Supplementary Information

EVIDENCE FOR THE FORMATION OF $UO_2(NO_3)_4^{2-}$
IN AN IONIC LIQUID BY EXAFS

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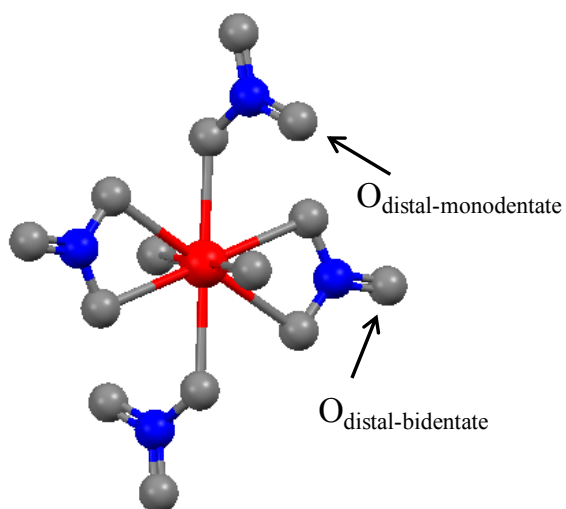
Figure S1: Scheme of $UO_2(\eta^2\text{-}NO_3)_2(\eta^1\text{-}NO_3)_2]^{2-}$.

Supplementary Information

Experimental procedure

Chemicals

The synthesis and purification of $UO_2(Tf_2N)_2$ (solid at RT) and of $[BMI][NO_3]$ (liquid at RT) have been published elsewhere.[1] Both compounds are highly hydroscopic, they were carefully dried on a vacuum line before use.

Two IL solutions were analyzed:

i) $UO_2(Tf_2N)_2$ was dissolved in dry $[BMI][NO_3]$ at a 10^{-2} M concentration. The solution was then degassed under vacuum at 60°C for one night. The final water content, measured by the Karl-Fischer technique after the XAS experiments, was found below the detection limit (50 ppm).

ii) $UO_2(NO_3)_2.6H_2O$ was dissolved in dry $[BMI][NO_3]$ at a 10^{-2} M concentration. As before, the solution was degassed and the final water content was found below 50 ppm.

After degassing, solutions were immediately sealed in polyethylene containers to prevent any water reabsorption, and kept away from the light. Due to high absorption of $[BMI][NO_3]$, it was not possible to analyze these solutions by UV-spectroscopy.

EXAFS data analysis

EXAFS measurements were led at the ROBL-ESRF beamline, at ambient temperature, using a double crystal Si(111) monochromator. Analysis were made at the U L_{III} (17166 eV) edge in transmission mode using argon-filled ionization chambers. The monochromator energy was calibrated by an yttrium foil (17038 eV). XAFS data reduction was made using the Athena software.[2] Data analysis was carried out with the FEFFIT code,[3] using phase and backscattering amplitude functions generated with the FEFF 8.1 code,[4] using the crystal structure of the cluster $[UO_2(NO_3)_4]^{2-}$ from Bradley et al.[5] Fits of the Fourier transform (FT) k^3-weighted EXAFS data to the EXAFS equation were performed in R-space between 0.8 and 4.3 Å. The k-range used was 3.0-16.8 Å^{-1}. Using these ranges, the distance resolution (i.e. the minimal distance between two shells that can be resolved by the fit) is of 0.11 Å. The amplitude reduction factor (S_0^2) was held constant to 1 for all fits. The shift in the threshold energy (E_0) was allowed to vary as a global parameter for all atoms. In all fits, the coordination number of the uranyl axial oxygen atoms (O_{ax}) was held constant at two. The 2-fold degenerated four-legged multiple scattering path U-O_{ax1}-U-O_{ax2} was included in the curve fit by constraining its Debye-Waller factor and its effective path length to twice the values of the U-O_{ax} single-scattering path. For all fits, coordination numbers of equatorial oxygen atoms, nitrogen atoms and distal oxygen atoms arising from monodentate groups were linked, the same procedure was applied for shells arising from bidentate nitrates. Multiple scatterings contributions from nitrate groups were also taken into account and their corresponding parameters were linked to those of single scatterings.

In order to conclude safely on the structure and stoichiometry of species present in solution, it was necessary to test different structural models for the data fit. Indeed, the number and coordination mode of nitrates bound to uranyl was not a priori known. We have first considered that uranyl is bound only by bidentate nitrate groups. The unsatisfactory fit obtained leads us to the conclusion that the mean coordination sphere of uranyl was formed by a mixture of bidentate and monodentate nitrates. A significant improvement of the fit quality is obtained using this model. Table S1 summarizes the main paths to be taken into account for fitting the complex $[UO_2(\eta^2\text{-}NO_3)_2(\eta^1\text{-}NO_3)_2]^{2-}$.

Supplementary Information

Table S1: Description of calculated paths by FEFF8 for the complex $[UO_2(\eta^2\text{-}NO_3)_2(\eta^1\text{-}NO_3)_2]^{2-}$, from ref.[5]

Path description[a]	Distance (Å)	Amplitude ratio from FEFF[b]
U-O_{ax}	1.765	100
U-O_{eq} monodentate	2.428	39
U-O_{eq} bidentate	2.525	35
U-N bidentate	2.968	20
U-N monodentate	3.329	14
U-O_{distal} monodentate	3.412	13
U-O_{eq}-N monodentate	3.530	12
U-O_{ax}-U-O_{ax}	3.529	69
U-O_{distal} bidentate	4.178	6
U-O_{distal}-N bidentate	4.178	20
U-N-O_{distal}-N bidentate	4.178	15

(a) "ax" is for "axial", "eq" is for equatorial, "monodentate" and "bidentate" indicate the mode of nitrate groups complexation in the uranium equatorial shell.
(b) Paths amplitude is normalized with respect to the highest amplitude, which is set to 100%.

In the following, fit results of different models are exposed, and the corresponding fit spectra are given in figures S2 and S3. For all models, coordination numbers are fixed, other parameters being fitted. Goodness of the fit is expressed by the "r-factor" and the reduced χ^2 which are defined in ref.[3]

$UO_2(NO_3)_3$ in [BMI][NO_3]

According to species in solution, uranium (VI) can be coordinated only by nitrates groups, bound either in a bidentate or monodentate fashion.
NB: in the following tables, * indicates fixed parameters during the fit, # are linked parameters.
Errors on coordination number N is ± 20%, on interatomic distance R ± 0.01 Å, on Debye-Waller factor is ± 0.001 Å².

i) U(VI) is coordinated only by bidentate nitrate groups
Model 1: number of bidentate groups fitted
Model 2: number of bidentate nitrates groups fixed to 3

shell	Model 1			Model 2		
	N	R (Å)	σ^2 (Å²)	N	R (Å)	σ^2 (Å²)
U-O_{axial}	2*	1.77	0.001	2*	1.76	0.001
U-$O_{eq\text{-}bidentate}$	4.7	2.53	0.008	6*	2.53	0.009
U-$N_{bidentate}$	2.4#	2.92	0.005	3*	2.92	0.005
U-$O_{dist\text{-}bidentate}$	2.4#	4.19	0.004	3*	4.19	0.006
E_0 (eV)	-9			-9		
R_{factor}	0.03			0.03		
Reduced χ^2	77			77		

3

Supplementary Information

ii)   U(VI) is coordinated by a mixture of monodentate and bidentate nitrate groups

Model 3: N fixed, 2 bidentate + 2 monodentate nitrate groups, total equatorial N = 6;
Model 4: N fixed, 1 bidentate + 3 monodentate nitrate groups, total equatorial N = 5;
Model 5: N fixed, 2 bidentate + 1 monodentate, total equatorial N = 5.

shell	Model 3			Model 4			Model 5		
	N	R (Å)	σ^2 (Å²)	N	R (Å)	σ^2 (Å²)	N	R (Å)	σ^2 (Å²)
U-O$_{axial}$	2*	1.76	0.001	2*	1.76	0.001	2*	1.76	0.001
U-O$_{eq-monodentate}$	2*	2.39	0.006	3*	2.46	0.009	1*	2.35	0.003
U-O$_{eq-bidentate}$	4*	2.53	0.004	2*	2.55	0.002	4*	2.52	0.004
U-N$_{bidentate}$	2*	2.92	0.005	1*	2.95	0.005	2*	2.93	0.005
U-N$_{monodentate}$	2*	3.18	0.005	3*	3.21	0.009	1*	3.40	0.004
U-O$_{dist-monodentate}$	2*	3.42	0.003	3*	3.40	0.004	1*	3.43	0.003
U-O$_{dist-bidentate}$	2*	4.19	0.004	1*	4.19	0.002	2*	4.19	0.004
E$_0$ (eV)	-10			-9			-10		
R$_{factor}$	0.01			0.02			0.01		
Reduced χ^2	29			45			30		

Strong improvement of the fit is observed when considering 2 bidentate nitrates groups, versus 3 or 1 bidentates groups. The best fit corresponds to model 3, i.e. a 1:4 stoichiometry with 2 bidentates and 2 monodentates nitrate groups bound to uranyl. Although the fit for model 5 looks good, results on distances for the monodentate nitrate group have no sense, the U-N distance being similar than the U-O$_{dist}$ one.
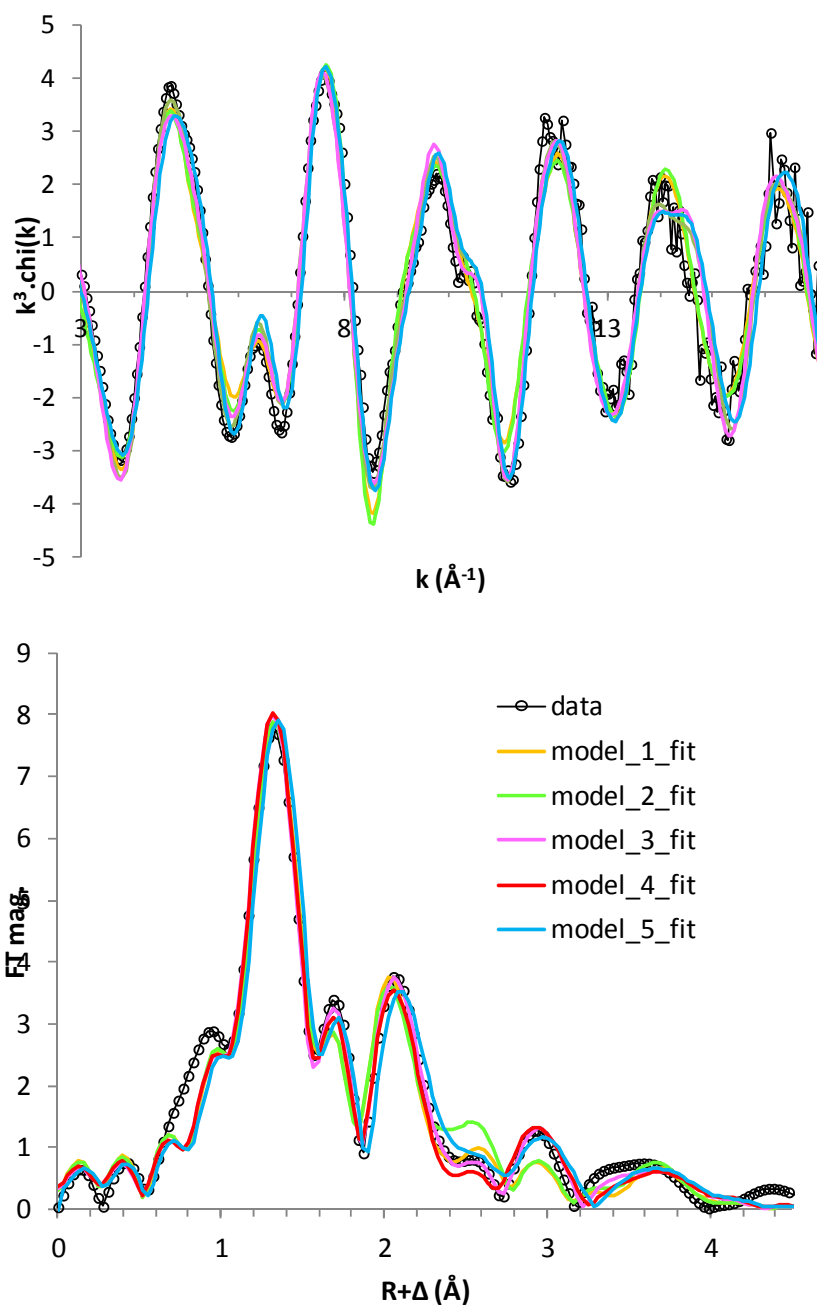
Supplementary Information

Figure S2: EXAFS and corresponding Fourier Transform spectra obtained for the sample of uranyl nitrate in [BMI][NO$_3$]: black dots and line = experimental data, coloured lines = tested fit models described in previous tables.

UO$_2$(Tf$_2$N)$_2$ in [BMI][NO$_3$]:

As explained in the main part of the article, it is very unlikely that Tf$_2$N$^-$ anions remain in the U(VI) coordination sphere: these anions have no affinity for uranyl and are removed from the U(VI) coordination sphere at much lower nitrate concentration.[6] Therefore, we have considered the sole presence of nitrate ions in the uranium coordination sphere, as for the previous sample.

Supplementary Information

NB: in the following tables, * indicates fixed parameters during the fit, # indicates linked parameters.

Errors on coordination number N is ± 20%, on interatomic distance R ± 0.01 Å, on Debye-Waller factor is ± 20%.

  i) U(VI) is coordinated only by bidentate nitrate groups
Model 1: number of bidentate groups fitted,
Model 2: 3 bidentate nitrate groups as fixed parameter

shell	Model 1			Model 2		
	N	R (Å)	σ^2 (Å^2)	N	R (Å)	σ^2 (Å^2)
U-O$_{axial}$	2*	1.76	0.002	2*	1.76	0.002
U-O$_{eq\text{-}bidentate}$	5.1	2.50	0.009	6*	2.51	0.011
U-N$_{bidentate}$	2.5#	2.97	0.005	3*	2.97	0.005
U-O$_{dist\text{-}bidentate}$	2.5#	4.18	0.004	3*	4.19	0.005
E$_0$ (eV)	-10			-10		
R$_{factor}$	0.05			0.05		
Reduced χ^2	17			17		

  ii) U(VI) is coordinated by a mixture of monodentate and bidentate nitrate groups;

Model 3: N fixed, 2 bidentate + 2 monodentate nitrate groups, total equatorial N = 6;
Model 4: N fixed, 1 bidentate + 3 monodentate nitrate groups, total equatorial N = 5;
Model 5: N fixed, 2 bidentate + 1 monodentate, total equatorial N = 5.

shell	Model 3			Model 4			Model 5		
	N	R (Å)	σ^2 (Å^2)	N	R (Å)	σ^2 (Å^2)	N	R (Å)	σ^2 (Å^2)
U-O$_{axial}$	2*	1.77	0.002	2*	1.77	0.002	2*	1.77	0.002
U-O$_{eq\text{-}monodentate}$	2*	2.38	0.008	3*	2.46	0.010	1*	2.35	0.004
U-O$_{eq\text{-}bidentate}$	4*	2.53	0.006	2*	2.54	0.004	4*	2.51	0.005
U-N$_{bidentate}$	2*	2.97	0.005	1*	2.98	0.005	2*	2.97	0.005
U-N$_{monodentate}$	2*	3.25	0.010	3*	3.28	0.010	1*	3.46	0.008
U-O$_{dist\text{-}monodentate}$	2*	3.45	0.005	3*	3.45	0.005	1*	3.47	0.003
U-O$_{dist\text{-}bidentate}$	2*	4.19	0.004	1*	4.21	0.002	2*	4.19	0.004
E$_0$ (eV)	-10			-9			-10		
R$_{factor}$	0.03			0.04			0.04		
Reduced χ^2	14			17			17		

As for the previous sample, a significant improvement of the fit is observed when considering only 2 bidentate nitrate groups bound to uranium (VI), versus 1 or 3 bidentate groups (see R-factors and fit spectra on the FT at distance above R+Δ = 2.5 Å). Then, the best fit is obtained considering 2 bidentate and 2 monodentate nitrate groups. Here again, model 5 leads to unrealistic U-N$_{monodentate}$ bond distance.
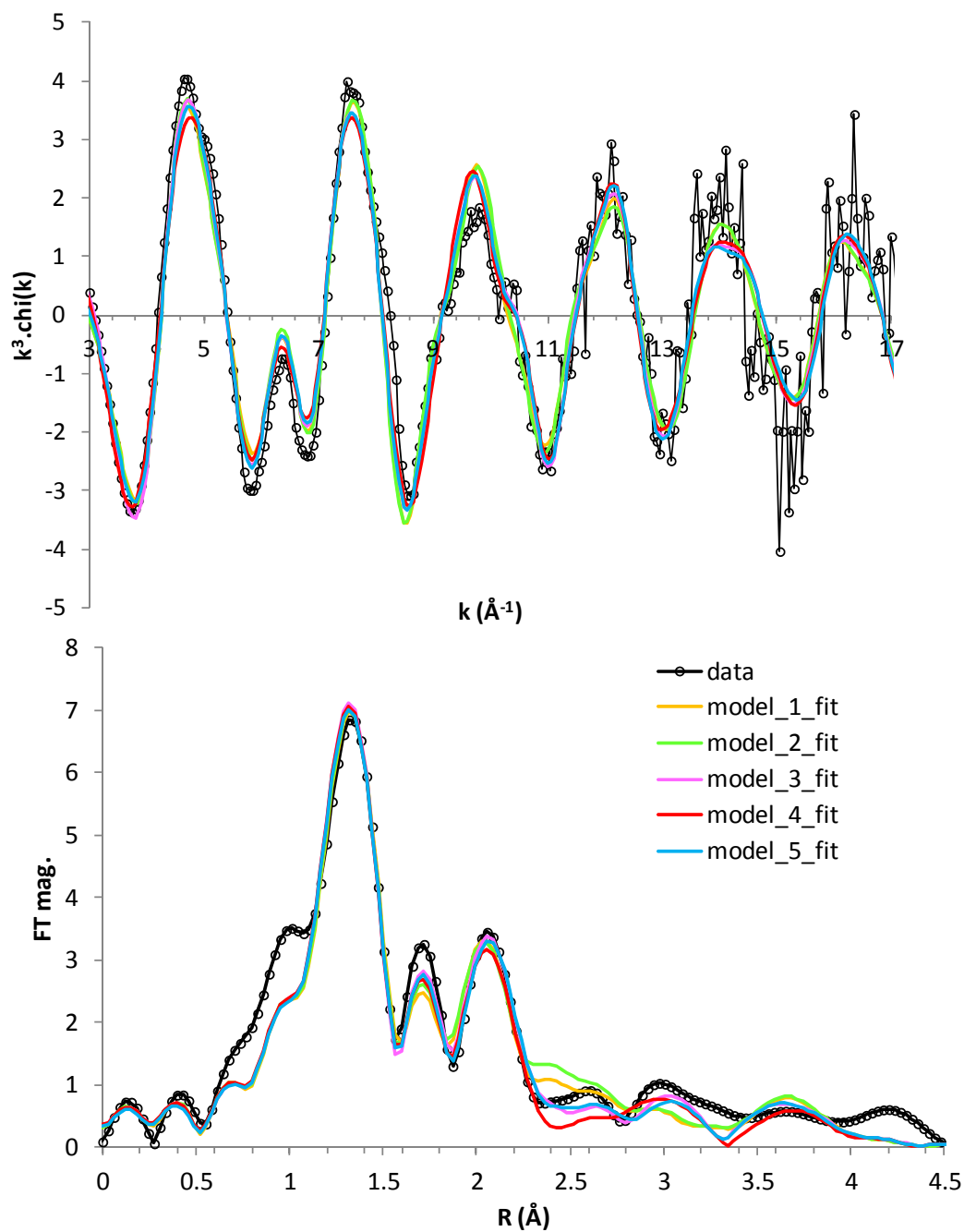
Supplementary Information

Figure S3: EXAFS and corresponding Fourier Transform spectra obtained for the sample of $UO_2(Tf_2N)_2$ in [BMI][NO_3]: black dots and line = experimental data, coloured lines = tested fit models described in previous tables.

References

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Supplementary Information

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