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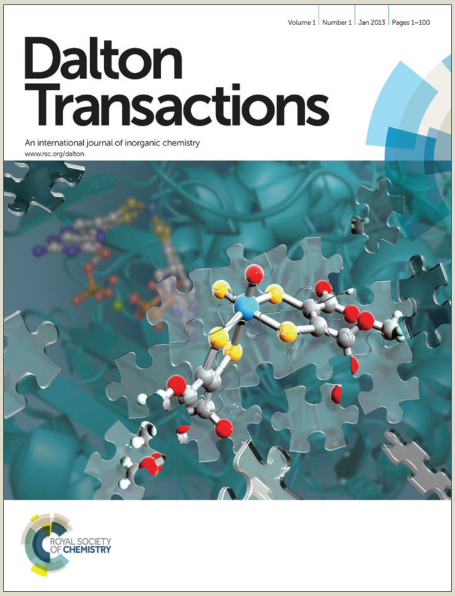

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Binary Lanthanide(III)/Nitrate and Ternary Lanthanide(III)/Nitrate/Chloride Complexes in an Ionic Liquid Containing Water: Optical Absorption and Luminescence Studies

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The formation of binary Ln(III)/nitrate and ternary Ln(III)/nitrate/chloride complexes in a water-saturated ionic liquid, 1-butyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)imide (denoted as BumimTf$_2$N), was investigated by absorption spectrophotometry and luminescence spectroscopy. Four successive binary complexes, $Nd(NO_3)^{2+}$, $Nd(NO_3)_2^+$, $Nd(NO_3)_3$, and $Nd(NO_3)_4^-$, were identified, and their stability constants in water-saturated BumimTf$_2$N are several orders of magnitude higher than those in aqueous solutions, but much lower than those observed in dry BumimTf$_2$N. The complexation of lanthanides with nitrate in wet BumimTf$_2$N proceeds via the replacement of water molecules by bidentate nitrate anions from the inner solvation spheres of Ln^{3+} cations. In the absence of nitrate, the precipitation of Ln(III)/chloride complex(es) occurs at low ratios of C_{Cl}/C_{Ln} (< 6) in BumimTf$_2$N, which precludes the determination of stability constants of binary Ln(III)/chloride complexes by spectrophotometry or luminescence spectroscopy. However, using a competition approach, the formation of two ternary complexes, $Ln(NO_3)_3Cl_2^{2-}$ and $Ln(NO_3)_2Cl_4^{3-}$, has been observed and their stability constants in wet BumimTf$_2$N were determined. Data indicate that both nitrate and chloride are stronger ligands than water for lanthanides in BumimTf$_2$N.

Introduction

Ionic liquids (ILs) have been widely studied as the "multi-purpose" solvents and have the potential to replace the usual molecular organic solvents in almost every field of chemistry. Both the cationic and the anionic components of ILs can be tailored easily to have specific sets of properties for particular applications, so that ILs are often referred to as the "design" solvents. A number of attractive properties, including thermal stability, non-flammability, and low vapour pressure, make the processes using ILs environmentally safer than those using volatile organic solvents. In the last decade, the chemistry of *f*-elements (lanthanides and actinides) in ILs has been a major focus of several research groups. The studies include coordination chemistry, spectroscopy, electrochemistry and electro-deposition, as well as the applications of ILs in organic synthesis, inorganic nanomaterial synthesis, and catalysis.[1-3] In particular, water-immiscible ILs with imidazolium-based cations and hydrophobic anions such as Tf_2N^- (bis(trifluoromethanesulfonyl)-imide) have been studied as an alternate solvent for metal ion separation in extraction process using target selective ligands.[4,5] Exciting results have been reported on the partitioning of actinides from acidic aqueous solutions with ILs containing extractants such as diglycolamides[6,7], CMPO (carbamoyl methylene phosphine oxide)[8,9] and malonamides.[10,11] Additionally, IL-based solvents have been studied for lanthanide/actinide separation in the TALSPEAK process.[12] ILs functionalized with suitable binding groups, known as task-specific ionic liquids, have also been studied for metal ion separation from aqueous solutions.[13-15] A few examples can also be found on the use of ILs in supercritical CO_2 extraction of organic compounds[16] or metallic moieties.[17]

Despite that numerous studies have been conducted on the use of ILs for metal separations, fundamental studies on the thermodynamics of the interactions of metal ions with ligands in ILs are rare. Few studies have been devoted to understanding the energetics of lanthanides/actinides complexation in ILs.[18-21] Of particular importance, since many ILs are highly hygroscopic and many separation processes involve aqueous solutions, the influence of water on the thermodynamics of metal/ligand interactions in ILs is not well understood. The presence of water strongly modifies the macroscopic physico-chemical properties of ILs such as viscosity, density, and electrochemical window.[22–24] Besides, the presence of water shows strong influence on the speciation of actinides and lanthanides in ILs, especially under metal extraction conditions in which the ILs are water saturated.[18-20] To bridge the gap in the understanding of the chemistry of actinides and lanthanides in ILs containing water, the present work has been conducted to quantify the complexation of lanthanides with nitrate and chloride, two most commonly used ligands in separations, in ILs saturated with water (denoted as "wet" ILs), and comparing the energetics of complexation in wet ILs with that in ILs free of water (denoted as "dry" IL). 1-Butyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)imide, denoted as BumimTf$_2$N, was chosen for this study because it has physico-chemical properties (such as water immiscibility and viscosity) favourable to applications in separation processes and it has been widely studied as a solvent in biphasic separations.[4,5] The fundamental information from this study is of critical importance to the development of practical applications of ILs in liquid/liquid extraction of metal ions.

For the binary Ln(III)/nitrate system, preliminary data on the complexation in wet $BumimTf_2N$ have been presented in a communication[19] and compared with the data in dry $BumimTf_2N$.[18] It has been demonstrated that the energetics of the Ln(III)/nitrate complexation in wet $BumimTf_2N$ is drastically different from that observed in dry $BumimTf_2N$. This paper presents additional luminescence data, detailed thermodynamic analysis, and insight into the solvent effect and the coordination modes of nitrate in the binary Ln(III)/nitrate complexes.

In comparison with the limited data on the binary Ln(III)/nitrate complexes in ILs, even fewer thermodynamic studies on the complexation of Ln/An with chloride in the ILs have been reported.[25-28] Data on Ln/chloride complexes in $BumimTf_2N$ are very scarce because of some experimental difficulties, such as the formation of precipitates at $C_{Cl}/C_{Ln} \approx 3$. The precipitates could dissolve at higher C_{Cl}/C_{Ln}, leading to the formation of $LnCl_6^{3-}$,[29] similar to the limiting hexa-chloride complex of lanthanides in aqueous solutions.[30] Due to such experimental difficulties, no stability constants of Ln(III)/chloride complexes in ILs are available in the literature. To by-pass the problem of precipitation of Ln(III)/chloride, we have studied the ternary Ln(III)/nitrate/chloride system in wet $BumimTf_2N$ in this work. The stability constants of the ternary complexes were determined for the first time. These data, in addition to those of the binary Ln(III)/nitrate complexes, will help to gain fundamental understanding of the metal-ligand interactions in the applications of ILs in separation processes.

Experimental

Materials

1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($BumimTf_2N$, Figure 1), procured from Sigma Aldrich (> 98%, CAS 174899-83-3), was equilibrated with an equal volume of Milli-Q water in a stoppered glass tube for 30 minutes. After equilibration, the tube was centrifuged to separate the aqueous and $BumimTf_2N$ layers. This water saturated $BumimTf_2N$, referred to as "wet" IL in this paper, was used throughout the present study. The water content of the $BumimTf_2N$ was calculated to be about 1 mol/L.[31] Neodymium and europium oxides were procured from Sigma Aldrich in the highest available purity. $Nd(Tf_2N)_3$ and $Eu(Tf_2N)_3$ salts were prepared by the reaction of the corresponding oxides with trifluoromethane sulfonimide (Sigma Aldrich, CAS 82113-65-3) according to the procedure in the literature.[18] A stock solution of $Nd(Tf_2N)_3$ or $Eu(Tf_2N)_3$ was prepared by dissolving appropriate amounts of the salts in $BumimTf_2N$. The concentration of Nd(III) or Eu(III) in the stock solutions was confirmed by volumetric titration with a standard EDTA solution using bromothymol blue as the indicator. Stock solutions of $BumimNO_3$ (Sigma Aldrich, CAS 179075-88-8) and BumimCl (Sigma Aldrich, CAS 79917-90-1) were prepared by dissolving known amounts of the vacuum-dried salts in $BumimTf_2N$. Other chemicals used were of analytical reagent grade and were used without further purifications.

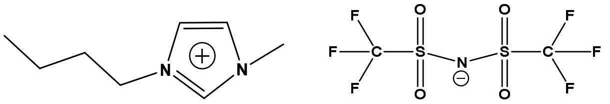

Figure 1. Structures of the cation and anion of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (denoted as $BumimTf_2N$ in this paper).

Spectrophotometric titration

Absorption spectra of Nd(III) were collected in the wavelength region 560 - 625 nm (0.1 nm interval) on a double beam Varian Cary-5G spectrophotometer using 10 mm path length Quartz cells. The temperature of the sample and reference cell holders was controlled by water circulation from a thermostated water bath. The initial concentration of Nd(III) in the cell was around 20 mmol/L. In each titration, appropriate aliquots of the titrant ($BumimNO_3$ or BumimCl) were added into the cell and mixed thoroughly for about 5 minutes before the spectrum was recorded. The mixing time was found to be sufficient to complete the complexation reaction. Usually a set of 20-25 spectra were recorded in each titration. The stability constants of the Nd(III) complexes were calculated by nonlinear least-squares regression analysis using the HypSpec program[32], based on equations (1) and (2) for the binary nitrate complexes and the ternary nitrate/chloride complexes, respectively.

$$M^{3+} + iNO_3^- = M(NO_3)_i^{(3-i)+} \qquad (1)$$

$$\beta_i = [M(NO_3)_i^{(3-i)+}]/([M^{3+}][NO_3^-]^i$$

$$M^{3+} + iNO_3^- + jCl^- = M(NO_3)_i(Cl)_j^{(3-i-j)+} \qquad (2)$$

$$\beta_{ij} = [M(NO_3)_i(Cl)_j^{(3-i-j)+}]/([M^{3+}][NO_3^-]^i[Cl^-]^j)$$

where M^{3+} represents the trivalent lanthanide cation. It should be pointed out that equations (1) and (2) are only "nominal" and the associated stability constants (β_i and β_{ij}) are best considered to be "conditional" as discussed previously.[19,21] Differing from the complexation in neutral solvents such as water where the electrical charges on the participating species (e.g., M^{3+}) do not vary as the degree of solvation changes, the charged species in ILs are surrounded by counter cations or anions of the medium so that the charges of the species participating in the complexation reaction vary as the degree of solvation changes, and are also dependent on the number of solvation shells taken into consideration.[33] Therefore, equations (1) and (2) are "nominal" expressions that do not accurately describe the electrical charges on the participating species.

Luminescence spectroscopy

Luminescence emission spectra and the lifetime of Eu(III) in aqueous and in $BumimTf_2N$ solutions were acquired on a Horiba Jobin Yvon IBH Fluorolog-3 fluorimeter, adapted for time-resolved measurements. A sub microsecond xenon flash lamp (Jobin Yvon, 5000XeF) was the light source, coupled with a double-grating excitation monochromator for spectral selection. A thermoelectrically cooled single photon detection module (Horiba Jobin Yvon IBH, TBX-04-D) equipped with a fast-rise-time photomultiplier tube, a wideband width preamplifier and a pico-second constant-fraction discriminator was used as the detector. The luminescence emission spectra were obtained in the wavelength region of 550–750 nm (0.5 nm/step) by excitation at 395 nm (5 nm bandwidth). Similarly, the luminescence lifetime data were obtained at an emission wavelength of (612 ± 5) nm and an excitation wavelength of (395 ± 5) nm. Signals were acquired using an IBH Data Station

Hub, and the data were analyzed using the commercially available DAS-6 decay analysis software package from Horiba Jobin Yvon IBH. The stability constants of the Eu(III) complexes with nitrate and nitrate/chloride were calculated from the emission spectra with the HypSpec program[32] based on equations (1) and (2).

Results and discussion

Binary Ln(III)/nitrate complexes in wet $BumimTf_2N$

Stability constants of Nd(III)/nitrate complexes: Absorption spectrophotometry. Figure 2(a) represents the spectrophotometric titration of Nd(III) with nitrate in wet $BumimTf_2N$. Nd^{3+} has well-defined absorption bands at about 575 nm, originating from the hypersensitive $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition.[34] Significant changes in the spectra were observed when the ratio of C_{NO3}/C_{Nd} increased from 0 to 8. The changes can be better discussed in the following three phases. In Phase I ($C_{NO3}/C_{Nd} = 0$ - 5), the absorption band at 575 nm was shifted to around 585 nm with simultaneous increase in the absorbance. In Phase II ($C_{NO3}/C_{Nd} = 5$ - 8), a new absorption band at around 580 nm appeared concomitantly with the decrease in the absorption band at 570 – 575 nm. The intensity of the band at 580 nm increased with the increase of the C_{NO3}/C_{Nd} ratio up to ~ 8. In Phase III ($C_{NO3}/C_{Nd} = 8$ - 20), few changes were observed in the spectra, implying that the "limiting" complex species was achieved at $C_{NO3}/C_{Nd} \leq 8$. A plot of the total peak area of the hypersensitive band ($^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$) versus the C_{NO3}/C_{Nd} ratio showed five sections with distinctly different slopes (Figure 2(b)). The nearly zero slope of the last section (where $C_{NO3}/C_{Nd} \geq 6$) indicates that the ML_4 species is the limiting complex.

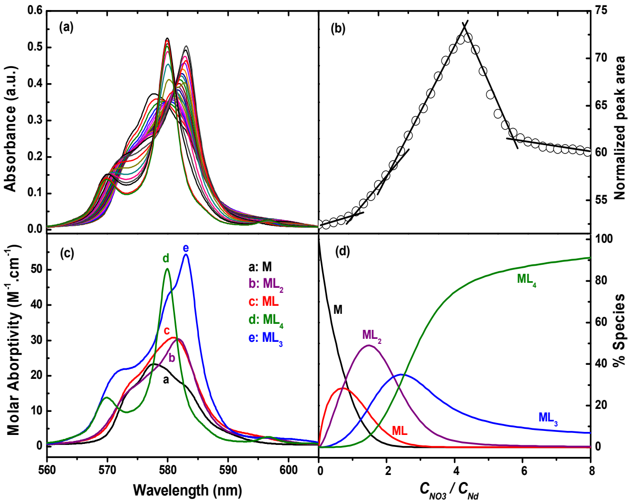

Figure 2. (a) Spectrophotometric titration of Nd(III) with nitrate, initial solution: 20 mmol/L $Nd(Tf_2N)_3$, titrant: 0.39 mol/L $BumimNO_3$.; (b) Total peak area of the normalized absorption band ($^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$) between 560 – 600 nm versus the C_{NO3}/C_{Nd} ratio; (c) Calculated molar absorptivities of free Nd(III) and Nd(III)/nitrate complexes (M, ML, ML_2, ML_3 and ML_4, where M denotes Nd, and L denotes nitrate); (d) Speciation of Nd(III) as a function of C_{NO3}/C_{Nd} ratio.

The above analysis suggests that the spectra can be described by the successive formation of four complexes (up to ML_4), consistent with the spectra factor analysis that indicated the presence of five absorbing species in the titrated system ("free" Nd(III) plus four complexes). Therefore, the spectra were fitted with the model shown by equation (1). The stability constants of $[Nd(NO_3)_i]^{(3-i)+}$, where i = 1, 2, 3, and 4, were calculated, and shown in Table 1. The calculated absorptivities of free Nd(III) and the four Nd(III)/nitrate complexes are shown in Figure 2(c). With the stability constants, the speciation of Nd(III) as a function of C_{NO3}/C_{Nd} was calculated and shown in Figure 2(d). Interestingly, the patterns of the curve for the total band area of the hypersensitive band (Figure 2(b)) correspond roughly with the speciation changes shown in Figure 2(d). The first section corresponds to the formation of ML (M + L = ML) and the first break point in the curve occurs when the ML species reached the maximum. Similar patterns are closely followed for the second and third break points as well. A decrease in the total band area after the third break point was ascribed to the significant decrease in the concentrations of ML_2 and ML_3 species, and the contribution to the band area was only from ML_4 species. A plateau region after the fourth break point confirmed the achievement of the limiting species, ML_4, as shown by the speciation diagram.

Table 1. Thermodynamic data on the complexation of lanthanides with nitrate and chloride in aqueous and $BumimTf_2N$ media at ambient temperature.

Equilibrium	Medium	logβ	Ref
$Nd^{3+} + NO_3^- = Nd(NO_3)^{2+}$	1 M $NaClO_4$	−(0.19 ± 0.02)	[35]
$Nd^{3+} + NO_3^- = Nd(NO_3)^{2+}$	Wet IL	3.23 ± 0.18	[p.w.][a]
$Nd^{3+} + 2NO_3^- = Nd(NO_3)_2^+$	Wet IL	6.58 ± 0.53	
$Nd^{3+} + 3NO_3^- = Nd(NO_3)_3$	Wet IL	9.06 ± 0.38	
$Nd^{3+} + 4NO_3^- = Nd(NO_3)_4^-$	Wet IL	11.4 ± 0.47	
$Nd^{3+} + NO_3^- = Nd(NO_3)^{2+}$	Dry IL	7.88 ± 0.10	[18]
$Nd^{3+} + 2NO_3^- = Nd(NO_3)_2^+$	Dry IL	13.3 ± 0.10	
$Nd^{3+} + 3NO_3^- = Nd(NO_3)_3$	Dry IL	21.2 ± 0.15	
$Nd^{3+} + 4NO_3^- = Nd(NO_3)_4^-$	Dry IL	27.1 ± 0.20	
$Nd^{3+} + Cl^- = NdCl^{2+}$	0.7 M $NaClO_4$	−0.37	[36]
$Nd^{3+} + 3NO_3^- + 2Cl^- = Nd(NO_3)_3Cl_2^{2-}$	Wet IL	13.89 ± 0.27	[p.w.]
$Nd^{3+} + 2NO_3^- + 4Cl^- = Nd(NO_3)_2Cl_4^{3-}$	Wet IL	15.68 ± 0.53	
$Eu^{3+} + 3NO_3^- + 2Cl^- = Eu(NO_3)_3Cl_2^{2-}$	Wet IL	13.77 ± 0.05	[p.w.][b]
$Eu^{3+} + 4NO_3^- + 4Cl^- = Eu(NO_3)_2Cl_4^{3-}$	Wet IL	15.15 ± 0.01	

[a] *These data have been presented in a previous communication [19].*

[b] *Determined by luminescence emission spectra on the assumption that the intensity is proportional to the concentration. It should be noted that this assumption may not always be valid.*

Stability constants of Eu(III)/nitrate complexes: Luminescence emission spectra. Figure 3 shows the luminescence emission spectra for the titration of Eu(III) with nitrate in wet $BumimTf_2N$. The emission bands at 590 nm and 612 nm originate from the transitions of $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$, respectively.[37] By nature, the $^5D_0 \rightarrow {}^7F_1$ band is of magnetic dipole transition and not sensitive to the ligand field, while the $^5D_0 \rightarrow {}^7F_2$ band is of electronic dipole transition and hypersensitive to the coordination environment of Eu(III). As shown by Figure 3 (left plot), when nitrate was added into the Eu(III) solution (C_{NO3}/C_{Eu} ratio increased from 0 to 10), the $^5D_0 \rightarrow {}^7F_2$ band (612 nm) was significantly intensified, but the $^5D_0 \rightarrow {}^7F_1$ band remained almost unaffected. Figure 3 (right plot) shows that the intensity ratio of the two bands (I_{612}/I_{590}) increases nearly linearly with the increase of the C_{NO3}/C_{Eu} ratio (from 0 to about 5), suggesting the formation of Eu(III)/nitrate complexes. The I_{612}/I_{590} ratio reaches a plateau at $C_{NO3}/C_{Eu} \approx 6 - 7$, indicating a limiting Eu(III)/nitrate complex is achieved. This observation parallels that in the spectrophotometric titration of Nd(III) with nitrate where the integrated absorption band intensity remains nearly constant when the C_{NO3}/C_{Nd} ratio is above 6 - 7 (Figure 2, upper right). In the case of the Nd(III)/nitrate system, the limiting complex in wet BumimTf$_2$N was found to be $Nd(NO_3)_4^-$. Therefore, it is reasonable to assume that the limiting Eu(III)/nitrate complex in the luminescence titration is also a tetra-nitrate complex, $Eu(NO_3)_4^-$. The best fit to the luminescence emission spectra was obtained with the model including four successive Eu(III)/nitrate complexes, $Eu(NO_3)_i^{(3-i)+}$ where i = 1, 2, 3, and 4. The constants (log β) were calculated to be 3.52, 7.21, 9.98, and 11.52, respectively. These values are very close to those of $Nd(NO_3)_i^{(3-i)+}$ shown in Table 1.

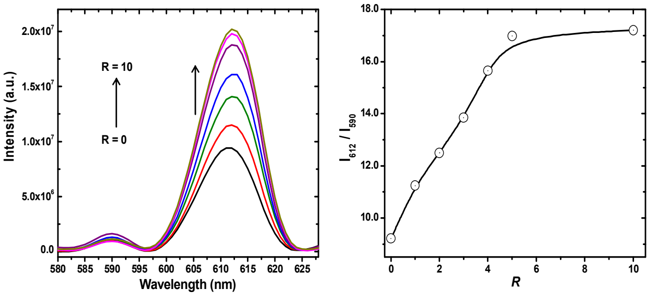

Figure 3. Emission spectra Eu(III)/nitrate in wet BumimTf$_2$N. Excitation wavelength: 395 nm. Cuvette solution: C_{Eu} = 10 mmol/L; C_{NO3} = 0.0 to 100 mmol/L. R refers to C_{NO3}/C_{Eu} in the solution.

Coordination mode of nitrate: Luminescence lifetime. In the absence of nitrate, a previous study showed that the luminescence lifetime of Eu(III) in dry BumimTf$_2$N was τ = 1.138 ms, suggesting the absence of water molecules in the primary coordination sphere of Eu(III) in dry BumimTf$_2$N.[18] In the present study, the lifetime of Eu(III) in wet BumimTf$_2$N was found to decrease as the water content of the IL increased, due to quenching of the luminescence by the water molecules in the primary coordination sphere of Eu(III). When the ratio of [H_2O]/[Eu] achieved 10 and above, the luminescence lifetime reached to a low plateau with τ = 0.105 – 0.112 ms, similar to that of Eu(III) in an aqueous medium ((0.110 ± 0.005) ms). This observation indicates that, in the absence of nitrate or other ligands, if the ratio of [H_2O]/[Eu] is above 10 in the wet BumimTf$_2$N, the Eu(III) is surrounded by the same number of water molecules as that in aqueous solutions (i.e., N_{H2O} = 9).

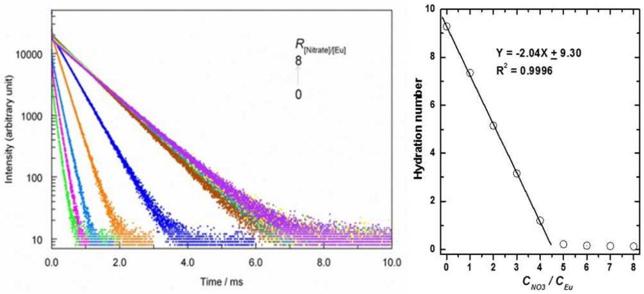

Figure 4. (left) Luminescence decay of Eu(III) in wet BumimTf$_2$N with increasing ratio of C_{NO3}/C_{Eu}; (right) Hydration number of Eu(III) as a function of C_{NO3}/C_{Eu}.

As nitrate was added into the Eu(III) solution in wet BumimTf$_2$N containing H_2O, the luminescence decay became slower as shown by Figure 4 (left plot). Parallel luminescence decay experiments with wet BumimTf$_2$N containing D_2O were also conducted. The values of lifetime (τ_{H2O} and τ_{D2O}) were calculated from the single-exponential decay function and listed in Table 2. As the data show, the lifetime in wet BumimTf$_2$N containing H_2O increased from 0.105 ms to 0.911 ms, but the lifetime in wet BumimTf$_2$N containing D_2O remained long and nearly unchanged (~ 1 ms) when the C_{NO3}/C_{Eu} ratio was increased from 0 to 8. Using equation (3) described by Horrocks and Sudnick[38] (where τ is in ms), the number of water molecules in the primary coordination sphere of Eu(III) was calculated, and shown as $N_{H2O\ (experimental)}$ in Table 2.

$$N_{H2O} = 1.05\left(\frac{1}{\tau_{H2O}} - \frac{1}{\tau_{D2O}}\right) \qquad (3)$$

Table 2. Luminescence lifetime of Eu(III) in BumimTf$_2$N containing H_2O/D_2O and the calculated number of water molecules (N_{H2O}) present in the primary coordination sphere. $[Eu(III)]_{total}$ = 0.018 mol/L; $[H_2O]_{total}$ or $[D_2O]_{total}$ = 0.27 mol/L.

$R_{nitrate/Eu}$	τ_{D2O} (ms)	τ_{H2O} (ms)	$N_{H2O\ (exp)}$	$N_{H2O\ (Cal)}$ [a]	$N_{H2O\ (Cal)}$ [b]
0	1.47	0.105	9.3	-	-
1	1.15	0.127	7.4	7.1	6.1
2	1.03	0.170	5.2	6.0	4.0
3	0.942	0.246	3.2	5.1	2.3
4	0.908	0.446	1.2	4.5	1.0
5	0.967	0.803	0.2	4.2	0.4
6	1.00	0.863	0.2	4.1	0.2
7	1.02	0.893	0.1	4.1	0.2
8	1.03	0.911	0.1	4.1	0.1

[a]: *assuming monodentate nitrate*, [b]: *assuming bidentate nitrate*

The data indicate that the number of water molecules in the primary hydration sphere of Eu(III) decreased from 9 (in the absence of nitrate) to nearly zero at C_{NO3}/C_{Eu} > 5. A plot of N_{H2O} vs. C_{NO3}/C_{Eu} shows a slope of -2.0 (Figure 4, right), suggesting that one nitrate ion replaces two water molecules. In other words, nitrate is bidentate in the binary Eu(III)/nitrate complexes and $Eu(NO_3)_4^-$ is the limiting complex (CN = 8, with no water in the primary coordination sphere) in wet BumimTf$_2$N. The results are consistent with those obtained by spectrophotometry which revealed that $Nd(NO_3)_4^-$ is the limiting complex in the same medium. The bidentate mode of nitrate in the complexes could be further validated by comparing the values of $N_{H2O\ (experimental)}$ directly obtained from the luminescence lifetime measurements, with those calculated from the speciation using the stability constants of $Eu(NO_3)_i^{(3-i)+}$ from this work assuming the nitrate is bidentate or monodentate. The comparison in Table 2 undoubtedly indicates that there is excellent agreement between the values of $N_{H2O\ (experimental)}$ and $N_{H2O\ (calculated)}$ from the assumption of bidentate nitrate. Data in the literature also show that the bidentate nitrato coordination is dominant in solid compounds such as $[Nd(NO_3)_2Cl]$[39] and $[Pr(NO_3)_2Cl_2]$.[30] EXAFS studies have also confirmed that the nitrate is bidentate in the Nd(III) complex obtained in aqueous solutions, with the two oxygen atoms at about 2.5 Å from the central metal atom.[40]

It should be pointed out that, while validating the bidentate mode of nitrate in the complexes, the luminescence lifetime data obviously demonstrate that the nitrate complexes of lanthanides in wet BumimTf$_2$N are of the "inner-sphere" type where the ligands (i.e., nitrate in this case) are in direct contact with the metal ions. Thermodynamic parameters (enthalpy and entropy of complexation) could often help to distinguish between the "inner-sphere" and "outer-sphere" complexes.[41] In aqueous solutions or wet BumimTf$_2$N containing water, inner-sphere complexation of nitrate should be accompanied by positive (endothermic) enthalpy and positive entropy because much energy is spent on dehydrate the metal cation and the ligand anion, and a significant degree of disorder is created when the water molecules are released into the bulk from the primary coordination sphere. As the data from direct calorimetric measurements show[19], the nitrate complexation with lanthanides in wet BumimTf$_2$N is indeed accompanied by positive enthalpy (endothermic) and positive entropy, consistent with the formation of inner-sphere complexes where nitrate replaces the water molecules from the primary coordination of Eu(III) ions.

Binding strength of nitrate in wet and dry BumimTf$_2$N: Solvent effect. As summarized in Table 1, the overall stability constants of Nd(III)/nitrate complexes in wet BumimTf$_2$N are several orders of magnitude lower than those observed in dry BumimTf$_2$N.[18] The difference can be best interpreted by the solvent effect on the energetics of the complexation. It has been shown that in a dry BumimTf$_2$N, in the absence of water, the metal ions are surrounded by the weakly solvating Tf$_2$N$^-$ anions of BumimTf$_2$N,[42,43] in contrast to the wet BumimTf$_2$N in which the primary coordination sphere of the metal ion contains strongly solvating H$_2$O molecules. The complexation of nitrate with lanthanides in the wet BumimTf$_2$N is weaker because the enthalpy of complexation is endothermic due to the large dehydration energy discussed in the previous section. In contrast to the aqueous solutions where nitrate is a very weak ligand for lanthanides[35], data for the wet BumimTf$_2$N from this work as well as the data for the dry BumimTf$_2$N, from previous work[18], have shown that nitrate is a remarkably strong ligand for lanthanides in BumimTf$_2$N. It could almost quantitatively replace water molecules from the primary hydration sphere of lanthanides in BumimTf$_2$N, as shown by the luminescence data discussed previously. The high binding strength of nitrate can be further manifested by Figure 5, where the absorption spectra of Nd(III) at different ratios of C_{NO3}/C_{Nd} in dry and wet BumimTf$_2$N are compared.

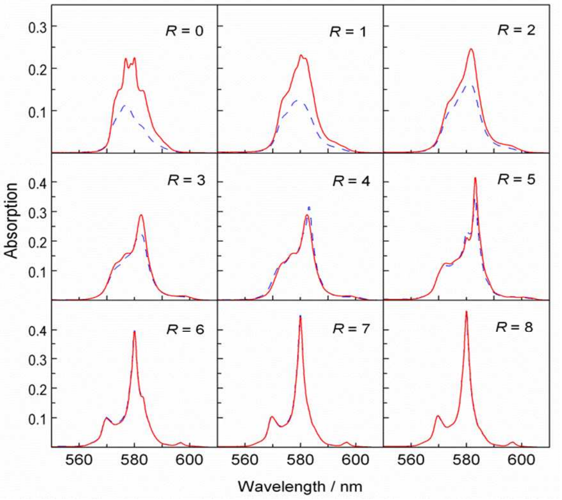

Figure 5. Comparison of the absorption spectra of Nd(III) in dry BumimTf$_2$N (solid line) and BumimTf$_2$N containing 100 mmol/L H$_2$O (dotted line) at different C_{NO3}/C_{Nd} ratios. $[Nd^{3+}]_{total}$ = 10.5 mmol/L. R refers to C_{NO3}/C_{Nd} in the solution.

As shown in Figure 5, in the absence of nitrate ($C_{NO3}/C_{Nd} = 0$), the absorption spectra of Nd(III) in dry and wet BumimTf$_2$N differ significantly, indicating that the coordination environment of Nd(III) is very different: Nd(III) is surrounded by the weakly solvating Tf$_2$N$^-$ anions in dry BumimTf$_2$N but by hydrating water molecules in wet BumimTf$_2$N. In fact, the spectra of Nd(III) in the wet BumimTf$_2$N are nearly identical to those of Nd(III) in aqueous solutions, indicating that the Nd(III) is fully hydrated in wet BumimTf$_2$N. As the C_{NO3}/C_{Nd} ratio was increased from 0 to 4, the difference in the absorption band in dry and wet BumimTf$_2$N became smaller, but was still identifiable when $C_{NO3}/C_{Nd} = 4$. The absorption bands became nearly identical when $C_{NO3}/C_{Nd} = 5$ and overlapped completely when $C_{NO3}/C_{Nd} > 5$ (Figure 5). These observations show that, in wet BumimTf$_2$N, nitrate gradually replaced the solvating water molecules of Nd(III) and the primary coordination sphere of Nd(III) in both dry and wet BumimTf$_2$N became identical as the C_{NO3}/C_{Nd} ratio was increased. In fact, the replacement of water by nitrate was nearly quantitative, because the limiting complex in wet BumimTf$_2$N, $Nd(NO_3)_4^-$, was almost achieved when $C_{NO3}/C_{Nd} = 5$. In other words, nitrate is a much stronger ligand than water in BumimTf$_2$N.

Ternary Ln(III)/nitrate/chloride complexes in wet BumimTf$_2$N

Nd(III)/nitrate/chloride complexes: Absorption spectrophotometry. To study the ternary Nd(III)/nitrate/chloride complexes, a solution of Nd(III)/nitrate in wet BumimTf$_2$N was titrated with BumimCl. The initial solution contains 15.6 mmol/L Nd(III) and 140 mmol/L nitrate ($C_{NO3}/C_{Nd} = 9$) so that the $Nd(NO_3)_4^-$ complex is dominant. Because $Nd(NO_3)_4^-$ is the limiting complex in the binary Nd(III)/nitrate system, no spectra changes should be observed as more nitrate is added. In contrast, the titration of this solution with chloride showed significant changes in the spectra, as shown in Figure 6. The intensities of the absorbance bands at 580 nm and 570 nm (that belong to $Nd(NO_3)_4^-$, see Figure 2) decreased and new bands at 580-590 nm appeared and intensified when chloride was added. The variations in the spectra clearly indicate the coordination environment of Nd(III) changed from that in $Nd(NO_3)_4^-$, implying the replacement of nitrate by chloride and the formation of ternary Nd(III)/nitrate/chloride complex(es). Various models were tested to fit the spectra and the best fit was obtained with the model containing the formation of $Nd(NO_3)_3Cl_2^{2-}$ and $Nd(NO_3)_2Cl_4^{3-}$, described by reactions (4) and (5).

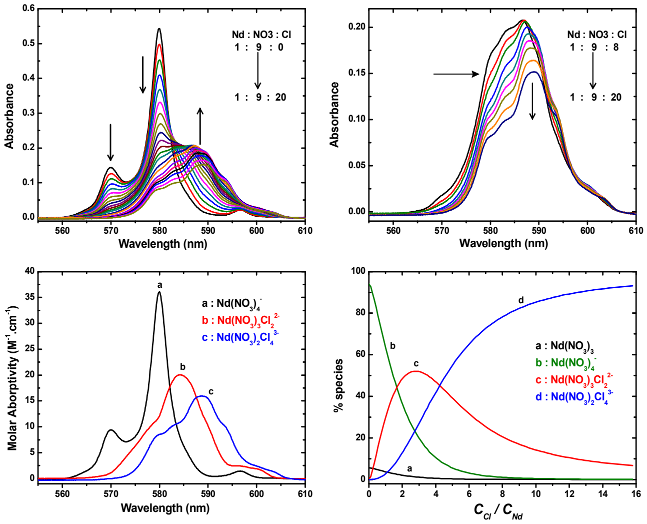

Figure 6. Spectrophotometric titration of the ternary Nd(III)/ nitrate/chloride system in wet BumimTf$_2$N (upper left); calculated molar absorptivities (lower left); an enlarged section of the titration (upper right); speciation of Nd(III) as a function of C_{Cl}/C_{Nd} (lower right). Initial cuvette solution: C_{Nd} = 15.6 mmol/L, C_{NO3} = 140 mmol/L (2.0 mL); titrant: 502 mmol/L BumimCl.

$$M^{3+} + 3NO_3^- + 2Cl^- = M(NO_3)_3(Cl)_2^{2-} \qquad (4)$$

$$M^{3+} + 2NO_3^- + 4Cl^- = M(NO_3)_2(Cl)_4^{3-} \quad (5)$$

The deconvoluted spectra of $Nd(NO_3)_4^-$, $Nd(NO_3)_3Cl_2^{2-}$, and $Nd(NO_3)_2Cl_4^{3-}$ complexes are shown in Figure 6 (lower left). In the calculation, the stability constants of the binary Nd(III)/nitrate complexes (Table 1) were all included and held constant. It seemed that the limiting ternary complex, $Nd(NO_3)_2Cl_4^{3-}$, achieved maximum at $C_{Cl}/C_{Nd} \approx 10$, beyond which little change in the spectra was observed.

Eu(III)/nitrate/chloride complexes: Luminescence spectroscopy. Luminescence titrations with Eu(III)/nitrate/chloride in wet $BumimTf_2N$ were conducted in parallel to the spectrophotometric titrations with Nd(III)/nitrate/chloride, with the objectives to validate the binding strength of the ternary complexes and provide insight into the coordination modes in these complexes. The luminescence data are shown in Figure 7. The observations could be summarized in two aspects and discussed in the following paragraphs, respectively.

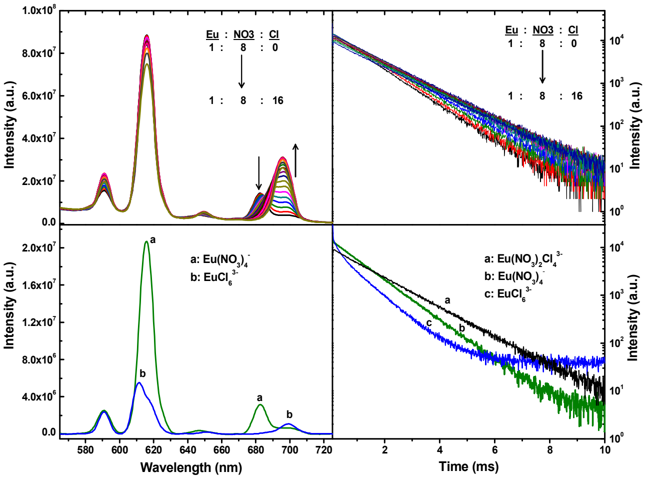

Figure 7. Emission spectra and luminescence life time of Eu(III) in wet $BumimTf_2N$. Excitation wavelength: 395 ± 5 nm; Emission wavelength: 612 ± 5 nm; Initial cuvette solution (2.0 mL): C_{Eu} = 15 mmol/L, C_{NO3} = 120 mmol/L; Titrant: 0.50 mol/L BumimCl. Individual spectrum of $EuCl_6^{3-}$ was recorded at C_{Cl}/C_{Eu} = 10:1 in the absence of nitrate.

Firstly, in contrast to the binary Eu(III)/nitrate system where significant changes were observed for the emission band at 612 nm ($^5D_0 \rightarrow {}^7F_2$) as nitrate was added, minor changes were seen for the band at 612 nm. Instead, the band at 680 - 700 nm ($^5D_0 \rightarrow {}^7F_4$) changed substantially as chloride was added (Figure 7, upper left). Using the HypSpec program, the spectra variations could be best fitted with a model comprising of ternary complexes, $Eu(NO_3)_3Cl_2^{2-}$ and $Eu(NO_3)_2Cl_4^{3-}$, described by reactions (4) and (5). The stability constants for the ternary Eu(III) complexes were in good agreement with those for corresponding Nd(III) complexes. It seems that, stepwise, two chloride anions would replace one bidentate nitrate anion. We cannot completely exclude the possibility of forming ternary complexes with other stoichiometry, such as $Eu(NO_3)_4Cl^{2-}$ where one chloride enters the coordination sphere and one nitrate becomes monodentate. However, the emission spectra did assume that only $Eu(NO_3)_3Cl_2^{2-}$ and $Eu(NO_3)_2Cl_4^{3-}$ were the most probably species that formed. The subsequent discussions on the symmetry of the complexes provide additional support for this assumption.

It is noticeable that the intensity ratio of the two transitions ($^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$), I_{612}/I_{590}, varied significantly in the binary system when Eu(III) was titrated with nitrate (Figure 3), but remained nearly unchanged when the Eu(III)/nitrate solution was titrated with chloride (Figure 7, upper left). This ratio, also referred as the "asymmetry parameter" in the literature,[44] can in fact be taken as a measure of the asymmetry of the Eu^{3+} site[45] and, in general, becomes larger as the Eu^{3+} site symmetry becomes lower and the interaction of Eu^{3+} with its neighbors becomes stronger.[44] As Figure 7 (upper left) shows, the I_{612}/I_{590} ratio in the ternary titrations with chloride was nearly unaffected even after the addition of excess chloride, implying that the symmetry of the complex around the central Eu^{3+} ions probably remained unchanged when chloride anions replaced the nitrate anions. This observation supports the previous assumption that, stepwise, two chloride anions replaced one nitrate anions and $Eu(NO_3)_3Cl_2^{2-}$ and $Eu(NO_3)_2Cl_4^{3-}$ were the most probable complexes that formed. The formation of ternary Eu(III)/nitrate/chloride complexes with other stoichiometry, e.g., $Eu(NO_3)_4Cl^{2-}$ where one nitrate would become monodentate, is less likely because it would result in significant change in the symmetry around the central Eu^{3+}, in disagreement with the observed nearly constant asymmetry parameter.

A comparison of the emission spectra of the two binary complexes, $Eu(NO_3)_4^-$ and $EuCl_6^{3-}$, in Figure 7 (lower left) also provides interesting information on the coordination symmetry and strength in these complexes. Because the intensity at 590 nm ($^5D_0 \rightarrow {}^7F_1$) is the same for all three complexes but the intensity at 612 nm ($^5D_0 \rightarrow {}^7F_2$) differ substantially, the asymmetry parameter decreases in the order: $Eu(NO_3)_4^- > EuCl_6^{3-}$. As pointed out previously, larger asymmetry parameter generally results from stronger interaction of Eu^{3+} with the surrounding ligands and lower symmetry of the Eu^{3+} site[44], data in Figure 7 (lower left) could suggest that nitrate has stronger binding strength with Eu(III) than chloride in wet $BumimTf_2N$ (although chloride could still replace nitrate at high chloride concentrations), and/or the Eu^{3+} site symmetry in $EuCl_6^{3-}$ is higher than that in $Eu(NO_3)_4^-$.

Secondly, the luminescence lifetime did not change much during the titration with chloride. The lifetimes of the initial solution ($C_{NO3}/C_{Nd}/C_{Cl}$ = 1/8/0 and $Eu(NO_3)_4^-$ is dominant), the final solution ($C_{NO3}/C_{Nd}/C_{Cl}$ = 1/8/16 and a limiting ternary $Eu(NO_3)_2Cl_4^{3-}$ complex achieved), and a separately prepared Eu(III)/chloride solution in the absence of nitrate where $EuCl_6^{3-}$ was expected to be the dominant species, were all in the vicinity of 1 ms (Figure 7, upper right), implying that no water molecules were in the primary coordination sphere of Eu(III) in these solutions. This observation indicates that the chloride anions just replaced the nitrate anions in the Eu(III) complex and no change in the hydration sphere of Eu(III) occurred. A similar phenomenon has been observed with uranyl ions in dry $BumimTf_2N$ in previous studies that showed chloride ions successfully replaced the nitrate ions from the inner coordination sphere of the uranyl cation.[25] The results from the present study have confirmed and extended the previous observations that ligands that are weak complexants in water (e.g., nitrate and chloride) could form strong complexes with metal ions (e.g., lanthanide and uranyl ions) in the ionic media.

Conclusions

Stability constants of binary Ln(III)/nitrate and ternary Ln(III)/nitrate/chloride complexes in $BumimTf_2N$ saturated with water were determined. Luminescence data helped to reveal the coordination modes and interpret the energetics of the complexation. The stability constants of binary

Ln(III)/nitrate complexes are several orders of magnitude higher than those in aqueous solution, but much lower than those observed in dry $\text{BumimTf}_2\text{N}$. This trend is attributed to the solvation effect arising from the difference in the solvation of Ln^{3+} and the ligand anions in these solvents. It has been demonstrated that both nitrate and chloride anions are strong ligands for lanthanides in $\text{BumimTf}_2\text{N}$, and, in fact, stronger than water. Stable binary Ln(III)/nitrate and ternary Ln(III)/nitrate/chloride complexes form readily in dry or wet $\text{BumimTf}_2\text{N}$. Data from this work is expected to help with the development of separation processes where ionic liquids are used in contact with aqueous solutions.

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Notes and references

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Graphical Abstract

Thermodynamic and spectroscopic data indicate that nitrate and chloride are stronger ligands than water for lanthanides in water saturated BumimTf$_2$N.