

## Supporting Information

### Experimental

**Synthesis. Caution!** *Whereas the uranium oxyacetate  $(\text{UO}_2)(\text{CH}_3\text{COO})_2 \cdot (\text{H}_2\text{O})_2$  used in this investigation contain depleted uranium, standard precautions for handling radioactive and toxic substances should be followed.*

**Materials.** The materials used in this study were purchased from Fischer Scientific at 96 % purity or higher and used as received.

#### **Synthesis of $[(\text{UO}_2\text{Cl}_4)(\text{C}_5\text{H}_5\text{NCl})_2]$ (**1**)**

Uranium oxyacetate (0.250 mg, 0.59 mmol, 1 equiv.) and 4-chloropyridine hydrochloride (177 mg, 1.18 mmol, 2 equiv.) were dissolved in distilled water (5 mL) to which conc. HCl (1.5 mL) was added. The mixture was sonicated to ensure complete dissolution of the reactants before being left to evaporate. Rod-shaped, yellow crystals suitable for single crystal X-ray analysis formed after several days.

#### **Synthesis of $[(\text{UO}_2\text{Cl}_4)(\text{C}_5\text{H}_5\text{NBr})_2]$ (**2**)**

Uranium oxyacetate (0.250 mg, 0.59 mmol, 1 equiv.) and 4-bromopyridine hydrochloride (229 mg, 1.18 mmol, 2 equiv.) were dissolved in distilled water (5 mL) to which conc. HCl (1.5 mL) was added. The mixture was sonicated to ensure complete dissolution of the reactants before being left to evaporate. Block-shaped yellow crystals of **2** were formed which were suitable for characterization by single-crystal XRD after several days

#### **Synthesis of $[(\text{UO}_2\text{Cl}_4)(\text{C}_5\text{H}_5\text{NI})_2]$ (**3**)**

Uranium oxyacetate (0.250 mg, 0.59 mmol, 1 equiv.) and 4-iodopyridine (242 mg, 1.18 mmol, 2 equiv.) were dissolved in distilled water (15 mL) to which conc. HCl (7.5 mL) was added. The mixture was sonicated to ensure complete dissolution of the reactants before being left to evaporate. Block-shaped yellow crystals of **3** were formed which were suitable for characterization by single-crystal XRD after several days

#### **Synthesis of $[(\text{UO}_2\text{Br}_4)(\text{C}_5\text{H}_5\text{NCl})_2]$ (**4**)**

Uranium oxyacetate (0.250 mg, 0.59 mmol, 1 equiv.) and 4-chloropyridine hydrochloride (177 mg, 1.18 mmol, 2 equiv.) were dissolved in distilled water (5 mL) to which conc. HBr (1.5 mL) was added. The mixture was sonicated to ensure complete dissolution of the reactants before being left to evaporate. Rod-shaped yellow crystals of **4** were formed which were suitable for characterization by single-crystal XRD after approximately a week.

#### **Synthesis of $[(\text{UO}_2\text{Br}_4)(\text{C}_5\text{H}_5\text{NBr})_2]$ (**5**)**

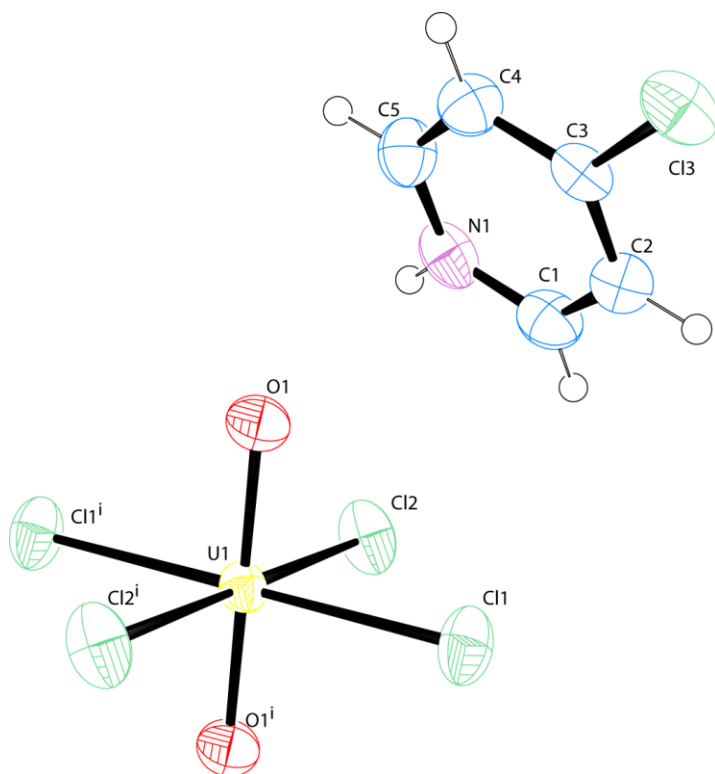
Uranium oxyacetate (0.250 mg, 0.59 mmol, 1 equiv.) and 4-bromopyridine hydrochloride (229 mg, 1.18 mmol, 2 equiv.) were dissolved in distilled water (5 mL) to which conc. HBr (1.5 mL) was added. The mixture was sonicated to ensure complete dissolution of the reactants before being left to evaporate. Rod-shaped yellow crystals of **5** were formed

which were suitable for characterization by single-crystal XRD after approximately a week.

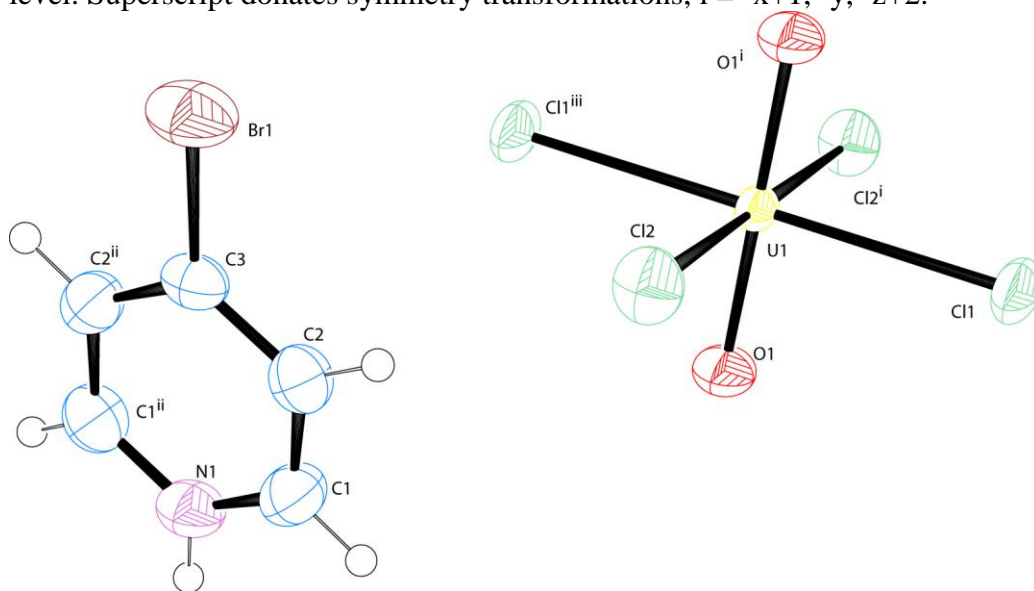
#### **Synthesis of $[(\text{UO}_2\text{Cl}_4)(\text{C}_5\text{H}_5\text{NI})_2]$ (**6**)**

Uranium oxyacetate (0.250 mg, 0.59 mmol, 1 equiv.) and 4-iodopyridine (242 mg, 1.18 mmol, 2 equiv.) were dissolved in distilled water (15 mL) to which conc. HBr (4.5 mL) was added. The mixture was sonicated to ensure complete dissolution of the reactants before being left to evaporate. Block-shaped yellow crystals of **6** were formed which were suitable for characterization by single-crystal XRD formed after approximately a week.

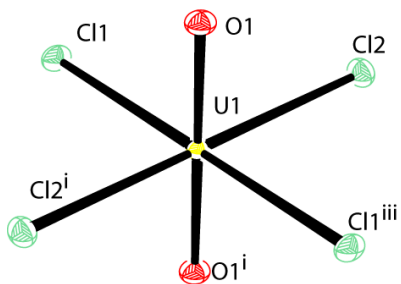
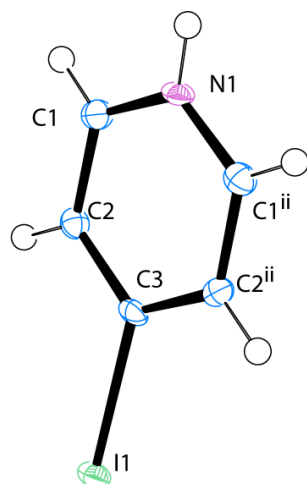
**X-ray Structure Determination.** A single crystal from each of the samples was isolated from the bulk and mounted on a MiTeGen micromount. Reflections were collected using a Bruker SMART diffractometer equipped with an APEX II CCD detector using Mo K  $\alpha$  radiation and a combination of  $0.5^\circ$   $\omega$  and  $\phi$  scans. The data were integrated with the *SAINTE* software package. The data were corrected for absorption using *SADABS*. All structures were solved using direct methods using *SIR92* and refined using *SHELXL-97*, (both within the *WinGX* software suite), and figures were made using *CrystalMaker*. Satisfactory refinements for all compounds as well as tests for missing symmetry, using *Platon*, indicated that no obvious space group changes were needed or suggested. All non-hydrogen atoms were located using difference Fourier maps and ultimately all non-hydrogen atoms were refined anisotropically. Hydrogen atoms residing on the carbon and nitrogen atoms of the aromatic rings were placed in calculated positions and bond distances were fixed at 0.97 Å.



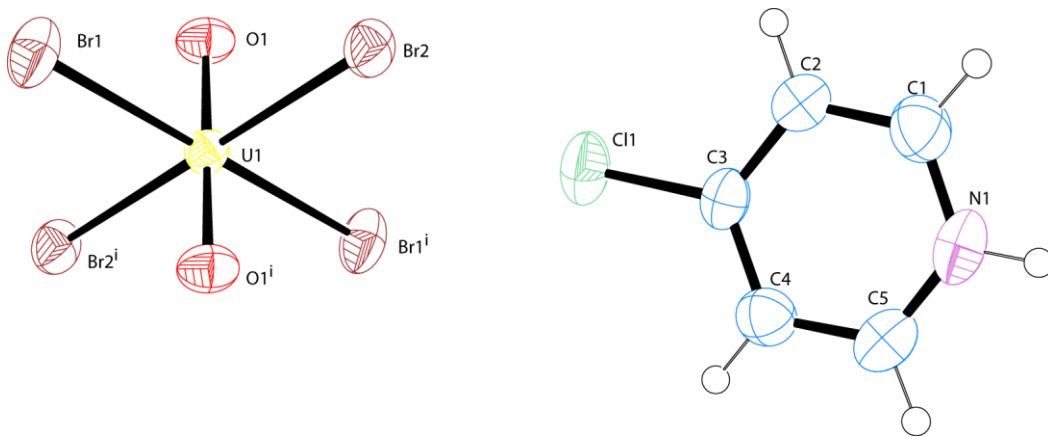
**Figure S1.** ORTEP illustration of Compound **1**. Ellipsoids shown at 50 % probability level. Superscript donates symmetry transformations,  $i = -x+1, -y, -z+2$ .



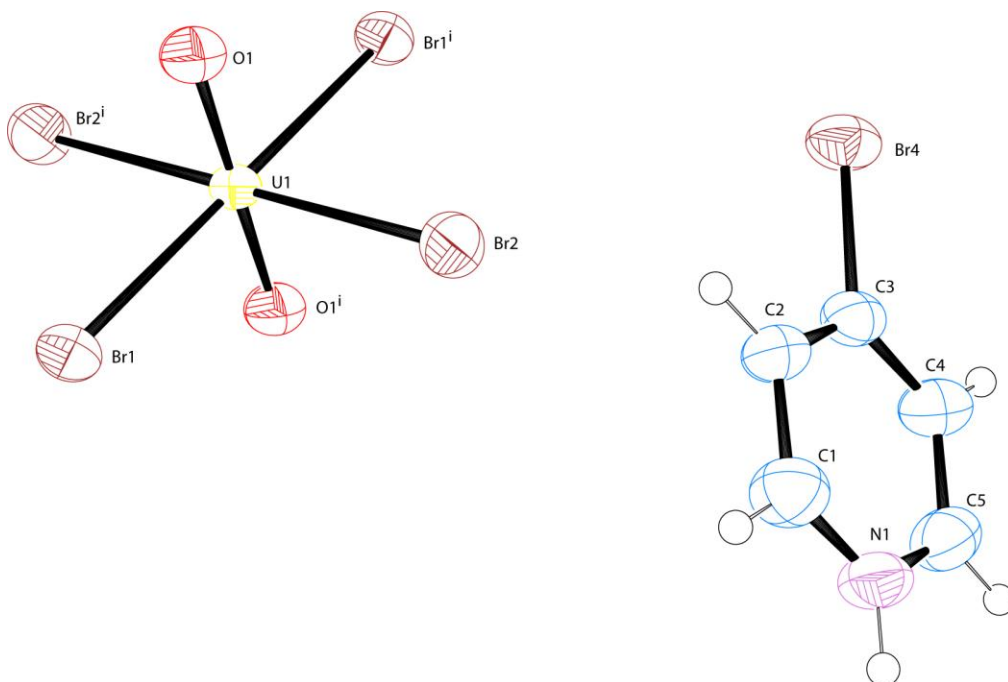
**Figure S2.** ORTEP illustration Compound **2**. Ellipsoids shown at 50 % probability level. Superscript donates symmetry transformations,  $i = -x+1, y, z$ ;  $ii = x, -y+2, z$ ;  $iii = x, -y+1, z$ .



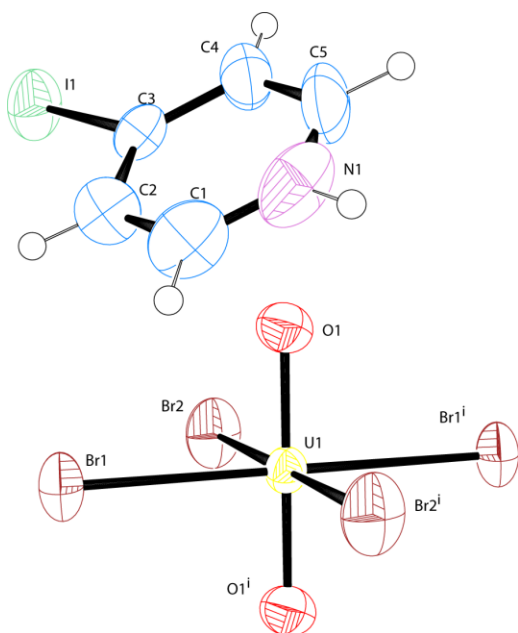
**Figure S3.** ORTEP illustration Compound 3. Ellipsoids shown at 50 % probability level. Superscript donates symmetry transformations,  $i = -x+1, y, -z$ ;  $ii = x, y+1/2, z$ ;  $iii = x, -y+1, z$ .



**Figure S4.** ORTEP illustration Compound 4. Ellipsoids shown at 50 % probability level. Superscript donates symmetry transformations,  $i = -x+1, -y+1, -z+2$



**Figure S5.** ORTEP illustration Compound 5. Ellipsoids shown at 50 % probability level. Superscript donates symmetry transformations,  $i = -x+1, -y+1, -z$



**Figure S6.** ORTEP illustration Compound 6. Ellipsoids shown at 50 % probability level. Superscript donates symmetry transformations,  $i = -x+1, -y+1, -z+1$