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Uranyl Complexes of Carboxyl-Functionalized Ionic Liquids

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Uranium(VI) oxide has been dissolved in three different ionic liquids functionalized with a carboxyl group: betainium bis[(trifluoromethyl)sulfonyl]imide, 1-(carboxymethyl)-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide, and *N*-(carboxymethyl)-*N*-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide. The dissolution process results in the formation of uranyl complexes with zwitterionic carboxylate ligands and bis[(trifluoromethyl)sulfonyl]imide (bistriflimide) counterions. An X-ray diffraction study on single crystals of the uranyl complexes revealed that the crystal structure strongly depends on the cationic core appended to the carboxylate groups. The betainium ionic liquid gives a dimeric uranyl complex, the imidazolium ionic liquid a monomeric complex, and the pyrrolidinium ionic liquid a one-dimensional polymeric uranyl complex. Extended X-ray absorption fine structure measurements have been performed on the betainium uranyl complex. The absorption and luminescence spectra of the uranyl betainium complex have been studied in the solid state and dissolved in water, in acetonitrile, and in the ionic liquid betainium bistriflimide. The carboxylate groups remain coordinated to uranyl in acetonitrile and in betainium bistriflimide but not in water.

Introduction

Ionic liquids are a remarkable class of solvents that entirely consist of ions.[1] They have possible applications in different fields ranging from nonaqueous solvents for electrodeposition of reactive metals, to electrolytes in batteries or dye-sensitized solar cells, to solvents for catalytic reactions and biomass processing.[2] Although ionic liquids are often touted as supersolvents and although they do possess remarkable solvent properties such as the ability to solubilize the high-molecular-weight bitumous matter in oil shale (kerogen),[3] ionic liquids with weakly coordinating anions (for instance, BF_4^-, PF_6^-, TfO^-, and Tf_2N^-) are poor solvents for metal salts and metal oxides. For instance, only 1.2 mg of LiCl or 0.7 mg of $LaCl_3$ can be dissolved in 100 g of 1-butyl-3-methylimidazolium hexafluorophosphate at room temperature.[4] On the other hand, many metal oxides have a reasonably good solubility in the ionic-liquid-like deep eutectic solvents, which consist of choline chloride in combination with a hydrogen-bond donor, e.g., urea or carboxylic acid.[5] Higher solubilities of metal oxides and other metal salts can be achieved by using *functionalized ionic liquids* (also called *task-specific ionic liquids*), i.e., ionic liquids with a functional group covalently linked to the cationic core,[6–8] or by using ionic liquids with strongly coordinating anions.[9] We have developed carboxyl-functionalized ionic liquids that are able to dissolve considerable

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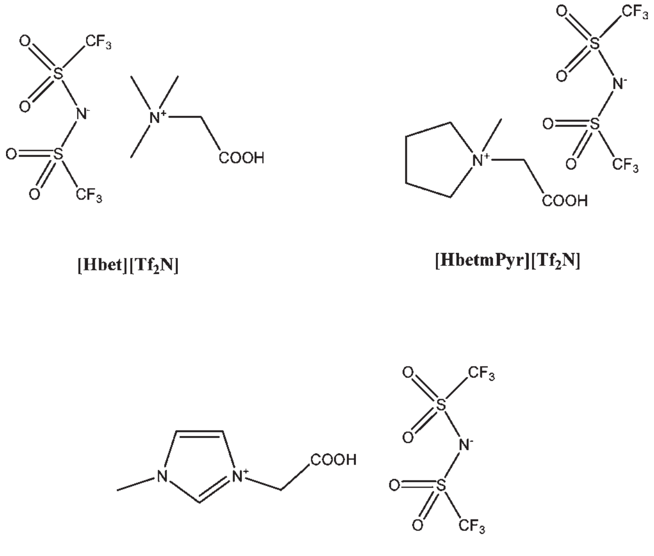
amounts of a wide range of metal oxides, including rare-earth oxides and uranium(VI) oxide.[7,10-12] Ionic liquids that can solubilize uranium oxides are of interest for applications in the nuclear fuel cycle, namely, for the extraction of uranium from ores and for the processing of spent nuclear fuel rods.[13] Uranium in ionic liquids has been the subject of several theoretical and experimental studies.[14] Uranium forms with oxygen the brown-black dioxide UO_2, the olive-green to black triuranium octoxide U_3O_8, and the yellow-orange trioxide UO_3.[15] UO_2 is insoluble in water and in alkaline solutions. It is sparingly soluble in most acids to form uranium(IV) salts. However, UO_2 can be dissolved by nitric acid upon oxidation to $UO_2(NO_3)_2$. UO_3 is an amphoteric oxide: it dissolves in acids HX to form uranyl salts $[UO_2]X_2$ and in basic solutions to form uranates $[UO_4]^{2-}$ or diuranates $[U_2O_7]^{2-}$.[15] U_3O_8 dissolves in acids and gives a mixture of uranium(IV) and uranyl salts. Recently, research has been directed toward the dissolution behavior of uranium oxides in ionic liquids. Bradley et al. were able to oxidatively dissolve UO_2 in the ionic liquid 1-butyl-3-methylimidazolium nitrate with the addition of concentrated nitric acid.[16] Billard and co-workers investigated the dissolution of UO_2 and UO_3 in the ionic liquid 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide.[17] Rao et al. compared the solubility of the uranium oxides UO_2, U_3O_8, and UO_3 in the carboxyl-functionalized ionic liquid betainium bis[(trifluoromethyl)sulfonyl]imide, [Hbet][Tf_2N].[18] These authors found that dissolution of UO_3 in [Hbet][Tf_2N] is fast and that the saturation concentration is 15 wt % of UO_3 at 100 °C, but for dissolution of UO_2 and U_3O_8, much harsher conditions are required. Only a little information is available on the coordination chemistry of uranium in carboxyl-functionalized ionic liquids.



[Hbet][Tf_2N]

[HbetmPyr][Tf_2N]

[HbetmIm][Tf_2N]

Figure 1. Structures of the carboxyl-functionalized ionic liquids [Hbet][Tf_2N], [HbetmPyr][Tf_2N], and [HbetmIm][Tf_2N].

In this paper, we report on uranyl complexes formed upon dissolution of uranium(VI) oxide (UO_3) in ionic liquids with a covalently bonded carboxyl group and with bis[(trifluoromethyl)sulfonyl]imide anions (Figure 1). This study comprises the structural determination of single crystals of complexes crystallized from these ionic liquids, as well as the measurement of absorption and luminescence spectra of the uranyl complex of betainium bis[(trifluoromethyl)sulfonyl]imide.

Experimental Section

Synthesis. The synthesis of the carboxyl-functionalized ionic liquids has been described elsewhere.[7,10]

$[(UO_2)_2(bet)_6(H_2O)_2][Tf_2N]_4$ (1). A mixture of the ionic liquid [Hbet][Tf_2N] (6 g, 15 mmol) and uranium trioxide dihydrate $UO_3 \cdot 2H_2O$ (1.15 g, 3.57 mmol) was stirred in 10 mL of water overnight at reflux temperature. The solvent was removed on a rotavap. The crude complex was redissolved in a minimum amount of water and recrystallized. The compound was obtained as bright-yellow crystals. Elem. anal. Calcd for $C_{19}F_{12}H_{33}N_5O_{16}S_4U \cdot 2H_2O$: C, 18.73; H, 3.06; N, 5.75. Found: C, 18.79. H, 3.09. N, 5.62. A crystal suitable for single-crystal X-ray diffraction was selected from this batch.

$[(UO_2)_2(betmPyr)_4(OH)][Tf_2N]_3 \cdot H_2O$ (2). To [HBetmPyrr][Tf_2N] (2.55 g, 6.1 mmol) was added 5 mL of deionized water. Under vigorous stirring, $UO_3 \cdot 2H_2O$ (1.13 g, 3.50 mmol) was added. The mixture was heated at reflux temperature for 24 h. Then another 0.1562 g (0.485 mmol) of $UO_3 \cdot 2H_2O$ was added, and the mixture was further refluxed for 12 h. The reaction mixture was filtered over a fritted glass filter (No. 4) while still hot. The residue was washed with small portions of ethanol (total 10 mL). The solvent was removed at the rotavap at 65 °C. From the glassy residue, a small particle was taken. The remainder was redissolved in the minimum amount of deionized water and put into a crystallization disk inside a desiccator

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equipped with anhydrous P_2O_5. After 3 days, the small dried parts of the uranyl complex were carefully put on top of the now oily complex in the crystallization disk and further dried. After 3 weeks, small deliquescent yellow crystals appeared, which weighed 2.48 g (95%). Elem. anal. Calcd for $C_{68}H_{110}F_{36}N_{14}O_{52}S_{12}U_4$: C, 20.53; H, 2.79; N, 4.93. Found: C, 20.18; H, 2.91; N, 5.07. A crystal suitable for single-crystal X-ray diffraction was selected from this batch.

$[(UO_2)(betmIm)_3][Tf_2N]_2$ (3). The ionic liquid [HbetmIm][Tf_2N] (5 g, 11.9 mmol) was first decolorized with activated charcoal at reflux conditions for 48 h in dichloromethane, followed by filtration over Celite. The solvent was removed by vacuum evaporation (rotavap, 45 °C, 650 mbar). Deionized water (10 mL) was added, followed by $UO_3 \cdot 2H_2O$ (1.60 g, 5.94 mmol). The reaction mixture was stirred overnight while maintaining a gentle reflux. The remaining solid was removed by filtration, and the filtrate was evaporated down to a glassy residue, which was redissolved in a minimum amount of deionized water at 60 °C. The solution was cooled in the refrigerator at 5 °C. After 8 h, the mother liquor was removed by decantation and the bright-yellow crystals were filtered and dried in a stream of dry air. A single crystal suitable for X-ray diffraction was selected from this batch. Yield: 4.04 g (95% with respect to the starting amount of ionic liquid). Elem. anal. Calcd for $C_{22}H_{24}F_{12}N_8O_{16}S_4U \cdot 2H_2O$: C, 20.53; H, 2.19; N, 8.71. Found: C, 20.11; H, 2.38; N, 8.14.

X-ray Crystallography. For all structures, X-ray intensity data were collected at room temperature on a SMART 6000 diffractometer equipped with a CCD detector using Cu Kα radiation (λ = 1.541 78 Å), using ϕ and ω scans. For compound **1**, the data were collected under a nitrogen gas cryostream at 100 K. The images were interpreted and integrated with the program *SAINT* from Bruker.[19] All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the *SHELXTL* program package.[20] Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode and isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups). For the structure of compound **2**, the hydrogen atoms on the solvent water molecule and the hydroxyl anion could be located from a difference electron density map and the O−H distances were restrained with a target value of 0.82 Å. CCDC-755956−755958 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, U.K., fax +44-1223-336033, or e-mail deposit@ccdc.cam.ac.uk).

Crystal Data for Compound 1:. $C_{38}H_{66}F_{24}N_{10}O_{34}S_8U_2$, M = 2395.63, monoclinic, Pc (No. 7), a = 11.276(3) Å, b = 10.216(3) Å, c = 33.95(1) Å, β = 90.32(1)°, V = 3911(2) Å^3, T = 100(2) K, Z = 2, ρ_{calcd} = 2.034 g cm^{-3}, μ(Cu Kα) = 14.892 mm^{-1}, F(000) = 2328, crystal size 0.2 × 0.1 × 0.05 mm, 14 523 independent reflections (R_{int} = 0.0782). Final R1 = 0.0392 for 14 073 reflections with $I > 2\sigma(I)$ and wR2 = 0.0965 for all data.

Crystal Data for Compound 2:. $C_{68}H_{110}F_{36}N_{14}O_{52}S_{12}U_4$, M = 3976.66, monoclinic, $P2/c$ (No. 13), a = 16.861(2) Å, b = 13.264(2) Å, c = 16.692(3) Å, β = 118.361(5)°, V = 3285.0(9) Å^3, T = 293(2) K, Z = 1, ρ_{calcd} = 2.010 g cm^{-3}, μ(Cu Kα) = 16.742 mm^{-1}, F(000) = 1916, crystal size 0.2 × 0.1 × 0.1 mm, 5733 independent reflections (R_{int} = 0.1410). Final R1 = 0.0714 for 4092 reflections with $I > 2\sigma(I)$ and wR2 = 0.1992 for all data.

Crystal Data for Compound 3:. $C_{22}H_{24}F_{12}N_8O_{16}S_4U$, M = 1250.80, monoclinic, $P2_1/c$ (No. 14), a = 16.834(3) Å, b = 27.155(3) Å, c = 9.510(2) Å, β = 104.927(8)°, V = 4200(1) Å^3, T = 293(2) K, Z = 4, ρ_{calcd} = 1.978 g cm^{-3}, μ(Cu Kα) = 13.912 mm^{-1}, F(000) = 2416, crystal size 0.3 × 0.2 × 0.1 mm, 7332 independent reflections (R_{int} = 0.1380). Final R1 = 0.0693 for 5250 reflections with $I > 2\sigma(I)$ and wR2 = 0.1848 for all data.

Extended X-ray Absorption Fine Structure (EXAFS). EXAFS measurements were carried out at the Rossendorf Beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France).[21] The monochromator, equipped with a Si(111) double crystal, was used in channel-cut mode. Higher harmonics were rejected by two platinum-coated mirrors. All experiments were performed at room temperature. The spectra were collected in transmission mode using argon-filled ionization chambers. The monochromator energy scale was calibrated to the K-edge of an yttrium metal foil (first inflection point assigned to 17 038 eV). The EXAFS oscillations were extracted from the raw absorption spectra by standard methods including a μ_0 spline approximation for the atomic background using the *EXAFSPAK* software package.[22] A standard shell fitting was performed by using theoretical phase and amplitude functions calculated with the FEFF 8.2 code.[23] The scattering interactions were calculated using a crystal structure determined from a single crystal of the dimeric complex **1**. The multiple-scattering path between uranium and the axiallly arranged *trans*-dioxo atoms (O_{ax}) was included in the curve fit by constraining its Debye−Waller factor and its effective path length to twice the values of the corresponding, freely fitted U−O_{ax} single-scattering path. The amplitude reduction factor, S_0^2, was defined as 0.9 in the free-energy force-field calculation and fixed to that value in the data fits. The solid complex was ground with boron nitride, pressed into a pellet, and sealed in a polyethylene sample holder (type SH01A), which was then heat-sealed in a polyethylene foil as the second confinement (ESRF regulations require a double confinement for all radioactive samples).

Spectroscopy. UV−vis absorption spectra were recorded on a Varian Cary 5000 spectrophotometer in the wavelength range between 300 and 600 nm. The spectra were measured at room temperature, unless otherwise stated. The luminescence spectra were recorded on an Edinburgh Instruments FS-900 spectrofluorimeter. The excitation was done with a 450 W xenon lamp. Emission spectra were recorded between 440 and 650 nm, with the excitation wavelength being 420 nm. The emission spectra were corrected for the wavelength-dependent sensitivity of the detector. For measurements in the solid state, the uranyl betainium complex **1** was ground to a fine powder and dispersed in vacuum grease (Dow Corning high-vacuum grease), and the resulting mull was squeezed to a thin film between two quartz plates. For measurements of the spectra of the complex in water and in acetonitrile, 4 × 10^{-2} mol L^{-1} solutions were prepared. The aqueous solution was acidified with a few drops of a 1 M $HClO_4$ solution, in order to prevent hydrolysis of the uranyl ion. The concentration of the solution of the uranyl complex in the ionic liquid [Hbet][Tf_2N] was 4 × 10^{-2} mol L^{-1}. Because of the high viscosity of the ionic liquid, the dissolution process was rather slow and the solution was prepared 4 days before measurement. The complex was dissolved at room temperature and was periodically agitated. Although the melting point of the ionic liquid [Hbet][Tf_2N] is 57 °C, this ionic liquid easily forms a supercooled liquid at room temperature when a uranyl complex is dissolved in it. The solution absorption and luminescence

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Table 1. Summary of Crystallographic Data

	$[(UO_2)_2(bet)_6(H_2O)_2][Tf_2N]_4$ (**1**)	$[(UO_2)_2(betmPyr)_4(OH)][Tf_2N]_3 \cdot H_2O$ (**2**)	$[(UO_2)(betmIm)_3][Tf_2N]_2$ (**3**)
formula	$C_{38}H_{66}F_{24}N_{10}O_{34}S_8U_2$	$C_{68}H_{110}F_{36}N_{14}O_{52}S_{12}U_4$	$C_{22}H_{24}F_{12}N_8O_{16}S_4U$
fw (g mol^{-1})	2395.63	3976.66	1250.80
cryst dimens (mm^3)	0.2 × 0.1 × 0.05	0.2 × 0.1 × 0.1	0.3 × 0.2 × 0.1
cryst syst	monoclinic	monoclinic	monoclinic
space group	*Pc* (No. 7)	$P2/c$ (No. 13)	$P2_1/c$ (No. 14)
a (Å)	11.276(3)	16.861(2)	16.834(3)
b (Å)	10.216(3)	13.264(2)	27.155(3)
c (Å)	33.95(1)	16.692(3)	9.510(2)
β (deg)	90.32(1)	118.361(5)	104.927(8)
V (Å^3)	3911(2)	3285.0(9)	4200(1)
Z	2	1	4
ρ_{calcd} (g cm^{-3})	2.034	2.010	1.978
$\mu_{Cu\ K\alpha}$ (mm^{-1})	14.892	16.742	13.912
abs corrn	refdelf	refdelf	refdelf
F(000)	2328	1916	2416
measd reflns	57 592	30 117	31 455
unique reflns	14 523	5733	7332
obsd reflns [$I_0 > 2\sigma(I_0)$]	14 073	4092	5250
param refined	1064	596	708
GOF on F^2	1.044	1.035	1.042
R1	0.0392	0.0714	0.0693
wR2	0.0954	0.1790	0.1699
R1 (all data)	0.0405	0.1043	0.0969
wR2 (all data)	0.0965	0.1992	0.1848

spectra were measured in quartz cuvettes with an optical path length of 1 cm (cuvettes with two polished sides for absorption measurements and four polished sides for luminescence measurements).

Nomenclature. We consider the carboxyl-functionalized ionic liquids [HbetmPyr][Tf_2N] and [HbetmIm][Tf_2N] as analogues of protonated betaine bis[(trifluoromethyl)sulfonyl]imide, [Hbet][Tf_2N], in which the betaine or *N*,*N*,*N*-trimethylglycine group is present. Therefore, all names contain "Hbet". We represent the cation betaine by *Hbet* rather than by *bet* because in [Hbet][Tf_2N] the carboxyl group is protonated. Protonated betaine can also be named as *betainium*.

Results and Discussion

Synthesis. The uranyl complexes were prepared by a reaction between uranium(VI) oxide dihydrate ($UO_3 \cdot 2H_2O$) and the corresponding ionic liquid in a small amount of water. In principle, the uranyl complex could also be formed by the direct dissolution of $UO_3 \cdot 2H_2O$ in the ionic liquid, but the dissolution kinetics are very slow and no single crystals suitable for X-ray diffraction could be obtained. It is assumed that water enhances the proton mobility of the carboxyl group and therefore facilitates the dissolution process. Although the first syntheses made use of an excess of $UO_3 \cdot 2H_2O$, we found that the purity of the uranyl complex is easier to control by using an excess of the ionic liquid, and an excess of the ionic liquid was used for the synthesis of the uranyl complex of the betainium ionic liquid [Hbet][Tf_2N]. The excess of ionic liquid could be removed during the purification step by washing with hot water (> 60 °C). In the case where an excess of $UO_3 \cdot 2H_2O$ was used, the resulting uranyl complexes were sometimes found to be contaminated with hydrolysis products. The uranyl ion is known to undergo hydrolysis in aqueous solutions with a pH > 2.5. At this pH, hydrolysis results in the formation of polynuclear complexes with the general formula $[(UO_2)_m(OH)_n]^{2m-n}$.[24,25] Two of the most frequently found complexes are the dimer $[(UO_2)_2(OH)_2]^{2+}$and the trimer $[(UO_2)_3(OH)_5]^{+}$. The excess of ionic liquid assures that the pH of the solution remained below 2.5.

Crystal Structures. The crystallographic data of complexes **1**−**3** are summarized in Table 1. The crystal structure of **1** consists of $[(UO_2)_2(bet)_6]^{4+}$ uranyl dimers with six coordinating betaine zwitterions and two water molecules, surrounded by four noncoordinating bistriflimide $[Tf_2N]^-$ counterions (Figure 2). Two of the betaine zwitterions coordinate via μ_2 bridging and link the two uranyl cations together. The other four carboxyl-functionalized betaine zwitterions are monodentately coordinated to each of the two uranyl cations in the asymmetric unit. The three bistriflimide anions in the asymmetric unit do not form hydrogen bonds with the terminal coordinating water molecules. This is in contrast to what is found, for instance, for comparable dimeric europium complexes that were previously reported by us.[12] Four of the coordinating betaine ligands and one water molecule form a slightly distorted pentagonal-bipyramidal coordination polyhedron around each of the uranium atoms. The uranyl O=U=O angles deviate from 180°, with 177.8° (U1) and 176.0° (U2). The noncoordinating bistriflimide anions are all, as to be expected, in the trans conformation. In the packing of the crystal structure of **1** viewed along the *a* axis (Figure 3), the dimers are packed into layers, parallel with (001), separated by layers of bistriflimide anions.

The crystal structure of **2** consists of polymeric strands of $[(UO_2)_2(betmPyr)_4(OH)]^{3+}$ along the *c* axis and three bistriflimide counterions. Figure 4 shows a cut-out of the polymeric strand of the linked uranyl cations. Each of the crystallographically equivalent uranyl cations is surrounded by one bidentately coordinating carboxylate-functionalized pyrrolidinium zwitterion (betmPyr), two

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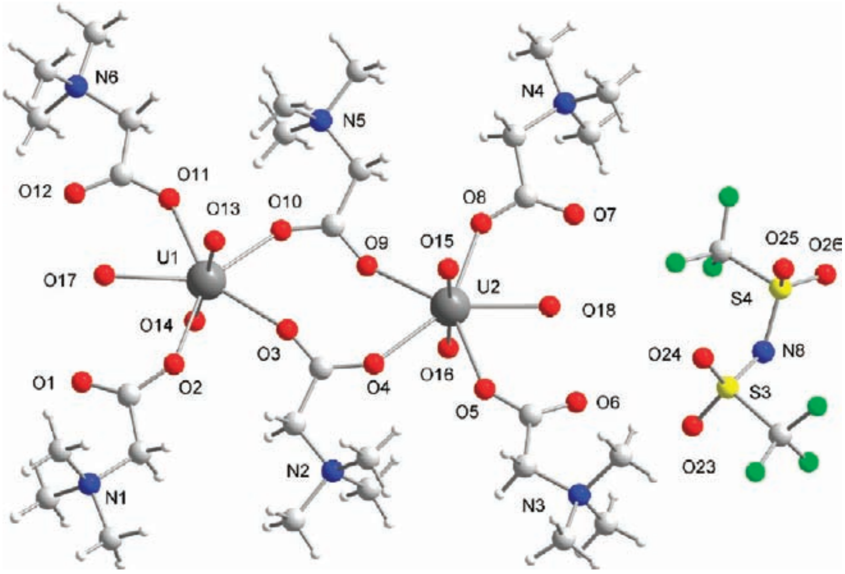

Figure 2. Structure and atom-labeling scheme of the $[(UO_2)_2(bet)_6(H_2O)_2]^{4+}$ dimers and one of the surrounding bistriflimide $[Tf_2N]^-$ anions in the crystal structure of **1**.

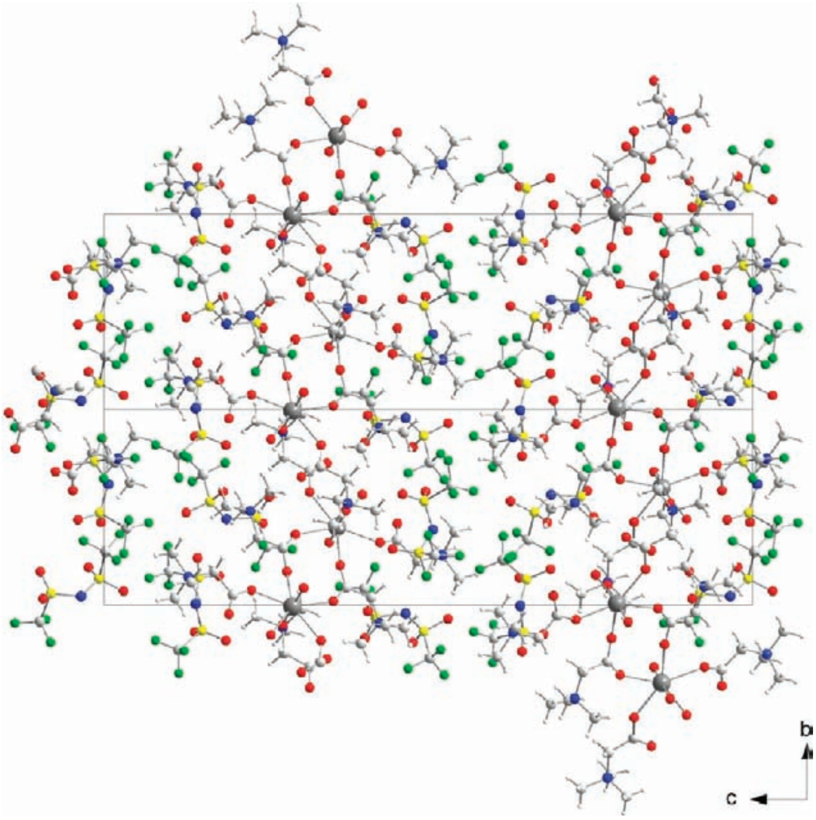

Figure 3. Packing in the crystal structure of **1** viewed along the *a* axis.

betmPyr ligands μ_2-bridging to an adjacent uranyl cation, and a hydroxyl group (OH^-) bridging to an adjacent uranyl cation at the opposite side. An inversion center is located between each betmPyr μ_2-bridged uranyl cations, and the OH group is located on the 2-fold axis. The U−O distances to the ligands range from 2.28 to 2.48 Å. The O═U═O angle deviates with 179.4° slightly from 180°. As shown in Figure 5, the bridging hydroxyl group shows strong hydrogen bonding with a noncoordinating water molecule (OH···O distance of 1.94 Å). The water molecule forms hydrogen bonds with two symmetry-equivalent bistriflimide anions (OH···O distance of 1.96 Å). Both bistriflimide anions in the asymmetric unit are strongly disordered. Figure 6 shows the uranyl strands in the packing of the crystal structure of **2**, viewed along the *c* axis.

The crystal structure of **3** consists of $[(UO_2)(betmIm)_3]^{2+}$ cations of three carboxyl-functionalized imidazolium zwitterions that coordinate bidentately to the uranyl and two noncoordinating bistriflimide counterions

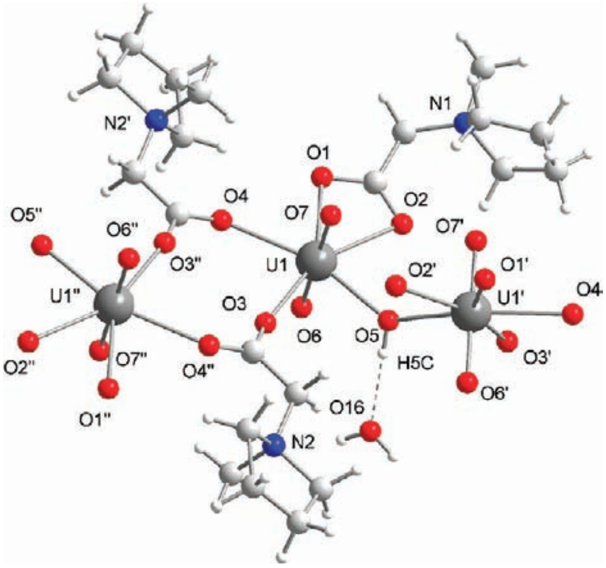

Figure 4. Cut-out from the polymeric strands of a uranyl linked by the bridging carboxy-functionalized pyrrolidinium zwitterions and a hydroxyl group in the crystal structure of **2**.

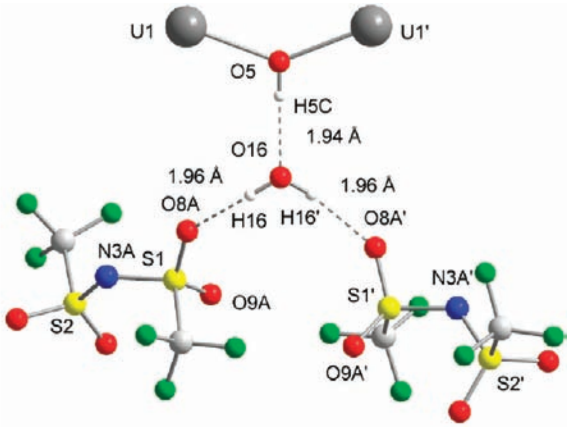

Figure 5. Hydrogen-bonding interaction in the crystal structure of **2**, between the bridging hydroxyl group, the noncoordinating water molecule, and two symmetry-equivalent bistriflimide anions.

($[Tf_2N]^-$) (Figure 7). One of the two bistriflimide anions in the asymmetric unit is strongly disordered. The U−O(carboxylate) bond lengths range from 2.46 to 2.48 Å. The three coordinating carboxylate groups are slightly out-of-plane with the O═U−O angles ranging from 86.3° to 93.8°. One imidazolium cation forms hydrogen bonds with a bistriflimide anion from the acidic hydrogen atom of the imidazolium ring to two oxygen atoms of the bistriflimide anions with CH−O distances of 2.35 and 2.40 Å, respectively (Figure 8). The second (disordered) bistriflimide anion is also contacting the acidic hydrogen atom of an imidazolium cation through a hydrogen bond (2.27 Å). Although the compound has been synthesized in the presence of water, no coordinating or noncoordinating water molecules were found in the crystal structure. In the packing of the crystal structure of **3**, as can be seen in Figure 9, the $[UO_2(betmIm)_3]^{2+}$ cations form double layers, which are separated by double layers of bistriflimide anions.

Because of the coordination of the neutral betaine (and related) zwitterions to the uranyl complex, the dipositive charge of the uranyl ion is not compensated for by the charge of the ligands and, as a consequence, the counterions of the uranyl complex are anions, namely, bistriflimide ions. In a search of the Cambridge Structural Database (CSD), it was found that most uranyl complexes with carboxylate ligands are anionic complexes with countercations.[26−30] The coordination of the uranyl ion in the crystal structure of **3** is similar to that found for complexes previously reported by Bismondo et al., with zwitterionic aminobutanoic acid as the ligand and perchlorate and nitrate as counterions, respectively.[31,32] A different arrangement exists of a uranyl cation, with two bidentately and two monodentately coordinating zwitterionic glycine ligands and nitrate counterions.[33] The dimeric structural units observed in the crystal structure of **1** are also observed in a structure reported by Grigor'ev et al., in which two acetate ligands are μ_2-bridging the two UO_2^{2+} cations together and in which one bidentate acetate ligand and one monodentate acetic acid molecule (via the carbonyl group) are coordinating to each of the uranyl cations.[34] Polymeric strands like those that occur in the crystal structure of **2** are also found in a structure described by Nierlich et al., where polymeric strands are formed by benzoate ligands, forming μ_2 bridges between the uranyl cations.[35] The coordination sphere of each uranyl cation is completed by a bidentately coordinating benzoate ligand and a water molecule. Another example is the structure of Alcock et al., containing uranyl dimers, built up by a μ_2-bridging furoate and additional hydroxyl anions (OH^-).[36] In the packing, these uranyl dimers form polymeric strands by additionally μ_2-bridging furoate molecules. Hence, this structure contains two different coordination environments for the uranyl cations; i.e., a first uranyl cation is surrounded by one hydroxyl anion and two monodentately and one bidentately coordinating furoate ligands, and a second uranyl cation coordinates with one hydroxyl anion, two monodentate furoate ligands, and two water molecules. The hydroxyl anion is also hydrogen-bonded to a water solvent molecule.

EXAFS Measurements. A solid sample of **1**, diluted with boron nitride, was investigated with uranium L_3-edge EXAFS spectroscopy. The rationale of this experiment was to use the EXAFS spectra to monitor the breakdown of the dimeric complex into a monomeric complex by the disappearance of the uranium−uranium

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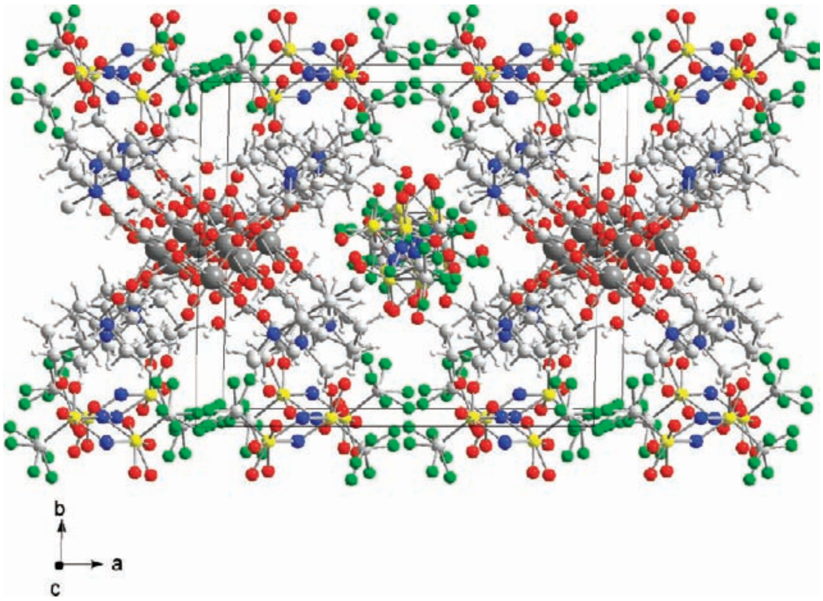

Figure 6. Packing in the crystal structure of **2** viewed along the *c* axis showing the uranyl strands in this direction.

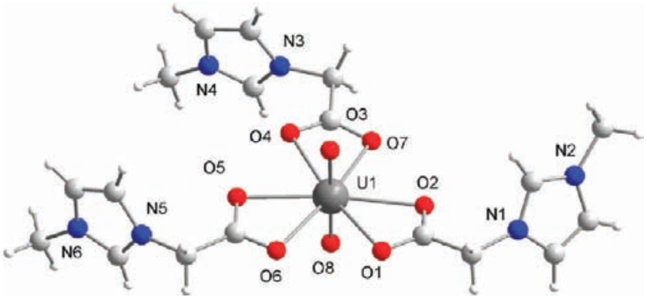

Figure 7. Structure and labeling of the $[UO_2(betmIm)_3]^{2+}$ cation in the crystal structure of **3**.

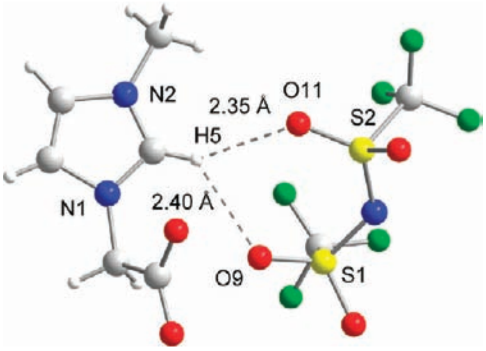

Figure 8. Hydrogen-bonding interaction between the undistorted bistriflimide anion and the carboxyl-functionalized imidazolium cation in the crystal structure of **3**.

backscattering signal upon dissolution of the uranyl complex. The raw k^3-weighted uranium L_3-edge EXAFS spectrum and the corresponding Fourier transform of the solid sample are shown in Figure 10. Because of limited data quality (probably related to nonideal sample preparation), the k range was truncated at $k = 12.5$ Å^{-1}. The Fourier transform is dominated by a distinctive signal at $R + \Delta =$ 1.32 Å, corresponding to a real distance of 1.77 Å, originating from the axial "yl" oxygen atoms of the uranyl ion, and another prominent signal at $R + \Delta = 1.85$ Å, corresponding to a real distance of 2.41 Å, originating from the equatorial oxygen shell. A small effect, which can be attributed to the multiple scattering signal from the axial "yl" oxygen atoms of the uranyl ion, can be noticed at a distance of $R + \Delta =$ 2.93 Å (real distance 3.53 Å) in the Fourier transform spectrum. Inclusion of the U$-$C shell in the shell-fitting procedure did not result in an improvement of the fit. The results of the shell-fitting procedure can be found in Table 2. There are two axial oxygen atoms at 1.77 ± 0.01 Å and five equatorial oxygen atoms at 2.41 ± 0.01 Å. A 5-fold coordination of the uranyl ion is characterized by a $U-O_{eq}$ distance between 2.34 and 2.42 Å. It is obvious that the symmetry-equivalent uranium atom at a distance of 5.84 Å cannot be observed in the EXAFS spectrum. Even though the uranium atom is a heavy scatterer, this distance is far too large for a significant signal to be detected by EXAFS. Thus, it has to be concluded that EXAFS alone cannot distinguish between the dimeric and monomeric forms of the uranyl betaine complex and therefore cannot determine whether the dimer would decompose into monomers upon dissolution in the ionic liquid $[C_4mim][Tf_2N]$. Possibly high-energy X-ray scattering might give more useful information on the dimeric or monomeric nature of the complex.[37]

Spectroscopy. In order to answer the question of whether the structure of the uranyl complex of the betainium bistriflimide ionic liquid retains its dimeric structure in solution, the absorption and luminescence spectra of the uranyl betainium complex in the solid state were compared with those of the complex dissolved in water, in acetonitrile, and in the ionic liquid betainium bistriflimide, $[Hbet][Tf_2N]$. The transitions observed in the uranyl spectra are caused by an oxygen-to-uranium charge-transfer excitation in which an electron is moved from a molecular orbital of odd parity (mainly from oxygen 2p orbitals) to the empty 5f shell. The fine structure is due to vibronic transitions, i.e., electronic transitions on which vibrational transitions are superimposed. Because of its linearity, the uranyl ion possesses

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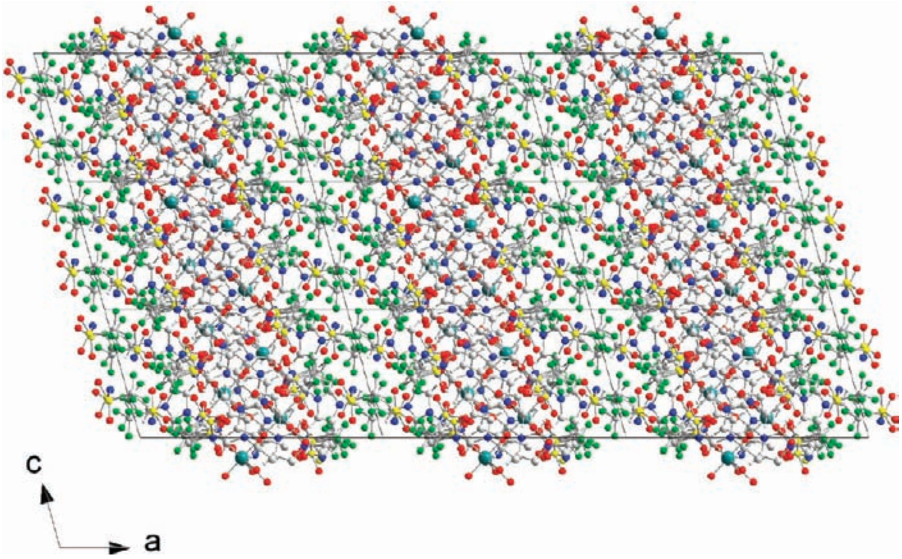

Figure 9. Packing in the crystal structure of **3** viewed along the *b* axis showing a layered structure (shown for a 3 × 3 × 3 supercell).

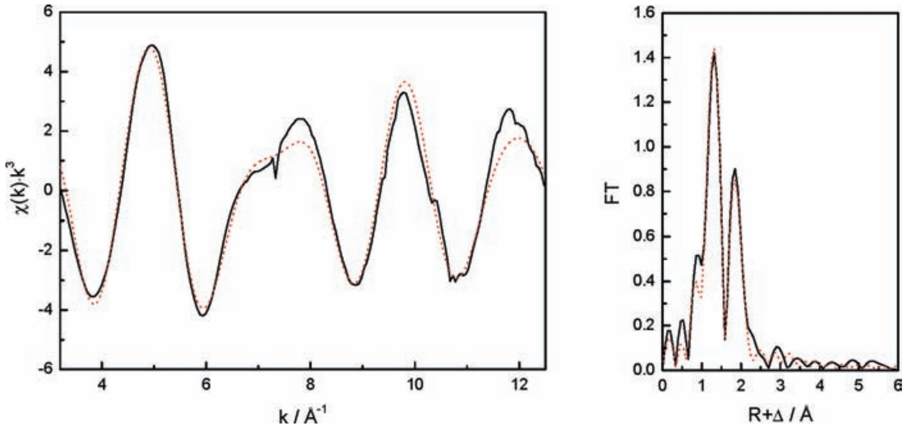

Figure 10. Raw k^3-weighted EXAFS (left) and the corresponding Fourier transform (right) of the solid uranyl betaine dimer complex **1** diluted with boron nitride. The solid black line represents experimental data; the dotted red curve represents fitted data.

Table 2. EXAFS Structural Parameters for Uranyl Betaine Dimer Complex **1** in the Solid State[a]

	R^b /Å	N^b	σ^2/Å^2
U−O$_{ax}$	1.77	2.2	0.0014
MS U−O$_{ax}$	3.54	2.2	0.0028
U−O$_{eq}$	2.41	4.8	0.0072

[a] *R*=distance; *N*=coordination number; σ^2=Debye−Waller factor; MS=multiple scattering. [b] Errors in distances *R* are ±0.01 Å; errors in coordination numbers *N* are ±10%. Δ*E* = −0.6 eV. Weighted *F* factor = 0.191.

three fundamental vibration modes: symmetric stretching, asymmetric stretching, and bending vibration. The bending vibration is 2-fold degenerate because bending can occur in two mutually perpendicular planes. In the uranyl ion, the symmetric vibration at 750 cm^{-1} is preferentially excited. In Figure 11, the absorption spectrum of the solid uranyl betaine complex **1** at room temperature is shown. The spectrum shows a pronounced vibrational fine structure that is very typical for a uranyl complex with D_{2h} symmetry, and it has an appearance very similar to that of the spectra of the uranyl diacetate dihydrate complex $UO_2(CH_3COO)_2\cdot 2H_2O$ with the uranyl ion at a site of D_{2h} symmetry.[38] These spectral features are in agreement with the approximate D_{2h} symmetry of the uranyl ion in the dimeric solid-state structure. Also, the luminescence spectrum of the uranyl betaine complex shows vibronic fine structure (Figure 12). The room-temperature luminescence spectrum shows a *hot band* at about 20 850 cm^{-1}, which disappears in the spectrum of the sample cooled to 77 K. Cooling of the sample to 77 K results in a strong narrowing of the emission lines.

The solution spectra of the uranyl betaine complex **1** are very different from those of the complex in the solid state. The absorption and luminescence spectra of the uranyl betaine complex dissolved in water show the same vibrational fine structure as the spectra obtained by dissolution of hydrated uranyl perchlorate, $UO_2(ClO_4)_2\cdot xH_2O$, in water (Figures 13 and 14).[39] A solution of $UO_2(ClO_4)_2\cdot xH_2O$ in water contains the hydrated uranyl ion $[UO_2(H_2O)_5]^{2+}$.[40] Consequently, the absorption spectrum

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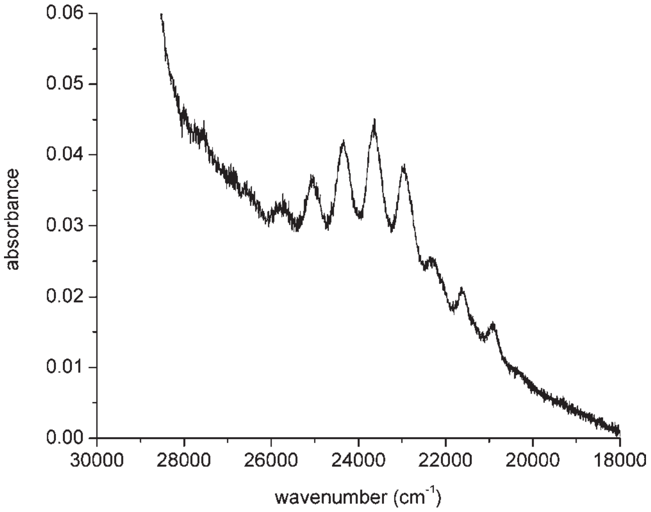

Figure 11. Room-temperature absorption spectrum of a powder of **1** dispersed in vacuum grease.

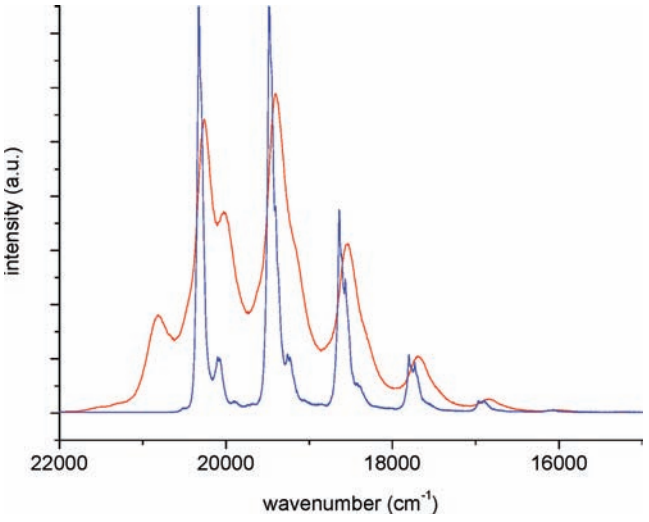

Figure 12. Luminescence spectrum of a powder of **1** dispersed in vacuum grease, measured at room temperature (red) and at 77 K (blue).

corresponds to that of a complex with D_{5h} coordination symmetry.[41,42] These experimental results show that the betaine ligands no longer coordinate to the uranyl ion in water and that they are replaced in the first coordination sphere by water molecules. No changes could be observed in the spectra of the uranyl betaine complex upon the addition of an excess of [Hbet][Tf$_2$N]. There was no indication for complex formation in water at a uranyl-to-[Hbet][Tf$_2$N] molar ratio of 1:15.

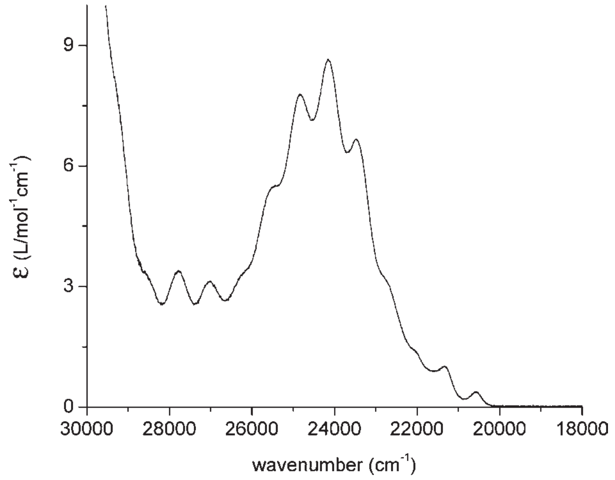

Figure 13. Room-temperature UV−vis absorption spectrum of the uranyl betaine complex **1** dissolved in water.

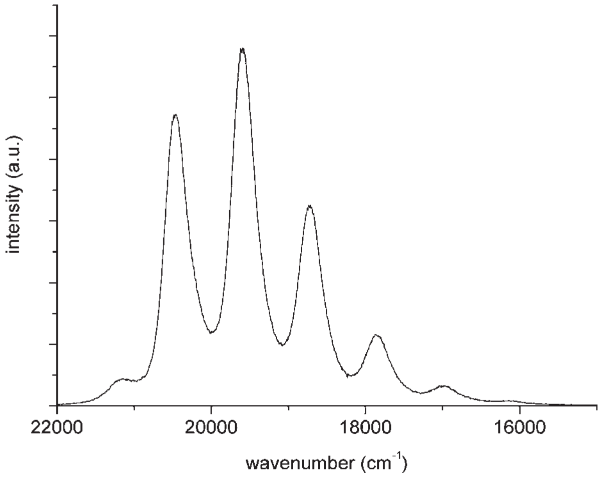

Figure 14. Room-temperature luminescence spectrum of the uranyl betaine complex **1** dissolved in water (excitation wavelength: 420 nm).

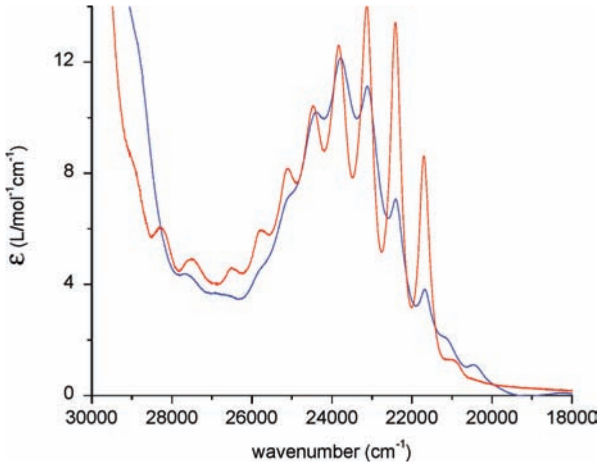

Figure 15. Room-temperature UV−vis absorption spectrum of the uranyl betaine complex **1** dissolved in acetonitrile (red) and in the ionic liquid betainium bistriflimide (blue).

The absorption spectrum of the uranyl betaine complex **1** dissolved in acetonitrile exhibits very sharp, intense peaks at the low-energy side of the spectrum (Figure 15). These sharp peaks are very typical for uranyl complexes with a trigonal D_{3h} symmetry, for example, the trinitrato, trioxalato, and triacetato complexes.[43] These “magnetic series” were named after the sharp peaks in the spectrum of CsUO$_3$(NO$_3$)$_3$, which were first discovered by Dieke

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and Duncan.[44] These results indicate that the dimeric structure of the uranyl betaine complex is lost upon dissolution in acetonitrile. However, in contrast to the aqueous solution, the carboxylate groups remain coordinated to the uranyl ion. The uranyl ion is coordinated by the carboxylate groups of three betaine ligands, forming the species $[UO_2(bet)_3]^-$ of D_{3h} symmetry. The absorption spectrum of the uranyl complex in the ionic liquid $[Hbet][Tf_2N]$ shows the same fine structure as the one observed in the spectra recorded in acetonitrile (Figure 15). This indicates that the structure $[UO_2(bet)_3]^-$ remains intact even in the presence of a large excess of betaine ligands. However, a distinct broadening of the peaks can be observed for the uranyl complex dissolved in $[Hbet][Tf_2N]$, compared to the same complex dissolved in acetonitrile. This broadening of the vibronic fine structure in the uranyl spectrum can be attributed to the high-viscosity or microheterogeneous nature of the ionic liquid. The spectra observed in the ionic liquid are intermediate to those observed in low-viscosity organic solvents and in glasses. It is indeed known that very broad vibronic transitions occur for uranyl in glasses.[45]

Conclusions

This work shows that uranium(VI) oxide can be dissolved in functionalized ionic liquids with appended carboxyl groups and that the structure of the resulting uranyl complexes strongly depends on the cationic core of the ionic liquids. Whereas a dimeric structure was observed for the uranyl complex of the betainium ionic liquid (complex **1**), a polymeric structure was found for the complex of the pyrrolidinium ionic liquid (complex **2**) and a monomeric structure for the complex of the imidazolium ionic liquid (complex **3**). These findings are further examples of the rich coordination chemistry of betaine and related ligands.[7,11,12,46-48] Spectroscopic studies revealed that the uranyl betaine complex **1** is decomposed in aqueous solution and that the carboxylate groups remain coordinated upon dissolution in acetonitrile and in the ionic liquid betainium bistriflimide. The absorption spectra in acetonitrile and in betainium bistriflimide are typical for uranyl complexes with D_{3h} symmetry. This reveals that three betaine ligands are coordinated via their carboxylate group to the uranyl ion. Even in the presence of an excess of the betaine ligand (as is the case of the solution in the betainium bistriflimide ionic liquid), no evidence for coordination of a fourth betaine ligand is found.

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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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