TRLFS and EXAFS investigations of lanthanide and actinide complexation by triflate and perchlorate in an ionic liquid

By S. Stumpf[1],*, I. Billard[2], C. Gaillard[2], P. J. Panak[3] and K. Dardenne[3]

[1] European Commission, JRC, Institute for Transuranium Elements, 76125 Karlsruhe, Germany
[2] IPHC/DRS, Chimie Nucléaire, BP. 28, 67037 Strasbourg, France
[3] Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgung, P.O. Box 3640, 76021 Karlsruhe, Germany

Summary. The solvation of the Eu-perchlorate (ClO_4^-) and triflate ($CF_3SO_3^-$, OTf^-) salts as well as of $Cm(ClO_4)_3$ and $Am(ClO_4)_3$ in the ionic liquid C_4mimTf_2N (1-butyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide) has been comparatively investigated by application of laser fluorescence spectroscopy and X-ray absorption spectroscopy. Moreover, the ClO_4^-/OTf^- ligand exchange reaction for the two actinide cations has been analyzed by the same spectroscopic techniques. A structural model for the different complexes was determined by the interpretation of the spectroscopic data. The lanthanide and the two actinide cations show the same coordination in C_4mimTf_2N. Moreover, a sequence for the strength of complexing ligands could be deduced from the spectroscopic data for the lanthanide and the two actinides: $ClO_4^- > OTf^- \geq Tf_2N^- > H_2O$.

1. Introduction

The separation of trivalent actinides (An(III)) from lanthanides (Ln(III)) is a key step in the partitioning and transmutation (P&T) strategy [1] with the aim of separating long-lived actinides from spent nuclear fuels and transmuting them by nuclear fission into shorter lived and stable isotopes. This procedure would have a positive impact on the long-term radiotoxicity of high-level nuclear wastes to be stored in a final geological repository.

There is much current research effort focused on the use of low melting organic salts (Ionic Liquids, IL) in separation schemes. Their outstanding properties of negligible flammability and volatility make them "green" solvents in regard to reducing environmental levels of volatile organic compounds (VOCs) that are traditionally used for separation purpose [2]. Moreover, depending on the choice of the cation and anion, ILs reveal different properties in terms of their density, viscosity, surface tension, melting point, and their hydrophobic and hydrophilic characteristics [3–5]. That is, the green aspect as well as the tunable physical properties

make ILs suitable as solvent and/or extracting phase for the Ln/An extraction.

The general problem of Ln/An separation is due to the strong similarities in chemical behaviour for the trivalent cations of the two f-element series because they show a similar range of ionic radii. Therefore, a separation using common oxygen-donor extractants which favourably complex hard acceptors such as An(III) and Ln(III) (HSAB principle) is not feasible in organic solvents. In traditional separation processes only complexation by soft donors like sulphur or nitrogen atoms in some respects yields selectivity [6].

The question arises if changing the solvent phase and using ionic liquids for separation purpose the same affinity of hard donors towards actinide and lanthanide complexation is observed. Therefore, in this study much interest is devoted to comparatively analyzing the complexation of the actinides Cm(III) and Am(III) and the lanthanide Eu(III) by the hard donors $CF_3SO_3^-$ (triflate, OTf^-) and ClO_4^- in the ionic liquid C_4mimTf_2N (1-butyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide) (Fig. 1). The spectroscopic investigations that are performed by time-resolved laser fluorescence spectroscopy (TRLFS) and X-ray absorption fine structure spectroscopy (XAFS) intend to point out differences and similarities in lanthanide and actinide complexation in ionic liquids by the cited ligands.
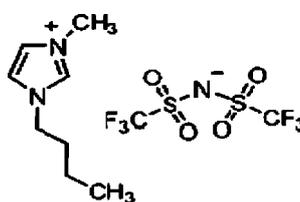

Fig. 1. Structural formular of C_4mimTf_2N.

2. Experimental

All experiments dealing with Eu(III) were performed at the laboratory of the IPHC 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 investiga-

*Author for correspondence (E-mail: silvia.stumpf@ec.europa.eu).

tions 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.

2.1 Chemicals

Eu(III)-trifluoromethanesulfonate (Eu(OTf)$_3$), Eu$_2$O$_3$, La$_2$O$_3$, concentrated HOTf and 70% HClO$_4$ were purchased from Sigma Aldrich and used as received. An aqueous solution of 0.2 M Eu-perchlorate was synthesized by dissolving Eu$_2$O$_3$ in HClO$_4$. A solution of 1 M La-triflate was prepared by dissolution of the oxide in HOTf. The ionic liquid 1-butyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide (C$_4$mimTf$_2$N) was from Solvionic SA (Vermiolle/France). Cm was extracted from a Cf-252 source (SR-CF 1007; United States Atomic Energy Commission (USAEC)). The composition of the perchlorate Cm(III) aqueous stock solution (6×10^{-6} M Cm(ClO$_4$)$_3$) was: 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.

Am$_2$O$_3$ was dissolved in concentrated HClO$_4$ and diluted in 0.1 M HClO$_4$. The final stock solution had a concentration of 0.01 mol/L Am(ClO$_4$)$_3$. The composition of the solution was 99.69% [243]Am and 0.309% [243/244]Cm. According to the preparation method ClO$_4$/Am $\gg$ 3.

2.2 Sample preparation

2.2.1 Eu(OTf)$_3$

Eu(OTf)$_3$ salt was dissolved in C$_4$mimTf$_2$N (419.36 g/mol; 1.43 kg/L) by treatment in an ultra sonic bath not longer than 10 minutes with respect to the prevention of ionic liquid degradation [7]. The Eu(III) concentration in this solution was 1×10^{-2} M. In order to dry the sample (initial water amount: 300 ppm H$_2$O) it was put to the vacuum line for 2 h at 70 °C and 2 mbar. The water content of the sample was then determined by Karl Fischer titration (Mettler Toledo DL 32; detection limit $< 5 \times 10^{-3}$ M) and Infrared Spectroscopy (Bruker Equinox 55; detection limit 50 ppm). The resulting value was < 50 ppm water which corresponds to less than 1 H$_2$O molecule per Eu(III).

2.2.2 Eu(ClO$_4$)$_3$

A sample of Eu-perchlorate in C$_4$mimTf$_2$N was prepared by dilution of the corresponding Eu(ClO$_4$)$_3$ stock solution (0.2 M) in the ionic liquid by a factor of 10 yielding a final Eu-perchlorate concentration of 2×10^{-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 determined as described above resulting in a value of < 50 ppm H$_2$O which again corresponds to less than 1 water molecule per Eu(III).

2.2.3 La(OTf)$_3$

Aqueous La-triflate stock solution (1 M La(OTf)$_3$) was added to C$_4$mimTf$_2$N to give the ionic liquid stock solution with a final concentration of 0.1 mol/L La-triflate. In order

to dry the solution, it was evaporated in the same manner as described for the Eu(ClO$_4$)$_3$ ionic liquid stock solution.

2.2.4 Cm(ClO$_4$)$_3$/OTf$^-$

For the preparation of the ionic liquid curium sample a droplet of the Cm(III) stock solution was put directly into a quartz cuvette and evaporated by heating at 100 °C for 30 minutes. After evaporation dry C$_4$mimTf$_2$N was added. The final Cm(III) concentration of this sample was 1.2×10^{-7} M. After the addition of C$_4$mimTf$_2$N the sample was put into an oven for 1 h at 70 °C and 2 mbar to get it as dry as possible.

In order to perform the ClO$_4$$^-$ $-$OTf$^-$ ligand exchange reaction the ionic liquid stock solution of La-triflate was added to the Cm-sample. Hereby, the concentration of the La-triflate was raised stepwise from 2×10^{-5} to 1.2×10^{-3} mol/L. Before measuring the luminescence emission and luminescence emission lifetime the sample was put in the oven for 1 h at 70 °C and 2 mbar to avoid the influence of minimal amounts of water absorbed during opening the cuvette.

2.2.5 Am(ClO$_4$)$_3$/OTf$^-$

35 μL of the Am-perchlorate stock solution (0.01 M) was evaporated in the oven at 70 °C. After evaporation Am(ClO$_4$)$_3$ was dissolved in 350 μL dry C$_4$mimTf$_2$N. The 1×10^{-3} molar solution was transferred into the final vessel for the EXAFS measurements and was then again evaporated for 4 hours in the oven. For experimental reason the temperature was 60 °C and the pressure was 5 mbar.

In order to perform the ClO$_4$$^-$ $-$OTf$^-$ ligand exchange reaction another Am-sample was prepared. 35 μL of the aqueous La-triflate stock solution was evaporated as described above. After evaporation 35 μL of the Am-perchlorate stock solution was added to the dry La(OTf)$_3$ salt. The mixture was again evaporated to dryness and dissolved in 350 μL dry C$_4$mimTf$_2$N. The sample (1×10^{-3} M Am(ClO$_4$)$_3$, 0.1 M La(OTf)$_3$) was transferred into the EXAFS vessel and evaporated at 60 °C and 5 mbar for 4 h.

2.3 Methods

In our previous studies, Eu(III) and Cm(III) luminescence spectroscopy (TRLFS) has been shown to be a suitable method for the characterization of different Eu and Cm species in C$_4$mimTf$_2$N [8]. For Eu(III) the strongest observed emission arises from the transition between the $^5D_0$ level and levels of the ground state manifold ^7F_J ($J = 0, 1, ..., 6$). The shapes and the luminescence intensities of the emission spectra are sensitive to their environment and thus informative about the coordination structure [9]. The relative intensities $R_{F2/F1}$ of the two $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions serve as a good indicator for examining a change of the symmetry and strength of the Eu-ligand field [10]. Supposing an unchanged complex symmetry, the increase of $R_{F2/F1}$ is associated with an increase of ligand field strength [11]. 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, *e.g.*, replacing a weaker ligand by a stronger one, induces a red shift (nephelauxetic effect [12]) of the Cm-luminescence spectrum [13, 14]. This

shift is due to an increasing covalence and decreasing value of repulsion parameter for the metal complex. The interpretation of the europium and curium luminescence emission lifetime (τ_{obs}) gives further structural information about different solvent species. Early work on Eu(III) and Cm(III) luminescence established that O−H oscillators of coordinated water molecules provide an efficient non radiative pathway for the de-excitation of the emissive state [15–18]. In aqueous systems the hydration number of different europium and curium complexes can be related to the decay constant k_{obs} ($k_{obs} = 1/\tau_{obs}$ [1/ms]) by the following empirical correlations [15, 16]:

$$n_{H_2O} = 0.65 k_{obs}(\text{Cm}) - 0.88 \,, \qquad (1)$$

$$n_{H_2O} = 1.07 k_{obs}(\text{Eu}) - 0.62 \,. \qquad (2)$$

As it was already published, these correlations cannot be directly transferred to an ionic liquid system but nevertheless, they represent a first approximation for the interpretation of lifetime data in such a solvent [8]. If europium or curium exist in multiple coordination environments, k_{obs} depends on the rate of exchange of the trivalent cation between its different coordination environments [19]. If the rate of exchange is fast compared to the luminescence decay rate, the observed luminescence lifetime shows a mono-exponential decay which represents an average of the lifetimes of each unique cation environment, whereas individual complexes in slow exchange result in multi-exponential decay of the luminescence. In the presented paper lifetime data will be expressed as τ_{obs}, the lifetime value, or as $k_{obs} = 1/\tau_{obs}$.

The Eu-emission spectra were recorded with a spectrofluorimeter (Photon Technology International). The measurements of the luminescence emission were not time resolved. Samples were excited at 394 nm and the luminescence was recorded in a range from 570 nm 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 the afore mentioned $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions. 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 emission 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 of the $^5D_0 \rightarrow {}^7F_2$ transition was analyzed at 612 nm.

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 luminescence emission was measured in the spectral range 580 nm 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, IRY 700G). The TRLFS instrumentation is described elsewhere in detail [20].

Americium L_3-edge spectra were recorded at the INE beamline at ANKA Synchrotron Light Source (Germany) operating at 2.5 GeV with a typical beam current of 150 mA. A double-crystal monochromator (DCM) equipped with a pair of Ge(422) crystals was used. Measurements were made in fluorescence mode, using a 5 elements LE-Ge detector with a sample orientation of 45° to the incident beam. Spectra were energy calibrated to the first inflection point in the XANES of a Nb metal foil (K edge at 18 986 eV). The data were analyzed by using IFEFFIT [21] and fits were performed in the R-space using FEFFIT [22]. The k-space range was set from 2.6 to 10.1 Å^{-1}. Theorical backscattering phase and amplitude functions used for fitting were calculated with the FEFF 8.2 code [23]. 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)$_3$ and Eu(ClO$_4$)$_3$ in C$_4$mimTf$_2$N

TRLFS investigations of the dissolution of Eu(OTf)$_3$ in C$_4$mimTf$_2$N have been already published by our group [8]. The corresponding europium luminescence emission spectrum together with its deconvolution is shown in Fig. 2.

The deconvolution results in two emission spectra corresponding to two different Eu-solution species. Hereby, the major component (species A; $\sim 70\%$) displays a luminescence lifetime of 2.5 ± 0.2 ms and a value of $R_{F2/F1} = 2.2 \pm 0.1$ whereas the remaining component (species B; $\sim 30\%$) has a lifetime of 1.0 ± 0.3 ms and a value of $R_{F2/F1} = 1.6$. It has already been shown [8] that the longer luminescence lifetime corresponds to a Eu(III)-species without water in the first coordination sphere whereas the shorter lifetime can be attributed to a Eu(III)-species with one additional water in the first coordination sphere.

The luminescence emission spectrum of Eu-perchlorate dissolved in C$_4$mimTf$_2$N together with the Eu-triflate spectrum is shown in Fig. 3.

With changing the Eu-anion also the shape of the $^5D_0 \rightarrow {}^7F_2$ emission changes. Its maximum is slightly shifted towards higher wavelength (611 nm) as compared to the emission of the Eu-triflate sample (610 nm). Moreover, Fig. 3 clearly demonstrates that the ratio of the two emission lines exceeds that one of the triflate sample. The calculation of $R_{F2/F1}$ for the perchlorate sample results in a value of 3.3 which is much greater than the determined values for the two Eu-triflate solution species (see above).
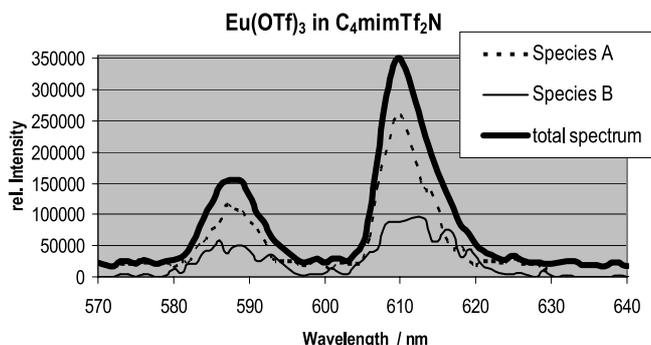

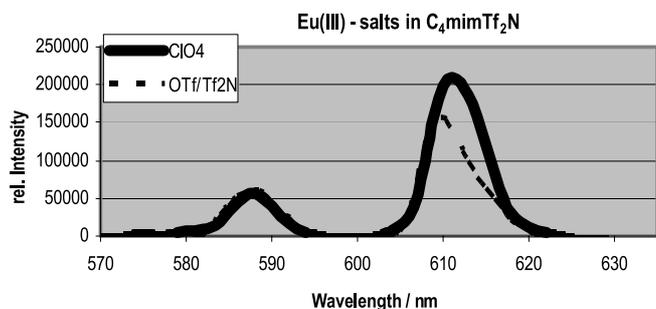**Fig. 2.** Total and deconvolved luminescence emission spectrum of Eu(OTf)$_3$ dissolved in C$_4$mimTf$_2$N.

Fig. 3. Luminescence emission spectra of Eu(OTf)$_3$ and Eu(ClO$_4$)$_3$ dissolved in C$_4$mimTf$_2$N normalized towards $^7F_1$ intensity.
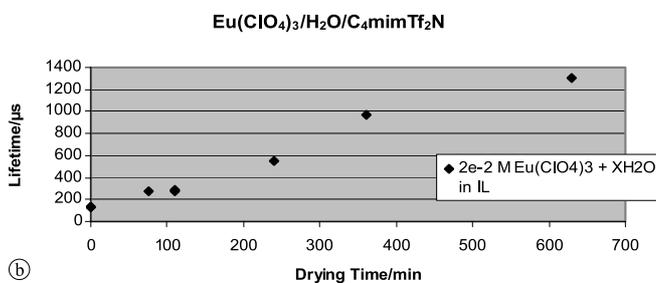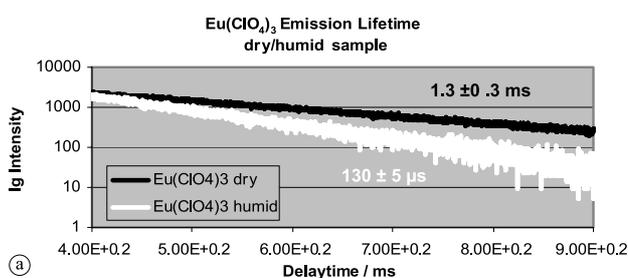
Fig. 4. (**a**) Mono-exponential luminescence decay behaviour of Eu(ClO$_4$)$_3$ dissolved in C$_4$mimTf$_2$N; fit depends on the water amount. (**b**) Linear correlation between luminescence emission lifetime and drying time *e.g.* water amount.

The emission lifetime analysis of a Eu-perchlorate dissolved in C$_4$mimTf$_2$N without further evaporation shows a mono-exponential decay behaviour of the Eu(III)-luminescence (Fig. 4).

The fit of the data gives a value of $130 \pm 2\,\mu s$ ($R_{F2/F1} = 0.9 \pm 0.1$; data not shown). This lifetime is slightly increased as compared to a value of $112 \pm 4\,\mu s$ for the aquo ion Eu(H$_2$O)$_9$ [16] ($R_{F2/F1} = 0.3 \pm 0.1$). Moreover, $R_{F2/F1}$ of this sample exceeds the corresponding value of the aquo ion. With the vacuum degassing of the sample the luminescence emission lifetime increases while the decay behaviour stays mono-exponential (Fig. 4). The fit results in a value of 1.3 ± 0.3 ms and can be attributed to a solution species with one water ligand in the first coordination sphere.

3.2 Cm(ClO$_4$)$_3$ in C$_4$mimTf$_2$N and Cm(ClO$_4$)$_3$ with La(OTf)$_3$ in C$_4$mimTf$_2$N

The results of the solvation of Cm(ClO$_4$)$_3$ in C$_4$mimTf$_2$N have been already published by the authors [8]. The luminescence emission spectrum of the Cm-perchlorate sample has a peak maximum at about 600 nm with a slight shoulder at ~ 596 nm (Fig. 5a). The luminescence emission decay
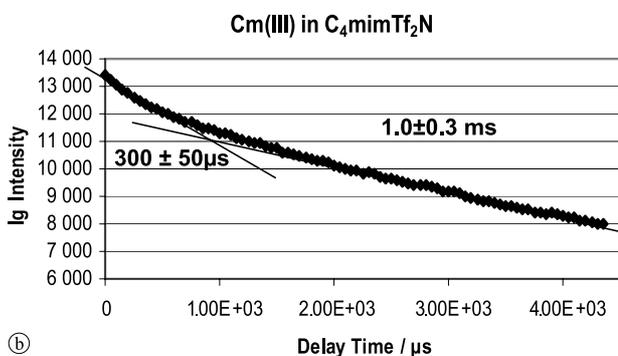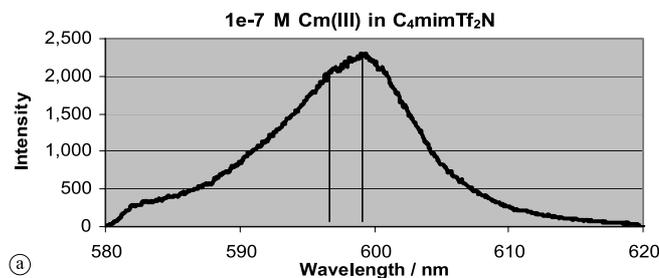

Fig. 5. (**a**) Luminescence emission spectrum and (**b**) corresponding bi-exponential luminescence emission decay of Cm(ClO$_4$)$_3$ dissolved in C$_4$mimTf$_2$N.

of this sample with time is shown in Fig. 5b and exhibits bi-exponential decay behaviour. The fit results in a longer luminescence lifetime of 1.0 ± 0.3 ms corresponding to the major species (species A) without water in the first coordination sphere (peak maximum at 600 nm). The shorter lifetime of $300 \pm 50\,\mu s$ can be attributed to a minor species (species B) with one additional water ligand in the curium inner coordination sphere (shoulder at 596 nm).

Fig. 5 shows the Cm-perchlorate emission spectra after addition of different concentrations of La-triflate. Increasing the triflate concentration up to 1.2×10^{-3} mol/L, corresponding to a concentration that is four orders of mag-
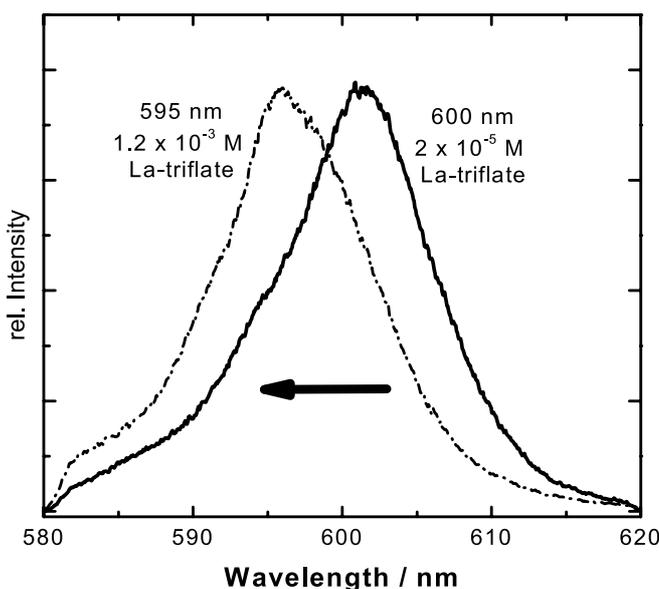

Fig. 6. Luminescence emission spectra of Cm(ClO$_4$)$_3$ dissolved in C$_4$mimTf$_2$N depending on a change of La-triflate concentration.

nitude higher than the Cm-concentration, the global peak maximum of the Cm-luminescence emission at 600 nm is shifted towards lower wavelength (595 nm). The shape of the emission spectrum in Fig. 6 is broadened and shows a shoulder at around 597 nm at this high triflate concentration indicating the presence of several Cm-solution species. The observed blue shift of the Cm-luminescence emission in Fig. 6 can be attributed to a change in the Cm-ligand field. The corresponding emission lifetimes show bi-exponential decay behaviour and the fit for all samples yields the values cited above (1 ms; 300 µs) within the error range.

3.3 Am(ClO₄)₃ in C₄mimTf₂N and Am(ClO₄)₃ with La(OTf)₃ in C₄mimTf₂N

Two Am−C₄mimTf₂N solutions were analyzed by EXAFS: in the first one, americium perchlorate was dissolved, and in the second one, a strong excess of triflate was added besides americium perchlorate. The EXAFS spectra and their corresponding Fourier transforms are displayed in Fig. 7, fit results are given in Table 1. Upon dissolution of americium perchlorate in C₄mimTf₂N, americium first coordination sphere is found to be composed of a shell of ~ 11 oxygen atoms at 2.42 Å. The weaker peak, observed on the FT at $R + \Delta \sim 3$ Å, could be modelled assuming a shell composed of chlorine or sulfur atoms, with $\sim$ 3–4 Cl/S at 3.60 Å. Addition of triflate ions to this solution entails a change in the americium coordination sphere, as can be observed on the FT with a slight shift of the main peak towards longer distances and the disappearance of the peak at $R + \Delta \sim 3$ Å. The weak features observed after ~ 2.5 Å on the FT are due

to the increased level of noise as compared to the previous sample. The fit to the data results in a Am coordination sphere composed of ~ 10 oxygen atoms at 2.48 Å.

4. Discussion

4.1 Eu(OTf)₃ in C₄mimTf₂N

Lanthanide cations behave as hard Lewis acids and therefore most strongly bind to hard bases such as oxygen (HSAB principle). In ionic liquid solution of C₄mimTf₂N the competing oxygen-ligands are represented by water, the ionic liquid anion Tf₂N⁻ ((F₃CSO₂)₂N) and the anion of the dissolved europium salt. As it was calculated by molecular dynamics simulations in "humid" C₄mimTf₂N Eu(III) forms fully hydrated Eu(H₂O)₉³⁺ complexes as in pure water [24, 25]. The solid state structures show a poor coordination by CF₃SO₃⁻ anions whereas Tf₂N⁻ is totally displaced in the first coordination sphere by H₂O. In the "less humid" ionic liquid one Eu(III) cation remains hydrated, another one is not hydrated at all [26, 27]. Finally, molecular dynamic simulations of undissociated Eu(OTf)₃ supposed in the "dry" C₄mimTf₂N the coordination of the metal ion by OTf⁻ and Tf₂N⁻ in the first coordination sphere giving a total coordination number of 9 to 10 [28]. Both hard Lewis bases, the OTf⁻ and the Tf₂N⁻ ligand, coordinate *via* their oxygen atoms of the sulfonic functional group [29]. Hereby, OTf⁻ is a stronger ligand than the ionic liquid anion Tf₂N⁻ [28]. The results described above are confirmed by TRLFS investigations performed by our group [8, 30]. A "humid" sample of Eu(OTf)₃ in C₄mimTf₂N (80 H₂O molecules per Eu(III)) showed mono-exponential decay behaviour (Fig. 8) which could be attributed to Eu(III) exclusively surrounded by H₂O ligands in the first coordination sphere. The decay behaviour of this sample became bi-exponential (Fig. 8) by vacuum degassing indicating the
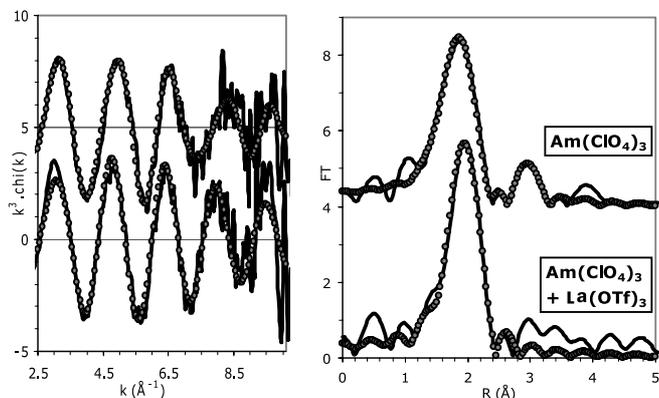

Fig. 7. EXAFS spectra and their corresponding Fourier transform (distance R not phase-shift corrected) of americium samples in C₄mimTf₂N. Lines = experimental data, dots = fits. For sake of clarity, spectra were shifted along the vertical axis.
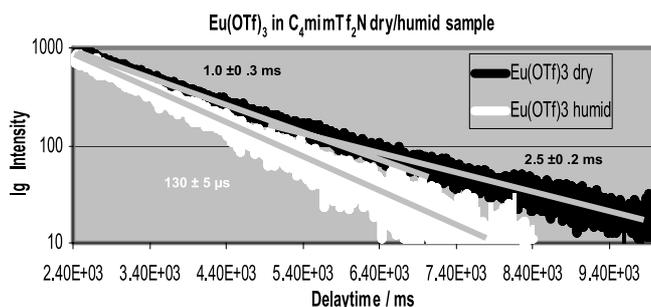
Fig. 8. Luminescence emission decay behaviour of Eu(OTf)₃ dissolved in C₄mimTf₂N depending on the water content of the sample.

Table 1. EXAFS structural parameters for americium samples. R_{factor} is the goodness of the fit, as defined in Ref. [22].

Sample	Shell	N	R (Å)	σ^2 (Å²)	ΔE_0 (eV)	R_{factor}
Am(ClO₄)₃ in C₄mimTf₂N	Am−O	10.9	2.42	0.014	−4.6	0.02
	Am−Cl/S	3.6	3.60	0.005		
Am(ClO₄)₃ + LaTf₃ in C₄mimTf₂N	Am−O	9.8	2.48	0.008	−2.2	0.04

formation of two specifiable Eu(III)-species with and without water in the first Eu coordination sphere.

The interpretation of the spectroscopic data of the actual study allows a further characterisation of the formed Eu-solvent species in C_4mimTf_2N. According to the calculated deconvolution in Fig. 2, the value of $R_{F2/F1} = 2.2$ can be attributed to the main component without water in the inner-sphere coordination whereas $R_{F2/F1} = 1.6$ corresponds to a Eu-species with one additional water in the first coordination sphere. The increase of $R_{F2/F1}$ is considered to be associated with a change from a weaker to a stronger ligand field provided that the symmetry of the complex stays invariable. Hence, the authors assume that in the analyzed system OTf^- and Tf_2N^- are stronger Lewis bases compared to H_2O and the following sequence of ligand strength is deduced for the Eu-complexation in C_4mimTf_2N:

$$OTf^- \geq Tf_2N^- > H_2O.$$

The question arises why H_2O stays coordinated to the lanthanide. Obviously, "ligand strength" cannot be the only driving force of complexation. In general, the stability of a complex is due to the positive change of total energy during complexation [31, 32]. Such a positive contribution to the total energy is given for example by the formation of hydrogen bonds. It is known from literature that in aqueous complexes of lanthanide triflate salts all water molecules form single hydrogen bonds to oxygen atoms of the coordinating anion [33]. These bridging bonds determine the arrangement of ligands around the trivalent metal ions by stabilizing the geometry of the complex formed and the hydration number of the central ion in solution. In the studied system, the stabilization of the different Eu-species in C_4mimTf_2N by the formation of hydrogen bonds of different type seems to be plausible. As cited above the OTf^- anion shows hydrogen bonding type interactions with water. Moreover, it is also known from literature [25] that the aromatic protons of the C_4mim^+ cation can coordinate to anions by formation of hydrogen bonds. Indeed, on the basis of these two types of hydrogen bonding Chaumont *et al.* report on two possible coordination configurations for Eu(III) dissolved in C_4mimTf_2N which can explain the presented TRLFS results [24, 25]. A schematic representation of both lanthanide species is given in Fig. 9. The Ln-species without water in the first coordination sphere (a) is surrounded by the complexing anions leading to a negatively charged complex. This complex is embedded in a second shell of C_4mim^+ cations and, if present, eventually H_2O. Both, the aquo ligand and the aromatic protons of the solvent cation display bridging hydrogen bonds to the first shell of the coordinating anion. The structural configuration for the second species (b) shows that part of the anionic ligands is located in the second coordination shell. This configuration is stabilized by hydrogen bonding interactions of the anionic ligand with one first shell aquo ligand on one side and by attraction with C_4mim^+ cations on the other side.

The described model of Chaumont *et al.* supports our assumption that the long luminescence lifetime of 2.5 ± 0.2 ms can be attributed to a Eu-species without water in the first coordination sphere whereas the shorter luminescence lifetime of 1.0 ± 0.3 ms is due to one additional water ligand in the
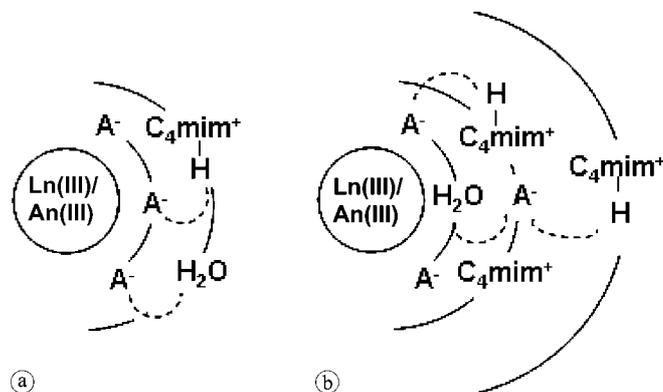

Fig. 9. Structural model for the Ln(III)-/An(III)-dissolution in C_4mimTf_2N. (**a**) No water ligand in the first coordination sphere. (**b**) One additional water ligand in the first coordination sphere.

first coordination shell resulting in luminescence quenching. The observed bi-exponential luminescence emission decay behaviour (Fig. 8) can thus be explained by the slow diffusion of the sterical demanding OTf^- and Tf_2N^- ligands and the resulting slow exchange reaction between the different configurations of the two Eu-species. The structural interpretation makes clear that not only the strength of the first coordination shell defined by the HSAB principle but also solvation effects such as hydrogen bond interactions play a very important role for the stabilization of different Eu-species in C_4mimTf_2N.
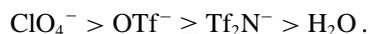
4.2 $Eu(ClO_4)_3$ in C_4mimTf_2N

Beside OTf^- and Tf_2N^- also ClO_4^- represents a hard Lewis base and can compete with more basic molecules such as H_2O in complexing small-sized and polarizing cations like lanthanides [34]. In aqueous solution the perchlorate salts of the trivalent metal ions such as La(III), Tb(III), Er(III) and Tl(III) normally form the hexa-hydrate $M(ClO_4)_3 \cdot 6H_2O$. In this complex the metal ion is solely surrounded by the water ligands in the first coordination shell which can be due to the excess of the aquo ligand compared to ClO_4^- in aqueous solution [35]. Nevertheless, Belin *et al.* report on the formation of the mono-hydrate $Yb(ClO_4)_3 \cdot H_2O$ where the perchlorato group is bi- and tridentate coordinated to the trivalent lanthanide [36]. Moreover, the formation of the anhydrous rare-earth perchlorate with monodentate coordinated ClO_4^- is reported in literature [37]. A detailed study on the perchlorate anion and its coordination modes in complexes is made up by Pascal and Favier [38].

Because the coordination sphere of rare earth ions is large enough to accept several bonds in organic solution, ClO_4^-, H_2O and organic ligands compete against each other. A study on anhydrous $Eu(ClO_4)_3$-complexes coordinated by amide ligands is reported by Teotonio *et al.* [39]. In anhydrous solutions of $Eu(ClO_4)_3$ in N,N-dimethylformamide (DMF) the perchlorate salt is completely dissociated. Eu(III) shows an inner-sphere coordination with DMF whereas the perchlorate anion stays in the outer-sphere of the lanthanide ion [40]. In contrast to these investigations, in anhydrous acetonitrile Bünzli *et al.* report on both, the outer- and inner-sphere interaction of ClO_4^- with Eu(III) [41]. The specified investigations give rise that also in ionic liquid solution

ClO_4^- represents a potential ligand beside H_2O and Tf_2N^- in the first europium coordination sphere.

In the actual study, the Eu-perchlorate sample before evaporation shows a mono-exponential luminescence lifetime with a value of $130 \pm 2\,\mu s$ (Fig. 4a). This value can be attributed to a Eu-species solely surrounded by H_2O. Nevertheless, since the luminescence lifetime of the europium aquo ion is $112 \pm 4\,\mu s$ the measured value of $130\,\mu s$ in our sample denotes a change of the Eu-ligand field in C_4mimTf_2N as compared to the europium environment in aqueous solution. The influence of ClO_4^- on the hydration sphere of metal ions is noticed by different authors since H_2O and ClO_4^- show hydrogen bonding interactions [42]. The influence of the perchlorate anion is apparently sufficient to change the environment of Eu(III) to an extent great enough to effect the luminescence lifetime [43]. Measurements of the Eu(III) luminescence in aqueous solution show an increase of hydrogen bonding interactions with increasing ClO_4^- concentration which results in a decrease of the $Eu-H_2O$ distance together with a decrease of luminescence emission lifetime [44]. Our observation of an increased lifetime is not in agreement with these studies and indicates the expulsion of the aquo ligand from the europium inner coordination sphere instead. Moreover, the determined $R_{F2/F1}$ value of 0.9 which exceeds the value of 0.3 for the europium aquo ion supposes that part of the H_2O is replaced by a stronger ligand. By drying the sample an increase of luminescence emission lifetime is observed (Fig. 4b). Obviously, the quenching of luminescence can be solely attributed to the influence of the water ligand and the increase of lifetime is equal to the further reduction of the Eu-hydration sphere. The fit of the mono-exponential luminescence emission decay of the dried sample gives a value of $1.3 \pm 0.3\,ms$. According to the interpretation of former lifetime measurements (Eu-triflate, s.a.), this value can be preliminary attributed to an europium solution species with one water in the first coordination sphere. But, since the determined water amount (Karl Fischer titration) of the dry sample gives a coordination by less than one water ligand per Eu(III), a species without water in the first coordination sphere must be also formed during dissolution. Therefore, we assume the formation of two species as described in Fig. 9. Obviously, the mono-exponential decay behaviour is due to a fast exchange of coordinating ligands that can be considered ($H_2O/ClO_4^-/Tf_2N^-$) and not to the formation of only one species. The determined luminescence lifetime therefore represents an average lifetime of both species a (2.5 ms) and b (1 ms) (Fig. 9) which also explains the slightly exceeded luminescence lifetime value of 1.3 ms. A further differentiation of coordinating ligands such as ClO_4^- and Tf_2N^- by interpretation of the lifetime data only is not possible since neither perchlorate nor triflate-imide influence the europium luminescence emission lifetime which is solely determined by the water ligand. The summarized emission spectra of Eu-triflate and Eu-perchlorate dissolved in C_4mimTf_2N (Fig. 3) exhibit different shapes and clearly show that the dissolution of the two Eu-salts results in the formation of different solution species with different coordination spheres. Moreover, the calculation of $R_{F2/F1}$ for the dry perchlorate sample gives a value of 3.3 which is much greater than the determined values for the two Eu-

triflate solution species (2.2; 1.6). That is, the dissolution of Eu-perchlorate gives the formation of a Eu-species which is also coordinated by ClO_4^- in the inner sphere. Moreover, assuming a comparable symmetry in the Eu-triflate and Eu-perchlorate solution species the comparison of the calculated $R_{F2/F1}$-values indicate a sequence of ligand strength as follows:

$$ClO_4^- > OTf^- \geq Tf_2N^- > H_2O.$$
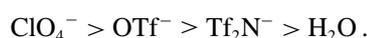
4.3 $Cm(ClO_4)_3$ in C_4mimTf_2N

Beside Ln(III), also An(III) behave as hard Lewis acids. As a result the trivalent cations of the two f-element series show strong similarities in their chemical behaviour. As indicated in the introduction, a separation of actinides from lanthanides using common oxygen-donor extractants is for given reason not feasible in organic solvents. By contrast the use of soft donors yields selectivity which is considered in literature to be due to a more covalent bonding to actinides as compared to lanthanides [45–48]. The actual study intends to verify if Ln(III) and An(III) show differences towards complexation by oxygen-donors switching to C_4mimTf_2N as solvent phase. The interpretation of the spectroscopic data shows that the dissolution of $Cm(ClO_4)_3$ in this ionic liquid results in the formation of two solution species that are structurally comparable to the corresponding Eu-species a and b (Fig. 9). Hereby, Cm(III) is either solely coordinated by the complexing anions or by one H_2O ligand in addition [8]. Whereas the dissolution of Eu-perchlorate results in mono-exponential decay behaviour of luminescence (Fig. 4) it is bi-exponential for the Cm-sample (Fig. 5b). Obviously, the kinetic of H_2O-anion ligand exchange in the latter sample is strongly reduced as compared to the Eu-sample. The spectroscopic observation indicates a difference in the chemical properties of the Ln-and An-perchlorate salts in ionic liquid solution. One possible explanation for the bi-exponential decay behaviour of the Cm-luminescence is the more covalent contribution of the metal-ligand bonding in the actinide complex as cited in literature [45–49]. If so, the difference of bonding in Ln- and An-complexes gains in importance by switching the solvent phase from organic solution to IL-solution since in organic solution no difference in exchange kinetics is observed for the different perchlorate salts.

4.4 $Cm(ClO_4)_3$ with $La(OTf)_3$ in C_4mimTf_2N

The addition of La-triflate to the Cm-perchlorate sample results in a blue shift [12] of the luminescence emission maximum of about 5 nm (Fig. 6). As described above the $^6D_{7/2} \rightarrow\ ^8S_{7/2}$ transition is sensitive to the coordination environment. The observed blue shift can be attributed to a change of the curium ligand field whereas a stronger ligand is replaced by a weaker one. Hereby, the latter is represented by OTf^- since only this ligand component is added to the system in large excess (four orders of magnitude). The replacement of H_2O from the inner-sphere can be excluded for two reasons. As it was already published by the authors a Cm-species which holds one aquo ligand in its first

coordination sphere such as b (Fig. 9) shows a peak maximum at ~ 596 nm [8]. Since the ligand field strength for the triflate-coordination environment nearly results in the same peak position a replacement of H_2O by OTf^- would not cause a blue shift. Moreover, the value of the measured luminescence emission lifetimes in this series stays constant and maintains its bi-exponential decay behaviour. Neither OTf^- nor ClO_4^- have a quenching influence on the Cm-luminescence emission. Only H_2O can cause a depopulation of excited states by non-radiative vibronic transitions. With this, the short lifetime of $300 \pm 50\,\mu s$ can be exclusively attributed to the Cm-species with one additional aquo ligand in the inner coordination sphere whereas the value of 1 ms corresponds to Cm whose luminescence is not affected by the coordinating ligand such as OTf^- or ClO_4^-. That is, a replacement of the aquo ligand would cause a disappearance of the shorter lifetime contribution together with a change of the decay behaviour from bi- to mono-exponential. With this, the blue shift can be solely explained by the replacement of ClO_4^- by OTf^- whereas H_2O stays coordinated to Cm(III). Obviously, the aquo ligand plays an important role in stabilizing the complex structure of the formed species. The broadened shape of the luminescence emission spectrum and the shoulder at higher wavelength after the addition of La-triflate indicate that the described ligand exchange reaction is not quantitative. The emission spectrum rather represents the sum of several contributions. Beside the predominant formation of a Cm-triflate solution species (peak maximum 595 nm) the shoulder of this spectrum still indicates the presence of the Cm-perchlorate species to a small amount. The broadened shape can be attributed to the formation of mixed Cm-triflate-perchlorate complexes.

The observed nephelauxetic effect in the Cm-compounds is directly correlated to the crystal field strength in the different complexes [19]. Instead, the deduced sequence of ligand strength for different Eu-salts dissolved in C_4mimTf_2N was not reliable since it was derived from the interpretation of $R_{F2/F1}$ values assuming comparable coordination symmetry of the examined solution species. With the interpretation of the Cm-data the postulated sequence of ligand strength can be confirmed and it follows:

$$ClO_4^- > OTf^- \geq Tf_2N^- > H_2O\,.$$

4.5 $Am(ClO_4)_3$ and $Am(ClO_4)_3$ in C_4mimTf_2N and $Cm(ClO_4)_3$ with $La(OTf)_3$ in C_4mimTf_2N

Considering the species in solution, the coordination sphere of americium upon its dissolution as a perchlorate salt in C_4mimTf_2N may be constituted by ClO_4^- and Tf_2N^- ions. In spite of the care taken to dry the samples, the presence of water molecules can also not be discarded. According to EXAFS result, americium is found coordinated by a shell of ~ 11 oxygen atoms at 2.42 Å. This distance is significantly shorter than the one obtained for aquo-species of americium (2.48 Å for a coordination number of ~ 10 oxygens) [50, 51]. Thus, we can discard the hypothesis of an exclusive coordination of americium with water molecules in our sample. As a matter of fact, a second coordination shell was evidenced, which could be well fitted assuming

~ 3–4 Cl/S atoms at 3.60 Å. The EXAFS technique can not discriminate between two atoms having comparable masses like sulfur and chlorine. Therefore, a discrimination between the coordinating ligands such as ClO_4^- and Tf_2N^- $((F_3CSO_2)_2N)$ is not possible.

To our knowledge, the structure of americium perchlorate or Tf_2N^- complexes in the liquid and solid state has never been characterized so far, but we may compare our results with lanthanides homologues. In the solid crystal of $Eu(ClO_4)_3$, europium is coordinated by 9 monodentate perchlorate groups, which results in a first coordination shell composed of 9 oxygen atoms at an average distance of 2.44 Å and a second shell formed by 9 chlorine atoms at an average distance of 3.75 Å [37]. Thus, we can discard the hypothesis that in our sample, americium is solely complexed by perchlorate ions even though there is an excess of ClO_4^- due to sample preparation. Such a complexation in the ionic liquid should result in the same coordination number for the oxygen shell and the chlorine shell.

Tf_2N^- anions have often been considered as weak ligands, but due to their high concentration in our ionic liquid sample, we have to consider their possible coordination to americium. A few solid state structures of Ln–Tf_2N^- complexes have been characterized [52]. Tf_2N^- ions appear to complex preferentially in a bidentate fashion, through the oxygens of their SO_2 groups, but monodentate coordination also occurs. Babai *et al.* [53] have characterized the structure of solid $[Ln(Tf_2N)_5][bmpyr]$ (Ln = Nd, Tb) in which Ln are coordinated by 4 bidentate Tf_2N^- and one monodentate Tf_2N^-. Both coordination give rise to Ln$-$S distances short enough to allow the S detection by EXAFS: between 3.68 and 3.81 Å for bidentate Tf_2N^- and 3.86 Å for monodentate Tf_2N^-. For the latter, the monodentate coordination entails a quasi-linear Ln$-$O$-$S configuration which would involve the presence of large multiple scattering interactions on the EXAFS spectrum. As a matter of fact, it was not possible to get a reliable fit of our data assuming a monodentate coordination of Tf_2N^- to americium. The bidentate Tf_2N^- coordination will lead to the same features on the EXAFS as the monodentate coordination of perchlorates, in particular it would also result in the same coordination number for the O_{Tf_2N} shell and the S shell. It is not the case in our sample ($N_O \sim 11$ and $N_{S/Cl} \sim 3$–4), so we can safely conclude that water molecules remain in the americium coordination sphere. This result is in good accordance with our TRLFS measurements and confirms the interpretation of luminescence lifetime data which indicate the Ln- and An-coordination of the perchlorate salts in C_4mimTf_2N also by water.

Addition of an excess of triflate ions in the perchlorate solution entails a change in the Am coordination, since the oxygen shell is shifted to a larger distance (2.48 Å *vs.* 2.42 Å) and no second Cl/S shell is detected, which means the removal of the ClO_4^-/Tf_2N^- from the Am coordination sphere. The Am-O distance is equivalent to the one in aquo-Am complexes ($Am(H_2O)_9$), but the formation of such an aquo species in the IL sample would imply an increase of the water amount by addition of the triflate solution. Due to the experimental procedure and the care taken to dry the samples, we can discard this hypothesis. Thus we conclude on the replacement of ClO_4^-/Tf_2N^- and on a complexation

of OTf$^-$ to americium instead. This result again supports the curium TRLFS observations which already indicated the Cm-coordination by OTf$^-$ in place of ClO$_4$$^-$/Tf$_2N^-$.

5. Conclusion

TRLFS results show different Cm(III) and Eu(III) salts dissolved in C$_4$mimTf$_2$N to have identical solution coordination structures. The interpretation of the spectroscopic data indicates the formation of a solution species without water in the metal first coordination sphere and a species with one additional aquo ligand in the metal inner-sphere coordination for each f-element cation. The coordination by both, the anionic ligands and the aquo ligand, is supported by EXAFS measurements.

TRLFS and EXAFS investigations of ligand exchange reactions in the lanthanide and actinide complexes in C$_4$mimTf$_2$N indicate the same sequence of ligand strength towards complexation with H$_2$O and the anions OTf$^-$, Tf$_2$N$^-$ and ClO$_4$$^-$.

$$\text{ClO}_4{}^- > \text{OTf}^- \geq \text{Tf}_2\text{N}^- > \text{H}_2\text{O}.$$
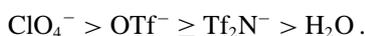
Hereby, the TRLFS studies reveal different ligand exchange kinetics for the complexation of Eu(III) and Cm(III) by ClO$_4$$^-$ in C$_4$mimTf$_2$N. Such a difference is not known for the two f-element cations in aqueous solution. Therefore, switching to Ils as solvent phase may provide the opportunity to stress the differences of Ln and An chemical properties which could result in an effective separation of lanthanides from actinides in the nuclear fuel cycle.

References

1. Actinide and fission product partitioning and transmutation, status and assessment report. OECD Nuclear Energy Agency, Paris (1999).
2. Rogers, R. D.; Seddon, K. R.: Ionic Liquids: Industrial Applications to Green Chemistry. ACS Symposium Series 818, American Chemical Society, Washington DC (2002).
3. Bonhôte, P., Dias, A.-P., Papageorgiou, N., Klyanasundaram, K., Grätzel, M.: Hydrophobic, highly conductive ambient-temperature molten salts. Inorg. Chem. **35**, 1168 (1996).
4. Visser, A. E., Swatloski, R. P., Rogers, R. D.: pH-dependent partitioning in room temperature ionic liquids provides a link to traditional solvent extraction behaviour. Green Chem. **1**, 1 (2000).
5. Holbrey, J. D., Seddon, K. R.: The phase behaviour of 1-alkyl-3-methylimidazolium tetrafluoroborates; ionic liquids and ionic liquid crystals. J. Chem. Soc. Dalton Trans. 2133 (1999).
6. Nash, K. L.: A review of the basic chemistry and recent developments in trivalent f-elements separations. Solvent Extr. Ion Exch. **11**(4), 729 (1993).
7. Oxley, J. D., Prozorov, T., Suslick, K. S.: Sonochemistry and sonoluminescence of room-temperature ionic liquids. J. Am. Chem. Soc. **125**, 11 138 (2003).
8. Stumpf, S., Billard, I., Panak, P. J., Mekki, S.: Differences of Eu(III) and Cm(III) chemistry in ionic liquids: investigations by TRLFS. Dalton Trans. 240 (2007).
9. Richardson, F. S.: Terbium(III) and europium(III) ions as luminescent probes and stains for biomolecular systems. Chem. Rev. **82**, 541 (1982).
10. Bünzli, J. C. G., Wessner, D.: Rare earth complexes with neutral macrocyclic ligands. Coord. Chem. Rev. **60**, 191 (1984).
11. Rao, L., Zanonato, P., Bernard, P. D., Bismondo, A.: Calorimetric and spectroscopic studies of Eu(III) complexation with tetramethylmalonamide and tetramethylsuccinamide in acetonitrile and dimethylsulfoxide. Inorg. Chim. Acta **306**, 49 (2000).
12. Karbowiak, M., Edelstein, N. M., Gajek, Z., Drozdzynski, J.: Crystal-field analysis of U^{3+} ions in K$_2$LaX$_5$ (X = Cl, Br or I) single crystals. Spectrochim. Acta A **54**, 2035 (1998).
13. Mochizuki, Y., Tatewaki, H.: On the electronic structure of Cm(H$_2$O)$_n$$^{3+}$ ($n = 1, 2, 4, 6$) by all-electron Dirac–Hartree–Fock calculations. J. Chem. Phys. **116**(20), 8838 (2002).
14. Beitz, J. V.: Laser-induced fluorescence studies of Cm^{3+} complexes in solution. Radiochim. Acta **52/53**, 35 (1991).
15. Kimura, T., Choppin, G. R.: Luminescence study on determination of the hydration number of Cm(III). J. Alloys Compd. **213/214**, 313 (1994).
16. Horrocks, W. D. Jr., Sudnick, D. R.: Lanthanide ion probes of structure in biology. Laser-induced luminescence decay constants provide a direct measure of the number of metal-coordinated water molecules. J. Am. Chem. Soc. **101**, 334 (1979).
17. Choppin, G. R., Peterman, D. R.: Applications of lanthanide luminescence spectroscopy to solution studies of coordination chemistry. Coord. Chem. Rev. **174**, 283 (1998).
18. Wang, Z., Choppin, G. R., Di Bernardo, P., Zanonato, P. L., Portanova, R., Tollazzi, M.: Luminescence spectroscopic study of europium(III) and terbium(III) with ethylenediamine in dimethyl sulfoxide. J. Chem. Soc. Dalton Trans. 2791 (1993).
19. Edelstein, N. M., Klenze, R., Fanghänel, Th., Hubert, S.: Optical properties of Cm(III) in crystals and solutions and their application to Cm(III) speciation. Coord. Chem. Rev. **250**, 948 (2006).
20. Chung, K. H., Klenze, R., Park, K. K., Paviet-Hartmann, P., Kim, J. I.: A study of the surface sorption process of Cm(III) on silica by time-resolved laser fluorescence spectroscopy (I). Radiochim. Acta **82**, 215 (1998).
21. Newville, M.: IFEFFIT: interactive XAFS analysis and FEFF fitting. J. Synchrotron Rad. **8**, 322 (2001).
22. Newville, M., Ravel, B., Haskel, D., Rehr, J. J., Stern, A., Yacoby, Y.: Analysis of multiple-scattering XAFS data using theoretical standards. Physica B **208**, 154 (1995).
23. Andukinov, A., Rehr, J. J.: Theory of solid-state contributions to the X-ray elastic scattering amplitude. Phys. Rev. B **62**, 2437 (2000).
24. Chaumont, A., Wipff, G.: Solvation of uranyl(II) and europium(III) cations and their chloro complexes in a room-temperature ionic liquid. A theoretical study of the effect of solvent "humidity". Inorg. Chem. **43**, 5891 (2004).
25. Chaumont, A., Wipff, G.: Solvation of uranyl(II), and europium(III) and europium(II) cations in basic room-temperature ionic liquids: a theoretical study. Chem. Eur. J. **10**, 3919 (2004).
26. Boumizane, K., Herzog-Cance, M. H., Jones, D. J., Pascal, J. L., Potier, J., Roziere, J.: Synthesis, vibrational spectroscopy and EXAFS analysis of some divalent and trivalent trifluoromethanesulfonato complexes. Polyhedron **10**, 2757 (1991).
27. Faithfull, D. L., Harrowfield, J. M., Ogden, M. I., Skelton, B. W., Third, K., White, A. H.: Synthetic and structural studies in the lanthanide toluene-4-sulfonate hydrates. Aust. J. Chem. **45**, 583 (1992).
28. Gaillard, C., Billard, I., Chaumont, A., Mekki, S., Ouadi, A., Denecke, M. A., Moutiers, G., Wipff, G.: Europium(III) and its halides in anhydrous room-temperature imidazolium-based ionic liquids: a combined TRES, EXAFS and molecular dynamics study. Inorg. Chem. **44**, 8355 (2005).
29. Hamidi, M., Pascal, J. L.: Synthesis and structural characterization of some anhydrous Ln(OTf)$_3$ complexes (Ln = Sc, La, Nd, Sm, Gd and Er; OTf = CF$_3$SO$_3$). Polyhedron **13**, 1787 (1994).
30. Billard, I., Mekki, S., Gaillard, C., Hesemann, P., Moutiers, G., Mariet, C., Labet, A., Bünzli, J.-C. G.: EuIII luminescence in a hygroscopic ionic liquid: effect of water and evidence for a complexation process. Eur. J. Inorg. Chem. 1190 (2004).
31. Choppin, G. R.: Factors in Ln(III) complexation. J. Alloys Compd. **249**, 1 (1997).
32. Choppin, G. R., Graffeo, A. J.: Complexes of trivalent lanthanide and actinide ions. II. Inner-sphere complexes. Inorg. Chem. **4**(9), 1254 (1965).

33. Abbasi, A., Lindqvist-Reis, P., Eriksson, L., Sandström, D., Lidin, S., Persson, I., Sandström, M.: Highly hydrated cations: defiency, mobility, and coordination of water in crystalline non-ahydrated scandium(III), yttrium(III), and lanthanoid(III) trifluoromethanesulfonates. Chem. Eur. J. **11**, 4065 (2005).

34. Huskowska, E., Legendziewicz, J., Schleid, Th., Meyer, J.: Do the lanthanides form inner sphere complexes with ClO_4^- ions in competition with H_2O molecules? Mater. Chem. Phys. **31**, 117 (1992).

35. Glaser, J., Johansson, G.: Crystal structures of the isomorphous perchlorate hexahydrates of some trivalent metal ions (M = La, Tb, Er, Tl). Acta Chim. Scand. A **35**, 639 (1981).

36. Belin, C., Favier, F., Pascal, J. L., Tillard-Charbonnel, M.: Triperchloratoytterbium(III) monohydrate, $Yb(ClO_4)_3 \cdot H_2O$. Acta Cryst. C **52**, 1872 (1996).

37. Wickleder, M. S.: $Eu(ClO_4)_3$: First single crystals of an anhydrous rare-earth perchlorate. Z. Anorg. Allg. Chem. **625**, 11 (1999).

38. Pascal, J.-L., Favier, F.: Inorganic perchlorato complexes. Coord. Chem. Rev. **178–180**, 865 (1998).

39. Teotonio, E. E. S., Espinola, J. G. P., Brito, H. F., Malta, O. L., Oliveira, S. F., de Faria, D. L. A., Izumi, C. M. S.: Influence of the N-[methylpyridyl]acetamide ligands on the photoluminescent properties of Eu(III)-perchlorate complexes. Polyhedron **21**, 1837 (2002).

40. Bünzli, J.-C. G., Yersin, J.-R.: Spectroscopic investigation of anhydrous solution of europium perchlorate and europium nitrate in *N,N*-dimethylformamide. Helvetica Chim. Acta **65**(8), 2498 (1982).

41. Bünzli, J.-C. G., Yersin, J.-R., Mabillard, C.: FTIR and fluorometric investigation of rare-earth and metallic ion solvation. 1. Europium perchlorate in anhydrous acetonitrile. Inorg. Chem. **21**, 1471 (1982).

42. Giuliani, J. F., Donohue, T.: Complex formation in dilute aqueous solutions of europium perchlorate detected through fluorescence lifetime measurements. Inorg. Chem. **17**(4), 1090 (1978).

43. Nehlig, A., Elhabiri, M., Billard, I., Albrecht-Gary, A. M., Lützenkirchen, K.: Photoexcitation of europium(III) in various electrolytes: dependence of the luminescence lifetime on the type of salts and the ionic strength. Radiochim. Acta **91**, 37 (2003).

44. Lis, S., Choppin, G. R.: Luminescence lifetimes of aqueous europium perchlorate, chloride and nitrate solutions. Mater. Chem. Phys. **31**, 159 (1992).

45. Nash, K. L.: In: *Handbook on the Physics and Chemistry of Rare Earths*. Vol. 18 (Gschneidner Jr., K. A., Eyring, L., Choppin, G. R., Lander, G. H., eds.) Elsevier Science, Amsterdam (1994).

46. Illemassene, M., Edelstein, N. M., Murdoch, K. M., Karbowiak, M., Cavellec, R., Hubert, S.: Site selective spectroscopy and crystal field analysis of Cm^{3+} diluted in $CsCdBr_3$. J. Luminescence **86**, 45 (2000).

47. Murdoch, K. M., Edelstein, N. M., Boatner, L. A., Abraham, M. M.: Excited state absorption and fluorescence line narrowing studies of Cm^{3+} in $LuPO_4$. J. Chem. Phys. **105**, 2539 (1996).

48. Thouvenot, P., Hubert, S., Edelstein, N. M.: Spectroscopic study and crystal-field analysis of Cm^{3+} in the cubic-symmetry site of ThO_2. Phys. Rev. B **50**, 9715 (1994).

49. Stumpf, Th., Fanghänel, Th., Grenthe, I.: Complexation of trivalent actinide and lanthanide ions by glycolic acid: a TRLFS study. J. Chem. Soc. Dalton Trans. 3799 (2002).

50. Stumpf, Th., Hennig, C., Bauer, A., Denecke, M. A., Fanghänel, Th.: An EXAFS and TRLFS study of the sorption of trivalent actinides onto smectite and kaolinite. Radiochim. Acta **92**, 133 (2004).

51. Allen, P. G., Bucher, J. J., Shuh, D. K., Edelstein, N. M., Craig, I.: Coordination chemistry of trivalent lanthanide and actinide ions in dilute and concentrated chloride solutions. Inorg. Chem. **39**, 595 (2000).

52. Bhatt, A. I., May, I., Volkovich, V. A., Collison, D., Helliwell, M., Polovov, I. B., Lewin, R.: Structural characterization of a lanthanum bistriflimide complex, $La(N(SO_2CF_3)_2)_3(H_2O)_3$, and an investigation of La, Sm, and Eu electrochemistry in a room-temperature ionic liquid, $[Me_3NnBu][N(SO_2CF_3)_2]$. Inorg. Chem. **44**, 4934 (2005).

53. Babai, A., Mudring, A.-V.: The first homoleptic bis(trifluoromethanesulfonyl)amide complex compounds of trivalent f-elements. Dalton Trans. 1828 (2006).