Electronic Supplementary Information for Dalton Transactions

Supporting Information for

Amine Templated Three- and Two-Dimensional Uranyl Sulfates*

Mohan S. Bharara and Anne E. V. Gorden*

Auburn University, Department of Chemistry and Biochemistry

Auburn, Alabama, USA 36849

Email: gordeae@auburn.edu

General Data

$UO_2(NO_3)_2 \cdot 6H_2O$, n-butylamine and Sulfuric acid were purchased from Acros and used as received. The IR data were recorded as KBr pellets on SHIMSDZU Inc. IR, Prestige-21 Fourier Transform Infrared Spectrophotometer in the range 400 – 4000 cm^{-1}. X-ray diffraction data for **1** – **3** were collected at -80 °C on a Bruker SMART APEX CCD X-ray diffractometer unit using Mo Kα radiation from crystals mounted in Paratone-N oil on glass fibers. SMART (v 5.624) was used for preliminary determination of cell constants and data collection control. Determination of integrated intensities and global cell refinement were performed with the Bruker SAINT software package using a narrow-frame integration algorithm. The program suite SHELXTL (v 5.1) was used for space group determination, structure solution, and refinement.[1] Refinement was performed against F^2 by weighted full-matrix least square, and empirical absorption correction (SADABS[2]) was applied. For compounds **1** and **2**, the disorder present in n-butylammonium cations contributes to the high s.u. values of the bond length and angles. The carbon atoms have apparently high displacement parameters and cannot be treated as anisotropic. Because of the disorder, SHELXL 97 (Sheldrick, 1997) restraints and constraints (DFIX, SADI, FLAT) were used in the refinement to control the geometry and displacement parameters of the atoms. H atoms were placed at calculated positions using suitable riding models with isotropic displacement parameters derived from their carrier atoms. The structures have been deposited at the Cambridge Crystallographic Data Center (724366 - 724368). Further information could be obtained from

http://www.ccdc.cam.ac.uk/deposit

CCDC, 12 Union Road, Cambridge CB2 1EZ, UK

Telephone: (44) 01223 762910

Experimental Section

$UO_2(NO_3)_2{\cdot}6H_2O$ (0.172 g, 0.3 mm), 0.5 mL 40 % H_2SO_4 and n-butyl amine (0.09 g, 1.1 mm) were added to 5 mL of DI water to make a homogenous solution and left to evaporate at room temperature. Two distinct types of crystals (needles (**1**) and blocks (**2**)) were observed after 2 - 3 days (combined yield = 40 %). Compounds **1** and **2** were separated carefully under the microscope for X-ray crystallography and IR analysis. A few block shaped yellow transparent crystal (**3**) were also observed under microscope (yield < 5 %), hence only crystallographic data could be obtained for **3**. IR (selected peaks for **1** - **2**, cm^{-1}): ≈ 3000 (N-H stretch); ≈ 1600 (N-H bend); ≈ 1100 (S-O stretches); ≈ 900 (U=O asymmetric); ≈ 800 (U=O symmetric).

Crystal data for $[HNC_4H_9]_8[(UO_2)_5(SO_4)_9]$ (H_2O) (1): Needles, 0.20 x 0.10 x 0.05 mm,: Orthorhombic, $P2_1$, a = 9.4586(8) Å, b = 26.769(2) Å, c = 32.377(3) Å, $\alpha = \beta = \gamma = 90^0$, V = 8197.9(12) $Å^3$, Z = 4, M = 2809.73, μ = 10.168, T = 193(2) K, 46987 measured reflections, 11719 unique, R_{int}= 0.0827; $R_1[I > 2\sigma(I)]$ = 0.0389, wR_2 (all) = 0.0664, Theta (max) = 23.27, Flack parameter = 0.407(7), maximum/minimum residual electron density: 1.036 and – 0.756 (e $Å^3$).

Crystal data for $[HNC_4H_9]_2[(UO_2)_6(SO_4)_7(H_2O)_2]$ (2): Blocks, 0.20 x 0.20 x 0.10 mm, Orthorhombic, $C222_1$, a = 10.2776(12) Å, b = 18.339(2) Å, c = 22.788(3) Å, $\alpha = \beta = \gamma = 90^0$, V = 4295.2(9) $Å^3$, Z = 4, M = 2472.86, μ = 23.003,T = 193(2) K, 12304 measured reflections, 3098 unique, R_{int}= 0.0770; $R_1[I > 2\sigma(I)]$ = 0.0462, wR_2 (all) = 0.1130, Theta (max) = 23.27, Flack parameter = 0.017(2), maximum/minimum residual electron density: 2.743 and –2.528 (e $Å^3$).

Crystal data for $[HNC_4H_9][(UO_2)_2(SO_4)_2(OH)](H_2O)_2$ (3): Blocks, 0.20 x 0.20 x 0.10 mm, Monoclinic, $P2_1$, a = 8.439(5) Å, b = 11.912(7) Å, c = 10.636(6) Å, $\alpha = \gamma = 90^0$, $\beta = 102.79^0$ (10), V = 1042.6(10) $Å^3$, Z = 2, M = 952.37, μ = 15.899, T = 193(2) K, 7141 measured reflections, 2934 unique, R_{int}= 0.0397; $R_1[I > 2\sigma(I)]$ = 0.0222, wR_2 (all) = 0.0524, Theta (max) = 23.28, Flack parameter = 0.021(9), maximum/minimum residual electron density: 0.859 and –0.853 (e $Å^3$).

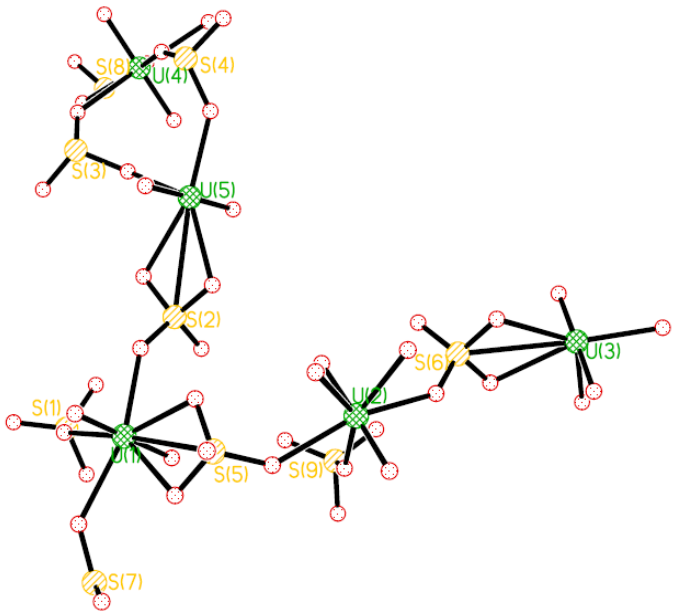

Fig S1. Asymmetric unit of **1** (thermal ellipsoids at 50 % probability). Amine and water molecules are not shown for clarity.

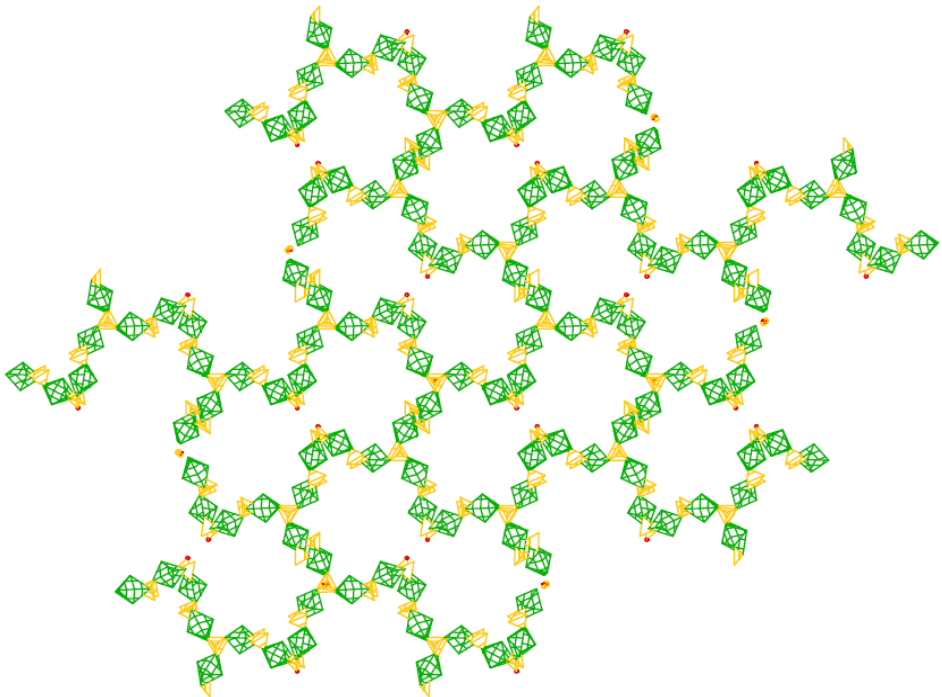

Fig S2. Structural view of **1** along the 'a' axis.

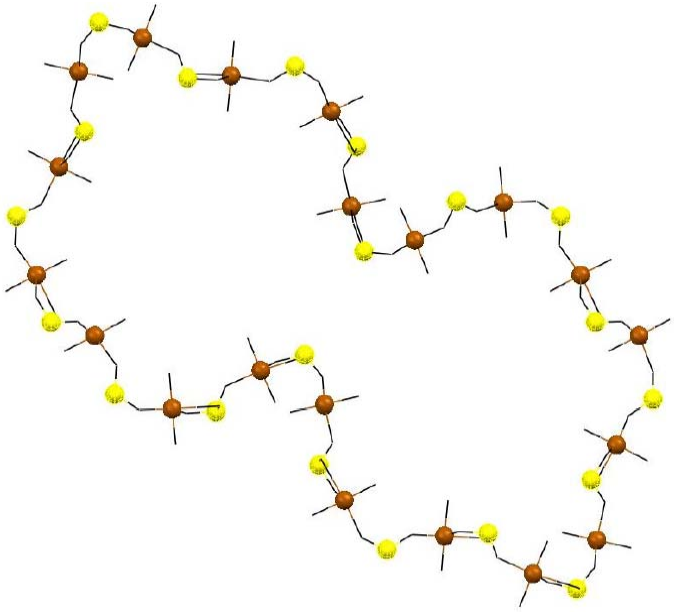

Fig S3. Ball and stick representation of 40 membered ring observed in **1** (red = UO_2 and yellow = SO_2) generated with the help of Mercury (CCDC).

Table S1. Selected bond distances (Å) and angles (^{0}) for **1**.

U1-O19:	1.735(8)	U1-O3:	1.742(7)	U1-O4:	2.297(9)
U1-O1:	2.317(10)	U1-O25:	2.424(9)	U1-O10:	2.487(9)
U1-O21:	2.494(8)	U2-O5:	1.737(8)	U2-O2:	1.754(8)
U2-O37:	2.282(10)	U2-O6:	2.363(10)	U2-O41:	2.397(9)
U2-O32:	2.478(8)	U2-O7:	2.495(9)	U2-S7:	3.119(4) $_1
U3-O13:	1.733(8)	U3-O18:	1.749(8)	U3-O30:	2.322(9) $_1
U3-O8:	2.342(9)	U3-O16:	2.355(9)	U3-O28:	2.478(8)
U3-O46:	2.489(9)	U4-O22:	1.719(9)	U4-O24:	1.754(9)
U4-O40:	2.338(10)	U4-O38:	2.340(10)	U4-O15:	2.377(10)
U4-O26:	2.445(9)	U4-O33:	2.465(11)	U5-O14:	1.729(8)
U5-O11:	1.759(8)	U5-O23:	2.321(10)	U5-O35:	2.320(9) $_1
U5-O17:	2.329(10)	U5-O27:	2.454(8)	U5-O31:	2.472(9)
S1-O45:	1.419(10)	S1-O36:	1.452(11)	S1-O35:	1.477(10)

S1-O4:	1.495(10)	S2-O29:	1.477(10)	S2-O1:	1.492(11)
S2-O31:	1.497(9)	S2-O27:	1.519(9)	S3-O47:	1.440(10)
S3-O15:	1.468(11)	S3-O17:	1.486(10)	S3-O8:	1.508(10) $_3
S4-O12:	1.438(10)	S4-O38:	1.465(10)	S4-O16:	1.474(10)$_3
S4-O23:	1.484(10)	S5-O34:	1.433(10)	S5-O10:	1.501(10)
S5-O41:	1.507(10)	S5-O21:	1.511(9)	S6-O39:	1.445(10)
S6-O6:	1.479(10)	S6-O28:	1.481(9)	S6-O46:	1.485(9)
S7-O20:	1.438(10)	S7-O7:	1.474(10)$_1	S7-O25:	1.482(10)
S7-O32:	1.483(9)$_1	S8-O44:	1.417(12)	S8-O33:	1.465(11)
S8-O40:	1.491(12)$_4	S8-O26:	1.494(10)	S9-O43:	1.437(10)
S9-O42:	1.456(11)	S9-O30:	1.482(10)	S9-O37:	1.521(11)

O19-U1-O3: 178.7(4)	O19-U1-O4: 91.0(4)	O3-U1-O4: 90.3(4)
O19-U1-O1: 89.6(4)	O3-U1-O1: 90.7(4)	O4-U1-O1: 82.4(3)
O19-U1-O25: 86.5(4)	O3-U1-O25: 93.7(4)	O4-U1-O25: 76.4(3)
O1-U1-O25: 158.3(3)	O19-U1-O10: 87.1(4)	O3-U1-O10: 91.9(4)
O4-U1-O10: 155.9(3)	O1-U1-O10: 73.6(3)	O25-U1-O10: 127.4(3)
O19-U1-O21: 94.9(3)	O3-U1-O21: 83.9(3)	O4-U1-O21: 147.3(3)
O1-U1-O21: 129.7(3)	O25 U1 O21: 72.0(3)	O10-U1-O21: 56.7(3)
O5-U2-O2: 178.1(4)	O5-U2-O37: 91.5(4)	O2-U2-O37: 88.8(4)
O5-U2-O6: 90.3(4)	O2-U2-O6: 91.5(4)	O37-U2-O6: 82.0(3)
O5-U2-O41: 86.1(4)	O2-U2-O41: 92.2(4)	O37-U2-O41: 76.8(4)
O6-U2-O41: 158.4(3)	O5-U2-O32: 94.7(3)	O2-U2-O32: 84.0(3)
O37-U2-O32: 148.4(3)	O6-U2-O32: 128.8(3)	O41-U2-O32: 72.7(3)
O5-U2-O7: 86.5(4)	O2-U2-O7: 93.9(4)	O37-U2-O7: 156.0(3)
O6-U2-O7: 74.1(3)	O41-U2-O7: 126.7(3)	O32-U2-O7: 55.5(3)
O5-U2-S7: 91.8(3)$_1	O2-U2-S7: 87.7(3)$_1	O37-U2-S7: 175.3(3)$_1

O6-U2-S7: 101.2(2)$_1 O41-U2-S7: 100.1(2)$_1 O32-U2-S7: 27.8(2)$_1
O7-U2-S7: 27.7(2))$_1 O13-U3-O18: 178.9(4) O13-U3-O30: 87.5(4)$_1
O18-U3-O30: 92.7(4)$_1 O13-U3-O8: 93.4(4) O18-U3-O8: 87.7(4)
O30-U3-O8: 79.4(3)$_1 O13-U3-O16: 89.3(4) O18-U3-O16: 91.0(4)
O30-U3-O16: 159.9(3)$_1 O8-U3-O16: 80.9(3) O13-U3-O28: 89.4(3)
O18-U3-O28: 89.6(3) O30-U3-O28: 72.8(3)$_1 O8-U3-O28: 151.9(3)
O16-U3-O28: 127.1(3) O13-U3-O46: 89.3(4) O18-U3-O46: 89.8(4)
O30-U3-O46: 128.8(3)$_1 O8-U3-O46: 151.8(3) O16-U3-O46: 71.0(3)
O28-U3-O46: 56.1(3) O22-U4-O24: 179.2(4) O22-U4-O40: 89.3(4)
O24-U4-O40: 90.1(5) O22-U4-O38: 92.1(4) O24-U4-O38: 88.3(4)
O40-U4-O38: 79.9(4) O22-U4-O15: 89.5(4) O24-U4-O15: 91.3(4)
O40-U4-O15: 157.6(3) O38-U4-O15: 77.7(3) O22-U4-O26: 89.2(4)
O24-U4-O26: 90.1(4) O40-U4-O26: 75.7(3) O38-U4-O26: 155.6(3)
O15-U4-O26: 126.7(3) O22-U4-O33: 91.0(4) O24-U4-O33: 89.0(4)
O40-U4-O33: 131.9(3) O38-U4-O33: 148.0(4) O15-U4-O33: 70.5(3)
O26-U4-O33: 56.2(3) O14-U5-O11: 178.9(4) O14-U5-O23: 95.7(4)
O11-U5-O23: 85.1(4) O14-U5-O35: 86.9(4)$_1 O11-U5-O35: 92.6(4))$_1
O23-U5-O35: 78.4(3)$_1 O14-U5-O17: 88.7(4) O11-U5-O17: 92.2(4)
O23-U5-O17: 77.9(3) O35-U5-O17: 155.4(3)$_1 O14-U5-O27: 91.7(3)
O11-U5-O27: 87.2(3) O23-U5-O27: 150.0(3) O35-U5-O27: 73.0(3)$_1
O17-U5-O27: 131.4(3) O14-U5-O31: 90.5(4) O11-U5-O31: 89.1(4)
O23-U5-O31: 151.5(3) O35-U5-O31: 129.8(3)$_1 O17-U5-O31: 74.4(3)
O27-U5-O31: 57.0(3)

$_1 = x, y, z; $_2 = -x+1/2, -y, z+1/2, $_3 = '-x, y+1/2, -z+1/2, $_4 = x+1/2, -y+1/2, -z

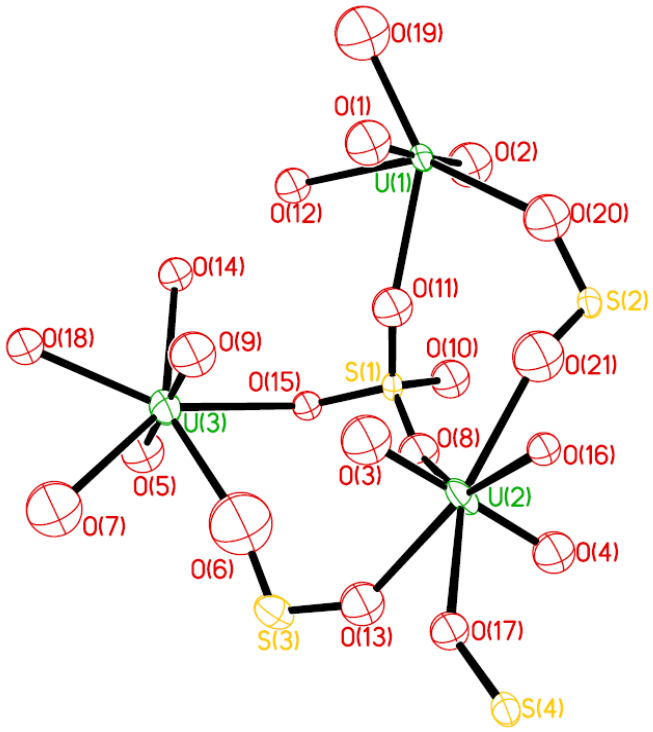

Fig S4. Asymmetric unit of **2** without ammonium cation (thermal ellipsoids at 50 % probability).

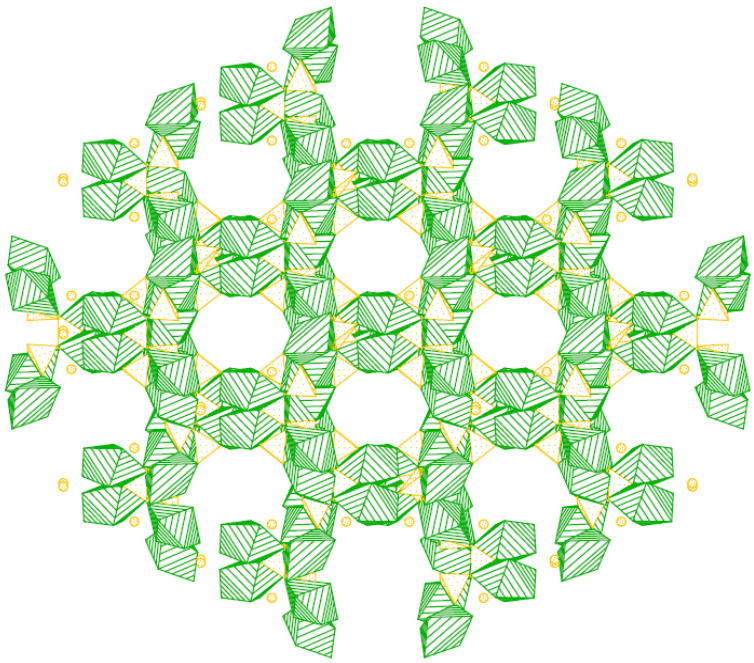

Fig S5. View of **2** along the ‘c’ axis.

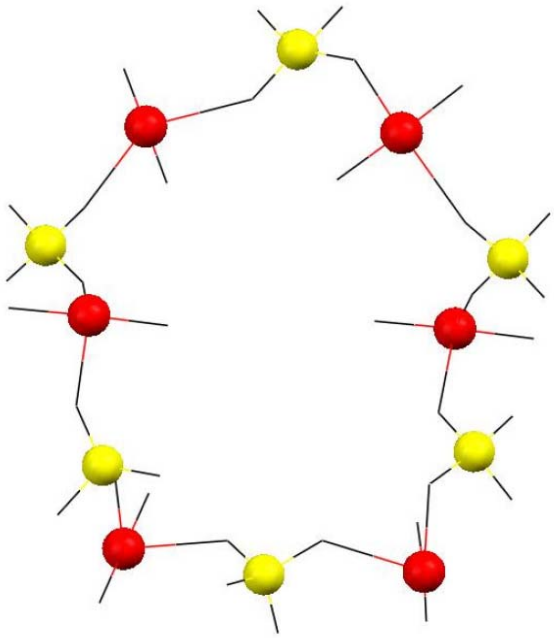

Fig S6. Ball and stick representation of 20 membered ring observed in **2** (red = UO_2 and yellow = SO_2) generated with the help of Mercury (CCDC).

Table S2. Selected bond distances (Å) and angles (^{0}) for **2**.

U1-O1:	1.67(2)	U1-O2:	1.67(2)	U1-O19:	2.27(2)
U1-O12:	.351(17)	U1-O20:	2.371(17)	U1-O11:	.379(17)
U1-O10:	2.379(17)$_5	U2-O4:	1.721(18)	U2-O3:	1.75(2)
U2-O21:	2.37(2)	U2-O17:	2.375(14)	U2-O13:	2.377(19)
U2-O16:	2.392(14)	U2-O8:	2.427(16)	U3-O5:	1.79(2)
U3-O9:	1.81(2)	U3-O18:	2.340(15)	U3-O6:	2.368(19)
U3-O15:	2.416(15)	U3-O14:	2.426(17)	U3-O7:	2.526(19)
S1-O8:	1.421(16)	S1-O1:1	1.458(19)	S1-O15:	1.466(16)
S1-O10:	1.505(17)	S2-O21:	1.44(2)	S2-O20:	1.449(19)
S2-O19:	1.48(2)$_5	S2-O16:	1.485(15)$_2	S3-O6:	1.42(2)$_1
S3-O6:	1.42(2)	S3-O13:	1.446(18)	S3-O13:	1.446(18)$_1
S4-O17:	1.461(16)	S4-O12:	1.479(17)$_3	S4-O14:	1.486(19)$_3

S4-O18:	1.516(17)$_4	O10-U1:	2.379(17)$_5	O12-S4:	1.479(17)$_3
O14-S4:	1.486(19)$_3	O16-S2:	1.485(15)$_2	O18-S4:	1.516(17)$_4
O19-S2:	1.48(2)$_5				

O1-U1-O2: 177.6(11)	O1-U1-O19: 85.4(11)	O2-U1-O19: 92.4(10)
O1-U1-O12: 92.4(7)	O2-U1-O12: 87.8(8)	O19-U1-O12: 72.0(6)
O1-U1-O20: 90.2(9)	O2-U1-O20: 90.9(8)	O19-U1-O20: 140.8(7)
O12-U1-O20: 147.2(6)	O1-U1-O11: 86.0(9)	O2-U1-O11: 96.3(8)
O19-U1-O11: 144.7(7)	O12-U1-O11: 74.3(6)	O20-U1-O11: 73.3(6)
O1-U1-O10: 87.6(8)$_5	O2-U1-O10: 90.8(8)$_5	O19-U1-O10: 71.7(6)$_5
O12-U1-O10: 143.6(5)$_5	O20-U1-O10: 69.2(6)$_5	O11-U1-O10: 141.9(6)$_5
O4-U2-O3: 177.3(9)	O4-U2-O21: 90.7(9)	O3-U2-O21: 91.9(9)
O4-U2-O17: 86.3(7)	O3-U2-O17: 91.1(8)	O21-U2-O17: 143.8(6)
O4-U2-O13: 88.5(8)	O3-U2-O13: 89.9(8)	O21-U2-O13: 143.6(6)
O17-U2- O13: 72.5(6)	O4-U2-O16: 96.8(7)	O3-U2-O16: 83.3(8)
O21-U2-O16: 70.9(5)	O17-U2-O16: 73.6(5)	O13-U2-O16: 145.3(5)
O4-U2-O8: 88.2(7)	O3-U2-O8: 93.3(8)	O21-U2-O8: 75.1(6)
O17-U2-O8: 140.7(6)	O13-U2-O8: 68.5(6)	O16-U2-O8: 145.7(6)
O5-U3-O9: 174.7(11)	O5-U3-O18: 92.1(7)	O9-U3-O18: 87.7(8)
O5-U3-O6: 101.2(13)	O9-U3-O6: 82.6(12)	O18-U3-O6: 134.3(7)
O5-U3-O15: 84.2(7)	O9-U3-O15: 93.4(7)	O18-U3-O15: 151.4(5)
O6-U3-O15: 74.1(7)	O5-U3-O14: 86.3(9)	O9-U3-O14: 88.5(8)
O18-U3-O14: 74.9(5)	O6-U3-O14: 148.7(7)	O15-U3-O14: 76.5(5)
O5-U3-O7: 88.8(10)	O9-U3-O7: 96.0(9)	O18-U3-O7: 67.0(6)

$_1: -x, y, -z+1/2; $_2 = x, -y, -z; $_3 = x+1/2, y+1/2, z; $_4 = -x+1/2, y+1/2, -z+1/2;

$_5 = x+1/2, -y+1/2, -z

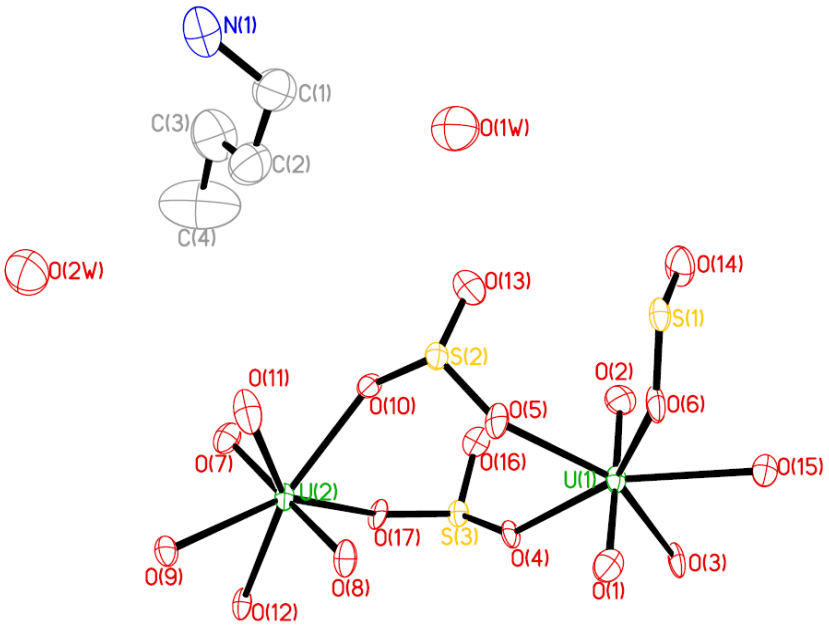

Fig S7. Asymmetric unit of **3** with thermal ellipsoids at 50 % probability.

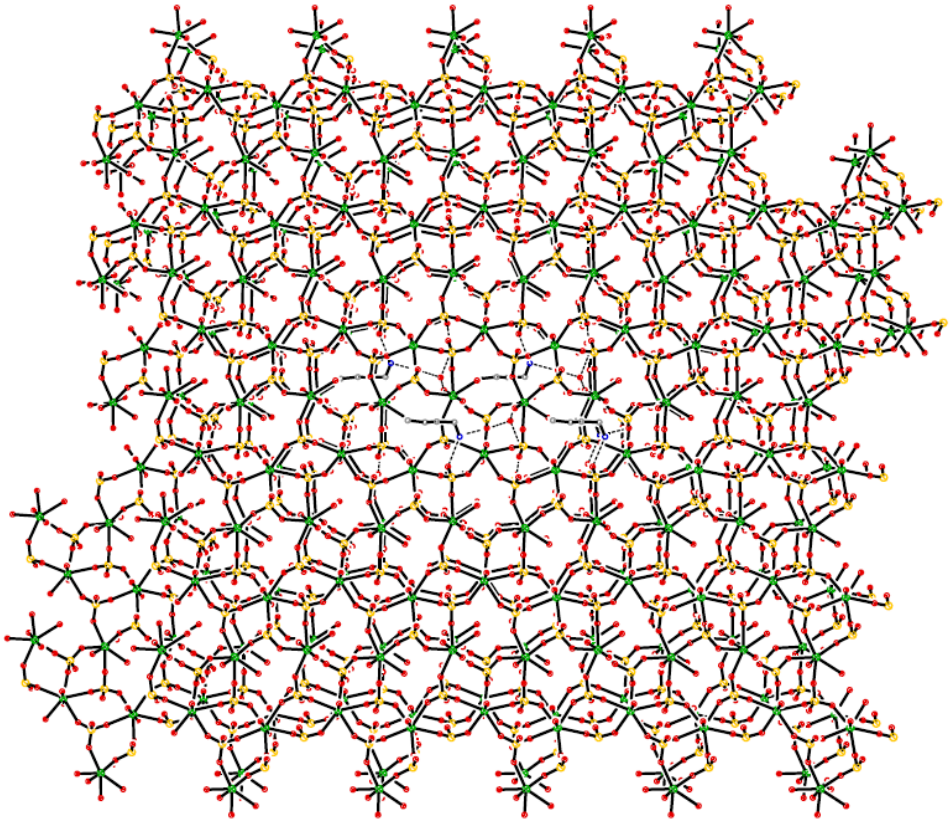

Fig S8. View of **3** along the 'c' axis.

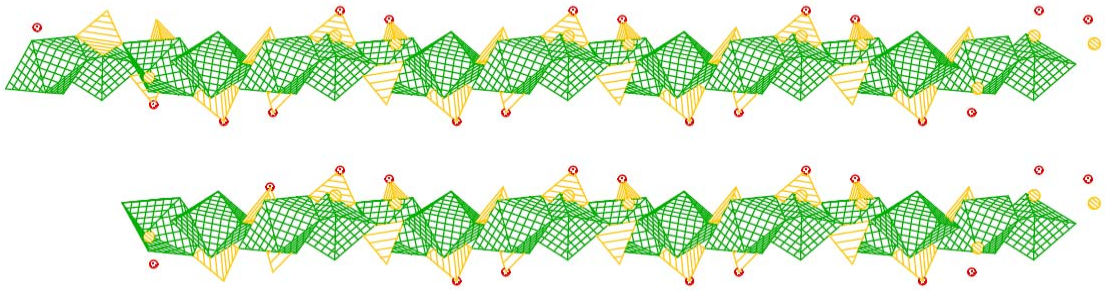

Fig S9. Polyehedra view of **3** along the 'b' axis.

Table S3. Selected bond distances (Å) and angles (^{0}) for **3**.

U1-O2:	1.757(8)	U1-O1:	1.758(8)	U1-O5:	2.353(7)
U1-O3:	2.369(7)	U1-O6:	2.381(7)	U1-O4:	2.416(7)
U1-O15:	2.453(8)	U2-O8:	1.753(7)	U2-O7:	1.778(7)
U2-O10:	2.377(7)	U2-O9:	2.377(6)	U2-O17:	2.389(7)
U2-O12:	2.418(7)	U2-O11:	2.455(8)	S1-O14:	1.445(8)
S1-O6:	1.460(8)	S1-O3:	1.482(8)$_2	S1-O9:	1.485(7)$_3
S2-O13:	1.438(8)	S2-O5:	1.467(8)	S2-O10:	1.478(7)
S2-O12:	1.509(7)$_3	S3-O16:	1.452(9)	S3-O15:	1.466(8)$_1
S3-O4:	1.481(7)	S3-O17:	1.499(7)	O3-S1:	1.482(8)$_1

O2-U1-O1: 178.1(4)	O2-U1-O5: 87.9(3)	O1-U1-O5: 91.5(3)
O2-U1-O3: 91.9(3)	O1-U1-O3: 87.8(3)	O5-U1-O3: 150.7(3)
O2-U1-O6: 95.7(3)	O1-U1-O6: 85.8(3)	O5-U1-O6: 71.5(2)
O3-U1-O6: 137.5(3)	O2-U1-O4: 91.6(3)	O1-U1-O4: 86.6(3)
O5-U1-O4: 75.7(3)	O3-U1-O4: 75.0(2)	O6-U1-O4: 146.1(3)
O2-U1-O15: 86.6(3)	O1-U1-O15: 95.0(3)	O5-U1-O15: 140.2(2)
O3-U1-O15: 68.9(2)	O6-U1-O15: 69.9(3)	O4-U1-O15: 143.7(2)
O8-U2-O7: 179.6(4)	O8-U2-O10: 93.5(3)	O7-U2-O10: 86.1(3)

O8-U2-O9: 88.4(3)	O7-U2-O9: 92.0(3)	O10-U2-O9: 137.3(2)
O8-U2-O17: 87.1(3)	O7-U2-O17: 92.6(3)	O10-U2-O17: 75.9(2)
O9-U2-O17: 146.7(2)	O8-U2-O12: 92.9(3)	O7-U2-O12: 87.4(3)
O10-U2-O12: 148.4(2)	O9-U2-O12: 73.8(2)	O17-U2-O12: 73.5(2)
O8-U2-O11: 89.6(3)	O7-U2-O11: 90.4(3)	O10-U2-O11: 67.9(3)

$_1 = -x+2, y-1/2, -z; $_2 = -x+2, y+1/2, -z; $_3 = -x+2, y+1/2, -z+1; $_4 = -x+2, y-1/2, -z+1

Table S4. Hydrogen bonding observed in **1** – **3**.

D-H—A	d(D-H) Å	d(H--A) Å	<DHA °
	1		
N1-H1--O26	0.77	2.910(14)	168.4
N2-H2--O47	0.77	2.834(14)	157.3
N4-H4--O12	0.77	2.918(14)	170.8
N5-H5--O28	0.77	2.872(14)	172.0
N6-H6--O27	0.77	2.832(13)	162.9
N7-H7--O43	0.77	2.939(15)	158.9
N8-H8--O20	0.77	2.949(14)	151.2
N8-H8--O21	0.77	3.010(12)	128.1
	2		
N1-H1--O3	0.77	2.88(13)	137.8
	3		
N1-H1--O16	0.77	2.889(14)	161.2

References

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2. G. M. Sheldrick, *SADABS-An empirical absorption correction program; Bruker Analytical X-ray Systems* Madison, WI, 1996.