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Time-Resolved Laser Fluorescence Spectroscopy and Extended X-Ray Absorption Spectroscopy Investigations of the N_3^- Complexation of Eu(III), Cm(III), and Am(III) in an Ionic Liquid: Differences and Similarities

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The complexation of the lanthanide Eu(III) and the actinides Cm(III) and Am(III) by N_3^- was investigated by application of time-resolved laser fluorescence spectroscopy (TRLFS) and X-ray absorption spectroscopy (XAFS) in the ionic liquid solution of C_4mimTf_2N (1-butyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide). TRLFS measurements show that the interaction of azide with $Eu(CF_3SO_3)_3$ and $Eu(ClO_4)_3$ results in both dynamic luminescence quenching by collisional encounters of N_3^- with Eu(III) and static luminescence quenching by inner-sphere complexation of Eu(III) by N_3^-. Hereby, the complexation of Eu-triflate by azide starts at a lower N_3^- concentration as compared to the perchlorate salt. The authors ascribe this phenomenon to a stronger bonding of ClO_4^- toward the metal ion than triflate, as well as to a stronger electrostatic repulsion of N_3^- by the perchlorate ligand. In both actinide samples ($Cm(ClO_4)_3$, $Am(ClO_4)_3$), the complexation with azide exhibits a clear kinetic hindrance. Nevertheless, mixed actinide-perchlorate-azide complexes are formed after several days in C_4mimTf_2N. The different reaction kinetics for the Ln- and An-complexation by azide may provide the opportunity for an effective separation of lanthanides from actinides in the nuclear fuel cycle by the use of N-based extractants in ionic liquid solution.

1. Introduction

Spent nuclear fuel is a complex mixture of fission products that contains beside the lanthanides also plutonium and the minor actinides neptunium, americium, and curium.[1] Plutonium and the minor actinides control the longterm radiotoxicity of nuclear wastes.[2] The separation of long-lived radionuclides (partitioning) and their fission (transmutation) into shortlived ones in nuclear reactors (P&T[3]) aims at minimizing the long-term radiotoxicity of spent nuclear fuels.[4] A key step in the partitioning and transmutation strategy is the separation of trivalent actinides (An(III)) from lanthanides (Ln(III)).This separation is required because lanthanides have high neutron cross-sections which results in a decrease in transmutation efficiency. The similar properties in chemical behavior of the Ln(III) and An(III) cations make their separation difficult.[5] Both behave as hard Lewis acids and therefore most strongly bind to hard Lewis bases such as oxygen (HSAB principle). In traditional liquid extraction processes a separation by the use of oxygen-donor extractants is therefore not feasible. Only complexation by soft donors such as nitrogen yields selectivity. With this, the partitioning of actinides from lanthanides has focused on the use of nitrogen containing extractants among others in organic solvents such as dodecane or kerosene.

Low melting organic salts known as ionic liquids (ILs) have been studied in view of their application in many fields

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of chemistry such as separation.[6–9] The main interest of these investigations is related to their "green" properties like the negligible flammability and volatility. Moreover, ILs show a high variability of physicochemical properties. Most of today's known ILs are fairly stable toward α and γ irradiation and can be generally considered as possible solvents for the Ln-An separation.[10] To this aim, the basic chemistry of Ln(III) and An(III) in IL solution has to be investigated. It was shown by our group that, switching to ILs as solvent phase, lanthanides and actinides exhibit different chemical reactivity toward their interaction with cations[11] and complexing anions.[12] In the cited studies, the differences in chemical behavior of the lanthanide and actinide was assumed to be related to the higher covalent contribution of the metal−ligand bonding in the actinide complexes as compared to the lanthanide complexes. As a continuation to the cited investigations and because N-based extractants are used in Ln-An separation schemes, the presented study intends to compare the complexation of the lanthanide cation Eu^{3+} and the actinide cations Cm^{3+} and Am^{3+} with the most simple donor N_3^- as a model system for organic N-based extractants.[13] In this context, different systems have been investigated by the authors: (1) The interaction of azide with $Eu(ClO_4)_3$ and $Eu(CF_3SO_3)_3$ in C_4mimTf_2N, and (2) the interaction of azide with $Cm(ClO_4)_3$ and $Am(ClO_4)_3$ in C_4mimTf_2N. Whereas the Am-perchlorate system is investigated by X-ray absorption spectroscopy (XAFS), the Eu- and Cm-samples are studied applying time-resolved laser fluorescence spectroscopy (TRLFS). A comparison of the results gained by the investigations of the lanthanide-samples and actinide-samples should provide a deeper insight into differences of the complexation of Ln and An by N-based ligands in ionic liquid solution which represents a basic approach in terms of lanthanide-actinide separation.

2. Experimental Section

All experiments dealing with Eu(III) were performed at the IPHC laboratory in Strasbourg/France. Preparation of Cm(III) and Am(III) samples were exclusively performed at the Institut für Nukleare Entsorgung (INE) of the Forschungszentrum Karlsruhe, Germany. TRLFS investigations of the Cm-samples were also performed at the INE in Karlsruhe. XAFS measurements of the Am(III) samples were carried out at ANKA (Karlsruhe, Germany) at the INE Beamline.[14]

2.1. Chemicals. Eu(III)-trifluoromethanesulfonate ($Eu(OTf)_3$), Eu_2O_3, 70% $HClO_4$, and tetrabutylammonium-azide ($C_{16}H_{36}N^+N_3^-$, TBAA) were purchased from Sigma Aldrich and used as received.

The ionic liquid 1-butyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide (C_4mimTf_2N, 99.5% purity) was from Solvionic SA (Vermiolle/France).

Cm was extracted from a Cf-252 source (SR-CF 1007) by the United States Atomic Energy Commission (USAEC). An aqueous Cm(III) stock solution (6×10^{-6} M $Cm(ClO_4)_3$) with the composition 89.68% ^{248}Cm, 0.07% ^{247}Cm, 9.38% ^{246}Cm, 0.14% ^{245}Cm, 0.30% ^{244}Cm, and 0.43% ^{243}Cm was prepared and provided by INE.

A stock solution of Am_2O_3 dissolved in 0.1 M $HClO_4$ (0.01 mol/L $Am(ClO_4)_3$) was provided by INE. The composition of the solution was 99.69% ^{243}Am and 0.309% $^{243/244}$Cm.

2.2. Preparation. $Eu(ClO_4)_3$ Stock Solution. An aqueous solution of 0.1 M Eu-perchlorate was prepared by dissolving Eu_2O_3 in 70% $HClO_4$.

TBAA Stock Solution. Stock solutions of 2×10^{-3} mol/L N_3^- (TRLFS measurements) and 0.1 mol/L N_3^- (XAFS measurements) were prepared by dissolving tetrabutylammonium-azide in C_4mimTf_2N. The samples were dried at the vacuum line for 4 h at 70 °C and 2 mbar. The water content of the samples, determined by Karl Fischer titration (Mettler Toledo DL 32; detection limit 5 $\times 10^{-3}$ M) and infrared (IR) spectroscopy (Bruker Equinox 55; detection limit 50 ppm), was below 50 ppm water.

$Eu(OTf)_3 + N_3^-$. $Eu(OTf)_3$ salt was dissolved in C_4mimTf_2N (419.36 g/mol; 1.43 kg/L) by treatment in an ultra sonic bath not longer than 10 min with respect to the prevention of ionic liquid degradation.[15] The Eu(III) concentration in this solution was 1×10^{-2} M. To dry the sample it was put at the vacuum line for 2 h at 70 °C and 2 mbar. The water content of the sample was determined as described above. The resulting value was <50 ppm water which corresponds to less than 1 H_2O molecule per Eu(III).

The azide concentration of the $Eu(OTf)_3$ sample was raised in several steps up to a value of 1.1×10^{-3} M N_3^-. The final concentration of Eu(III) in this sample was 9.2×10^{-3} M. For each concentration step, the emission spectra and lifetimes were recorded. The measurements were performed within a day. The water content of the luminescence sample was determined after each addition of azide solution by IR spectroscopy. No macroscopic uptake of water could be detected.

$Eu(ClO_4)_3 + N_3^-$. For the dissolution of Eu-perchlorate in C_4mimTf_2N, the corresponding stock solution (0.1 M $Eu(ClO_4)_3$) was diluted in the ionic liquid by a factor of 10 yielding a final Eu-perchlorate concentration of 1×10^{-2} M. After addition, the sample was evaporated at the vacuum line for 2 h at 70 °C and 2 mbar. The water content of the sample was again <50 ppm corresponding to less than 1 H_2O molecule per Eu(III).

TBAA stock solution was added to the Eu-perchlorate sample in several concentration steps (1×10^{-5} M to 1.1×10^{-3} M). The final concentration of Eu(III) in this sample was 9.2×10^{-3} M. As described above, emission spectra and lifetimes were recorded after each azide addition. No macroscopic uptake of water could be detected during the measurements.

$Cm(ClO_4)_3 + N_3^-$. For the preparation of the ionic liquid curium sample, a droplet of the Cm(III) stock solution was put directly

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into a quartz cuvette and evaporated by heating at 100 °C for 30 min. This treatment does not result the formation of the oxide. After evaporation, dry C_4mimTf_2N was added. The final Cm(III) concentration of this sample was 1.2×10^{-7} M. Then, the sample was put into an oven for 1 h at 70 °C and 2 mbar to get it as dry as possible. The concentration of N_3^- in the Cm(III) sample was varied within a day from 2×10^{-8} to 1×10^{-5} mol/L by adding the according amount of ionic liquid TBAA stock solution. The final concentration of Cm(III) in this sample was 1.1×10^{-7} M. Before measuring the luminescence and emission lifetime at different N_3^- concentrations, the Cm-sample was put in the oven for 1 h at 70 °C and 2 mbar to avoid the influence of minimal amounts of absorbed water during the opening of the cuvette. After another 7 days, the same Cm sample was measured again. To avoid the penetration of water during the waiting period, the sample was stored in a glovebox under nitrogen atmosphere.

$Am(ClO_4)_3 + N_3^-$. A 35 μL volume of the $Am(ClO_4)_3$ stock solution (1×10^{-2} M) was evaporated (5 mbar) in the oven at 70 °C. After evaporation, the salt was dissolved in 350 μL of the 0.1 M N_3^- ionic liquid stock solution. The 1 mM solution was transferred into the final vessel for the XAFS measurements, was then again put into the oven at 60 °C, and was evaporated (5 mbar) for 4 h. The sample was analyzed by XAFS right after its preparation. Another sample was prepared in the same manner and measured 8 days after its preparation. To avoid the penetration of water during the waiting period, the sample was hermetically sealed.

2.3. Methods. It is well-known that beside XAFS,[16] the luminescence spectroscopy of Eu(III) and Cm(III) is a useful tool in studying the structure and chemical reactivity of the two f-element cations in solution,[11,12] as well as at the solid-solution interface[17] and in solid matrixes.[18,19] The emission bands of Eu(III) originate from electronic transitions from the lowest excited state $^5D_0$ to the ground-state manifold ^7F_J ($J = 0, 1, ..., 6$). The intensity, splitting, and energy of the luminescence bands as well as the relative intensities of the two $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions ($R_{F2/F1}$) are very sensitive to the symmetry and the nature of the ligand environment.[20–22] For Cm(III) the $^6D_{7/2} \rightarrow {}^8S_{7/2}$ transition is sensitive to the coordination environment. A change of the curium ligand field results in a spectral shift (nephelauxetic effect[23]) of the Cm-luminescence spectrum.[24,25] Beside the interpretation of emission spectra, structural information is gained by analyzing the europium and curium emission lifetime (τ_{obs}). Various processes including excited-state reactions, complex formation, and collisional encounters can result in a depopulation of excited states causing a decrease of the luminescence intensity together with a decrease of the emission lifetime for a given fluorophore.[26–28] Quenching resulting from collisional encounters between fluorophore and quencher is also called dynamic quenching whereas quenching which is due to complex formation is called static quenching. In aqueous solution, the dominant mode of luminescence quenching of the excited ions occurs via coupling of the excited-state to O−H oscillators coordinated to the metal ions. Hereby, the reciprocal Eu- and Cm-luminescence lifetime is linearly proportional to the number of aqua ligands in the inner coordination sphere of the lanthanide[29] and the actinide ion.[30] Ligands with oscillators, having vibronic frequencies similar to the O−H ones, are also effective as nonradiative deactivators of the fluorophore. In aqueous, as well as in nonaqueous, solution the quenching influence of pseudohalides such as $NCSe^-$, NCS^-, NCO^-, and N_3^- is reported.[31–33] In general, dynamic luminescence quenching can be described by the Stern−Volmer equation[26]

$$k_{obs} = k + k_{SV}[Q] \tag{1}$$

where [Q] is the concentration of the quencher, k_{SV} is the bimolecular quenching constant, k_{obs} is the decay rate of the fluorophore, and k is the decay rate of the fluorophore in absence of a quencher.

A plot of k_{obs} versus [Q] yields a straight line with a slope equal to k_{SV}. In many instances the fluorophore can be quenched both by collisional encounters (outer-sphere interaction; dynamic quenching) and by complex formation (inner-sphere interaction; static quenching) with the same quencher. Then, the Stern−Volmer plot deviates from linearity, and an upward curvature is observed. With this, the interpretation of Stern−Volmer plots makes a separation between the two contributions possible and allows the differentiation of outer-sphere interaction and inner-sphere complex formation.

The Eu-emission spectra were recorded with a spectrofluorimeter (Photon Technology International). The measurements of the emission were not time-resolved in this setup. Samples were excited at 394 nm and recorded in a range from 570 to 635 nm with a step size of 0.5 nm. The emission spectra were characterized by the two emitting lines that can be attributed to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions. The intensity ratio of these two lines, $R_{F2/F1}$, was used in addition to give a further interpretation of the system. Lifetime measurements were performed using a Nd:YAG laser set up (10 Hz, 6 ns pulse duration, 1.2 mJ, GCR 11, Spectra Physics). The Eu(III) luminescence was excited at 266 nm and detected by a monochromator (Jobin-Yvon, H20, precision ± 0.5 nm) connected to a photomultiplier (Philips, XP2254B) and an oscilloscope (Tektronik, 500 MHz, 10000 channels, 8 bit resolution). The decay was analyzed at 612 nm. The two different set ups for measuring the Eu luminescence and the emission lifetime have no influence on the spectroscopic properties of the characterized species.

The Cm(III) speciation by TRLFS was performed using an excimer-pumped dye laser system (Lambda Physics, EMG 201 and FL 3002). Cm was excited at 375 nm, and the resulting emission was measured in the spectral range of 580 to 620 nm, using a delay time of 1.2 μs at a gate width of 1.3 ms. An optical multichannel analyzer was used for detection, which consists of a polychromator (Jobin Yvon, HR 320) with a 1200 lines/mm grating and an intensified photodiode array (Spectroscopy instruments, ST 180,

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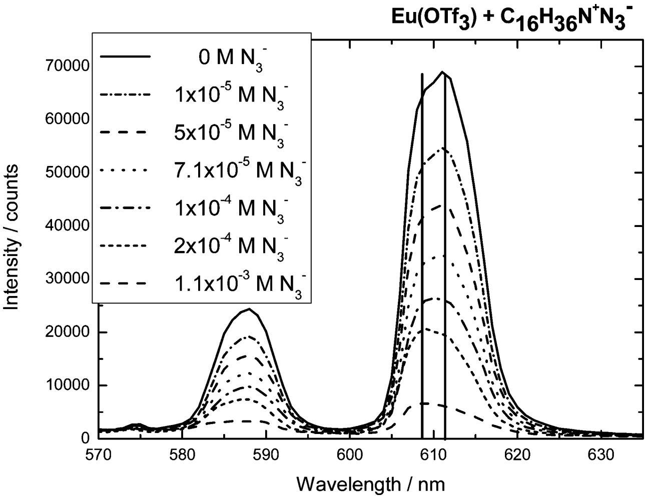

Figure 1. Luminescence spectra of 1 × 10^{-2} M $Eu(OTf)_3$ dissolved in C_4mimTf_2N at different $C_{16}H_{36}N^+N_3^-$ concentrations. With increasing N_3^- concentration, the luminescence decreases and the shape of the emission signal changes.

IRY 700G). The TRLFS instrumentation is described elsewhere in detail.[34] In the presented paper, lifetime data will be expressed as τ_{obs}, the lifetime value, or as $k_{obs} = 1/\tau_{obs}$.

Americium L_3-edge spectra were recorded at the INE beamline at ANKA (Germany) using a double-crystal monochromator equipped with a pair of Ge(422) crystals. The radioactive samples were sealed with polyethylene foils. Measurements were made in fluorescence mode using a five elements Ge detector with a sample orientation of 45° to the incident beam. The energy calibration was performed using a Nb metal foil (K edge at 18986 eV). The data were analyzed using IFEFFIT, [35] and fits were performed in the *R*-space (0.8−4 Å) using FEFFIT.[36] The *k*-space range was set from 2.6 to 10.1 $Å^{-1}$. Theoretical backscattering phase and amplitude functions used for fitting were calculated with the FEFF 8.2 code.[37] The overall scaling factor S_0^2 was held constant to 1. Distances are determined with an error of ± 0.02 Å and coordination numbers with an error of ± 20%.

3. Results

3.1. $Eu(OTf)_3 + N_3^-$. The emission spectrum of 1 × 10^{-2} M $Eu(OTf)_3$ at different N_3^- concentrations (Figure 1) exhibits two peak maxima at 588 and 611 nm that can be attributed to the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions.[11,12] The luminescence decay of the sample before addition of N_3^- shows biexponential behavior (Figure 2). According to the literature, the fit results in a longer emission lifetime of 2.5 ± 0.2 ms which can be attributed to a Eu(III)-species without water in the first coordination sphere. The shorter lifetime of 1.0 ± 0.3 ms corresponds to a Eu(III)-species with one additional water in the first coordination sphere. The ratio of the two luminescence transitions gives a value of $R_{F2/F1} = 2.5 \pm 0.1$ and is in good accordance with the published data.[11,12]

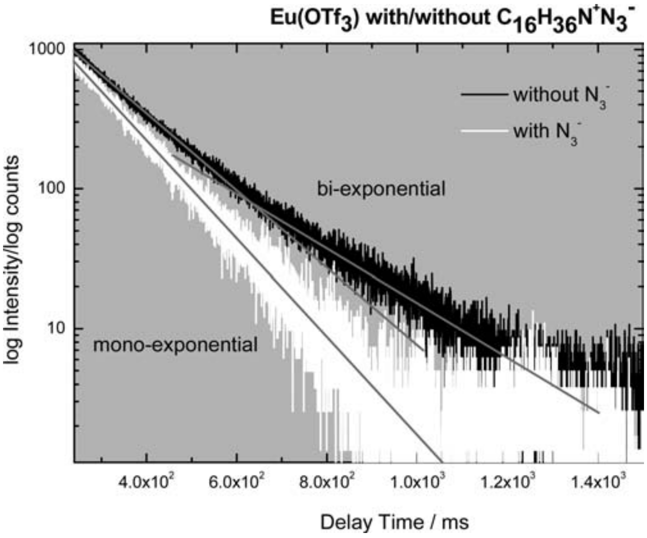

Figure 2. Luminescence of 1 × 10^{-2} M $Eu(OTf)_3$ dissolved in C_4mimTf_2N reveals a biexponential decay behavior. With the addition of 1 × 10^{-5} M $C_{16}H_{36}N^+N_3^-$ the decay behavior becomes monoexponential.

With increasing N_3^- concentration, the Eu luminescence is affected in two respects. In the range from 1 × 10^{-5} M to 1.1 × 10^{-3} M azide, the luminescence intensity decreases by nearly 1 order of magnitude (Figure 1). This decrease is not due to dilution effects as it was shown by the authors in another experimental series (unpublished data) without the quenching ion. Beside this decrease also the shape of the emission signals changes. Beginning with a N_3^-concentration of 1 × 10^{-4} M, the peak maximum of the $^5D_0 \rightarrow {}^7F_2$ transition starts to shift from 611 nm toward 609 nm (Figure 1). This shift is accompanied by a decrease of $R_{F2/F1}$ from 2.5 ± 0.1 to a value of 2 ± 0.1. Regarding the Eu luminescence lifetime, the introduction of N_3^- results in a change from a biexponential (without N_3^-) to a monoexponential (with N_3^-; Figure 2) decay of luminescence intensity for the whole series. Moreover, the Eu emission lifetime decreases with increasing azide concentration from τ_{obs} = 830 ± 20 μs at 1 × 10^{-5} M N_3^- to τ_{obs} = 240 ± 30 μs at 1.1 × 10^{-3} M N_3^-. The corresponding Stern−Volmer plot of the Eu-triflate/azide interaction (Figure 3) clearly deviates from linearity, and an upward curvature is observed instead.

3.2. $Eu(ClO_4)_3 + N_3^-$. Figure 4 shows the luminescence spectrum of 1 × 10^{-2} M $Eu(ClO_4)_3$ dissolved in C_4mimTf_2N at different N_3^- concentrations. In the absence of the quencher the ratio of the two emission bands has a value of $R_{F2/F1} = 3.8 \pm 0.1$. The corresponding emission lifetime exhibits a monoexponential decay behavior (τ_{obs} = 1.3 ± 0.1 ms) which is due to a fast exchange of coordinating ligands (H_2O, ClO_4^-, OTf^-, Tf_2N^-). That is, the determined luminescence lifetime represents an average lifetime of the different solution species.[12]

With increasing azide concentration up to 1.1 × 10^{-3} M, the emission intensity decreases. Again, this effect is not due to the dilution of Eu(III). No change, neither in the shape of the spectrum nor of $R_{F2/F1}$, is observed in this concentration range. Beside the decrease of emission intensity also the emission lifetime decreases with increasing quencher concentration (τ_{obs} = 1.3 ± 0.1 ms without N_3^-; 1.0 ± 0.1 ms

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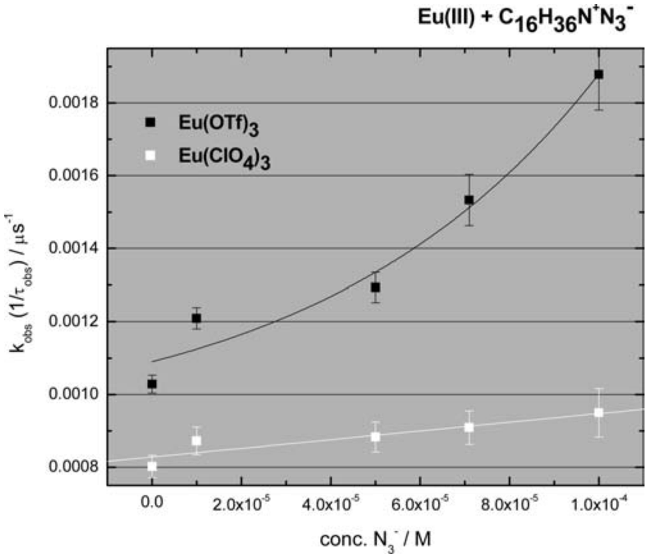

Figure 3. Stern−Volmer plot of the N_3^- interaction with 1 × 10^{-2} M Eu-triflate and 1 × 10^{-2} M Eu-perchlorate in C_4mimTf_2N. A plot of k_{obs} versus a changing concentration of azide yields a straight line for the perchlorate ($R = 0.92$), whereas it deviates from linearity in the case of the triflate.

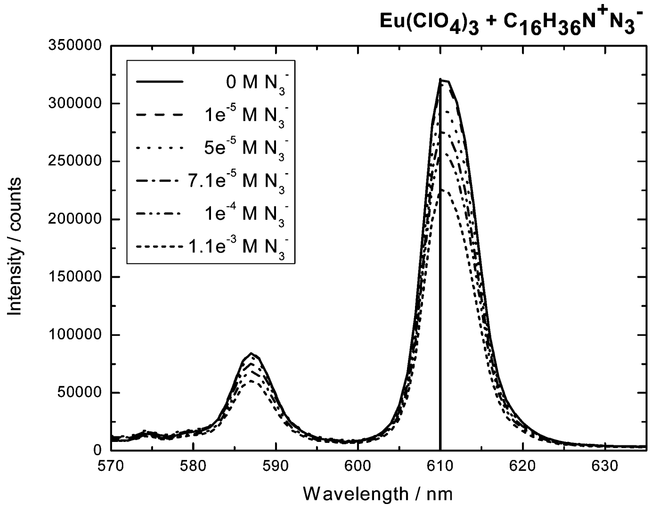

Figure 4. Luminescence spectra of 1 × 10^{-2} M $Eu(ClO_4)_3$ dissolved in C_4mimTf_2N at different $C_{16}H_{36}N^+N_3^-$ concentrations. Solely the emission is affected by N_3^- and decreases with increasing azide concentration.

at 1.1 × 10^{-3} M N_3^-). The corresponding Stern−Volmer plot for this process together with the data points of the triflate sample is shown in Figure 3. The linear fit gives a value of $k_{SV} = 1.5 \times 10^6$ M^{-1} s^{-1} (regression factor R = 0.92). With further addition of N_3^- (5 × 10^{-1} M) to the solution, the intensity of the emission signal again decreases but equally also a change of $R_{F2/F1}$ is observed as displayed in Figure 5 ($R_{F2/F1} = 2.6 \pm 0.1$). As shown in Figure 5, there is no further change neither of the intensity nor of the shape of this spectrum after waiting for a period of 5 days.

3.3. $Cm(ClO_4)_3 + N_3^-$. According to already published data,[11,12] the luminescence spectrum of 1.2 × 10^{-7} M $Cm(ClO_4)_3$ in C_4mimTf_2N shows a peak maximum at 600 nm with a slight shoulder at ∼595 nm (Figure 6). The fit of the corresponding biexponential emission lifetime results in a value of 1.0 ± 0.3 ms and can be attributed to a species without water in the first coordination sphere (peak maximum at 600 nm). The shorter lifetime of 300 ± 50 μs corresponds to a species with one additional water ligand in the curium inner coordination sphere (shoulder at 595 nm).

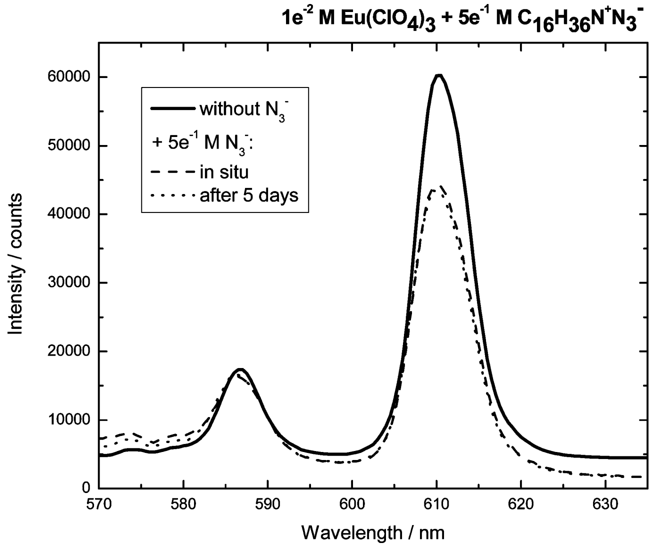

Figure 5. Luminescence spectra of 1 × 10^{-2} M $Eu(ClO_4)_3$ dissolved in C_4mimTf_2N without azide and at a concentration of 5 × 10^{-1} M $C_{16}H_{36}N^+N_3^-$. At this high azide concentration, a change of $R_{F2/F1}$ from $R_{F2/F1} = 3.8 \pm 0.1$ without to $R_{F2/F1} = 2.6 \pm 0.1$ with azide is observed which stays constant over a period of 5 days.

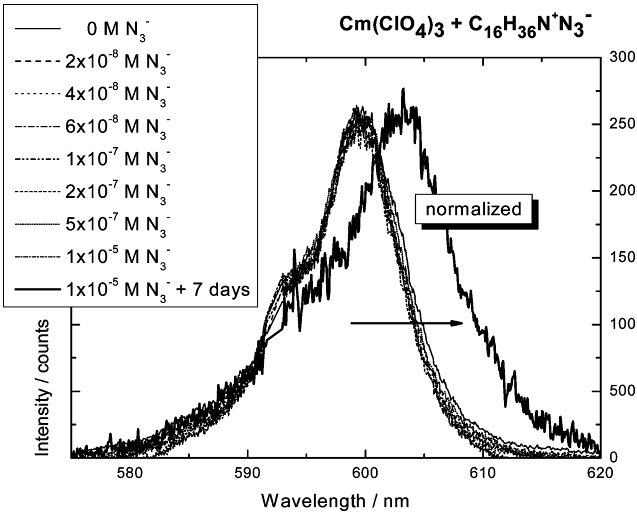

Figure 6. Luminescence spectra of 1.2 × 10^{-7} M $Cm(ClO_4)_3$ dissolved in C_4mimTf_2N at different $C_{16}H_{36}N^+N_3^-$ concentrations. The Cm-luminescence is affected by the Cm-interaction with N_3^- but not until 7 days when a shift of the emmission maximum to higher wavelength together with a decrease of intensity (normalized spectrum shown) is observed.

As it is shown in Figure 6, the increase of azide concentration in the Cm sample within a day has no effect neither on the intensity and shape of the luminescence nor on the emission lifetime which displays the same lifetime values independent of the amount of N_3^-. Waiting a period of 7 days, the emission spectrum in Figure 6 is shifted to higher wavelength (603.5 nm). Furthermore, the emission intensity of the broadened spectrum is decreased by a factor of 7 (normalized spectrum displayed for sake of clarity). At the same time, the curium emission lifetime is decreased as demonstrated in Figure 7. Moreover, the luminescence decay changes from a bi- to a multiexponential behavior.

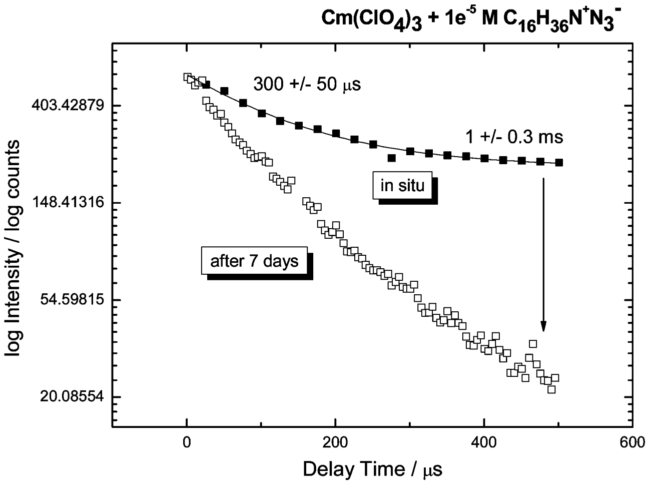

Figure 7. Luminescence decay of 1.2×10^{-7} M $Cm(ClO_4)_3$ dissolved in C_4mimTf_2N at a concentration of 1×10^{-5} M $C_{16}H_{36}N^+N_3^-$. The biexponential decay behavior of the Cm luminescence is affected by the Cm interaction with N_3^- not until 7 days when the luminescence lifetime decreases and becomes multiexponential.

3.4. $Am(ClO_4)_3 + N_3^-$. Three americium samples were analyzed by extended X-ray absorption (EXAFS) spectroscopy, in which 1×10^{-3} M americium perchlorate was dissolved in C_4mimTf_2N. For two of them, a hundredfold excess of azide was added, either 8 days before the XAFS measurements ("old" sample) or only 4 hours before the measurements ("fresh" sample). The corresponding EXAFS spectra of the three samples are presented in Figure 8, together with their Fourier transforms (not phase shift corrected). Fit results are given in Table 1.

The EXAFS spectrum of dissolved $Am(ClO_4)_3$ exhibits a main peak at 2.42 Å and a second peak at $R + \Delta \sim 3$ Å. The addition of azide to the Am perchlorate solution results in a change of the americium coordination sphere which is expressed in the FT by a disappearance of the peak at $R + \Delta \sim 3$ Å for the "fresh" sample. For the "old" sample beside the main peak at 2.40 Å, a second peak can be again observed on the FT at $R + \Delta \sim 2.9$ Å.

4. Discussion

4.1. $Eu(OTf)_3 + N_3^-$. According to the soft−hard classification, lanthanides are hard acceptors and therefore should show lower affinity to N-based ligands than to OH_2, ClO_4^-, or OTf^-. In fact, spectroscopic investigations of the $Eu(NO_3)_3$ dissolution in anhydrous *N*,*N*-dimethylformamide show the favored coordination of the lanthanide by the O-ligand.[38] Nevertheless, Bünzli et al. report on spectroscopic investigations of the inner-sphere complexation of $Eu(ClO_4)_3$ by acetonitrile[39] and by *N*,*N*-dimethylformamide.[38] In both complexes ClO_4^- is ejected from the inner coordination sphere of the cation by the N-based ligand. Borkowski et al. report on the Ln- and An-complexation by pseudohalides and the effect of complexation on the solvent extraction.[13] In the cited study, with increasing π-electron charge in the series $NCSe^-$, NCS^-, NCO^-, and N_3^- they observe an increasing inner-sphere complexation together with the destabilization of the bond between the central metal ion and the coordinating O-based ligands such as H_2O. Beside the cited extraction experiments[13] also spectroscopic investigations of the Ln(III) inner-sphere coordination by N_3^- are reported in literature.[31–33,40] The azide ion is as effective in quenching of the luminescent excited-state of several trivalent lanthanides (Nd, Sm, Eu, Gd, Tb, Dy) as H_2O. Its deactivating power is even stronger than O−H oscillators of coordinated water molecules. Borkowski et al.[40] who investigated the interaction of azide with Eu(III) in perchloric solution by luminescence lifetime measurements interpret the decrease of europium luminescence lifetime in terms of the lanthanide inner-sphere complexation by the quencher (static quenching). But, as it was described above, the depopulation of excited states is not mandatory to an inner-sphere complexation process. It can be also a result of an outer-sphere interaction between the fluorophore and the quencher (dynamic quenching). To distinguish between these two quenching contributions and finally between inner- and outer-sphere interaction the interpretation of luminescence lifetime data together with the accordant luminescence spectra is essential. Only the decrease of emission lifetime together with a spectral shift definitely indicates the inner-sphere complexation of the fluorophore by the quencher N_3^-.

Actual investigations of the influence of azide on the Eu luminescence of dissolved $Eu(OTf)_3$ up to a concentration of 7.1×10^{-5} M N_3^- give rise that the Eu luminescence is quenched by collisional encounters with N_3^- (dynamic quenching) without further complexation by the quenching anion because only the luminescence intensity is decreasing whereas signal shape and $R_{F2/F1}$ are not affected at all. However, it is surprising that the addition of N_3^- causes a change of the decay behavior from bi- to monoexponential (Figure 2) already at very low azide concentrations of about 1×10^{-5} M. In general, monoexponential decay behavior can be interpreted in terms of the presence of only one solution species with one according luminescence lifetime or it can be explained by the presence of different species which show a fast exchange of their coordinating ligands with regard to the lifetime of the excited state. In this case, the observed lifetime represents an average value of the lifetimes of each unique cation environment.[41] The biexponential decay behavior of Eu-triflate dissolved in C_4mimTf_2N was explained by the authors by the formation of two different solution species in this ionic liquid which show a slow exchange of coordinating ligands.[11,12] It is obvious that in the studied azide concentration range (1×10^{-5} M to 7.1×10^{-5} M N_3^-) the formation of a single species can be ruled out since the addition of N_3^- cannot result in the total replacement of the coordinating Eu-ligands such as H_2O ($\approx 1 \times 10^{-3}$ M), OTf^-, or Tf_2N^-. Obviously, small quantities of N_3^- disturb the arrangement of coordinating ligands and catalyze the fast conformational exchange of the different

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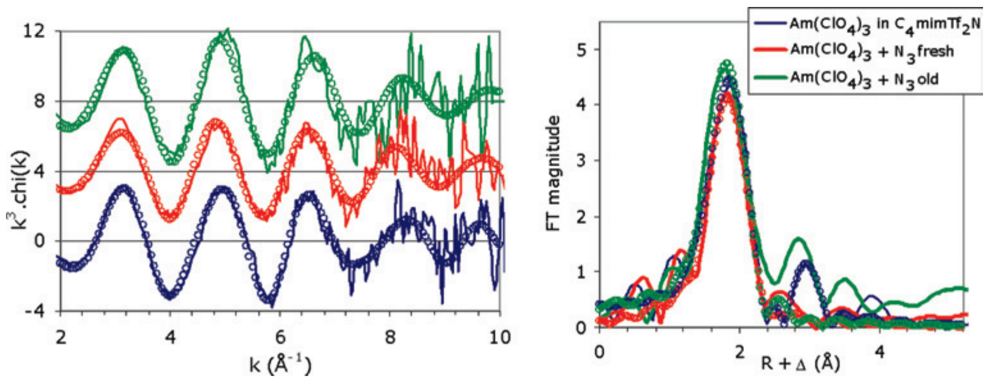

Figure 8. EXAFS spectra and their corresponding Fourier transform of 1 × 10^{-3} M americium perchlorate solutions in C_4mimTf_2N, in the presence and in the absence of 0.1 M azide. For sake of clarity, EXAFS spectra were shifted along the *y*-axis. Experimental data are lines, fits are represented by dots.

Table 1. EXAFS Structural Parameters for Americium Samples[a]

sample	shell	N	R (Å)	σ^2 (Å^2)	E_0 (eV)	R_{factor}
$Am(ClO_4)_3$ in C_4mimTf_2N[12]	Am−O	10.9	2.42	0.014	−4.6	0.02
	Am−Cl/S	3.6	3.60	0.005	−4.6	0.02
$Am(ClO_4)_3 + N_3^-$ in C_4mimTf_2N, fresh	Am−N/O	8.7	2.43	0.012	−4.2	0.03
$Am(ClO_4)_3 + N_3^-$ in C_4mimTf_2N, old	Am−N/O	11.7	2.40	0.014	−4.8	0.03[b]

[a] N is the coordination number (±20%), R the interatomic distance (±0.02 Å), σ^2 the Debye−Waller factor (±0.001 Å^2), E_0 the shift in energy, and R_{factor} the goodness of the fit as defined in ref. 36. [b] R range of the fit: 0.8−2.5 Å.

solvent species. Hereby, the observed monoexponential luminescence lifetime is determined by both the H_2O and the N_3^- quenching contributions.

Because the azide anion is electronically attracted by Eu^{3+}, its approach toward the metal ion can be generally assumed during the described ligand exchange. With this, also small amounts of Eu species that are inner-sphere coordinated to N_3^- are certainly present at low azide concentration, and an additional quenching contribution that can be due to complex formation seems to be conceivable in the Eu-triflate sample. The missing change of the emission signal that should arise from such inner-sphere interaction can be due to the low spectral resolution at these N_3^- concentrations. However, the Stern−Volmer plot in Figure 3 deviates from linearity and is represented by an upward curvature instead. This observation can be definitely assigned to the presence of two quenching contributions caused by inner- and outer-sphere interaction of fluorophore and quencher. Nevertheless, our data are not precise enough to determine the quantity and the composition of the formed complexes at low azide concentration.

The above postulated complexation by N_3^- becomes evident at higher quencher concentration (1 × 10^{-4} M to 1.1 × 10^{-3} M N_3^-), where the maximum of the $^5D_0 \rightarrow {}^7F_2$ transition is shifted from 611 to 609 nm, and a decrease of the $R_{F2/F1}$ value is observed (2.5 ± 0.1 to 2.0 ± 0.1). Both observations indicate a complexation process. It is known from the literature that in C_4mimTf_2N a Eu-triflate species with one water ligand in the first coordination sphere displays a peak maximum at 611 nm whereas it is at 609 nm for a Eu-triflate species without water in the first coordination sphere.[11,12] The observed shift is in good accordance with the cited peak positions, and we consider a complexation of Eu(III) by azide together with a replacement of the water ligand. Such a dehydration of the metal inner-sphere coordination by Ln−N interaction has been already postulated by Lis et al.[42] and Borkowski et al.[13] However, our data are not precise enough to quantify this exchange reaction and to specify the formed complexes which are supposed to be of a mixed nature.

4.2. $Eu(ClO_4)_3 + N_3^-$. Because the addition of azide to the perchlorate sample neither result in a change of the emission signal shape nor in a change of $R_{F2/F1}$ (Figure 4), indicating a complexation process, the spectroscopic data give evidence that the depopulation of the europium excited states in this sample is only due to collisional encounters between the quencher N_3^- and the fluorophore Eu(III) and is not a result of inner-sphere complex formation with the quencher as it was proposed at these low azide concentrations for the Eu-triflate sample. According to this, a plot of $1/\tau$ versus the azide concentration results in a straight line (k_{SV} = 1.5 × 10^6 M^{-1} s^{-1}; R = 0.92) in contrast to the Stern−Volmer plot of the Eu-triflate/azide interaction which deviates from linearity (Figure 3). Because the depopulation of excited states is due to a single quenching interaction in the perchlorate sample whereas in the triflate sample two mechanisms coexist, the quenching efficiency in the latter should exceed that one in the perchlorate sample. As a matter of fact, the decrease of luminescence intensity by adding the azide ion is less intense for the Eu-perchlorate thanfor the Eu-triflate. At an azide concentration of 1 × 10^{-5} M, the Eu-perchlorate emission is not affected at all (Figure 4) whereas it is decreased for the Eu-triflate by a factor of 1.3 (Figure 1). Moreover, the emission lifetime at this azide concentration is less quenched in the perchlorate sample (1.1 ± 0.1 ms) than in the triflate sample (0.80 ± 0.02 ms).

The difference in the nature of Eu(III)-N_3^- interaction obviously depends on the anion of the dissolved europium salt. It was already published by the authors that in ionic liquid solution of C_4mimTf_2N the anion ClO_4^- represents a stronger ligand than OTf^-.[12] In general, the strength of coordinated ligands determines if a replacement by other coordinating ligands such as N_3^- is more or less difficult. Moreover, the approach of the ligand can be influenced by

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sterical or electrostatic effects. Both, triflate and perchlorate represent sterical demanding anions and a different influence on the approach of N_3^- for sterical reasons can be therefore ruled out. In the case of triflate, the negative charge of the anion is located at the oxygen atoms of the coordinating SO_3 functional group.[43] Beside this, the fast conformational exchange of coordinating ligands in the Eu-triflate sample allows a closer or more frequent approach of fluorophore and quencher which also explains an increased collisional interaction and the spectroscopic observation of a stronger quenching effect. In contrast, the negative charge of the ClO_4^- anion is distributed over all O atoms that can alternately coordinate to the central ion. This makes the approach of a negatively charged ligand toward the Eu(III) central ion more difficult. The given considerations of ligand strength and electrostatic effects explain well why N_3^- at low concentrations shows inner- as well as outer-sphere interaction with Eu-triflate species whereas only outer-sphere interaction is observed for the perchlorate species. The increase of N_3^- concentration by a factor of approximately 50 toward Eu^{3+} finally enforces the inner-sphere complexation of the europium−perchlorate species by azide. This complexation is expressed by a dramatic change of $R_{F2/F1}$ from 3.8 to 2.6 which does not change over a period of 5 days. However, the quality of the spectroscopic data does not allow a further specification of the formed complexes.

4.3. $Cm(ClO_4)_3 + N_3^-$. As described in section 3.3, even a hundredfold excess of N_3^- does not affect the curium luminescence properties of $Cm(ClO_4)_3$ in contrast to $Eu(ClO_4)_3$. This means that a depopulation of excited states neither by outer-sphere interaction (dynamic quenching) nor by inner-sphere interaction or complexation (static quenching) takes place. Because Eu(III) and Cm(III) exhibit the same spectroscopic properties in aqueous solution,[29,30] the question arises why $Eu(ClO_4)_3$ dissolved in C_4mimTf_2N shows quenching interaction with N_3^- in contrast to $Cm(ClO_4)_3$. In C_4mimTf_2N both Ln(III) and An(III) exhibit the same structural conformation,[12] and a sterical reason for the observed spectroscopic deviation can be ruled out. It is known from the literature that the 5f-radial functions of the actinide series show a higher extension toward the 6s and 6p orbitals as compared to the 4f-radial functions of the lanthanide series.[44] The delocalization of the 5f orbitals in inner-sphere complexes is therefore increased for actinides as compared to lanthanides, and a more covalent contribution in the An complexes than in the corresponding Ln complexes is proposed by several authors.[45,46] In this study the observed monoexponential decay behavior for dissolved $Eu(ClO_4)_3$ is explained by the fast exchange of coordinating ligands and is in good agreement with the postulated low covalency of the metal−ligand bond in the Eu species which allows such a reaction. Moreover, the biexponential decay behavior of the corresponding Cm perchlorate species can be explained by a higher covalent contribution causing a slow ligand exchange instead.

The difference in covalency is also considered responsible in the actual study for the spectroscopic deviation observed for the quenching interaction of dissolved $Eu(ClO_4)_3$ and $Cm(ClO_4)_3$ with azide. Dynamic quenching requires the overlap of the fluorophore's and the quencher's dipoles. The stronger bonding in actinide complexes can result in a stronger splitting of the curium f-energy levels preventing the required overlap. A comparable interpretation of spectroscopic data was given by the authors who investigated the Eu(III) and Cm(III) interaction with the quencher Cu(II) in C_4mimTf_2N.[11] Also in the cited study it was solely the Eu luminescence being influenced by Cu(II) and a missing overlap of Cm(III) and Cu(II) dipoles caused by a strong ligand field splitting was taken into consideration by the authors.

Beside the different spectroscopic observations for the N_3^- interaction with Eu(III) and Cm(III), the proposed stronger metal to ligand bond in the actinide complexes can explain the hindered complexation reaction with N_3^-. Not until after waiting a period of 7 days is the emission signal shifted to 603.5 nm (Figure 6) which can be due to a change of the curium ligand field. Because the spectral shift is accompanied by a decrease of emission intensity by a factor of 7 (normalized spectrum shown) together with a decrease of emission lifetime (Figure 7), the change of the curium ligand field can be directly attributed to a complexation by the quencher N_3^- which causes a depopulation of excited states by static quenching. The shifted luminescence spectrum exhibits a broadened shape indicating the formation of mixed $Cm- ClO_4^- - H_2O - N_3^-$ complexes with variable composition.[24,25] The coexistence of mixed complexes is confirmed by the corresponding multiexponential decay behavior of the Cm luminescence. The recorded different luminescence lifetimes can not only be attributed to different species but also be interpreted in terms of a slow conformational exchange of coordinating ligands in the Cm inner-sphere probably caused by the relatively high covalent contribution in the metal−ligand bond of these complexes.

4.4. $Am(ClO_4)_3 + N_3^-$. Because of its ionic nature, C_4mimTf_2N represents a solvent which has been shown to be quite organized for a liquid. The dissolution of $Am(ClO_4)_3$ entails the embedding of the actinide in such an organized structure. As a result the FT not only gives evidence for a first but also a second coordination shell allowing a relative precise characterization of the solvent species. According to our previous investigations in C_4mimTf_2N,[2] the main peak of dissolved $Am(ClO_4)_3$ at 2.42 Å can be attributed to a first shell of ∼11 oxygen atoms coming from coordinated ClO_4^-, Tf_2N^- ($(F_3CSO_2)_2N^-$), and H_2O ligands. The second peak at $R + \Delta \sim 3$ Å corresponds to a second coordination shell composed of ∼3−4 chlorine or sulfur atoms of the aforementioned ligands. Because of the comparable masses of Cl and S, a discrimination is not possible. The addition of azide to the system obviously destroys the organized arrangement

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of the coordinating ligands which is expressed in the disappearance of the peak at R + Δ ∼ 3 Å and a reduction of the first shell oxygen atoms from ∼11 to ∼9 ($R \sim 2.43$ Å) in the "fresh" sample. The postulation of a destroyed ligand arrangement is in good accordance with the interpretation of the Eu(III) TRLFS data in the actual study. However, such a disorganization of the Am and Eu coordination sphere is not detected in the case of curium, which luminescence properties (emission intensity, peak position, emission lifetime) remain the same within 1 day after the azide addition. We may attribute the observed phenomenon for europium and americium to concentration effects and their influence on the solvent in which the species are immerged. Indeed, the concentration ranges are very different between Am = 10^{-3} M, Eu = 10^{-2} M, and Cm = 1.2×10^{-7} M. The addition of N_3^- to the Am perchlorate solution does not result in an instantaneous complexation of the actinide by azide as it is the case for $Eu(OTf)_3$ and $Eu(ClO_4)_3$. A complexation should result in a shift of the main peak but it keeps unchanged (2.43 Å) instead. This result is in good accordance with the presented TRLFS investigations of the azide addition to the Cm-perchlorate solution. Whatever the N_3^- concentration is, no instantaneous Cm complexation can be observed.

Waiting for a period of 8 days, the first coordination sphere of Am in the "old" sample does not significantly change (main peak at 2.40 Å; ∼12 coordinating atoms). But new features are observed on the FT at R + Δ > 2.9 Å which cannot be attributed to a sole Cl/S shell. FEFF calculations performed from the cluster $[Am(N_3)_8]$[47] reveal the presence of three strong multiple scatterings, occurring from the linear structure of the azide molecules, that may give rise to this feature on the FT. Nevertheless, it was never possible to get a reliable fit of the "old" sample data assuming a total complexation of azides to americium. We can thus postulate that after 8 days of reaction, the complexation of Am-perchlorate to azides is not total, and mixed complexes may be formed in solution in contrast to the "fresh" sample. Such a mixture could explain the slight increase of the first-shell coordination number from ∼11 to ∼12. The formation of mixed complexes has been already postulated in this study for the complexation of Eu-triflate and Eu-perchlorate by azide and is evidenced for the Cm-perchlorate sample. The result of mixed complexes can be basically interpreted by two hypotheses: (1) the complexation is to be total (exclusive coordination by N_3^-) but the slow kinetics entails that the final species are not obtained after more than 1 week or (2) the final equilibrium has been reached and the azide complexation is never total. Because the addition of 5×10^{-1} M N_3^- to $Eu(ClO_4)_3$ instantaneously results in the complexation of Eu(III) and because the luminescence spectrum does not change over a period of 5 days (Figure 5), the authors assume the rightness of the second hypothesis.

The EXAFS results of slow reaction kinetics for the Am complexation by azide confirm well the interpretation of the Cm TRLFS data. So far slow kinetics measured in ionic liquid solution were explained by the effect of the solvent viscosity and its relative organization due to its ionic nature.[48,49] The interesting feature in our experiments is that we do not observe such slow kinetics in the case of europium. With this, the low complexation kinetics can be definitely assigned to different chemical properties of lanthanides and actinides in ionic liquid solution.

Conclusion

The intention of the actual studies was to exhibit differences in chemical behavior regarding the complexation of lanthanides and actinides by N-based ligands in ionic liquid solution. TRLFS and EXAFS measurements were successfully applied for recording the azide complexation of $Eu(OTf)_3$, $Eu(ClO_4)_3$, $Cm(ClO_4)_3$, and $Am(ClO_4)_3$ dissolved in C_4mimTf_2N. In both Eu-samples, the lanthanide is instantaneously complexed by N_3^- and forms mixed complexes. In the case of the Eu-triflate salt, the complexation process starts at lower azide concentration as compared to the perchlorate salt. This effect can be due to the fact that ClO_4^- represents the stronger ligand as compared to OTf^-. Moreover, the authors propose a stronger electrostatic repulsion of N_3^- by the perchlorate ligand which is less for the triflate ligand. In contrast to an instantaneous reaction for the lanthanide, a decreased complexation kinetics is evidenced by TRLFS and EXAFS measurements for the interaction of N_3^- with the two actinides Am(III) and Cm(III) which finally also results in the formation of mixed complexes. The TRLFS and EXAFS results clearly show that the slow complexation kinetics is not a result of solution or concentration effects. One possible explanation could be an increased delocalization of the 5f orbitals in An inner-sphere complexes resulting in a stronger metal to ligand bond as compared to the corresponding Ln complexes. Obviously, this difference becomes more evident in ionic liquid solution than in aqueous solution.

The presented study provides an important basis for further fundamental investigations of Ln- and An-chemistry in ionic liquid solution with regard to their separation by the use of N-based extractants.

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