Mechanisms of Metal Ion Transfer into Room-Temperature Ionic Liquids: The Role of Anion Exchange

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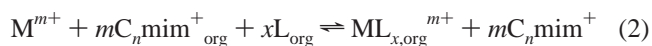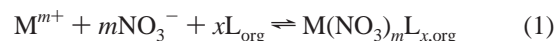
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Abstract: The structure and stoichiometry of the lanthanide(III) (Ln) complexes with the ligand 2-thenoyl-trifluoroacetone (Htta) formed in a biphasic aqueous room-temperature ionic liquid system have been studied by complementary physicochemical methods. Equilibrium thermodynamics, optical absorption and luminescence spectroscopies, high-energy X-ray scattering, EXAFS, and molecular dynamics simulations all support the formation of anionic $Nd(tta)_4^-$ or $Eu(tta)_4^-$ complexes with no water coordinated to the metal center in 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ($C_4mim^+Tf_2N^-$), rather than the hydrated, neutral complexes, $M(tta)_3(H_2O)_n$ ($n = 2$ or 3), that form in nonpolar molecular solvents, such as xylene or chloroform. The presence of anionic lanthanide complexes in $C_4mim^+Tf_2N^-$ is made possible by the exchange of the ionic liquid anions into the aqueous phase for the lanthanide complex. The resulting complexes in the ionic liquid phase should be thought of as weak $C_4mim^+Ln(tta)_4^-$ ion pairs which exert little influence on the structure of the ionic liquid phase.

Introduction

Room-temperature ionic liquids (RTILs) are being considered as replacement solvents for a host of synthetic, catalytic, electrochemical, and separations processes.[1–3] They possess fundamentally unique combinations of properties,[4] such as being nonvolatile and able to dissolve both ionic and nonionic species. At the same time, a subset of ionic liquids retain important properties of certain conventional, molecular organic solvents, such as immiscibility with water. Studies have demonstrated that the mechanisms of numerous synthetic reactions are the same in molecular solvents and in RTILs,[5] but this is not universally true.[6]

In biphasic systems, like those used in phase transfer catalysis or those used for the separation or purification of a metal ion containing complex by liquid−liquid partitioning, the differences between the chemical equilibria observed in RTILs and conventional (molecular) organic solvents can be especially large.[7] Recent studies of the partitioning mechanism of Sr^{2+}-crown

ether[8,9] and UO_2^{2+}-carbamoylmethylenephosphine oxide complexes[10] showed that substituting a water immiscible 1-alkyl-3-methylimidazolium-based ionic liquid for molecular organic solvents in biphasic aqueous−organic solvent systems altered the stoichiometry, charge, and structure of the metal ion complexes in the organic phase. At the same time, the partitioning mechanism changed from ion pairing (eq 1) to cation exchange (eq 2). (Species present in the organic phase are indicated by the subscript org.)

$$M^{m+} + mNO_3^- + xL_{org} \rightleftharpoons M(NO_3)_mL_{x,org} \qquad (1)$$

$$M^{m+} + mC_nmim^+_{org} + xL_{org} \rightleftharpoons ML_{x,org}^{m+} + mC_nmim^+ \quad (2)$$

In the cation exchange reaction (eq 2), the partitioning of the cationic metal complex into the RTIL phase is accompanied by the transfer of 1-alkyl-3-imidazolium cations from the RTIL into the aqueous phase. These findings suggest that some RTILs may not be suitable for use in biphasic systems, prompting us to systematically examine other partitioning reactions to understand if the formation of *cationic* metal−ligand complexes in the RTIL phase, driven by cation exchange, is a general phenomenon of 1-alkyl-3-methylimidazolium-based ionic liquids in biphasic systems. Consequently, we studied the RTIL-phase complexes of trivalent lanthanide cations (Ln^{3+}) with the common β-diketone ligand 2-thenoyltrifluoroacetone (Htta, 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione) in biphasic aqueous/

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RTIL solutions. The ionic liquid used as the organic solvent, 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ($C_4mim^+Tf_2N^-$), was chosen to increase the likelihood of *cation* exchange into the aqueous phase by employing a cation containing a shorter alkyl chain (butyl vs pentyl, hexyl, or octyl methylimidazolium cations) than had been used in previous systems where cation exchange had been identified.[8-10]

We report three key findings regarding the nature of the ionic liquid and the formation of Ln^{3+}-tta^- complexes in the biphasic aqueous/$C_4mim^+Tf_2N^-$ system. Under the common-place conditions employed for this reaction, $C_4mim^+Tf_2N^-$ behaves as a liquid *anion* exchanger, promoting the formation of the anionic complex, $Ln(tta)_4^-$, in the RTIL phase in contrast to the neutral complexes commonly observed in molecular organic solvents or the cationic complexes previously reported in RTILs. Unlike common liquid anion exchangers, though, the cationic components of the RTIL do not form large aggregates[11] in the organic phase when these anionic metal—ligand complexes are present. In addition, despite the significant water content of the equilibrated $C_4mim^+Tf_2N^-$ phase (1.05 M) and in contrast to the recent reports of the formation of hydrated complexes through cation exchange reactions in RTILs,[9,10] all of the water is expelled from the inner coordination sphere of the metal ion of this complex.

Experimental Section

Materials and Sample Preparation. 2-Thenoyltrifluoroacetone (99%, Aldrich) was purified by vacuum sublimation, yielding fine pale yellow needles. Weighed amounts of Htta were dissolved in *o*-xylene (99%, Acros Organics) or the ionic liquid $C_4mim^+Tf_2N^-$ (Covalent Associates), which were used as received. Solutions containing Htta were stored in the dark when not in use to avoid photodecomposition of the ligand. Aqueous solutions of $Eu(ClO_4)_3$ or $Nd(ClO_4)_3$ and 0.001–0.02 M $HClO_4$ with sufficient $NaClO_4$ to maintain the ionic strength of the aqueous phase at 1.0 M were prepared and standardized as previously described.[12] For measurements of the Eu or Na distribution ratios, 1 μL aliquots of radiochemically pure ^{152,154,155}Eu or ^{22}Na radiotracer solutions in 0.01 M $HClO_4$ were added to 400 μL portions of aqueous 1.0 M $(Na,H)ClO_4$ of known acidity. The Nd concentration in the RTIL phase and the Nd distribution ratios were calculated from the difference in the Nd concentration in the aqueous phase before and after extraction, which was determined spectrophotometrically using the Nd—Arsenazo III complex after dilution.[13]

Ln^{3+}-tta^- complexes were formed by mixing equal volumes of a pre-equilibrated *o*-xylene or $C_4mim^+Tf_2N^-$ solution, containing a known amount of Htta (0.05–0.5 M), and an aqueous 1.0 M $(Na,H)ClO_4$ solution, containing Eu^{3+} or Nd^{3+} ($\leq 10^{-8}$ – 0.06 M Ln^{3+}), at 295 $\pm$ 1 K. Equilibrium was attained within 60 min of mixing. For the preparation of samples containing more than 0.001 M of the lanthanide complex, a known amount of NaOH also was added to the aqueous phases to drive the complexation equilibria. The concentrations of C_4mim^+ and Htta in the aqueous phase were determined spectrophotometrically at 210 nm ($\epsilon = 4560$ M^{-1} cm^{-1}) and 266 nm ($\epsilon = 9840$ M^{-1} cm^{-1}), respectively, after dilution in 0.01 M HCl. The water content of the RTIL phase was determined by Karl Fischer titration.

The concentration of Tf_2N^- in the aqueous phase was determined as the colored ion pair, bis[(trifluoromethyl)sulfonyl]imide bis(2,9-dimethyl-1,10-phenanthroline)copper(I) in ethyl acetate using a modification of the indirect spectrophotometric procedure for anion analysis developed by Collinson and Boltz.[14] Chloride salts replaced perchlorate salts as the background electrolyte in this set of experiments to avoid severe interference from perchlorato bis(2,9-dimethyl-1,10-phenanthroline)copper(I) in the analysis. Known concentrations of $LiTf_2N$ (Aldrich) were used to calibrate the background corrected absorption response, which followed the Beer—Lambert law to the highest concentration measured, 4.7×10^{-5} M Tf_2N^- in the diluted aqueous analyte, with a molar absorptivity of $(2.33 \pm 0.02) \times 10^4$ M_{aq}^{-1} cm^{-1} at 456 nm (M_{aq} = molar concentration of Tf_2N^- in the aqueous copper solution before extraction into ethyl acetate).

The crystalline complex 1,4-dimethylpyridinium tetrakis(2-thenoyltrifluoroacetonato)europate(III), $(1,4-Me_2py)Eu(tta)_4$ was prepared as a standard for X-ray absorption measurements according to literature procedures.[15]

Spectroscopic and Scattering Measurements. Optical absorption spectra of the Nd containing samples were measured in 1.000 cm quartz cuvettes with a computer-controlled Cary-14 spectrophotometer (OLIS, Inc.). Time-resolved laser-induced fluorescence measurements of Eu containing organic phases were made after contact with aqueous phases containing H_2O or 99.9% D_2O. The emission spectra of the samples were measured after excitation at 355 or 532 nm. The lifetime of the Eu $^5D_0$ state was measured by monitoring the $^5D_0 \rightarrow {}^7F_2$ transition, analyzing the data as described previously.[16] The measured lifetimes were independent of the excitation wavelength.

X-ray absorption spectra at the Eu L_3-edge were measured of a $C_4mim^+Tf_2N^-$ solution containing 0.2 M Htta and 0.015 M Eu in a 4 mm inner diameter polyethylene tube and of solid $(1,4-Me_2py)Eu(tta)_4$ diluted with boron nitride contained in a 2.2 mm thick holder with Kapton windows. Measurements were made in the fluorescence mode with a 13-element Ge detector (Canberra) at the Advanced Photon Source bending magnet beamline 12-BMB.[17] The energy scale was calibrated against the first inflection point of the K-edge of an Fe foil (7.112 keV). Two spectra of each sample were averaged, and the k^3-weighted Eu EXAFS were isolated and analyzed by standard procedures[18] using the program Ifeffit[19] and the phase and amplitude functions generated by FEFF7.02[20] from the atomic positions derived from the crystal structures of $Eu(tta)_3(H_2O)_2$[21] or $(1,4-Me_2py)Eu(tta)_4$.[15] The threshold energy, E_0, was set to the first inflection point of the measured Eu L_3 absorption edge, 6.982 keV.

The EXAFS of crystalline $(1,4-Me_2py)Eu(tta)_4$, which is known to contain discrete, octacoordinate $Eu(tta)_4^-$,[15] was fit to the FEFF phase and amplitude functions with fixed coordination numbers ($N_O = N_C = 8$), while allowing the Debye—Waller factors, σ^2, to vary. The resulting value of σ^2 for the coordinated oxygen atoms, 0.0045 ± 0.0017 Å^2, was then used as a fixed parameter to fit the EXAFS of the RTIL phase sample, allowing the number of coordinated oxygen atoms, N_O, to vary. The amplitude reduction factor, S_0^2, was held equal to unity for both fits. The uncertainty in the coordination number derived from the fitting, ± 1.0, includes both the intrinsic uncertainty in the fit of N_O and the uncertainty in the value of σ^2 from fitting the standard.

High-energy X-ray scattering experiments (HES) were conducted at beamline 11-ID[22] of the Advanced Photon Source at a beam current of 100 mA and an energy of 98 keV. Samples were enclosed in thin

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walled (0.01 mm) silica tubes with a 3 mm outer diameter (Glas Müller). Data were collected in two regions, 0.48 Å^{-1} < Q < 3.5 Å^{-1} and 0.6 Å^{-1} < Q < 30 Å^{-1}, with $Q = 4\pi/\lambda \sin \theta$. After correction for the detector dead time and instrumental background, the different scan regions were merged into a single data set for each sample and were further corrected for geometry and polarization before normalization as previously described.[23]

Molecular Dynamics Simulations. Molecular dynamics simulations were done using the MOSCITO 3.9 code.[24] The simulations employed 125 C$_4$mim$^+$ and 125 Tf$_2$N$^-$ ions, 38 H$_2$O molecules, and 8 enolic Htta molecules in a cubic box with periodic boundary conditions to reproduce the water saturated Htta/RTIL solution at a temperature of 300 K. For simulations of solutions containing the Eu(tta)$_4^-$ complex, the eight enolic protons were replaced with two Eu^{3+} ions, yielding two Eu(tta)$_4^-$ anions. All ions were represented by charged 12−6 Lennard−Jones sites bound together by harmonic bond distance, bond bending (angular), and dihedral potentials. Each C−H unit was treated as a pair of united atoms, and intramolecular 1,2- and 1,3-interactions were neglected. Intermolecular interactions were calculated to a distance of 17.0 Å, incorporating long-range electrostatic interactions through the particle mesh Ewald technique.[25] The Lennard−Jones parameters were taken from the Amber 4.1 force fields,[26] except for the Eu ion, which used the parameters of van Veggel and Reinhouldt.[27] Lorenz−Berthelot rules were used throughout for the mixed Lennard−Jones terms. The atomic charges[28,29] and estimates of the geometric parameters[28,30] were taken from the literature. The time step of the simulations was 1 fs with 500 ps of equilibration and an additional 500 ps for averaging.

Results

The fundamental metal/proton/ligand stoichiometry of the Ln^{3+}−tta$^-$ complexes in the RTIL phase was determined by equilibrium measurements of the Eu^{3+} partitioning between the aqueous and RTIL phases as a function of the aqueous phase acidity and the initial concentration of Htta in the RTIL, as shown in Figure 1. Slope analysis[31] of the data indicates the participation of 4.0 ± 0.4 Htta molecules in the partitioning equilibrium accompanied by the release of 4.2 ± 0.2 protons to the aqueous phase for each Eu^{3+} that moves from the aqueous phase to the C$_4$mim$^+$Tf$_2$N$^-$ phase. As illustrated in Figure 2, sodium ions do not participate in the partitioning equilibrium, but the extraction of the Ln^{3+}−tta$^-$ complex does cause a linear increase in the aqueous phase concentration of Tf$_2$N$^-$ from the initial aqueous Tf$_2$N$^-$ concentration of 0.0139 M.

Other data from the solutions represented in Figure 2 provide independent confirmation of the stoichiometry of the complexes in the RTIL phase through the stoichiometric correspondence between the amount of OH$^-$ added to drive the Ln^{3+} partitioning and the amount of Ln^{3+} in the RTIL phase. Addition of 26 ± 1 μmol of OH$^-$ causes the extraction of 5.8 ± 0.6 μmol of Eu
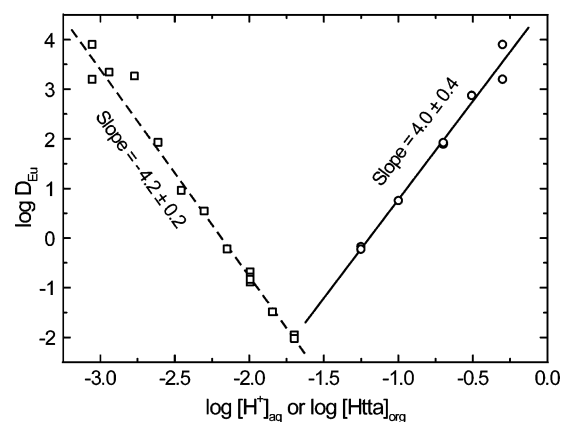
Figure 1. Dependence of the partitioning of Eu^{3+} from aqueous 1.0 M NaClO$_4$ into C$_4$mim$^+$Tf$_2$N$^-$ on the aqueous phase acidity (□, [Htta]$_{org}$ = 0.5 M) and on the concentration of Htta in the RTIL phase (○, log[H$^+$]$_{aq}$ = −3.05). Lines represent best fit by linear least-squares regression.
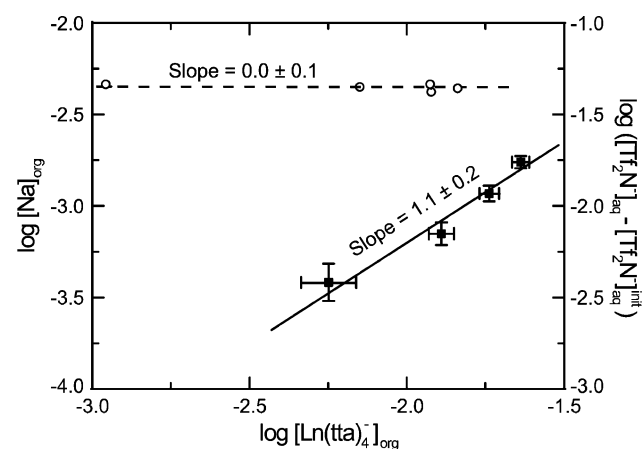
**Figure 2.** Dependence of the partitioning of Na$^+$ into C$_4$mim$^+$Tf$_2$N$^-$ on the organic phase concentration of Eu(tta)$_4^-$ (○, 1.0 M NaClO$_4$) and the dependence of the partitioning of Tf$_2$N$^-$ into the aqueous phase on the organic phase concentration of Nd(tta)$_4^-$ (■, 1.0 M NaCl). Lines indicate best fit of data by linear least-squares regression.

into the RTIL. This agrees with the 6.4 ± 0.3 μmol of Eu that would partition if Eu(tta)$_4^-$ is formed in the RTIL through an anion exchange mechanism. In contrast, if neutral Eu(tta)$_3$(H$_2$O)$_3$ or Eu(tta)$_3$(Htta) complexes or the anionic Eu(tta)$_3$(Tf$_2$N)$^-$ complex is formed in the RTIL phase, 8.6 ± 0.4 μmol of Eu would be extracted. Furthermore, measurement of the change in the amount of uncomplexed Htta and tta$^-$ in the system when macro concentrations of Nd partition in the RTIL phase confirms the Ln/tta stoichiometry of the complex. The transfer of 14.9 ± 0.5 μmol of Nd into the RTIL phase decreased the amount of uncomplexed ligand from 152 ± 1 μmol to 89 ± 3 μmol. Therefore, 64 ± 3 μmol of tta$^-$ are bound to 14.9 ± 0.5 μmol of Nd^{3+}, which gives a bound tta/Nd ratio of 4.3 ± 0.3 in the RTIL phase of solutions used to determine the spectrum of Nd(tta)$_4^-$ in Figure 3.

Optical spectroscopy confirms that the bulk of the Ln ions in the RTIL are present as Ln(tta)$_4^-$, in accord with the equilibrium stoichiometry derived at the tracer and macro scales. The absorption spectra of the Nd^{3+}−tta$^-$ complexes in *o*-xylene, C$_4$mim$^+$Tf$_2$N$^-$, and *o*-xylene containing 0.02 M tricaprylm-ethylammonium perchlorate (TCMA$^+$ClO$_4^-$), a liquid anion exchanger known to form ion pairs with Ln(tta)$_4^-$ in molecular solvents,[32] are compared in Figure 3 (also see the Supporting Information). The Nd^{3+} $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transition depicted

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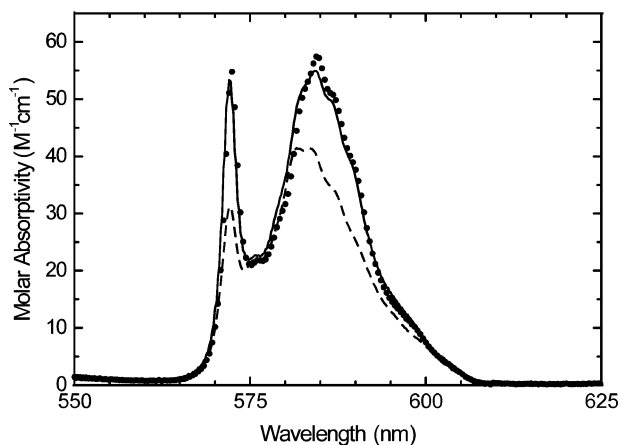
Figure 3. Visible absorption spectra of $Nd(tta)_3(H_2O)_3$ in *o*-xylene (dashed line), $Nd(tta)_4^-$ in $C_4mim^+Tf_2N^-$ (solid line), and $Nd(tta)_4^-$ in *o*-xylene containing 0.02 M tricaprylmethylammonium perchlorate (●).

in Figure 3 is a hypersensitive $4f \rightarrow 4f$ transition. The energy of this transition shows little sensitivity to the ligand environment, but the shape and intensity of these absorption bands are very sensitive to changes in the Nd^{3+} coordination environment.[33] The shape and intensities of the absorption bands of the Nd complex in the RTIL bear little resemblance to those of $Nd(tta)_3(H_2O)_3$ in *o*-xylene, clearly demonstrating the change in the Nd coordination environment. At the same time, the spectrum of the $Nd^{3+}-tta^-$ complex in the RTIL is very similar to the spectrum of $[TCMA^+][Nd(tta)_4^-]$ in *o*-xylene. The increase in the maximum molar absorptivities of the 572 nm (71% increase) and 584 nm (28% increase) bands and the 28% increase in the integrated intensity of the $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition (565–610 nm) of the $Nd(tta)_4^-$ complex as compared to $Nd(tta)_3(H_2O)_3$ in *o*-xylene are well within the range commonly observed for the replacement of coordinated water molecules with an anionic oxygen-bearing ligand.[34] The slightly lower intensity of the Nd absorption in the RTIL as compared to the $[TCMA^+][Nd(tta)_4^-]$ ion pair in *o*-xylene is within experimental error of this determination of the Nd concentration in these organic phases (±3%). In addition, the single peak of the $^5D_0 \rightarrow {}^7F_0$ transition of the $Eu^{3+}-tta^-$ containing RTIL solutions (Supporting Information) indicates that the metal ion is present primarily in a single coordination geometry[35] and that any other complexes present are below the limit of detection of the combined fluorescence spectral and lifetime measurements (ca. 5% of the total Eu concentration in the RTIL).

Luminescence lifetime measurements of the Eu complexes in the water-equilibrated RTIL phase also support the assignment of the complexes as the anionic $Eu(tta)_4^-$ complexes. The number of water molecules directly coordinated to Eu, N_{H_2O}, was calculated from the well-established correlation between

Table 1. Number of Water Molecules Coordinated to Eu in the RTIL Phase Determined from Fluorescence Lifetime Measurements

$[Htta]_{org}$, M	k_{H_2O}, msec^{-1}	k_{D_2O}, msec^{-1}	N_{H_2O}, Eu[a]
0.2	2.154 ± 0.020	1.976 ± 0.027	0.2
0.5	2.378 ± 0.035	2.294 ± 0.041	0.1

[a] Estimated uncertainty ± 0.5 H_2O.
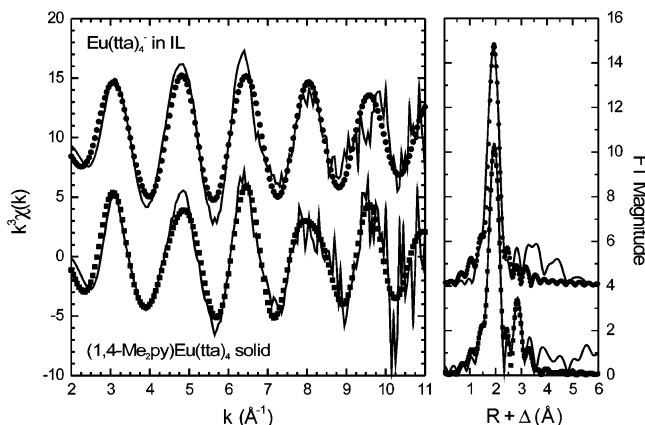
Figure 4. k^3-weighted Eu L_3-edge EXAFS of $Eu(tta)_4^-$ in $C_4mim^+Tf_2N^-$ (offset vertically) and $(1,4-Me_2py)Eu(tta)_4$ solid standard. Solid lines represent the experimental data, while the points represent the best fit.

N_{H_2O} and the difference in the fluorescence decay constants, k, of trivalent Eu complexes containing H_2O and D_2O,[36]

$$N_{H_2O} = 1.05(k_{H_2O} - k_{D_2O}) \quad (3)$$

The results (Table 1) demonstrate that the tta^- anions displace all of the coordinated water molecules from the Eu inner coordination sphere. This is in contrast to the hydrated, neutral 1:3 Ln/tta complexes found in the solid state[21] and solution[37,38] but is in accord with the fully dehydrated 1:4 Ln/tta^- complexes observed in the solid state.[39,40] The absolute uncertainty in N_{H_2O}, ±0.5 H_2O, was previously estimated from the agreement between standards with a known hydration number and the measured N_{H_2O}.[36]

Structural parameters of the $Eu^{3+}-tta^-$ complex in the RTIL were determined by EXAFS and HES. The results are summarized in Figures 4 and 5 and in Table 2. The EXAFS signals of both the RTIL sample and the $Eu(tta)_4^-$ solid standard (Figure 4) are dominated by the shell of oxygens directly coordinated to the Eu ion at 2.4 Å. The next shell of atoms, the ketone carbons of the tta^- ligands, is obviously present in the solid standard at 3.4 Å but is of sufficiently small intensity in the RTIL sample that it was not considered in the analysis. The absence of a detectable Eu–C distance in the EXAFS data would appear to arise from greater disorder in this shell of atoms for the complex in solution and the inherently low

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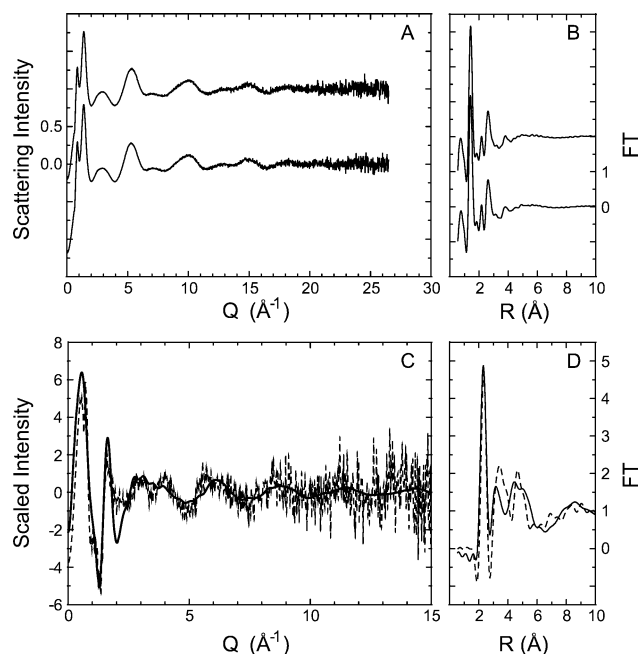
Figure 5. Background corrected high energy scattering of $C_4mim^+Tf_2N^-$ solutions equilibrated with aqueous 1.0 M (Na,H)ClO_4 and containing a total of 0.2 M Htta. (A) Top, scattering of 0.2 M Htta with 0 M Eu. Bottom, scattering of 0.2 M Htta with 0.046 M Eu. (B) Fourier transformation of scattering data in panel A using the Lorch function.[41] (C) Comparison of the scattering of $Eu(tta)_4^-$ from the scaled difference of the samples in panel A (dotted line) and the scattering intensity predicted from molecular dynamics simulations of octacoordinate $Eu(tta)_4^-$ in $C_4mim^+Tf_2N^-$ (solid line). (D) Fourier transformation of scattering data in panel C using the Lorch function.[41]

Table 2. Metrical Parameters from Fitting the EXAFS and HES of the $Eu(tta)_4^-$ Complexes

	N	R, Å	$\sigma^2, 10^{-3} Å^2$	ΔE_0, eV
$(1,4-Me_2py)Eu(tta)_4$ solid				
Eu−O EXAFS	8[a]	2.40 ± 0.01	4.5 ± 1.7	8.9 ± 1.4
Eu−C EXAFS	8[a]	3.40 ± 0.03	3.7 ± 3.1	
$Eu(tta)_4^-$ in RTIL				
Eu−O EXAFS	8.7 ± 1.0	2.39 ± 0.01	4.5[a]	8.8 ± 2.1
Eu−O HES	7.5 ± 0.6	2.35 ± 0.01		

[a] Fixed parameter.

backscattering of the C shell caused by the rapid decrease in scattering intensity with increasing distance. The absence of a Eu−O−S scattering peak at 3.8 Å in the RTIL sample is consistent with the absence of significant amounts of Eu coordinated to Tf_2N^- through the sulfonyl oxygens, as expected from the equilibrium partitioning measurements.
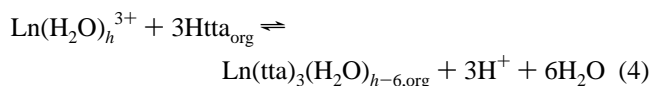
The HES data were fit to the scattering calculated for models based on the structures of $Eu(Tf_2N)_3$, $Eu(tta)_3(H_2O)_2$, or $Eu(tta)_4^-$ in the RTIL derived from molecular dynamics simulations, allowing the number of coordinated oxygens, N_O, and the Eu−O bond distances to vary. The fit of the HES data to the $Eu(tta)_4^-$ model (Figure 5) was significantly better than that to either the $Eu(Tf_2N)_3$ or $Eu(tta)_3(H_2O)_2$ models, which were unable to reproduce the Eu−O scattering peak at 2.35 Å without requiring unreasonable values for the parameters. The good agreement between the scattering calculated from the simulation of $Eu(tta)_4^-$ in the RTIL and the experimental scattering data is demonstrated in Figure 5C and D, which show the simulated scattering of $Eu(tta)_4^-$ before fitting N_O or the Eu−O bond distances to the experimental data.

These structural measurements are most consistent with Eu coordination by eight oxygen atoms from four bidentate tta^- anions. The coordination numbers determined from EXAFS and HES (Table 2) agree within the fitting error and indicate the presence of eight oxygen atoms in the Eu inner coordination sphere in the RTIL phase. Furthermore, the average Eu−O bond distance in the RTIL sample (Table 2) is consistent with octacoordination, agreeing well with the average Ln−O distances reported for crystalline $Ln(tta)_4^-$ complexes (expected average Eu−O distance = 2.39 Å),[15,40] while being considerably shorter than the average Eu−O distance reported in the hydrated octacoordinate complex $Eu(tta)_3(H_2O)_2$, 2.44 Å.[21]
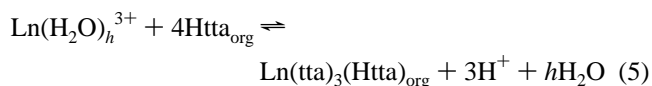
The molecular dynamics simulations also are in accord with the picture derived from the structural, thermodynamic, and spectroscopic measurements. The simulations indicate that the $Eu(tta)_4^-$ anion is more stable in water-saturated $C_4mim^+Tf_2N^-$ containing 0.2 M Htta than are either the $Eu(Tf_2N)_3$ or $Eu(tta)_3(H_2O)_2$ complexes.

Discussion

Mechanism of Eu Partitioning. The reactions of β-diketone ligands with trivalent lanthanide cations (Ln^{3+}) are well characterized, varied, and have been studied in aqueous, organic, and biphasic aqueous−organic solvent systems. Among these, the reactions of Htta with lanthanides in biphasic systems have been the subject of particularly intensive study, forming an extensive basis for comparing partitioning reactions in different solvents. In biphasic systems, both cationic[42] and anionic[32,43,44] $Ln(tta)_n^{3-n}$ complexes ($n = 2$ or 4) may form ion pairs in molecular organic solvents in the presence of an appropriate counterion. These are special cases, however. The neutral complexes $Ln(tta)_3(H_2O)_{h-6}$[38] and $Ln(tta)_3(Htta)$[45] are much more commonly observed in molecular organic solvents. The formation and partitioning of these neutral complexes into conventional solvents are governed by the equilibria

$$Ln(H_2O)_h^{3+} + 3Htta_{org} \rightleftharpoons$$
$$Ln(tta)_3(H_2O)_{h-6,org} + 3H^+ + 6H_2O \quad (4)$$

and

$$Ln(H_2O)_h^{3+} + 4Htta_{org} \rightleftharpoons$$
$$Ln(tta)_3(Htta)_{org} + 3H^+ + hH_2O \quad (5)$$

where h, the hydration number of a given lanthanide aquo cation, varies between 9 and 8 as the atomic number of the lanthanides increases.[46] Equilibria 4 and 5 both display characteristic dependencies on the $[Htta]_{org}$ and $[H^+]_{aq}$, as described in Table 3, reactions A and B.

In contrast to the species observed in conventional solvents (eqs 4 and 5), our combined thermodynamic, spectroscopic, and X-ray absorption and scattering measurements, together with molecular dynamics simulations, demonstrate that the Ln^{3+}−

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Table 3. Expected Dependence of the Ln Distribution Ratio on the Aqueous Proton, Organic Htta, and Aqueous Na Concentrations for Various Hypothetical Partitioning Equilibria

	slope of log D_{Ln} vs log		
reaction	$[H^+]_{aq}$	$[Htta]_{org}$	$[Na]_{aq}$
A. $Ln^{3+} + 3Htta_{org} + 3H_2O \rightleftharpoons Ln(tta)_3(H_2O)_{3,org} + 3H^+$	−3	3	0
B. $Ln^{3+} + 4Htta_{org} \rightleftharpoons Ln(tta)_3(Htta)_{org} + 3H^+$	−3	4	0
C. $Ln^{3+} + 4Htta_{org} + H_2O \rightleftharpoons [H_3O^+][Ln(tta)_4^-]_{org} + 3H^+$	−3	4	0
D. $Ln^{3+} + 4Htta_{org} + Na^+ \rightleftharpoons [Na^+][Ln(tta)_4^-]_{org} + 4H^+$	−4	4	1
E. $Ln^{3+} + 4Htta_{org} + [C_4mim^+][Tf_2N^-]_{org} \rightleftharpoons$ $[C_4mim^+][Ln(tta)_4^-]_{org} + Tf_2N^- + 4H^+$	−4	4	0
F. $Ln^{3+} + 4Htta_{org} + [C_4mim^+][Tf_2N^-]_{org} \rightleftharpoons$ $[C_4mim^+][Ln(tta)_4^-]_{org} + H(Tf_2N)_{org} + 3H^+$	−3	4	0
G. $Ln^{3+} + 2Htta_{org} + 5H_2O + [C_4mim^+][Tf_2N^-]_{org} \rightleftharpoons$ $[Ln(tta)_2(H_2O)_5^+][Tf_2N^-]_{org} + C_4mim^+ + 2H^+$	−2	2	0

tta$^-$ complexes in $C_4mim^+Tf_2N^-$ exist as discrete, octacoordinate $Ln(tta)_4^-$ anions. The dissolution or formation of a number of anionic complexes already has been identified in various RTIL systems.[2,47] What is different about the $Ln(tta)_4^-$ anions in this system is that they form in the RTIL phase of this biphasic system (or at the interface of the phases) through an anion exchange reaction. In fact, the aqueous phase concentration of tta$^-$ is so low under our experimental conditions (1×10^{-7} to 9×10^{-6} M) that appreciable aqueous concentrations of $Ln(tta)_4^-$ complexes would not exist even in the absence of a second phase.[44] This is born out by the optical spectra of Nd in the aqueous phase after contact with the Htta/RTIL solution where only the Nd^{3+} aquo ion is observed.

Although 1-alkyl-3-methylimidazolium-based RTILs are effective solvents for a variety of ionic solutes,[1] the net charge must be zero in both the RTIL and the aqueous phases at equilibrium. Having experimentally demonstrated that the Nd and Eu complexes in the RTIL phase are present as the $Ln(tta)_4^-$ anion, the negative charge of the complex anion in the RTIL phase must be balanced either by transferring a cation from the aqueous phase or by displacing an anion from the organic phase. From the vantage point of a Ln^{3+} cation forming a tta$^-$ complex and moving from the aqueous phase into the RTIL phase, the equilibrium described by Figure 1 is

$$Ln(H_2O)_h^{3+} + 4Htta_{org} \rightleftharpoons Ln(tta)_4^-{}_{org} + 4H^+ + hH_2O \quad (6)$$
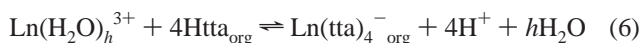
As written above, eq 6 is obviously incomplete because it creates a charge imbalance in both phases by separating one cation−anion pair ($[H_3O^+][Ln(tta)_4^-]$) between two phases. Charge balanced versions of this reaction (Table 3, reactions B, C, and F) are at odds with our experimental results (Figure 1), which require four protons to remain in the aqueous phase. Only reactions D and E in Table 3 are consistent with the measured Ln^{3+}/H^+ and $Ln^{3+}/Htta$ ratios in Figure 1 and the requirement for a charge neutral reaction. Because the partitionings of Na^+ and Eu^{3+} into the RTIL are independent (Figure 2), reaction D, which involves the correct number of Htta molecules and protons but requires a 1:1 relationship between the Ln and Na concentrations in the RTIL phase, is also at odds with the experimental results. Therefore, only an anion exchange

mechanism with the formation of $[C_4mim^+][Ln(tta)_4^-]$ ion pairs (Table 3, reaction E) is consistent with the observations of $Ln(tta)_4^-$ in the RTIL phase, the release of four protons to the aqueous phase, the independence of the Ln partitioning on the sodium concentration, and the absolute requirement of charge balance at equilibrium in both phases.

Further proof of the importance of anion exchange and the formation of the $Ln(tta)_4^-$ complex in the RTIL phase is given by the direct relationship between the concentration of Tf_2N^- in a 1.0 M (Na,H)Cl aqueous phase and the amount of $Nd(tta)_4^-$ that partitions into the RTIL phase (Figure 2). Switching the anion of the background electrolyte from noncomplexing ClO_4^- to weakly complexing Cl^- was necessary to avoid severe interference of colored ClO_4^- ion pairs in the Tf_2N^- optical analysis. The presence of 1.0 M Cl^- in the aqueous phase depresses the Nd^{3+} distribution ratio by a factor of 2 through the formation of aqueous $NdCl^{2+}$ complexes, but it does not alter the fundamental metal ion partitioning equilibria or the structure or stoichiometry of the complex formed in the RTIL phase, as evidenced by the optical spectrum of the Nd-loaded RTIL. Taking the participation of Tf_2N^- into account, the full equilibrium describing Ln^{3+} partitioning into the $C_4mim^+Tf_2N^-$ phase (ignoring the role of H_2O and ClO_4^- as spectator species) is

$$Ln^{3+} + 4Htta_{org} + [C_4mim^+][Tf_2N^-]_{org} \rightleftharpoons$$
$$[C_4mim^+][Ln(tta)_4^-]_{org} + 4H^+ + Tf_2N^- \quad (7)$$
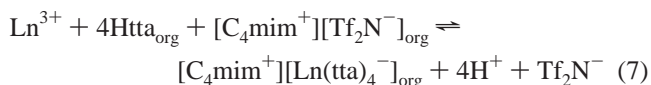
Protonation of Tf_2N^- in the aqueous phase is not a major reaction under the conditions of these experiments because of its low pK_a, 1.2.[48]

The anion exchange of $Ln(tta)_4^-$ into organic solvents is not unique to ionic liquids. As demonstrated by the spectroscopic data in Figure 3, $Ln(tta)_4^-$ anions are known to partition into low polarity molecular solvents such as xylene in the presence of liquid anion exchangers. In that particular case, one ClO_4^- anion was exchanged for each $Nd(tta)_4^-$ anion, and $[TCMA^+]$-$[Nd(tta)_4^-]$ ion pairs were formed. Given the similarity of the cations favored for making RTILs and the cations commonly employed as liquid anion exchangers,[49] metal ion partitioning through anion exchange is not surprising. Nevertheless, two particularly interesting aspects of the partitioning mechanism are implied by eq 7.

The availability of the anion exchange pathway in the two phase aqueous/RTIL system drives the formation of the anionic 1:4 Ln/tta complex under conditions that favor the formation of neutral 1:4 complexes in molecular organic solvents. With chloroform as the organic solvent, 36% of the Eu in the organic phase would be present as the neutral 1:3 complex while 64% would be the neutral 1:4 complex when the $[Htta]_{org} = 0.5$ M.[45] When $C_4mim^+Tf_2N^-$ is substituted for chloroform, only anionic 1:4 complexes are observed in the RTIL phase under these conditions. While the RTIL could simply solvate neutral 1:3 or 1:4 complexes, the experimental free energies of extraction demonstrate that the anion exchange reaction in $C_4mim^+Tf_2N^-$

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is favored by more than 10 kJ/mol over the formation of the neutral 1:4 complex in chloroform when $-\log [H^+]_{aq} = 3$ and $[Htta]_{org} = 0.5$ M.

The exchange of the $Ln(tta)_4^-$ anion for the RTIL's Tf_2N^- anion also implies that the $Ln^{3+}-tta^-$ complex is more than a solute in the ionic liquid, in contrast to $Ln(tta)_3(H_2O)_n$ or $Ln(tta)_3(Htta)$ in conventional solvents. By displacing anions from the RTIL phase, the anionic lanthanide complex becomes part of the ionic liquid. The ultimate recovery of the metal complex from the RTIL phase as part of a catalytic or separations cycle will eventually destroy the ionic liquid unless the complex anions are replaced by other anions. A similar problem was encountered in the studies that demonstrated the cation exchange of Sr^{2+} and UO_2^{2+} complexes into RTILs from aqueous solutions.[8,10] Unlike the incorporation of the cationic Sr^{2+} and UO_2^{2+} complexes into the RTILs, though, the proton dependence of eq 7 provides a realistic mechanism for recovering the lanthanide cation from the RTIL phase and reconstituting the RTIL. Contacting the RTIL phase with aqueous 0.01−0.1 M $H(Tf_2N)$ will reverse the lanthanide partitioning equilibrium in eq 7 and replace the complex anions with Tf_2N^- anions without breaking down the RTIL. Thus, the primary chemical limitations of using this RTIL for large-scale chemical processes with this type of anion exchange system would be the modest solubility of the RTIL in the aqueous phase and, more importantly, the initial loss of Tf_2N^- to the aqueous phase in exchange for $Ln(tta)_4^-$. While the RTIL in this chemical system can easily be regenerated when the metal ion is recovered from the RTIL phase, the contamination of the aqueous phase with components of the RTIL can hardly be considered "green."[50]

Structure of the Eu Loaded RTIL. Solvent ordering in ionic liquids can be quite important[51] and is well demonstrated by the formation of liquid crystals by RTILs with the appropriate alkyl chains.[52] In addition to this, cations commonly used in RTILs, the tetraalkylammonium and *N*-alkylpyridinium ions, are well-known to form inverse micelles in nonpolar, molecular organic solvents. These micelles can contain as many as 50 tetraalkylammonium cations in the presence of certain anionic complexes.[11,53] Could significant ordering of the RTIL phase be responsible for the strong energetic preference for the anion exchange mechanism in lanthanide partitioning?

The HES results and molecular dynamics simulations both suggest that the presence of the $Ln(tta)_4^-$ complex does not significantly alter the solution structure of the RTIL phase. In the absence of $Eu(tta)_4^-$, the HES scattering data (Figure 5A) do not show large structures in the water-equilibrated RTIL phase. After formation of the anionic lanthanide complex in the RTIL phase, the small changes in the scattering peaks are
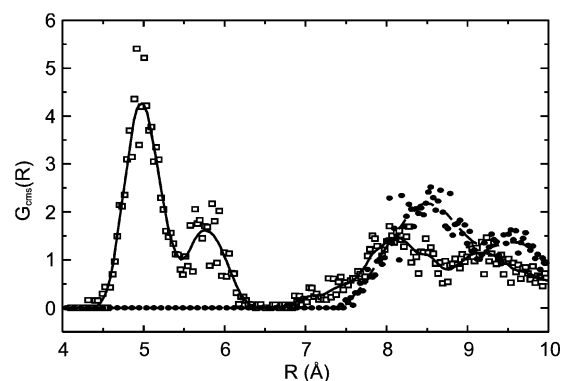
Figure 6. $Eu(tta)_4^- - C_4mim^+$ and Tf_2N^- distance correlations from molecular dynamics simulations of $Eu(tta)_4^-$ in $C_4mim^+Tf_2N^-$. $Eu(tta)_4^- - C_4mim^+$ distances (□) and $Eu(tta)_4^- - Tf_2N^-$ distances (●). Distances are between Eu and the center of mass of C_4mim^+ or Tf_2N^-.

well accounted for by the presence of $Eu(tta)_4^-$ (Figure 5C). In contrast to the extraction-driven reverse micelle formation found for some anion exchange reactions involving alkylammonium salts in benzene,[11] evidence for larger structures around the extracted metal anions is not observed in the RTIL phase. Reverse micelle formation also is not supported by the molecular dynamics simulations. Simulations of $Eu(tta)_4^-$ loaded $C_4mim^+Tf_2N^-$ suggest some ordering of C_4mim^+ cations around each $Eu(tta)_4^-$ anion (Figure 6), with a set of C_4mim^+ cations at a distance (between centers of mass) of 5−6 Å. However, this cation−anion ordering is weak. An average of only two C_4mim^+ cations near each $Eu(tta)_4^-$ anion is found. Beyond this pair of C_4mim^+ cations, beginning ca. 7 Å from the center of mass of the $Eu(tta)_4^-$ complex, C_4mim^+ and Tf_2N^- ions are mixed together and no additional medium range ordering of the ionic liquid components is observed. Taken together, the experimental and computational evidence show that the partitioning of the $Ln^{3+}-tta^-$ complexes is not enhanced by ordering in the RTIL phase and that direct interactions between C_4mim^+ and $Ln(tta)_4^-$ are present but minimal.

Role of Water in the Partitioning Mechanism. In previous studies of cation exchange in biphasic RTIL systems, some sites in the inner coordination sphere of the extracted metal ions appeared to be occupied by water molecules.[9,10] Low polarity, water-immiscible molecular organic solvents are generally poor solvents for ions and for water. Although this makes the presence of hydrated complexes in conventional organic solvents less common, the hydrated complex $Ln(tta)_3(H_2O)_n$ ($n = 2$ or 3) is the most commonly encountered form of $Ln^{3+}-tta^-$ complexes in nonpolar, molecular solvents. The high water content of the hydrophobic methylimidazolium-based RTILs in equilibrium with water would seem to increase the likelihood that a hydrated complex will form in the RTIL phase. This is not the case in the $Ln^{3+}-tta^- -C_4mim^+Tf_2N^-$ system. The fluorescence lifetimes of the $Eu^{3+}-tta^-$ complex in $C_4mim^+Tf_2N^-$ indicate complete dehydration of the lanthanide inner coordination sphere when the $Ln(tta)_4^-$ complex forms in the RTIL phase despite the 1.05 mol/L H_2O in the $C_4mim^+Tf_2N^-$ phase before and after loading with the $Ln(tta)_4^-$ complex and the general stability of the $Ln(tta)_3(H_2O)_n$ complexes in molecular solvents. The molecular dynamics simulations indicate that the $Eu(tta)_4^-$ complex in water-saturated 0.2 M $Htta/C_4mim^+Tf_2N^-$ is 5 kJ/mol more stable than the hydrated $Eu(tta)_3(H_2O)_2$ complex in the same media. Thus, while the high water content of RTILs

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may affect the formation of certain organic phase complexes,[10] the enhanced partitioning of metal ions into RTILs as compared to molecular solvents does not always arise from the ability of RTILs to dissolve hydrated species.

Conclusion

Despite the previous observations of the partitioning of metal complexes into RTIL solutions through *cation* exchange, $Ln^{3+}-tta^-$ complexes partition from aqueous solution into the $C_4mim^+Tf_2N^-$ RTIL by an *anion* exchange mechanism under the conditions we studied. The presence of the C_4mim^+ cation and the availability of the anion exchange pathway in a second phase enables a complex that otherwise would not be present in the aqueous system to dominate the speciation. The required charge balance is maintained by exchange of $Ln(tta)_4^-$ anions with Tf_2N^- anions from the ionic liquid, and the resulting $[C_4mim^+][Ln(tta)_4^-]$ ion pairs become part of the ionic liquid without greatly altering the general structure of the RTIL phase. Although the loss of the Tf_2N^- anion to the aqueous phase as part of the anion exchange reaction (eq 7) may make this class of RTILs unsuitable for practical application in some types of biphasic catalysis or separations, the steep acid dependence of the $Ln(tta)_4^-$ partitioning provides a realistic mechanism for recovering the lanthanide from the RTIL phase through treatment with the acidic form of the anion, $H(Tf_2N)$. This mechanism for recovering the lanthanide complex was not available in the previously studied systems where cation exchange was the mechanism for metal ion partitioning into RTILs.[8,10]

Supporting Information Available: Fluorescence and absorption spectra of the Eu and Nd complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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