Electronic Supplementary Material (ESI) for CrystEngComm.

Complexation of tetravalent uranium cations by the $As_4W_{40}O_{140}$ cryptand

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Supplementary informations

The supplementary informations contain the table S1 with the main crystallographic data for compounds **1-3** and the table S2 with the wavelength of the main W-O vibrations in the three compounds. The S1-S4 Figures are available below. Figure S1 contain the TGA measurements for compounds **1-3**, Figure S2 the IR spectroscopy of compounds **1-3** in comparison with the $[As_4W_{40}O_{140}]^{28-}$ cryptant and the formate ligand, Figure S3 highlight the environment of the uranium cations in compounds **1-3** and, Figure S4 shows the IR spectra of precipitated cationic mixtures with CsCl.

Some comments on the A and B alerts have also been added on the crystal structure refinement of the three compounds.

Table S1: Crystal data and structure refinement for compounds **1-3**.

	(1)	**(2)**	**(3)**
Formula	$As_4W_{40}O_{182.4}Na_{5.35}U_2$	$As_8W_{80}O_{373}Na_{15}U_4C_7$	$As_4W_{40}O_{226}Na_{13}U_4C_{3.5}$
Formula weight	11171.14	22656.4	12562.71
Temperature/K	100	100	100
Crystal color	brown	brown	brown
Crystal size/mm	0.15 x 0.05 x 0.05	0.15 x 0.1 x 0.1	0.1 x 0.08 x 0.08
Crystal system	Tetragonal	Triclinic	Orthorhombic
Space group	*I-4*	*P-1*	*Pmmn*
a/Å	19.8185(5)	19.5645(7)	23.184(2)
b/Å	19.8185(5)	26.6677(10)	29.532(3)
c/Å	26.1867(6)	38.3039(15)	14.5168(13)
α/°	90	106.064(2)	90
β/°	90	96.373(2)	90
γ°	90	90.129(2)	90
Volume/Å^3	10285.4(6)	19074.3(13)	9939.2(16)
Z, $\rho_{calculated}$/g.cm^{-3}	2, 3.607	2, 3.945	2, 4.198
μ/mm^{-1}	24.579	26.516	15.660
Θ range/°	1.555 – 26.412	1.293 – 26.421	1.386 – 20.544
Limiting indices	$-21 \le h \le 24$ $-20 \le k \le 24$ $-32 \le l \le 28$	$-24 \le h \le 24$ $-32 \le k \le 33$ $-47 \le l \le 47$	$-28 \le h \le 28$ $-36 \le k \le 36$ $-18 \le l \le 18$
Collected reflections	26582	212649	171581
Unique reflections	10354 [R(int) = 0.0576]	77648 [R(int) = 0.0753]	10581 [R(int) = 0.0714]
Parameters	537	2421	753
Goodness-of-fit on F^2	0.994	1.030	1.049
Final R indices [I>2σ(I)]	R1 = 0.0457 wR2 = 0.0917	R1 = 0.0769 wR2 = 0.1439	R1 =0.0408 wR2 = 0.1149
R indices (all data)	R1 = 0.0743 wR2 = 0.1017	R1 = 0.1385 wR2 = 0.1674	R1 =0.0524 wR2 =0.1380

Largest diff. peak and hole/e.Å^{-3}	1.42 and -2.39	3.70 and -3.44	6.44 and -5.94

Table S2: Comparison of $\{SiW_9O_{34}\}$ main vibrations (cm^{-1}) of compounds **1- 3**.

	W-Od	W-Ob-W	W-Oc-W
Compound **1**	944	866 and 842	779, 694, 621 and 576
Compound **2**	944	865 and 838	778, 691, 620 and 572
Compound **3**	947	869 and 829	772, 684, 617 and 566
$As_4W_{40}O_{140}$	946	866	792, 699, 620 and 558

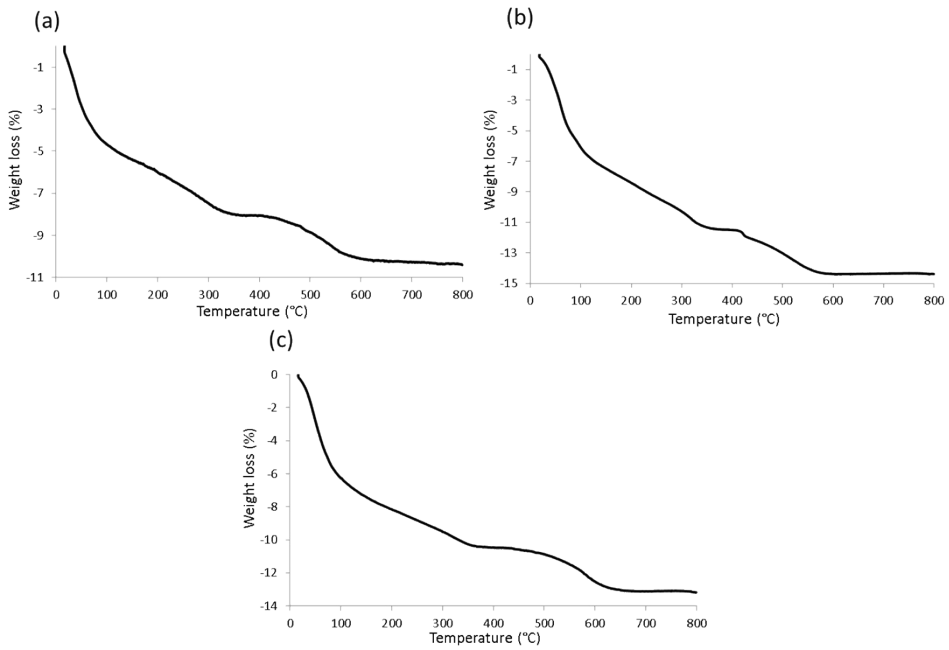

Figure S1: TGA curves of compound **1** (a), compound **2** (b) and compound **3** (c).

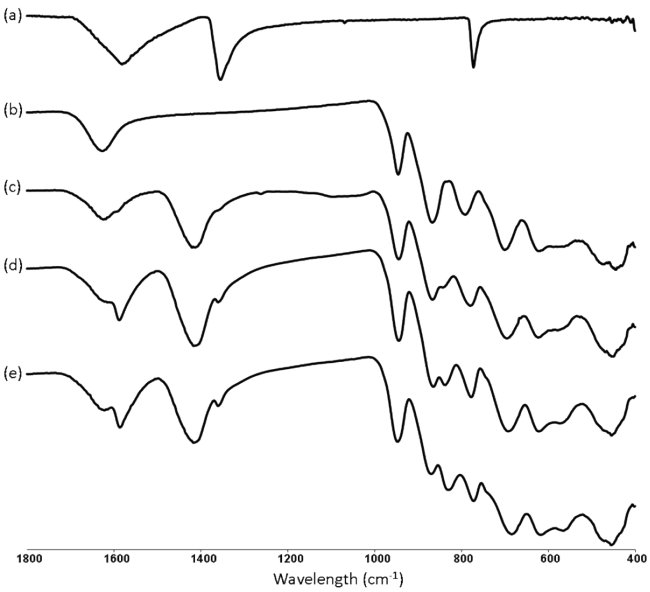

Figure S2: IR spectra in the region 400-1800 cm^{-1} of HCOONa (a), $[As_4W_{40}O_{140}]^{28-}$ (b), Compound 1 (c), Compound 2 (d) and Compound 3 (e).

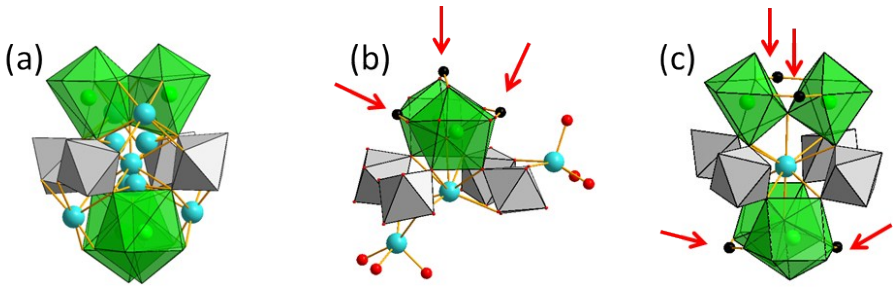

Figure S3: Highlight on the environment of the embedded uranium cations (green polyhedron) in compound **1** (a), compound **2** (b) and compound **3** (c) with the directly interacting sodium cations (light blue sphere). Red arrows highlight the bridging formate ligands.

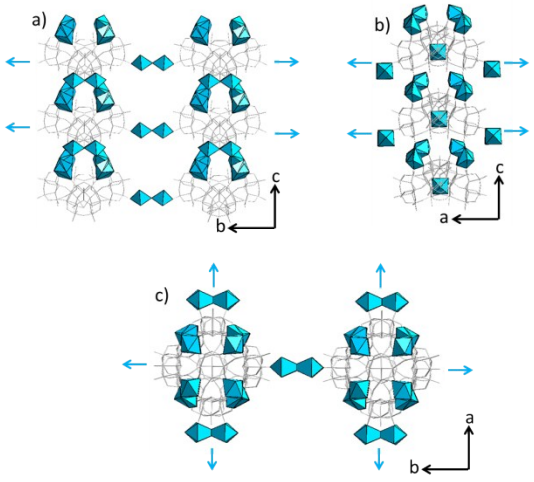

Figure S4: representation of the sodium-POM interaction in the lattice of compound **3** along the a, b and c axis. Blue polyhedron represents bridging dimers of sodium cations. The blue arrows highlight the directions of the stacking of the POM entities.

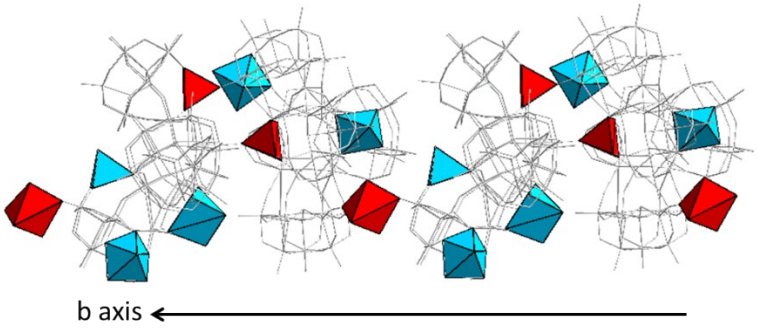

Figure S5: representation of the sodium-POM interaction in the lattice of compound **2** along the b axis. The red polyhedrons represent the square pyramidal and octahedral geometries of the bridging sodium environment. Blue polyhedrons represent surface interacting sodium cations.

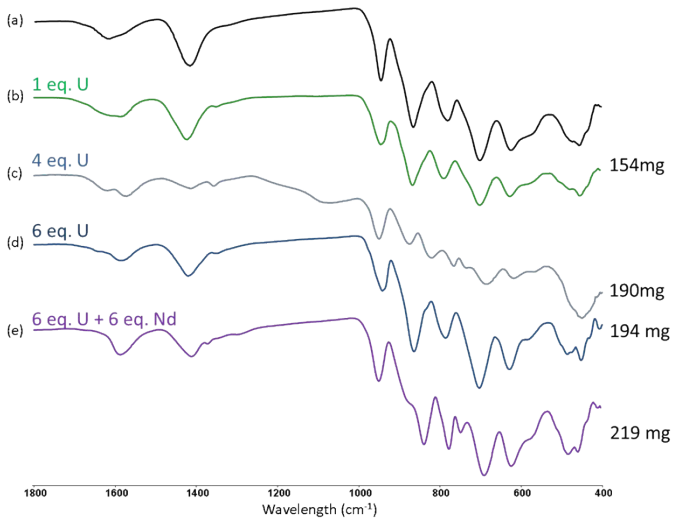

Figure S6: Comparison of the IR spectra of $[As_4W_{40}O_{140}]^{28-}$ (a) and the precipitated powder from the synthetic composition of compound **1** (b), compound **2** (c), compound **3** (d) and of a mixture containing 6eq of U^{IV} and 6 eq. of Nd^{III} (e).

Special details on the refinement of compounds **1-3**:

Compound **1**:

Alert B:

`Isolated Oxygen Atom (H-atoms Missing ?)`

This alert is due to the presence of the oxygen atoms of the water molecules present in the lattice of the crystals. Generally, in polyoxometalate structural resolution, hydrogen atoms are not added on calculated position to these water-oxygen atoms because they do not reflect the disorder that can be present around them.

`Number of (Iobs-Icalc)/SigmaW > 10 Outliers`

The reflexions associated to this problem have been identified and are not affected by the beam-stop. They are slightly above 10 and this error is mainly due to the fact that too much grease was present over the crystal,

generating some diffusion of the X-ray where these 3 intensities appear. As it was not too far from the limit, we decided to keep them for the refinement.

`The Flack x is >> 0 - Do a BASF/TWIN Refinement`

A Twin refinement was performed but didn't detect any other domain or transformations associated with the space group used for the refinement.

Compound **2**:

Alert A:

`Isotropic non-H Atoms in Anion/Solvent`

All the solvent water molecules were refined isotropically. As the model is quite complex, the oxygen atoms of the polyanionic part were not refined anisotropically. Furthermore, when doing anisotropic refinement, some oxygen atoms appear to be NPD. To avoid having a mixture of isotropic and anisotropic oxygen atoms, we decided to refine all of the same way. Only the heaviest atoms were refined anisotropically in this compound.

`Check Calcd Resid. Dens.`

These residual densities are relatively close from solvent oxygen atoms and are due to some disorder of the solvent molecules. These disorders were not modeled and the SQUEEZE procedure was applied to remove most of these electronic densities related to the solvent disorder.

Alert B:

`Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 10 Ratio`

`High 'MainMol' Ueq as Compared to Neighbors of C3`

These alerts are due to the thermal mobility of one carbon atom in one of the formate ligand generating larger U(eq) value in comparison of the two neighboring oxygen atoms. It might be due to some disorder on this atom that we didn't model.

`Isolated Oxygen Atom (H-atoms Missing ?)`

This alert is due to the presence of the oxygen atoms of the water molecules present in the lattice of the crystals. Generally, in polyoxometalate structural resolution, hydrogen atoms are not added on calculated position to these water-oxygen atoms because they do not reflect the disorder that can be present around them.

`Number of (Iobs-Icalc)/SigmaW > 10 Outliers`

Like in compound **1**, the reflexions associated to this problem have been identified and are not affected by the beam-stop. They are slightly above 10 and this error is mainly due to the fact that too much grease was present over the crystal, generating some diffusion of the X-ray were these 3 intensities appears. As it was not too far from the limit, we decided to keep them for the refinement.

Compound **3**:

Alert A:

`Number of (Iobs-Icalc)/SigmaW > 10 Outliers`

These reflexions were checked and appears to be close to the beam-stop but seems to be unaffected by it as none of them are overlapped by it. Thus, we have decided to leave them for the refinement of this compound.

`Check Calcd Residual Density 0.79A From W8 7.81 eA-3`

Some residual densities can be observed around heavy atoms in this structure. They are due to some ghost residue peaks as it can sometimes occur for heavy atoms.

Alert B:

`Atom Ow26 (Anion/Solvent) ADP max/min Ratio`

This alert is due to a water molecule in the lattice that is disordered on two positions and was not modeled on these two positions generated an elongated ellipsoid anisotropy.

`Non-Solvent Resd 1 O Ueq(max)/Ueq(min) Range`

This alert is due to the thermal mobility of one oxygen atom in one of the formate ligand generating larger U(eq) value in comparison of the two neighboring oxygen atoms.

`Isolated Oxygen Atom (H-atoms Missing ?)`

This alert is due to the presence of the oxygen atoms of the water molecules present in the lattice of the crystals. Generally, in polyoxometalate structural resolution, hydrogen atoms are not added on calculated position to these water-oxygen atoms because they do not reflect the disorder that can be present around them.

`Reflection # Likely Affected by the Beamstop`

After checking these reflexions, they are not affected by the beam-stop. The alert may be due to some X-Ray diffusion in the grease used to glue the crystals.

`Large Value of Not (SHELXL) Weight Optimized S . 103.40 Check`

This alert is probably generated by the presence of the four affected reflexions reported just above.

`Check Calcd Residual Density 0.53A From`

In the case of oxygen atoms of water molecules (OwXX), this alert is due to the presence of residual disorder around these oxygen atoms. We were not able to model all the disorder around some of the water molecules of the lattice.

In the case of heavier atoms (As, U, W) these residual densities are due to some ghost residue peaks as it can sometimes occur for heavy atoms.