Electronic Supplementary Information

Benchtop Access to Anhydrous Actinide N-donor Coordination Complexes using Ionic Liquids

Steven P. Kelley,[a] Volodymyr Smetana,[b] Stephen D. Emerson,[c] Anja-Verena Mudring,[b] Robin D. Rogers*[,b,c]

[a]Department of Chemistry, University of Missouri, Columbia, MO 65211, USA

[b]Department of Materials and Environmental Chemistry, Stockholm University, 106 91 Stockholm, Sweden

[c]College of Arts & Sciences, The University of Alabama, Tuscaloosa, AL 35487, USA

Table of Contents:

Materials and Methods:

Caution! ^{238}*U and* ^{232}*Th are radioactive. Comply with all local regulations regarding handling and disposal of radioisotopes.*

$Th(NO_3)_4·4H_2O$ (IBI Labs, Boca Raton, FL), 1,2,4-triazole (Sigma Aldrich, St. Louis, MO), 5-aminotetrazole (Sigma Aldrich), 4,4'-bipyridyl (4,4'-bipy, Sigma Aldrich), imidazole (H-im, Sigma Aldrich), methanol (EMD Chemicals, Darmstadt, Germany), and concentrated nitric acid (Sigma Aldrich) were used as received from their commercial sources. 1-methylimidazole was obtained from Sigma Aldrich and purified by distillation at 145 ^{o}C under reduced pressure. Acetonitrile (EMD Chemicals) was dried by shaking for 24 h over anhydrous potassium carbonate (Alfa-Aesar, Ward Hill, MA). 1-ethyl-3-methylimidazolium nitrate ([C_2mim][NO_3]) was used as received (Iolitec-USA, Tuscaloosa, AL) or prepared by reacting 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc], Iolitec-USA) with nitric acid: [C_2mim][OAc] was combined with 1.1 eq. of 3 M HNO_3 and heated overnight to give a slightly tinted liquid which crystallized when cooled to room temperature following the addition of a seed crystal of [C_2mim][NO_3]. Deionized water was obtained from an in-house deionizer (Culligan, International, Rosemont, IL; typical resistivity = 17.8 MΩ·cm). Compressed air was obtained from a house line, and N_2 was obtained from liquid nitrogen boil-off (Airgas, Radnor, PA).

$UO_2(NO_3)_2·6H_2O$ was prepared as follows: 2 g UO_3, (Strem Chemicals, Newburyport, MA) 2 g deionized water, and 2 g concentrated nitric acid were combined in a 20 mL scintillation vial with magnetic stirring at room temperature to give a yellow solution. The solution was in open atmosphere in a sand bath at ca. 100 ^{o}C for a day, yielding a yellow solid. The solid was allowed to cool to room temperature and mixed by hand with several drops of DI water to give a slurry. This mixture was heated for 2-5 min. at ca. 100 ^{o}C, resulting in partial liquefaction. The liquid was decanted away from the remaining solid. Upon standing at room temperature, the liquid crystallized into long, yellow-green prismatic crystals of $UO_2(NO_3)_2·6H_2O$.

IR spectra were recorded by measuring attenuated total reflectance of neat samples using a Bruker Alpha FT-IR spectrometer with a diamond ATR accessory (Bruker Optics, Billerica, MA). Powder X-ray diffraction was measured on a Bruker D2 Phaser diffractometer (Bruker-AXS, Madison, WI) equipped with a Lynxeye linear position-sensitive detector using Ni-filtered Cu-Kα radiation (1.54056 Å). Single crystal X-ray diffraction was measured on a Bruker diffractometer equipped with a PLATFORM 3-circle goniometer and an Apex II CCD area detector using graphite-monochromated Mo-Kα radiation (0.71073 Å). Crystals were mounted on a glass fiber with silicone grease and cooled under a cold nitrogen stream using an N-Helix cryostat (Oxford Cryosystems, Oxford, UK). Data was collected using a strategy of phi and omega scans with 0.5^{o} frame widths. Data collection, unit cell determination, integration, and scaling were performed using the Apex 2 software package (Bruker AXS).[1]

Preparation of [C_2mim]$_2$[$Th(NO_3)_6$] and [H(1-mim)$_2$][$Th(NO_3)_5$(1-mim)$_2$] (1): A 20 mL glass scintillation vial was loaded with 2.0103 g $Th(NO_3)_4·4H_2O$ and 4.1 g methanol and swirled by hand to give a colorless solution. A separate 20 mL glass vial was loaded with 1.1038 g [C_2mim][NO_3] and 2.6 g methanol and swirled by hand to give a colorless solution. The solutions were combined by adding the [C_2mim][NO_3] solution dropwise into the $Th(NO_3)_4·4H_2O$ solution and then transferring the solution back and forth between the two vials. Colorless crystals began forming during mixing. The reaction mixture was sealed with a threaded cap and allowed to stand at room temperature for one day. The mother liquor was decanted from the colorless crystals, and additional solid [C_2mim][NO_3] (not weighed) was added directly to it and dissolved with swirling. The resulting solution was allowed to stand for another day, yielding another crop of colorless crystals. The mother liquor was decanted off, and the two batches of crystals were dried for 2 h at 70 ^{o}C in a temperature controlled oven. The two batches were combined, and the IR analysis has been performed for residual methanol. The total mass of isolated [C_2mim]$_2$[$Th(NO_3)_6$] was 2.5429 g (84.533% yield).

Alternatively 51 mg of $Th(NO_3)_4 \cdot 4H_2O$ and 85 mg [C_2mim][NO_3] were dissolved in 0.805 and 0.204 mg of deionized water, respectively. The IL solution was added to the Th^{4+} solution, and the resulting mixture was heated at ~90 ^{o}C overnight to remove water. The resulting product contained a mixture of liquid and well-formed crystals, one of which was isolated by hand and analyzed by SCXRD revealing a second polymorph of [C_2mim]$_2$[$Th(NO_3)_6$].

A series of reactions of [C_2mim]$_2$[$Th(NO_3)_6$] with 1,2,4-triazole (1,2,4-TAZ) and 1-methylimidazole (1-mim) were conducted as follows: 1,2,4-TAZ was weighed into glass culture tubes and combined with varying amounts of 1-mim (from 1 to 8 molar equivalents in approximately integer amounts). The resulting mixtures were liquefied by grinding and heating temporarily with a heat gun. [C_2mim]$_2$[$Th(NO_3)_6$] (obtained using the first route above) was then weighed out at a 1:1 molar ratio with 1,2,4-TAZ and added to each reaction mixture. The vials were allowed to stand sealed at room temperature for 36 hours before being opened. The solids present in each system were removed and analyzed by powder X-ray diffraction. Single crystals of compound **1** were prepared by weighing 0.0830 g of [C_2mim]$_2$[$Th(NO_3)_6$] and 0.0079 g 1,2,4-triazole into two separate glass culture tubes, dissolving each in 1-mim, adding the 1,2,4-triazole solution to the [C_2mim]$_2$[$Th(NO_3)_6$] solution, and allowing the mixture to stand in a capped vial at room temperature. Colorless crystals of **1** were observed after 3 days.

Crystallization of [C_2mim][$UO_2(NO_3)_3$]: [C_2mim][NO_3] was dissolved in an equal mass of concentrated nitric acid, and 0.048 g of this solution was weighed into a tared glass culture tube to which 0.056 g $UO_2(NO_3)_2 \cdot 6H_2O$ was added. The culture tube was placed in a sand bath at ~90 ^{o}C overnight while open to atmosphere, yielding a viscous yellow liquid. The culture tube was sealed with parafilm and allowed to stand at room temperature. Yellow crystals of [C_2mim][$UO_2(NO_3)_3$] were observed after several days.

Crystallization of Compounds 2-4: For each reaction, [C_2mim][NO_3] was weighed into a tared, empty culture tube. One molar eq. $UO_2(NO_3)_2 \cdot 6H_2O$ was calculated and measured onto a tared sheet of weighing paper and transferred into the culture tube. The mixture was placed in a temperature controlled oil bath at 70 ^{o}C. A slow stream of air or N_2 was directed into the culture tube using the end of a pipette. The resulting yellow to red-orange liquids were analyzed by IR to confirm that water had been removed. The shade of yellow or orange was not consistent among all batches of [C_2mim][$UO_2(NO_3)_3$] prepared this way, but the differences were never correlated with any differences in the IR spectra.

*Crystallization of [C_2mim]$_2$[$(UO_2(NO_3)_3)_2$(4,4'-bipy)]$\cdot$2{$UO_2(NO_3)_2$(4,4'-bipy)}(**2**):* 1 eq. of 4,4'-bipy was weighed onto a tared sheet of weighing paper and added to the hot [C_2mim][$UO_2(NO_3)_3$]. The mixture remained at 70 ^{o}C under a stream of N_2 and gave a heterogeneous mixture of yellow and orange solids. Single crystals of **2** were found in this reaction mixture.

*Crystallization of $UO_2(NO_3)_2$(1-mim)$_2$ (**3**)*: 2 eq. of 5-aminotetrazole and 4 eq. of 1-mim were weighed into a tared culture tube, heated with a heat gun, and swirled by hand to give a homogeneous solution. This solution was added to hot [C_2mim][$UO_2(NO_3)_3$]. The reaction mixture was transferred to a sand bath at 110-120 ^oC and heated overnight. Single crystals of **3** could be isolated from the resulting mixture of orange solids and gel.

Crystallization of $UO_2(NO_3)_2$*(H-im)*$_2$ ***(4)***: 2 eq. of H-im was weighed out and dissolved in ~0.5 mL dried acetonitrile. Liquid [C_2mim][$UO_2(NO_3)_3$] was dissolved in ~0.5 mL of acetonitrile after dehydration. The H-im solution was added to the $[UO_2]^{2+}$ containing solution, and the resulting mixture was evaporated in a Drierite-filled desiccator at reduced pressure. Crystals of **4** were observed after 4 days. Crystals of **4** were noticeably occluded within minutes of exposure to air.

Crystal Structure Determination: A polyhedral single crystal of [C_2mim]$_2$[$Th(NO_3)_6$] isolated using the first method above measuring 0.17x0.13x0.10 mm was analyzed by SCXRD at -173 ^oC. The structure was solved by direct methods and refined by full matrix least squares refinement about F^2. Non-hydrogen atoms were located from the difference map and refined anisotropically. Hydrogen atoms were placed in calculated positions, and their coordinates and thermal displacement parameters were allowed to ride on the carrier atoms.

A colorless polyhedral crystal of [C_2mim]$_2$[$Th(NO_3)_6$] obtained using the second method above measuring 0.17x0.13x0.10 mm was analyzed by SCXRD at -173 ^oC. The structure was solved by direct methods and refined by full matrix least squares refinement about F^2. Non-hydrogen atoms were located from the difference map and refined anisotropically. Hydrogen atoms were placed in calculated positions, and their coordinates and thermal displacement parameters were allowed to ride on the carrier atoms. After refinement, larger than expected residual difference map peaks were located near the metal atom. These peaks are likely artifacts due to under-correction for absorption.

A colorless polyhedral crystal of **1** measuring 0.17x0.14x0.10 mm was analyzed by SCXRD at -173 ^oC. Due to an instrument malfunction, part of the data collection strategy was not executed resulting in about 30 low-angle reflections not being recorded. Regardless, the overall completeness of the data was 98.9% out to 56^o 2θ, and the data-to-parameters ratio was more than sufficient for refinement. The structure was solved by locating the Th atom from a Patterson refinement. Non-hydrogen atoms were located from the difference map and refined anisotropically. A difference map peak atom was found within bonding distance to the basic 1-mm nitrogen atom and modeled as a hydrogen atom with half occupancy. The coordinates of this hydrogen atom were refined freely, and the thermal displacement parameters were constrained to ride on the carrier atom. All other hydrogen atoms were placed in calculated positions, and their coordinates and thermal displacement parameters were allowed to ride on the carrier atoms.

An irregular yellow crystal of [C_2mim][$UO_2(NO_3)_3$] was analyzed by SCXRD at room temperature (ca. 19 ^oC). The structure was solved by direct methods and refined by full matrix least squares refinement about F^2. Non-hydrogen atoms were located from the difference map and refined anisotropically. Hydrogen atoms were placed in calculated positions, and their coordinates and thermal displacement parameters were allowed to ride on the carrier atoms.

An irregular yellow crystal of **2** measuring 0.16x0.10x0.08 mm was analyzed by SCXRD at -100 ^oC. The structure was solved by direct methods and refined by full matrix least squares refinement about F^2. Non-hydrogen atoms were located from the difference map and refined anisotropically. Hydrogen atoms were placed in calculated positions, and their coordinates and thermal displacement parameters were allowed to ride on the carrier atoms.

An irregular yellow crystal of **3** measuring 0.12x0.06x0.02 mm was analyzed by SCXRD at -100 ^oC. The structure was solved by locating the uranium atom using a Patterson refinement. Non-hydrogen atoms were located from the difference map and refined anisotropically. Hydrogen atoms were placed in calculated positions, and their coordinates and thermal displacement parameters were allowed to ride on the carrier atom.

A blocky yellow crystal of **4** measuring 0.30x0.13x0.02 mm was analyzed by SCXRD at -100 ^{o}C. The structure was solved by intrinsic phasing using an iterative dual space approach. Atoms located from the solution were given the expected element assignment, and any remaining non-hydrogen atoms were located from the difference map. All non-hydrogen atoms were refined anisotropically by full matrix least squares refinement about F^2. The hydrogen atom bonded to the H-Im ligand was located from the difference map, and its coordinates were allowed to refine freely while the thermal displacement parameters were constrained to ride on the carrier atom. All other hydrogen atoms were placed in calculated positions, and their coordinates and thermal displacement parameters were allowed to ride on the carrier atoms.

Space group determination, crystal structure solution by direct or Patterson methods, refinement, and generation of probability ellipsoid plots were conducted using the Bruker SHELXTL software suite.[2] Structures were refined using SHELXL 2014.[3] by intrinsic phasing was done using SHELXT. Analysis of short contacts and packing plots were done using the CCDC software Mercury.[4]

Table S1. U−O and Th−O distances in the crystal structures of the investigated compounds.

Compound	**CN$_{Th, U}$**	***d*$_{Th,U−O}$**
$[C_2mim]_2[Th(NO_3)_6]$-LT	12	2.546−2.581
$[C_2mim]_2[Th(NO_3)_6]$-HT	12	2.548−2.573
$[H(1\text{-}mim)_2][Th(NO_3)_5(1\text{-}mim)_2]$	12	2.578−2.595
$[C_2mim][UO_2(NO_3)_3]$	8	2.425−2.468
	8	2.511−2.513
$UO_2(NO_3)_2(H\text{-}Im)_2$	8	2.512−2.513
$UO_2(NO_3)_2(1\text{-}mim)_2$	8	2.490−2.513
$[C_2mim]_2[(UO_2(NO_3)_3)_2(4,4'\text{-}bipy)]\cdot2\{UO_2(NO_3)_2(4,4'\text{-}bipy)\}$	9	2.493−2.653

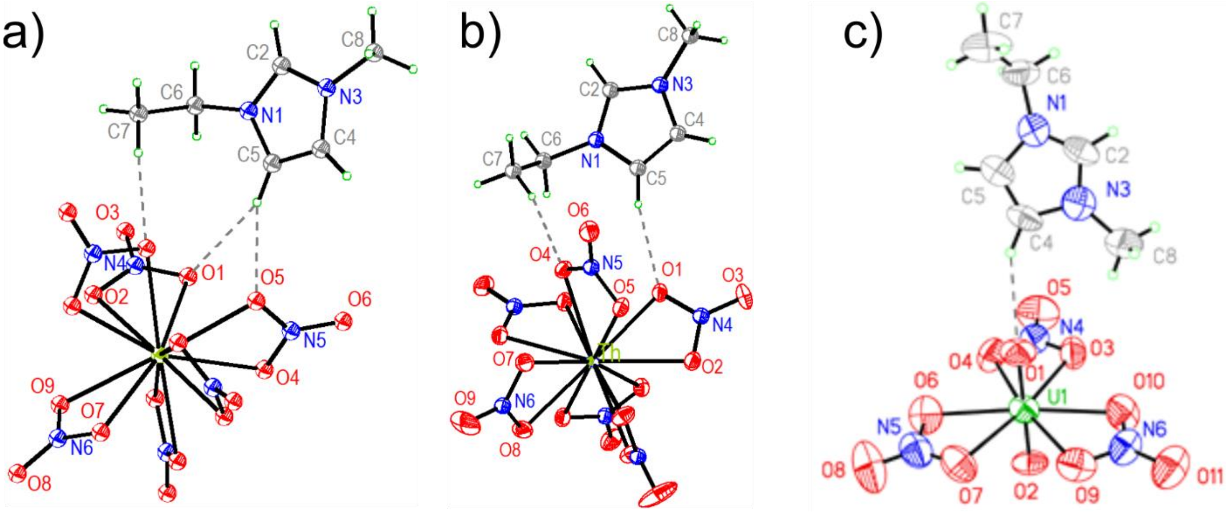

Fig. S1. 50% probability ellipsoid plot of the formula units of $[C_2mim]_2[Th(NO_3)_6]$ (Method 1) (a), $[C_2mim]_2[Th(NO_3)_6]$ (Method 2) (b), and $[C_2mim][UO_2(NO_3)_3]$ (c). Dashed lines indicate shortest contacts between ions.

Additional Spectra

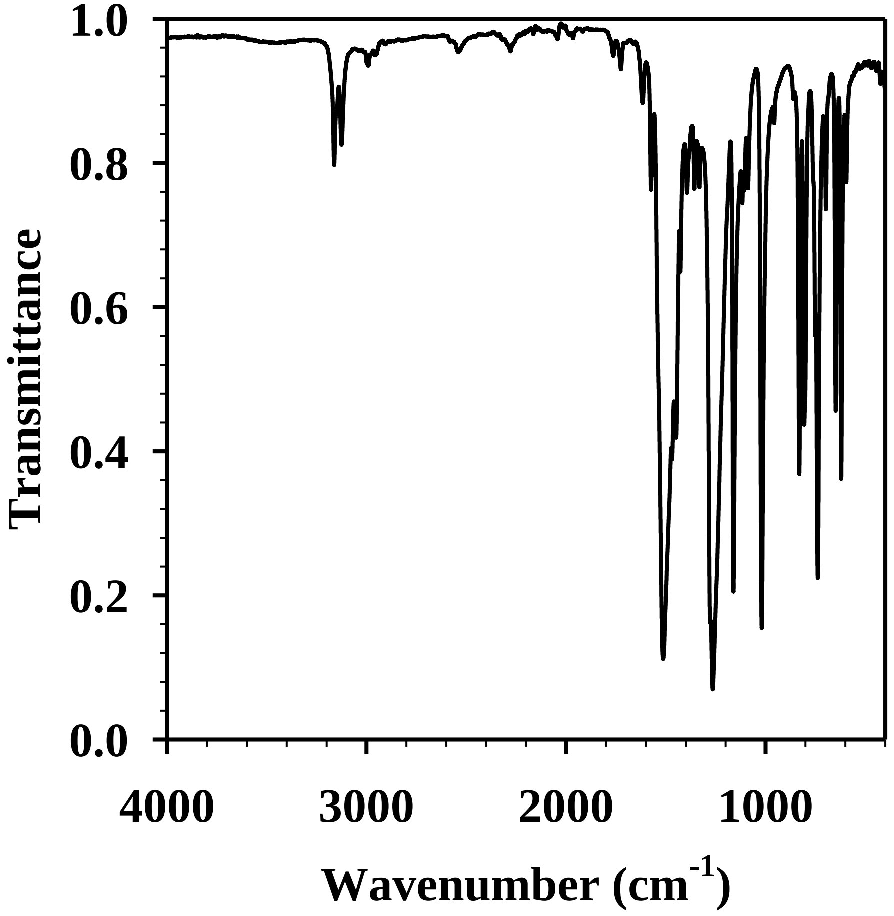

Fig. S2: FT-IR spectrum of isolated LT-[C_2mim]$_2$[Th(NO_3)$_6$]

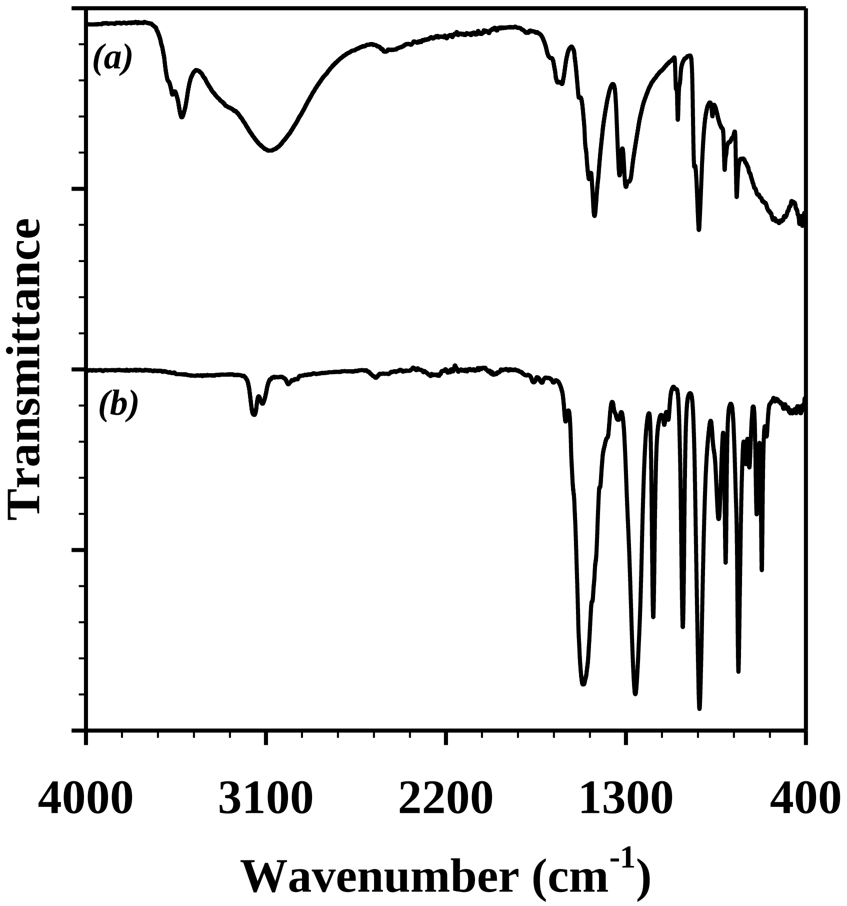

Fig. S3: IR spectra of $UO_2(NO_3)_2 \cdot 6H_2O$ (*a*) *vs.* 1:1 mixture of $[C_2mim][NO_3]$ and $UO_2(NO_3)_2 \cdot 6H_2O$ after heating (*b*). Dehydration is indicated by change in O-H stretching region (3500-2800 cm^{-1})

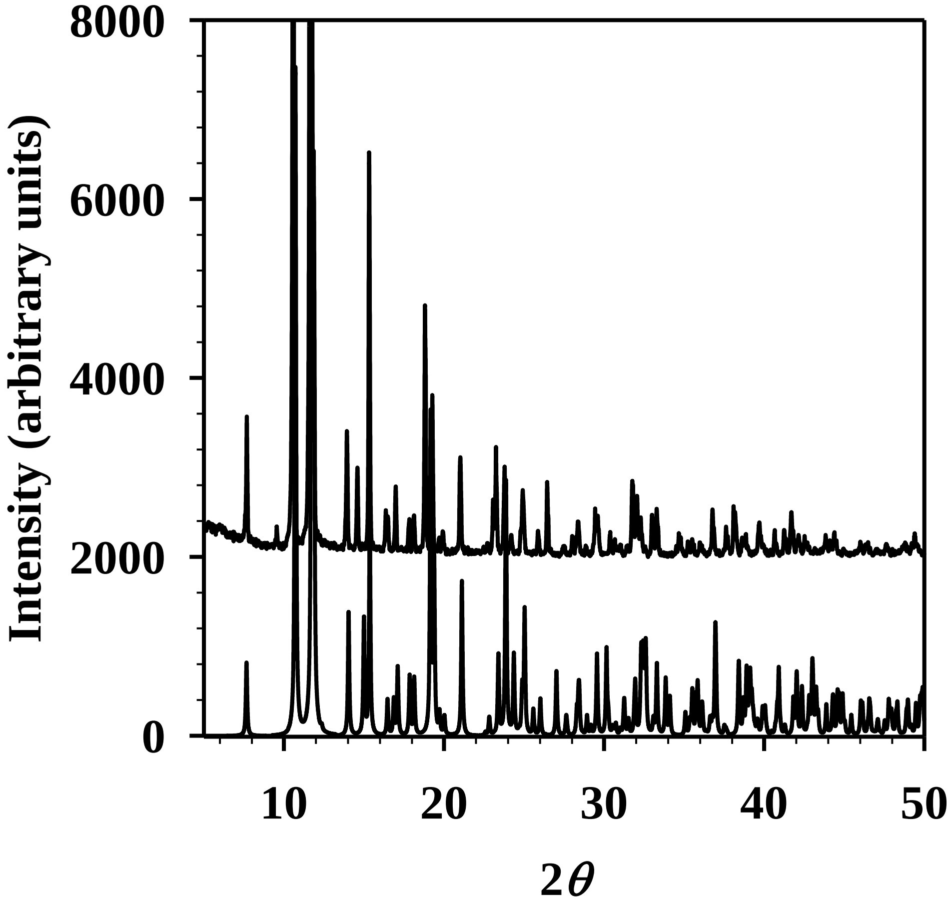

Fig. S4: PXRD of isolated LT-[C_2mim]$_2$[Th(NO_3)$_6$] (*top*) vs. calculated PXRD pattern from low-temperature crystal structure (bottom).

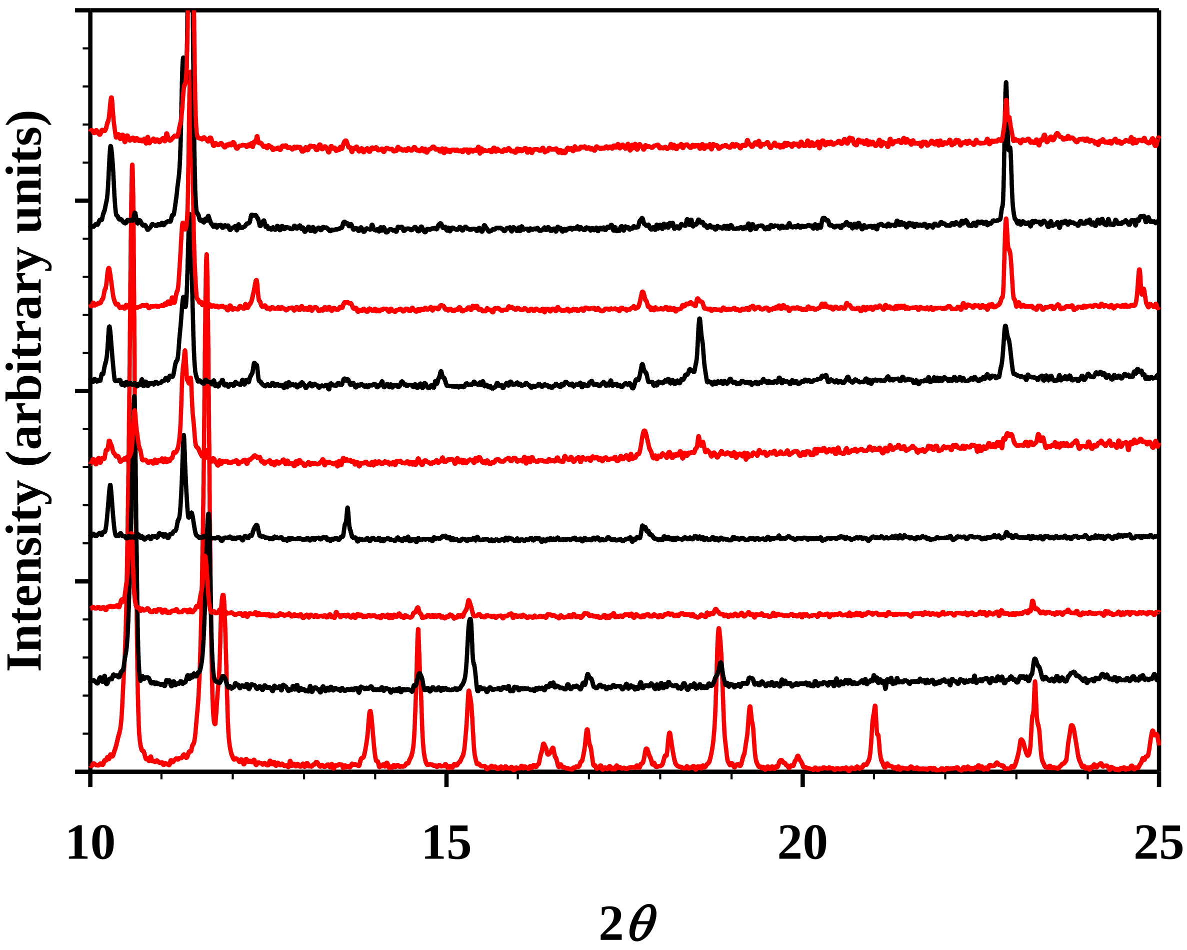

Fig. S5: PXRD patterns of [C_2mim]$_2$[Th(NO_3)$_6$] (very bottom) *vs*. mixtures of 1:1:*n* [C_2mim]$_2$[Th(NO_3)$_6$]:1,2,4-TAZ:1-methylimidazole (*n* varies from 1 to 8, increasing from bottom to top).

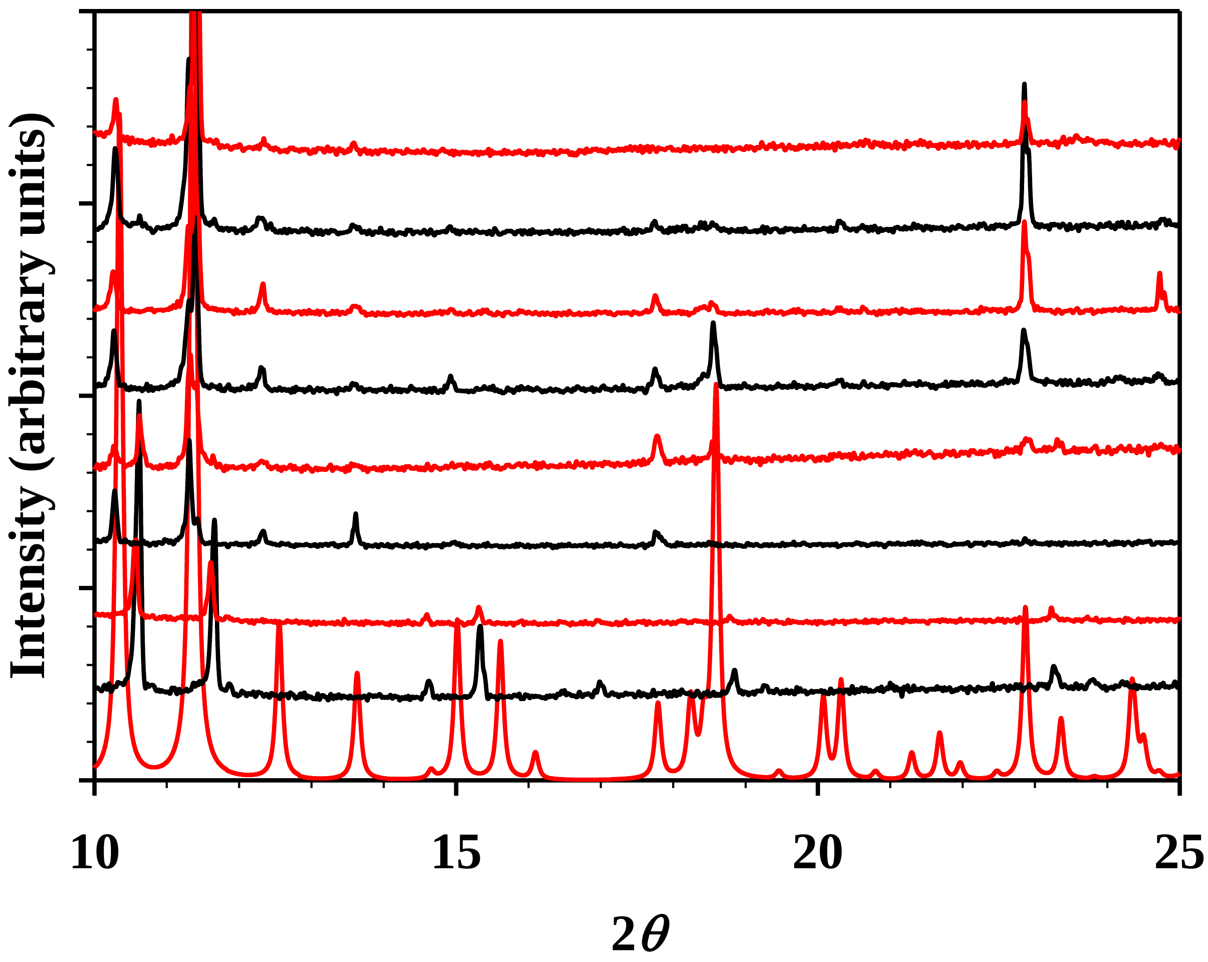

Fig. S6: PXRD patterns of $[H(1\text{-mim})_2][Th(NO_3)_5(1\text{-mim})_2]$ (simulated, very bottom) *vs.* mixtures of 1:1:*n* $[C_2mim]_2[Th(NO_3)_6]$:1,2,4-TAZ:1-methylimidazole (*n* varies from 1 to 8, increasing from bottom to top).

Additional Crystallographic Information

Thorium: $[H(1\text{-mim})_2][Th(NO_3)_5(1\text{-mim})_2]$ crystallizes in the monoclinic space group *C*2/*c* with Z = 4. The Th atom resides on a crystallographic 2_1 axis which also passes through a $[NO_3]^-$ anion. The complex counterion, $[H(1\text{-mim})_2]^+$, is similar to $[H(1,2\text{-dimethylimidazolium})_2]^+$ structurally characterized as its chloride salt.[5] Complexes of $[Th(NO_3)_5L_2]^-$ anions with the same geometry are known for neutral O-donor ligands such as water,[6] *however, there are only two crystallographically characterized Th-imidazole coordination complexes reported to date* – bis(1,3-di-t-butyl-cyclopentadienyl)-((2,4,6-tri-t-butylphenyl)phosphanyl)-(1-methyl-imidazol-2-yl)-thorium and bis(η^5-1,2,4-tri-t-butylcyclopentadienyl)-bis(1-methyl-1H-imidazol-2-yl)-thorium.[7] Besides that a unique Th(U)-tetrazole complex $(C_5Me_5)_2$*An*[η^2-(N,N′)-tetrazolate]$_2$ (*An* = Th, U) has been structurally characterized.[8] The $[NO_3]^-$ groups and imidazole groups are separated into distinct and very ordered zones, suggesting that interactions between the $[H(1\text{-mim})_2]^+$ cations and 1-mim ligands are very important in the formation of this structure.

Uranium: Since $[C_2mim][UO_2(NO_3)_3]$ could be isolated as either a crystalline solid or a supercooled liquid, both solventless and solution-based reactions were potentially available. Stoichiometric amounts of 1,2,4-triazole, 5-aminotetrazole, H-Im, 1-mim, and 4,4'-bipy were observed to either dissolve in hot $[C_2mim][UO_2(NO_3)_3]$ or react with it to give solids after cooling.

Combining 1 eq. of 4,4'-bipy to hot $[C_2mim][UO_2(NO_3)_3]$ at 70 °C under a stream of N_2 yielded a heterogeneous mixture of yellow and orange solids. Orange single crystals obtained from the mixture were characterized by SCXRD to be $[C_2mim]_2[(UO_2(NO_3)_3)_2(4,4'\text{-bipy})]\cdot 2\{UO_2(NO_3)_2(4,4'\text{-bipy})\}$. This cocrystal contains both anionic, dinuclear complexes and neutral, infinite coordination polymers where $[UO_2]^{2+}$ centers are bridged by 4,4'-bipy ligands. The neutral polymers and anionic molecules represent differing levels of substitution of $[NO_3]^-$ by 4,4'-bipy that would be expected to coexist in solution, and their co-crystallization likely occurs as a result of the neutral polymer buffering the extreme size difference between $[(UO_2(NO_3)_3)_2(4,4'\text{-bipy})]^{2-}$ and $[C_2mim]^+$. We have observed similar, complicated crystalline phases to form when neutral co-formers are added to an IL with potentially strong intermolecular interactions.[9]

The anionic $[(UO_2(NO_3)_3)_2(4,4'\text{-bipy})]^{2-}$ has an extremely uncommon 9-coordinate uranyl center in which one $[NO_3]^-$ is twisted out of the equatorial plane in a conformation that certainly weakens the metal-ligand interaction. It is interesting to note that this binding mode has only been observed for uranyl nitrate complexes, and many of these involve coordination to an N-donor ligand.[10] One of the U–O bonds in the anion is bent resulting in $\angle O-U-O \approx 168.61°$. The twisted axial $[NO_3]^-$ anion is almost perpendicular to the mean equatorial plane favoring strong charge transfer, inducing the bending of the linear uranyl fragment by repulsive electrostatic interactions.

The bending mechanism of uranyls has been analyzed based on density functional calculations, which showed that the bending of the uranyl unit has electrostatic origins.[11] The increase in bond distances may indicate a reduced positive charge on the metal centers (which would both weaken the metal-$[NO_3]^+$ interactions and increase the metal ionic radii). This indicates that despite the lack of a negative charge, the N-heterocycles are better electron N-donors than $[NO_3]^-$ which is consistent with the fact that they are stronger bases.

The reaction of 1 eq. of 5-AT with 2 eq. of 1-mim to form a putative IL produced a homogeneous solution after heating with a heat gun. Adding this solution to hot $[C_2mim][UO_2(NO_3)_3]$ and heating at 110-120 °C overnight, resulted in a mixture of orange solids and gel from which single crystals of $UO_2(NO_3)_2(1\text{-mim})_2$ could be isolated. $UO_2(NO_3)_2(1\text{-mim})_2$ has been detected in solution[12] and predicted in the gas phase,[13] but has never been isolated as a crystalline solid, probably due to hydrolysis at higher concentrations. It is practically isostructural to the reported $UO_2(OAc)_2(1\text{-mim})_2$ (OAc = acetate anion)[13] where the U atom resides on a crystallographic inversion center with overall hexagonal bipyramidal geometry. The biggest difference has been observed in the mutual orientation of the imidazole and nitrate/acetate planes being almost orthogonal (~89°) in the former and forming an 81° angle in the latter.

Finally, we investigated the use of a solvent to control the crystallization. Two eq. of H-Im and supercooled $[C_2mim][UO_2(NO_3)_3]$ were dissolved in ~1 mL of dry acetonitrile. The resulting mixture was evaporated in a Drierite-filled desiccator at reduced pressure to produce large yellow crystals of $UO_2(NO_3)_2(H\text{-Im})_2$ after 4 days. This compound exhibits U coordination identical to $UO_2(NO_3)_2(1\text{-mim})_2$ and $UO_2(OAc)_2(1\text{-mim})_2$ but crystallizes in the monoclinic space group $P2_1/n$ (Table S1). The higher crystal symmetry of this compound is combined with even larger rotational freedom of the ligands – the angle between the nitrate and imidazole planes has been further reduced down to ~74°.

The N-heterocyclic ligands appear to have a significant effect on metal-$[NO_3]^-$ interactions. It is known that actinide metal-ligand bonds are correlated with coordination number, but in all cases where the coordination number remained unchanged, coordination of the N-heterocyclic ligand resulted in a significant increase of all metal-$[NO_3]^-$ bond distances (**Table S1**). Besides geometric reasons this may serve as a proof of enhanced metal−N-donor interactions. On the other hand, N-heterocyclic ligands are also known to have significant influence on the crystal packing not at least due to non-covalent interactions.[14]

Hydrogen bonding, π−π, and H−π stacking or lp−π repulsion were found to be prominent in all structures. For example, in the crystals structure of $[H(1\text{-mim})_2][Th(NO_3)_5(1\text{-mim})_2]$ we do not only observe classic π−π-H−π chains, but maximal separation of imidazole rings and nitrate groups; however, the layers perfectly interact through the extended hydrogen bond network involving $[NO_3]^-$ and aromatic CH groups. Due to the smaller proportion of the imidazolium groups the structural situation in $UO_2(NO_3)_2(1\text{-mim})_2$ is slightly different including separated chains instead of separated layers, though the same building principles can still be observed. 1-mim π−π-H−π zigzag chains alternate with NO_3 zigzag chains both along the *ab* and *-ab* diagonals, involving just hydrogen bonding along the latter.

Classic π−π stacking is missing in the crystal structure of $[C_2mim]_2[(UO_2(NO_3)_3)_2(4,4'\text{-bipy})]\cdot 2\{UO_2(NO_3)_2(4,4'\text{-bipy})\}$, however, single H−π interactions between C_2mim CH_2 groups and bipy rings can be observed. Overall, hydrogen bonding here appears to play the dominant role. The same is valid also for the pseudo-1D structure of $UO_2(NO_3)_2(H\text{-Im})_2$ with an extended network of relatively short CH···O bonds and supporting CH−π interactions between the aromatic rings of the neighboring chains, though only along the *bc* diagonals.

The protonation of H-Im and 4,4'-bipy by $UO_2(NO_3)_2\cdot 6H_2O$ to give ammonium salts is established in the literature.[15] The structures here are all analogous to $UO_2(NO_3)_2(OH_2)_2$[16] except for the $[(UO_2(NO_3)_3)_2(4,4'\text{-bipy})]^{2-}$ anion which has a 9-coordinate uranium center. Thus, while a number of reactions of $UO_2(NO_3)_2\cdot 6H_2O$ with N-heterocycles (including 1-mim, H-Im, and 4,4'-bipy) have already been reported, *the crystallization of uranyl nitrate complexes with these ligands is unprecedented*. It is difficult to obtain the crystals of uranyl nitrate complexes with N-heterocycles from aqueous medium as N-heterocycles can readily be protonated and also the actinides tend to hydrolyze in concentrated aqueous solutions. Here, we successfully obtained the crystals of those novel complexes by simply reacting N-heterocycles with liquid anhydrous uranyl nitrate.

While complexes with N-heterocyclic ligands can be isolated in the presence of more basic anions, the use of more weakly binding $[NO_3]^-$ counterions should lead to greater flexibility of the $[UO_2]^{2+}$ coordination geometry. This has been illustrated here by the fortuitous isolation of two distinct species in the crystal structure of $[C_2mim]_2[(UO_2(NO_3)_3)_2(4,4'\text{-bipy})]\cdot 2\{UO_2(NO_3)_2(4,4'\text{-bipy})\}$. By comparison, six crystalline complexes of $[UO_2]^{2+}$ with N-heterocycles have also been crystallized from reactions with $UO_2(NO_3)_2\cdot 6H_2O$ and acetylacetone in solution.[17] However, this approach only resulted in the isolation of complexes with the same coordination geometries (two bidentate acetylacetonate ions and one unidentate N-donor), and prevented the isolation of any complexes with a bidentate N-heterocycle (2,2'-bipyridyl).

References

1. Bruker, APEX 2 AXScale and SAINT, version 2010; Bruker AXS, Inc.: Madison, WI.
2. G. Sheldrick, SHELXTL, Version 6.14, Bruker AXS Madison, WI
3. G. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112-122.
4. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466-470.
5. S. P. Kelley, A. Narita, J. D. Holbrey, K. D. Green, W. M. Reichert and R. D. Rogers, *Cryst. Growth Des.*, 2013, **13**, 965-975.
6. G. E. Sigmon and P. C. Burns, *J. Solid State Chem.*, 2010, **183**, 1604-1608.
7. (a) C. Zhang, G. Hou, G. Zi and M. D. Walter, *Dalton Trans.*, 2019, **48**, 2377-2387; (b) C. Zhang, G. Hou, G. Zi, W. Ding and M. D. Walter, *Inorg. Chem.*, 2019, **58**, 1571-1590.
8. K. P. Browne, K. A. Maerzke, N. E. Travia, D. E. Morris, B. L. Scott, N. J. Henson, P. Yang, J. L. Kiplinger and J. M. Veauthier, *Inorg. Chem.*, 2016, **55**, 4941-4950.
9. H. M. Titi, S. P. Kelley, M. E. Easton, S. D. Emerson and R. D. Rogers, *Chem. Commun.*, 2017, **53**, 8569-8572.
10. J.-C. Berthet, P. Thuéry, J.-P. Dognon, D. Guillaneux and M. Ephritikhine, *Inorg. Chem.*, 2008, **47**, 6850-6862.
11. K. P. Carter, M. Kalaj, A. Kerridge, J. A. Ridenour and C. L. Cahill, *Inorg. Chem.*, 2018, **57**, 2714-2723.
12. A. Marzotto and H. Kozłowski, *Inorg. Chim. Acta*, 1982, **67**, 87-90.
13. K. E. Gutowski, V. A. Cocalia, S. T. Griffin, N. J. Bridges, D. A. Dixon and R. D. Rogers, *J. Am. Chem. Soc.*, 2007, **129**, 526-536.
14. E. A. Meyer, R. K. Castellano and F. Diederich, *Angew. Chem. Int. Ed.*, 2003, **42**, 1210-1250.
15. (a) D. L. Perry, H. Ruben, D. H. Templeton and A. Zalkin, *Inorg. Chem.*, 1980, **19**, 1067-1069; (b) N. W. Alcock and D. J. Flanders, *Acta Crystallogr. C*, 1987, **43**, 1267-1269.
16. D. Hall, A. D. Rae and T. N. Waters, *Acta Crystallogr.*, 1965, **19**, 389-395.
17. T. Kawasaki, T. Nishimura and T. Kitazawa, *Bull. Chem. Soc. Jpn.*, 2010, **83**, 1528-1530.