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Speciation of Uranyl Complexes in Ionic Liquids by Optical Spectroscopy

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Uranyl complexes dissolved in room-temperature ionic liquids have diagnostic absorption and emission spectra which reflect the molecular symmetry and geometry. In particular, the characteristic vibrational fine structure of the absorption spectra allows identification of the molecular symmetry of a uranyl complex. The concept of speciation of uranyl complexes is illustrated for the hydrated uranyl ion, the tetrachloro complex $[UO_2Cl_4]^{2-}$, the trinitrato complex $[UO_2(NO_3)_3]^-$, the triacetato complex $[UO_2(CH_3COO)_3]^-$, and the crown ether complex $[UO_2(18\text{-crown-}6)]^{2+}$ in imidazolium and pyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquids. The competition between 18-crown-6 and small inorganic ligands for coordination to the uranyl ion was investigated. The crystal structures of the hydrolysis product $[(UO_2)_2(\mu_2\text{-}OH)_2(H_2O)_6]$ $[UO_2Br_4](18\text{-crown-}6)_4$ and imidazolium salt $[C_6mim]_2[UO_2Br_4]$ are described.

Introduction

Liquid−liquid extraction is being used for the reprocessing of spent nuclear reactor fuels.[1−4] Uranium and plutonium are separated from fission products and heavier actinides to recover the fissile ^{235}U and ^{239}Pu radionuclides as well as the fertile ^{238}U radionuclide. The best known nuclear reprocessing process is the PUREX process (*plutonium and uranium recovery by extraction*).[5,6] After dissolution of the used nuclear fuel rods in concentrated nitric acid, uranium (as the uranyl ion) and plutonium (as the Pu^{4+} ion) are extracted into the organic phase which consists of 30% tributylphosphate (TBP) and kerosene. The fission products and heavy actinides (neptunium, americium, curium) remain in the aqueous phase. In subsequent process steps separation of uranium and plutonium can be achieved. Ionic liquids could offer an alternative for the organic phase in this type of liquid−liquid extraction processes.[7−13] Advantages of ionic liquids include a low vapor pressure and low inflammability. Moreover, boron-containing ionic liquids (for instance, tetrafluoroborate salts) are strongly neutron absorbing, so that the risks of criticality accidents during the reprocessing of nuclear fuel can be considerably reduced. Recent experiments have shown that the mechanism of extraction of metal species from an aqueous phase into an ionic liquid is not necessarily the same as the mechanism for extraction into a conventional organic phase.[14,15] Knowledge of the solvation of metal ions in ionic liquids is of prime importance for understanding extraction processes involving ionic liquids. Several authors

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have investigated the behavior of uranium in ionic liquids, and these studies have been reviewed.[12] In particular, the dioxouranium(VI) ion (uranyl ion) is often the subject of experimental and theoretical investigations.[16−24] Whereas recent studies on uranium in ionic liquids focus on solvents with weakly coordinating anions like the bis(trifluoromethylsulfonyl)imide, hexafluorophosphate, tetrafluoroborate, and triflate anions, older studies are mainly about the redox behavior of uranium in haloaluminate ionic liquids.[25−31]

Given the complexity of the ionic liquid medium, speciation of uranyl complexes is not an easy task. Experimental techniques that are often used for such studies include optical spectroscopy (UV−vis absorption spectroscopy) and extended X-ray absorption fine structure (EXAFS) spectroscopy. However, we are convinced that the potential of optical spectroscopy for speciation of uranyl complexes in ionic liquids has not fully been explored.

In uranyl, uranium occurs in its most stable oxidation state, +VI. The uranyl ion is formally a $5f^0$ system and consists of a uranium atom covalently bound to two oxygen atoms. The electronic structure of the uranyl ion can be described in terms of the molecular orbitals formed by the 5f and 6d valence orbitals of uranium and the 2s and 2p orbitals of the oxygen atoms.[32,33] The bonding molecular orbitals σ_g^+, σ_u^+, π_g, and π_u accommodate the 12 valence electrons of UO_2^{2+}, with σ_u^+ being the highest occupied molecular orbital (HOMO).[32−36] The lowest unoccupied molecular orbitals (LUMO) are the nonbonding δ_u (f_{xyz}, $f_{z(x^2-y^2)}$) and ϕ_u ($f_{y(3x^2-y^2)}$, $f_{x(x^2-3y^2)}$), originating from the 5f orbitals of uranium. The ground state is Σ_g^+ ($D_{\infty h}$ symmetry label). The UV−vis absorption spectra of uranyl compounds can be explained in terms of excitations from the σ_u^+ orbital to the δ_u and ϕ_u orbitals: $(\sigma_u^+)^2 \rightarrow \sigma_u^+\delta_u$ and $(\sigma_u^+)^2 \rightarrow \sigma_u^+\phi_u$. In the free uranyl ion, i.e., in the uranyl ion without any ligands in its equatorial plane, the nonbonding orbitals δ_u and ϕ_u have approximately the same energy. However, when ligands are surrounding the uranyl ion in the equatorial plane, the energy of the ϕ_u orbital increases due to interactions with the equatorial field. In most cases, the ϕ_u orbital is about 2000 cm^{-1} above the δ_u orbital. All electronic transitions in uranyl spectra are parity forbidden by the Laporte selection rule.[33,35−37] Therefore, intensity must be induced either by the static ligand field (e.g., $[UO_2(NO_3)_3]^-$ D_{3h}) or by the dynamic ligand field, also referred to as *vibronic coupling* (e.g., $[UO_2Cl_4]^{2-}$ D_{4h}). Electric dipole transitions induced by the static ligand field can only be observed in noncentrosymmetric point groups, whereas vibronic coupling can occur in both centrosymmetric and noncentrosymmetric point groups. The symmetric stretching vibration ν_s is always superimposed on all electronic transitions as a progression.[38] Ungerade vibrational modes, i.e., the asymmetric stretching vibration ν_a and the bending mode ν_b of the uranyl ion itself and ungerade equatorial ligand vibrations, are coupled to the gerade electronic states in the vibronic coupling intensity mechanism. The absorption spectra of uranyl complexes show a characteristic vibronic fine structure, which is diagnostic for a certain symmetry (and geometry) of the first coordination sphere.[39,40] The chemical nature of the ligands has a minor influence on the spectral fine structure. Several reviews describing the luminescence and photophysical properties of the uranyl ion are available.[41−44]

In this paper, the typical spectra of the ligands has a minor influence on the spectral fine structure. The typical spectra of the hydrated uranyl ion as well as of $[UO_2Cl_4]^{2-}$, $[UO_2(NO_3)_3]^-$, $[UO_2(CH_3COO)_3]^-$, and $[UO_2(18\text{-crown-}6)]^{2+}$ in the hydrophobic ionic liquids 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_4mim][Tf_2N]$, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_6mim][Tf_2N]$, and *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide $[C_4mpyr][Tf_2N]$ are discussed. It will be shown that water has a pronounced effect on the spectroscopic behavior of uranyl in ionic liquids with weakly coordinating anions. Competition experiments between 18-crown-6 and small inorganic ligands (NO_3^-, Cl^-, Br^-) for coordination to the uranyl ion have been performed.

Experimental Section

General. UV−vis absorption spectra were measured at room temperature on a Varian Cary 5000 spectrophotometer between 300 and 600 nm. Luminescence measurements have been carried out

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at room temperature on an Edinburgh Instruments FS-900 spectrofluorimeter. The light source used was a 450 W xenon arc lamp. Emission spectra were recorded between 430 and 650 nm. The excitation wavelength depended on the uranyl complex present in the ionic liquid solution: 418.5 nm for the chloro complexes, 438.5 nm for the nitrato complexes, 420.0 nm for the acetato complexes, and 429.0 nm for the 18-crown-6 complexes. Magnetic circular dichroism (MCD) spectra were recorded at room temperature on an AVIV 62DS circular dichroism spectrometer (extended with an electromagnet to create a magnetic field of 1 T) over the wavelength interval between 300 and 570 nm.

Synthesis of the Ionic Liquids. The ionic liquid *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [C_4mpyr][Tf_2N], was kindly provided by Merck. The ionic liquids [C_4mim][Tf_2N], [C_6mim][Tf_2N], [C_6mim][Br], and [C_6mim][Cl], where C_4mim stands for 1-butyl-3-methylimidazolium and C_6mim for 1-hexyl-3-methylimidazolium, were synthesized in spectrograde purity according to literature procedures.[45] All compounds are liquid at room temperature. To reduce the water content, the ionic liquids [$C_n$mim][Tf_2N] were dried in vacuo at 70 °C on a rotavap before preparing the solutions for spectroscopic measurements. Karl Fischer titrations indicated that the water content of the ionic liquids was less than 100 ppm. The absorption bands of the ionic liquids [$C_n$mim][Tf_2N] ($n = 4$ or 6), [C_6mim][Br], [C_6mim][Cl], and [C_4mpyr][Tf_2N] do not interfere with the absorption spectrum of the uranyl ion because these ionic liquids do not show any appreciable light absorption in the wavelength region between 300 and 600 nm.

Synthesis of Uranyl Salts. $UO_2(ClO_4)_2 \cdot xH_2O$. UO_3 was dissolved in perchloric acid (2 mol L^{-1}). The solution was boiled to expel free chlorine gas. After dilution with water, the solution was subsequently evaporated close to dryness. This procedure was repeated until whitish fumes were no longer formed. Finally, a yellow powder was obtained. Various hydrates of uranyl perchlorate $UO_2(ClO_4)_2 \cdot xH_2O$ ($x = 0-7$) have been reported in the literature.[46,47] Treatment of the initial solid probably governs the degree of hydration. However, it is difficult to determine the exact number of water molecules in the uranyl perchlorate salt due to its hygroscopic behavior. Even if we could determine the exact number of water molecules in the initial batch, this number could have changed during the course of the experiments. Therefore, to have more or less an idea about the uranyl concentration in our samples, we use the molecular weight of the hexahydrate for calculating concentrations ($M_w = 577.02$ g mol^{-1}). Comparison of the ϵ values of an aqueous solution of the uranyl ion with 5, 6, or 7 water molecules in the initial perchlorate salt yields an error of about 3%.

CAUTION: Perchloric acid can be hazardous.[48] It is very corrosive to skin and eyes and should be handled with the utmost care. Organic material such as cloth or wood can ignite or explode in contact with perchloric acid. Perchlorate salts are shock sensitive. Scraping of a spatula on the side of the container and/or crushing perchlorate salt crystals with a metal pestle can initiate an explosion.

UO_2Br_2. Hydrogen bromide (1.25 mL of an aqueous solution of HBr (47%), which corresponds to 0.01 mol of HBr) was added to a suspension of UO_3 (4 g, 0.014 mol) in water while stirring and heating the solution. The excess of UO_3 was filtered off, and the filtrate was evaporated in a beaker. The remaining amount of water was expelled under reduced pressure. UO_2Br_2 is a yellow powder. Due to its hygroscopic character, UO_2Br_2 was kept in a desiccator.

$UO_2(Tf_2N)_2 \cdot xH_2O$. In a first step, lithium bis(trifluoromethylsulfonyl)imide was converted into the corresponding acid by mixing 30 mL of an aqueous solution of Li(Tf_2N) (2 mol L^{-1}) with an excess of a 20% aqueous H_2SO_4 solution. H(Tf_2N) and Li_2SO_4 were formed. The colorless aqueous phase was extracted several times with diethyl ether. The organic phase and aqueous phase contained the desired acid and Li_2SO_4, respectively. The organic phase was then washed several times with water to remove possible traces of Li_2SO_4. Evaporation of diethyl ether under reduced pressure gave hydrogen bis(trifluoromethylsulfonyl)imide H(Tf_2N). In the second step, uranyl bis(trifluoromethylsulfonyl)imide was synthesized by reaction between uranium(VI)oxide and hydrogen bis(trifluoromethylsulfonyl)imide. Into a round-bottom flask, equipped with a magnetic stirrer and a cooler, a small excess of H(Tf_2N) (9 g; 0.033 mol) was added to a suspension of UO_3 (0.023 mol) in water. This reaction mixture was stirred at 50 °C for 3 days. Then the temperature was raised to 80 °C, thereby stirring the mixture for another 24 h. Water was evaporated under reduced pressure until a yellow oil-like substance was obtained. This substance was washed with dichloromethane to remove the remaining traces of the acid H(Tf_2N). Under stirring and slightly heating for 1 h, methanol was added to dissolve the obtained product. The nonreacted UO_3 was filtered off, resulting in a bright yellow solution. Finally, methanol was expelled on a rotary evaporator under reduced pressure, leaving the viscous, dark yellowish $UO_2(Tf_2N)_2 \cdot xH_2O$ in the flask.

Preparation of the Sample Solutions. "Free" uranyl ion. Solutions of the "free" uranyl ion (hydrated uranyl ion) were obtained by dissolving either $UO_2(Tf_2N)_2 \cdot xH_2O$ or $UO_2(ClO_4)_2 \cdot xH_2O$ in the ionic liquids [$C_n$mim][Tf_2N] ($n = 4$ or 6) and [C_4mpyr][Tf_2N]. The uranyl concentration was approximately 10^{-2} mol L^{-1} for $UO_2(Tf_2N)_2 \cdot xH_2O$ and 5×10^{-2} mol L^{-1} for $UO_2(ClO_4)_2 \cdot xH_2O$.

Chloro Complexes. Earlier studies of the complex formation of the uranyl ion with chloride ions in acetone and acetonitrile have indicated that the maximum number of chloro ligands that can be coordinated to the uranyl ion is four and that in this case the tetrachloro complex $[UO_2Cl_4]^{2-}$ is formed.[49,50] Addition of an excess of chloride ions did not result in further changes in the absorption spectra. In order to achieve the maximum number of coordinated chloride ions to the uranyl in ionic liquids, we used a 1:5 uranyl-to-chloride ratio for our studies in ionic liquids. $UO_2(ClO_4)_2 \cdot xH_2O$ was mixed with tetrabutylammonium chloride in [C_4mim][Tf_2N] and [C_4mpyr][Tf_2N] in a uranyl-to-chloride ratio of 1:5. The uranyl concentration was approximately 5×10^{-2} mol L^{-1}.

Nitrato Complexes. Two experimental approaches have been used to obtain the $[UO_2(NO_3)_3]^-$ complex in ionic liquids. In the first approach, $UO_2(NO_3)_2 \cdot 6H_2O$ was dissolved in the ionic liquid and an excess of tetrabutylammonium nitrate was added so that the uranyl-to-nitrate ratio in the final ionic liquid solution was 1:4. No further changes were observed by raising the nitrate concentration above a uranyl-to-nitrate ratio of 1:4, which shows that the maximum coordination of uranyl with nitrate ions in the equatorial plane has been reached. Notice that a formal 1:4 uranyl-to-nitrate ratio in solution does not mean that four nitrate ions are bound to

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the uranyl ion, as the discussion below will show. A second method for preparing the $[UO_2(NO_3)_3]^-$ complex consisted of dissolving uranium(VI) oxide (UO_3) with concentrated nitric acid in the ionic liquid $[C_4mim][Tf_2N]$. A similar sample preparation was found in the literature for the oxidative dissolution of uranium(IV) oxide.[51,52] Concentrated nitric acid contains a certain amount of water. Because the ionic liquid $[C_4mim][Tf_2N]$ is immiscible with water, a phase separation resulted. The UV−vis absorption spectrum was taken from the ionic liquid phase, separated from the aqueous phase with a separatory funnel.

Acetato Complexes. $UO_2(CH_3COO)_2\cdot 2H_2O$ was mixed with tetrabutylammonium acetate in $[C_4mim][Tf_2N]$ in a total uranyl-to-acetate ratio of 1:4. The uranyl concentration was approximately 5×10^{-2} mol L^{-1}.

Complexes with 18-Crown-6. $UO_2(ClO_4)_2\cdot xH_2O$ was mixed with 18-crown-6 in $[C_4mim][Tf_2N]$ and $[C_4mpyr][Tf_2N]$ in a uranyl-to-ligand ratio of 1:2. The uranyl concentration was approximately 5×10^{-2} mol L^{-1}. To study the influence of small inorganic ligands on the uranyl crown ether complex in ionic liquids, UO_2Br_2 and UO_2Cl_2 were dissolved in $[C_6mim][Br]$ and $[C_6mim][Cl]$, respectively, in the presence of the crown ether 18-crown-6 in such an amount that the uranyl concentration was approximately 2×10^{-2} mol L^{-1}.

The total dissolution of the uranyl salt and ligand in the ionic liquid was often only observed after 3 days, yielding a transparent, yellow-colored solution. The initial spectroscopic measurements on mixtures of the uranyl salt and ligand in the ionic liquid did not allow observing the characteristic UV−vis absorption spectrum of the corresponding uranyl complex. However, when these mixtures were measured again after several days, the typical absorption bands were clearly visible. This indicates that the kinetics for formation of uranyl complexes in ionic liquids are slow. Gaillard et al. found a correlation between this kinetic effect and the viscosity of ionic liquids.[53] Thus, we can assume that the absence of a typical vibronic fine structure in the initial spectra of uranyl complexes in ionic liquids is due to the slow kinetics of anion exchange, which is related to the viscosity of the ionic liquid.

Crystallography. Yellow single crystals of $[C_6mim]_2[UO_2Br_4]$ were obtained after slowly cooling a 2:1 mixture of $[C_6mim][Br]$ and UO_2Br_2 to room temperature. Suitable yellow single crystals of $[(UO_2)_2\mu_2\text{-}(OH)_2(H_2O)_6][UO_2Br_4]$ (18-crown-6)$_4$ were obtained after 3 days by slowly evaporating an aqueous solution containing $[C_6mim][Br]$, UO_2Br_2, and 18-crown-6 at room temperature.

$[C_6mim]_2[UO_2Br_4]$. $C_{20}H_{38}Br_4N_4O_2U$, $M = 924.17$ g mol^{-1}, trigonal, R-3 (No. 148), $a = 33.297(5)$ Å, $c = 7.1671(14)$ Å, $V = 6881.6(19)$ Å^3, $T = 100(2)$ K, $Z = 9$, $\rho_{calc} = 2.007$ g cm^{-3}, μ(Cu Kα) = 21.228 mm^{-1}, $F(000) = 3906$, crystal size $0.3 \times 0.1 \times 0.1$ mm^3, 2932 independent reflections ($R_{int} = 0.0771$). Final $R = 0.0357$ for 2518 reflections with $I > 2\sigma(I)$ and $\omega R2 = 0.0822$ for all data.

$[(UO_2)_2(\mu_2\text{-}OH)_2(H_2O)_6]$ $[UO_2Br_4]$ (18-crown-6)$_4$. $C_{48}H_{110}Br_4O_{38}U_3$, $M = 2329.05$ g mol^{-1}, monoclinic, $P2_1/c$ (No. 14), $a = 12.1149(9)$ Å, $b = 17.6649(11)$ Å, $c = 17.7492(10)$ Å, $\beta = 99.113(4)°$, $V = 3750.5(4)$ Å^3, $T = 100(2)$ K, $Z = 2$, $\rho_{calc} = 2.062$ g cm^{-3}, μ(Cu Kα) = 21.285 mm^{-1}, $F(000) = 2236$, crystal size $0.25 \times 0.14 \times 0.1$ mm^3, 7179 independent reflections ($R_{int} = 0.1178$). Final $R = 0.0516$ for 5442 reflections with $I > 2\sigma(I)$ and $\omega R2 = 0.1166$ for all data.

X-ray intensity data were collected on a SMART 6000 diffractometer, equipped with a CCD detector, using Cu Kα radiation ($\lambda = 1.54178$ Å). The images were interpreted and integrated with the program SAINT from Bruker.[54] Both structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.[55] Non-hydrogen atoms were anisotropically refined, and the hydrogen atoms in the riding mode with isotropic temperature factors were fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups). CCDC-663904 and CCDC-663905 contain the supplementary crystallographic data for this paper and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44−1223-336033; or deposit@ccdc.cam.ac.uk).

Results and Discussion

Hydrated Uranyl Ion ("Free Uranyl Ion"). The UV−vis absorption spectra of $UO_2(Tf_2N)_2\cdot xH_2O$ in $[C_6mim][Tf_2N]$ and $UO_2(ClO_4)_2\cdot xH_2O$ in $[C_4mim][Tf_2N]$ and $[C_4mpyr][Tf_2N]$ were recorded for the wavenumber range between 18 000 and 30 000 cm^{-1} (Figure 1). Both the bis(trifluoromethylsulfonyl)imide and perchlorate anion are known to be weakly coordinating anions.[53,56] They will not coordinate to the metal center in the presence of other competing ligands. Comparison of the UV−vis absorption spectra in Figure 1 reveals the same spectral features regardless which uranyl salt has been dissolved or which type of ionic liquid has been used. Moreover, the three absorption spectra exhibit the same vibrational fine structure as the spectrum of the hydrated uranyl ion in aqueous solution.[57] The absorption maxima are observed at 24 085, 23 946, and 23 929 cm^{-1} for $UO_2(Tf_2N)_2\cdot xH_2O$ in $[C_6mim][Tf_2N]$, $UO_2(ClO_4)_2\cdot xH_2O$ in $[C_4mim][Tf_2N]$, and $UO_2(ClO_4)_2\cdot xH_2O$ in $[C_4mpyr][Tf_2N]$, respectively. These values are similar to the absorption maxima of $UO_2(ClO_4)_2\cdot xH_2O$ in aqueous solution (24 140 cm^{-1}) and acetonitrile (24 079 cm^{-1}). The vibronic spacing of approximately 876 cm^{-1} can be attributed to the frequency of the symmetric stretching vibration (ν_s) of the uranyl ion in the ground state. It is generally accepted that the uranyl ion is coordinated by five water molecules in the equatorial plane.[58−62] Consequently, the UV−vis absorption spectrum corresponds to a D_{5h} coordination symmetry.[63,64] In this

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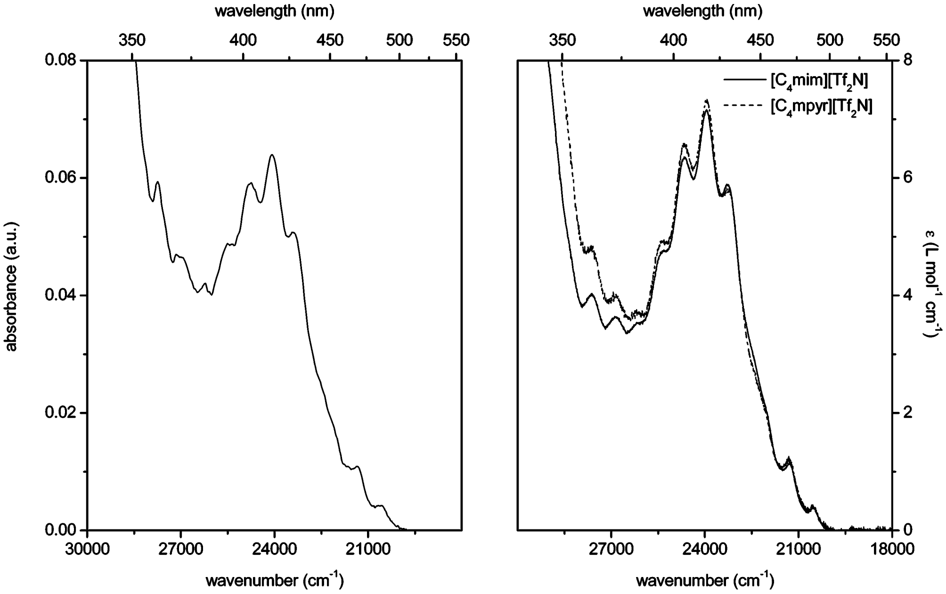

Figure 1. UV−vis absorption spectra of $UO_2(Tf_2N)_2 \cdot xH_2O$ in [C$_6$mim][Tf$_2$N] (left) and $UO_2(ClO_4)_2 \cdot xH_2O$ in [C$_4$mim][Tf$_2$N] and [C$_4$mpyr][Tf$_2$N] (right) at room temperature. The uranyl concentration is 5×10^{-2} mol L^{-1}.

symmetry group, no intense transitions are observed in the absorption spectrum. The spectroscopic data indicate that even in ionic liquids dried to a water content lower than 100 ppm, the [Tf$_2$N]$^-$ anion does not coordinate to the uranyl ion in these ionic liquids. The main species in solution is the hydrated uranyl ion, $[UO_2(H_2O)_5]^{2+}$, in which five water molecules are bound to the uranium atom in the equatorial plane. It can be concluded that under normal circumstances of handling the hydrated uranyl ion is formed upon dissolution of uranyl salts with weakly coordinating anions (Tf$_2$N$^-$ or ClO_4^-) in ionic liquids with bis(trifluoromethylsulfonyl)-imide anions.

The ionic liquids [C$_4$mim][Tf$_2$N] and [C$_6$mim][Tf$_2$N] are strongly fluorescing between 14 000 and 20 000 cm^{-1}, which is the same spectral region as the green luminescence of the uranyl ion. The emission intensity of the uranyl ion in [C$_4$-mpyr][Tf$_2$N] is also not strong enough to overcome the background fluorescence (due to trace impurities?) of the pyrrolidinium ionic liquid. Therefore, the luminescence spectrum of the hydrated uranyl ion could not be measured in the ionic liquids used for this study.

Tetrachloro Complex. The UV−vis absorption spectra of the uranyl ion in the presence of chloride ions (1:5 uranyl-to-chloride ratio) in the ionic liquids [C$_4$mim][Tf$_2$N] and [C$_4$-mpyr][Tf$_2$N] are shown in Figure 2. The spectra of the two ionic liquid solutions exhibit the same remarkable vibrational fine structure, which is typical for the $[UO_2Cl_4]^{2-}$ species with D_{4h} coordination symmetry.[65,66] Thus, the uranyl tetrachloro complex is formed in the ionic liquids [C$_4$mim]-[Tf$_2$N] and [C$_4$mpyr][Tf$_2$N] when a mixture of $UO_2(ClO_4)_2 \cdot xH_2O$ and an excess of tetrabutylammonium chloride is dissolved in these solvents. The nature of these ionic liquids

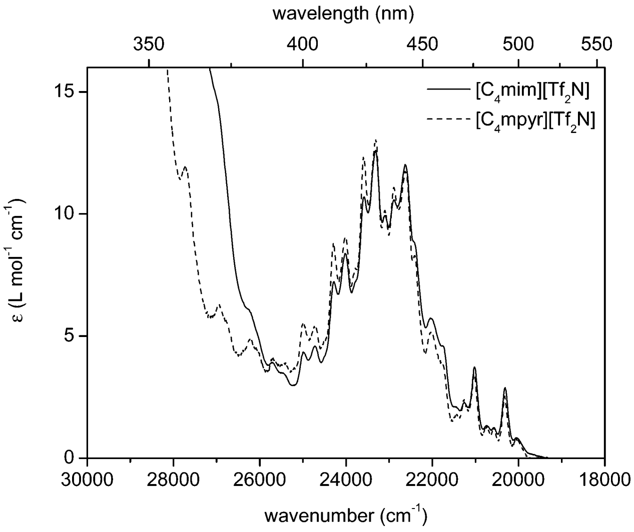

Figure 2. UV−vis absorption spectra of $[UO_2Cl_4]^{2-}$ in [C$_4$mim][Tf$_2$N] and [C$_4$mpyr][Tf$_2$N] at room temperature, where $[UO_2^{2+}]/[Cl^-] = 1{:}5$. The uranyl concentrations are 5×10^{-2} mol L^{-1} in [C$_4$mim][Tf$_2$N] and 10^{-2} mol L^{-1} in [C$_4$mpyr][Tf$_2$N].

and in particular the cationic part of the ionic liquid has no significant influence on the maxima of the absorption bands in the UV−vis absorption spectrum of $[UO_2Cl_4]^{2-}$. There is good agreement between the absorption maxima in [C$_4$mim]-[Tf$_2$N] and [C$_4$mpyr][Tf$_2$N], which in turn correspond well to the positions of the absorption peaks in acetonitrile. On the other hand, the cation of the ionic liquid has an influence on the intensity of the transitions. The transitions of $[UO_2Cl_4]^{2-}$ have a slightly higher absorbance value in [C$_4$-mpyr][Tf$_2$N] than in [C$_4$mim][Tf$_2$N], with the exception of the transitions at 20 312 and 21 021 cm^{-1} in [C$_4$mim][Tf$_2$N] and 20 321 and 21 039 cm^{-1} in [C$_4$mpyr][Tf$_2$N]. These two transitions have a comparable absorbance value in the two ionic liquids. Sornein et al. also noticed that the absorbance values of the transitions of $[UO_2Cl_4]^{2-}$ are a little larger in [MeBu$_3$N][Tf$_2$N] than in [C$_4$mim][Tf$_2$N], except for the peaks at 21 008 and 20 325 cm^{-1}.[17] Ryan explained the intensity

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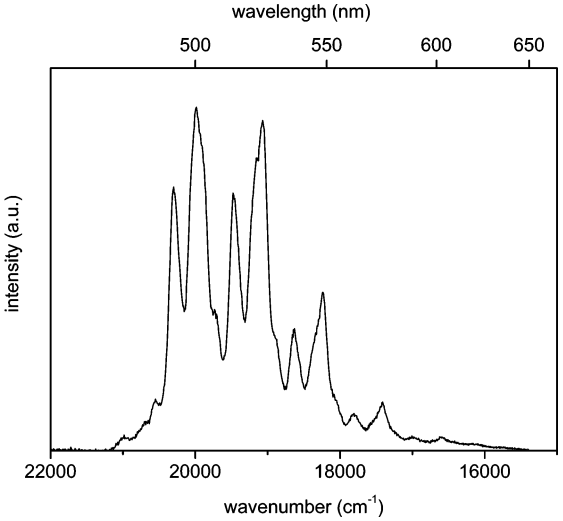

Figure 3. Emission spectrum of $[UO_2Cl_4]^{2-}$ in $[C_4mpyr][Tf_2N]$ at room temperature. The uranyl concentration is 10^{-2} mol L^{-1}. The excitation wavelength is 418.5 nm.

of these two peaks at the low-energy end (longer wavelength end) of the spectrum of $[UO_2Cl_4]^{2-}$ with respect to the other transitions to hydrogen bonding of the uranyl tetrachloro complex to a hydrogen donor.[67] Therefore, Sornein et al. could assign the intensity enhancement at 21 008 and 20 325 cm^{-1} from $[MeBu_3N][Tf_2N]$ to $[C_4mim][Tf_2N]$ to the ability of the imidazolium cations to form C−H···Cl hydrogen bonds.[17] Similar conclusions were made by Deetlefs et al.[23] On the basis of these investigations, we attribute the intensity behavior of the transitions at 20 312 and 21 021 cm^{-1} in $[C_4mim][Tf_2N]$ to hydrogen bonding of the $[UO_2Cl_4]^{2-}$ complex with the imidazolium cation of the ionic liquid. The photoluminescence spectrum of $[UO_2Cl_4]^{2-}$ in $[C_4mpyr][Tf_2N]$ shows the typical splitting of the emission bands, which was also observed for $[UO_2Cl_4]^{2-}$ in acetonitrile and acetone (Figure 3).[49,50] Furthermore, the emission maxima in $[C_4mpyr][Tf_2N]$ correspond well to the maxima in the spectrum of $[UO_2Cl_4]^{2-}$ in these nonaqueous solvents. The ground-state frequency of the symmetric stretching vibration ν_s is approximately 825 cm^{-1}. This value is in good agreement with the frequency of ν_s, i.e., 832 cm^{-1}, obtained from the FT Raman spectrum of $[UO_2Cl_4]^{2-}$ in a 40:60 $AlCl_3$-$[C_2mim][Cl]$ chloroaluminate ionic liquid.[68]

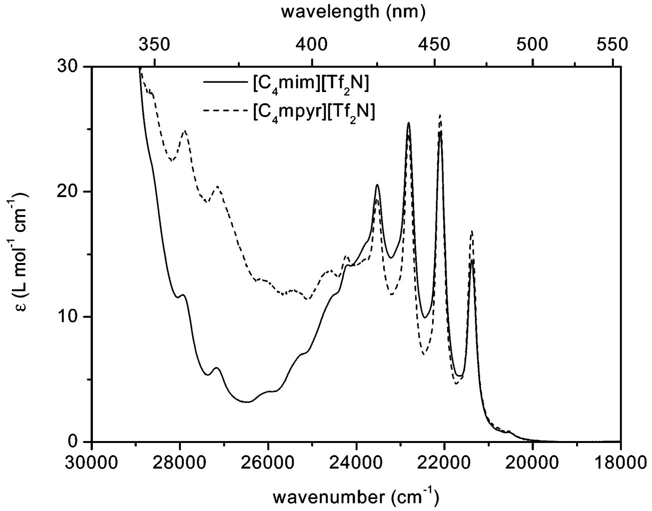

Figure 4. UV−vis absorption spectra of $[UO_2(NO_3)_3]^-$ in $[C_4mim][Tf_2N]$ and $[C_4mpyr][Tf_2N]$ at room temperature, where $[UO_2^{2+}]/[NO_3^-]_{tot} = 1:4$. The uranyl concentrations are 5×10^{-2} mol L^{-1} in $[C_4mim][Tf_2N]$ and 10^{-2} mol L^{-1} in $[C_4mpyr][Tf_2N]$.

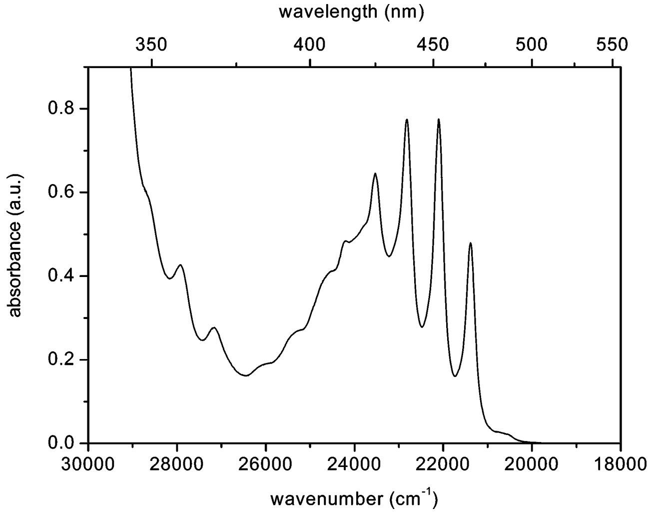

Figure 5. UV−vis absorption spectrum of $[UO_2(NO_3)_3]^-$ in $[C_4mim][Tf_2N]$ at room temperature by dissolving UO_3 in $HNO_3/[C_4mim][Tf_2N]$. The initial uranyl concentration was 5×10^{-2} mol L^{-1}.

Trinitato Complex. The UV−vis absorption spectra of solutions prepared by dissolving $UO_2(NO_3)_2 \cdot 6H_2O$ and tetrabutylammonium nitrate (uranyl-to-nitrate ratio = 1:4) in the ionic liquids $[C_4mim][Tf_2N]$ and $[C_4mpyr][Tf_2N]$ are shown in Figure 4. The more pronounced increase of the baseline in the absorption spectrum of $[C_4mpyr][Tf_2N]$ is possibly caused by the presence of colloidal particles in the solution, which are not visible by the naked eye. The absorption spectrum shown in Figure 5 is that of a solution obtained by dissolving uranium(VI) oxide (UO_3) with concentrated nitric acid in the ionic liquid $[C_4mim][Tf_2N]$. The *Y* axis is expressed in absorbance values because we do not exactly know the uranyl concentration in the ionic liquid after the equilibrium has been established. This is not a major problem since we are mainly interested in the qualitative features of the absorption spectra. In the ionic liquids, the absorption coefficient of the uranyl ion in the presence of nitrate ions is of the same order of magnitude as in acetonitrile. The UV−vis absorption spectra of $UO_2(NO_3)_2 \cdot 6H_2O$ with nitrate ions added in $[C_4mim][Tf_2N]$ and $[C_4mpyr][Tf_2N]$ as well as the spectrum of UO_3 in $HNO_3/[C_4mim][Tf_2N]$ display four very intense, sharp peaks between 21 000 and 24 000 cm^{-1}. This observation is a first indication of the formation of $[UO_2(NO_3)_3]^-$ in the ionic liquids. Dieke and Duncan were the first to discover these sharp peaks in the spectrum of $CsUO_2(NO_3)_3$. In earlier papers, these peaks at the low-energy end of the spectrum were called the *“magnetic series”*.[38] Although two different synthesis methods were used for the preparation of the uranyl nitrate complexes, the trinitrato complex is formed in both cases.

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Additional evidence for formation of the trinitrate complex originates from the corresponding magnetic circular dichroism (MCD) spectra.[69,70] The MCD technique is based on the Zeeman effect. The differential absorption of left and right circularly polarized light of a sample in a longitudinal magnetic field is measured. In a longitudinal magnetic field, the magnetic field lines are parallel to the light beam. An MCD spectrum is often described as the superposition of so-called *A*, *B*, and *C* terms.[71] The *A* term has the shape of the first derivative of an absorption curve. An *A* term is positive if left circularly polarized light is absorbed to the upper Zeeman component.[72] This implicates that a positive *A* term has its positive lobe at the high wavenumber side. A negative *A* term has its positive lobe at the low wavenumber side. MCD spectroscopy is a spectroscopic technique that gives complementary information to absorption spectra.[73] Very intense negative *A* terms are typical for the MCD spectra of the $[UO_2(NO_3)_3]^-$ complex.[70,74] The MCD spectra of both $UO_2(NO_3)_2{\cdot}6H_2O$ with added nitrate ions in $[C_4mim][Tf_2N]$ and UO_3 in $HNO_3/[C_4mim][Tf_2N]$ yield the expected very intense negative *A* terms (Figure 6). The photoluminescence spectrum of $[UO_2(NO_3)_3]^-$ in $[C_4mpyr][Tf_2N]$ shows the typical vibrational fine structure of the uranyl trinitrato complex (Figure 7). Three sharp and intense peaks are observed between 19 000 and 22 000 cm^{-1}. The ground state value of ν_s is approximately 867 cm^{-1}, which resembles the value in acetonitrile (872 cm^{-1}).[74]

Triacetato Complex. The absorption spectra of solutions prepared by dissolving $UO_2(CH_3COO)_2{\cdot}2H_2O$ and tetrabutylammonium acetate (uranyl-to-acetate ratio = 1:4) in the ionic liquid $[C_4mim][Tf_2N]$ have an appearance similar to that of the trinitrato complex (Figure 8). This supports the hypothesis that the triacetato complex $[UO_2(CH_3COO)_3]^-$ is formed in the ionic liquid solution. Indeed, the presence of very sharp, intense peaks in the UV−vis absorption spectra are typical for uranyl complexes with D_{3h} symmetry.[40]

18-Crown-6 Complex. A remarkable vibrational fine structure in the UV−vis absorption spectra can also be observed when the uranyl ion forms an inclusion complex with a crown ether.[75,76] This fine structure is not present in the absorption spectra of outer-sphere complexes of uranyl with crown ethers. The UV−vis absorption spectrum of the uranyl ion in the presence of the crown ether 18-crown-6 in $[C_4mim][Tf_2N]$ and $[C_4mpyr][Tf_2N]$ is shown in Figure 9. From comparison with the UV−vis absorption spectrum in acetonitrile,[76] it is obvious that the spectra in the ionic liquids $[C_4mim][Tf_2N]$ and $[C_4mpyr][Tf_2N]$ exhibit spectral features which are characteristic for inclusion of the uranyl ion in the crown ether ring. Thus, the uranyl ion is extracted from an aqueous phase into the ionic liquid as the inclusion complex $[UO_2(18\text{-crown-}6)]^{2+}$. The cavity of 18-crown-6

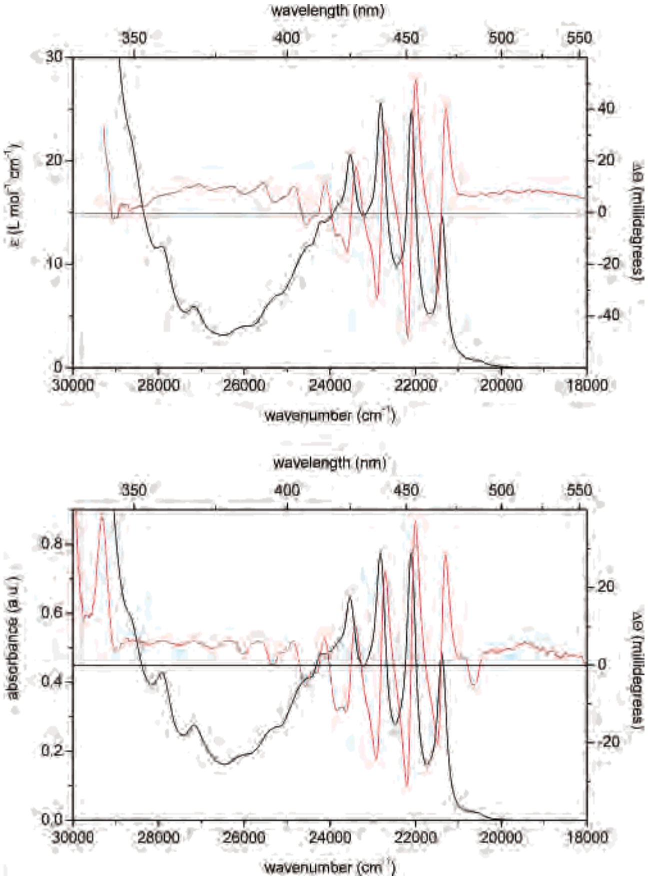

Figure 6. UV−vis absorption (black line) and MCD (red line) spectra of $[UO_2(NO_3)_3]^-$ in $[C_4mim][Tf_2N]$ (upper graph) and UO_3 in $HNO_3/[C_4mim][Tf_2N]$ (lower graph) at room temperature. The uranyl concentration is 5×10^{-2} mol L^{-1}.

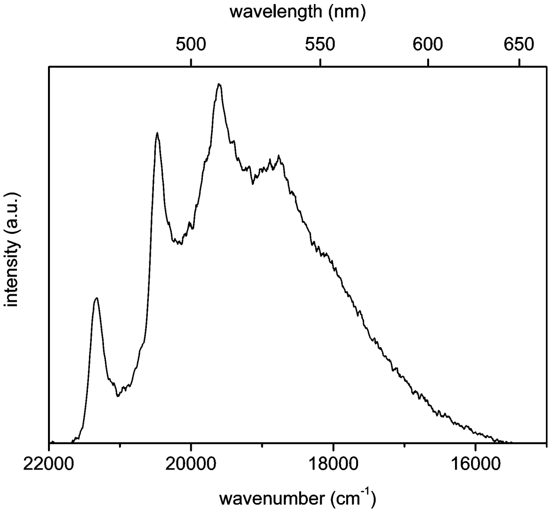

Figure 7. Emission spectrum of $[UO_2(NO_3)_3]^-$ in $[C_4mpyr][Tf_2N]$ at room temperature. The concentrations are $[UO_2^{2+}] = 10^{-2}$ mol L^{-1} ($UO_2(NO_3)_2{\cdot}6H_2O$) and $[NO_3^-] = 2 \times 10^{-2}$ mol L^{-1} (total metal-to-ligand ratio = 1:4). The excitation wavelength is 438.2 nm.

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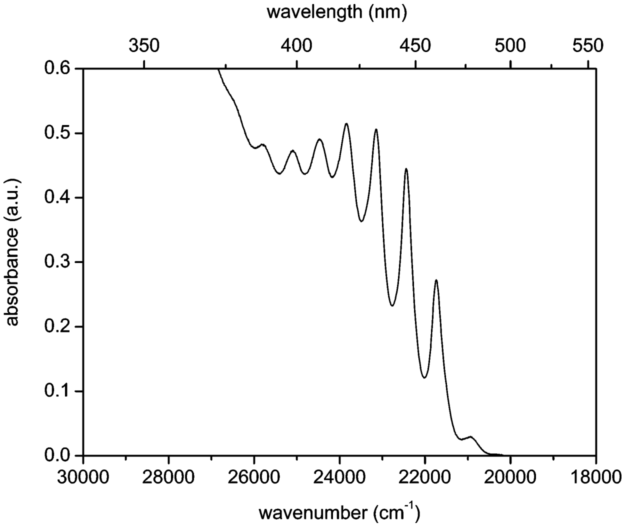

Figure 8. UV−vis absorption spectrum of $[UO_2(CH_3COO)_3]^-$ in [C$_4$mim][Tf$_2$N] at room temperature. The uranyl concentration is 5×10^{-2} mol L^{-1}. The metal-to-ligand ratio is 1:4.

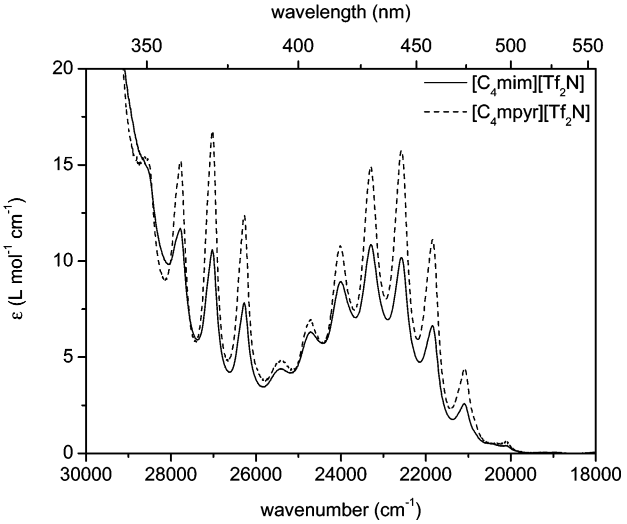

Figure 9. UV−vis absorption spectra of $[UO_2(18\text{-crown-}6)]^{2+}$ in [C$_4$mim][Tf$_2$N] and [C$_4$mpyr][Tf$_2$N] at room temperature. The uranyl concentrations are 5×10^{-2} and 10^{-2} mol L^{-1} in [C$_4$mim][Tf$_2$N] and [C$_4$mpyr][Tf$_2$N], respectively. The metal-to-ligand ratio is 1:2.

(2.6−3.2 Å) matches well with the ion diameter of the uranyl ion, 2.8 Å. The cationic and anionic parts of the ionic liquid seem to have little influence on the positions of the absorption maxima of the $[UO_2(18\text{-crown-}6)]^{2+}$ complex. Just like in the case of the uranyl tetrachloro complex, the absorbance values of the uranyl crown ether complex are higher for the complex dissolved in [C$_4$mpyr][Tf$_2$N] compared to the complex dissolved in [C$_4$mim][Tf$_2$N]. The vibrational fine structure in the spectrum of $[UO_2(18\text{-crown-}6)]^{2+}$ can be explained in terms of a D_{3d} (D_3) coordination symmetry. The special features between 26 000 and 29 000 cm^{-1} can only be attributed to the transition $\Gamma_g \leftarrow \Sigma_g^+$. This transition, arising from the $\sigma_u^+\phi_u$ configuration, is typical for a D_3 coordination symmetry. The luminescence of the $[UO_2(18\text{-crown-}6)]^{2+}$ complex could not be measured in [C$_4$mpyr][Tf$_2$N] due to the intense background fluorescence of the ionic liquid.

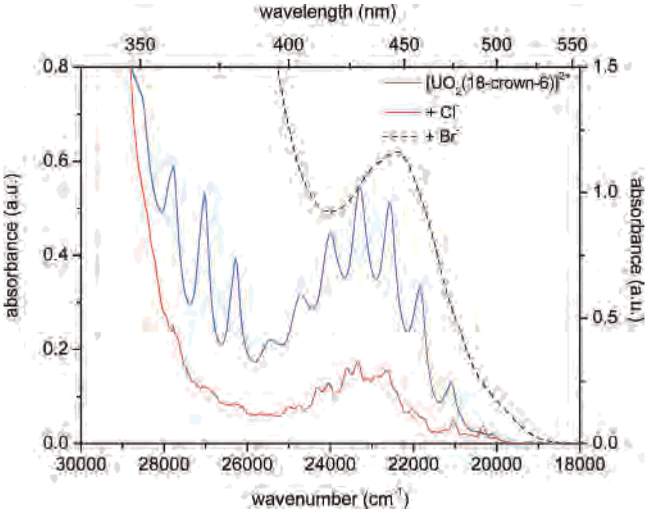

Figure 10. UV−vis absorption spectrum of $[UO_2(18\text{-crown-}6)]^{2+}$ with an excess of chloride and bromide ions at room temperature. The ionic liquids used are [C$_6$mim][Cl], [C$_6$mim][Br], and [C$_4$mim][Tf$_2$N]. Notice the difference in absorbance values for the bromide system (*Y* axis at right-hand side).

Ligand Competition Experiments. When UO_2Cl_2 is dissolved in [C$_6$mim][Cl] in the presence of the crown ether 18-crown-6, the absorption spectrum of the $[UO_2Cl_4]^{2-}$ species and not that of the $[UO_2(18\text{-crown-}6)]^{2+}$ is observed (Figure 10). This indicates that 18-crown-6 cannot form an inclusion complex with uranyl when chloride ions are present. The effect of addition of bromide ions to the $[UO_2(18\text{-crown-}6)]^{2+}$ complex in ionic liquids was investigated as well. UO_2Br_2 was dissolved in [C$_6$mim][Br] together with the crown ether 18-crown-6. The corresponding UV−vis absorption spectrum, displayed in Figure 10, coincides with neither the spectrum of $[UO_2(18\text{-crown-}6)]^{2+}$ nor the spectrum of $[UO_2Br_4]^{2-}$.[77] Instead, a broad, intense band without any fine structure is observed. In addition, the charge-transfer band is shifted toward lower energies. However, literature data reveal that such a broad structureless band can be attributed to the hydrolysis products of the uranyl ion. The uranyl ion is prone to hydrolysis in solutions with a pH value ≥ 2.5.[78] With increasing pH, uranyl hydrolysis results in polynuclear species with the general formula $[(UO_2)_m(OH)_n]^{2m-n}$. Two of the most predominant complexes are the dimer $[(UO_2)_2(OH)_2]^{2+}$ and trimer $[(UO_2)_3(OH)_5]^+$. When a certain amount of water is present in the ionic liquid, these water molecules can coordinate to the uranyl ion. This coordination to the uranyl ion results in a higher acidity of the protons of water. The deprotonation of the coordinated water molecules at the pH conditions in the ionic liquid leads to the formation of hydrolysis products and the corresponding structureless band in the UV−vis absorption spectrum.

Partial evidence for the presence of multinuclear hydrolysis products was obtained from the structure of crystals formed from an aqueous solution of [C$_6$mim][Br], UO_2Br_2 and 18-crown-6. The molecular structure and crystal packing of $[(UO_2)_2(\mu_2\text{-OH})_2(H_2O)_6]$ $[UO_2Br_4](18\text{-crown-}6)_4$ are shown

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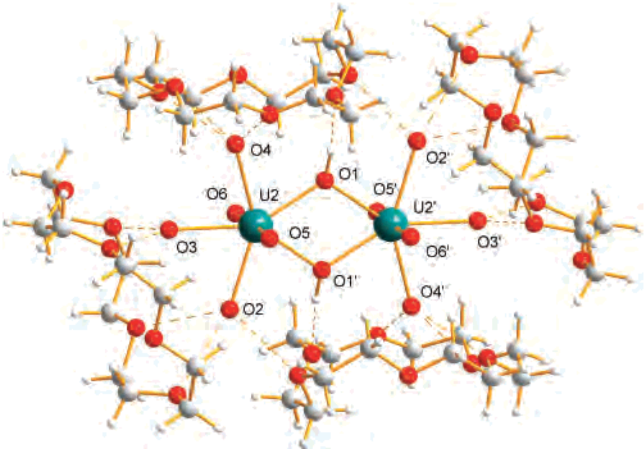

Figure 11. Part of the crystal structure of $[(UO_2)_2(\mu_2\text{-}OH)_2(H_2O)_6][UO_2Br_4](18\text{-crown-}6)_4$, showing the $[(UO_2)_2(\mu_2\text{-}OH)_2(H_2O)_6]^{2+}$ cation surrounded by four 18-crown-6 moieties, attached by strong hydrogen bonding.

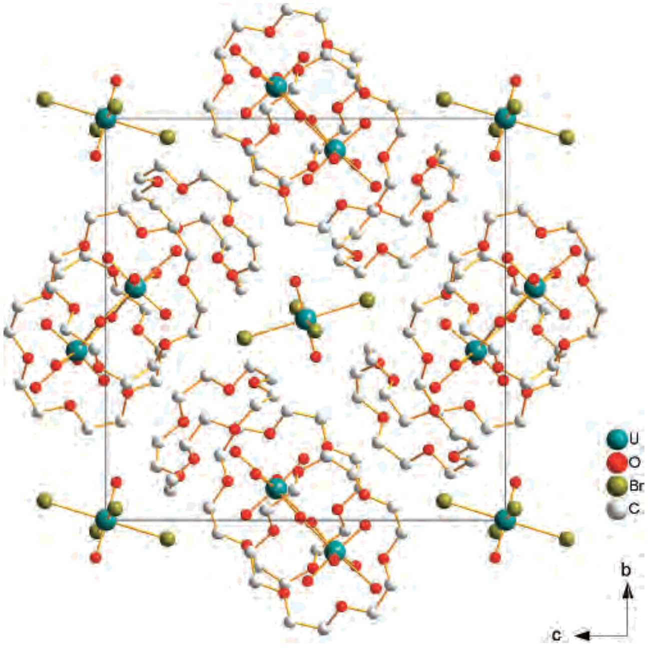

Figure 12. Packing diagram of the crystal structure of $[(UO_2)_2(\mu_2\text{-}OH)_2(H_2O)_6][UO_2Br_4](18\text{-crown-}6)_4$. Hydrogen atoms have been omitted for clarity.

in Figures 11 and 12. The hydrolysis product consists of two uranyl units, bridged by two hydroxide groups. The uranyl ions have completed their coordination sphere with water molecules, thereby achieving an equatorial coordination number of five. Strong hydrogen bonding is found for all coordinated water molecules and hydroxide groups. Besides the hydrolysis product of the uranyl ion, the $[UO_2Br_4]^{2-}$ species is present in the crystal structure as well. However, the typical spectrum of the $[UO_2Br_4]^{2-}$ species was not detected by UV−vis absorption spectroscopy due to the high molar absorptivity of the hydrolysis product $[(UO_2)_2(\mu_2\text{-}OH)_2(H_2O)_6]^{2+}$. From this crystal structure determination it is obvious that the uranyl ion prefers coordination to bromide ions rather than to the crown ether 18-crown-6. The $[(UO_2)_2(\mu_2\text{-}OH)_2(H_2O)_6]^{2+}$ cations are surrounded by four 18-crown-6 molecules.

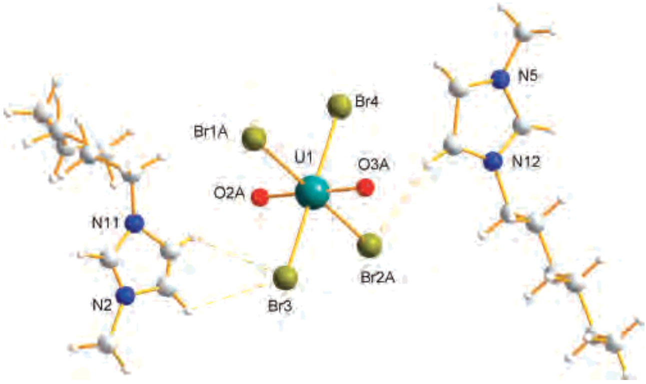

Figure 13. Part of the crystal structure of $[C_6mim]_2[UO_2Br_4]$, showing the $[UO_2Br_4]^{2-}$ anion with weak hydrogen bonding to two surrounding $[C_6mim]^+$ cations.

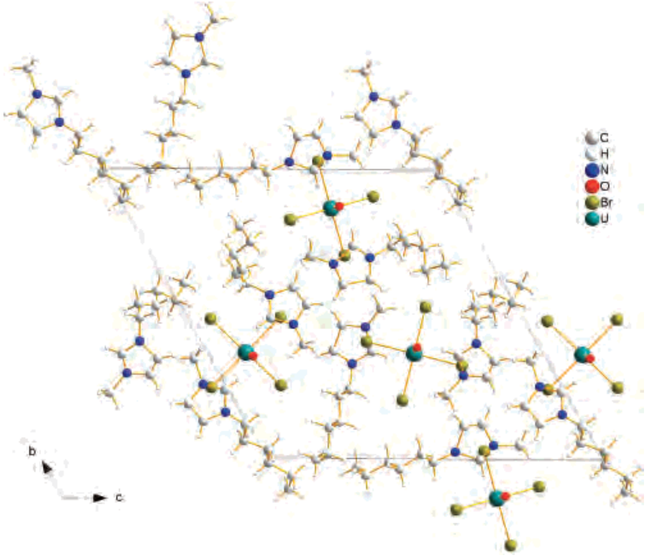

Figure 14. Packing diagram of the crystal structure of $[C_6mim]_2[UO_2Br_4]$, viewed along the *a* axis.

Upon addition of hydrogen bromide, hydrolysis of the uranyl ion is repelled and the $[UO_2Br_4]^{2-}$ complex is formed. This is evident from the crystal structure of $[C_6mim]_2[UO_2Br_4]$ shown in Figures 13 and 14. These crystals were grown from an aqueous solution of $[C_6mim][Br]$, UO_2Br_2 and 18-crown-6 at pH < 2.5. The first coordination sphere of the uranyl ion in $[C_6mim]_2[UO_2Br_4]$ consists of four bromide ions, which confirms again the preference of the uranyl ion to coordinate to small inorganic ligands (NO_3^-, Cl^-, Br^-) rather than to oxacrown ethers. Each $[UO_2Br_4]^{2-}$ unit is surrounded by two imidazolium cations of the ionic liquid, which is consistent with the results of molecular dynamics simulations of the coordination environment of $[UO_2Cl_4]^{2-}$ in imidazolium ionic liquids.[18] Weak hydrogen-bonding interactions are found between the bromide ions and the acidic hydrogen atoms of the imidazolium cations. A literature example of a crystal structure similar to that of $[C_6mim]_2[UO_2Br_4]$ is that of $[C_2mim]_2[UO_2Cl_4]$.[79]

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(79) Deetlefs, M.; Hitchcock, P. B.; Hussey, C. L.; Mohammed, T. J.; Seddon, K. R.; van den Berg, J.-A.; Zora, J. A. *ACS Symp. Ser.* **2005**, *901*, 47−67.

Conclusion

In this paper, we applied the method of speciation of uranyl complexes by optical spectroscopy to uranyl complexes dissolved in the ionic liquids 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide. It was shown that the spectra of tetrachloro, trinitrato, triacetato, and 18-crown-6 complexes in these ionic liquids are very similar to the spectra of these complexes in the nonaqueous solvents acetone and acetonitrile. Both the cation and the weakly coordinating anion bis(trifluoromethylsulfonyl)imide have only a minor influence on the spectra of the uranyl complexes, and it can therefore be assumed that the ionic liquid matrix only marginally disturbs the geometry and symmetry of the uranyl complexes. In wet ionic liquids, the absorption spectrum of the hydrated uranyl ion (“free” uranyl ion) is observed. This indicates that the uranyl ion is surrounded by a shell of water molecules. 18-Crown-6 forms inclusion complexes with the uranyl ion in ionic liquids with the weakly coordinating bis(trifluoromethylsulfonyl)imide anion, but it cannot compete with chloride or bromide ions for coordination to the uranyl ion: once appreciable amounts of chloride or bromide ions are present in the ionic liquid, the crown ether is removed from the first coordination sphere. Although the symmetry of uranyl complexes can be determined on the basis of the characteristic absorption spectra, optical spectroscopy does not allow determination of the coordination number and interatomic distances. However, this information can be obtained by EXAFS. The combination of optical spectroscopy and EXAFS is a powerful tool for the speciation of uranyl complexes in the liquid state, including uranyl complexes dissolved in ionic liquids.

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Supporting Information Available: CIF files of the crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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