

Electronic Supporting Information

The Exploration of Supramolecular Interactions Stemming from the $[\text{UO}_2(\text{NCS})_4(\text{H}_2\text{O})]^{2-}$ Tecton and Substituted Pyridinium Cations

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Synthesis of Compounds 1-8

$(\text{C}_5\text{H}_5\text{NCl})_2[\text{UO}_2(\text{NCS})_4(\text{H}_2\text{O})]$ (1)

Compound **1** was prepared by dissolving uranyl acetate dihydrate (0.18mmol) and potassium thiocyanate (2.12mmol) in 5mL of water in a glass scintillation vial. The clear bright yellow solution was stirred as 4-chloropyridine · HCl (0.35mmol) and diluted hydrochloric acid were added to reach a pH of 1.40. The resulting clear bright yellow solution was left to evaporate at room temperature to the open atmosphere. Yellow crystalline material formed after several weeks and was harvested. X-ray quality crystals of **1** were obtained by crushing the bulk product to obtain crystalline shards suitable for diffraction.

$(\text{C}_5\text{H}_5\text{NBr})_2[\text{UO}_2(\text{NCS})_4(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (2) *

Compound **2** was prepared by dissolving uranyl acetate dihydrate (0.24mmol) and potassium thiocyanate (1.41mmol) in 5mL of water in a glass scintillation vial. The clear bright yellow solution was stirred and gently heated as 4-bromopyridine · HCl (0.47mmol) and (2M) hydrobromic acid were added to reach a pH of 1.00. The resulting clear bright yellow solution was removed from the heat and allowed to evaporate at room temperature to the open atmosphere. After three weeks an orange crystalline material formed and was harvest from solution. X-ray quality crystals of **2** were obtained by crushing the bulk product to obtain crystalline shards suitable for diffraction

*Retarding the conversion of 4-bromopyridine to 4-thiocyanatopyridine was troublesome and thus **2** often cocrystallized with **4**. By limiting the quantity of water to 1-2mL the product distribution is favored to that of **2**.

(C₅H₅NI)₂[(UO₂(NCS)₄(H₂O)] · (H₂O) (3)

Compound **3** was prepared by dissolving uranyl acetate dihydrate (0.24mmol) and potassium thiocyanate (1.41mmol) in 6mL of water in a glass scintillation vial. The clear bright yellow solution was stirred and moderately heated as 4-iodopyridine (0.54mmol) and (2M) hydrochloric acid were added to reach a pH of 1.00. After several minutes of stirring and heating, the remaining clear yellow solution was slowly cooled and allowed to evaporate at room temperature to the open atmosphere. Clear colorless and clear orange crystals co-formed after several weeks and were harvested from solution. Orange single crystals suitable for diffraction were grown via rapid evaporation of the mother liquor on a plastic petri dish.

Note: **3** was also observed to form at pH values of 1.40 and 1.94.

(C₆H₅N₂S)₂[UO₂(NCS)₄(H₂O)] · 4(H₂O) (4)

Compound **4** was prepared by dissolving uranyl acetate dihydrate (0.24mmol) and potassium thiocyanate (1.24mmol) in 5mL of water in a glass scintillation vial. The solution was heated gently and stirred as 4-bromopyridine · HCl (0.48mmol) and dilute hydrochloric acid were added to reach a pH of 1.0. The resulting clear bright yellow solution was removed from the heat and left to evaporate at room temperature to the open atmosphere. Large bright orange crystals were harvested after several weeks from the solution. The large crystals were cut with a razor blade in order to obtain a smaller crystal suitable for diffraction.

(C₆H₈N)₂[UO₂(NCS)₄(H₂O)] (5)

Compound **5** was prepared by stirring uranyl nitrate hexahydrate (0.20mmol) and potassium thiocyanate (1.2mmol) in 5mL of acetone in a roundbottom flask. Upon dissolution of the potassium thiocyanate a white solid (KNO₃) precipitated and the resulting bright yellow solution was stirred overnight. The solution was decanted, transferred to a glass scintillation vial, stirred and heated to reduce the volume to near dryness. The resulting orange yellow solid and remaining liquid was removed from the heat and re-dissolved in 4mL of water. The solution was stirred as 4-picoline (0.40mmol) and dilute hydrochloric acid was added to reach a pH to 1.25. The clear bright yellow solution was allowed to evaporate at rt .to the open atmosphere. A yellow crystalline material formed after several weeks and was harvested. The bulk crystalline product was cut with a razor blade in order to obtain a smaller crystal suitable for X-ray diffraction.

(C₆H₈N)₂[UO₂(NCS)₄(H₂O)] (6)

Compound **6** was prepared by stirring uranyl nitrate hexahydrate (0.05mmol) and potassium thiocyanate (0.30mmol) in 7mL of acetone in a roundbottom flask. Upon dissolution of the potassium thiocyanate a white solid (KNO₃) precipitated and the resulting bright yellow solution was stirred overnight. The solution was decanted, transferred to a glass scintillation vial, stirred and heated to reduce the volume to near dryness. The remaining orange yellow solid and remaining liquid was removed from the heat and re-dissolved in 3mL of water. The solution was stirred as 4-picoline (0.10mmol) and dilute hydrochloric acid was added to reach a pH of 1.20. The clear bright yellow clear solution was allowed to evaporate at room temperature to the open atmosphere. A light yellow crystalline material formed after several weeks and was harvested. The bulk crystalline product had to be cut with a razor blade in order to obtain a smaller crystal suitable for X-ray diffraction.

(C₅H₇N₂)₂[UO₂(NCS)₄(H₂O)] (7)

Compound **7** was prepared by stirring uranyl nitrate hexahydrate (1.92mmol) and potassium thiocyanate (1.20mmol) in 5mL of acetone in a roundbottom flask. Upon dissolution of the potassium thiocyanate a white solid (KNO₃) precipitated and the resulting bright yellow solution was stirred overnight. The solution was decanted, transferred to a glass scintillation vial, stirred and heated to evaporate the solution to near dryness. The remaining orange yellow solid and liquid was removed from the heat and re-dissolved in 4mL of water. The clear yellow solution was stirred as 4-aminopyridine (0.44mmol) and dilute hydrochloric acid were added to reach a pH of 1.05. The solution was allowed to evaporate at room temperature to the open atmosphere. A yellow crystalline material formed after several days and was harvested. The crystalline material was cut into smaller pieces in order to obtain a shard suitable for X-ray diffraction.

(C₇H₁₁N₂)₂[UO₂(NCS)₄(H₂O)] (8)

Compound **8** was prepared by stirring uranyl nitrate hexahydrate (1.92mmol) and potassium thiocyanate (1.20mmol) in 5mL of acetone in a roundbottom flask. Upon dissolution of the potassium thiocyanate a white solid (KNO₃) precipitated and the resulting clear bright yellow solution was stirred overnight. The solution was decanted, transferred into a glass scintillation vial, stirred and heated to reduce the volume to near dryness. The remaining orange yellow solid and liquid was re-dissolved in 4mL of water. The solution was gently heated and stirred as 4-dimethylaminopyridine (0.40mmol) and dilute hydrochloric acid was added to reach a pH of 1.05. The solution was removed from the heat and allowed to evaporate at room temperature to the open atmosphere. A yellow crystalline material formed

after several days and was harvested. The bulk crystalline material was cut with a razor blade to obtain smaller crystals suitable for X-ray diffraction.

Additional Synthetic Notes

As previously noted in the accompanying manuscript, the synthetic conditions under which compound **6** was observed to form varied and often coincided with those of **5**. Provided below are several alternate conditions (from those listed above) that resulted in the synthesis of **6**.

Table 1: Selected synthetic conditions that led to the formation of compound **6**.

Result	6 *	6 *
UO₂(NO₃)₂ · 6H₂O	0.050g (0.099mmol)	0.100g (0.199mmol)
KSCN	0.060g (0.618mmol)	0.166g (1.71mmol)
4-Methylpyridine	0.020mL (0.205mmol)	0.041mL (0.422mmol)
H₂O	2.0mL	4.0mL
HCl (2M)	pH = 1.25	pH = 0.75

*Denotes that compound **5** has been synthesized using the same conditions.

Local Coordination Geometry of the Uranyl Isothiocyanate Tecton in Compound **8**

Table 2: Selected bond lengths and angles of the uranyl isothiocyanate tecton from **8**.

Bond	Length (Å)	Angle (°)
U(1)-N(1)	2.4347(16)	-
N(1)-C(1)	1.165(2)	-
C(1)-S(1)	1.6243(18)	-
N(1)-C(1)-S(1)	-	178.94(17)
U(1)-N(1)-C(1)	-	148.78(14)
U(1)-N(2)	2.4409(16)	-
N(2)-C(2)	1.165(2)	-
C(2)-S(2)	1.6305(19)	-
N(2)-C(2)-S(2)	-	178.78(18)
U(1)-N(2)-C(2)	-	171.35(15)

Additional Figures

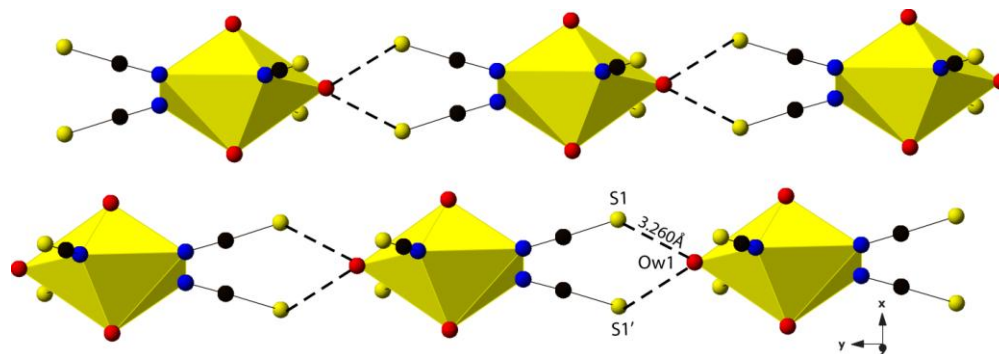


Figure 1: The anti-parallel chains of uranyl tectons in **1** that propagate along the [010] direction.

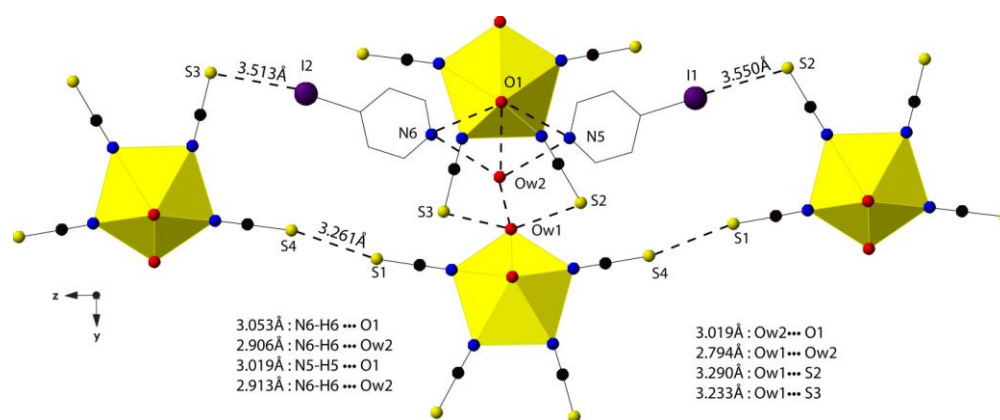


Figure 2: The supramolecular interactions of **3** are shown and viewed down the [100] direction. The iodine atoms are represented as purple spheres and the hydrogen atoms have been omitted for clarity.

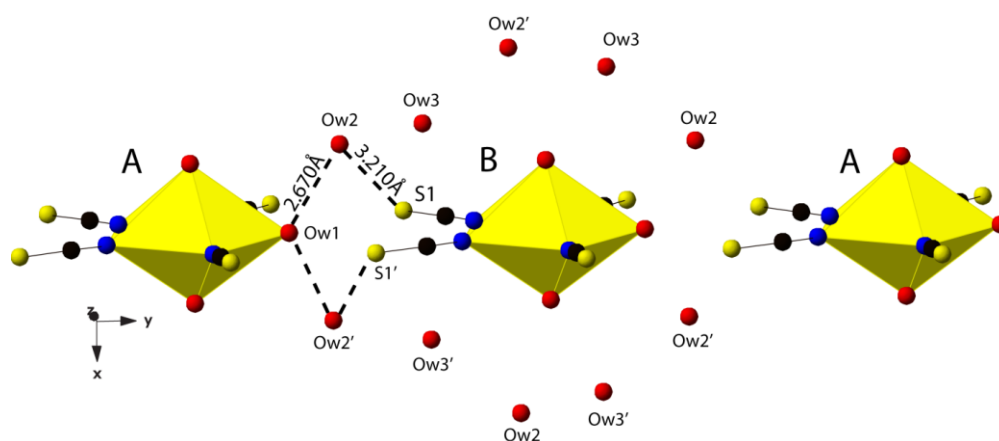


Figure 3: Compound **4**, viewed down the [001] direction, incorporates two solvent water molecules that form hydrogen bonds linking the uranyl tectons together to form a 1D chain. The hydration sphere is displayed around tecton **B** but has been omitted surround **A** for clarity. The hydrogen atoms have been omitted for clarity.

Compound 3RT

Table 3: Selected crystallographic data and structural information of 3RT

Compound	3RT
Empirical formula	C₁₄H₁₄I₂N₆O₄S₄U
Formula mass	950.45
Crystal system	Orthorhombic
a/Å	6.7452(4)
b/Å	15.1032(8)
c/Å	25.9377(14)
α /°	90.00
β /°	90.00
γ /°	90.00
Unit cell volume/Å ³	2642.4(3)
Temperature/K	293(2)
D _{calc} /g cm ⁻³	2.344
Space group	<i>Pbcm</i>
No. of formula units per unit cell, Z	4
Radiation type	Mo K α
Absorption coefficient, μ /mm ⁻¹	8.821
No. of reflections measured	26739
No. of independent reflections	3910
R _{int}	0.0612
Final R ₁ values ($I > 2\sigma(I)$)	0.0358
Final wR ₂ (F ²) values ($I > 2\sigma(I)$)	0.0648
Final R ₁ values (all data)	0.0720
Final wR ₂ (F ²) values (all data)	0.0752
Goodness of fit on F ²	1.001
CCDC number	967157

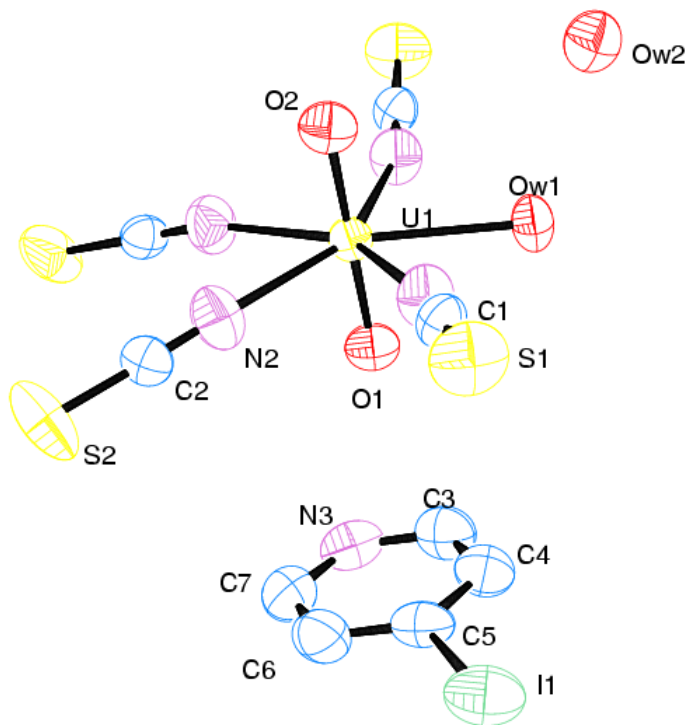


Figure 4: ORTEP illustration of **3RT**. Ellipsoids are shown at 50% probability level.

Thermal Ellipsoids Plots 1-8

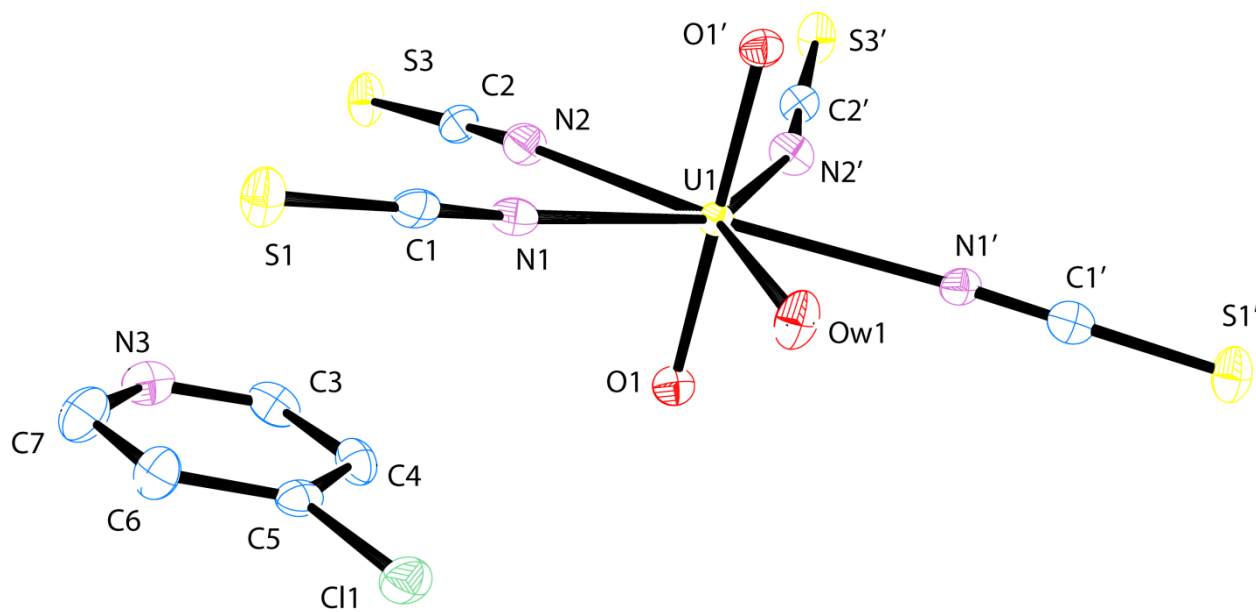


Figure 5: ORTEP illustration of **1**. Ellipsoids are shown at 50% probability level.

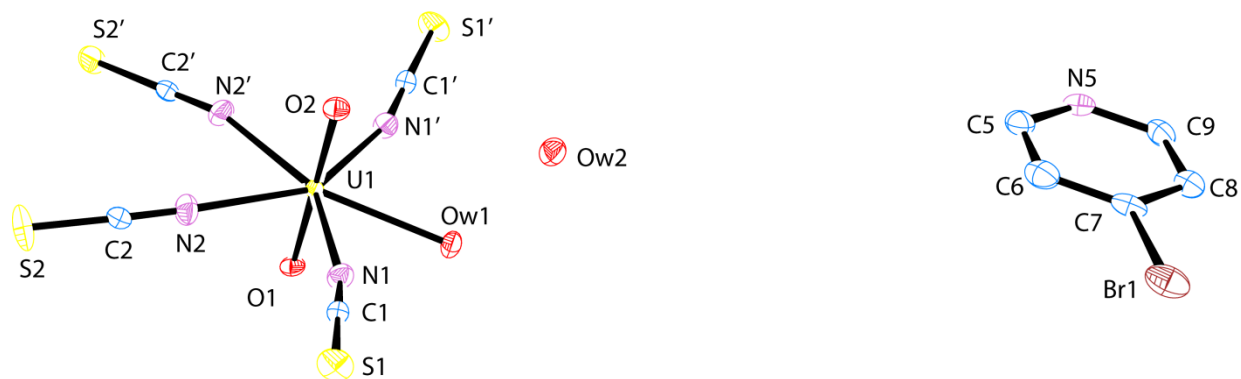


Figure 6: ORTEP illustration of 2. Ellipsoids are shown at 50% probability level.

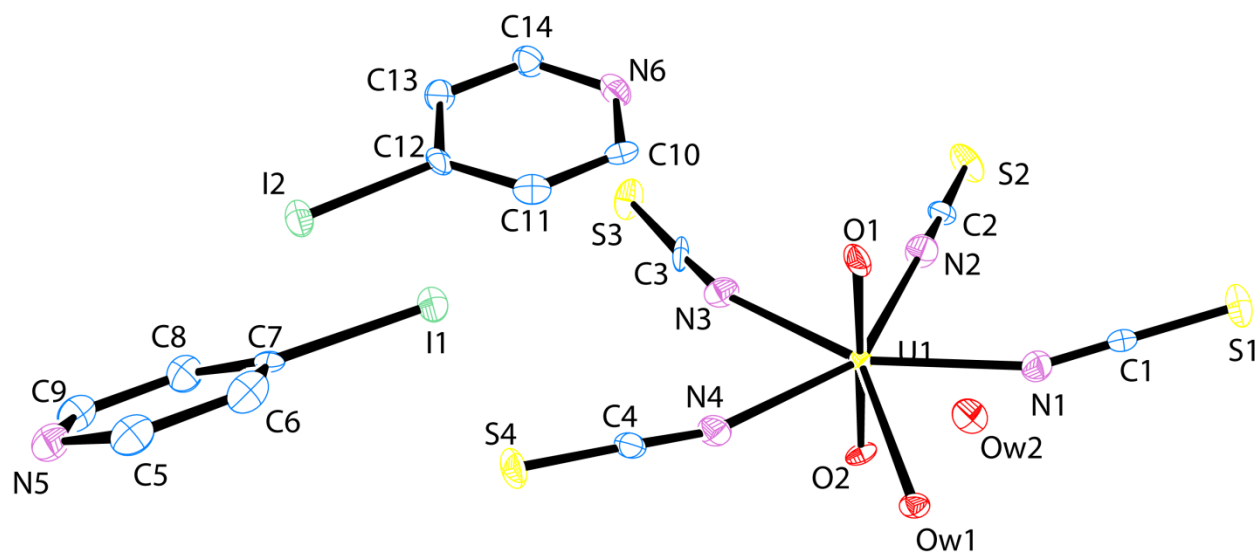


Figure 7: ORTEP illustration of 3. Ellipsoids are shown at 50% probability level.

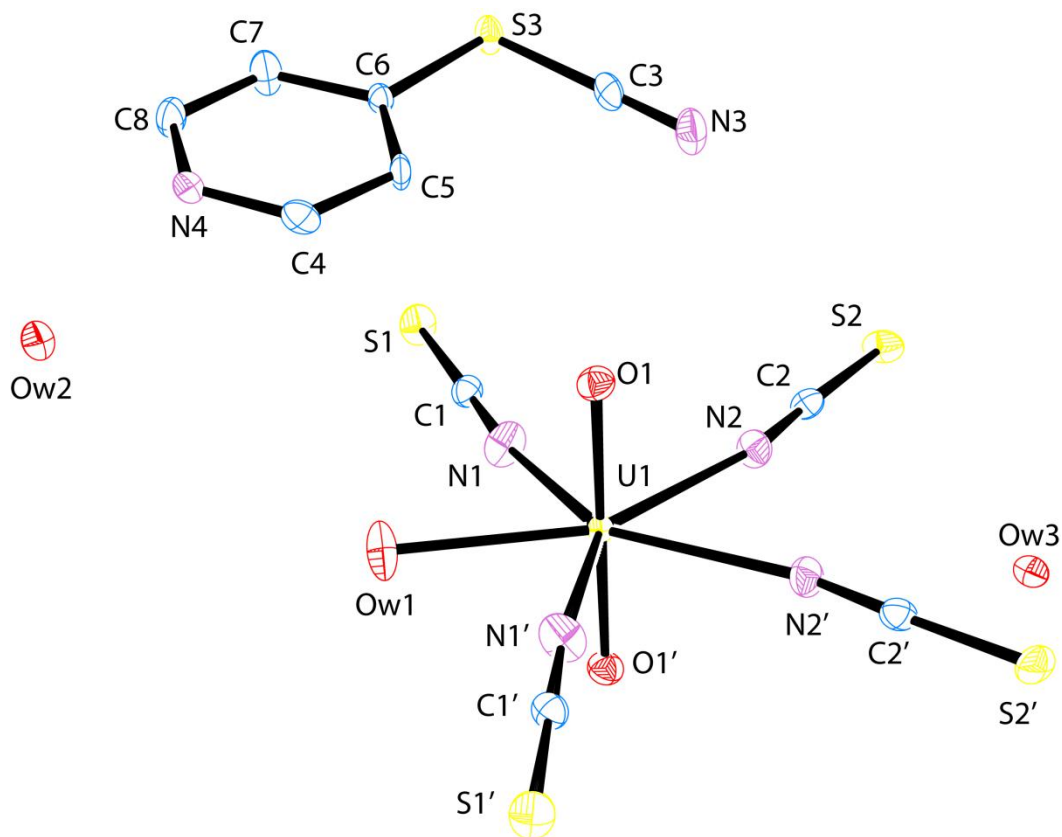


Figure 8: ORTEP illustration of 4. Ellipsoids are shown at 50% probability level.

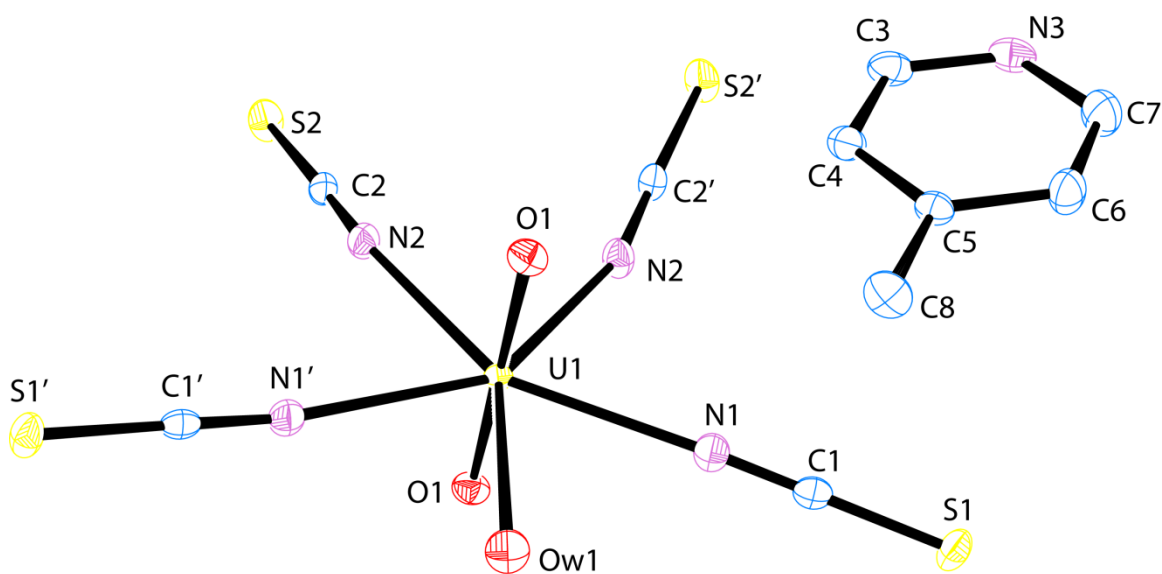


Figure 9: ORTEP illustration of 5. Ellipsoids are shown at 50% probability level.

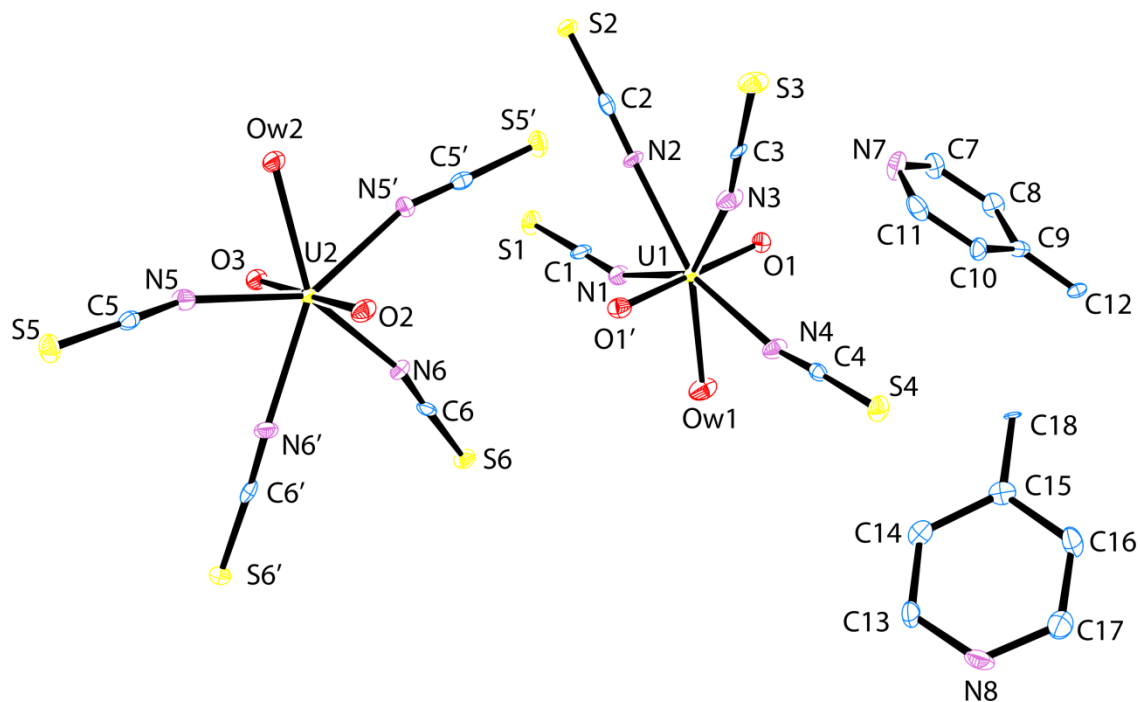


Figure 10: ORTEP illustration of 6. Ellipsoids are shown at 50% probability level.

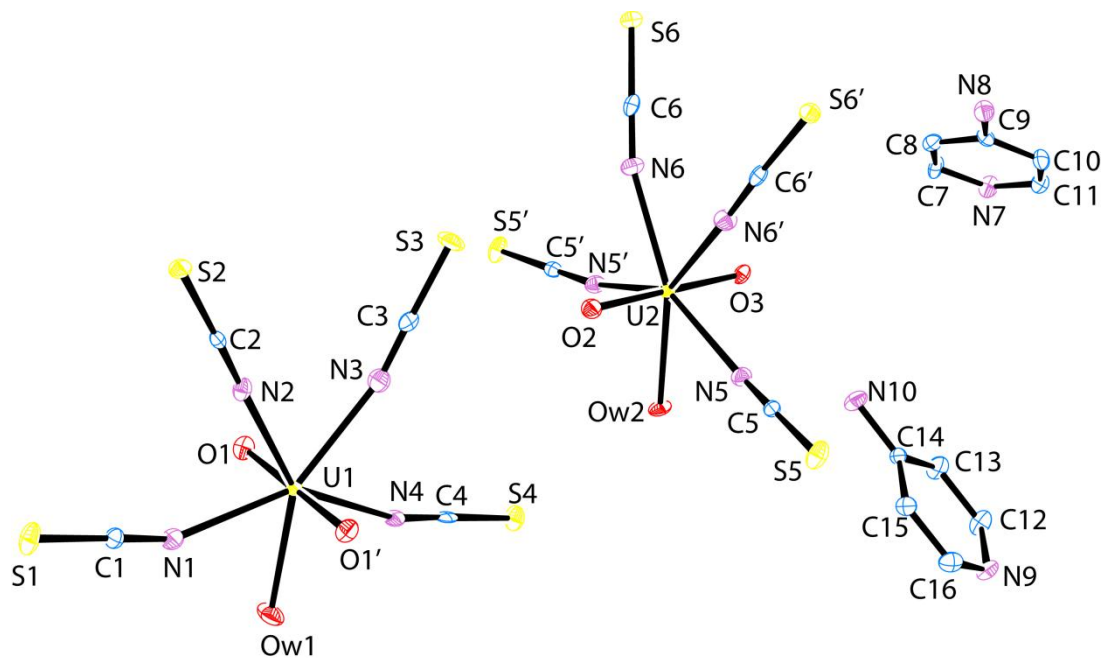


Figure 11: ORTEP illustration of 7. Ellipsoids are shown at 50% probability level.

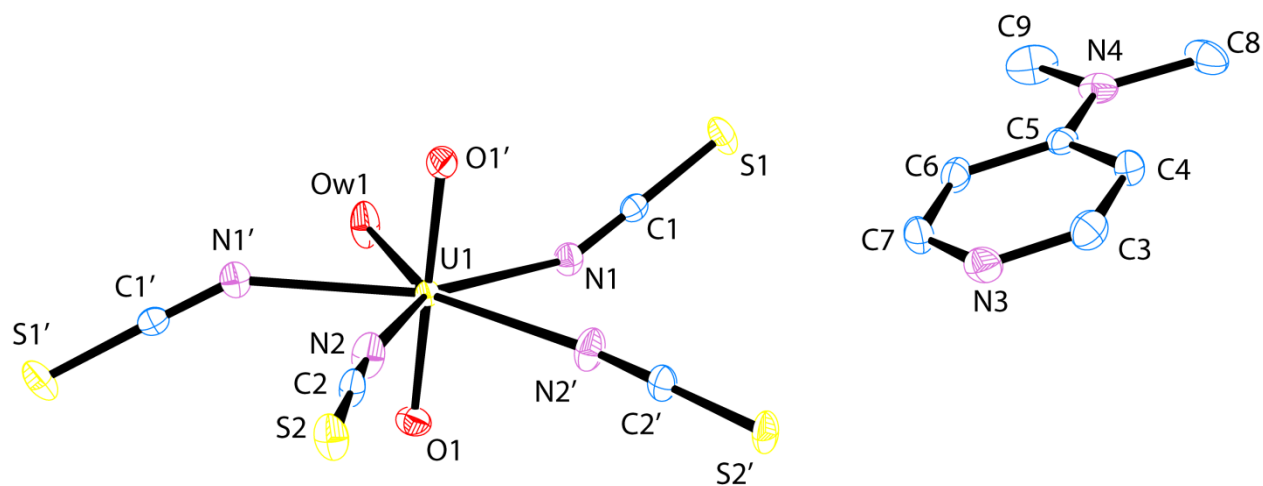


Figure 12: ORTEP illustration of **8**. Ellipsoids are shown at 50% probability level.