

Supplementary Information

Table S1. Crystallographic data and refinement parameters for compounds **2**, **3**, **5**, **6**, **7**, **8**.

Compound	2	3	5
Formula	$\text{K}_3(\text{H}_3\text{O})[(\text{UO}_2)_3(\text{SO}_4)_5(\text{H}_2\text{O})_2](\text{H}_2\text{O})_5$	$\text{K}_{3.5}(\text{H}_3\text{O})_{0.5}[(\text{UO}_2)_3(\text{SO}_4)_5(\text{H}_2\text{O})](\text{H}_2\text{O})_{1.5}$	$\text{K}_2[(\text{UO}_2)_2(\text{SO}_4)_3(\text{H}_2\text{O})_2](\text{H}_2\text{O})_3$
Formula Weight	1552.69	1481.74	996.44
Space Group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Z	4	4	8
T, °C	296	296	296
a, Å	12.774(4)	9.8901(3)	17.3051(2)
b, Å	11.339(3)	16.1105(5)	12.56130(10)
c, Å	20.734(6)	17.2862(5)	17.3240(2)
α , °	90	90	90
β , °	92.088(6)	98.038(2)	96.5770(10)
γ , °	90	90	90
V, Å ³	3001.1(16)	2727.23(14)	3741.01(7)
μ , mm ⁻¹	17.036	18.800	18.172
2 θ range, °	3.932–54.998	3.472–54.984	3.536–55.000
D _{calc} , g/cm ³	3.399	3.593	3.503
Total ref.	25339	26393	8580
Unique ref.	6880	6259	8580
Unique $ F_o \geq 4\sigma_F$	5958	4615	7674
R _{int}	0.0378	0.0648	Merged*
R ₁	0.0252	0.0358	0.0212
wR ₂	0.0530	0.0724	0.0523
GOF	1.045	1.036	1.034
$\rho_{\text{max}}, \rho_{\text{min}}$, e/Å ³	1.49 / -1.01	1.73 / -1.62	1.38/-0.91
CSD	1996652	1996653	1996656

Table S1. Continued.

Compound	6	7	8
Formula	$\text{K}_2[(\text{UO}_2)_2(\text{SO}_4)_3(\text{H}_2\text{O})_2](\text{H}_2\text{O})_3$	$\text{K}_2[(\text{UO}_2)_2(\text{SO}_4)_3(\text{H}_2\text{O})](\text{H}_2\text{O})$	$\text{K}(\text{H}_5\text{O}_2)[(\text{UO}_2)_2(\text{SO}_4)_3(\text{H}_2\text{O})]$
Formula Weight	996.44	942.47	922.40
Space Group	<i>Pnma</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
Z	4	4	4
T, °C	296	100	296
a, Å	11.465(7)	8.229(6)	11.1337(15)
b, Å	12.605(7)	14.862(10)	10.0463(13)
c, Å	12.944(8)	13.921(14)	14.697(2)
α , °	90	90	90
β , °	90	92.921(14)	101.280(3)
γ , °	90	90	90
V, Å ³	1870.7(19)	1626.8(19)	1612.2(4)
μ , mm ⁻¹	18.171	20.871	20.809
2 θ range, °	4.51–54.994	4.11–54.98	3.73–54.998
D _{calc} , g/cm ³	3.503	3.848	3.800
Total ref.	14744	9109	28887
Unique ref.	2237	3728	3707
Unique $ F_o \geq 4\sigma_F$	1719	3092	3514
R _{int}	0.0532	0.0334	0.0267
R ₁	0.0291	0.0238	0.0126
wR ₂	0.0560	0.0431	0.0298
GOF	1.064	0.986	1.120
ρ_{max} , ρ_{min} , e/Å ³	1.19/-1.15	1.12/-0.98	0.84/-0.46
CSD	1996654	1996651	1996655

*The compound 5 was refined using twin law with the creation of HKLF5-type reflection file. MERG code changed to 0 for compatibility with HKLF and BASF parameters.

Infrared Spectroscopy

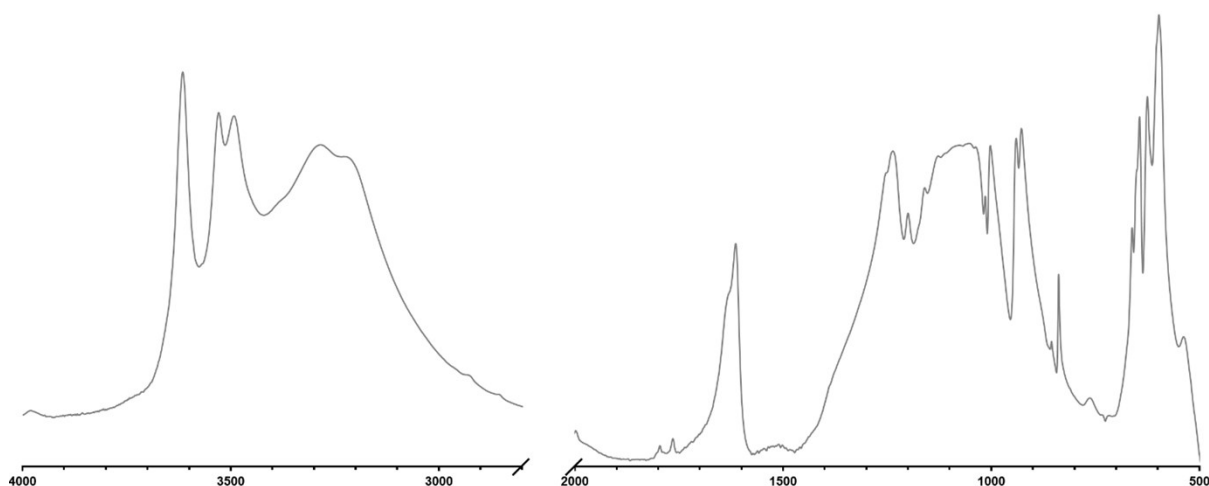


Figure S1. Infrared spectroscopy for compound 7.

The IR spectrum of **7** (Figure S1) was recorded using KBr pellets on the Bruker Vertex 70 spectrometer via Attenuated Total Reflection method in the region 4000-500 cm^{-1} . A MIRacle ATR accessory (Pike Technologies) with a Ge ATR crystal was used. In order to subtract the baseline and integrate peaks, the spectrum was processed using OriginPro software.

Infrared bands at 3615, 3528, 3492, 3284 and 3227 cm^{-1} are assigned to the ν O–H stretching vibrations of symmetrically nonequivalent H_2O molecules. According to the correlation given by Libowitzky (1999), listed values of infrared bands correspond to the O–H \cdots O hydrogen bond distances range between 3.2 to 2.7 Å, which is in a good agreement with the values obtained from single crystal X-ray analysis (3.190–2.735 Å). Two infrared bands at 1634 and 1613 cm^{-1} are attributed to the ν_2 (δ) bending vibrations of structurally non-equivalent H_2O molecules.

There are ten bands in the spectrum in the range from 1300 to 1000 cm^{-1} which are assigned to stretching vibrations of $(\text{SO}_4)^{2-}$ groups. The bands at 1257, 1236, 1199, 1160, 1127, 1076 and 1053 are attributed to the split triply degenerate ν_3 antisymmetric stretching vibrations, whereas next three bands at 1037, 1014 and 1001 cm^{-1} are assigned to the ν_1 symmetric stretching vibrations. Two strong bands at 940 and 927 cm^{-1} are attributed to the ν_3 antisymmetric

stretching vibrations of the uranyl ion, UO_2^{2+} . Next two weak bands at 855 and 838 cm^{-1} are assigned to the ν_1 symmetric stretching vibrations of uranyl ion. A broad weak band at 763 cm^{-1} may be associated with the libration modes of H_2O molecules. Medium-strong infrared bands at 661, 643 and 624 cm^{-1} are attributed to the ν_4 (δ) triply degenerate antisymmetric stretching vibrations of SO_4 tetrahedra. The strongest band among all the spectrum at 596 cm^{-1} is assigned to the split triply degenerate ν_4 (δ) bending vibrations of SO_4 .