Supporting Information

Construction of a Microporous Inorganic-Organic Hybrid Compound with Uranyl Units

Zhen-Tao Yu, Zuo-Lei Liao, Yu-Sheng Jiang, Guang-Hua Li, Guo-Dong Li and Jie-Sheng Chen*

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China

To whom correspondence should be addressed: Professor Jie-Sheng Chen, College of Chemistry, Jilin University, Changchun 130012, P. R. China.
E-mail: chemcj@mail.jlu.edu.cn.

Materials and methods: All reagents were of reagent grade and commercially available and used as received without further purification. Elemental microanalyses (C, H, N) were carried out on a Perkin-Elmer 2400 elemental analyzer. The metal contents were determined by inductively coupled plasma (ICP) analysis on a Perkin-Elmer optima 3300DV ICP spectrometer.

The powder X-ray diffraction (XRD) patterns (scan rate 2^{o} min^{-1}, Cu-Kα radiation λ = 1.5418 Å) were recorded on a Siemens D5005 diffractometer with a graphite monochromator at room temperature. The FT-IR spectra of the samples were obtained using KBr pellets within 4000-500 cm^{-1} on a Nicolet Impact 410 FTIR spectrometer. The differential thermal (DT) and the thermogravimetric analyses (TGA) were conducted on a Netzsch STA 449C thermal analyzer, under a flow of dry air at a heating rate of 10 K min^{-1}.

Synthesis and general characterization: Single crystals of **1** suitable for X-ray diffraction were synthesized from an aqueous solution that contained uranium component and organic ligands under a hydrothermal condition. The pure single-phase product of **1** was obtained, as confirmed by ICP and C, H and N elemental analysis, and by comparison of the observed powder XRD pattern with that generated from the single-crystal X-ray data.

The IR spectrum of **1** shows peaks at about 3000-3600 and 1600-1700 cm^{-1}, corresponding to water stretching and bending modes in the compound. Main IR features (KBr): υ = 3475w, 3370s, 3113w, 2925w, 2357w, 1625m, 1584s, 1526s, 1472m, 1414s, 1387m, 1274w, 1220w, 1162w, 1117m, 1063w, 1014w, 965w, 905s, 856w, 821m, 775w, 717m, 664m, 565m cm^{-1}.

Single-crystal X-ray data for **1** were collected at 293(2) K on a Bruker Smart-CCD diffractometer (Mo-Kα, λ = 0.71073 Å). The structure was solved by direct methods (SHELXTL Version 5.10), and refined with the full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically and the aromatic hydrogen atoms were calculated ($d_{C\text{-}H}$ = 0.93 Å) and fixed with thermal parameters based on the carbon atoms to which they are bonded. The six H atoms attached to the oxygen atoms (Ow) of three water molecules in the empirical formula (([Ni(H_2O)QA (bipy)$U_{2.5}O_7$(H_2O)OAc]·H_2O) were not located. Of the 7063 reflections measured ($2.43 \leqslant\theta\leqslant 25.01^{o}$), 4979 symmetry-independent reflections were used to solve the structure. Based on all these data and 397 refined parameters, $R1$ = 0.0346 [$I > 2\sigma(I)$], $wR2$ = 0.0943, and the goodness-of-fit on F^2 was 1.046. The water molecules disordered over three crystallographically unique sites in the crystal structure of **1** was assigned partial occupancy factors, for a better structural resolution.

Adsorption measurement: the adsorption isotherms of H_2O were obtained at 293 K by measuring the increase in weight at equilibrium as a function of relative pressure. Measurements were performed using a CAHN 2000 electrogravimetric balance. A known weight (typically 20-40 mg) of the as-synthesized sample was placed in a cylindrical Pt bucket, and then subjected to a heating program (300 ^{o}C, 3h) at vacuum in order to remove the guest water molecules. A point isotherm was recorded at the equilibrium state (the stage when no further weight change was observed).

Photocatalytic testing: photocatalytic reactions in aqueous phase were conducted in a water-cooled quartz (for Hg lamp UV light) or Pyrex (for xenon lamp light) cylindrical cell configuration. The reaction mixture inside the cell was maintained at 20 ± 2 ^{o}C by a continuous flow of water through an external cooling coil with magnetic

stirring, and were illuminated from an internal light source with about 2 cm optical path length. The UV light source was a 125 W high-pressure mercury lamp (HPML, main output 313.2 nm). The solar light experiments were performed using a 400 W xenon lamp (radiation wavelength > 400 nm). After the suspension containing a catalyst (160 mg) and the fresh aqueous solution of MB (80 mL, 0.10 $mmolL^{-1}$) was ultrasonicated for 5 min and magnetically stirred in the dark for ca. 30 min to establish an adsorption/desorption equilibrium confirmed by monitoring the absorbance (at λ = 600 nm) characteristic of the target MB (after stirred in the dark 30 min, no change for the absorbance), the lamp was inserted into the suspension. At given irradiation time intervals, 2 mL samples were collected, filtered through a Millipore filter to remove catalyst particles, and analyzed immediately by UV-vis spectroscopy with a Perkin-Elmer Lambda 20 UV-vis spectrometer. The photocatalytic performance of the catalysts was estimated by monitoring the variation of the dye concentrations through UV-vis spectroscopy.

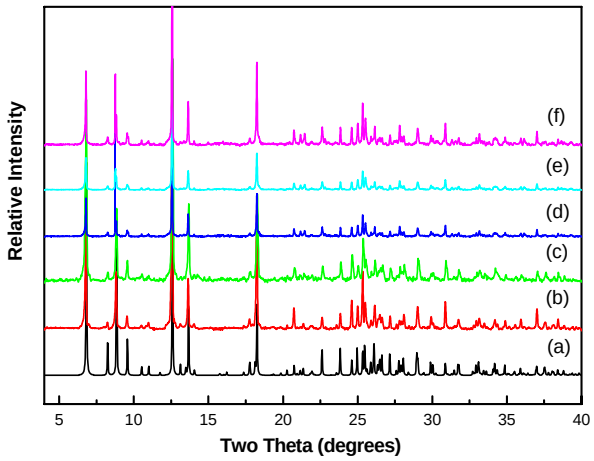

Figure S1. Comparison of the simulated XRD pattern (a) for the as-synthesized **1** on the basis of the single crystal structure with the experimental XRD patterns for the as-synthesized compound (b), for the samples calcined at 300 °C for 3 h (c), for the samples after photocatalysis testing (MB) by UV irradiation (d), for the samples after photocatalysis testing (MB) by visible light irradiation (e) and for the samples after dehydration-rehydraton process (f).

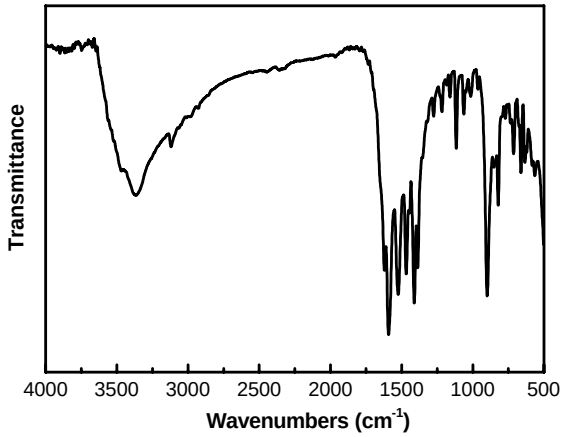

Figure S2. Infrared spectrum of **1**.

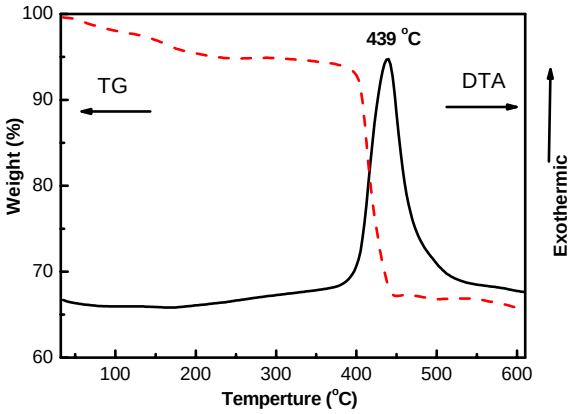

Figure S3. TG and DTA curves of **1**.

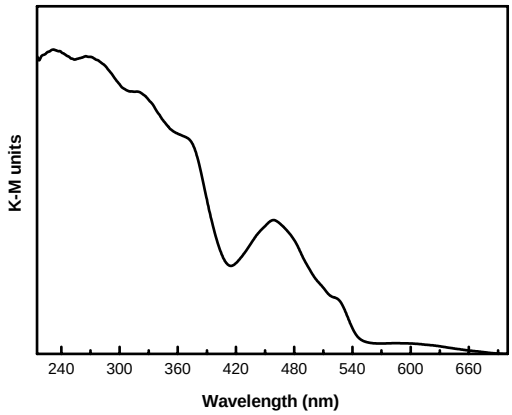

Figure S4. UV-vis diffuse reflectance spectrum for **1** using $BaSO_4$ as the background.

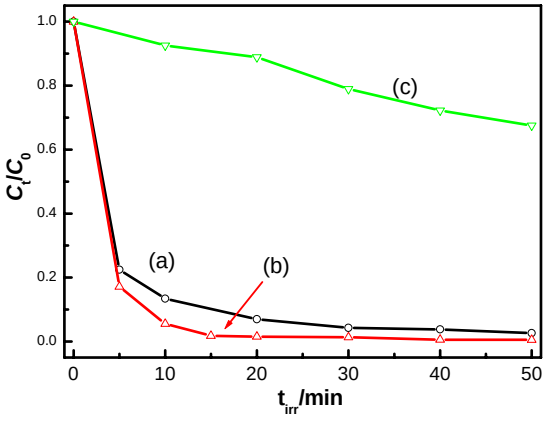

Figure S5. Concentration changes of MB under UV irradiation in the presence of (a) **1** (160 mg), (b) the commercial TiO_2 Degussa P-25 (160 mg) and (c) no photocatalyst. It is seen that the photocatalytic activity of **1** is comparable with that of TiO_2 which is being widely used as a photocatalyst.

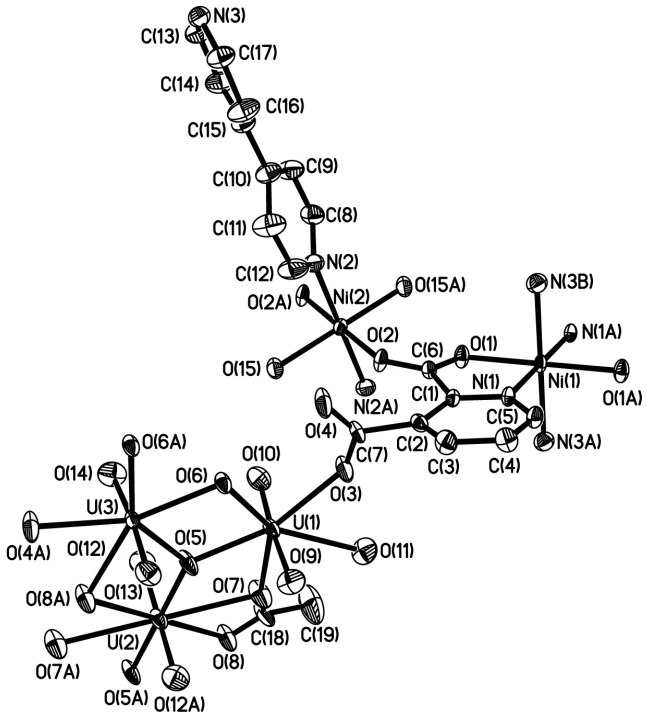

Figure S6. ORTEP drawing of the asymmetric unit of **1**. Thermal ellipsoids are shown at 50 % probability.

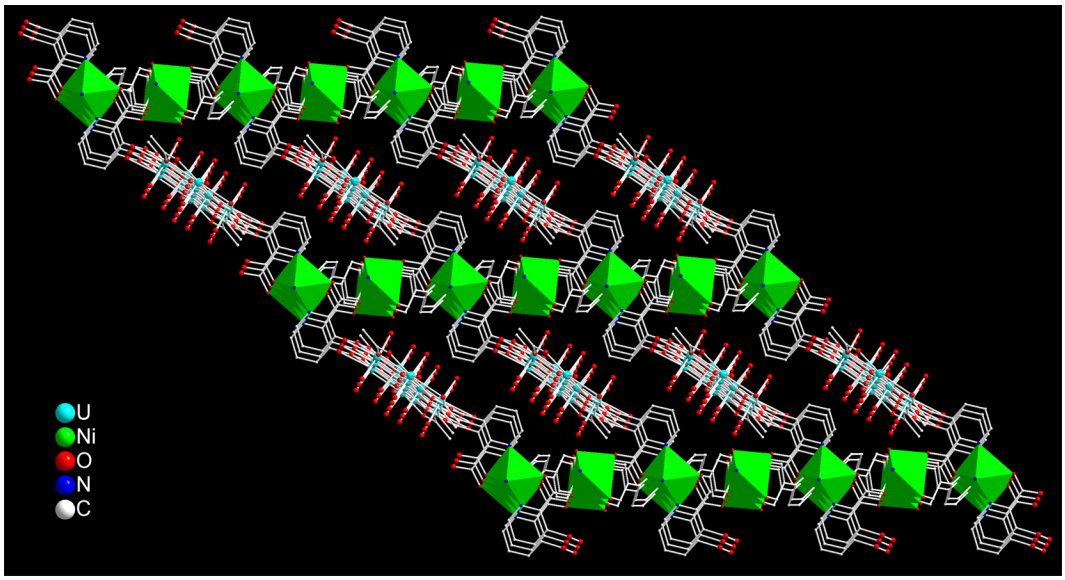

Figure S7. View of the structure of **1** along the *b* axis. Channels are obvious along this direction.

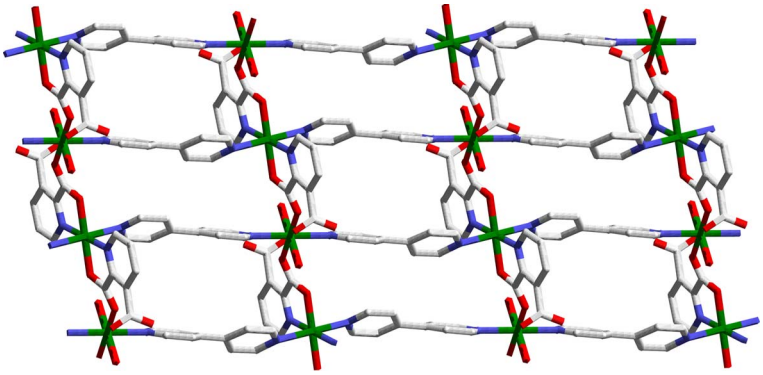

Figure S8. View of the Ni-organic layer along the *ab* plane in **1**.

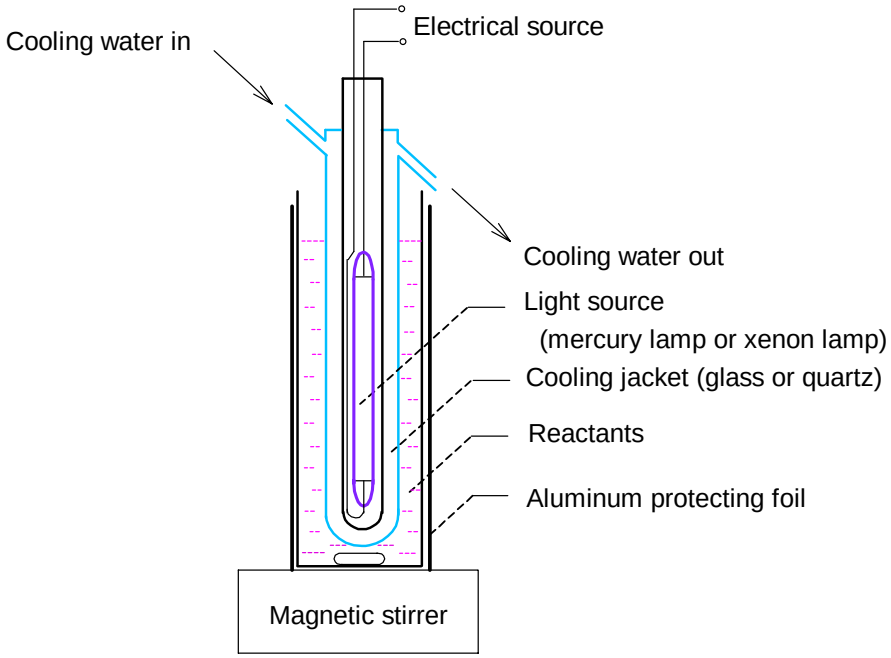

Figure S9. Schematic diagram of the photoreactor. When irradiated with UV light (mercury lamp), water-cooled quartz cylindrical cell configuration was used; while irradiated with xenon-lamp light, water-cooled Pyrex configuration was used.

Table S1. Crystal data and structure refinement for **1**.

empirical formula	$C_{19}H_{20}N_3NiO_{16}U_{2.5}$
formula weight	1200.17
temperature [K]	293(2)
crystal system	Triclinic
space group	*P*-1
a [Å]	10.5466(2)
b [Å]	10.8779(2)
c [Å]	13.4741(3)
α [°]	89.1470(10)
β [°]	74.0720(10)
γ [°]	80.1120(10)
V [Å^3]	1463.54(5)
Z	2
ρ [Mg/m^3]	2.723
μ [mm^{-1}]	14.053
F(000)	1082
theta range [°]	2.43-25.01
limiting indices	-12≤h≤7, -12≤k≤12, -16≤l≤15
reflections collected / unique	7063/4979
completeness to theta = 25.01	96.4 %
data / parameters	4979/397
GooF	1.046
$R1^a/wR2^b$ [I>2σ(I)]	0.0346/0.0943
*R*1/*wR*2 (all data)	0.0371/0.0958

[a] $R_1 = \sum \| F_o \| - | F_c \| / \sum | F_o |$, [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$.

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)[a]
U(1)	3298(1)	2518(1)	3947(1)	22(1)
U(2)	5000	5000	5000	26(1)
U(3)	5514(1)	1335(1)	5534(1)	18(1)
Ni(1)	0	0	0	17(1)
Ni(2)	5000	0	0	18(1)
O(1)	1873(5)	186(5)	33(4)	24(1)
O(2)	3227(5)	-212(5)	1052(4)	22(1)
O(3)	2305(6)	1078(5)	3190(5)	36(2)
O(4)	2957(7)	-925(5)	3392(5)	39(2)
O(5)	4554(7)	3097(5)	4870(5)	37(2)
O(6)	4217(6)	773(5)	4527(5)	26(1)
O(7)	3342(8)	4816(6)	3884(6)	48(2)
O(8)	4003(7)	6590(5)	3871(5)	39(2)
O(9)	1886(7)	2720(6)	5081(5)	39(2)
O(10)	4597(7)	2400(6)	2740(5)	35(2)
O(11)	1469(7)	3580(6)	3113(5)	41(2)
O(12)	6427(7)	4632(6)	3889(6)	42(2)
O(13)	4119(6)	1466(6)	6675(5)	33(1)
O(14)	6976(7)	1297(6)	4461(5)	40(2)
O(15)	5630(6)	424(6)	1265(4)	30(1)
O(1W)	8996(14)	2678(14)	3425(14)	58(4)
O(2W)	8320(30)	6130(30)	2740(20)	48(7)
O(2W')	9150(30)	5670(20)	3088(19)	38(6)
N(1)	-179(6)	-318(5)	1542(5)	17(1)
N(2)	5833(7)	-1862(6)	157(5)	25(2)
N(3)	9251(7)	-8045(6)	356(5)	26(2)
C(1)	941(7)	-217(6)	1795(6)	18(2)
C(2)	1033(8)	-314(6)	2807(6)	19(2)
C(3)	-35(9)	-642(8)	3526(6)	29(2)
C(4)	-1204(9)	-788(8)	3277(6)	27(2)
C(5)	-1223(7)	-586(7)	2275(6)	21(2)
C(6)	2117(7)	-48(7)	898(6)	20(2)
C(7)	2209(8)	-36(7)	3143(6)	23(2)
C(8)	6619(9)	-2546(8)	-674(6)	30(2)
C(9)	7297(10)	-3727(8)	-626(7)	36(2)
C(10)	7159(9)	-4298(8)	327(7)	31(2)
C(11)	6351(11)	-3591(9)	1198(7)	44(2)
C(12)	5704(10)	-2395(8)	1077(7)	38(2)

C(13)	9761(9)	-7203(8)	-311(7)	33(2)
C(14)	9118(10)	-5992(8)	-331(7)	35(2)
C(15)	7883(9)	-5569(8)	389(7)	31(2)
C(16)	7397(10)	-6409(8)	1109(7)	37(2)
C(17)	8087(9)	-7608(8)	1076(7)	34(2)
C(18)	3368(11)	5896(8)	3540(8)	42(2)
C(19)	2763(17)	6276(13)	2672(12)	76(4)

Table S3. Bond lengths [Å] and angles [º] for **1**[a].

U(1)-O(9)	1.803(7)	U(1)-O(10)	1.806(7)
U(1)-O(6)	2.213(5)	U(1)-O(5)	2.217(6)
U(1)-O(3)	2.406(5)	U(1)-O(7)	2.507(6)
U(1)-O(11)	2.588(6)		
U(2)-O(12)	1.800(7)	U(2)-O(12)#1	1.800(7)
U(2)-O(5)	2.220(5)	U(2)-O(5)#1	2.220(5)
U(2)-O(7)	2.633(7)	U(2)-O(7)#1	2.633(7)
U(2)-O(8)	2.566(6)	U(2)-O(8) #1	2.566(6)
U(3)-O(14)	1.796(6)	U(3)-O(13)	1.800(6)
U(3)-O(6)#2	2.261(5)	U(3)-O(5)	2.297(5)
U(3)-O(6)	2.326(5)	U(3)-O(4)#2	2.431(6)
U(3)-O(8)#1	2.584(6)		
Ni(1)-O(1)	2.033(5)	Ni(1)-O(1)#3	2.033(5)
Ni(1)-N(1)	2.063(6)	Ni(1)-N(1)#3	2.063(6)
Ni(1)-N(3)#4	2.150(7)	Ni(1)-N(3)#5	2.150(7)
Ni(2)-O(2)	2.060(5)	Ni(2)-O(2)#6	2.060(5)
Ni(2)-O(15)	2.075(5)	Ni(2)-O(15)#6	2.075(5)
Ni(2)-N(2)	2.097(6)	Ni(2)-N(2)#6	2.097(6)
O(3)-U(1)-O(11)	65.9(2)	O(3)-U(1)-O(7)	136.3(2)
O(5)-U(1)-O(7)	67.44(19)	O(5)-U(1)-O(11)	137.5(2)
O(5)-U(1)-O(3)	156.16(19)	O(6)-U(1)-O(3)	81.82(19)
O(6)-U(1)-O(5)	74.3(2)	O(6)-U(1)-O(7)	141.6(2)
O(6)-U(1)-O(11)	146.7(2)	O(7)-U(1)-O(11)	71.5(2)
O(9)-U(1)-O(10)	174.1(3)	O(9)-U(1)-O(7)	92.2(3)
O(9)-U(1)-O(6)	91.4(3)	O(9)-U(1)-O(5)	89.7(3)
O(9)-U(1)-O(3)	90.6(3)	O(9)-U(1)-O(11)	81.2(3)
O(10)-U(1)-O(6)	93.7(3)	O(10)-U(1)-O(7)	85.5(3)
O(10)-U(1)-O(5)	94.4(3)	O(10)-U(1)-O(11)	92.9(3)
O(10)-U(1)-O(3)	87.3(3)		
O(5)-U(2)-O(7)	65.09(19)	O(5)#1-U(2)-O(7)	114.91(19)
O(5)#1-U(2)-O(7)#1	65.09(19)	O(5)#1-U(2)-O(8)	66.22(19)
O(5)-U(2)-O(7)#1	114.91(19)	O(5)-U(2)-O(8)	113.78(19)
O(5)-U(2)-O(8)#1	66.22(19)	O(5)#1-U(2)-O(8)#1	113.78(19)
O(5)#1-U(2)-O(5)	180.000(1)	O(8)#1-U(2)-O(8)	180.0(2)
O(8)#1-U(2)-O(7)#1	49.06(19)	O(8)-U(2)-O(7)#1	130.94(19)
O(12)-U(2)-O(12)#1	180.000(1)	O(12)-U(2)-O(8)#1	93.7(3)
O(12)-U(2)-O(5)#1	90.7(3)	O(12)#1-U(2)-O(8)#1	86.3(3)
O(12)#1-U(2)-O(5)#1	89.3(3)	O(12)-U(2)-O(8)	86.3(3)
O(12)-U(2)-O(5)	89.3(3)	O(12)#1-U(2)-O(8)	93.7(3)
O(12)#1-U(2)-O(5)	90.7(3)	O(12)-U(2)-O(7)#1	88.6(3)

O(12)-U(2)-O(7)	91.4(3)	O(12)#1-U(2)-O(7)#1	91.4(3)
O(12)#1-U(2)-O(7)	88.6(3)	O(8)#1-U(2)-O(7)	130.94(19)
O(7)#1-U(2)-O(7)	180.000(1)	O(8)-U(2)-O(7)	49.06(19)
O(4)#2-U(3)-O(8)#1	69.86(19)	O(5)-U(3)-O(8)#1	64.91(19)
O(5)-U(3)-O(4)#2	134.6(2)	O(5)-U(3)-O(6)	70.7(2)
O(6)#2-U(3)-O(8)#1	152.23(19)	O(6)#2-U(3)-O(4)#2	82.37(19)
O(6)-U(3)-O(8)#1	135.55(18)	O(6)-U(3)-O(4)#2	154.59(19)
O(6)#2-U(3)-O(6)	72.2(2)	O(6)#2-U(3)-O(5)	142.7(2)
O(13)-U(3)-O(8)#1	87.6(3)	O(13)-U(3)-O(4)#2	89.6(3)
O(13)-U(3)-O(6)#2	92.6(3)	O(13)-U(3)-O(5)	92.0(3)
O(13)-U(3)-O(6)	91.2(3)	O(14)-U(3)-O(6)#2	90.8(3)
O(14)-U(3)-O(5)	87.9(3)	O(14)-U(3)-O(8)#1	87.3(3)
O(14)-U(3)-O(6)	94.0(3)	O(14)-U(3)-O(4)#2	86.5(3)
O(14)-U(3)-O(13)	174.5(3)		
O(1)-Ni(1)-O(1)#3	180.0	O(1)#3-Ni(1)-N(3)#5	92.1(2)
O(1)-Ni(1)-N(1)	81.0(2)	N(1)-Ni(1)-N(3)#5	89.7(2)
O(1)#3-Ni(1)-N(1)	99.0(2)	N(1)#3-Ni(1)-N(3)#5	90.3(2)
O(1)-Ni(1)-N(1)#3	99.0(2)	N(3)#4-Ni(1)-N(3)#5	180.0(4)
O(1)#3-Ni(1)-N(1)#3	81.0(2)	O(1)-Ni(1)-N(3)#5	87.9(2)
N(1)-Ni(1)-N(1)#3	180.0(3)	N(1)-Ni(1)-N(3)#4	90.3(2)
O(1)-Ni(1)-N(3)#4	92.1(2)	N(1)#3-Ni(1)-N(3)#4	89.7(2)
O(1)#3-Ni(1)-N(3)#4	87.9(2)		
O(2)#6-Ni(2)-O(2)	180.0(3)	O(15)-Ni(2)-N(2)	86.7(2)
O(2)#6-Ni(2)-O(15)	93.8(2)	O(15)#6-Ni(2)-N(2)	93.3(2)
O(2)-Ni(2)-O(15)	86.2(2)	O(2)#6-Ni(2)-N(2)#6	90.9(2)
O(2)#6-Ni(2)-O(15)#6	86.2(2)	O(2)-Ni(2)-N(2)#6	89.1(2)
O(2)-Ni(2)-O(15)#6	93.8(2)	O(15)-Ni(2)-N(2)#6	93.3(2)
O(15)-Ni(2)-O(15)#6	180.0(3)	O(15)#6-Ni(2)-N(2)#6	86.7(2)
O(2)#6-Ni(2)-N(2)	89.1(2)	N(2)-Ni(2)-N(2)#6	180.0
O(2)-Ni(2)-N(2)	90.9(2)		

[a] Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+1,-y,-z+1 #3 -x,-y,-z #4 x-1,y+1,z

#5 -x+1,-y-1,-z #6 -x+1,-y,-z #7 x+1,y-1,z

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^2U11+ ... + 2hkabU12]$.

	U11	U22	U33	U23	U13	U12
U(1)	33(1)	18(1)	22(1)	2(1)	-18(1)	-6(1)
U(2)	40(1)	15(1)	30(1)	1(1)	-23(1)	-6(1)
U(3)	21(1)	17(1)	20(1)	1(1)	-11(1)	-5(1)
Ni(1)	13(1)	23(1)	15(1)	2(1)	-7(1)	-3(1)
Ni(2)	12(1)	22(1)	20(1)	-1(1)	-5(1)	-2(1)
O(1)	18(3)	40(3)	16(3)	4(2)	-8(2)	-7(2)
O(2)	11(3)	36(3)	22(3)	6(2)	-7(2)	-6(2)
O(3)	45(4)	24(3)	52(4)	1(3)	-36(3)	-7(3)
O(4)	47(4)	28(3)	62(4)	8(3)	-44(4)	-11(3)
O(5)	68(5)	15(3)	46(4)	3(2)	-45(4)	-7(3)
O(6)	33(3)	17(3)	36(3)	1(2)	-24(3)	-6(2)
O(7)	72(5)	27(3)	62(5)	8(3)	-48(4)	-8(3)
O(8)	68(5)	20(3)	48(4)	8(3)	-44(4)	-11(3)

O(9)	44(4)	38(4)	33(4)	6(3)	-8(3)	-1(3)
O(10)	43(4)	32(3)	33(3)	2(3)	-11(3)	-15(3)
O(11)	46(4)	41(4)	36(4)	12(3)	-17(3)	-4(3)
O(12)	48(4)	35(4)	44(4)	0(3)	-13(3)	-6(3)
O(13)	32(3)	40(4)	27(3)	-2(3)	-1(3)	-13(3)
O(14)	33(4)	43(4)	40(4)	0(3)	2(3)	-13(3)
O(15)	22(3)	43(3)	27(3)	-7(3)	-10(2)	-5(3)
O(1W)	33(6)	47(7)	91(9)	26(6)	-12(6)	-11(5)
O(2W)	59(11)	45(10)	41(10)	-1(8)	-6(8)	-21(8)
O(2W')	37(9)	31(9)	32(9)	-13(7)	13(7)	-1(8)
N(1)	10(3)	22(3)	21(3)	2(2)	-5(3)	-4(2)
N(2)	24(4)	27(4)	22(4)	-1(3)	-6(3)	0(3)
N(3)	26(4)	28(4)	25(4)	3(3)	-8(3)	-2(3)
C(1)	16(4)	19(3)	21(4)	-3(3)	-8(3)	-2(3)
C(2)	26(4)	14(3)	20(4)	1(3)	-12(3)	-4(3)
C(3)	31(5)	36(5)	21(4)	2(3)	-10(4)	-3(4)
C(4)	28(5)	35(4)	19(4)	5(3)	-5(3)	-10(4)
C(5)	15(4)	29(4)	20(4)	1(3)	-3(3)	-5(3)
C(6)	16(4)	21(4)	24(4)	1(3)	-8(3)	-6(3)
C(7)	26(4)	27(4)	21(4)	-2(3)	-13(3)	-9(3)
C(8)	41(5)	31(4)	17(4)	1(3)	-11(4)	-2(4)
C(9)	46(6)	31(5)	25(4)	-3(4)	-8(4)	5(4)
C(10)	31(5)	26(4)	32(5)	7(3)	-5(4)	-1(4)
C(11)	62(7)	32(5)	25(5)	5(4)	-1(5)	4(4)
C(12)	50(6)	33(5)	21(4)	-2(4)	-2(4)	4(4)
C(13)	28(5)	30(4)	36(5)	-1(4)	-2(4)	-3(4)
C(14)	40(5)	23(4)	37(5)	0(4)	-2(4)	-5(4)
C(15)	35(5)	27(4)	29(4)	4(3)	-8(4)	-3(4)
C(16)	38(5)	31(5)	29(5)	3(4)	6(4)	5(4)
C(17)	37(5)	26(4)	33(5)	2(4)	-6(4)	1(4)
C(18)	67(7)	18(4)	57(6)	-1(4)	-43(6)	-9(4)
C(19)	103(8)	70(7)	87(8)	21(6)	-68(7)	-32(6)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	*U*(eq)
H(3)	16	-772	4198	80
H(4)	-1931	-1011	3767	80
H(5)	-2005	-639	2097	80
H(8)	6709	-2198	-1320	80
H(9)	7848	-4150	-1226	80
H(11)	6246	-3916	1852	80
H(12)	5154	-1942	1663	80
H(13)	10593	-7453	-783	80
H(14)	9502	-5456	-823	80
H(16)	6598	-6164	1619	80
H(17)	7735	-8149	1576	80
H(19A)	2320	5629	2524	80
H(19B)	3456	6407	2069	80
H(19C)	2126	7035	2869	80