

Characterization of Uranyl(VI) Nitrate Complexes in a Room Temperature Ionic Liquid Using Attenuated Total Reflection-Fourier Transform Infrared Spectrometry

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Received June 15, 2010

Room temperature ionic liquids form potentially important solvents in novel nuclear waste reprocessing methods, and the solvation, speciation, and complexation behaviors of actinides and lanthanides in room temperature ionic liquids is of current interest. In this study, the coordination environment of uranyl(VI) in solutions of the room temperature ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide containing either tetrabutylammonium nitrate or nitric acid was characterized using attenuated total reflection-Fourier transform infrared spectrometry. Both $\text{UO}_2(\text{NO}_3)_2$ and $\text{UO}_2(\text{NO}_3)_3^-$ species were detected in solutions containing tetrabutylammonium nitrate. $\nu_{\text{as}}(\text{UO}_2)$ for these two species were found to lie at 951 and 944 cm^{-1} , respectively, while $\nu_{\text{as}}(\text{UO}_2)$ arising from uranyl(VI) coordinated by bis(trifluoromethylsulfonyl)imide anions in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide was found to lie at 968 cm^{-1} . In solutions containing nitric acid, only $\text{UO}_2(\text{NO}_3)_2$ was detected, due to the high water content. The $\text{UO}_2(\text{NO}_3)^+$ species was not detected under the conditions used in this study. From the results shown here, we conclude that infrared spectroscopy forms a valuable addition to the suite of tools currently used to study the chemical behavior of uranyl(VI) in room temperature ionic liquids.

Introduction

Reprocessing of spent nuclear fuel with recycling of fissile isotopes is necessary to optimize energy extraction from actinide resources and to minimize waste product production. A number of solvent extraction processes have been used in order to separate plutonium and uranium from fission products in spent nuclear fuel, with the most widely used process being the plutonium and uranium recovery by extraction (PUREX) process.¹ In the PUREX process, tri-*n*-butylphosphate (TBP) is dissolved in a paraffinic hydrocarbon and used to extract uranium and plutonium from nitric acid solutions, thus allowing the recovery of these elements from fission products.² This technique requires the use of potentially hazardous organic solvents with relatively high disposal costs. Separations processes that can safely and effectively separate the useful components of discharged nuclear fuel from the wastes, while dramatically reducing their volume and toxicity, are currently being developed.^{3,4} A new three-step extraction technique for the extraction of actinides and lanthanides from a solid or an aqueous phase

into a room temperature ionic liquid (RTIL) phase and then from the RTIL phase into a supercritical CO_2 (sc- CO_2) phase has been proposed as an alternative “green” technology for nuclear waste treatment, because the physical and chemical properties of RTILs and sc- CO_2 make them attractive replacements for volatile organic solvents.^{3,4} New, greener separations methods are needed to help improve public acceptance of nuclear power.

Extractions of actinides and lanthanides into RTILs and sc- CO_2 are still in the initial stages of development and little is known about the extraction mechanisms at work in these solvents. In order to gain insight into extraction mechanisms and optimize extraction efficiencies for the different radionuclide species, it is important to understand the solvation, speciation, and complexation behaviors of actinides and lanthanides in RTILs, sc- CO_2 , and RTIL/sc- CO_2 mixtures. While the chemistry of actinides and lanthanides in sc- CO_2 has been little studied, there is currently a great deal of interest in the speciation and coordination chemistry of actinides and lanthanides in RTIL, and several review articles have recently been published on this topic.^{5–7} To date, the bulk of the spectroscopic studies on uranium complexes in RTIL has been completed using UV–visible spectrophotometry and/or extended X-ray absorption fine structure (EXAFS) spectroscopy. However, vibrational spectroscopy

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(1) Choppin, G. R. *Solvent Extr. Res. Dev., Jpn.* **2005**, *12*, 1.
(2) McKibben, J. M. *Radiochim. Acta* **1984**, *36*, 3.
(3) Mekki, S.; Wai, C. M.; Billard, I.; Moutiers, G.; Burt, J.; Yoon, B.; Wang, J. S.; Gaillard, C.; Ouadi, A.; Heseemann, P. *Chem.—Eur. J.* **2006**, *12*, 1760.
(4) Wang, J. S.; Sheaff, C. N.; Yoon, B.; Addleman, R. S.; Wai, C. M. *Chem.—Eur. J.* **2009**, *15*, 4458.

(5) Cocalia, V. A.; Gutowski, K. E.; Rogers, R. D. *Coord. Chem. Rev.* **2006**, *250*, 755.
(6) Binnemans, K. *Chem. Rev.* **2007**, *107*, 2592.
(7) Billard, I.; Gaillard, C. *Radiochim. Acta* **2009**, *97*, 355.

can also provide important information regarding uranyl(VI) complexation and coordination in solution and has been extensively used for that purpose.^{8–16} The Raman active $\nu_s(\text{UO}_2)$ mode and the infrared active $\nu_{as}(\text{UO}_2)$ mode are sensitive to changes in the uranyl(VI) coordination environment. Complexation of uranyl(VI) weakens the O=U=O bonds, causing $\nu_s(\text{UO}_2)$ and $\nu_{as}(\text{UO}_2)$ to shift to lower wavenumbers. The extent of this shift can be correlated to the complex formed and can be used to track uranyl(VI) speciation in solution. In this study, we use attenuated total reflection-Fourier transform infrared spectrometry to characterize the complexes formed in solutions of the RTIL 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][Tf₂N]) containing uranyl(VI) and either tetrabutylammonium nitrate (TBAN) or HNO₃.

Experimental Section

Chemicals and Reagents. Uranium trioxide, UO₃, and uranyl nitrate hexahydrate, UO₂(NO₃)₂·6H₂O, were purchased from International Bio-Analytical Industries, Inc. (Boca Raton, FL). Concentrated nitric acid (70% w/w), tri-*n*-butylphosphate (TBP), 1-butyl-3-methylimidazolium chloride, [BMIM]Cl, and lithium bis(trifluoromethane) sulfonimide, [LiN(CF₃SO₂)₂] were purchased from Sigma-Aldrich (Milwaukee, WI). Acetonitrile and methylene chloride were purchased from Fisher Scientific (Pittsburgh, PA). Toluene was purchased from EMD Chemicals Inc. (Gibbstown, NJ). Deuterated chloroform (99.8% D) and D₂O (99.9% D) were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA).

Instruments. A Bruker Avance 500 MHz NMR spectrometer was used to check the purity and water content of [BMIM][Tf₂N] after synthesis. Absorption spectra were acquired using a model 440 UV–visible spectrophotometer with a CCD array detector (Spectral Instruments Inc., Tucson AZ). ATR-FTIR spectra were acquired using a Nicolet Magna 760 FTIR spectrometer equipped with a DTGS detector. ATR-FTIR measurements were made with a SplitPea attenuated total reflection accessory (Harrick Scientific Corporation). A silicon internal reflection element was used as a reflection medium. Silicon is relatively inert and resistant to corrosive materials, while zinc selenide is not compatible with acids and strong bases, and germanium is soluble in nitric acid. ATR-FTIR spectra were acquired using 500 coadded scans at 2 cm⁻¹ resolution with Happ–Genzel apodization. A single-beam reference spectrum of the silicon ATR internal reflection element was acquired at the start of each experiment, and each single-beam sample spectrum collected was ratioed against this background reference spectrum. Spectra were not otherwise corrected. Each sample spectrum required ~17 min to collect.

Synthesis of 1-Butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide [BMIM][Tf₂N]. [BMIM][Tf₂N] was synthesized from the metathesis of [BMIM]Cl and [LiN(CF₃SO₂)₂] following an established literature procedure.³ The resulting ionic liquid was washed and extracted with dichloromethane and deionized water.

The excess dichloromethane was removed by evaporation under reduced pressure using a rotary evaporator. The sample was left under vacuum overnight at 68 °C to remove excess water. The purity and water content of the ionic liquid were evaluated using ¹H NMR, and the chloride content was determined by neutron activation analysis at the Washington State University (Pullman, WA) Nuclear Radiation Center. The water concentration was determined as follows: a known volume and mass of [BMIM][Tf₂N] was placed in a 5 mm diameter NMR tube. An insert containing 66 μL of 99.9% D₂O was placed in the NMR tube with the sample, and a ¹H NMR spectrum was acquired. Residual HDO (chemical shift 4.74 ppm) arising from the D₂O in the insert was used as a reference. Water in the [BMIM][Tf₂N] sample gave rise to a ¹H NMR signal at 2.38 ppm. This signal (*I*_{H₂O}) was integrated and compared to the integrated signal of a butyl chain CH₂ proton triplet (*I*_{CH₂}, 1.8 ppm). The number of water protons (*n*_{H₂O}) could be calculated using the relationship $n_{\text{H}_2\text{O}}/n_{\text{CH}_2} = I_{\text{H}_2\text{O}}/I_{\text{CH}_2}$. The number of protons giving rise to the CH₂ proton triplet (*n*_{CH₂}) was calculated using the sample mass and molecular weight, and, since the sample volume was also known, the concentration of water in the sample could be determined. The concentration of water in the final product was 10 mM, while the chloride concentration was 0.008 mM.

Synthesis of Uranyl(VI) Bis(trifluoromethylsulfonyl)imide. Uranyl(VI) bis(trifluoromethylsulfonyl)imide (UO₂(Tf₂N)₂·*x*H₂O) was synthesized according to the method of Nockemann et al.¹⁷ The synthesis began with the conversion of lithium bis(trifluoromethylsulfonyl)imide (2 M) into the corresponding acid, H(Tf₂N), with the addition of excess 20% H₂SO₄. In the process of converting the salt into an acid, lithium sulfate was produced. The desired acid was extracted with diethyl ether and washed with water to remove trace amounts of lithium sulfate. Evaporation of diethyl ether under reduced pressure using a rotary evaporator gave H(Tf₂N). In the next step, uranium(VI) oxide (0.023 mol) was suspended in water in a round-bottom flask, and a small excess of H(Tf₂N) (0.033 mol) was added. This mixture was allowed to react for 3 days at 50 °C with stirring, following which the temperature was increased to 75 °C for an additional 24 h. Water was removed under reduced pressure, and a viscous yellow product was obtained. This product was washed with dichloromethane to remove unreacted H(Tf₂N), then dissolved in methanol, and stirred for 1 h. Unreacted UO₃ was filtered off, giving a clear yellow solution. Excess methanol was removed under reduced pressure using a rotary evaporator, leaving a viscous dark yellow substance. The sample was left under vacuum overnight for further solvent removal. The final product was stored in a desiccator.

Sample Preparation. Samples were prepared by dissolving uranyl(VI) nitrate hexahydrate and uranyl(VI) bis(trifluoromethylsulfonyl)imide in [BMIM][Tf₂N] to a final concentration of 0.1 M. Nitrate was added in the form of TBAN or concentrated HNO₃. Nitrate concentrations ranged from 0.05 to 0.5 M in [BMIM][Tf₂N]. The samples were sonicated to completely homogenize all solutes in the ionic liquid. A small droplet of sample was placed directly on the silicon internal reflection element prior to analysis by ATR-FTIR. Samples were exposed to the atmosphere during analysis. In order to evaluate the extent of water uptake from the atmosphere, a sample of [BMIM][Tf₂N] was placed on the internal reflection element, and water $\nu_s(\text{OH})$ modes at 3636 and 3565 cm⁻¹ were monitored over the course of 17 min, the time required to collect a typical spectrum. No increase was seen in the intensities of these modes during this time, indicating little water is absorbed from the atmosphere during spectral acquisition under our laboratory conditions.

(8) Brooker, M. H.; Huang, C.-H.; Sylwestrowicz, J. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1431.

(9) Toth, L. M.; Begun, G. M. *J. Phys. Chem.* **1981**, *85*, 547.

(10) Gal, M.; Goggin, P. L.; Mink, J. *Spectrochim. Acta* **1992**, *48A*, 121.

(11) Nguyen-Trung, C.; Begun, G. M.; Palmer, D. A. *Inorg. Chem.* **1992**, *31*, 5280.

(12) Quiles, F.; Burneau, A. *Vib. Spectrosc.* **1998**, *18*, 61.

(13) Quiles, F.; Burneau, A. *Vib. Spectrosc.* **2000**, *23*, 231.

(14) Nguyen-Trung, C.; Palmer, D. A.; Begun, G. M.; Peiffert, C.; Mesmer, R. E. *J. Solution Chem.* **2000**, *29*, 101.

(15) Pasilis, S. P.; Pemberton, J. E. *Inorg. Chem.* **2003**, *42*, 6793.

(16) Muller, K.; Brendler, V.; Foerstendorf, H. *Inorg. Chem.* **2008**, *47*, 10127.

(17) Nockemann, P.; Servaes, K.; Van Deun, R.; Van Hecke, K.; Van Meervelt, L.; Binnemans, K.; Goerller-Walrand, C. *Inorg. Chem.* **2007**, *46*, 11335.

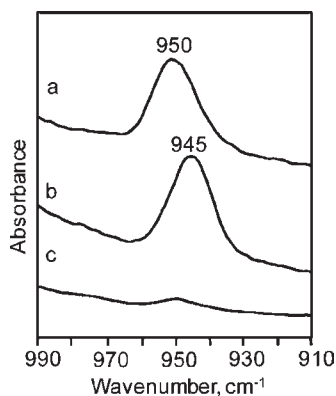


Figure 1. ATR-FTIR spectra showing the $\nu_{\text{as}}(\text{UO}_2)$ region for solutions of [BMIM][Tf₂N] containing (a) 0.1 M UO₂(NO₃)₂·6H₂O, (b) 0.1 M UO₂(NO₃)₂·6H₂O with 0.1 M TBAN, and (c) 0.1 M TBAN.

Results and Discussion

The effect of changing uranyl(VI) coordination environment on $\nu_{\text{as}}(\text{UO}_2)$ is illustrated in the infrared spectra shown in Figure 1a,b. Figure 1a shows a spectrum acquired from a solution of 0.1 M uranyl nitrate hexahydrate dissolved in [BMIM][Tf₂N], while Figure 1b shows a spectrum acquired from a 0.1 M solution of uranyl nitrate hexahydrate in [BMIM][Tf₂N] to which 0.1 M TBAN had been added. Figure 1c shows a spectrum acquired from a 0.1 M solution of TBAN. TBAN does not have any significant vibrational modes in the $\nu_{\text{as}}(\text{UO}_2)$ region. When uranyl nitrate hexahydrate is dissolved in [BMIM][Tf₂N], a complex is formed having $\nu_{\text{as}}(\text{UO}_2)$ at 950 cm⁻¹, as shown in Figure 1a. With the addition of nitrate in the form of TBAN, such that the total concentration of nitrate in solution is 0.3 M, the uranyl(VI) coordination environment is changed and $\nu_{\text{as}}(\text{UO}_2)$ is shifted to 945 cm⁻¹ (Figure 1b). Previous work using UV–visible spectrophotometry and EXAFS to examine uranyl(VI) nitrate complexes formed in RTIL has indicated that the major species are UO₂(NO₃)⁺, UO₂(NO₃)₂, and UO₂(NO₃)₃⁻.^{17–20} Servaes et al.¹⁹ and Georg et al.²⁰ have shown that UO₂(NO₃)₃⁻ is the major species in RTIL solutions when nitrate is present in excess. Thus, we assign the mode at 945 cm⁻¹ (Figure 1b) to UO₂(NO₃)₃⁻. The mode at 950 cm⁻¹ can then be assigned to the dinitrato complex, UO₂(NO₃)₂ (Figure 1a). The formation of the two uranyl(VI) nitrate complexes may also be followed through the growth of a $\nu(\text{NO})$ mode at 1537 cm⁻¹ (Figure 2a,b). This mode is diagnostic for nitrate that is coordinated to a metal ion²¹ and offers further evidence that nitrate forms a complex with uranyl(VI) in [BMIM][Tf₂N]. The $\nu(\text{NO})$ mode increases in intensity when TBAN is added to the solution (Figure 2b). Figure 2c simply shows a solution of [BMIM][Tf₂N] to which TBAN has been added. TBAN does not have vibrational modes in the $\nu(\text{NO})$ region.

To more easily detect any uranyl(VI) nitrate complexes formed, UO₂(Tf₂N)₂ was used as a source of uranyl(VI). The

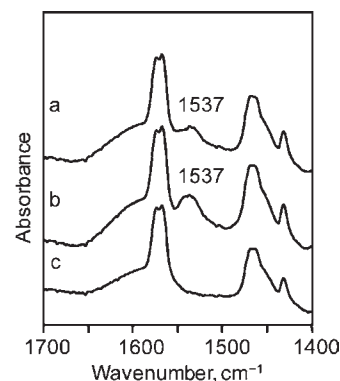


Figure 2. ATR-FTIR spectra showing the $\nu(\text{NO})$ region for solutions of [BMIM][Tf₂N] containing (a) 0.1 M UO₂(NO₃)₂·6H₂O, (b) 0.1 M UO₂(NO₃)₂·6H₂O with 0.1 M TBAN, and (c) 0.1 M TBAN.

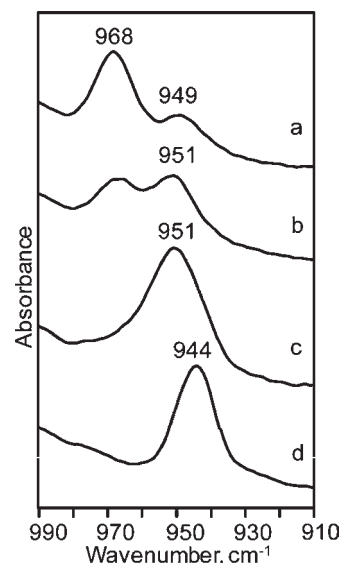


Figure 3. ATR-FTIR spectra showing the $\nu_{\text{as}}(\text{UO}_2)$ region for solutions of 0.1 M UO₂(Tf₂N)₂ in [BMIM][Tf₂N] containing (a) no TBAN, (b) 0.1 M TBAN, (c) 0.2 M TBAN, and (d) 0.3 M TBAN.

bis(trifluoromethylsulfonyl)imide anion is easily displaced by nitrate.^{18,20} In order to track uranyl(VI) speciation in the presence of nitrate, the molar ratio of uranyl(VI) to TBAN was systematically varied and the infrared spectra acquired. The spectra are shown in Figure 3a–d. When UO₂(Tf₂N)₂ is dissolved in [BMIM][Tf₂N], the $\nu_{\text{as}}(\text{UO}_2)$ mode appears at 968 cm⁻¹ (Figure 3a). This mode can be assigned to uranyl(VI) coordinated by Tf₂N⁻ anions. A small peak at ~950 cm⁻¹ arises from [BMIM][Tf₂N]. With the addition of 0.1 M TBAN, the $\nu_{\text{as}}(\text{UO}_2)$ mode at 968 cm⁻¹ decreases in intensity, while a new $\nu_{\text{as}}(\text{UO}_2)$ mode begins to grow in at 951 cm⁻¹, indicating that a uranyl(VI) nitrate complex has formed in solution (Figure 3b). When the solution TBAN concentration is increased to 0.2 M, the intensity of the $\nu_{\text{as}}(\text{UO}_2)$ mode at 951 cm⁻¹ also increases, while the $\nu_{\text{as}}(\text{UO}_2)$ mode at 968 cm⁻¹ disappears completely (Figure 3c). The uranyl(VI) nitrate complex formed may be assigned to a UO₂(NO₃)₂ species, based on the peak position of $\nu_{\text{as}}(\text{UO}_2)$ for uranyl nitrate hexahydrate dissolved in [BMIM][Tf₂N]

(18) Gaillard, C.; Chaumont, A.; Billard, I.; Hennig, C.; Ouadi, A.; Wipff, G. *Inorg. Chem.* **2007**, *46*, 4815.

(19) Servaes, K.; Hennig, C.; Billard, I.; Gaillard, C.; Binnemans, K.; Gorller-Walrand, C.; Van Deun, R. *Eur. J. Inorg. Chem.* **2007**, 5120.

(20) Georg, S.; Billard, I.; Ouadi, A.; Gaillard, C.; Petitjean, L.; Picquet, M.; Solov'ev, V. *J. Phys. Chem. B* **2010**, *114*, 4276.

(21) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley & Sons: New York, 1986.

(22) Kaplan, L.; Hildebrandt, R. A.; Ader, M. *J. Inorg. Nucl. Chem.* **1956**, *2*, 153.

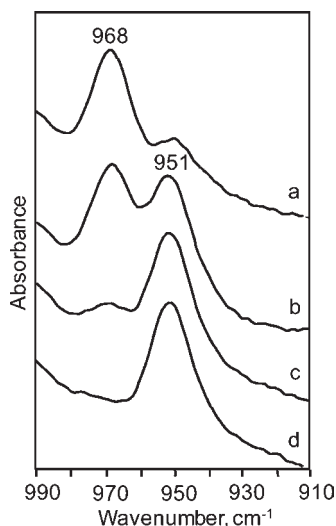


Figure 4. ATR-FTIR spectra showing the $\nu_{\text{as}}(\text{UO}_2)$ region for solutions of 0.1 M $\text{UO}_2(\text{Tf}_2\text{N})_2$ in $[\text{BMIM}][\text{Tf}_2\text{N}]$ containing (a) no HNO_3 , (b) 0.1 M HNO_3 , (c) 0.2 M HNO_3 , and (d) 0.3 M HNO_3 .

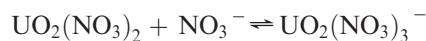
(Figure 1a). Upon addition of a third aliquot of TBAN, such that the total nitrate concentration in solution is 0.3 M, the $\nu_{\text{as}}(\text{UO}_2)$ mode shifts to 944 cm^{-1} (Figure 3d). This shift in $\nu_{\text{as}}(\text{UO}_2)$ represents the formation of the $\text{UO}_2(\text{NO}_3)_3^-$ complex. In our study, the absorption bands diagnostic for $\text{UO}_2(\text{NO}_3)_3^-$ ^{22,23} can be seen in a UV–visible absorption spectrum acquired from this solution (Supporting Information, Figure 1). These bands can also be seen, albeit at a lower intensity, in a UV–visible absorption spectrum acquired from the solution of 0.1 M $\text{UO}_2(\text{Tf}_2\text{N})_2$ in $[\text{BMIM}][\text{Tf}_2\text{N}]$ containing 0.2 M TBAN, indicating that some $\text{UO}_2(\text{NO}_3)_3^-$ is present there as well, (Supporting Information, Figure 1). On the basis of the presence of these characteristic absorption bands for $\text{UO}_2(\text{NO}_3)_3^-$ in a solution prepared by dissolution of uranyl nitrate hexahydrate in $[\text{BMIM}][\text{Tf}_2\text{N}]$, Gaillard et al.¹⁸ have suggested that $\text{UO}_2(\text{NO}_3)_2$ can dissociate into $\text{UO}_2(\text{NO}_3)^+$ and $\text{UO}_2(\text{NO}_3)_3^-$. In our ATR-FTIR spectra, the diagnostic mode for $\text{UO}_2(\text{NO}_3)_2$ ($\nu_{\text{as}}(\text{UO}_2)$ 951 cm^{-1}) is rather broad and may include a small component at 944 cm^{-1} . Interestingly, the infrared spectra show no evidence for a $\nu_{\text{as}}(\text{UO}_2)$ mode that could be assigned to the $\text{UO}_2(\text{NO}_3)^+$ species; however, as the $\nu_{\text{as}}(\text{UO}_2)$ modes are relatively broad, it is possible that a small mode between $\nu_{\text{as}}(\text{UO}_2)$ 968 cm^{-1} and $\nu_{\text{as}}(\text{UO}_2)$ at 951 cm^{-1} would not be detected. As in the case for the uranyl nitrate hexahydrate/TBAN system discussed earlier, the presence of a $\nu(\text{NO})$ mode at 1536 cm^{-1} indicates that nitrate is indeed complexed to uranyl(VI) (Supporting Information, Figure 2).

In the three-step extraction method for actinides and lanthanides mentioned above, uranium dioxide is first dissolved in a RTIL containing a mixture of HNO_3 and tributyl phosphate and the resulting uranyl complex is then extracted into *sc*- CO_2 . Thus, it is of interest to examine the uranyl complexes formed when HNO_3 is used as a nitrate source instead of TBAN. Figure 4a–d shows a series of infrared spectra acquired from solutions of 0.1 M $\text{UO}_2(\text{Tf}_2\text{N})_2$ in $[\text{BMIM}][\text{Tf}_2\text{N}]$ to which varying amounts of HNO_3 have been added. $\nu_{\text{as}}(\text{UO}_2)$ for a solution 0.1 M in $\text{UO}_2(\text{Tf}_2\text{N})_2$ in

$[\text{BMIM}][\text{Tf}_2\text{N}]$ in the absence of any HNO_3 appears at 968 cm^{-1} , assigned above to uranyl(VI) coordinated by Tf_2N^- anions (Figure 3a). When HNO_3 is added to the solution such that its final concentration is 0.1 M, the $\nu_{\text{as}}(\text{UO}_2)$ mode at 968 cm^{-1} decreases in intensity as a new uranyl(VI) nitrate complex having $\nu_{\text{as}}(\text{UO}_2)$ at 951 cm^{-1} forms (Figure 4b). $\nu_{\text{as}}(\text{UO}_2)$ at 968 cm^{-1} disappears almost completely when the concentration of HNO_3 is increased to 0.2 M (Figure 4c). The $\nu_{\text{as}}(\text{UO}_2)$ mode at 951 cm^{-1} can be assigned to the $\text{UO}_2(\text{NO}_3)_2$ species. However, no new $\nu_{\text{as}}(\text{UO}_2)$ modes are detected in the infrared spectra when the concentration of HNO_3 is increased beyond 0.2 M. The characteristic trinitrate absorption bands^{22,23} can be clearly seen in the UV–visible absorption spectra of a solution 0.3 M in HNO_3 , indicating that some $\text{UO}_2(\text{NO}_3)_3^-$ is indeed present (Supporting Information, Figure 3). However, the $\text{UO}_2(\text{NO}_3)_3^-$ anion is not a major species, existing at concentrations which cannot be detected using infrared spectroscopy under the experimental conditions used for this study.

As was the case in the TBAN/ $[\text{BMIM}][\text{Tf}_2\text{N}]$ system, the $\nu(\text{NO})$ mode at 1536 cm^{-1} appears to grow as the concentration of HNO_3 increases, indicating that nitrate is coordinated to uranyl(VI) (Supporting Information, Figure 4). The $\nu_{\text{as}}(\text{NO}_2)$ stretching mode can be seen at 1670 cm^{-1} when HNO_3 concentrations reach 0.2 M (Supporting Information, Figure 4b,c).

A major difference between the TBAN/ $[\text{BMIM}][\text{Tf}_2\text{N}]$ and the HNO_3 / $[\text{BMIM}][\text{Tf}_2\text{N}]$ systems is that the amount of H_2O introduced into solution is greater in the HNO_3 / $[\text{BMIM}][\text{Tf}_2\text{N}]$ experiment, because, a solution of 70% wt/wt HNO_3 was used as a nitrate source. Kaplan et al.²² studied the formation of the $\text{UO}_2(\text{NO}_3)_3^-$ complex in organic solvents using UV–visible spectrophotometry. The authors noted that the equilibrium reaction



is affected by the presence of water and suggested that a nitrate ion and water molecules compete for a coordination position around the uranyl(VI) ion. Billard et al.²³ also noted that the formation of the $\text{UO}_2(\text{NO}_3)_3^-$ complex in $[\text{BMIM}][\text{Tf}_2\text{N}]$ is affected by the presence of water. In our study, no significant shifts in $\nu_{\text{as}}(\text{UO}_2)$ were seen in solutions of 0.1 M $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or 0.1 M $\text{UO}_2(\text{Tf}_2\text{N})_2$ in $[\text{BMIM}][\text{Tf}_2\text{N}]$ to which aliquots of water were deliberately added. Thus, water is not a strong enough ligand in $[\text{BMIM}][\text{Tf}_2\text{N}]$ to displace NO_3^- or otherwise affect the $\text{O}=\text{U}=\text{O}$ bond strength.

Conclusions

We have conducted a detailed spectroscopic examination of the uranyl(VI) nitrate system in $[\text{BMIM}][\text{Tf}_2\text{N}]$, using ATR-FTIR spectrometry to characterize the coordination environment of uranyl(VI) in solutions of $[\text{BMIM}][\text{Tf}_2\text{N}]$ containing either TBAN or HNO_3 . Both $\text{UO}_2(\text{NO}_3)_2$ and $\text{UO}_2(\text{NO}_3)_3^-$ species were detected. $\nu_{\text{as}}(\text{UO}_2)$ for these two species were found to appear at 951 and 944 cm^{-1} , respectively, while $\nu_{\text{as}}(\text{UO}_2)$ arising from uranyl(VI) coordinated by Tf_2N^- anions in $[\text{BMIM}][\text{Tf}_2\text{N}]$ appears at 968 cm^{-1} . The $\text{UO}_2(\text{NO}_3)^+$ species was not detected under the conditions used in this study. Formation of the uranyl(VI) nitrate complexes may also be followed through the growth of the $\nu(\text{NO})$ mode at 1537 cm^{-1} , which is diagnostic for nitrate that

is coordinated to a metal ion. The $\text{UO}_2(\text{NO}_3)_3^-$ complex did not form in solutions of [BMIM][Tf₂N] containing HNO₃ under our experimental conditions, likely as a result of competition from water. More research is needed to examine the role that water and other potentially competing species play in uranyl(VI) solution chemistry in RTIL. Overall, our results indicate that infrared spectroscopy can form a valuable addition to the suite of tools currently used to study the chemical behavior of uranyl(VI) in RTIL.

Acknowledgment. S.P.P. gratefully acknowledges start-up funding from the University of Idaho College of Science. C.M.W. and D.L.Q. acknowledge the DOE Nuclear Energy University Programs (NE-UP Grant No. TO 00058) for financial support.

Supporting Information Available: UV–visible and infrared spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.