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Luminescence Properties and Water Coordination of Eu^{3+} in the Binary Solvent Mixture Water/1-Butyl-3-methylimidazolium Chloride

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The effect of relative water content on the luminescence properties and speciation of Eu^{3+} ions in solutions of $EuCl_3$ in the binary solvent mixture water/[BMI]Cl is presented, where [BMI]Cl is the ionic liquid (IL) 1-butyl-3-methylimidazolium chloride. Using luminescence techniques, the binding properties of water to Eu^{3+} are determined for samples with mole ratios of water-to-IL ranging from 0 to 5. Very little water binds to Eu^{3+} at mole ratios of water-to-IL less than 1, above which binding increases rapidly with increasing water concentration. It is shown that only certain hydration numbers for Eu^{3+} complexes are stable in the water/IL solutions. The data presented suggest that the Eu^{3+} species present are $[EuCl_x]^{3-x}$, $[EuCl_y(H_2O)_{3-4}]^{3-y}$, $[EuCl_z(H_2O)_6]^{3-z}$, and $[Eu(H_2O)_{8-9}]^{3+}$ (where $x > y > z$). Comparison of the positions of the ${}^5D_0 \leftarrow {}^7F_0$ transitions of the Eu^{3+} complexes in IL solution with those of model crystal systems provides insight into the extent of Cl^- complexation. This study suggests that [BMI]Cl is a promising medium for luminescent lanthanide (Ln) compounds due to the low-energy phonon environment of the $[LnCl_x]^{3-x}$ complex and to the fact that moderate water contamination does not result in direct binding of water to Ln^{3+}, which would result in luminescence quenching.

Introduction

Despite the wealth of literature on the use of ionic liquids (ILs) as ‘green solvents’ for organic reactions, as catalysts, and as unique solvents for IL/aqueous extractions, there are relatively few studies on the luminescence properties of trivalent lanthanide ions (Ln^{3+}) in IL.[1−9] This is surprising, because the ‘designer solvent’ qualities of IL which make them so attractive as solvents for chemical reactions and extractions also make them interesting hosts for luminescent lanthanides and lanthanide complexes. ILs can be either hydrophobic or hydrophilic, and the IL anions can be chosen to be either strongly or weakly coordinating. By using ILs with weakly coordinating anions, it is possible to study the properties of lanthanide chelates which do not exist in traditional solvents due to binding competition from solvent molecules.[5] Also, IL matrices provide low-energy phonon environments relative to many common solvents. For example, reasonably efficient NIR emission has been reported from Nd^{3+}, Er^{3+}, and Yb^{3+} in ILs.[3−5]

Most of the work to date on Ln^{3+} emission in ILs has focused on ILs with weakly coordinating anions, which form biphasic IL/aqueous systems. This is not surprising, given the interest in using ILs to extract lanthanide and actinide ions.[10] There are, however, disadvantages to using these ILs as hosts for Ln^{3+}. Although not miscible with water, these ILs do tend to be hygroscopic, and several investigators have reported that Ln^{3+} emission is quenched by even trace amounts of water.[1,5,6,8] Billard et al. have reported that solutions of Eu^{3+} in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide required degassing in order to avoid aqueous emulsions, into which the Eu^{3+} ions were

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(1) Billard, I.; Mekki, S.; Gaillard, C.; Hesemann, P.; Moutiers, G.; Mariet, C.; Labet, A.; Bünzli, J.-C. G. *Eur. J. Inorg. Chem.* **2004**, *6*, 1190.

(2) Guillet, E.; Imbert, D.; Scopelliti, R.; Bünzli, J.-C. G. *Chem. Mater.* **2004**, *16*, 4063.

(3) Driesen, K.; Nockemann, P.; Binnemans, K. *Chem. Phys. Lett.* **2004**, *395*. 306.

(4) Puntus, L.; Schenk, K. J.; Bünzli, J.-C. G. *Eur. J. Inorg. Chem.* **2005**, 4739.

(5) Arenz, S.; Babai, A.; Binnemans, K.; Driesen, K.; Giernoth, R.; Mudring, A.-V.; Nockemann, P. *Chem. Phys. Lett.* **2005**, *402*, 75.

(6) Babai, A.; Mudring, A.-V. *Chem. Mater.* **2005**, *17*, 6230.

(7) Gaillard, C.; Billard, I.; Chaumont, A.; Mekki, S.; Ouadi, A.; Denecke, M. A.; Moutiers, G.; Wipff, G. *Inorg. Chem.* **2005**, *44*, 8355.

(8) Mudring, A.-V., Babai, A.; Arenz, S.; Giernoth, R.; Binnemans, K.; Driesen, K.; Nockemann, P. *J. Alloys Compds.* **2006**, *418*, 204.

(9) Lunstroot, K.; Driesen, K.; Nockemann, P.; Görller-Walrand, C.; Binnemans, K.; Bellayer, S.; Le Bideau, J.; Vioux, A. *Chem. Mater.* **2006**, *18*, 5711.

(10) Nakashima, K.; Kubota, F.; Maruyama, T.; Goto, M. *Ind. Eng. Chem. Res.* **2005**, *44*, 4368, and references therein.

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apparently extracted.[1] This latter observation illustrates a more general concern when dealing with solutions of Ln^{3+} in non-coordinating ILs, namely, the solution state of Ln^{3+} in these systems can be tenuous and that great care must be taken to ensure that the Ln^{3+} or Ln^{3+} complex is truly solvated by the IL, rather than being present as an emulsion or suspension.

Here, we present a study of the luminescence properties of Eu^{3+} in the binary solvent mixture water/1-butyl-3-methylimidazolium chloride ([BMI]Cl). The ionic liquid [BMI]Cl has a strongly coordinating anion and is miscible with water. The effect of water content on the luminescence properties and speciation of Eu^{3+} ions in water/[BMI]Cl is examined at water-to-IL mole ratios up to 5:1. Our results show that Eu^{3+} luminescence efficiency is largely unaffected by water up to a 1:1 mole ratio of water to [BMI]Cl, above which water binding to Eu^{3+} increases rapidly with increasing water concentration. The speciation of Eu^{3+} is characterized and the hydration number associated with each species is determined for the higher-water-content solutions. Our data strongly indicate that only certain hydration numbers of Eu^{3+} are stable. This study suggests that [BMI]Cl and related ILs are promising media for luminescent lanthanide (Ln) compounds due to the low-energy phonon environment of the $[LnCl_x]^{3-x}$ complex and to the fact that moderate water contamination does not result in direct binding of water to Ln^{3+}, which would result in luminescence quenching.

Experimental Section

Sample Preparation. Anhydrous $EuCl_3$ (Acros Organics, 99.9%) and [BMI]Cl (Solvent Innovation, Lot-No. 99/603, 99.4%) were stored in a controlled-atmosphere glove box prior to use. According to the manufacturer's analysis for the specific lot used in this study, the IL contained no detectable fluoride, bromide, sulfate, or phosphate contamination. Deuterium oxide (Aldrich, 99.9 atom % D) was purchased in sealed 1 mL ampules and opened immediately prior to use.

Solutions of $EuCl_3$ in [BMI]Cl were prepared inside the glove box in an argon atmosphere by heating the IL slightly above its melting point, adding anhydrous $EuCl_3$, and stirring for ~24 h. (Although the $EuCl_3$ appeared to dissolve readily, we used the extended stirring time to ensure complete dissolution.) Prior to removal from the glove box, the clear solutions were transferred to weighed fluorescence cuvettes with septum caps. Water or deuterium oxide was added to the solution using a syringe. The amount of water or deuterium oxide added was determined by reweighing the cuvette following each addition. The initial water content of the solutions prior to D_2O or H_2O addition was determined by Karl Fischer titration (Titrando 841, Metrohm) to be ≤ 0.2 wt %.

Spectroscopic Measurements. Luminescence data were acquired using a PC-controlled system consisting of nitrogen laser/dye laser excitation (Laser Photonics models UV-12 and DL-14, respectively), a 0.46 M flat-field monochromator (Jobin-Yvon HR460), and a time-resolved photon-counting detection system consisting of a fast, red-sensitive, side-window photomultiplier (Hamamatsu R2949) and a multichannel scaler (Stanford Research SR430). The wavelengths reported here are accurate to within ±1 Å.

Samples were mounted in a thermostated cuvette holder for 65 °C (338 K) measurements. For 77 K measurements, $EuCl_3$/water/[BMI]Cl solutions were placed in 9 mm (inner diameter) Vycor ampules and quickly immersed in a liquid-nitrogen-filled optical Dewar.

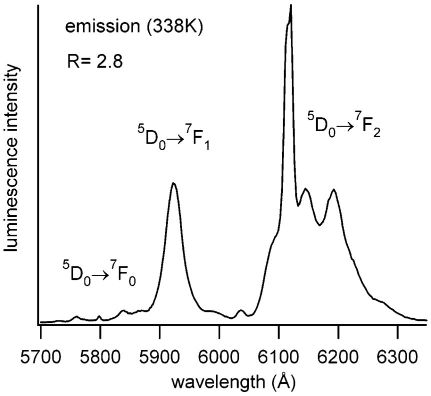

Figure 1. $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2$) emission spectrum of 0.3 mol % $EuCl_3$ in [BMI]Cl at 338 K (65 °C). The asymmetry factor, R, is the ratio of the integrated intensity of the $^5D_0 \rightarrow {}^7F_2$ transition to the $^5D_0 \rightarrow {}^7F_1$ transition. Emission was produced by laser excitation at 5263 Å. Spectral resolution is 4 Å. The spectrum is corrected for instrument response such that luminescence intensities are proportional to d(photons)/dt/dλ.

Results and Discussion

Anhydrous Solutions of $EuCl_3$ in [BMI]Cl. Figure 1 shows the $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2$) emission spectrum of an anhydrous solution of 0.3 mol % $EuCl_3$ in [BMI]Cl at 338 K (65 °C), produced by laser excitation into the $^5D_1 \leftarrow {}^7F_0$ transition at 5263 Å. The slightly elevated temperature was required to ensure that the sample remained fluid. The water content of the solution was determined by Karl Fischer titration to be ≤ 0.2 wt %. The asymmetry factor, R, which is the ratio of the integrated intensity of the $^5D_0 \rightarrow {}^7F_2$ transition to the $^5D_0 \rightarrow {}^7F_1$ transition, is 2.8. R is useful for making qualitative comparisons of Eu^{3+} site symmetry.[11] The observation of only one electronic origin in the $^5D_0 \rightarrow {}^7F_0$ region indicates that there is probably only one Eu^{3+} species present in the anhydrous solution. The fact that $R > 1$ suggests that the complex has low symmetry.

The most interesting feature of the emission spectrum is the easily discernible vibronic structure associated with the nondegenerate $^5D_0 \rightarrow {}^7F_0$ transition at 5798 Å, which is similar to that reported by Guillet et al. for 5%$EuCl_3$ in 1-dodecyl-3-methylimidazolium chloride, $[C_{12}\text{-mim}]Cl$. Figure 2 shows an expanded view of the $^5D_0 \rightarrow {}^7F_0$ emission region at 338 K (bottom spectrum) in which the symmetrical vibronic structure on either side of the electronic origin is clearly visible. The vibronic transitions are labeled according to their energy separation from the electronic origin. The assignment of these peaks as being vibronic in nature is confirmed (see Figure 2) by comparison of the 338 K emission spectrum with the 77 K $^5D_0 \rightarrow {}^7F_0$ emission spectrum (top spectrum). In the 77 K emission spectrum, the intensity of the anti-Stokes lines on the high-energy side of the origin is greatly reduced relative to 338 K, while the Stokes lines on the low-energy side of the origin retain their intensity. The 77 K $^5D_0 \leftarrow {}^7F_0$ excitation spectrum (middle spectrum) further

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[11] Kirby, A. F.; Foster, D. F.; Richardson, F. S. *Chem. Phys. Lett.* **1983**, *95*, 507.

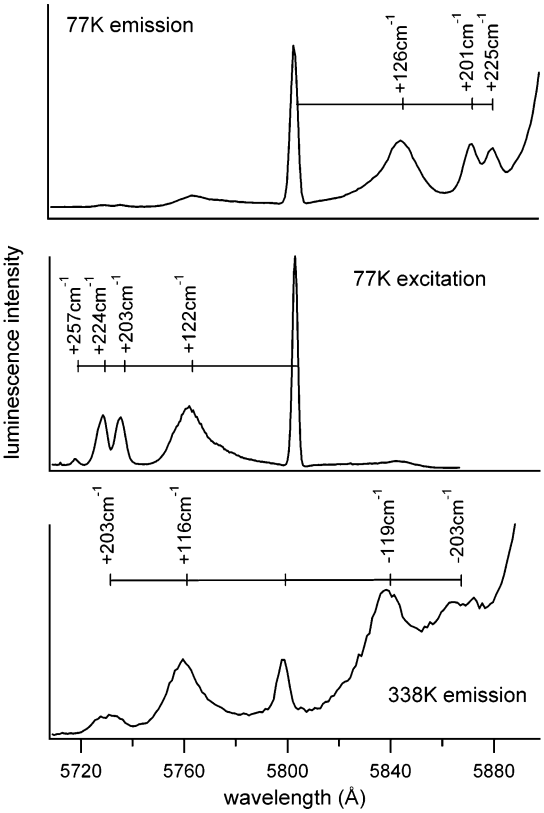

Figure 2. Comparison of the 77 and 338 K $^5D_0 \rightarrow {}^7F_0$ emission spectra and the 77 K $^5D_0 \leftarrow {}^7F_0$ excitation spectrum of 0.3 mol % $EuCl_3$ in [BMI]-Cl. The vibronic transitions associated with the pure electronic $^5D_0 \leftrightarrow {}^7F_0$ transition are labeled according to their energy separation from the electronic origin. For 77 K emission, laser excitation was at 5268 Å, and the signal integration was delayed for 500 μs following the laser pulse to avoid interference from $^5D_1$ emission. The 77 K excitation spectrum was obtained by monitoring $^5D_0 \rightarrow {}^7F_2$ emission at 6121 Å with 7 Å resolution. For the 338 K emission spectrum, laser excitation was at 5259 Å and signal integration was delayed for 20 μs following the laser pulse to avoid interference from $^5D_1$ emission. The excitation spectrum is corrected for the wavelength dependence of laser excitation intensity.

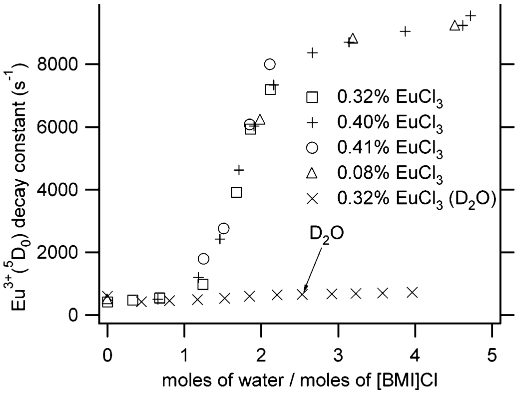

Figure 3. Dependence of the $Eu^{3+}(^5D_0)$ luminescence decay constant on mole ratio of water to [BMI]Cl for various solutions of $EuCl_3$ in water/[BMI]Cl at 338 K. The concentration of $EuCl_3$ is given as mol % relative to [BMI]Cl. The dependence of the $Eu^{3+}(^5D_0)$ luminescence decay constant on the mole ratio of D_2O to [BMI]Cl in 0.32 mol % $EuCl_3$ in D_2O/[BMI]-Cl at 338 K is shown for reference. Decay constants were obtained by fitting luminescence decay curves to an exponential function. Decay curves were produced by laser excitation at ~5263 Å, monitoring emission at 6117 Å.

supports the vibronic nature of the satellite peaks by exhibiting the 'mirror' vibronic structure of the 77 K emission spectrum, corresponding to simultaneous excitation of electronic and vibrational transitions. The vibronic structure in the emission and excitation spectra is most likely attributable to vibrational modes of the $[EuCl_x]^{3-x}$ complex in solution. The energies of the vibronics associated with the $^5D_0 \leftarrow {}^7F_0$ transition are consistent with vibrational energies observed for $[LnCl_x]^{3-x}$ complexes in lanthanide halide−alkali halide binary melts, which have a cutoff of ~260−270 cm^{-1}.[12]

$Eu^{3+}(^5D_0)$ Decay Constants: Water Complexation vs Water-to-[BMI]Cl Mole Ratio. Because the presence of water in the first coordination sphere of Eu^{3+} quenches $^5D_0$ luminescence, the $Eu^{3+}(^5D_0)$ luminescence decay constant is a direct measure of the extent of Eu^{3+}−water complexation. Unlike water, D_2O does not quench $Eu^{3+}(^5D_0)$ emission, so that the difference in the decay rate constants in H_2O and D_2O is an accurate measure of the effect of water on the $Eu^{3+}(^5D_0)$ decay constant. The $Eu^{3+}(^5D_0)$ decay constant can be quantitatively related to the number of water molecules bound to Eu^{3+}, n_{H_2O}, by the following equation:[13]

$$n_{H_2O} = (1.05 \times 10^{-3})(k_{H_2O} - k_{D_2O}) \tag{1}$$

where k_{H_2O} and k_{D_2O} are the $Eu^{3+}(^5D_0)$ luminescence decay constants (s^{-1}) measured in the presence of water and D_2O, respectively. Equation 1 is considered reliable to ±0.5 water molecules.

Figure 3 shows the dependence of the $Eu^{3+}(^5D_0)$ luminescence decay constant, k_{H_2O}, on the mole ratio of water to [BMI]Cl for various solutions of $EuCl_3$ in water/[BMI]Cl at 338 K. The dependence of the $Eu^{3+}(^5D_0)$ luminescence decay constant on D_2O content, k_{D_2O}, in 0.32 mol % $EuCl_3$ in D_2O/[BMI]Cl at 338 K is shown for reference. As discussed in the next section, it is known that multiple Eu^{3+} species exist in solution when adequate water is present. We note that $Eu^{3+}(^5D_0)$ luminescence decay curves were exponential for all samples and that the decay constants were not sensitive to the choice of excitation or emission wavelength. This indicates that the various Eu^{3+} species are in rapid equilibrium on the scale of the lifetime of $Eu^{3+}(^5D_0)$ and that the observed decay constants represent the weighted average rate constants for all species in solution.[14]

Figure 4 shows the average number of water molecules, n_{H_2O}, in the first coordination sphere of Eu^{3+} as a function of the mole ratio of water to [BMI]Cl in various solutions of $EuCl_3$ in water/[BMI]Cl at 338 K. n_{H_2O} was calculated according to eq 1 using the rate constant data in Figure 3.

Interestingly, it is clear from Figures 3 and 4 that very little direct binding of water to Eu^{3+} occurs at water-to-[BMI]-Cl molar ratios of <1. This observation suggests that each mole of [BMI]Cl effectively sequesters 1 mol of water, making it inaccessible to Eu^{3+}. In general, the solubility of water in ionic liquids appears to be determined primarily by the anion.[15] Theoretical studies on water in 1-ethyl-3-

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(12) Photiadis, G. M.; Børresen, B.; Papatheodorou, G. N. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2605.

(13) Horrocks, W. D.; Sudnick, D. R. *Acc. Chem. Res.* **1981**, *14*, 384.

(14) Horrocks, W. D.; Arkle, V. K.; Liotta, F. J.; Sudnick, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 3455.

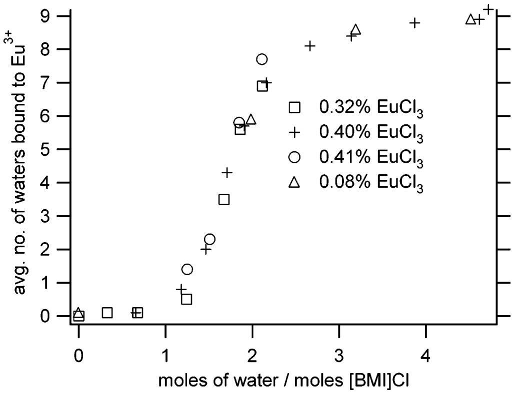

Figure 4. Average number of water molecules, $n_{\mathrm{H_2O}}$, in the first coordination sphere of Eu^{3+} as a function of the mole ratio of water to [BMI]Cl in solutions of $EuCl_3$ in water/[BMI]Cl at 338 K. $n_{\mathrm{H_2O}}$ was calculated according to eq 1 using the rate constant data in Figure 3.

methylimidalozium chloride by Wang et al.[16] and in 1,3-dimethylimidalozium chloride by Hanke et al.[17] indicate that water is solvated primarily through hydrogen-bonding interactions with the Cl^- anion. Hanke's molecular dynamics calculations describe each water molecule as being strongly hydrogen-bonded to two Cl^- ions. The quantum-mechanical-level calculations of Wang, however, show two types of complexes, $Cl^-{-}W$ and $2Cl^-{-}2W$ (W = water), both having 1:1 ratios of water to Cl^-. Moreover, X-ray structural analysis of [1-alkyl-3-methylimidazolium]Cl·H_2O single crystals show strong hydrogen-bonding interactions between the Cl^- ions and water molecules leading to the formation of an $O{-}H\cdots Cl^-$ chain.[18] Our results would certainly be consistent with a 1:1 binding ratio of water to chloride in the ionic liquid.

Above water-to-[BMI]Cl mole ratios of 1, $n_{\mathrm{H_2O}}$ increases rapidly to $n_{\mathrm{H_2O}} \approx 8$ at a water-to-[BMI]Cl mole ratio of $\sim$2.7, after which $n_{\mathrm{H_2O}}$ asymptotically approaches a value of $\sim$9. We note that $n_{\mathrm{H_2O}} \approx 9$ is the value obtained using eq 1 for the Eu^{3+} aquo complex in dilute aqueous solutions of $EuCl_3$. It is then reasonable to conclude that, at the highest water-to-[BMI]Cl mole ratios used in this study, Eu^{3+} exists primarily as the aquo complex. The preponderance of evidence in the literature indicates that the Eu^{3+} aquo complex involves an equilibrium between $n_{\mathrm{H_2O}} = 8$ and $n_{\mathrm{H_2O}} = 9$ species.[19,20] Therefore, it is possible that the asymptotic limit of $n_{\mathrm{H_2O}} \approx 9$ for the water−IL solutions shown in Figure 4 is slightly overestimated by eq 1.

Effect of Mole Ratio of Water to [BMI]Cl on Eu^{3+} Emission and Excitation Spectra at 338 K. The ${}^5D_0 \leftarrow {}^7F_0$ excitation spectrum of Eu^{3+} is useful for analyzing the coordination properties of Eu^{3+} because the nondegenerate nature of both the initial and final states ensures that each electronic origin observed in this region corresponds to a distinct Eu^{3+} species in solution.[21]

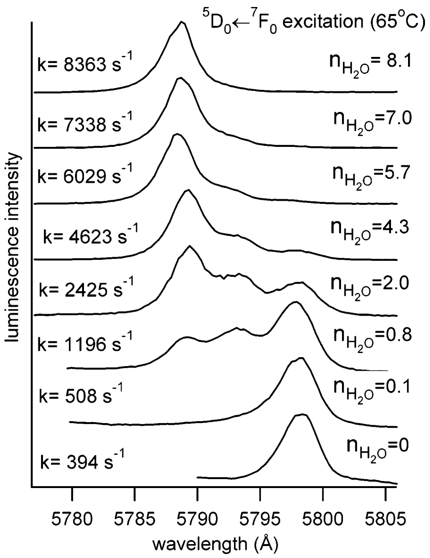

Figure 5. ${}^5D_0 \leftarrow {}^7F_0$ excitation spectra of 0.3 mol % $EuCl_3$ in water/[BMI]Cl at 338 K as a function of the mole ratio of water to [BMI]Cl. The mole ratio of water to [BMI]Cl is (top to bottom) 2.7, 2.1, 1.9, 1.7, 1.5, 1.1, 0.6, and 0. Emission was monitored at 6120 Å with 7−10 Å resolution. Decay constants, *k*, were obtained by fitting luminescence decay curves to an exponential function. Decay curves were produced by laser excitation at $\sim$5263 Å, monitoring emission at 6117 Å. The average number of water molecules, $n_{\mathrm{H_2O}}$, in the first coordination sphere of Eu^{3+} was calculated according to eq 1.

Figure 5 shows the ${}^5D_0 \leftarrow {}^7F_0$ excitation spectrum of 0.3 mol % $EuCl_3$ in water/[BMI]Cl at 338 K as a function of water content. The mole ratio of water to [BMI]Cl is (top to bottom) 2.7, 2.1, 1.9, 1.7, 1.5, 1.1, 0.6, and 0. Emission was monitored at 6120 Å with 7−10 Å resolution. The luminescence decay constant associated with each spectrum, as well as $n_{\mathrm{H_2O}}$ (calculated using eq 1), is also indicated in Figure 5.

As mentioned previously, in the dry solution (bottom spectrum) only one peak is observed (at 5798 Å), indicating the presence of only one Eu^{3+} species. The observed decay constant of 394 s^{-1} is in the range of radiative rate constants commonly observed for Eu^{3+} compounds and, therefore, indicates inefficient multiphonon relaxation. This is consistent with the low-energy phonon environment of a $[EuCl_x]^{3-x}$ complex. Guillet et al. report a luminescence decay constant of 355 s^{-1} (at RT) for 5% $EuCl_3$ in [C_{12}-mim]Cl and estimate a quantum efficiency of 61 ± 2%.[2]

As water is added to the sample, two additional peaks appear in the excitation spectrum at shorter wavelengths, 5793 and 5789 Å. It is well known that decreasing the negative charge in the first coordination sphere of Eu^{3+} tends to shift the position of the ${}^5D_0 \leftarrow {}^7F_0$ peak to shorter wavelengths.[22] The species corresponding to these additional peaks, therefore, presumably have successively fewer chloride ions in the first coordination sphere compared to the initial species. Accompanying the appearance of the additional peaks is an increase in $n_{\mathrm{H_2O}}$, as calculated using eq

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(15) Cammarata, L.; Kazarian, P. A.; Salter, P. A.; Welton, T. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192.

(16) Wang, Y.; Li, H.; Han, S. *J. Phys. Chem. B* **2006**, *110*, 24646.

(17) Hanke, C. G.; Atamas, N. A.; Lynden-Bell, R. M. *Green Chem.* **2002**, *4*, 107.

(18) Downard, A.; Earle, M. J.; Hardacre, C.; McMath, E. J.; Nieuwenhuyzen, M.; Teat, S. J. *Chem. Mater.* **2004**, *16*, 43.

(19) Helm, L.; Merbach, A. E. *Coord. Chem. Rev.* **1999**, *187*, 151.

(20) Tilkens, L.; Randall, K.; Sun, J.; Berry, M. T.; May, P. S.; Yamase, T. *J. Phys. Chem. A* **2004**, *108*, 6624, and references therein.

(21) See, for example: Choppin, G. R.; Peterman, D. R. *Coord. Chem. Rev.* **1998**, *174*, 283.

(22) Albin, M.; Horrocks, W. D. *Inorg. Chem.* **1985**, *24*, 895.

1. Our interpretation of the data is that, as water content increases, additional species appear in solution corresponding to complexes in which some of the chloride ions bonded to Eu^{3+} have been displaced by water molecules.

The position of the peak at 5789 Å, corresponding to the most hydrated complex in the spectrum, is close to that observed for the $[Eu(H_2O)_n]^{3+}$ ($n = 8-9$) aquo complex at 5787 Å.[23] However, it is unlikely that the 5789 Å peak in Figure 5 corresponds to the aquo complex. As discussed in the following section, the 5789 Å peak corresponds to a Eu^{3+} species with only ~6 waters in the first coordination sphere, compared to 8 or 9 for the aquo complex. This is not to say, however, that the aquo complex is not present in any of the samples represented in Figure 5; we have noted earlier that the aquo complex is likely to dominate at the highest water-to-[BMI]Cl mole ratios used in this study. It is simply that the $^5D_0 \leftarrow {}^7F_0$ aquo peak is not discernible in these samples. Because of the extremely low oscillator strength of the $^5D_0 \leftarrow {}^7F_0$ transition for the aquo complex, it is difficult to detect the aquo peak in the presence of other, lower-symmetry Eu^{3+} complexes. The fact that the 5789 Å peak is easily observable at $n_{H_2O} = 0.8$ (see Figure 5) would indicate that the intrinsic oscillator strength of the corresponding species is relatively high. In summary, it seems likely that this peak corresponds to a Eu^{3+} species that is not fully hydrated and has one or more chlorides still present in the first coordination sphere.

We note that excitation into any of the three $^5D_0 \leftarrow {}^7F_0$ peaks yields identical luminescence spectra and lifetimes for a given solution, which indicates that the equilibrium between the various Eu^{3+} species is fast compared to the $Eu^{3+}(^5D_0)$ lifetime.[14]

Figure 6 shows the $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2$) emission spectrum of 0.3 mol % $EuCl_3$ in water/[BMI]Cl at 338 K as a function of water content. The mole ratio of water to [BMI]Cl is (top to bottom) 3.3, 2.1, 1.7, 1.3, 0.9, and 0. The asymmetry factor, *R*, and average number of water molecules in the first coordination sphere of Eu^{3+}, n_{H_2O}, corresponding to each spectrum is indicated. Emission was produced by laser excitation into $^5D_1$ at 5263 Å. Because of the fast equilibrium between the various Eu^{3+} species in solution, each emission spectrum in Figure 6 represents a weighted sum of the emission spectra of all species in solution.[14]

Referring to Figure 6, as water is added, the average asymmetry factor, *R*, initially increases, reflecting the appearance of partially hydrated, lower-symmetry Eu^{3+} complexes in solution. As the mole ratio of water to [BMI]Cl is increased further, *R* reduces steadily due to the increasing concentration of more symmetrical, increasingly hydrated complexes, including, but not necessarily limited to, the aquo complex.

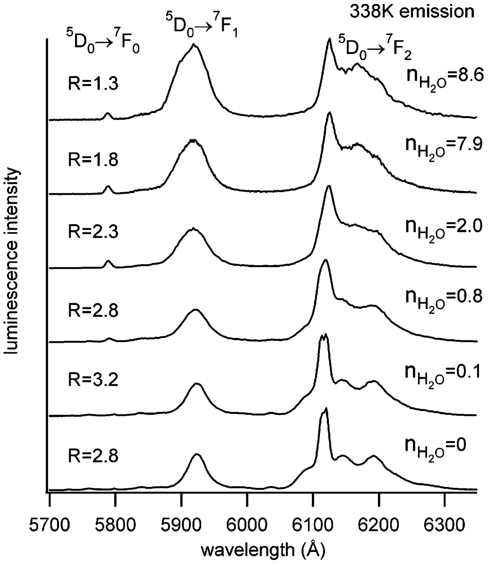

Figure 6. $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2$) emission spectrum of 0.3 mol % $EuCl_3$ in water/[BMI]Cl at 338 K as a function of water content. The mole ratio of water to [BMI]Cl is (top to bottom) 3.3, 2.1, 1.7, 1.3, 0.9, and 0. The asymmetry factor, *R*, is the ratio of the integrated intensity of the $^5D_0 \rightarrow {}^7F_2$ transition to the $^5D_0 \rightarrow {}^7F_1$ transition. Average number of water molecules, n_{H_2O}, in the first coordination sphere of Eu^{3+} was calculated according to eq 1. Emission was produced by laser excitation at 5263 Å. Spectral resolution is 5 Å. Spectra are corrected for instrument response such that luminescence intensities are proportional to d(photons)/d*t*/d*λ*.

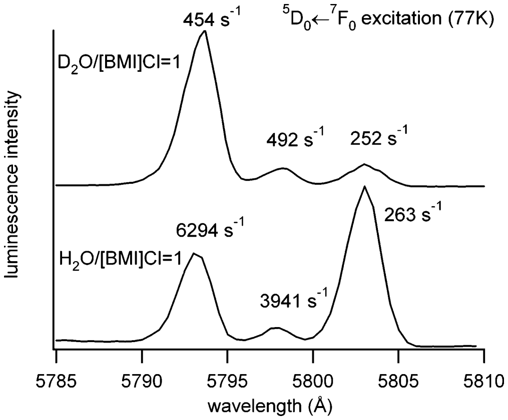

Figure 7. Comparison of the $^5D_0 \leftarrow {}^7F_0$ excitation spectra of 0.3 mol % $EuCl_3$ in D_2O/[BMI]Cl at 77 K (upper spectrum) in which the mole ratio of D_2O/[BMI]Cl is ~1 and in water/[BMI]Cl (lower spectrum) in which the mole ratio of H_2O to [BMI]Cl is ~1. Emission was monitored with the monochromator in zeroth order using a 610 nm Schott cutoff filter. The luminescence decay constant associated with each peak is given. Decay constants were obtained from luminescence decay curves generated by excitation directly into the individual $^5D_0 \leftarrow {}^7F_0$ peaks and monitoring the resulting $^5D_0 \rightarrow {}^7F_2$ emission.

Site-Selective Spectroscopy at 77 K. At 338 K, the rapid equilibrium between Eu^{3+} species in water/[BMI]Cl solutions prevents spectroscopic determination of the number of waters associated with the two partially hydrated species corresponding to the 5793 and 5789 Å peaks in the $^5D_0 \leftarrow {}^7F_0$ excitation spectrum in Figure 5. However, by cooling the solutions to 77 K, the three Eu^{3+} species visible in Figure 5 can be isolated out of equilibrium and studied individually using site-selective spectroscopy.

Figure 7 shows a comparison of the 77 K $^5D_0 \leftarrow {}^7F_0$ excitation spectra of Eu^{3+} in 1:1 D_2O/[BMI]Cl (upper spectrum) and in 1:1 H_2O/[BMI]Cl (lower spectrum). In order to observe all species present in the samples, emission was monitored with the monochromator in zeroth order using a 610 nm Schott cutoff filter. The difference in the relative

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(23) Frey, S. T.; Horrocks, W. D. *Inorg. Chim. Acta* **1995**, *229*, 383.

intensities of the $^5D_0 \leftarrow {}^7F_0$ peaks in the upper and lower spectra is due to differences in the quantum efficiencies of the hydrated species in the H_2O- and D_2O-containing samples.

The luminescence decay constant associated with each peak is also given in Figure 7. Decay constants were obtained from luminescence decay curves generated by excitation directly into the individual $^5D_0 \leftarrow {}^7F_0$ peaks and monitoring the resulting $^5D_0 \rightarrow {}^7F_2$ emission. The decay constants associated with the upper spectrum correspond to k_{D_2O}, and those with the lower spectrum to k_{H_2O}. We note that the $^5D_0 \leftarrow {}^7F_0$ peak positions at 77 K are slightly red-shifted compared to those at 338 K (see Figure 5). Red-shifting of the $^5D_0 \leftrightarrow {}^7F_0$ transition upon cooling is not uncommon[24] and is probably due to a shortening of the $Eu^{3+}-Cl^-$ bonds, which tends to increase bond covalency and reduce the splitting between the SL terms in the 4f electron configuration via the so-called 'nephelauxetic effect.'[23]

Using eq 1 and the k_{D_2O} and k_{H_2O} values shown in Figure 7, we can estimate the number of waters in the first coordination sphere for each complex in the excitation spectrum. The right-most peak at 5803 Å corresponds the anhydrous $[EuCl_x]^{3-x}$ complex, as reflected in the very similar (and low) values for k_{D_2O} and k_{H_2O} The middle peak at 5798 Å corresponds to a Eu^{3+} complex with $n_{H_2O} = 3.6$, while the left-most peak at 5793 Å corresponds to a Eu^{3+} complex with $n_{H_2O} = 6.1$. We note that the luminescence decay curves produced by exciting into the three peaks in Figure 7 can all be fit quite well to an exponential function, indicating that only one species is associated with each peak (as opposed to there being multiple unresolved species represented within a given peak). This would suggest that there is only one complex associated with the 5798 Å peak (for which $n_{H_2O} = 3.6$) and that there is, in reality, an integral number of waters, either 3 or 4, in its first coordination sphere. This result is consistent with the claimed uncertainty of ±0.5 waters using eq 1.

Note that, at high water concentrations, the average n_{H_2O} can approach a value of ∼9 (see Figure 4), while the most hydrated complex isolated in the 77 K $^5D_0 \leftarrow {}^7F_0$ excitation spectra (Figure 7) has a value of $n_{H_2O} = 6.1$. Clearly, there are Eu^{3+} species in solution for which $n_{H_2O} > 6$ that are not observable in the $^5D_0 \leftarrow {}^7F_0$ excitation spectra. As stated in the previous section, these observations are most easily explained in terms of the presence of the highly symmetrical $[Eu(H_2O)_{8-9}]^{3+}$ aquo complex, which exhibits a very weak $^5D_0 \leftarrow {}^7F_0$ transition. In summary, the four Eu^{3+} species present in the H_2O/[BMI]Cl solutions are $[EuCl_x]^{3-x}$, $[EuCl_y(H_2O)_{3-4}]^{3-y}$, $[EuCl_z(H_2O)_6]^{3-z}$, and $[Eu(H_2O)_{8-9}]^{3+}$ (where $x > y > z$).

The results outlined above lead to a very interesting conclusion; namely, water molecules do not bind to Eu^{3+} in a one-at-a-time manner as water concentration is increased. There appear to be large differences in the stabilities of Eu^{3+} complexes with different hydration numbers, which leads to only specific observable hydration numbers in solution: $n_{H_2O} = 3-4$, 6, and 8−9.

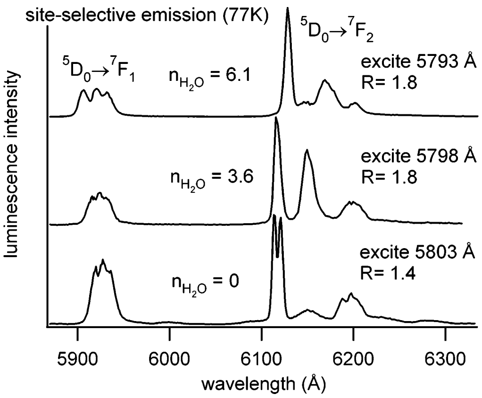

Figure 8. Site-selective 77 K emission spectra of 0.3 mol % $EuCl_3$ in D_2O/[BMI]Cl, in which the mole ratio of D_2O/[BMI]Cl is ∼1. Emission spectra were generated by excitation into each of the three $^5D_0 \leftarrow {}^7F_0$ peaks shown in Figure 7. The asymmetry factor, *R*, is the ratio of the integrated intensity of the $^5D_0 \rightarrow {}^7F_2$ transition to the $^5D_0 \rightarrow {}^7F_1$ transition. The number of water molecules in the first coordination sphere of Eu^{3+}, n_{H_2O}, is calculated using eq 1.

One final observation of interest regarding the 77 K $^5D_0 \leftarrow {}^7F_0$ excitation spectra is that, while prominent $^5D_0 \leftarrow {}^7F_0$ vibronic structure is associated with the anhydrous $[EuCl_x]^{3-x}$ complex (see Figure 2), we see no evidence of $^5D_0 \leftarrow {}^7F_0$ vibronic structure associated with the $[EuCl_y(H_2O)_{3-4}]^{3-y}$ and $[EuCl_z(H_2O)_6]^{3-z}$ complexes.

Figure 8 shows the site-selective 77 K $^5D_0 \rightarrow {}^7F_J$ ($J = 1$, 2) emission spectra of $[EuCl_x]^{3-x}$ (bottom), $[EuCl_y(H_2O)_{3-4}]^{3-y}$ (middle), and $[EuCl_z(H_2O)_6]^{3-z}$ (top) in a 1:1 D_2O/[BMI]Cl solution. Emission spectra were generated by excitation into each of the three $^5D_0 \leftarrow {}^7F_0$ peaks shown in Figure 7. The values of *R* and n_{H_2O} associated with each spectrum is also given. Note that the asymmetry factor, *R*, for the anhydrous $[EuCl_x]^{3-x}$ complex (bottom spectrum) at 77 K is much lower compared to its 338 K value: $R = 1.4$ at 77 K vs $R = 2.8$ at 338 K (see Figure 1). The lowering of the *R* factor upon cooling is probably at least partially due to the loss of vibronic intensity in the $^5D_0 \rightarrow {}^7F_2$ emission.

Correlation of $^5D_0 \leftarrow {}^7F_0$ Excitation Spectra with $Eu^{3+}-Cl^-$ Complexation. On the basis of the $Eu^{3+}(^5D_0)$ luminescence lifetime data and 77 K site-selective spectroscopy, we are able to estimate the hydration numbers associated with each complex in solution. However, we have not yet discussed what our data tell us about the Cl^- coordination for the various Eu^{3+} complexes we have identified.

As noted previously, the position of the $^5D_0 \leftrightarrow {}^7F_0$ transition is influenced by the Eu^{3+} coordination environment. Although an empirical model has been presented that correlates the $^5D_0 \leftrightarrow {}^7F_0$ transition with total negative charge in the first coordination sphere,[22] it appears that the effect is most probably due to covalent interactions between Eu^{3+} and its ligands.[23] As covalency is increased, the transition shifts to lower energies.

In practice, it is difficult to deduce the exact nature of the coordination environment on the basis of the position of the $^5D_0 \leftrightarrow {}^7F_0$ transition. This position is dependent not only on

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[24] See, for example: (a) Xiao, L. S.; Lang, M.; May, P. S. *J. Phys. Chem. A* **2000**, *104*, 209. (b) Berry, M. T.; May, P. S.; Xu, H. *J. Phys. Chem.* **1996**, *100*, 9216.

the chemical identity of the ligands but is also quite sensitive to Eu^{3+}–ligand bond distances, which, in turn, are affected by the overall coordination environment.[23] Still, we can gain some insight into the extent of chloride complexation by comparing the peak positions observed in our 338 K $^5D_0 \leftarrow {}^7F_0$ excitation spectra (Figure 5) with appropriate model compounds for which the structure is known.

With regard to the anhydrous $[EuCl_x]^{3-x}$ complex, the literature contains both experimental and theoretical results that might lead one to suspect $[EuCl_6]^{3-}$ as a likely candidate. Raman spectra of molten YCl_3–ACl (A = Cs, K, Li) mixtures indicate the presence of $[YCl_6]^{3-}$.[25] Similar results were obtained from Raman studies on melts of $NdCl_3$–ACl (A = Li, Na, K, Cs).[12] Neutron diffraction data on molten MCl_3 (M = Tb, Y, Ho, Er) indicate the presence of $[YCl_6]^{3-}$.[26] Also, single crystals of tris(1-ethyl-3-methylimidazolium) hexachlorolanthanate, $[EMI]_3[LaCl_6]$, have been grown from solutions of $LaCl_3$ in the IL [EMI]Cl–$AlCl_3$.[27] However, the vacuum-corrected position of the $^5D_0 \leftarrow {}^7F_0$ transition for the anhydrous $[EuCl_x]^{3-x}$ complex in [BMI]Cl at 338 K is 17 242 cm^{-1}. This transition occurs at significantly higher energy than that observed for $[EuCl_6]^{3-}$moieties in the crystal systems 0.1%Eu/$CsMgCl_3$ (17 203 cm^{-1}),[24a] 1%Eu/$CsNaYCl_6$ (17 212 cm^{-1}),[28] and $CsNaEuCl_6$ (17 208 cm^{-1}).[29] On the basis of this comparison, it seems unlikely that the anhydrous moiety in the ionic liquid is $[EuCl_6]^{3-}$, *unless the Eu^{3+}–Cl^- bond lengths are significantly longer than in the model crystal systems*.

Chaumont and Wipff have published molecular dynamics studies of the solvation of Eu^{3+} and its chloro complexes in $[BMI]PF_6$ and $[EMI]AlCl_4$ and have noted the importance of the metal hexachloro complex.[30,31] However, they report that the stability of this complex in the IL is due not to its intrinsic stability but to solvation forces.[31] If the anhydrous species in [BMI]Cl is not $[EuCl_6]^{3-}$, it is probably due to the different solvation forces in [BMI]Cl compared to the systems discussed above.

Because the $^5D_0 \leftarrow {}^7F_0$ transition is blue-shifted relative to our hexachloro model systems, it is tempting to infer that there are fewer than six chlorides inside the first coordination sphere of $[EuCl_x]^{3-x}$. However, coordination numbers >6 could also result in a blue-shift of the $^5D_0 \leftarrow {}^7F_0$ transition relative to the hexachloro complex if the increased coordination number results an expansion of the $[EuCl_x]^{3-x}$ complex, which would then reduce the covalent character of the Eu^{3+}–Cl^- bonds. For example, in anhydrous $EuCl_3$, in which the Eu^{3+} coordination sphere contains nine Cl^- ions,[32] the $^5D_0 \leftarrow {}^7F_0$ transition energy is 17 258 cm^{-1},[33] which is significantly blue-shifted relative to our model hexachloro compounds.

The vacuum-corrected position of the $^5D_0 \leftarrow {}^7F_0$ transition for the hexahydrate complex, $[EuCl_z(H_2O)_6]^{3-z}$, in water/[BMI]Cl at 338 K is 17 268 cm^{-1}. This transition energy is only slightly higher than the value of 17 263 cm^{-1} observed for the hexahydrate complex $[EuCl_2(H_2O)_6]^+$ in crystalline $EuCl_3 \cdot 6H_2O$.[22,23] This would be consistent with either one or two chlorides in the inner coordination sphere of the hexahydrate complex, $[EuCl_z(H_2O)_6]^{3-z}$ (i.e., $z = 1-2$).

Conclusion

Our study of the effect of water content on the luminescence properties and speciation of Eu^{3+} ions in solutions of $EuCl_3$ in water/[BMI]Cl has yielded several interesting and notable results. First, there is essentially no direct binding of water to Eu^{3+} up to a 1:1 mole ratio of water to [BMI]Cl, so that Eu^{3+} emission remains efficient even at relatively high levels of water content. It seems logical to view this behavior in terms of the IL matrix sequestering the water, making it unavailable for binding to Eu^{3+}. This result is in stark contrast with the reported behavior of Eu^{3+} luminescence in $[BMI]Tf_2N$ (Tf_2N = bis(trifluormethylsulfonyl)-imide) which shows high sensitivity to even trace amounts of water.[1] $[BMI]Tf_2N$ forms biphasic systems with aqueous solutions and has non-coordinating anions. In these systems, water is not as strongly solvated by the non-coordinating anions of the IL, and the relative affinity of added water for Eu^{3+} is apparently quite high. Therefore, although [BMI]Cl is not suitable for metal-ion separations (due to its miscibility with water), it is a very attractive matrix for Ln^{3+} ion luminescence due to its high tolerance of moisture content and to the low-energy phonon environment within the $[LnCl_x]^{3-x}$ complex. In fact, depending on the application, some moisture may be desirable, since we have observed that the melting point drops below room temperature at water content levels far below 1:1 water/[BMI]Cl.

As water content increases, we conclude that there are most probably four Eu^{3+} species in solution, which are in rapid equilibrium at 338 K. The Eu^{3+} species present are $[EuCl_x]^{3-x}$, $[EuCl_y(H_2O)_{3-4}]^{3-y}$, $[EuCl_z(H_2O)_6]^{3-z}$, and $[Eu(H_2O)_{8-9}]^{3+}$ (where $x > y > z$). The strong preference for only certain hydration numbers in the Eu^{3+} complex is very interesting and implies large stability differences between the possible Eu^{3+} coordination environments in solution.

Although it is not possible, based on our data, to accurately assess the nature or extent of chloride complexation in the various Eu^{3+} species, the position of the $^5D_0 \leftarrow {}^7F_0$ transition for the $[EuCl_z(H_2O)_6]^{3-z}$ hexahydrate complex is consistent with $z = 1-2$. The position of the $^5D_0 \leftarrow {}^7F_0$ transition for the anhydrous $[EuCl_x]^{3-x}$ moiety is not consistent with a hexachloro complex, but we are unable to draw further conclusions as to the extent of chloride binding with any

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(25) Papatheodorou, G. N. *J. Chem. Phys.* **1977**, *66*, 2893.

(26) Wasse, J. C.; Salmon, P. S. *J. Phys.: Condens. Matter* **1999**, *11*, 9293.

(27) Matsumoto, K.; Tsuda, T.; Nohira, T.; Hagiwara, R.; Ito, Y.; Tamada, O. *Acta Crystallogr. C* **2002**, *58*, m186.

(28) Moran, D. M.; May, P. S.; Richardson, F. S. *Chem. Phys.* **1994**, *186*, 77.

(29) Tanner, P. A.; Liu, Y.-L.; Chua, M.; Reid, M. F. *J. Alloys Compds.* **1994**, *207–208*, 83.

(30) Chaumont, A.; Wipff, G. *J. Phys. Chem. B* **2004**, *108*, 3311.

(31) Chaumont, A.; Wipff, G. *Inorg. Chem.* **2004**, *43*, 5891.

(32) Morosin, B. *J. Chem. Phys.* **1968**, *49*, 3007.

(33) Chen, G.; Stump, N. A.; Haire, R. G.; Peterson, J. R. *Appl. Spectrosc.* **1992**, *46*, 1198.

(34) Hardacre, C. *Annu. Rev. Mater. Res.* **2005**, *35*, 29.

confidence. We are currently planning EXAFS studies to determine the nature of chloride binding in the chloride-containing complexes.[34]

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Supporting Information Available: Tables of rate constants and water/IL ratios used to generate Figures 3 and 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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