Inorg. Chem. **2006**, *45*, 10419–10421

Inorganic Chemistry
Communication

Uranyl Complexation by Chloride Ions. Formation of a Tetrachlorouranium(VI) Complex in Room Temperature Ionic Liquids [Bmim][Tf_2N] and [$MeBu_3N$][Tf_2N]

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Received September 15, 2006

The tetrachlorouranium(VI) complex is formed in [Bmim][Tf_2N] and [$MeBu_3N$][Tf_2N] from a uranium(VI) solution in the presence of a stoichiometric quantity of chloride ions. The [$U^{VI}O_2Cl_4$]$^{2-}$ absorption and emission spectra show bands splitting in comparison with the [$U^{VI}O_2$]$^{2+}$ spectra, as observed in the solid state, organic solvents, and chloroaluminate-based ionic liquids. The fluorescence lifetime of [UO_2Cl_4]$^{2-}$ in [$MeBu_3N$][Tf_2N] is 0.7 ± 0.1 μs. The reduction potential of this complex is –1.44 and –1.8 V vs Ag/Ag$^+$ respectively in [Bmim][Tf_2N] and [$MeBu_3N$][Tf_2N] and does not depend on the chloride concentration. The mechanism proposed for the redox process is a monoelectronic reduction to form [$U^VO_2Cl_4$]$^{3-}$, followed by a chemical reaction. The tetrachlorouranium(V) complex seems more stable in [Bmim][Tf_2N] than in [$MeBu_3N$][Tf_2N]. The electrochemical analysis put in evidence specific interactions of the ionic liquid cation with the uranium anionic species.

Room temperature ionic liquids (RTILs) have currently gained interest in many chemical processes such as catalysis, organic synthesis, or electrochemistry. They display negligible vapor pressure, high thermal stability, high electrical conductivity, and a large electrochemical window, and their physicochemical properties can be adjusted by a suitable choice of a cation/anion combination.[1] These criteria make them good candidates to replace organic solvents and especially the volatile organic compounds. Recently, electrochemical and spectroscopic studies of actinides in RTILs have shown their potentiality in the nuclear industry.[2] However, fundamental knowledge on the behavior of actinides in ionic liquids is necessary to perform nuclear fuel reprocessing by extraction or electrodeposition. Most studies on actinides are investigated in chloroaluminate-based ionic liquids, which are extremely air- and water-sensitive.[3−6] Only a few papers deal with the uranium behavior in non-chloroaluminate-based RTILs.[7−11]

In this context, we are particularly interested in understanding the solvation, complexation, and redox properties of uranium in hydrophobic ionic liquids with the bis(trifluoromethanesulfonyl)imide anion (Tf_2N^-). For that purpose, three techniques were used: absorption spectroscopy, time-resolved laser spectroscopy (TRLS), and electrochemistry. In this Communication, we present the results obtained on the chloride complexation of [$U^{VI}O_2$]$^{2+}$ in 1-butyl-3-methylimidazolium ($Bmim^+$) and tri-*n*-butylmethylammonium ($MeBu_3N^+$), with both of them being associated with Tf_2N^-.

The uranyl salt used to prepare the solutions in both ionic liquids was [UO_2][OTf]$_2$, synthesized according to the procedure described in ref 12. The chloride ions were added to the uranyl(VI) solution as [Bmim]Cl and [$MeBu_3N$]Cl respectively in [Bmim][Tf_2N] (H_2O: 125 ± 20 ppm) and [$MeBu_3N$][Tf_2N] (H_2O: 175 ± 30 ppm). The uranyl salt and the ionic liquids were stocked in an argon-filled drybox, and all samples were prepared in this drybox.

The absorption spectra of [UO_2][OTf]$_2$ (0.01 M) alone and in presence of 6 equiv of [$MeBu_3N$]Cl in [$MeBu_3N$][Tf_2N]

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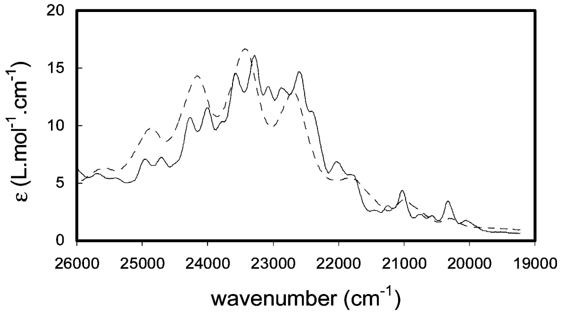

Figure 1. Absorption spectra of $[UO_2][OTf]_2$ (0.01 M) with 6 equiv of $[MeBu_3N]Cl$ (solid line) and without $[MeBu_3N]Cl$ (dotted line) in $[MeBu_3N][Tf_2N]$ at 60 °C. Details of the spectral data are available as Supporting Information.

are reported Figure 1. The absorption spectra are the same if 4, 6, or 9 equiv of Cl^- is added to the uranyl solution, and similar spectra are observed in $[Bmim][Tf_2N]$ (Figure S1 in the Supporting Information). In the presence of Cl^- (>4 equiv), the absorption spectra show a remarkable band splitting in comparison with the spectrum obtained for $[UO_2][OTf]_2$. The separation within a series of vibrational peaks is 700 ± 25 cm^{-1}. This spectrum corresponds to those obtained for the tetrachlorouranyl(VI) complex in the solid state,[13,14] organic solvents,[15] and chloroaluminate-based ionic liquids.[3-5] Then, the spectrophotometric analysis clearly shows the formation of $[UO_2Cl_4]^{2-}$ in both ionic liquids if a stoichiometric quantity of chloride ions is added to the uranyl solution. While the ionic liquid cation has no significant effect on the peak positions of the $[UO_2]^{2+}$ and $[UO_2Cl_4]^{2-}$ spectra, the absorbance is a little higher in $[MeBu_3N][Tf_2N]$ than in $[Bmim][Tf_2N]$, except for the peaks at 21 008 and 20 325 cm^{-1} of the $[UO_2Cl_4]^{2-}$ spectrum. Indeed, the molar extinction coefficients of these two peaks are quite sensitive to the uranium(VI) environment. Ryan has shown that the intensities of these two peaks increase if the tetrachlorouranyl(VI) complex is hydrogen-bonded.[14] The increase of the intensities at 21 008 and 20 325 cm^{-1} from $[MeBu_3N][Tf_2N]$ to $[Bmim][Tf_2N]$ can thus be assigned to the ability of the imidazolium cations to form C−H···Cl hydrogen bonds with the $[UO_2Cl_4]^{2-}$ complex.[3]

The fluorescence intensity of $[UO_2][OTf]_2$ (0.01 M) in $[Bmim][Tf_2N]$ alone or in the presence of chloride ions is very low. As was already described in the case of imidazolium-based ionic liquids, $[Bmim][Tf_2N]$ fluoresces in the 20 000−14 000-cm^{-1} range.[16,17] The spectra of uranyl solutions can thus not be well detected. Moreover, the samples were degraded under laser irradiation, as was already observed for $[Bmim][PF_6]$.[16] Therefore, the TRLS analysis was not achieved in this ionic liquid.

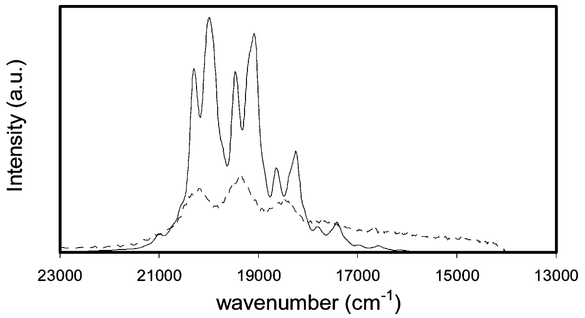

Figure 2. Emission spectra of $[UO_2][OTf]_2$ (0.01 M) alone (dotted line) and with 6 equiv of $[MeBu_3N]Cl$ (solid line) in $[MeBu_3N][Tf_2N]$ at 60 °C. The intensity is given in arbitrary units. $\lambda_{exc} = 425$ nm. Details of the spectral data are available as Supporting Information.

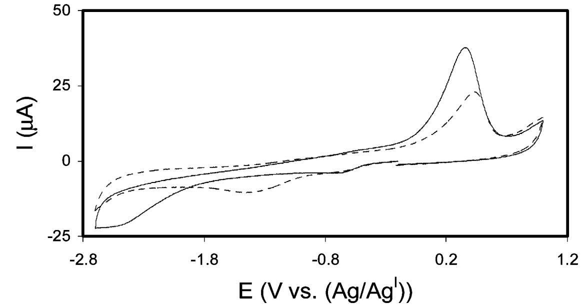

Figure 3. Cyclic voltammograms of $[UO_2][OTf]_2$ (0.01 M) in $[Bmim][Tf_2N]$ at 25 °C (solid line) and in $[MeBu_3N][Tf_2N]$ at 60 °C (dotted line). $v = 100$ mV/s; GC electrode area = 0.07 cm^2; $E_i = E_f = -0.2$ V; $E_{inv1} = -2.7$ V; $E_{inv2} = 1$ V.

Figure 2 shows the emission spectra of $[UO_2][OTf]_2$ (0.01 M) alone and with 6 equiv of $[MeBu_3N]Cl$ in $[MeBu_3N][Tf_2N]$. For the $[UO_2][OTf]_2$ solution, a broad band is observed from 20 000 to 14 000 cm^{-1} due to the fluorescence of $[MeBu_3N][Tf_2N]$. However, in the presence of 4, 6, and 9 equiv of Cl^-, a remarkable increase of the fluorescence intensity is observed. Like the absorption spectrum, the emission spectrum of the uranyl(VI) solutions containing chloride ions (>4 equiv) is characterized by the band splitting, with a separation of 850 ± 25 cm^{-1} within a series of vibrational peaks. This spectrum is similar to the $[UO_2Cl_4]^{2-}$ spectrum in organic solvents[15] and in chloroaluminate-based ionic liquids.[4] For samples containing 4−9 equiv of $[MeBu_3N]Cl$, a single-exponential decay with a fluorescence lifetime of 0.7 ± 0.1 μs is observed for the coordinated uranium(VI). Therefore, TRLS confirms the formation of one chloro complex, $[UO_2Cl_4]^{2-}$, if a stoichiometric quantity of chloride ions is added to the uranyl(VI) solution in $[MeBu_3N][Tf_2N]$.

The cyclic voltammograms of $[UO_2][OTf]_2$ (0.01 M) in both ionic liquids are recorded at a glassy carbon electrode (Figure 3) with respect to an Ag/Ag^I reference electrode. Two broad cathodic signals are observed (−0.6 and −2.5 V in $[Bmim][Tf_2N]$; −0.6 and −1.4 V in $[MeBu_3N][Tf_2N]$) and are associated with an anodic peak at the reverse scan (0.37 V in $[Bmim][Tf_2N]$; 0.45 V in $[MeBu_3N][Tf_2N]$). This oxidation peak is observed after either the first or the second reduction peak, and its shape is characteristic of a redissolution anodic peak. Thus, a species should be deposited after the reduction of uranium(VI) in $[Bmim][Tf_2N]$ and $[MeBu_3N][Tf_2N]$. This result is confirmed by linear voltammetry because a cathodic peak is obtained instead of a wave and an anodic redissolution peak is observed if the potential is

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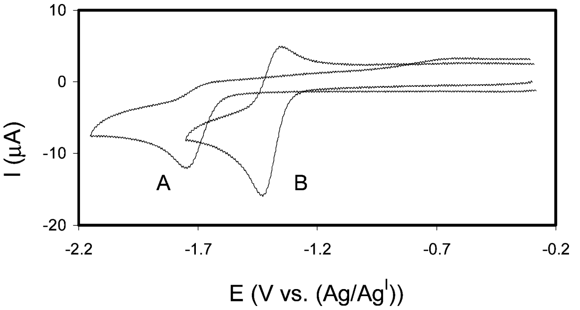

Figure 4. Cyclic voltammogram of $[UO_2][OTf]_2$ (0.01 M) with 6 equiv of $[MeBu_3N]Cl$ in $[MeBu_3N][Tf_2N]$ at 60 °C (A) and $[UO_2][OTf]_2$ (0.01 M) with 8.8 equiv of [Bmim]Cl in $[Bmim][Tf_2N]$ at 25 °C (B). $\upsilon = 100$ mV/s; GC electrode area = 0.07 cm^2; $E_i = E_f = -0.3$ V; $E_{inv} = -2.15$ V (A) and -1.75 V (B).

then scanned in the positive direction (Figure S2 in the Supporting Information). This phenomenon could be assigned to the formation of a $U^{IV}O_2$ passivating film because it was already described for uranyl nitrate complexes in $[Bmim][NO_3]$.[9] In organic solvents, the reduction of $[U^{VI}O_2]^{2+}$ occurs via both monoelectronic and bielectronic transfer.[18] Then, we suggest that the first cathodic peak corresponds to the reduction of $[U^{VI}O_2]^{2+}$ in $[U^{V}O_2]^{+}$ followed by a chemical reaction leading to the formation of $U^{IV}O_2$. The second cathodic peak would be the direct reduction of $[U^{VI}O_2]^{2+}$ in $U^{IV}O_2$.

As soon as 4 equiv of Cl^- is added to the $[UO_2][OTf]_2$ (0.01 M) solution, the cyclic voltammogram presents a new cathodic peak at −1.44 V in $[Bmim][Tf_2N]$ and at −1.8 V in $[MeBu_3N][Tf_2N]$ (Figure 4). In both ionic liquids, the potential of these new cathodic peaks does not change with the chloride concentration. Thus, the redox process does not involve any chloride exchange reaction. The cyclic voltammogram of [Bmim]Cl in $[Bmim][Tf_2N]$ and $[MeBu_3N]Cl$ in $[MeBu_3N][Tf_2N]$ (Figure S3 in the Supporting Information) allowed us to determine the concentration of the free Cl^- in the samples. The peak intensities obtained for the free Cl^- in the uranyl samples containing more than 4 equiv of Cl^- in both ionic liquids (Table S4 in the Supporting Information) confirm the formation of the tetrachlorouranium(VI) complex observed by UV−visible and TRLS.

In $[Bmim][Tf_2N]$, at the reverse scan, an oxidation peak is observed only in the presence of more than 4 equiv of [Bmim]Cl, and its intensity is lower than the cathodic peak intensity. The ratio I_{pa}/I_{pc} goes from 0.4 to 0.7 for potential scan rates from 0.025 to 5 V/s (Figure S4 in the Supporting Information). In $[MeBu_3N][Tf_2N]$, whatever the chloride content (until 8 equiv) and the potential scan rate (until 5 V/s), no anodic peak is observed at the reverse scan. Therefore, the reduction of $[U^{VI}O_2Cl_4]^{2-}$ should involve the formation of a tetrachloro complex, probably $[U^{V}O_2Cl_4]^{3-}$. This complex seems more stable in $[Bmim][Tf_2N]$ than in $[MeBu_3N][Tf_2N]$. In $[Bmim][Tf_2N]$, the stability of this complex is a function of the chloride concentration, as was observed for $U^{V}Cl_6^-$ in a chloroaluminate-based ionic liquid.[19] A difference of 360 mV is measured for the cathodic peak potential in the two ionic liquids. This phenomenon was already observed for the hexachlorouranium(IV) complex and was attributed to a difference of solvation.[7] Because of C−H···Cl hydrogen bonds between the imidazolium ring and the uranium complex, the $[Bmim]^+$ cation would interact more strongly than $[MeBu_3N]^+$. Works are in progress to study in detail the redox mechanism of $[U^{VI}O_2Cl_4]^{2-}$ in RTILs.

In conclusion, the three techniques put in evidence the formation of tetrachlorouranium(VI) in $[Bmim][Tf_2N]$ and $[MeBu_3N][Tf_2N]$. The uranium absorption and emission spectra are similar in the presence of 4 equiv or more of Cl^-. The complexation is then totally achieved as soon as a stoichiometric quantity of Cl^- is added. The absorption and emission spectra of $[UO_2Cl_4]^{2-}$ in both ionic liquids show a vibrational fine structure with band splitting like in the solid state, organic solvents, and chloroaluminate-based ionic liquids. Because a solution containing the tetrachlorouranium complex alone can be prepared, the electrochemical behavior of this species was studied. The redox process should involve a monoelectronic transfer to form a tetrachlorouranium(V) complex followed by a chemical reaction. A difference of 360 mV measured for the reduction potential of $[UO_2Cl_4]^{2-}$ in the ionic liquids under study shows a different interaction of these solvents. Our work is currently focused on the solvent effect. The possible formation of other chlorouranium(VI) complexes $[UO_2Cl_x]^{-(x-2)}$ is also investigated in the Tf_2N^--based RTILs.

Acknowledgment. This work was supported by European Actinet network and GDR PARIS (French organization).

Supporting Information Available: Description of the materials and methods used, absorption and emission data for $[UO_2][OTf]_2$ and $[UO_2Cl_4]^{2-}$, anodic peak intensities of free Cl^- in both ionic liquids, absorption spectra of $[UO_2][OTf]_2$ and $[UO_2Cl_4]^{2-}$ in $[Bmim][TF_2N]$, linear voltammograms of $[UO_2][OTf]_2$ in $[Bmim][Tf_2N]$, and cyclic voltammograms of [Bmim]Cl in $[Bmim][Tf_2N]$ and $[MeBu_3N]Cl$ in $[MeBu_3N][Tf_2N]$ and also of $[UO_2][OTf]_2$ + 8.8 equiv of [Bmim]Cl in $[Bmim][TF_2N]$ at different potential scan rates. This material is available free of charge via the Internet at http://pubs.acs.org.

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