

## Uranyl-Tc(VII)/Tc(V) hybrid clusters

<sup>a</sup>Mohammad Shohel and <sup>a</sup>May Nyman\*

<sup>a</sup>Department of Chemistry, Oregon State University, Corvallis, Oregon 97331, USA

\*Corresponding author: may.nyman@oregonstate.edu

### 1. Synthetic procedure

*Caution!! Radioactive materials were used for synthesis, which contained <sup>99</sup>Tc (β-emitter) and <sup>238</sup>U (α-emitter). The experiments in this study were conducted by trained personnel in a licensed research facility with special precautions taken towards the handling, monitoring, and disposal of radioactive materials.*

Chemicals used in the synthesis,  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (SPI), 30%  $\text{H}_2\text{O}_2$  (Macron Chemicals), and  $\text{HReO}_4$  (Sigma-Aldrich) were used as received. The  $\text{NH}_4\text{TcO}_4$  was obtained from Oakridge National Lab. Solutions utilized in this study were prepared by using deionized water ( $18.2 \text{ M}\Omega \cdot \text{cm}$ ).  $\text{HTcO}_4$  was prepared by our previously published method<sup>1</sup>. In a typical synthesis, the as received  $\text{NH}_4\text{TcO}_4$  was added to water and then reflux until boil. Then 30%  $\text{H}_2\text{O}_2$  added dropwise in the boiling mixture to convert  $\text{TcO}_2$  impurities into  $\text{TcO}_4^-$ . The resulting clear 0.5M  $\text{NH}_4\text{TcO}_4$  solution was cooled down and then passed through a Dowex™ 50WX8-100 cation exchange resin.

#### 1.1 Synthesis of $\text{U}_5\text{Re}_2 [(\text{UO}_2)_5(\text{O})_2(\text{OH})_2(\text{H}_2\text{O})_6(\text{ReO}_4)_2(\text{CH}_3\text{COO})_2]$ and $\text{U}_4\text{Re}_2 [(\text{UO}_2)_4(\text{O})_2(\text{H}_2\text{O})_2(\text{ReO}_4)_2(\text{CH}_3\text{COO})_4\text{Na}_2(\text{H}_2\text{O})_2]$

0.12 M uranyl acetate solution (400  $\mu\text{L}$ , 48  $\mu\text{mol}$ ) was combined with 0.12 M perrhenic acid solution (200  $\mu\text{L}$ , 24  $\mu\text{mol}$ ) in a 4 mL glass scintillation vial. The solution was evaporated at 30 °C inside a fume hood. After 7 days when the solution has evaporated down to less than 80% of its initial volume, blocky orange colored crystals of  $\text{U}_5\text{Re}_2$  started to appear. After evaporating this solution for additional 3 days, thin light yellow plate-shaped crystals of  $\text{U}_4\text{Re}_2$  can be observed at the bottom of vial sticking to the glass surface under the  $\text{U}_5\text{Re}_2$  crystals. The percent yield of bulk crystalline material was 80% based on uranium. The yield of  $\text{U}_4\text{Re}_2$  appears to be very low compared to  $\text{U}_5\text{Re}_2$  because of less amount of  $\text{Na}^+$  in reaction solution but part of crystal structure and coming from impurities/leaching glass. The yield of  $\text{U}_4\text{Re}_2$  can be increased by addition of 0.12 M sodium acetate (100  $\mu\text{L}$ , 12  $\mu\text{mol}$ ) in the initial uranyl acetate and perrhenic acid solution.

#### 1.2 Synthesis of $\text{U}_5\text{Tc}_2 [(\text{UO}_2)_5(\text{O})_2(\text{OH})_2(\text{H}_2\text{O})_6(\text{TcO}_4)_2(\text{CH}_3\text{COO})_2]$ , $\text{U}_4\text{Tc}_2 [(\text{UO}_2)_4(\text{O})_2(\text{H}_2\text{O})_2(\text{TcO}_4)_2(\text{CH}_3\text{COO})_4\text{Na}_2(\text{H}_2\text{O})_2]$ and $\text{U}_4\text{Tc} [(\text{UO}_2)_4(\text{TcO})(\text{O})_4(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_4 \cdot \text{H}_3\text{O} \cdot \text{H}_2\text{O}]$

0.12 M uranyl acetate solution (200  $\mu$ L, 24  $\mu$ mol) was combined with 0.12 M pertechnetic acid solution (100  $\mu$ L, 12  $\mu$ mol) in a 4 mL glass scintillation vial. The solution was evaporated at 30 °C inside fume hood. After 7 days when the solution had evaporated down to less than 90% of its initial volume, blocky orange colored crystals of **U<sub>5</sub>Tc<sub>2</sub>** started to appear along with dark yellow elongated plate crystals of **U<sub>4</sub>Tc**. After evaporating this solution for additional 3 days, thin light yellow colored plate shaped crystals of **U<sub>4</sub>Tc<sub>2</sub>** can be observed at the bottom of vial under **U<sub>5</sub>Tc<sub>2</sub>** crystals. The yields of the crystalline material was not measured to avoid radioactive contamination. Similar to **U<sub>4</sub>Re<sub>2</sub>**, the yield of **U<sub>4</sub>Tc<sub>2</sub>** appears to be very low compared to **U<sub>5</sub>Tc<sub>2</sub>** and **U<sub>4</sub>Tc**. The yield of **U<sub>4</sub>Re<sub>2</sub>** can be improved by addition of 0.12 M sodium acetate (50  $\mu$ L, 6  $\mu$ mol) in the initial uranyl acetate and pertechnetic acid solution.

## 2. Single Crystal X-ray diffraction (SCXRD)

Single Crystal X-ray diffraction experiments were conducted using a Rigaku Oxford Synergy system equipped with PhotonJet Cu source ( $\lambda=1.54178$  Å) and hyPix-6000HE photon counting detector. The data was collected at 150K/223K and then processed with CrysAlisPro Version 171.40.64.53 (Rigaku Oxford Diffraction, 2018)<sup>2</sup>. Analytical absorption and empirical absorption (spherical harmonic, image scaling, detector scaling) corrections were applied after integrating all frames<sup>3</sup>. All structures were solved by Intrinsic Phasing method from SHELXT<sup>4</sup> program, developed by successive difference Fourier syntheses, and refined by full-matrix least square on all F<sup>2</sup> data using SHELX<sup>5</sup> via OLEX2 interface<sup>6</sup>. The crystals of **U<sub>4</sub>Re<sub>2</sub>** and **U<sub>4</sub>Tc<sub>2</sub>** exhibited non-merohedral twinning. OLEX2 was used to find the twin law and write hkl5 file for the structural refinement. The selected crystallographic information for the isolated structures are in **Table S1**. The crystallographic information files of the refined structures can be requested with their deposition number **2332264-2332268** in the Cambridge crystallographic data center website <https://www.ccdc.cam.ac.uk/structures/>.

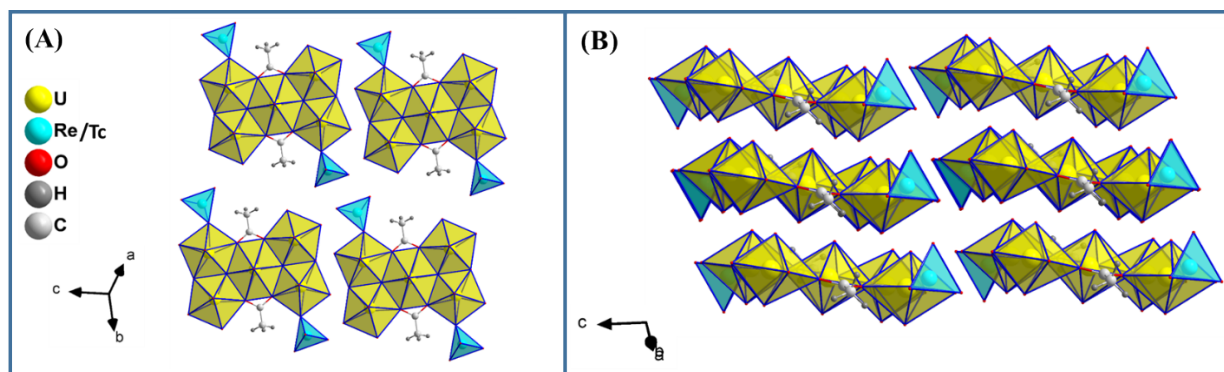
**Table S1.** Selected crystallographic information for the isolated structures.

	<b>U<sub>5</sub>Re<sub>2</sub></b>	<b>U<sub>4</sub>Re<sub>2</sub></b>	<b>U<sub>5</sub>Tc<sub>2</sub></b>	<b>U<sub>4</sub>Tc<sub>2</sub></b>
Empirical formula	C <sub>4</sub> H <sub>18</sub> O <sub>32</sub> Re <sub>2</sub> U <sub>5</sub>	C <sub>8</sub> H <sub>12</sub> Na <sub>2</sub> O <sub>30</sub> Re <sub>2</sub> U <sub>4</sub>	C <sub>4</sub> H <sub>6</sub> O <sub>32</sub> Tc <sub>2</sub> U <sub>5</sub>	C <sub>8</sub> H <sub>12</sub> Na <sub>2</sub> O <sub>30</sub> Tc <sub>2</sub> U <sub>4</sub>
Moiety formula	(UO <sub>2</sub> ) <sub>5</sub> (O) <sub>2</sub> (OH) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> (ReO <sub>4</sub> ) <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub>	(UO <sub>2</sub> ) <sub>4</sub> (O) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (ReO <sub>4</sub> ) <sub>2</sub> (CH <sub>3</sub> COO) <sub>4</sub> Na <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	(UO <sub>2</sub> ) <sub>5</sub> (O) <sub>2</sub> (OH) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> (TcO <sub>4</sub> ) <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub>	(UO <sub>2</sub> ) <sub>4</sub> (O) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (TcO <sub>4</sub> ) <sub>2</sub> (CH <sub>3</sub> COO) <sub>4</sub> Na <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>
Formula weight	2142.75	963.34	1952.24	1782.28
Temperature/K	149.98(10)	223.00(10)	172.97(10)	223.00(10)
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	P-1	C2/m	P-1	C2/m
a/Å	7.7354(3)	15.2417(5)	7.7451(3)	15.2356(8)
b/Å	8.4717(3)	8.1267(2)	8.4501(2)	8.1216(3)
c/Å	12.7820(4)	15.0583(5)	12.7565(5)	15.0053(7)
$\alpha$ /°	94.029(3)	90	93.982(3)	90
$\beta$ /°	99.086(3)	113.798(4)	99.211(3)	114.061(6)

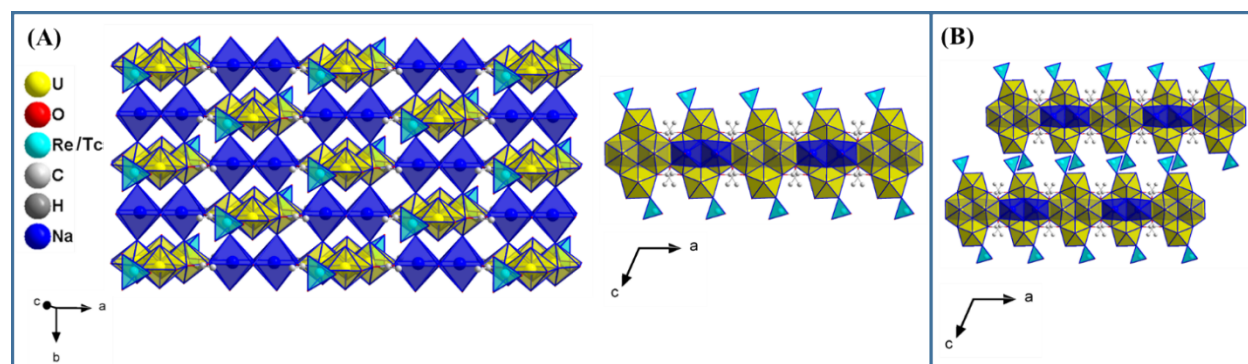
$\gamma/^\circ$	109.920(3)	90	109.708(3)	90
Volume/ $\text{\AA}^3$	770.66(5)	1706.60(10)	768.96(5)	1695.39(15)
Z	1	2	1	2
$\rho_{\text{calc}}/\text{g/cm}^3$	4.613	3.749	4.216	3.491
$\mu/\text{mm}^{-1}$	34.100	67.259	81.160	60.650
F(000)	908.0	1648.0	832.0	1552.0
Crystal size/ $\text{mm}^3$	$0.08 \times 0.08 \times 0.08$	$0.04 \times 0.04 \times 0.01$	$0.04 \times 0.04 \times 0.02$	$0.05 \times 0.02 \times 0.01$
Radiation	Mo K $\alpha$ ( $\lambda = 0.71073$ )	Cu K $\alpha$ ( $\lambda = 1.54184$ )	Cu K $\alpha$ ( $\lambda = 1.54184$ )	Cu K $\alpha$ ( $\lambda = 1.54184$ )
2 $\Theta$ range for data collection/ $^\circ$	5.722 to 52.742	6.416 to 136.472	7.082 to 136.34	6.45 to 136.502
Index ranges	$-9 \leq h \leq 9, -10 \leq k \leq 10, -15 \leq l \leq 15$	$-18 \leq h \leq 16, 0 \leq k \leq 9, 0 \leq l \leq 18$	$-9 \leq h \leq 9, -10 \leq k \leq 10, -14 \leq l \leq 15$	$-18 \leq h \leq 16, 0 \leq k \leq 9, 0 \leq l \leq 18$
Reflections collected	9602	1669	10031	1678
Independent reflections	3149 [ $R_{\text{int}} = 0.0361$ , $R_{\text{sigma}} = 0.0357$ ]	1669 [ $R_{\text{int}} = ?$ , $R_{\text{sigma}} = 0.0403$ ]	2797 [ $R_{\text{int}} = 0.0361$ , $R_{\text{sigma}} = 0.0274$ ]	1678 [ $R_{\text{int}} = ?$ , $R_{\text{sigma}} = 0.0426$ ]
Data/restraints/parameters	3149/2/208	1669/0/110	2797/0/198	1678/0/111
Goodness-of-fit on $F^2$	1.040	1.049	1.109	1.123
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0197$ , $wR_2 = 0.0443$	$R_1 = 0.0698$ , $wR_2 = 0.1901$	$R_1 = 0.0260$ , $wR_2 = 0.0663$	$R_1 = 0.0678$ , $wR_2 = 0.1884$
Final R indexes [all data]	$R_1 = 0.0241$ , $wR_2 = 0.0455$	$R_1 = 0.0727$ , $wR_2 = 0.1941$	$R_1 = 0.0287$ , $wR_2 = 0.0681$	$R_1 = 0.0715$ , $wR_2 = 0.1926$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	2.31/-1.42	6.71/-8.17	2.05/-1.92	9.15/-5.44

	<b>U<sub>4</sub>Tc</b>
Empirical formula	C <sub>8</sub> H <sub>20</sub> O <sub>25.75</sub> TcU <sub>4</sub>
Moiety formula	(UO <sub>2</sub> ) <sub>4</sub> (TcO)(O) <sub>4</sub> (CH <sub>3</sub> COO) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> .H <sub>3</sub> O.H <sub>2</sub> O
Formula weight	1578.36
Temperature/K	222.99(10)
Crystal system	orthorhombic
Space group	Pbcn
a/ $\text{\AA}$	14.3710(3)
b/ $\text{\AA}$	13.8231(3)
c/ $\text{\AA}$	14.8033(3)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	2940.70(11)
Z	4

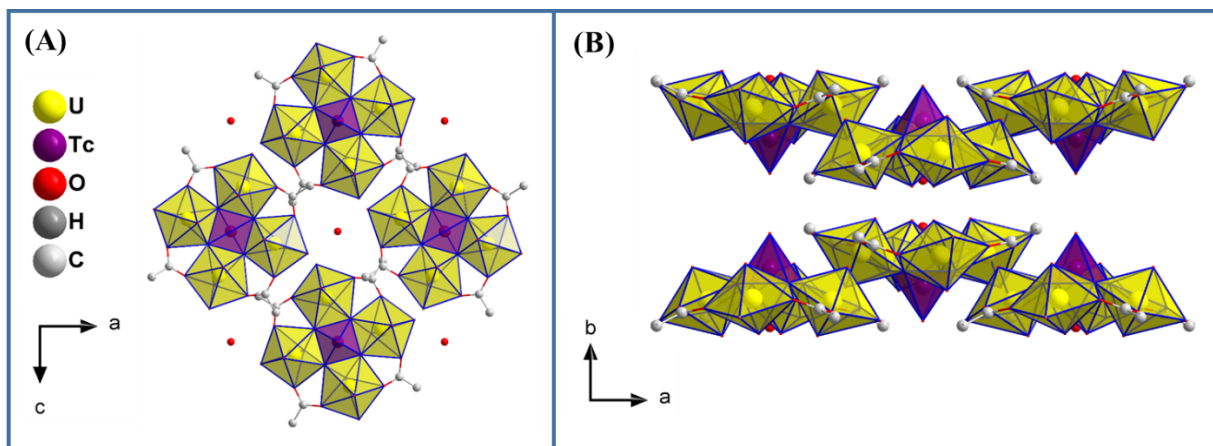
$\rho_{\text{calc}}/\text{cm}^3$	3.565
$\mu/\text{mm}^{-1}$	65.775
F(000)	2740.0
Crystal size/ $\text{mm}^3$	$0.08 \times 0.02 \times 0.01$
Radiation	Cu K $\alpha$ ( $\lambda = 1.54184$ )
2 $\Theta$ range for data collection/ $^\circ$	8.876 to 136.5
Index ranges	$-17 \leq h \leq 17$ , $-15 \leq k \leq 16$ , $-16 \leq l \leq 17$
Reflections collected	36295
Independent reflections	2695 [ $R_{\text{int}} = 0.0847$ , $R_{\text{sigma}} = 0.0276$ ]
Data/restraints/parameters	2695/0/182
Goodness-of-fit on $F^2$	1.066
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0383$ , $wR_2 = 0.0992$
Final R indexes [all data]	$R_1 = 0.0408$ , $wR_2 = 0.1013$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.39/-2.57



**Figure S1.** Polyhedral representation of the extended crystal lattice of  $\text{U}_5\text{Re}_2$  and  $\text{U}_5\text{Tc}_2$ , viewed from different crystallographic directions.



**Figure S2.** Polyhedra representation of extended crystal structure of  $\text{U}_4\text{Re}_2$  and  $\text{U}_4\text{Tc}_2$  from different crystallographic direction.



**Figure S3.** Polyhedra representation of extended crystal structure of  $\text{U}_5\text{Tc}$  from different crystallographic direction.

**Table S2.** Bond valence sum (BVS) values of selected fully occupied metal center and oxygen sites from isolated structures.

$\text{U}_5\text{Re}_2$		$\text{U}_4\text{Re}_2^1$		$\text{U}_5\text{Tc}_2$		$\text{U}_4\text{Tc}_2$		$\text{U}_4\text{Tc}$	
Site	BVS	Site	BVS	Site	BVS	Site	BVS	Site	BVS
U1	6.01	U1	6.19	U1	6.09	U001	6.04	U1	6.13
U2	5.98	U2	6.08	U2	6.03	U002	6.09	U2	6.12
U3	6.04	O9	2.07	U3	6.02	Tc003	6.52	Tc3	5.35
Re4	6.86	O7	2.05	Tc4	6.78	O00B	2.06	O4	1.76
O17	2.12	O6	1.74	O7	1.96	O00C	2.60	O9	1.99
O15	0.53	O18	2.27	O9	0.44	O00D	2.04	O16	2.03
O18	1.69	O11	2.14	O13	0.44	O00E	2.02	O6	1.93
O7	2.18	O13	1.78	O10	0.52	O00F	2.15	O10	1.95
O10	1.74	O8	2.24	O16	2.32	O00H	1.75	O14	0.38
O5	1.96	O10	2.52	O8	1.00	O00I	0.38	O7	1.78
O9	1.72	O19	1.93	O18	1.62	O00J	2.21	O5	1.84
O11	1.02	O5	0.38	O17	2.09	O00K	0.42	O8	1.73
O16	0.44	O21	0.40	O14	2.21	O1	1.34	O15	2.09
O13	1.78	Na20	1.38	O11	1.72	O13	1.81	O12	0.41
O14	1.79			O12	1.78	Na4	1.39	O11	2.26
O12	0.45			O5	1.81			O13	1.94
O20	1.77			O6	1.84				
O6	1.71			O15	1.73				
O8	2.20			O20	1.78				
O19	1.73			O19	1.73				

<sup>1</sup>BVS for Re was not calculated due to extensive disorder. However, based on charge-balance and the tetrahedra geometry and bond distances, we are certain it is Re(VII).



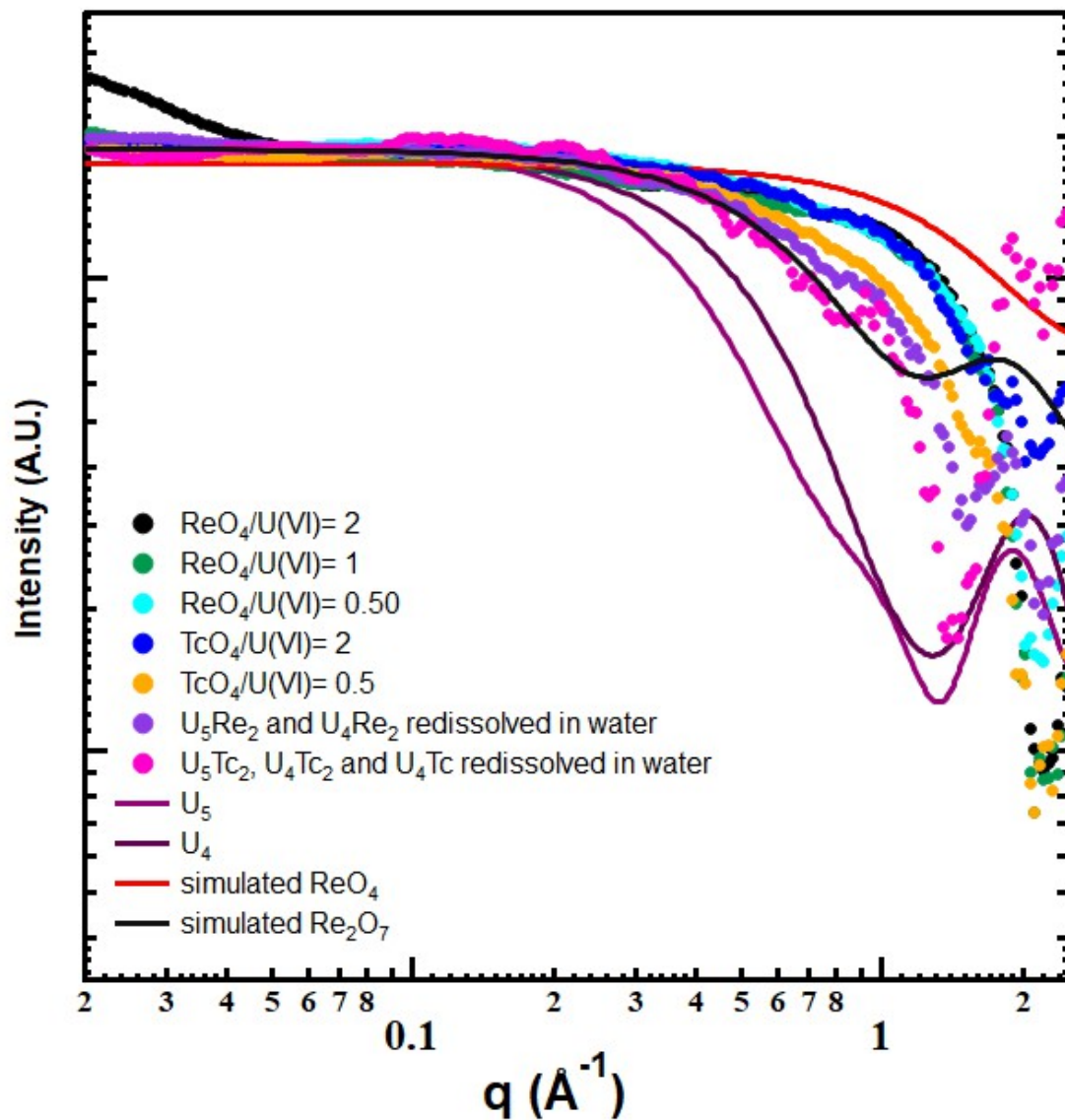
**Table S3.** Average metal to oxygen bond length comparison for [Tc(V)O<sub>5</sub>] umbrella core.

Bond	Bond length (Å)			
	This study	Abrams <i>et al.</i> 1991 <sup>7</sup>	Rochon <i>et al.</i> 1992 <sup>8</sup>	Davison <i>et al.</i> 1987 <sup>9</sup>
<b>Tc=O<sub>ax</sub></b>	1.656	1.646	1.635	1.648
<b>Tc-O<sub>eq</sub></b>	1.896± 0.009	1.955± 0.008	1.965± 0.010	1.957± 0.002

\*ax= axial, eq= equatorial

### 3. Small Angle X-ray scattering (SAXS)

Small angle X-ray scattering data was collected on an Anton Paar SAXSess instrument using Cu-K $\alpha$  radiation (1.54 Å) equipped with line collimation. A 2-D image plate was used for data collection in the  $q = 0.018$ - $2.5 \text{ Å}^{-1}$  range. The lower  $q$  resolution is limited by the beam attenuator. The SAXS samples for redissolved crystals were made using HPLC grade acetonitrile. About 5 mg of crystals were added in 0.5 mL acetonitrile/water and sonicated. Then undissolved crystals were filtered out using a 0.45  $\mu\text{m}$  membrane filter. The filtered solution was filled in a 1.5 mm glass capillaries (Hampton Research) to collect SAXS data. In case of Tc-99 containing solution, the sample was filled in 1.5 mm Kapton polyamide tubing (Cole-Palmer). Scattering data of neat solvent in glass/Kapton tube was also collected for background subtraction. Scattering was measured for 30 min for each experiment. SAXSQUANT software was used for data collection and post processing (normalization, primary beam removal, background subtraction, desmearing, and smoothing to remove the extra noise created by the desmearing routine). Data was analyzed by using IRENA macros with IgorPro 6.3 (Wavemetrics) software<sup>10</sup>. Simulated scattering pattern of Zr/Hf clusters were generated using SolX utilizing structural files (.xyz) containing the selected portion of the structure without solvent or coordinated ligands<sup>11</sup>.



**Figure S4.** SAXS scattering curve of mother liquor for different reaction solution and redissolved bulk crystals in water.

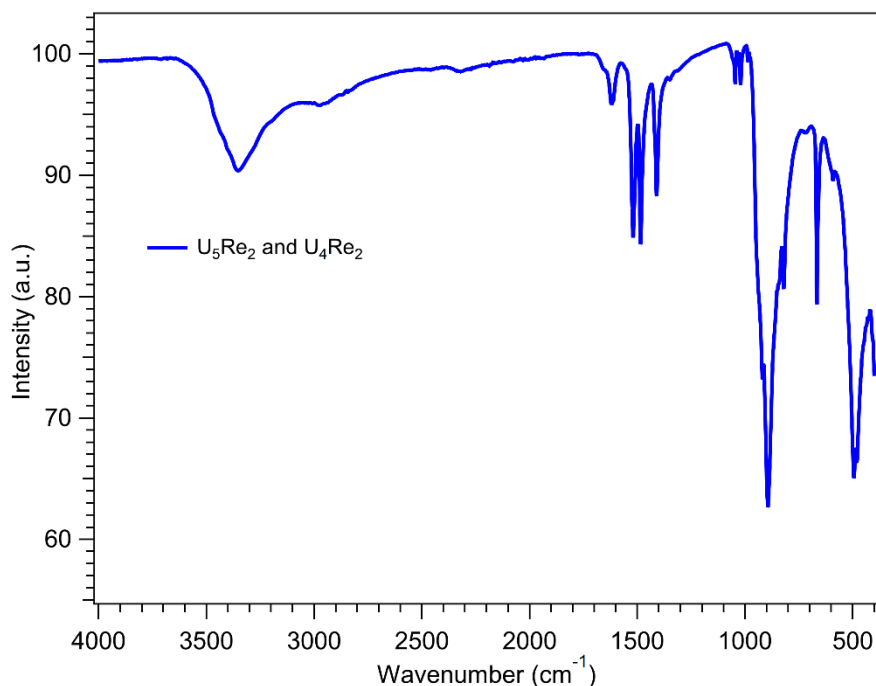
#### 4. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra was collected by using a PerkinElmer Spectrum Two Spectrometer system equipped with a  $\text{LiTaO}_3$  MIR detector. The scanning range for experiment was from 4000 to  $400 \text{ cm}^{-1}$  at a resolution of  $4 \text{ cm}^{-1}$ .

The FTIR spectra of the crystalline materials from the reaction between uranium acetate and perrhenic acid shows a characteristic band for an -OH stretching in between  $3600\text{--}3100 \text{ cm}^{-1}$ , from both  $\text{H}_2\text{O}$  and hydroxyl groups (**Figure S5**). Vibrational frequency corresponds to different group present in  $\text{CH}_3\text{COO}^-$  can be found in between  $1520\text{--}1420 \text{ cm}^{-1}$  and assigned in **Table S4**. A



wide peak in between 990-780  $\text{cm}^{-1}$  corresponds to  $\text{UO}_2$  and  $\text{ReO}_4$  stretching. Similar to previous studies, the stretching bands corresponding to these separate group metal-oxo moieties overlap<sup>12</sup>.



**Figure S5.** FT-IR spectra of crystalline materials isolated from reaction between uranium acetate and perrhenic acid.

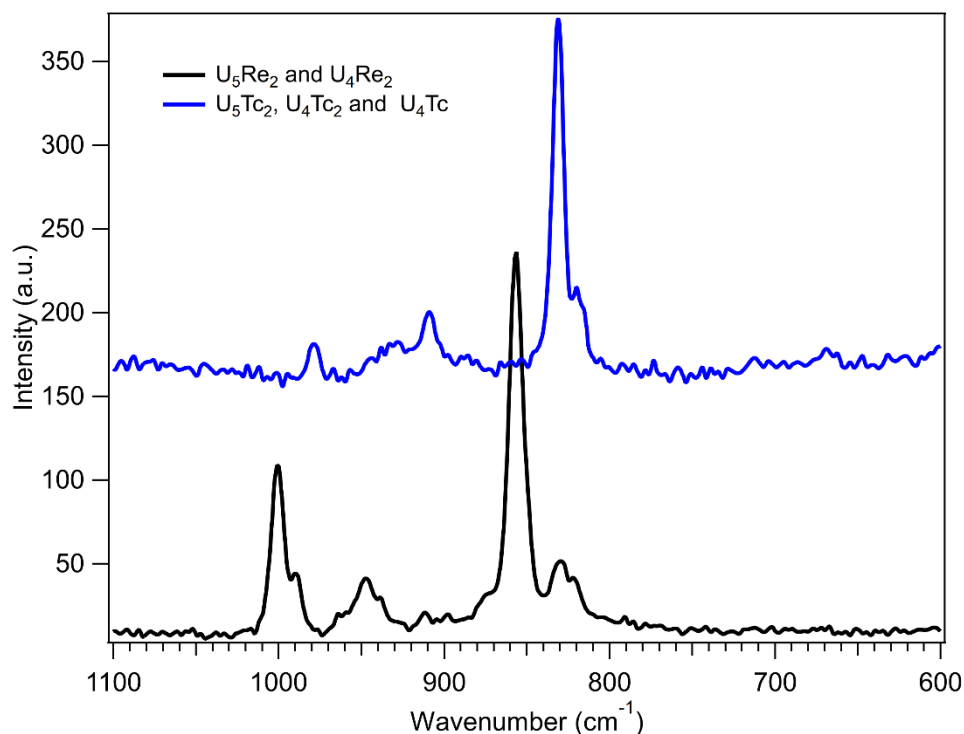
**Table S4.** Analysis of functional groups and their vibration from FTIR spectra.

Group	Wavenumber ( $\text{cm}^{-1}$ )	Assignment
$\text{H}_2\text{O}$	3600-3100	antisymmetric and symmetric OH stretching <sup>13</sup>
	1624	$\text{H}_2\text{O}$ bending <sup>13</sup>
$\text{CH}_3\text{COO}$	1521	COO antisymmetric stretching <sup>13</sup>
	1486	$\text{CH}_3$ bending <sup>13</sup>
	1411	COO symmetric stretching <sup>13</sup>
	667	COO bending/wagging <sup>13</sup>
	497	CH bending/ COO rocking <sup>13</sup>
$\text{ReO}_4^-/\text{UO}_2^{2+}$	990-780	$\text{UO}_2$ asymmetric stretch <sup>14</sup> / $\text{ReO}_4$ stretching <sup>15</sup>

## 5. Raman Spectroscopy

The Raman spectra of air-dried crystalline materials were collected using a Thermo Scientific DXR spectrometer with a 760 nm laser source, between wavelengths of 600 and 1200  $\text{cm}^{-1}$ .

The Raman spectra (**Figure S6**) were found to be useful in distinguishing the groups. The Raman active  $\nu_1$  and  $\nu_3$  stretching of  $\text{ReO}_4$  can be observed in  $998\text{ cm}^{-1}$ ,  $946\text{ cm}^{-1}$  and  $856\text{ cm}^{-1}$ .<sup>15-16</sup> In case of crystalline materials from reaction between uranium acetate and pertechnic acid, this stretching shift into lower wavenumber for  $\text{TcO}_4^-$  at position  $978\text{ cm}^{-1}$ ,  $908\text{ cm}^{-1}$  and  $830\text{ cm}^{-1}$ .<sup>17</sup> The Raman active  $\nu_1$  stretching of uranyl group can be also observed at  $828\text{ cm}^{-1}$  for perrhenate compounds and  $820\text{ cm}^{-1}$  for pertechnetate compounds.<sup>14, 16</sup> The vibrational mode at  $908\text{ cm}^{-1}$  can also be assigned to  $\text{Tc}^{\text{VO}}$ , based on prior vibrational spectroscopy data of pentavalent technetium.<sup>18</sup>

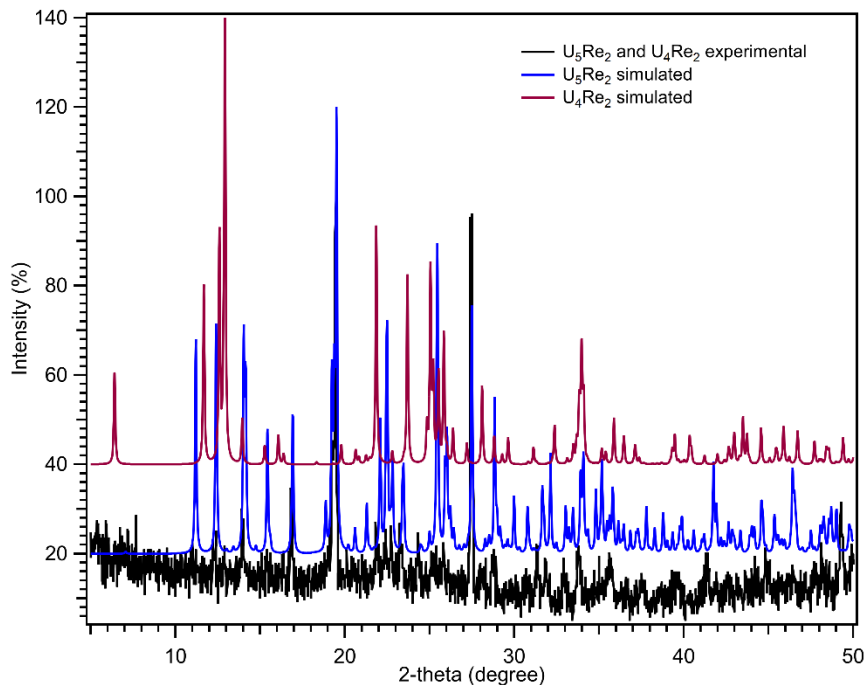


**Figure S6.** Raman spectra of crystalline materials isolated from reaction between uranium acetate, perrhenic acid and pertechnic acid.

## 6. Powder X-ray Diffraction (PXRD)

The PXRD experiments were done by using a Rigaku Miniflex diffractometer with  $\text{Cu K}\alpha$  ( $\lambda = 1.54056\text{ \AA}$ ) from  $5$  to  $50^\circ 2\theta$  at a rate of  $2^\circ\text{ min}^{-1}$ . The air-dried samples were crushed into powder prior to analysis. A silicon zero diffraction plate was used to collect diffraction data.

PXRD patterns of crystalline materials isolated from reaction between uranium acetate and perrhenic acid show peaks corresponds to  **$\text{U}_5\text{Re}_2$**  and  **$\text{U}_4\text{Re}_2$**  (**Figure S7**). However, preferred crystallographic orientation, similar peak positions for the different phases, as well as loss of crystallinity due to lattice dehydration renders peak assignment difficult.

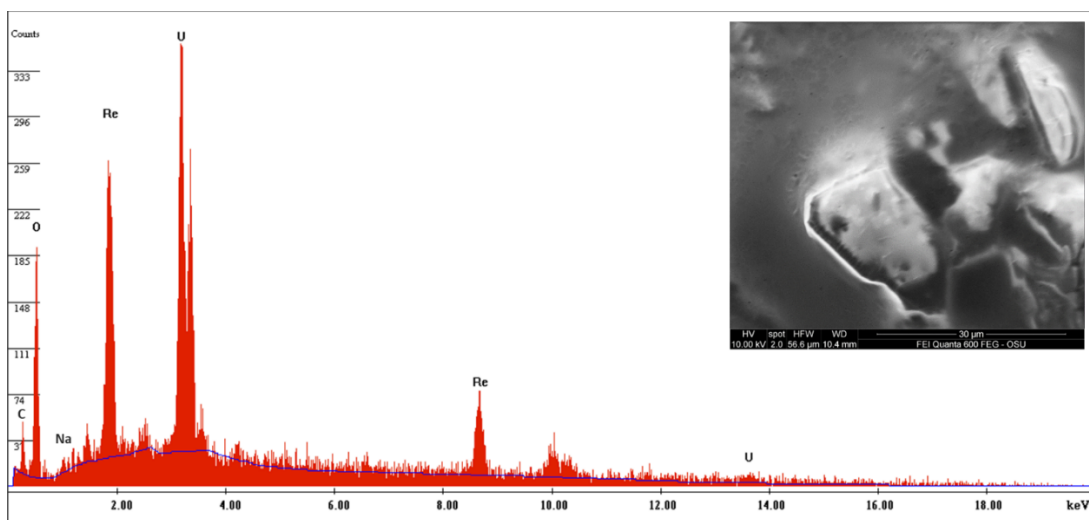


**Figure S7.** PXRD pattern of crystalline materials isolated from reaction between uranium acetate and perrhenic acid.

## 7. Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS)

SEM analysis was done using a FEI Quanta 600F SEM system equipped with energy dispersive spectroscopy (EDS) capability through 10 mm<sup>2</sup> Si(Li) detector (EDAX inc). The crystalline materials were fixed on a carbon conductive before the analysis. The analyses were performed under high vacuum using accelerating voltage 10-20 kV for SEM and 30 kV for EDS analysis.

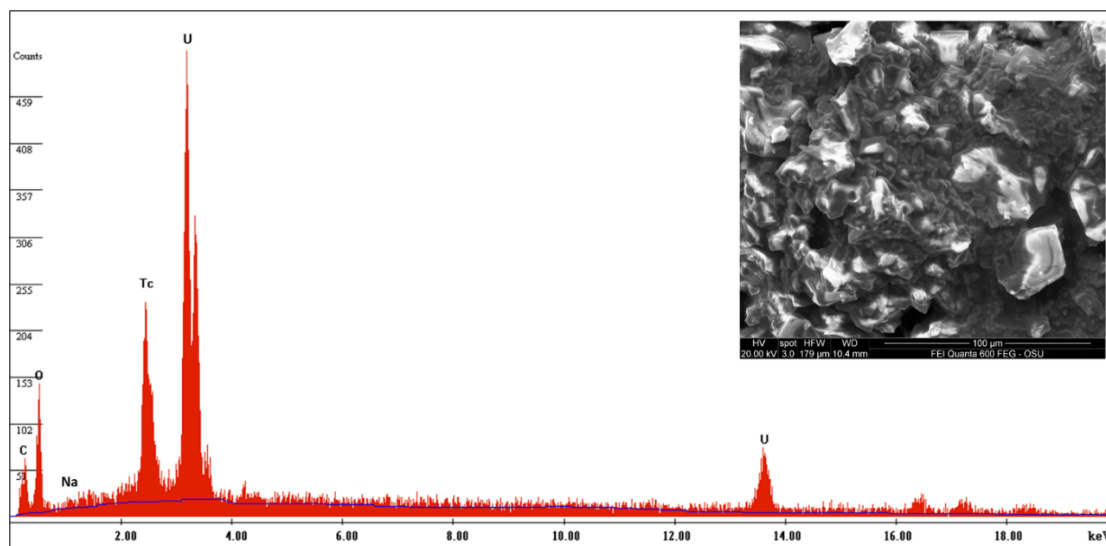
Scanning electron microscopy (SEM) analysis on crystalline materials reveal irregular shaped crystals (**Figure S8 and S9**). The energy dispersive spectroscopy (EDS) agreed well with elucidated compositions from SCXRD by showing peaks corresponding to U, Tc/Re, and Na, C and O in the crystalline materials (**Figure S8 and S9**). The results of EDS semi-quantitative elemental analysis are summarized in **Table S5 and Table S6**.



**Figure S8.** SEM image and EDS pattern of crystalline materials isolated from reaction between uranium acetate and perrhenic acid.

**Table S5.** EDS analysis result of crystalline materials isolated from reaction between uranium acetate and perrhenic acid.

Elements	Weight (%)	Atom (%)
C	4.77	22.9
O	15.4	55.6
Re	28.4	8.84
U	51.5	12.5



**Figure S9.** SEM image and EDS pattern of crystalline materials isolated from reaction between uranium acetate and pertechnic acid.

**Table S6.** EDS analysis result of crystalline materials isolated from reaction between uranium acetate and pertechnic acid.

Elements	Weight (%)	Atom (%)
C	6.83	22.5
O	25.7	63.5
Tc	11.7	4.74
U	55.7	9.26

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