Structural Clues to UO_2^{2+}/VO_2^{+} Competition in Seawater Extraction using Amidoxime-Based Extractants

Steven P. Kelley, Patrick S. Barber, Peter H. K. Mullins, and Robin D. Rogers*

SUPPLEMENTARY INFORMATION

Contents:

Materials and Methods:

Chemicals and Instrumentation: All commercially acquired chemicals were used as received without additional purification. Methanol (BDH Chemicals) was obtained from VWR International (Radnor, PA). NH_2OH, as a 50 wt% solution in water, was obtained from Alfa-Aesar (Ward Hill, MA). V_2O_5 and 4,5-dicyanoimidazole were obtained from Sigma-Aldrich (St. Louis, MO). Deionized water was obtained from an in-house system (Culligan Water Systems, Rosemont, IL) with a typical resistivity of 17.4 MΩ·cm (the exact resistivity was not measured prior to these experiments).

$UO_2(NO_3)_2{\cdot}6H_2O$ was prepared as follows (*Caution!* All isotopes of uranium are radioactive. Comply with local regulations regarding handling and disposal.): 1 g of UO_3 (Strem Chemicals, Inc., Newburyport, MA), 1.1 molar eq. of concentrated nitric acid (Sigma-Aldrich), and 1 g of deionized water were combined in a 20 mL borosilicate glass vial and dissolved with magnetic stirring at room temperature to give a clear yellow solution. This solution was evaporated to dryness by heating overnight at 80-90 ^{o}C in a heated sand bath to give a yellow powder. A few drops of water were added to this powder and ground to give a slurry which was then heated for 2 min at 80 ^{o}C. The liquid fraction was decanted while hot and allowed to stand at room temperature whereupon it completely froze into a mass of yellow-green prismatic crystals of $UO_2(NO_3)_2{\cdot}6H_2O$.

Synthesis of 4,5-(diamidoximyl)imidazole (4,5-(DAO)Im): Caution! Pure NH_2OH and concentrated solutions are explosive. Evaporation of NH_2OH containing solutions should be avoided.

In a round-bottom flask 0.5 g 4,5-dicyanoimidazole was dissolved in 50 mL of methanol with magnetic stirring at room temperature. To this solution was added 1.5 g of 50 wt% NH_2OH solution in water (5 to 6 molar eq. NH_2OH). The flask was fitted with a water-cooled double walled condenser, and the reaction was heated to reflux overnight with stirring. During the course of the reaction, the clear solution became opaque with suspended solids. After approximately 12 h of heating, the reaction flask was removed from heat. Solid product was isolated by gravity filtration, and the filtrate was collected in a glass beaker and evaporated on a hot plate. When crystals were observed to form from the filtrate, heating was stopped, and the beaker was covered with Parafilm and allowed to stand for several hours at room temperature. The remaining liquid was decanted and all isolated solids were combined and allowed to air-dry. ^1H NMR and comparison of the measured and calculated powder X-ray diffraction (PXRD) patterns confirmed the product to be pure 4,5-(DAO)Im. Single crystals for X-ray diffraction were obtained by dissolving a small amount of this material in *ca.* 20 mL of water and allowing the solvent to evaporate under ambient conditions for several weeks.

Reaction of 4,5-(DAO)Im with $UO_2(NO_3)_2{\cdot}6H_2O$: A series of solutions of $UO_2(NO_3)_2{\cdot}6H_2O$ were prepared by weighing $UO_2(NO_3)_2{\cdot}6H_2O$ into borosilicate glass culture tubes and dissolving each in a known volume of water to give yellow solutions. Solid 4,5-(DAO)Im was added freely to these solutions and swirled, resulting in a color change to dark red in all cases. When no further dissolution could be observed visually upon adding fresh 4,5-(DAO)Im, each solution was filtered through a glass Pasteur pipette packed with Whatman No. 6 filter paper and collected in a clean culture tube. The solutions were covered and allowed to stand. The time over which crystallization was observed ranged from less than 1 h to overnight and was correlated with the concentration. Exact masses of $UO_2(NO_3)_2{\cdot}6H_2O$ and water are given in Table S1.

Table S1: Masses of reagents used in crystallization of UO_2(4,5-(DAO)Im)$(OH_2)_2{\cdot}3H_2O$

Mass $UO_2(NO_3)_2{\cdot}6H_2O$ (g)	0.028	0.021	0.059	0.025	0.030
Volume H_2O (mL)	0.1	0.2	0.5	1.0	1.5

The largest, most strongly diffracting crystals were obtained by adding 4,5-(DAO)Im to a solution of a 30.0 mg $UO_2(NO_3)_2{\cdot}6H_2O$ in 1.5 mL deionized water.

Reaction of V_2O_5 with 4,5-(DAO)Im: 2.64 mg V_2O_5 was dissolved in 4.1250 g deionized water to give a yellow-green solution. To this solution was added 10.0 mg of 4,5-(DAO)Im, which dissolved with no obvious changes. Yellow-green crystals formed on standing after several days, one of which was used for X-ray diffraction analysis.

^{1}H NMR Spectrum of 4,5-(DAO)Im

^{1}H NMR was measured on a Bruker Avance 300 MHz NMR spectrometer (Bruker Biospin Corporation, Billerica, MA) in DMSO-d_6 (Cambridge Isotope Laboratories, Inc., Tewksbury, MA). The spectrum was referenced to the DMSO solvent peak at 2.50 ppm. The main expected impurities, methanol and 4,5-dicyanoimidazole, could not be detected. Acetone was observed as a contaminant from the NMR tube.

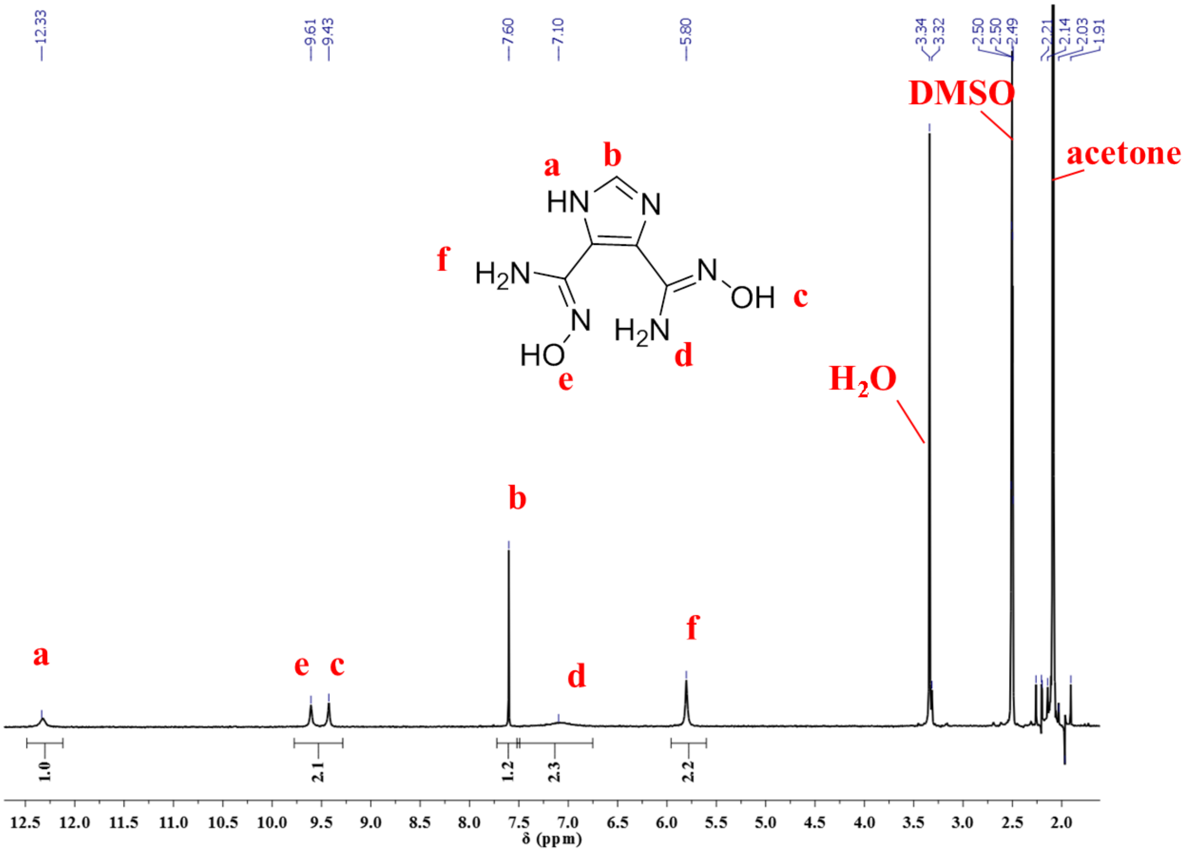

Fig. S1: ^{1}H NMR spectrum of 4,5-(DAO)Im in DMSO-d_6.

Powder X-ray diffraction analysis of 4,5-(DAO)Im

Powder X-ray diffraction (PXRD) was measured on a Bruker D2 Phaser desktop diffractometer with a Linxeye linear position-sensitive detector (Bruker-AXS, Madison, WI) using Ni-filtered Cu-Kα radiation. A thin layer of 4,5-(DAO)Im powder (used as isolated from the reaction) was spread onto a silicon low-background PXRD sample holder using vacuum grease to fix the sample to the surface. Diffraction data was measured across a 2*θ* range of 5 to 60^{o} using a continuous fast scanning mode with a rate of 0.4 s/0.02^{o}.

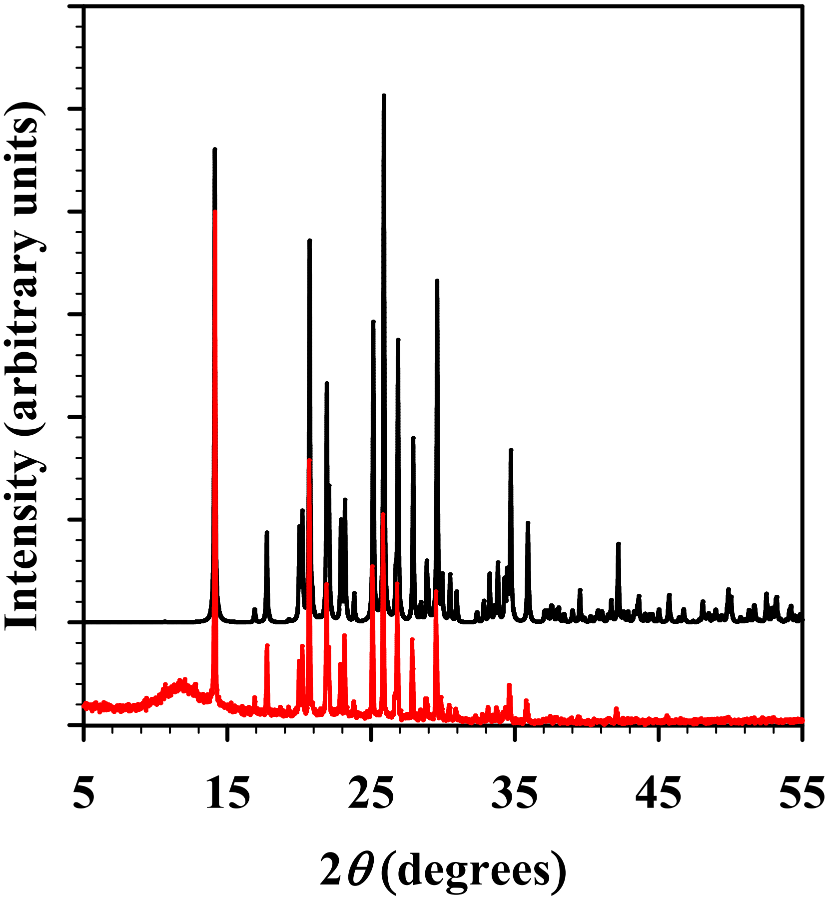

Fig. S2: PXRD pattern of 4,5-(DAO)Im (red) *vs.* calculated PXRD from the single crystal structure (*black*). All major diffraction peaks match with expected peaks. The broad elevated intensity at ca. 11^{o} is background from the vacuum grease.

Single Crystal X-ray Diffraction Experimental and Refinement Details

Crystal structures were determined from single crystal X-ray diffraction (SCXRD) data collected on a Bruker diffractometer equipped with a Platform 3-circle goniometer and an Apex II CCD area detector (Bruker-AXS) using graphite monochromated Mo-Kα radiation. Crystals were mounted on a glass fiber using silicone grease and cooled to their respective temperatures by a cold stream of N_2 gas using an N-Helix cryostat (Oxford Cryosystems, Oxford, UK). Data was collected in 0.5° frames using a strategy of scans about the omega and phi axes. Data collection, unit cell determination, data reduction and integration, absorption correction, and scaling were performed using the Apex2 software suite from Bruker.[1]

Refinement Details for 4,5-(DAO)Im and (VO_2(4,5-(DAO)Im)$_2$·2H_2O: The crystal structures of 4,5-(DAO)Im and (VO_2(4,5-(DAO)Im)$_2$·2H_2O were solved by direct methods and refined by full matrix least squares refinement against F^2. All non-hydrogen atoms were located from the difference map and refined anisotropically. Difference map peaks for hydrogen atoms in 4,5-(DAO)Im could be clearly discriminated from noise peaks in the difference map. All hydrogen atoms were located from the difference map, and their coordinates were allowed to refine freely while their thermal parameters were constrained to ride on the carrier atom. For (VO_2(4,5-(DAO)Im)$_2$·2H_2O, hydrogen atoms bonded to carbon were placed in calculated positions. Hydrogen atoms bonded to nitrogen and oxygen could be located from the difference map, and their coordinates were refined with distance restraints applied where necessary to keep the N-H and O-H bond distances chemically reasonable. Space group determination, structure solution and refinement, and generation of ORTEPs were carried out using the Bruker SHELXTL software package.[2]

Refinement Details for $UO_2(4,5\text{-}(DAO)Im)(OH_2)_2{\cdot}3H_2O$: Prismatic maroon crystals of UO_2(4,5-(DAO)Im)$(OH_2)_2{\cdot}6H_2O$ were grown by saturating a solution of $UO_2(NO_3)_2{\cdot}6H_2O$ in deionized water with 4,5-(DAO)Im and allowing it to stand overnight at room temperature. Crystals appeared free of flaws during inspection but inevitably showed signs of polycrystallinity in their diffraction patterns. Changing the starting concentration of $UO_2(NO_3)_2{\cdot}6H_2O$ allowed for the growth of much larger and more strongly diffracting crystals, but did not affect the polycrystallinity, which appears to be an intractable feature of the crystals grown under these conditions.

Numerous attempts were made to solve the structure from SCXRD data integrated against a single domain. While non-hydrogen atom positions could be easily determined from these datasets, anisotropic refinement resulted in non-positive definite thermal displacement parameters for some light atoms, and hydrogen atom positions for strong hydrogen bond donors could not be located from the difference map. Ultimately, using a crystal measuring 0.32 x 0.06 x 0.05 mm it was possible to collect a dataset which could be integrated as a two-component twin with the components related by the following twin law:

$$\begin{bmatrix} -0.964 & 0.001 & 0.074 \\ 0.013 & 1.000 & 0.022 \\ -0.102 & 0.010 & -1.030 \end{bmatrix}$$

Indexing was done using CELL_NOW,[3] integration was performed using the Apex2 software suite,[1] and scaling and absorption corrections were applied using TWINABS.[4]

The structure was solved in $P2_1/c$ with two formula units per asymmetric unit. The asymmetric unit appears as though it could be reduced by additional symmetry when viewed in isolation. However, the structure was tested and found not to have higher symmetry using the program PLATON.[5] When the packing was examined beyond a single asymmetric unit, it became clear that the unit cell was not consistent with these pseudo-symmetry elements.

Symmetry inequivalent metal complexes can be related to each other by pseudo-translation in some cases and pseudo-inversion in others but never both, which itself indicates symmetry inequivalence between the two. Additionally, the six unique water molecules form a network which cannot be reduced by symmetry.

Hydrogen atoms could not be located from the difference map for most of the hydrogen bond donor groups, so hydrogen atom positions were calculated by adding hydrogen atoms along expected hydrogen bond vectors, applying appropriate distance and angle constraints, refining to convergence, and fixing the final positions. The resulting hydrogen atom placements illustrate the expected strong donor-acceptor interactions although they are not perfectly accurate, resulting in some accidental D-H···H-D contacts.

Refinement of the structure against detwinned HKLF-5 format data improved the R-factor and allowed all non-hydrogen atoms to be refined anisotropically without non-positive definite ellipsoids. The final structure does have some problems such as unexpectedly high electron density peaks near the oximate groups and severely oblate thermal ellipsoids on some light atoms. The oblate thermal parameters on atoms C7A and O1B resulted in level A CheckCIF alerts. While these errors *can* indicate incorrect element assignments, the two particular affected atoms can be confidently assigned as correct: The carbon atom is associated with the skeleton of 4,5-(DAO)Im ligand whose structure can be reliably confirmed from the other two structure determinations, and the oxygen atom is associated with the UO_2^{2+} ion, the structure of which is highly conserved across all compounds in which it is found. Level B alerts are associated with a large difference map peak, but the proximity of this peak to the uranium atom (0.08 Å) indicates that this peak is associated with a discrepancy in the position or thermal parameter of this atom rather than unassigned electron density.

These artifacts indicate contamination of the data with unresolved contributions from other domains. This is further supported by the fact that F_{obs} is much greater than F_{calc} for the most disagreeable reflections, indicating that these reflections are systematically brighter than expected from the structure. Since these artifacts do not call into question the identity of the compound, it was decided to leave them in rather than employ an excessive number of restraints or twin domains.

Additional Crystal Structure Details

4,5-(DAO)Im: The compound crystallized in the orthorhombic space group *Pbca* with Z = 8. The ring has the typical planar geometry and asymmetric C2-N bond distances of protonated imidazoles. Compared to the starting material, 4,5-dicyanoimidazole, the C5-N1 and C4-N3 bond distances have increased significantly while all other ring bond distances are similar.[6] The N-O and C-N single bonds on the oximes are significantly different from each other. N7, which acts as the intramolecular hydrogen bond donor, has a significantly longer bond to C7 than the corresponding bond between C6 and N5 (1.368(2) *vs.* 1.350(2) Å). N4, which is the intramolecular hydrogen bond acceptor, has a significantly shorter bond to O1 than the corresponding N6-O2 bond (1.415(2) *vs.* 1.436(2) Å). The shortening of the N4-O1 bond may be due to increased polarity caused by increasing positive charge on N4, while the lengthening of the C7-N7 bond may be due to a decrease in double bond character due to the electron density received by N7 from the hydrogen bond to N4. The hydrogen bond donor amidoxime group is relatively co-planar with the ring while the acceptor group is tilted highly out of the plane of the ring. The amino nitrogen atoms N5 and N7 have bond angles that are intermediate between planar and pyramidal, indicating some resonance with the oxime double bonds.

The crystal has very dense packing, with each molecule making short (less than the sum of the van der Waals radii) contacts to 12 neighboring molecules. Oxime to oxime O-H···N hydrogen bonds, which are reported to be a conserved motif,[7] including among amidoximes,[8] are present although the intramolecular hydrogen bond blocks one of the oximes from acting as an acceptor. O2-H···N4 hydrogen bonds link the molecules into infinite hydrogen bonded chains. along the *a* axis.

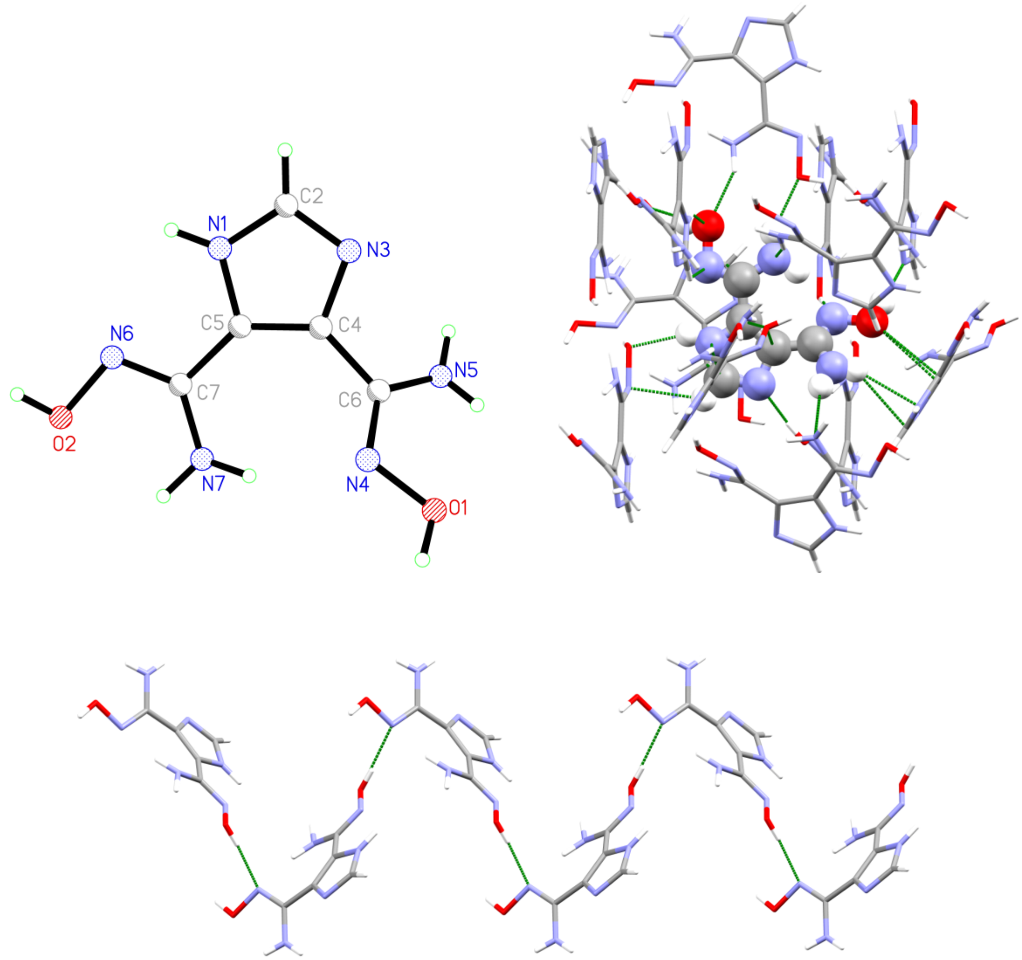

Fig. S3: Labeled ball-and-stick diagram of 4,5-(DAO)Im (*top left*) and packing diagrams of short contact environment around one molecule of 4,5-(DAO)Im *(top right)* and oxime-to-oxime hydrogen bonded catemer along *a (bottom)*. Green lines indicate short contacts.

Adjacent chains along the *b* axis are linked to each other through a very dense network of complementary hydrogen bonds and other interactions to form layers. The remaining oxime O-H group donates a hydrogen bond to the basic imidazole nitrogen atom, the acidic imidazole hydrogen atom is donated to an oxime oxygen atom, adjacent amidoxime groups on two chains dimerize through N-H···O hydrogen bonds, and dimeric short contacts are present between the amidoxime groups and imidazole rings where they overlap with one another in a coplanar fashion.

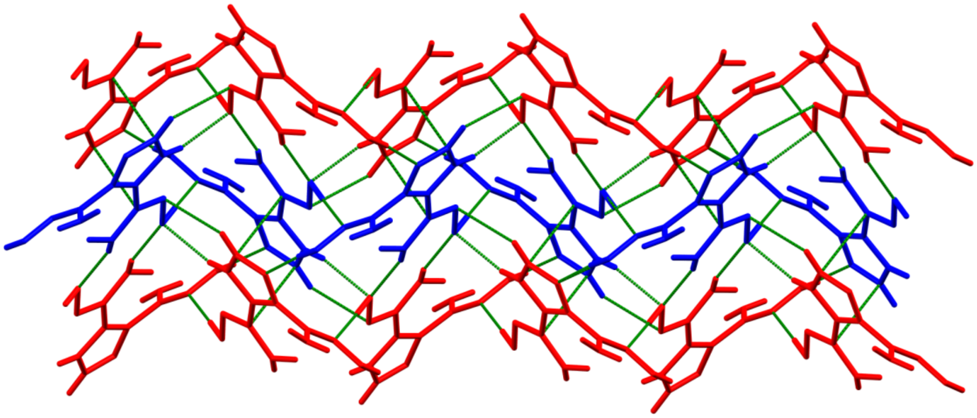

Fig. S4: Packing diagram showing oxime-to-oxime hydrogen bonded catemers interacting with each other to form layers parallel to the *ab* plane. Molecules of the same color are connected by oxime-to-oxime hydrogen bonds along the *a* axis, and molecules of different colors are connected by interactions along the *b* axis.

The hydrogen atoms on amino nitrogen N5 point roughly perpendicular to these layers and donate the hydrogen bonds which bridge the layers along *c* into a complete 3D network. These hydrogen bonds are donated to imidazole ring carbon and nitrogen atoms through contacts that are perpendicular to the ring, indicating an N-H···π interaction, as well as to the lone pair on amino nitrogen N7. Short contacts between O2, the oxygen atom on the same amidoxime group, and carbon atoms C4 and C5 on the neighboring imidazole ring are also observed.

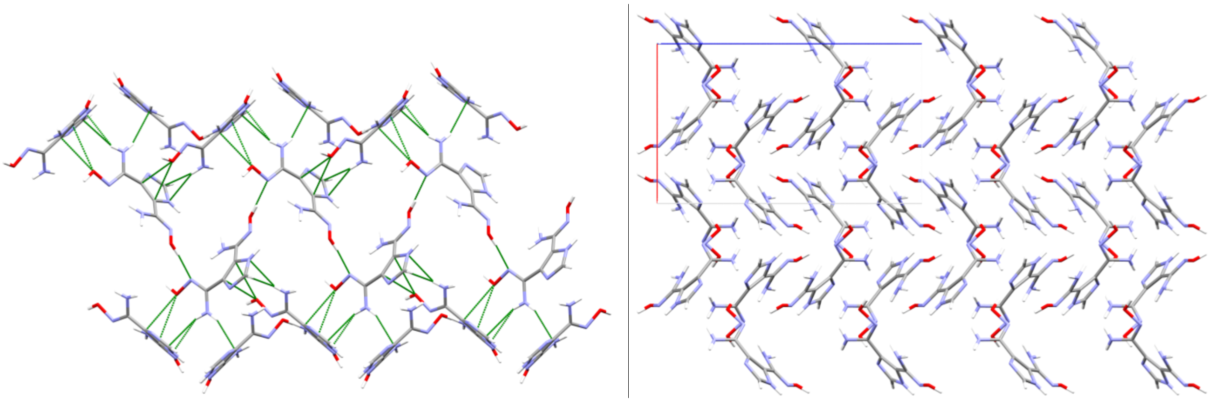

Fig. S5: Packing diagrams showing the reciprocal interactions between amidoxime groups and rings for an oxime-to-oxime hydrogen bonded catemer and its neighbors along the *c* axis (*left*) and a 2x2x2 unit cell packing down *b* (*right*).

$UO_2(4,5\text{-}(DAO)Im)(OH_2)_2\cdot 3H_2O$: The compound crystallized in space group $P2_1/c$ with Z = 8. The structure is typical of uranyl complexes, with uranium bonded two axial oxo ligands with short bonds and six nearly coplanar equatorial atoms which include two deprotonated oxime groups and two water molecules. This coordination mode is both exclusive to and almost universally prevalent among complexes of UO_2^{2+} with anionic oximate ligands found in the CSD, strongly supporting the assignment of the ligand as a dianion.

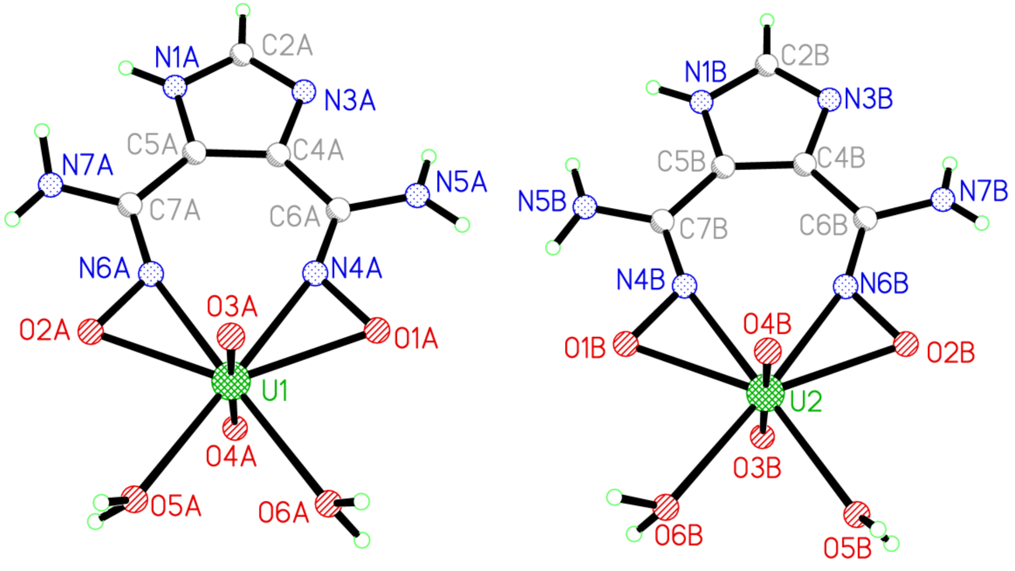

Fig. S6. Labeled 50% probability ORTEP plots of both unique $UO_2(4,5(DAO)Im)(OH_2)_2$ formula units.

The entire ligand is approximately planar and oriented nearly perpendicular to the O-U-O uranyl bond axis. Although there are six atoms in the equatorial coordination plane the geometry of the four oxygen atoms is closer to ideal for pentagonal bipyramidal, with the fifth point of the pentagon being in between the two nitrogen atoms. The oxime U-N bonds are significantly shorter than the U-O bonds (N4A-U1 = 2.292(9) Å, O1A-U1 = 2.443(9) Å, N6A-U1 = 2.298(7) Å, O2A-U1 = 2.385(8) Å, N4B-U2 = 2.31(1) Å, O1B-U2 = 2.414(9) Å, N6B-U2 = 2.297(7) Å, O2B-U2 = 2.446(8) Å), which is highly unusual and reported in only one other uranyl oximate complex.[9] This is likely a result of the geometry of the binding site which causes the uranium atom to be closer to the nitrogen atoms. U1 makes asymmetric bonds and is closer to O2A than O1A, while the U2 oxime bond distances are equivalent within experimental uncertainty. This is the only clear structural difference between the two unique complexes.

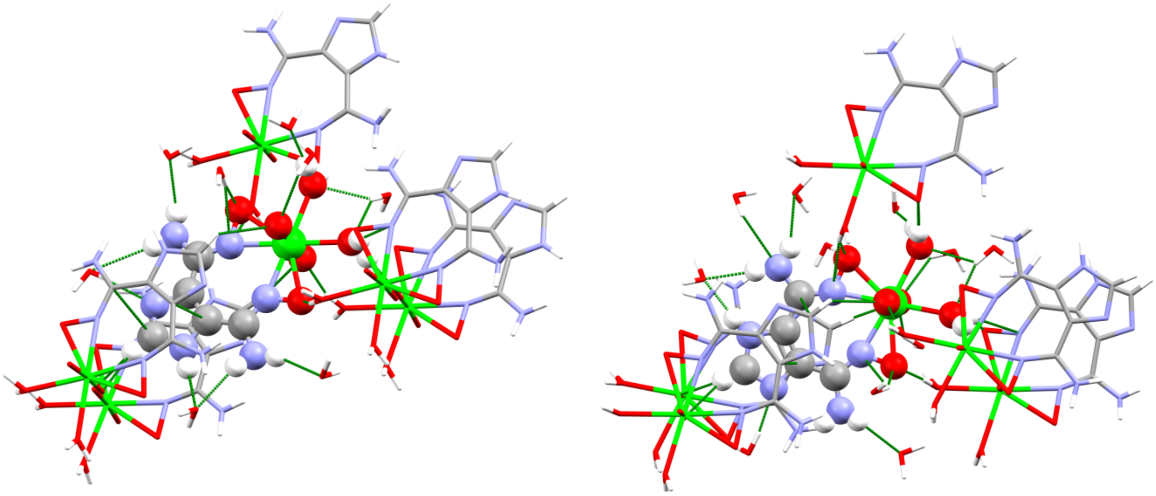

Fig. S7: Packing diagrams showing short contact environments around the unique UO_2(4,5-(DAO)Im)$_2$(OH_2)$_2$ formula units.

Complex A makes short contacts to 5 neighboring complexes and 8 lattice water molecules. Complex B makes short contacts to 5 neighboring complexes and 11 lattice water molecules. Both complexes interact with their symmetry equivalent neighbors via O-H···O hydrogen bonds between coordinated water molecules and oximate oxygen atoms to form infinite catemers along *c*. The catemers composed of complex A are antiparallel to those of complex B, and these chains interact with each other via hydrogen bonds between coordinated water molecules and uranyl oxygen atoms to form pseudo-centrosymmetric ribbons.

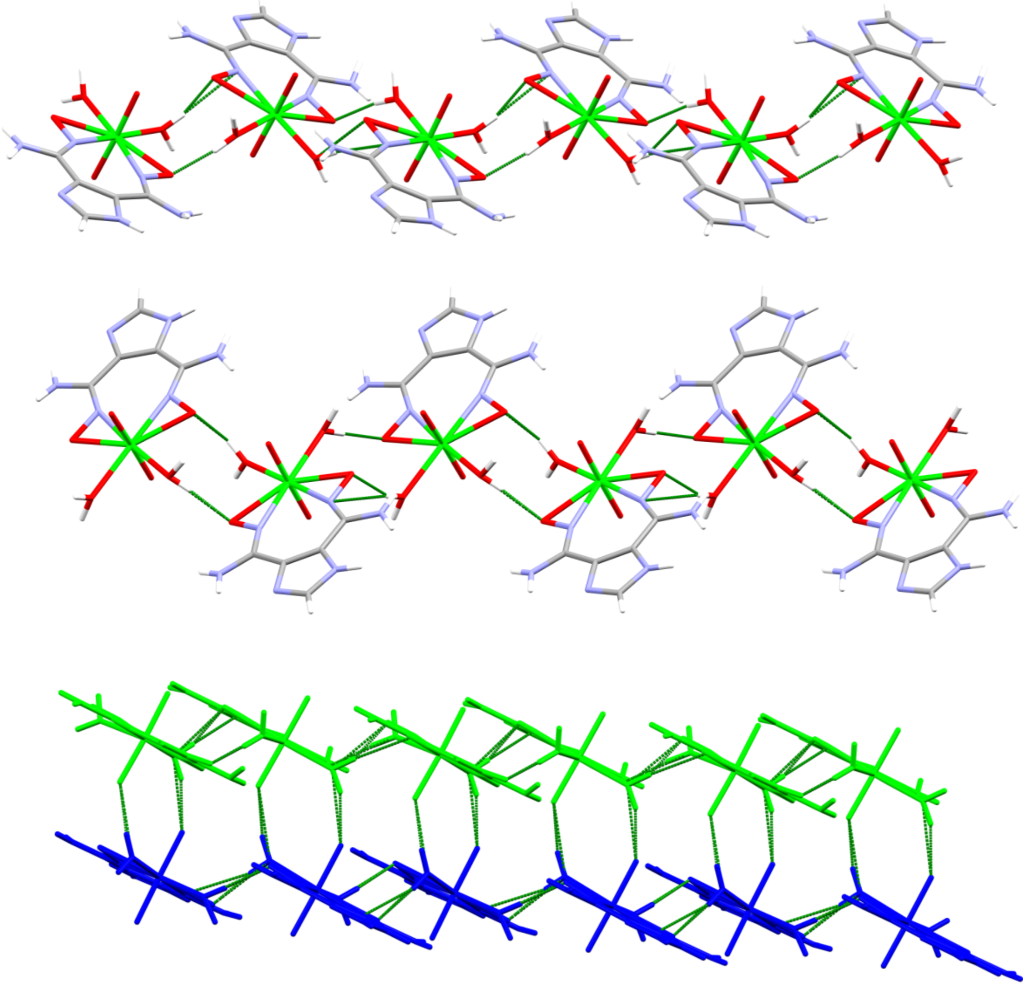

Fig. S8: Packing diagrams showing hydrogen bonding between symmetry equivalent units A (*top*) and B (*middle*) and between adjacent chains of symmetry inequivalent units (*bottom*, different colors indicate symmetry inequivalence).

These ribbons are bridged to each other along both *ab* diagonals through a variety of interactions creating the 3D network, which can be observed by viewing packing down *c*. These interactions include hydrogen bonds mediated by lattice water molecules, hydrogen bonds directly between coordinated water molecules and acceptors on neighboring ribbons, and head-to-tail stacking interactions between the imidazole and oxime portions of the ligand.

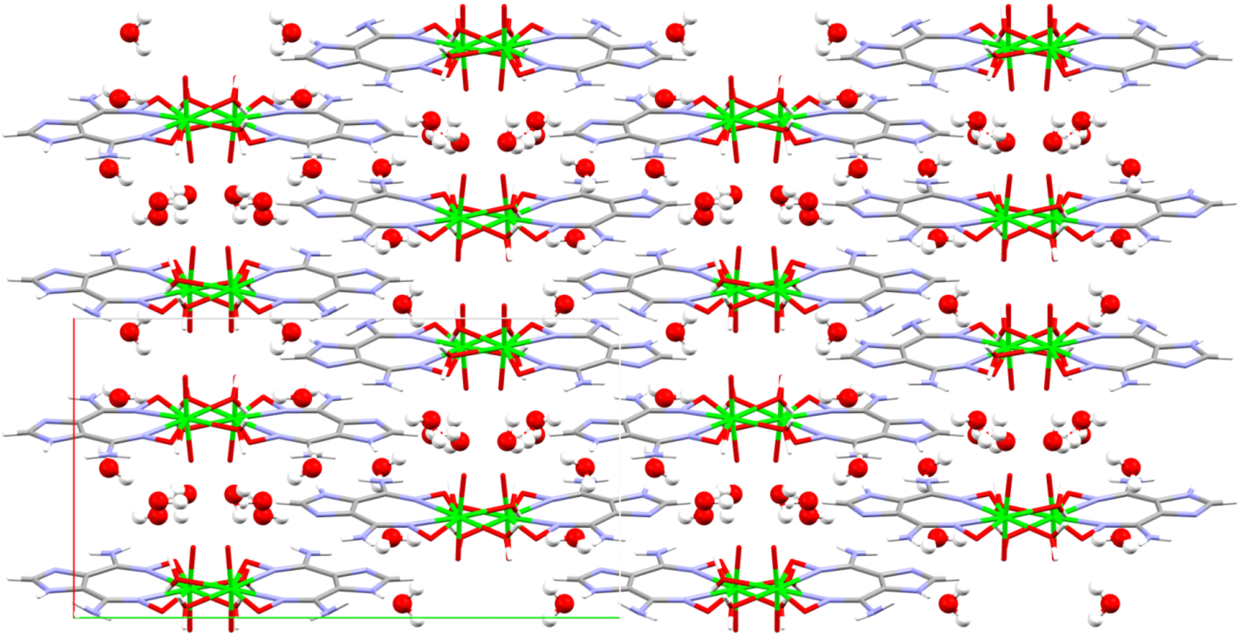

Fig. S9: 2x2x2 Unit cell packing diagram down the *c* axis.

$(VO_2(4,5\text{-}(DAO)Im))_2\cdot 2H_2O$: The compound crystallized in the space group *C*2/*c* with Z = 4. The molecule consists of two VO_2^+ ions coordinated to two nitrogen atoms from one 4,5-(DAO)Im ligand and a deprotonated oxime oxygen atom from a second, forming a 6-membered ring. A crystallographic 2-fold axis passes directly through the center of this ring. The vanadium coordination environment is a distorted trigonal bipyramid with the oxime oxygen and imidazole nitrogen atoms forming the axial bonds. Coordination to the oxime group results in little change to the N-O bond involving the deprotonated oxygen but significant lengthening of the C6-N4 double bond. The C6-N5 bond becomes more double-bond like as a result, indicated by significant shortening relative to the uncoordinated amidoxime (1.323(2) *vs.* 1.350(3) Å) and a more planar arrangement of the $–NH_2$ group. The near tetrahedral N4-O1-V1 bond angle (116.0(1)^o) and the length of the N-O bond indicate mostly sp^3 character around the oxygen

atom. The 4,5-(DAO)Im anions are mostly flat, but O1-V1 bond is angled out of the plane of the molecule, giving the dimer a V-shape.

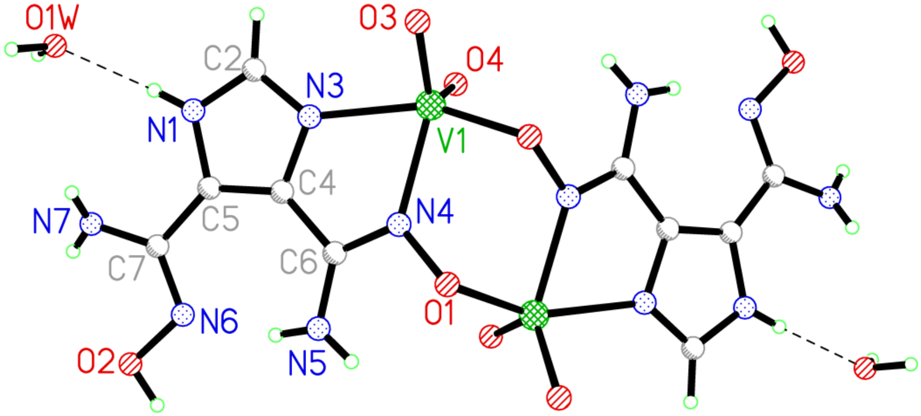

Fig. S10: Labeled 50% probability ORTEP plot of $(VO_2(4,5\text{-}(DAO)Im))_2 \cdot 2H_2O$

Twenty-three complexes of vanadium with oximes and oximates were found in the CSD. The structures are diverse, but most features present in this structure are observed in others, such as the short V-O oxime bond. The V-O bond is usually coplanar with the oxime but is oriented out of the plane to a similar extent observed in $(VO_2(4,5\text{-}(DAO)Im))_2 \cdot 2H_2O$ in a few cases.

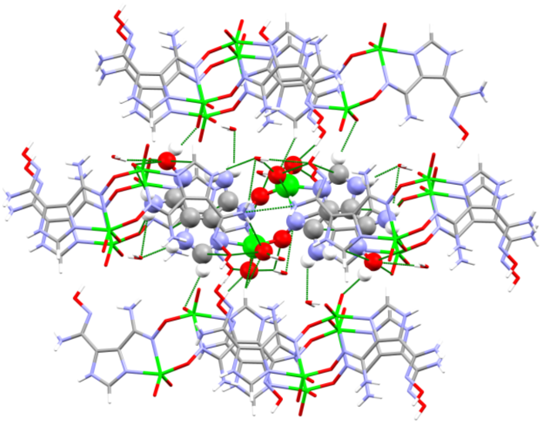

Fig. S11: Packing diagram showing short contact environment around on unit of $(VO_2(4,5\text{-}(DAO)Im))_2$.

Each $(VO_2(4,5\text{-}(DAO)Im))_2$ complex makes short contacts to 10 other complexes and 10 water molecules. The noncoordinating oxime nitrogen atom is occupied by the intramolecular hydrogen bond to the neighboring amine, so there are no oxime-to-oxime hydrogen bonds. The oxime O-H groups donated in hydrogen bonds to VO_2^+ oxygen atoms to form infinite 2-dimensional hydrogen bonded sheets perpendicular to *c*. These sheets interleave with each other and interact through head-to-tail stacking interactions between the imidazolium ring and amidoxime groups and hydrogen bonds between the amino groups and coordinated oxygen atoms, propagating the network along the *c* axis. The water molecules appear to fill space and interact with hydrogen bond donors such as the acidic imidazole nitrogen atom which are not involved in the network formed by the main moiety.

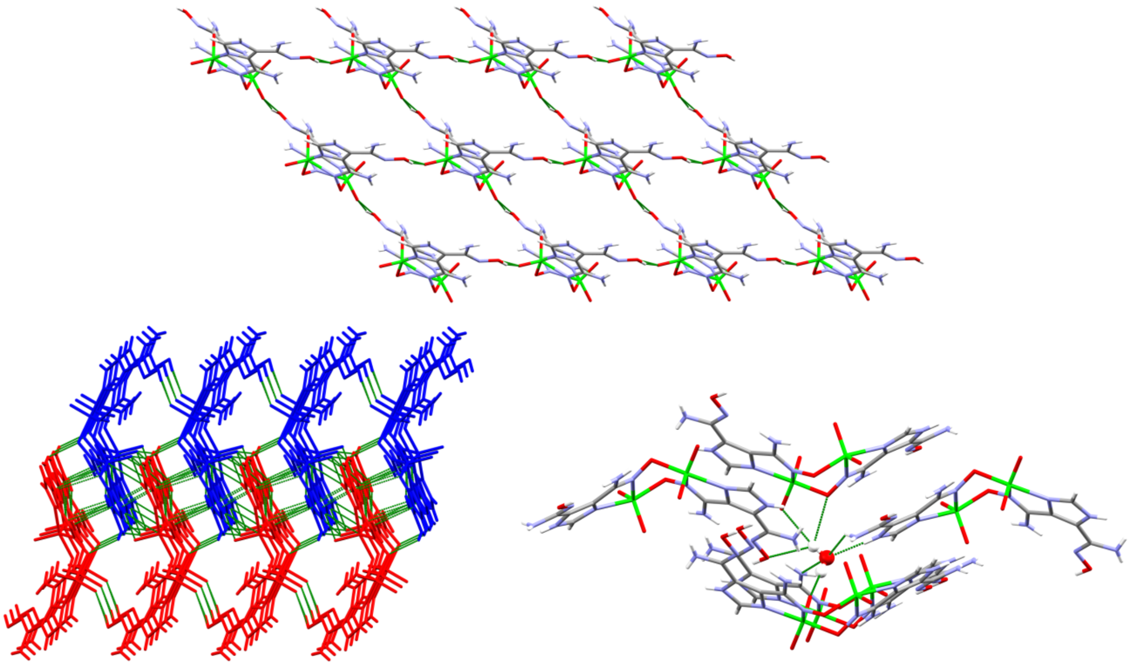

Fig. S12: Packing diagrams showing 2-dimensional network of $(VO_2(4,5\text{-}(DAO)Im))_2$ units linked by O-H···O-V hydrogen bonds (*top*), the stacking of these sheets along the *c* axis (*bottom left*, molecules of same color are hydrogen bonded through O-H···O-V interactions), and the short contact environment around one water molecule (*bottom right*).

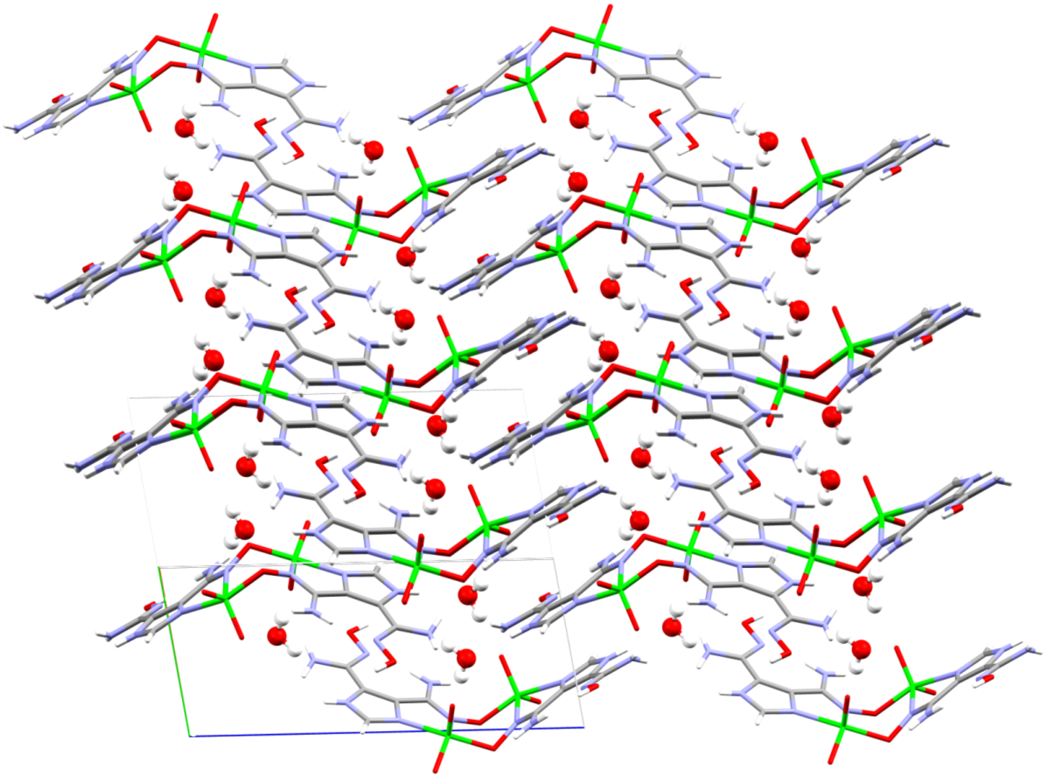

Fig. S13: 2x2x2 Unit cell packing diagram viewed down diagonal of *ab* plane.

Differential Scanning Calorimetry of $UO_2(4,5\text{-}(DAO)Im)(OH_2)_2 \cdot 3H_2O$

Differential scanning calorimetry (DSC) was measured on a Mettler-Toledo DSC 1 Star system (Mettler-Toledo International, Inc., Columbus, OH). A known mass of material was weighed into a tared aluminum crucible. An aluminum lid was crimped onto the pan to seal it and was perforated with a single pin hole. Three cycles of cooling to -70 °C followed by warming to 100 °C were measured using a temperature ramp rate of 5 °C/min and 10 min isotherms at the end of every dynamic step. Heat flow was referenced against an empty sample pan. The DSC of an empty pan was also measured to serve as a blank.

The irreversible endothermic transition observed on first warming with an onset of approximately 51 °C and peak at 68.3 °C has been assigned to dehydration of the crystal. No other transitions appear in the measurement range.

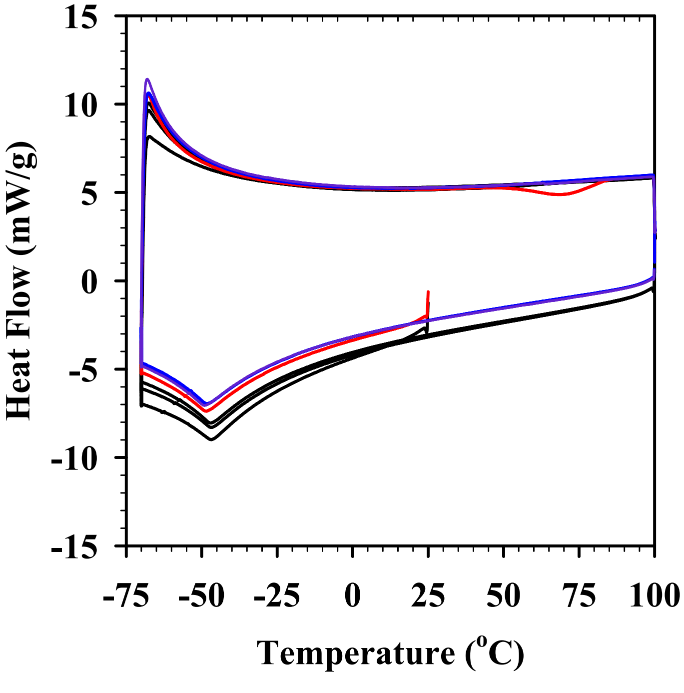

Fig. S13: DSC of UO_2(4,5-(DAO)Im)$(OH_2)_2$·$3H_2O$: Red – 1st cycle, blue – 2nd cycle, violet – 3rd cycle, black – empty pan (all 3 cycles).

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