H/^{15}N correlation spectra, providing new insights into the metal ion-

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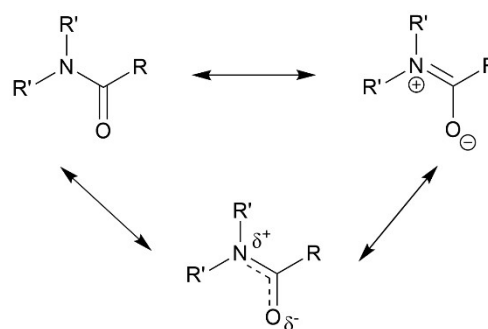Heidelberg University, Institute of Physical Chemistry, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany

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Figure 1. Structure of TEDGA and alternative structures of the amide bond.

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ligand interaction and exploring the solvent's influence on speciation and complex stability.

Results and Discussion

Effect of solvent polarity on the NMR speciation

In the literature, the formation of 1:1, 1:2 and 1:3 TEDGA complexes has been documented for a variety of lanthanide and actinide ions.[4a,6b,c,8] NMR-titration experiments were conducted in D_2O to determine the speciation in the samples. The ^1H NMR spectrum was continuously monitored at 300 K after each titration step. In Figure 2 (on the left), the progression of the ^1H NMR spectra of the weakly paramagnetic Sm(III) ion at different metal ion-to-ligand ratios is presented. In general, all five ligand signals are detected within the 5 ppm and 0 ppm range. The signals from the CH_2 groups H_1 and H_3 experience noticeable shifts as the ligand concentration increases. In addition, significant line broadening is observed for H_1, H_3, H_4 and H_5 at a Sm:L ratio of 1:4. Conducting a similar experiment with La(III), a comparable shift is observed (cf. supporting information Figure S1). In contrast to La(III) and Sm(III), no shift of H_1 with increasing ligand concentration is noted for Lu(III) (as depicted in Figure 2 on the right). In fact, at a Lu:L ratio of 1:4 a new signal emerges at 4.41 ppm, corresponding to the H_1 protons of the free ligand. A distinctive feature of the proton spectrum at a Lu:L=1:3 is the line broadening of H_1 and H_3, resulting from limited ligand flexibility in the complex. Consequently, the protons of these CH_2-groups become diastereotopic. For H_1, the shift difference between both protons is relatively small, leading to a broadening of the singlet. As for H_{3a}/H_{3b}, two separate signals are observed at 3.51 ppm and 3.37 ppm. Like Sm(III), significant line broadening of H_1, H_3, H_4 and H_5 occurs at high ligand concentration (Lu:L>1:3). The titration experiment with Y(III) shows a comparable trend to what was observed with Lu(III) (cf. supporting information
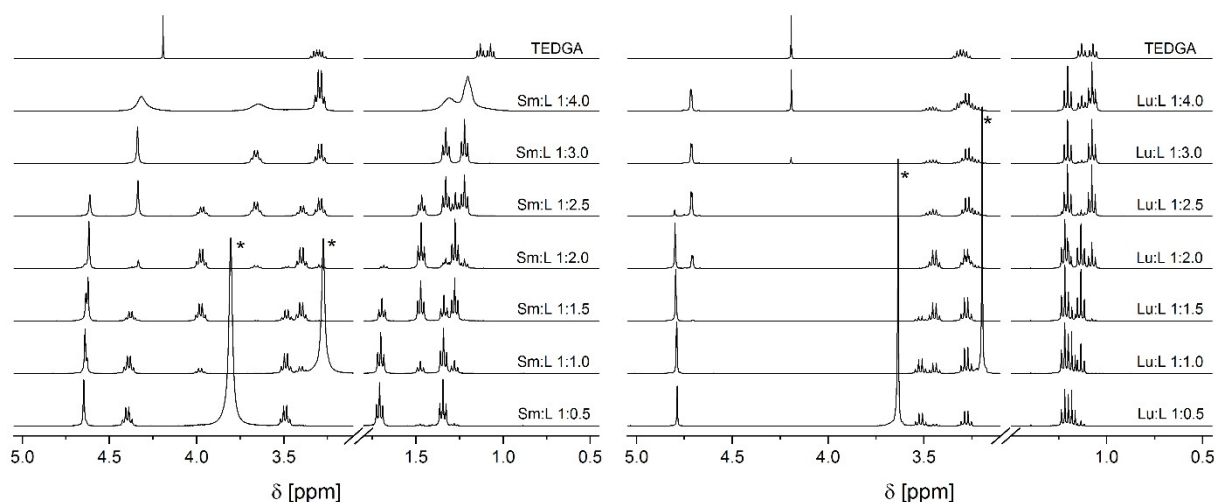
Figure S2). This indicates the formation of the 1:3 complex $[M(TEDGA)_3]^{3+}$ for M=Y(III) and Lu(III). However, the titration experiments for Sm(III) and La(III) do not conclusively confirm the formation of the 1:3 complex. In all experiments, there is a broadening of individual proton signals at high ligand concentrations, which arises from an exchange between the free ligand and the complex. In case of Y(III) and Lu(III), the exchange rate appears to be relatively slow, resulting in split signals for both the complex and the free ligand.

To determine the stoichiometry of the Sm(III)- and La(III) complexes, we prepared solutions with a M:L ratio of 1:3 (where M=La, Sm, Lu, Y) in D_2O. These solutions were then subjected to analysis using electrospray ionization mass spectrometry (ESI-MS) in positive mode. The mass spectra obtained for all ions are provided in Supplementary Information. The spectra reveal three major signals: $[M(TEDGA)_3(NO_3)]^{2+}$, $[M(TEDGA)_2(NO_3)_2]^+$, and $[M(TEDGA)_3(NO_3)_3+M(NO_3)_2]^+$ with $[M(TEDGA)_2(NO_3)_2]^+$ consistently appearing as the most prominent signal. It is worth noting that while the MS speciation does not precisely mirror the actual speciation in solution, MS fragmentation remains consistent across the complex series. Considering the NMR data for Lu(III) and Y(III), the MS data suggest the formation of $[M(TEDGA)_3]^{3+}$ for Sm(III) and La(III) under the given experimental conditions.

To faciliate a comparison between Ln(III) to Am(III), the Am(III)-TEDGA complex was synthesized using a 1:3 metal-to ligand ratio. Proton and carbon NMR analyses revealed line broadening of the CH_2 bridging protons and carbonyl carbon atom, respectively (Figure S33/S34 in the Supporting Information). Considering the comparable ionic radius of Am(III) and Nd(III), we expect a similar exchange process for the $[Am(TEDGA)_3]^{3+}$ complex in D_2O. This behavior is expected to resemble the observed interactions of Sm(III) and La(III). Adjusting the solvent polarity might mitigate this exchange process, potentially enabling the characterization of individual complexes. Consequently, we substituted D_2O with deuterated acetonitrile (CD_3CN). In Figure 3 (on the left), we present the
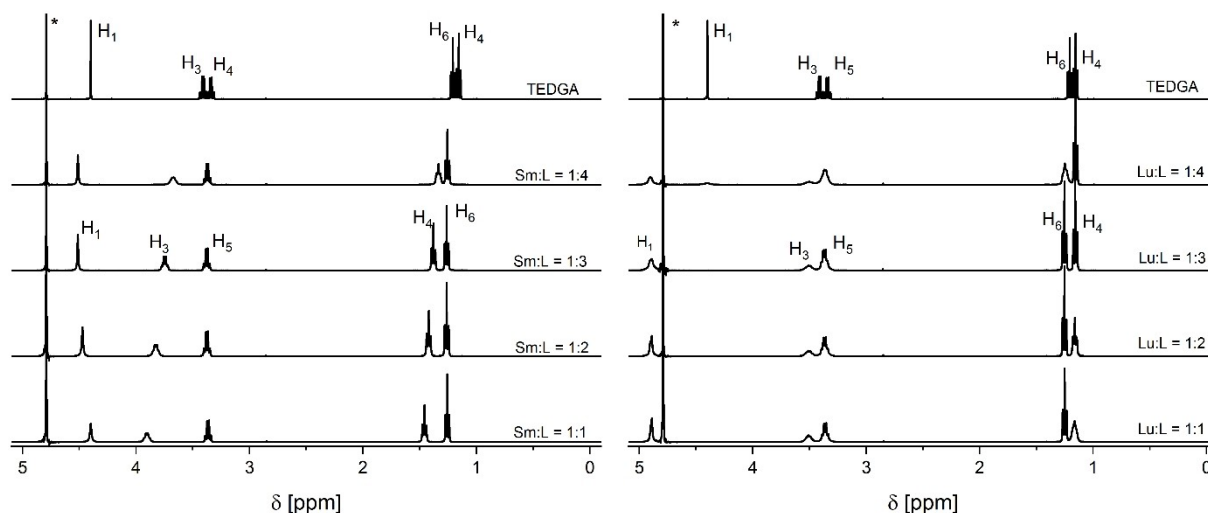
Figure 2. ^1H-NMR spectra (400.13 MHz, 300 K) of Sm(III) and Lu(III) ($[M]_{ini}=2.0\cdot10^{-2}$ mol L^{-1}, n(M) = 10 μmol) as a function of the TEDGA/metal ion ratio in D_2O (* δ(H$_2$O) = 4.79 ppm).

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Figure 3. ^{1}H-NMR spectra (400.13 MHz, 300 K) of Sm(III) and Lu(III) ([M]$_{ini}$ = $2.0 \cdot 10^{-2}$ mol L^{-1}, n(M) = 10 µmol) as a function of the TEDGA/metal ion ratio in CD$_3$CN (* δ(H$_2$O)).

evolution of the ^{1}H NMR spectra during the Sm(III) titration at different metal-to-ligand ratios. In contrast to the previous experiment in D$_2$O, the spectra reveal the formation of three complex species: Species 1 is evident between Sm:L 1:0.5–1.5; Species 2 emerges at Sm:L 1:1–2.5 and the third species forms at higher TEDGA concentrations. This observation strongly suggests the progressive formation of the [Sm(TEDGA)$_n$]$^{3+}$ complexes (with n = 1–3) in acetonitrile. In cases where there is an excess of ligand (Sm:L > 1:3), the signals from the complex become noticeably broader. Additionally, no signals of the free ligand are observed in the spectrum. This indicates that a rapid exchange is occurring. In retrospect, this reaffirms the formation of the 1:3 complex in aqueous solution, as previously discussed. A similar trend is observed for La(III), leading to the conclusion that La(III) also forms 1:1, 1:2 and 1:3 complexes which exhibit rapid exchange processes. In comparison, the titration of Lu(III) is displayed in Figure 3 (on the right). Once again, we observed the formation of three distinct complex species, indicating a gradual formation of [Lu(TEDGA)$_n$]$^{3+}$ (n = 1–3). As previously noted, the presence of unbound ligand signals in the proton NMR spectrum at Lu:L > 1:3 suggests only a slow exchange between coordinated and uncoordinated

ligand within the NMR timescale. Y(III) follows the same pattern as Lu(III), confirming the formation of [Y(TEDGA)$_n$]$^{3+}$ (n = 1–3).

Based on the results presented, we prepared Am(III) complexes with TEDGA at Am:L 1:1.75 and Am:L 1:3.25 (see Figure 4). The NMR spectrum at Am:L 1:1.75 shows three singlet signals at 4.56 ppm, 4.35 ppm, and 4.24 ppm. These signals can be assigned from the left to right as follows: 1:3, 1:2 and 1:1 complex. The spectrum at Am:L 1:3.25 displays only one set of signals, presumably from the 1:3 complex. Due to the exchange, the signals are broadened and shifted compared to the spectrum obtained at Am:L 1:1.75. No signals of the free ligand are detected, underscoring the similarity between Am(III) and the lighter Ln(III) ions.

Comparison of the [Ln(TEDGA)$_3$]$^{3+}$ and [Am(TEDGA)$_3$]$^{3+}$ complexes

Based on the speciation provided in the initial NMR section, we synthesized [M(TEDGA)$_{1-3}$]$^{3+}$ complexes for M=Am, La, Sm, Y, and Lu, and characterized them using 1D and 2D NMR techniques. Table 1 presents the carbon NMR shifts of C$_1$ and C$_2$ for each respective metal ion within [M(TEDGA)$_{1-3}$]$^{3+}$. For the

Table 1. ^{13}C chemical shifts (100.63 MHz, 300 K) of the carbonyl atom of the amide group C$_2$ and the CH$_2$ group C$_1$ of TEDGA and [M(TEDGA)$_3$]$^{3+}$ ([M] = $1 \cdot 10^{-2}$ mol L^{-1} M=La, Sm, Lu, Y; [Am] = $6.7 \cdot 10^{-3}$ mol L^{-1}) in D$_2$O.

	δ(C$_1$)$_{CD3CN}$ [ppm]			δ(C$_2$)$_{CD3CN}$ [ppm]			δ(C$_2$)$_{D2O}$ [ppm]
Metal ion	1:1	1:2	1:3	1:1	1:2	1:3	1:3
La	71.4	71.5	71.6	172.0	171.8	171.9	170.3
Sm	71.2	71.3	70.6	175.0	174.2	173.5	172.1
Lu	71.0	71.0	70.0	172.4	172.2	171.8	170.8
Y	71.1	70.9	70.4	171.9	171.7	171.5	170.4
Am	69.8	70.2	71.0	179.8	179.8	181.0	176.5
TEDGA	70.1			168.8			169.8

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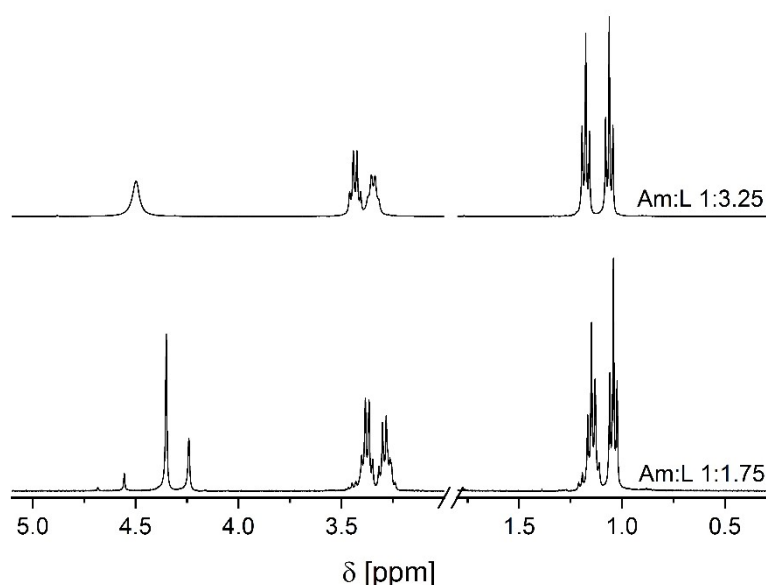
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Figure 4. ^{1}H-NMR spectra (400.13 MHz, 300 K) of Am(III) ([M] $= 6.7 \cdot 10^{-3}$ mol L^{-1}) depending on the TEDGA/metal ion ratio in CD$_3$CN.

bridging CH$_2$ group C$_1$, the NMR shifts exhibit relatively consistent values across the 1:1, 1:2, and 1:3 complexes and the metal ion series.

C$_2$, on the other hand, exhibits more intriguing results across the metal ion series. As shown in Table 1, a consistent downfield shift of 3–13 ppm is observed in all complexes, underscoring the immediate influence of oxygen coordination on the metal ion. Am(III) and Sm(III) display the most pronounced changes in chemical shift compared to diamagnetic ions. Among them, Am(III) shows the most significant shifts overall. Table 1 also provides the chemical shifts of the respective 1:3 complexes prepared in D$_2$O. Although a direct comparison of shifts is not feasible, it is worth noting that the same trends observed in CD$_3$CN also apply in aqueous solution. Additionally, NMR shifts in CD$_3$CN are more pronounced compared to the aqueous system, indicating a stronger overall ligand-metal interaction.

The carbonyl data are crucial for enhancing our understanding of the metal-ligand interaction in these complexes. Given the nature of the amide bond, changes in electron density distribution in the coordinating oxygen atoms should be reflected in the attached carbon atom and the neighboring nitrogen atom. The noticeable shifts in the carbonyl atoms, compared to the remaining CH$_2$ and CH$_3$ groups, directly reflect the immediate impact of complexation. A closer examination of the carbon shifts reveal that Am(III) complexes exhibit the most significant shifts. This trend may be caused by a slight difference in the metal-ligand interaction. However, to gain comprehensive insights, it is crucial to consider the chemical shifts of the nitrogen atom within the amide group. Table 2 displays the ^{15}N shifts, obtained using a ^{1}H/^{15}N HMQC sequence. In CD$_3$CN, the NMR shifts for the complexes range from 139 to 141 ppm. These shifts are notably affected by coordination when

Table 2. ^{15}N chemical shifts of TEDGA and [M(TEDGA)$_{1-3}$]$^{3+}$ ([M] $= 1 \cdot 10^{-2}$ mol L^{-1} M $=$ La, Sm, Lu, Y; [Am] $= 6.7 \cdot 10^{-3}$ mol L^{-1}) determined from the ^{1}H/^{15}N HMQC spectra.

	$\delta(^{15}$N$)_{CD3CN}$ [ppm]	$\delta(^{15}$N$)_{D2O}$ [ppm]
Metal ion	1:1/1:2/1:3	1:3
La	139–138	137
Sm	138–136	138
Lu	140–138	138
Y	140–139	139
Am	140–139	139
TEDGA	127	134

compared to the chemical shift of the free ligand. Due to the inherent ^{1}H/^{15}N coupling signal, distinguishing specific trends between the individual complex species proved to be challenging. Nevertheless, the NMR data reveals minimal differences, suggesting a consistent electron density distribution across all complex species. The table also includes the chemical shifts of the 1:3 complexes determined in D$_2$O. The same trends as observed in CD$_3$CN are evident, although the complex shifts are less pronounced when compared to the free ligand.

Considering the carbon and nitrogen data, it appears that the metal-ligand interaction remains relatively consistent across the series of metal ions. Consequently, we conclude that there is not a discernible difference in the metal-ligand interaction between Am(III) and the trivalent lanthanide ions. However, a small deviation in carbon shifts is noticeable between the Am(III) complexes and the Ln(III) complexes.

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TRLFS study of the Cm(III) complexation

The results presented here underscore the substantial impact of solvent selection on the speciation of TEDGA complexes. Shifting from D_2O to CD_3CN appears to enhance the stability of the complex species, as the coordination of solvent molecules does not pose significant competition to TEDGA. To confirm the observed solvent effect, we employed time-resolved laser fluorescence spectroscopy (TRLFS) to determine the complex stability constant for Cm(III) complexes in acetonitrile with 10 Vol.% H_2O.

Figure 5 presents the normalized emission spectra of Cm(III) in relation to the TEDGA concentration. In the absence of TEDGA, the solvent species exhibits an emission band at 594.6 nm. This species has been previously documented in the literature and can be attributed to a partial replacement of water molecules in the first coordination sphere.[9] With gradual increase in ligand concentration, three new emission bands appear at 597.8 nm, 602.8 nm, and 608.8 nm. These signify the progressive coordination of TEDGA with the Cm(III) ion. These emission bands correspond to $[Cm(TEDGA)]^{3+}$, $[Cm(TEDGA)_2]^{3+}$, and $Cm(TEDGA)_3]^{3+}$. The distinctive characteristics of these narrow emission bands and their maxima are consistent with those found in diglycolamide complexes in the existing literature.[3a,6b,10] The measured emission spectrum represents a superposition of individual Cm(III) species. The relative fraction of each species can be determined through peak deconvolution. This method allows for a detailed understanding the of the composition of the overall spectrum. A detailed description of this procedure is provided in the Supporting Information. In Figure 6, the speciation of Cm(III) with TEDGA, resulting from the applied deconvolution procedure, is displayed. It illustrates

the gradual formation of $[Cm(TEDGA)_n]^{3+}$ with $n=1-3$. This coordination process adheres to the following equilibrium (Eq. 1)

$$[Cm(TEDGA)_{n-1}]^{3+} + TEDGA \rightleftharpoons [Cm(TEDGA)_n]^{3+} \tag{1}$$
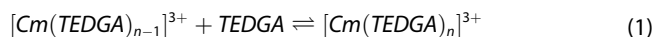
Applying the mass action law provides Equation 2

$$\frac{[Cm(TEDGA)_n]^{3+}}{[Cm(TEDGA)_{n-1}]^{3+} \cdot [TEDGA]_{free}} = K_n' \tag{2}$$

With K_n' being the conditional stability constants. Stability constants are calculated based on Equation 3

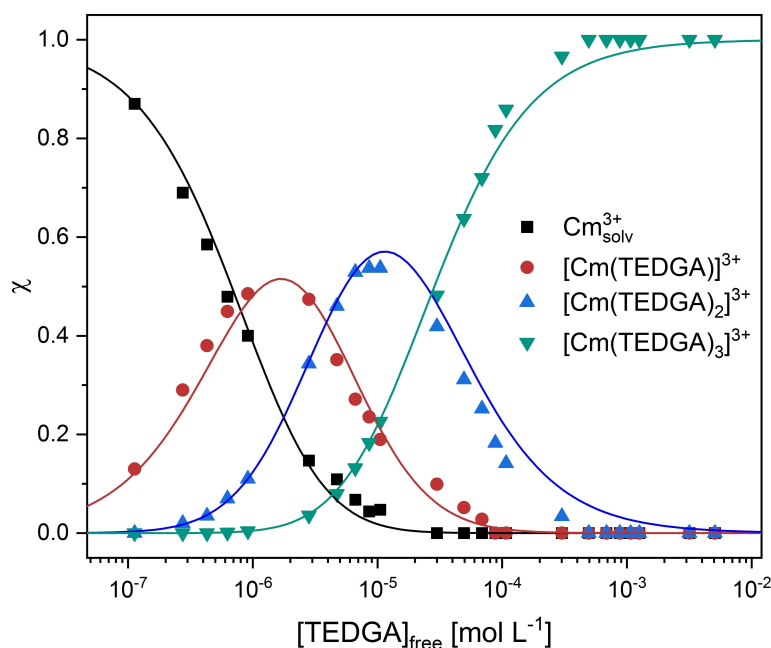$$\log\beta_n' = \log\left(\frac{[Cm(TEDGA)_n]^{3+}}{[Cm_{Solv.}]^{3+} \cdot [TEDGA]_{free}^n}\right) \tag{3}$$

The determined stability constants for $[Cm(TEDGA)_n]^{3+}$ with $n=1-3$ in $CH_3CN + 10$ Vol.% H_2O are as follows: $\log \beta_1 = 6.1$, $\log \beta_2 = 11.5$, and $\log \beta_3 = 16.1$. These values are also provided in Table 3, alongside the previously reported $\log \beta$ values for Cm(III) complexes with TEDGA and TODGA. TEDGA forms a 1:3 complex in acetonitrile with stability constants differing by almost eight orders of magnitude compared to those determined in 10^{-3} mol L^{-1} $HClO_4$. This underscores the significant impact of reduced solvent polarity on complex stability.

The stability constants determined in this work fall within the range of known literature data for TODGA, a lipophilic extractant structurally related to TEDGA. Differences in complex stability arise from the variations in solvent polarity (EtOH vs. ACN), water content, and potential steric effects. NMR experiments revealed that Am(III) behaves similarly to early lanthanide
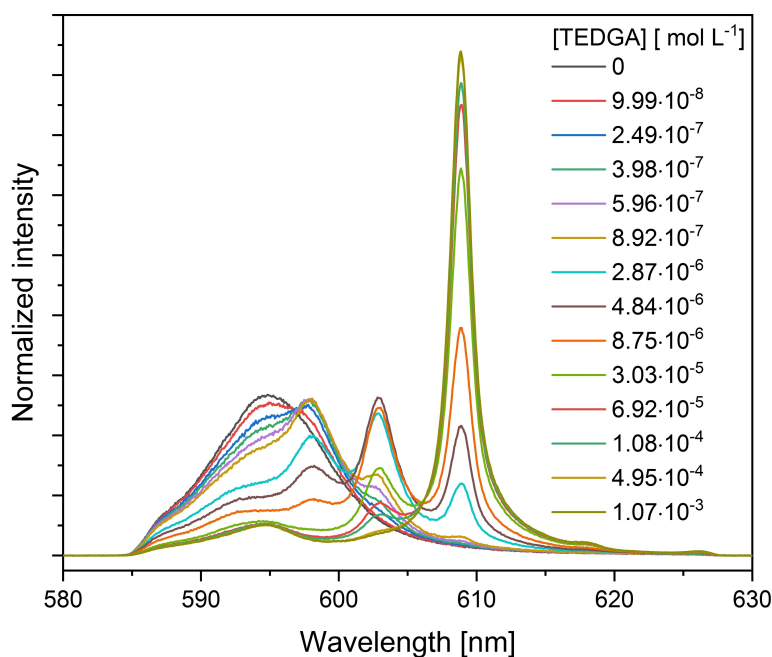
Figure 5. Normalized Cm(III) emission spectra for the complexation of Cm(III) with TEDGA in acetonitrile containing 10 Vol.% H_2O as a function of the TEDGA concentration. $[Cm(III)]_{ini} = 1 \cdot 10^{-7}$ mol L^{-1}.

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Figure 6. Relative fractions of the Cm(III) solvent species and the $[Cm(TEDGA)_n]^{3+}$ complexes (n = 1–3) as a function of the free TEDGA concentration. Dots denote experimental data. Lines are calculated using log $\beta_1 = 6.1$, log $\beta_2 = 11.5$ and log $\beta_3 = 16.1$. Fl factors: $Fl(Cm_{solv}) = 1$, $Fl(Cm_{1:1}) = 1.1$, $Fl(Cm_{1:2}) = 1.1$, $Fl(Cm_{1:3}) = 3.5$.

Table 3. Stability constants of $[Cm(TEDGA)_n]^{3+}$ and $[Cm(TODGA)_n]^{3+}$ (n = 1–3).

	log β_1	log β_2	log β_3	Solvent	Literature
TEDGA	6.1 ± 0.3	11.5 ± 0.3	16.1 ± 0.4	ACN + 10 Vol.% H_2O	this work
TEDGA	3.3 ± 0.3	6.6 ± 0.3	8.3 ± 0.3	$1 \cdot 10^{-3}$ HClO$_4$	[6b]
TODGA	6.25 ± 0.15	–	14.92 ± 0.3	EtOH	[3a]

ions in terms of speciation. The indicate similarities in the ligand-metal interaction between Ln(III) and An(III), supporting Pearson's principle. This fundamental concept proposes that hard trivalent lanthanide and actinide ions tend to form strong complexes with hard donor atoms such as oxygen.

Conclusions

Utilizing NMR spectroscopy, this study offers novel insights into the M(III)-TEDGA interaction within Am(III) and Ln(III) complexes. ^{15}N and ^{13}C NMR data substantiate the claim that the metal-ligand interaction between Am(III)–O and Ln(III)–O in the respective $[M(TEDGA)_n]^{3+}$ complexes is nearly identical. These findings closely align with extraction and TRLFS data for TEDGA and analogous digylcolamide ligands as reported in existing literature. Notably, our study confirms the similar behavior of Am(III) and early lanthanide ions such as Nd(III).

Experimental section

Material and methods

Deuterated solvents were purchased from Euriso-Top GmbH. Chemicals for synthesis were purchased from VWR International and used as-is. TEDGA was synthesized according to the literature.[11]

TRLFS experiments were performed at 298 K with a Nd:YAG (Surelite II laser, Continuum) pumped dye laser system (NarrowScan D-R; Radiant Dyes Laser Accessories GmbH). A wavelength of 396.6 nm (Cm(III)) was used to excite the metal ions. Spectral decomposition was performed with a spectrograph (Shamrock 303i, ANDOR) with 300, 1199 or 2400 lines per mm gratings. The fluorescence was detected by an ICCD Camera (iStar Gen III, ANDOR). A delay of 1 μs was used to discriminate short-lived organic fluorescence and light scattering.

NMR spectra were recorded on a Bruker Avance III 400 spectrometer operating at 400.13 MHz for ^{1}H, 100.63 MHz for ^{13}C and 40.58 MHz for ^{15}N at 300 K. The spectrometer was equipped with a broadband observe probe (BBFOplus) with direct x-magnetization detection for proton and heteronuclear detection experiments. Chemical shifts are referenced internally to TMS (δ(TMS) = 0 ppm) for ^{1}H and ^{13}C and to ^{15}NH$_4$Cl with δ(^{15}NH$_4$Cl) = 0 ppm for ^{15}N. For all spectra, standard Bruker pulse sequences were used. 1D spectra of ^{1}H and 13 C were recorded with 32k data points and are zero filled to 64k data points. ^{15}N data at natural abundance were obtained

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from high resolution ^{1}H,^{15}N-HMQC spectra with a resolution of 4k data points in the indirect dimension. Signal multiplicity was determined as s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sex (sextet), sept (septet), m (multiplet) and br. s (broad signal).

Mass spectra using ESI ionization methods were recorded using a Bruker ApexQe FT-ICR instrument.

Sample preparation

Preparation of TRLFS samples

122 mg TEDGA were dissolved in 0.5 mL acetonitrile containing 10 Vol.% H_2O and dilutions were prepared.

TRLFS samples were prepared by adding 5.0 μL of a Cm(III) stock solution (2. 10^{-5} mol L^{-1} Cm(ClO$_4$)$_3$ in 0.01 mol L^{-1} HClO$_4$: ^{248}Cm: 89.7%, ^{246}Cm: 9.4%, ^{243}Cm: 0.4%, ^{244}Cm: 0.3%, ^{245}Cm: 0.1%, ^{247}Cm: 0.1%) to 900 μL of acetonitrile and 95 μL H_2O, respectively, resulting in initial concentrations of 10^{-7} mol L^{-1} Cm(III).

NMR sample preparation

Titration experiments

Initially, 10 μmol of Ln(III) salt (either as NO$_3$ or OTf) were dissolved in 480 μL D$_2$O/acetonitrile-d$_3$ and subsequently transferred to an NMR tube. 50 μmol TEDGA (12.22 mg) were dissolved in 200 μL D$_2$O/acetonitrile-d$_3$ and then added to the NMR tube in 20 μL increments (20 μL = 0.5 eq. = 5 μmol TEDGA). After thorough shaking, a ^{1}H NMR spectrum was recorded.

General synthesis of [Ln(TEDGA)$_{1-3}$](OTf)$_3$

In a 2 mL screw-cap glass vial, an exact amount of TEDGA (4.5–18 μmol, 0.75–3.0 eq.) was dissolved in 600 μL CD$_3$CN. The ligand solution was added to 6 μmol Ln(OTf)$_3$ and then transferred into a high-resolution NMR tube.

General synthesis of [Ln(TEDGA)$_3$](NO$_3$)$_3$

In a 2 mL screw-cap glass vial, 18 μmol TEDGA (4.40 mg, 3.0 eq.) was dissolved in 600 μL D$_2$O. The ligand solution was added to 6 μmol Ln(NO$_3$)$_3$·H$_2$O and then transferred into a high-resolution NMR tube.

Synthesis of [Am(TEDGA)$_{1-3}$](OTf)$_3$

250 μL of an ^{243}Am(III)-stock solution (4 g/L Am(III) in 10^{-3} mol L^{-1} HOTf) were evaporated slowly in a 2 mL screw-cap glass vial. A specific amount of TEDGA (7.2/13.3 μmol, 1.75/3.25 eq.) was dissolved in 600 μL CD$_3$CN. The ligand solution was added to the solid Am(OTf)$_3$ residue (1 mg, 4.1 μmol, 1 eq). The solution was then carefully shaken and transferred into a J. Young type NMR tube.

Synthesis of [^{243}Am(TEDGA)$_3$](NO$_3$)$_3$

333 μL (4.12 μmol ^{243}Am(NO$_3$)$_3$), 1 eq) of an ^{243}Am^{3+}-stock solution (3 g/L Am^{3+}, 0.5 M HNO$_3$) were evaporated slowly in a 2 mL screw-cap glass vial. 3.02 mg (12.36 μmol, 3 eq) TEDGA were dissolved in 600 μL D$_2$O. The ligand solution was added to the Am(NO$_3$)$_3$ precipitate. The solution was then carefully shaken and transferred into a J. Young type NMR tube.

Associated Content

Supporting Information available: ^{1}H, ^{13}C, ^{1}H/^{15}N HMQC NMR spectra for all complexes, ESI MS spectra and additional TRLFS data.

Conflict of Interests

There are no conflicts to declare.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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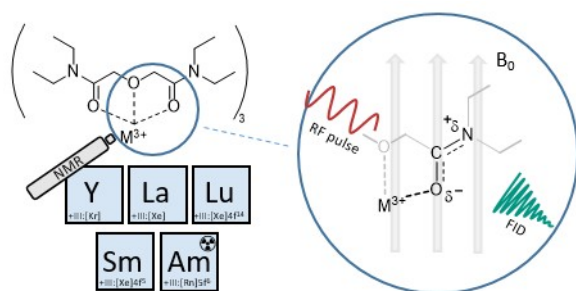
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Spectroscopic Study on the Complexation of trivalent Actinide and Lanthanide ions with TEDGA in Solution

By using NMR spectroscopy, this study provides novel insights into the M(III)-TEDGA interaction in [M-(TEDGA)$_3$]$^{3+}$ complexes (M=Ln, Am).

The chemical shift analyses solidify the assumption of almost identical metal-ligand interaction between Am(III)—O and Ln(III)—O.