Time-controlled synthesis of the 3D coordination polymer U(1,2,3-*H*btc)$_2$ followed by the formation of molecular poly-oxo cluster {U_{14}} containing hemimellitate uranium(IV)

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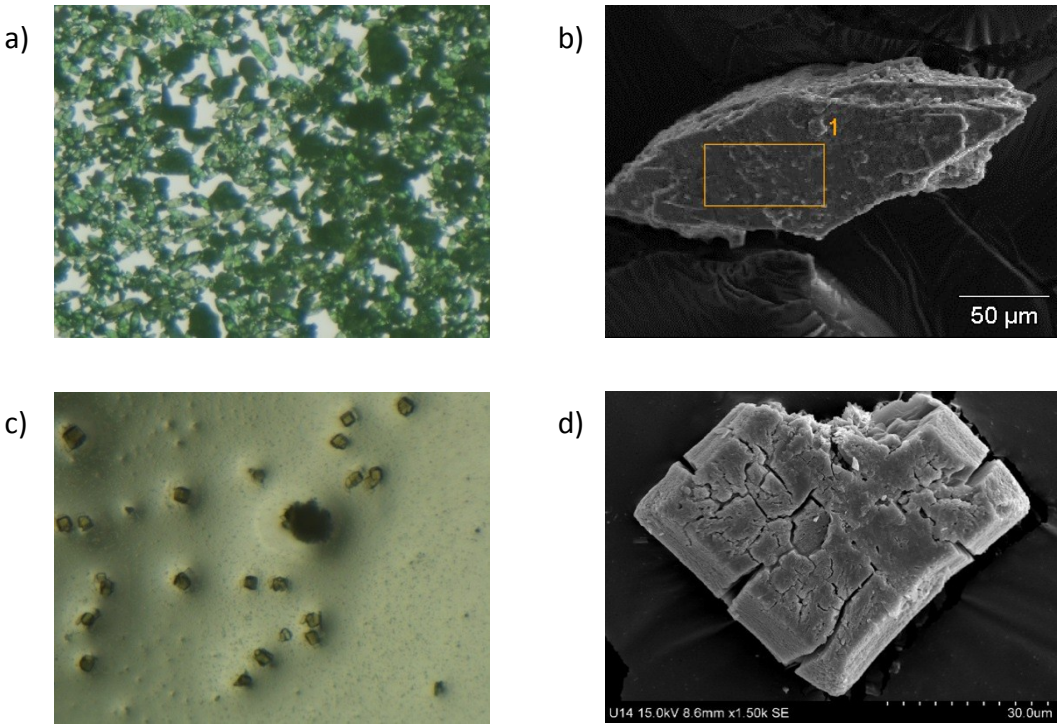

Figure S1: Optical microscope (left) and SEM images (right) of compound **1** (a and b) and compound **2** (c and d).

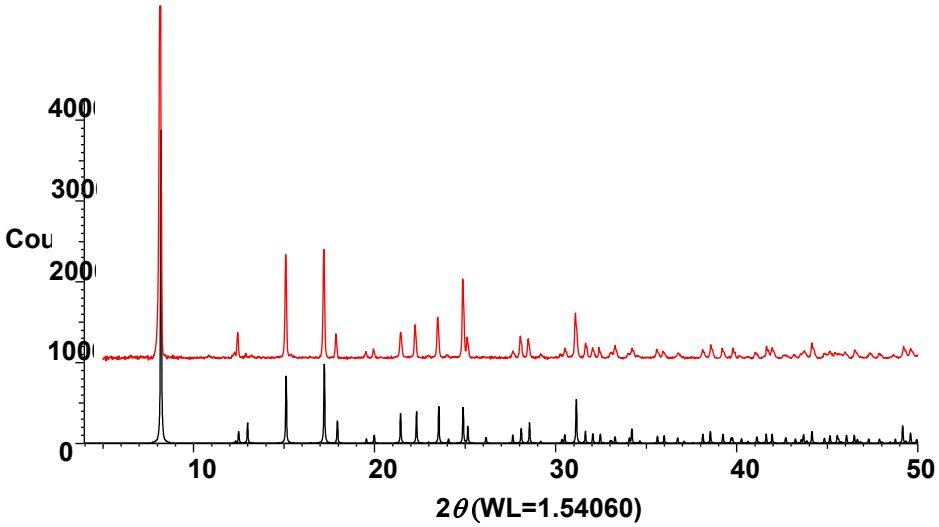

Figure S2a: Powder X-ray diffraction patterns of compound **1**; simulated (black line) and experimental patterns (red line) (Cu Kα radiation).

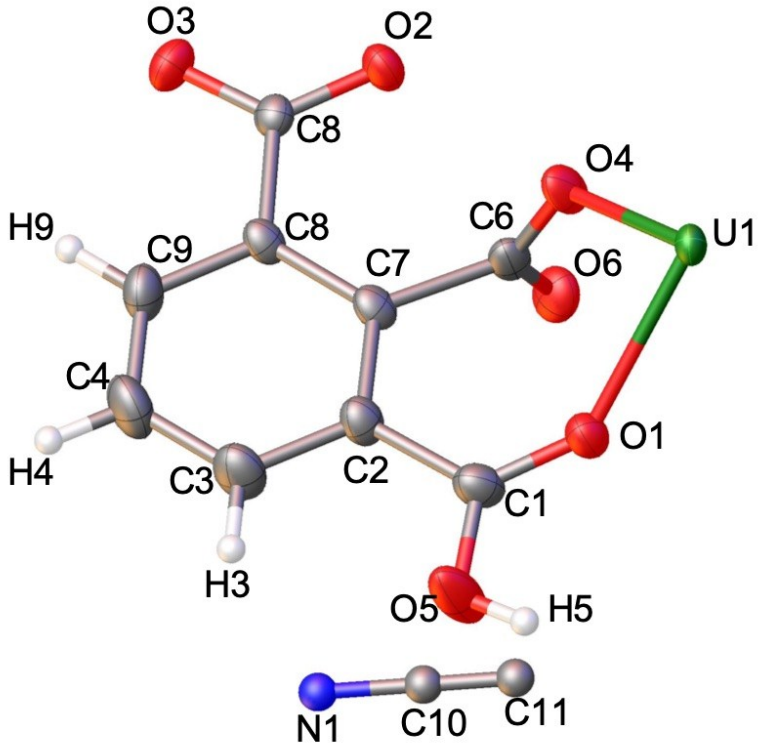

Figure S2b: Ortep view of the asymmetric unit in compound **1**. Green: U; red: O; blue: N; grey: C; white: H.

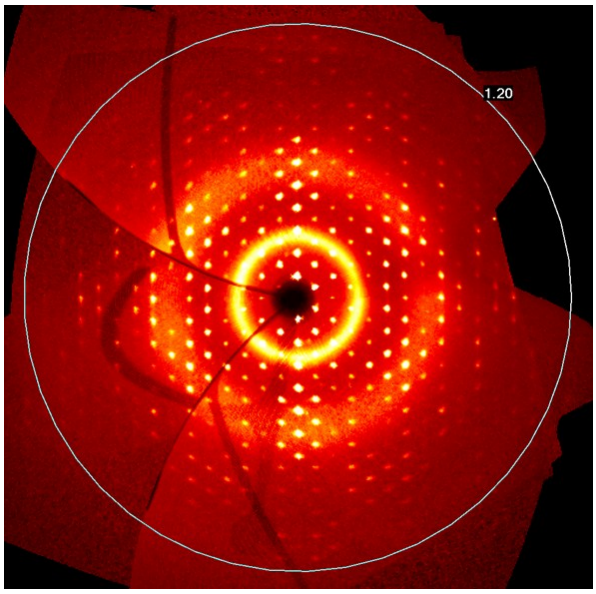

Figure S3: 0kl precession frame showing the low resolution (~1.20Å) obtained for the crystals of compound **2**.

Alert A for compound 2: explanations

The value of sine(theta_max)/wavelength is less than 0.550 Calculated sin(theta_max)/wavelength

Despite several measurements attempts performed at 100K, we can see on the 0kl precession frame on Figure S3 that no intensities are observed above the 1.25 Å resolution and the integration of the data considering this limit only give a relatively bad R_{int} of 12.73%. It would have been useless to integrate the data further this point. The examination of the intensities from the precession frames shows that the crystal appears to be well crystallized.

Isotropic non-H Atoms in Main Residue(s)

This alert is due to the quality of the bad data generating numerous NPD atoms if we refined them anisotropically.

Large Hirshfeld Difference U4 --Cl2

This problem could not be resolved using a DELU or SIMU restraint. It might be due to the high thermal agitation of the chloride atom.

Short Inter D...A Contact

These shorts contacts take place between water molecules that appears to be present with an occupancy factor generally below 0.5 indicating a disorder between them. This disorder is also the reason of the presence of the non modelled solvent accessible void.

The absolute value of parameter shift to su ratio > 0.20 Absolute value of the parameter shift to su ratio given 0.688 Additional refinement cycles may be required.

This alert is due to the hydrogen atoms localized on the oxygen atom O16, belonging to a free carboxylate arm and to the carbon atom C20 belonging to the CH_3 of the highly agitated acetate ligands bonded on the uranium cations. On these two atoms, the refinement of the hydrogen atoms is not stable and always gives this alert. It is worth noting that this alert disappears if we remove these four hydrogen atoms but we choose to add all possible hydrogen atoms on the corresponding molecules.

VERY LARGE Solvent Accessible VOID(S) in Structure

Due to the low resolution of the data, a SQUEEZE procedure to remove this alert was not performed. Doing it results in a model that did not converge.

Alert B for compound 2: explanations

Poor Data / Parameter Ratio (Zmax > 18)

This is due to the low resolution of the collected data.

Large Hirshfeld Difference U3 --Cl1

This problem could not be resolved using a DELU or SIMU restraint. It might be due to the high thermal agitation of the chloride atom.

High 'MainMol' Ueq as Compared to Neighbors of

This alert is also probably due to the high thermal parameter of the Cl2 atom in comparison of the uranium centers bonded to it.

Isolated Oxygen Atom (H-atoms Missing ?)

Generally, in cluster or polyoxoanion chemistry, the hydrogen of the water solvent molecule is never added. In absence of a clear hydrogen bond network in the lattice, these hydrogen atoms could not converge on calculated positions.

Singly Bonded Carbon Detected (H-atoms Missing)

See the last Alert A on the converging of the structural model

Short Inter D...A Contact O3W ..O9W

See answer on the A alert.

D-H Without Acceptor O8 --H8

This alert is due to the absence of modeled water molecule in the lattice of this compound due to their probable high disorder combined with the low resolution of the measurement.

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

A BASF/TWIN refinement did not give any information on a possible twinning in this crystal.

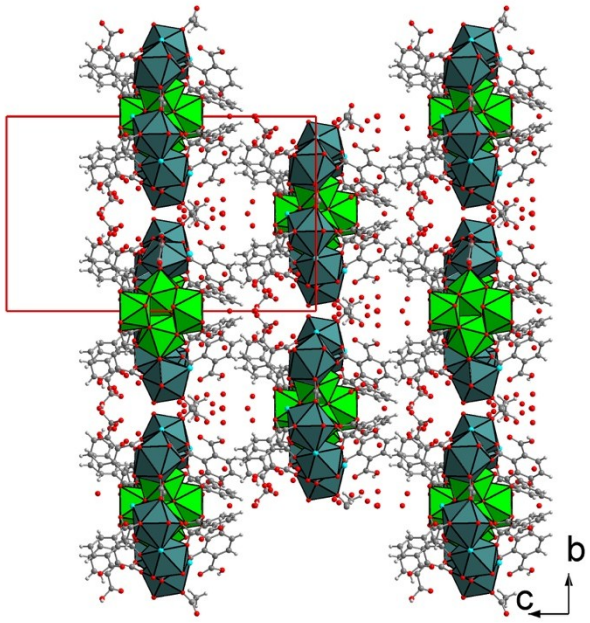

Figure S4: Crystal packing of the $\{U_{14}\}$ clusters in compound **2** along the c axis.

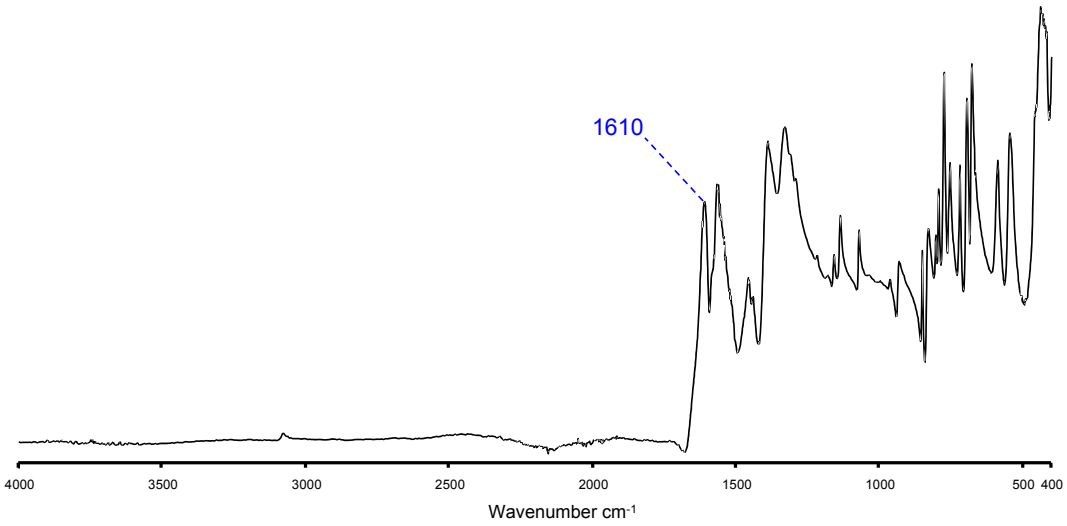

Figure S5: Infrared spectrum of compound **1**, after washing with ethanol at room temperature.

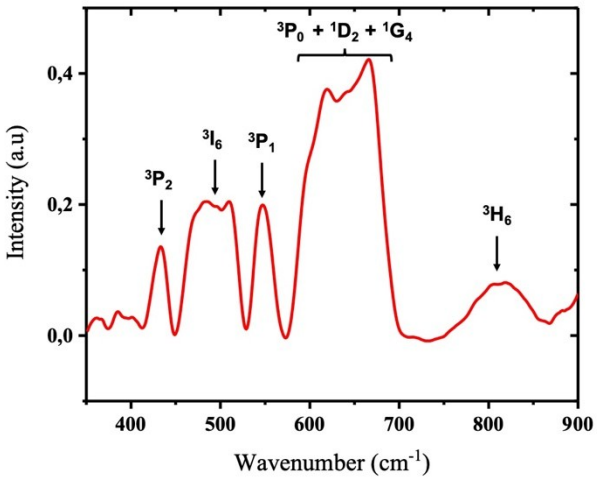

Figure S6: Solid-state UV-Visible absorption spectrum of compound **1** at room temperature.

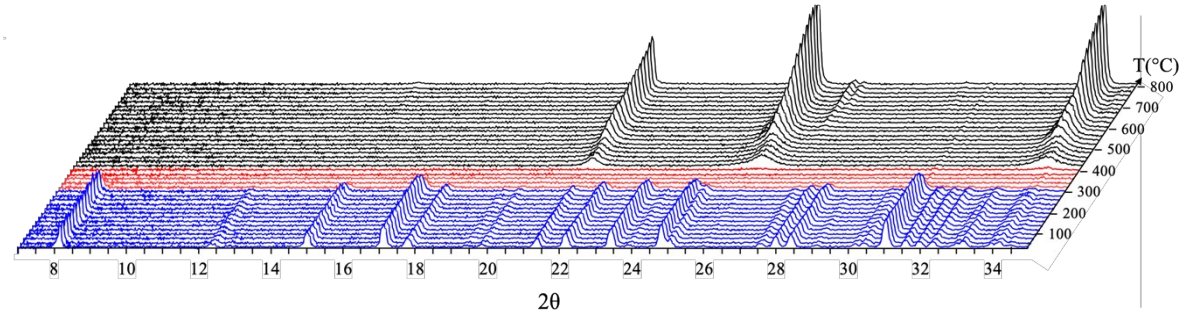

Figure S7: X-ray thermodiffractograms of compound **1** after washing with ethanol (Cu Kα radiation).

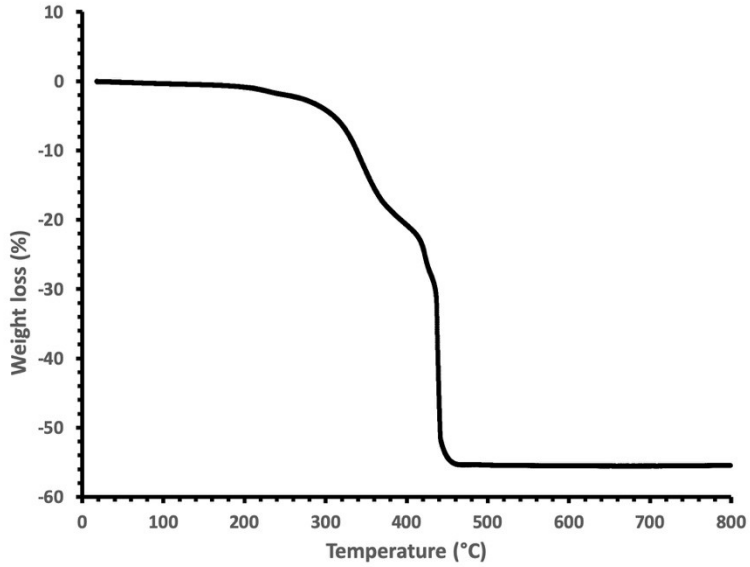

Figure S8: Thermogravimetric curve of compound **1** under air gas flow with a heating rate of 5 °C.min^{-1}.

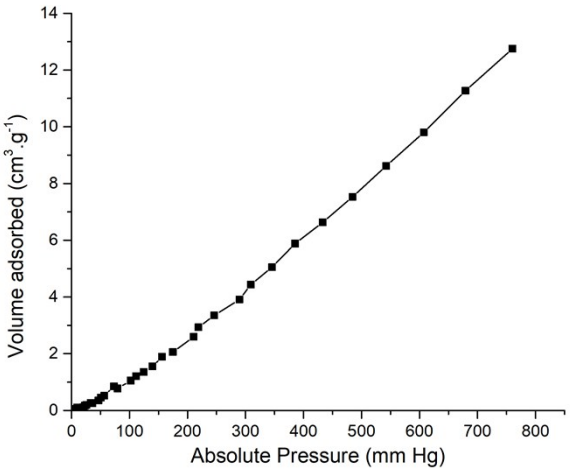

Figure S9: CO_2 adsorption isotherm of compound **1** at 273.15 K.