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Solvothermal Synthesis and Crystal Structure of Uranyl Complexes with 1,1-Cyclobutanedicarboxylic and (1*R*,3*S*)-(+)-Camphoric Acids – Novel Chiral Uranyl-Organic Frameworks

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Reaction of the 1,1-cyclobutanedicarboxylic (H_2L^1) or (1*R*,3*S*)-(+)-camphoric (H_2L^2) acids with uranyl nitrate under solvothermal conditions gives novel uranyl-organic assemblages. The complex $[Hpy]_2[UO_2L^1(NO_3)]_2$ (**1**), obtained in pyridine, is a dimeric, dinuclear species in which the closeness of the two carboxylate groups prevents the formation of a more extended architecture. The chiral complexes $[UO_2L^2(py)_2]\cdot py$ (**2**) and $[UO_2L^2MeOH]\cdot MeOH$ (**3**), obtained with the enantiopure, divergent camphorate ligand in either pyridine (**2**) or methanol/water (**3**), are comprised of zigzag chains defining channels and a microporous assemblage or of undulated sheets based on tessellated 8- and 32-membered rings, respectively. Apart from a zinc(II) complex previously described, compounds **2** and **3** are the only examples of metal complexes with camphoric acid crystallographically characterized.

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Introduction

Several research groups have recently illustrated the potential of hydrothermal methods for the synthesis of uranyl-organic polymers, with a particular emphasis on obtaining microporous or luminescent materials.[1] Most of the compounds thus investigated include organic polycarboxylic acids as ligands and exploit the huge variety of this class of molecules. Even polyacid complexes recalcitrant to other crystallization procedures can be obtained in this way, as evidenced lately by the cases of uranyl citrate and tricarballylate.[2] Among organic polyacids, particularly interesting are those which, through a proper choice of geometry and rigidity, can assemble uranyl ions to form metallacycles, as is the case for tetrahydrofuran-2*r*,3*t*,4*t*,5*c*-tetracarboxylic acid.[3] The latter reacts with uranyl ions in organic solvents at room temperature to give tri- or tetranuclear cyclic species. Other candidates that seemed promising in this context are 1,1-cyclobutanedicarboxylic (H_2L^1) and (1*R*,3*S*)-(+)-camphoric (H_2L^2) acids, but these two ligands, when treated with uranyl nitrate in the presence of bases such as triethylamine or alkali metal hydroxides, did not give crystals, neither in organic solvents at room temperature nor under hydrothermal conditions. Suitable crystals could only be obtained, albeit in very low yields, under solvothermal conditions, using pyridine or methanol/water as the solvent and the crystal structures of the three species thus characterized are reported herein. A search of the Cambridge Structural Database (CSD, Version 5.27)[4] indicates that, apart from a polymeric terbium(III) complex,[5] all the metal complexes of 1,1-cyclobutanedicarboxylic acid which have been crystallographically characterized include 3d ions [platinum(II) and palladium(II) in particular]. In the case of (1*R*,3*S*)-(+)-camphoric acid, only one zinc(II) complex has been reported.[6] The present complexes are thus the first with an actinide ion for both ligands and with an f element for the second. Much work has recently been devoted to the synthesis of chiral nanoporous materials, with potential applications in enantioselective separation or heterogeneous asymmetric catalysis.[7] A particularly simple way to obtain such assemblages is the use of enantiopure chiral ligands, such as L- or D-tartaric acid,[7e,7g,7h] as metal bridges. The present results show that (1*R*,3*S*)-(+)-camphoric acid deserves to be considered as a useful building block in this context.

Results and Discussion

In the presence of pyridine, the diacid H_2L^1 gives the centrosymmetric, dinuclear complex $[Hpy]_2[UO_2L^1(NO_3)]_2$ (**1**), represented in Figure 1. The L^1 dianions chelate each of the metal ions, one of them through one oxygen atom of each acid group (O3, O5) and the other by a single acid group (O5, O6). The oxygen atoms O5 and O5′ are thus bridging the two metal centres in a μ_2 fashion. The four U–$O_{carboxy}$ bond lengths are quite different (Table 1), likely as a result of the constraints arising from the rigid geometry of the ligand, the shortest being U–O3 and the longest U–O6′; the average U–(O5,O5′) bond [2.45(3) Å] is longer

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than U–O3 due to the bridging nature of these oxygen atoms. All these values are in the range of U–$O_{carboxy}$ distances for uranyl complexes reported in the CSD, 2.24–2.64 Å [mean value 2.42(7)]. The coordination sphere of the metal atom is completed by a bidentate nitrate ion, with an average U–O bond length of 2.509(3) Å, close to the mean value for bidentate nitrate ions in the CSD, 2.52(3) Å. The uranium atom is thus in a hexagonal-bipyramidal environment, quite usual when small-bite bidentate ligands are used, and is located at 0.0820(8) Å from the mean plane defined by the six equatorial donor atoms (r.m.s. deviation 0.039 Å). The coordination polyhedra of the two metal atoms share a common edge (O5–O5′), with a U···U′ distance of 4.2896(3) Å. A similar coordination mode is observed with other diacids, such as adipic acid, in which case the uranyl dimers are further linked in a three-dimensional network.[1c] The double negative charge of the complex is balanced by the positive charges of two pyridinium ions, which are involved in hydrogen bonds with the uncoordinated carboxylic oxygen atoms O4 and O4′ [N2···O4 2.677(4) Å, N2–H2···O4 170°]. It appears that, in contrast with tetrahydrofuran-2*r*,3*t*,4*t*,5*c*-tetracarboxylic acid, in which the acid groups are in the β- or γ-position relative to one another, their α-position in L^1 and the ensuing easy chelation of the metal ion through one oxygen atom from each result in these acid groups being nearly coplanar [dihedral angle between the two COO planes 34.3(4)°]. This ligand thus appears badly adapted to the synthesis of cyclic uranyl complexes.

Table 1. Environment of the uranium atoms: selected bond lengths [Å] and angles [°].

1[a]	U–O1	1.766(3)	O1–U–O2	177.47(13)
	U–O2	1.758(3)	O3–U–O5	68.09(10)
	U–O3	2.327(4)	O5–U–O5′	58.01(14)
	U–O5	2.424(2)	O5′–U–O6′	51.36(9)
	U–O5′	2.481(3)	O6′–U–O8	63.40(10)
	U–O6′	2.544(3)	O8–U–O7	51.03(11)
	U–O7	2.512(3)	O7–U–O3	68.02(9)
	U–O8	2.506(3)		
2[b]	U–O1	1.759(6)	O1–U–O2	178.6(3)
	U–O2	1.772(7)	O3–U–O4	52.3(2)
	U–O3	2.420(6)	O4–U–N1	63.7(2)
	U–O4	2.471(6)	N1–U–O5′	65.4(2)
	U–O5′	2.464(6)	O5′–U–O6′	52.6(2)
	U–O6′	2.441(6)	O6′–U–N2	63.6(2)
	U–N1	2.552(6)	N2–U–O3	63.0(2)
	U–N2	2.569(7)		
3[c]	U1–O1	1.766(9)	O1–U1–O2	177.4(4)
	U1–O2	1.753(8)	O5–U1–O9	85.5(3)
	U1–O5	2.312(9)	O9–U1–O13	76.9(3)
	U1–O9	2.354(8)	O13–U1–O11′	71.1(2)
	U1–O11′	2.519(7)	O11′–U1–O12′	52.8(2)
	U1–O12′	2.414(7)	O12′–U1–O5	74.1(3)
	U1–O13	2.393(8)		
	U2–O3	1.741(8)	O3–U2–O4	178.1(4)
	U2–O4	1.755(8)	O6–U2–O10	79.4(3)
	U2–O6	2.330(8)	O10–U2–O7"	77.3(3)
	U2–O10	2.294(7)	O7"–U2–O8"	52.6(3)
	U2–O7"	2.412(8)	O8"–U2–O14	72.8(3)
	U2–O8"	2.497(7)	O14–U2–O6	78.1(3)
	U2–O14	2.365(8)		

[a] Symmetry code: ′: $1 - x$, $1 - y$, $2 - z$. [b] Symmetry code: ′: $1.5 - x$, $-y$, $0.5 + z$. [c] Symmetry codes: ′: $1 - x$, $0.5 + y$, $1 - z$; ″: $-x$, $y - 0.5$, $-z$.

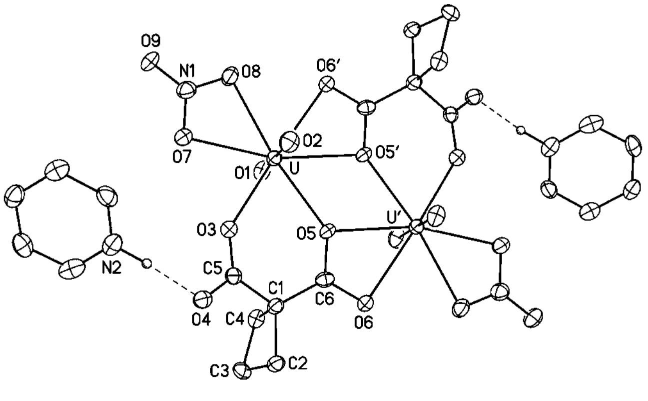

Figure 1. View of the complex $[Hpy]_2[UO_2L^1(NO_3)]_2$ (**1**). Hydrogen atoms not involved in hydrogen bonds have been omitted for clarity. Hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 50% probability level. Symmetry code: ′: $1 - x$, $1 - y$, $2 - z$.

When treated with uranyl nitrate under conditions similar to those leading to complex **1**, H_2L^2 gives the complex $[UO_2L^2(py)_2]\cdot py$ (**2**). The two acid groups being in γ-positions with respect to one another and separated by the bulky methyl substituents, metal ion chelation through one atom from each group is no longer possible. Each acid group chelates a metal ion instead, giving rise to a one-dimensional polymer in which the motifs are related to one another by a binary screw axis (Figure 2a). The uranium atom is in a hexagonal-bipyramidal environment, being bound, in addition to the two oxo atoms, to four carboxylic oxygen atoms [mean U–$O_{carboxy}$ bond length 2.45(2) Å] and two pyridine molecules in *trans* positions [mean U–N bond length 2.561(8) Å]. The metal atom is located at 0.010(3) Å from the mean equatorial plane (r.m.s. deviation 0.083 Å) and the dihedral angle between the equatorial planes of two successive metal atoms along the chain is 72.80(11)°. The geometry of the rigid ligand is not modified by metal ion coordination since the dihedral angle between the two COO planes is 63.2(8)° in **2**, whereas values in the range 61.9–63.4° are observed in the uncomplexed camphoric acid.[8,9] Such a value of the angle between uranyl equatorial planes and the overall coordination geometry could in principle lead to a cyclic species, but five units would be necessary for ring closure, giving a large complex probably less stable than the chiral, undulated chain which is formed instead. The packing of these chains gives rise to chiral channels directed along the *a*-axis in the crystal structure, in which the solvent pyridine molecules are located (Figure 2b) and which could in principle be interesting for the recognition of chiral guests. The absence of any significant π-stacking or CH···π interactions between host and guest suggests that the included pyridine molecules, held primarily by van der Waals interactions, have at most little contribution in the framework formation. This assemblage presents some similitude with several hydrogen-bonded organic-organic polymers including H_2L^2 and polyamines recently reported.[9] With polyamines such as 1,2-bis(4-pyridyl)ethane or DABCO (1,4-diazabicyclo[2.2.2]octane), zigzag chains with curved parts defined by camphoric acid are observed, whereas 4,4′-bipyridine gives a spiral arrangement and other polyamines give more intricate sheets or frameworks. The coordination bonds with uranyl ions being much more directional than hydrogen bonds, the chains in **2** appear more regular (the polyamine complexes are highly disordered) and the separation between camphoric acid units is reduced. Moreover, no channels are formed in the case of the organic-organic chains analogous to those in complex **2**. This analogy between linear spacers such as 4,4′-bipyridine, which is much used, in association with 3d transition metal ions, to generate squares, boxes or cubes,[10] and the stereochemically constrained uranyl ion has been pointed out previously and several examples have been given of the use of uranyl ions as edge- or face-defining units.[3,11]

The presence of coordinated pyridine in complex **2** can be thought of as preventing the formation of a more extended assemblage. For this reason, the reaction between camphoric acid and uranyl nitrate under solvothermal conditions was repeated in a methanol/water solution and in the presence of NaOH as a base. The chiral complex thus obtained, $[UO_2L^2MeOH]\cdot MeOH$ (**3**), differs markedly from **2**. Each camphorate dianion bridges three uranium atoms, two of them in a monodentate (μ_2-carboxylato-*O,O′*) and the other in a bidentate, chelating fashion (Figure 3a). Each metal atom is bound in its turn to three L^2 molecules [average $U–O_{carboxy}$ bond length 2.32(2) Å for the μ_2-carboxylato-*O,O′* groups and 2.46(5) Å for the chelating groups] and its environment is completed by a methanol molecule [average U–O bond length 2.379(14) Å, in agreement with the mean value from the CSD, 2.39(11) Å]. The metal atom environment is thus pentagonal-bipyramidal, as

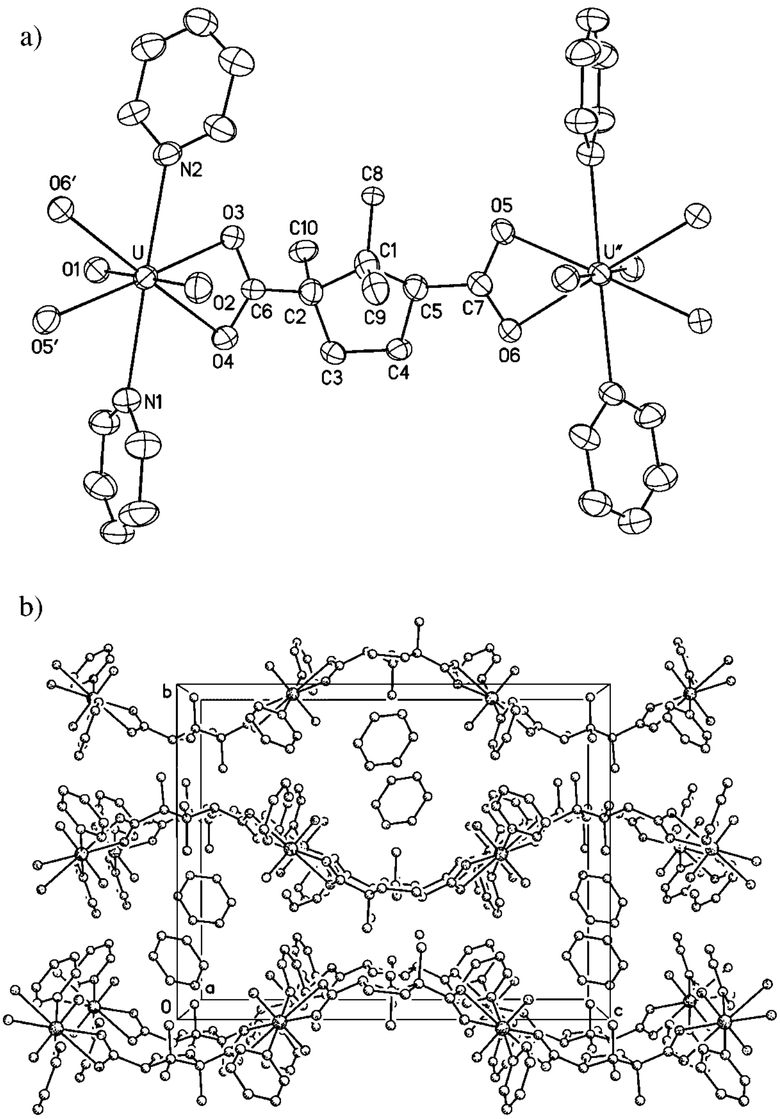

Figure 2. (a) View of the complex $[UO_2L^2(py)_2]\cdot py$ (**2**). Hydrogen atoms and solvent molecules have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. Symmetry codes: ′: 1.5 – *x*, –*y*, 0.5 + *z*; ″: 1.5 – *x*, –*y*, *z* – 0.5. (b) View of the packing along the *a*-axis. A single chain is shown at the top.

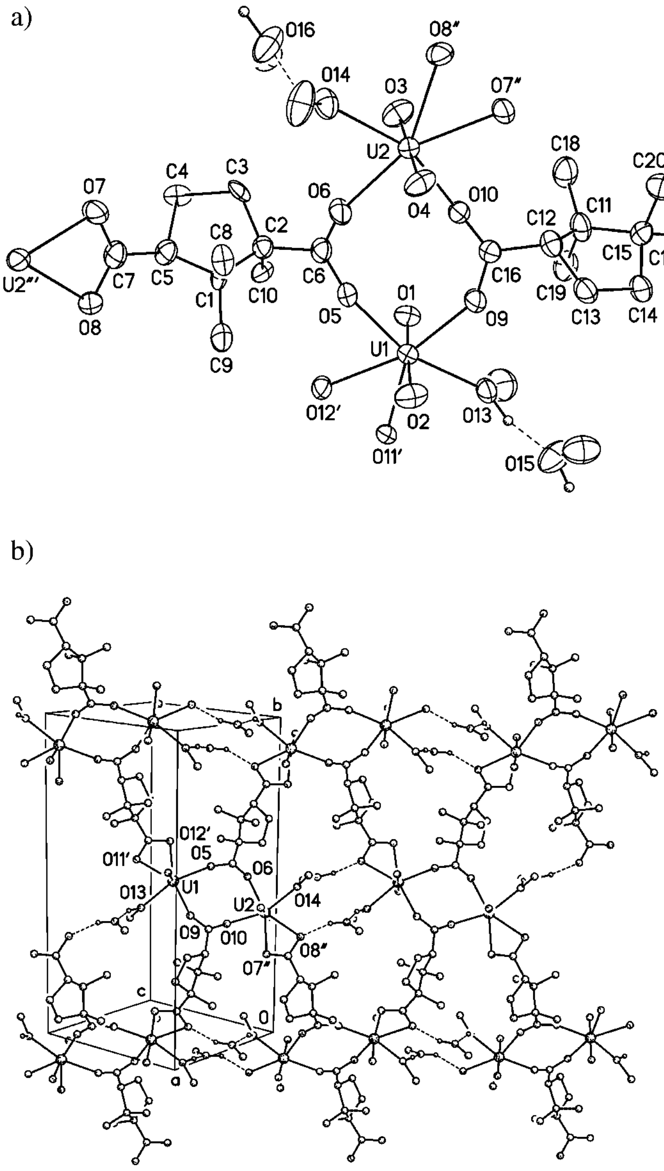

Figure 3. (a) View of the complex $[UO_2L^2MeOH]\cdot MeOH$ (**3**). Hydrogen atoms not involved in hydrogen bonds have been omitted for clarity. Hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: ′: 1 – *x*, 0.5 + *y*, 1 – *z*; ′′: –*x*, *y* – 0.5, –*z*; ′′′: –*x*, 0.5 + *y*, –*z*; ′′′′: 1 – *x*, *y* – 0.5, 1 – *z*. (b) View of the two-dimensional assemblage in **3**.

expected since only one ligand is chelating. The metal centres are displaced by 0.004(4) and 0.003(4) Å from the associated equatorial mean planes (r.m.s. deviations 0.09 and 0.04 Å). The two uranium atoms linked by the μ_2-carboxylato-*O*,*O′* groups are separated by 5.5737(5) Å and they are part of a nearly planar eight-membered ring subunit [the dihedral angle between the two average uranyl equatorial planes is 7.2(4)°]. The four L^2 molecules which diverge from each subunit further assemble these subunits to form undulated sheets in which the curved parts correspond to the L^2 linkers [dihedral angle between the two COO planes: 66.2(12) and 63.3(10)° in the two independent molecules]. Larger, 32-membered elongated rings are formed in the process, which unite four L^2 ligands and four uranyl ions and are doubly bridged in their centre by the hydrogen-bonded and coordinated methanol molecules (Figure 3b). However, no channel is formed through the packing of these sheets, which does not involve inter-sheet hydrogen bonding. By contrast with the case of compound **2** in which it behaves as a simple spacer, L^2 appears in **3** to be able to act as a ring assembler, although not as a molecular metallacycle linker.

Conclusions

The two acids investigated in this work present some characteristics, such as multiple coordination sites and rigidity, which make them attractive ligands for the synthesis of uranyl complexes, in the wake of the results previously obtained with other polyacids. However, the proximity of the two carboxylic groups in the α-diacid H_2L^1 favours uranyl chelation through one oxygen atom from each group, leading, with further chelation of a second metal atom by one of the carboxylate groups, to the formation of a dimeric, dinuclear species. Conversely, the separation of the two carboxylic acid functions in the γ-diacid H_2L^2 prevents similar chelation, but, due to the insufficient curvature of the ligand, either chiral zigzag chains or undulated sheets are formed instead of a molecular metallacycle, which should likely be pentanuclear. Camphoric acid appears nevertheless to be a versatile ligand for metal complexation, leading to very different, one- or two-dimensional assemblages upon varying reaction conditions, and it should therefore benefit from a reappraisal in metal coordination chemistry, particularly for its potential in the synthesis of built-in chiral frameworks. The present results also illustrate the potential of solvothermal synthesis, which can permit the obtention of species unattainable through the more widely used hydrothermal method and also the synthesis of different species from the same building blocks with different organic solvents.

Experimental Section

Starting Materials: 1,1-Cyclobutanedicarboxylic acid and (1*R*,3*S*)-(+)-camphoric acid were purchased from Aldrich and used without further purification.

$[Hpy]_2[UO_2L^1(NO_3)]_2$ (1): 1,1-Cyclobutanedicarboxylic acid (57 mg, 0.40 mmol), $UO_2(NO_3)_2·6H_2O$ (100 mg, 0.20 mmol) and pyridine (3 mL) were placed in a 15-mL tightly closed vessel and heated at 145 °C under autogenous pressure. A few light-yellow single crystals of complex **1** were obtained in about two weeks.

$[UO_2L^2(py)_2]·py$ (2): (1*R*,3*S*)-(+)-Camphoric acid (61 mg, 0.30 mmol), $UO_2(NO_3)_2·6H_2O$ (151 mg, 0.30 mmol) and pyridine (4 mL) were placed in a 20-mL tightly closed vessel and heated at 125 °C under autogenous pressure. Light-yellow single crystals of complex **2** were obtained within 2 d.

$[UO_2L^2MeOH]·MeOH$ (3): (1*R*,3*S*)-(+)-Camphoric acid (61 mg, 0.30 mmol), $UO_2(NO_3)_2·6H_2O$ (151 mg, 0.30 mmol), NaOH (12 mg, 0.30 mmol), demineralized water (1.5 mL) and methanol (3 mL) were placed in a 20-mL tightly closed vessel and heated at 140 °C under autogenous pressure. Light-yellow single crystals of complex **3** were obtained within 3 d.

X-ray Crystallography: The data were collected at 100(2) K with a Nonius Kappa-CCD area detector diffractometer[12] using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The crystals were introduced in glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit-cell parameters were determined from ten frames, then refined on all data. The data (φ- and ω-scans) were processed with HKL2000.[13] The structures were solved by Patterson map interpretation (**1** and **2**) or by direct methods (**3**) with SHELXS-97 and subsequent Fourier difference synthesis and refined by full-matrix least squares on F^2 with SHELXL-97.[14] Absorption effects were corrected empirically with SCALEPACK.[13] All non-hydrogen atoms were refined with anisotropic displacement parameters. The solvent pyridine molecule in **2** was refined as an idealized hexagon with restraints on displacement parameters. The hydrogen atoms bound to the nitrogen atom of the pyridinium ion in compound **1** and to the oxygen atoms of the methanol molecules in **3** were found on Fourier difference maps and all the others were introduced at calculated positions; all were treated as riding atoms with an isotropic displacement parameter equal to 1.2 (OH, NH, CH, CH_2) or 1.5 (CH_3) times that of the parent atom. The absolute configuration in compounds **2** and **3** indicated by the value of the Flack parameter[15] is in agreement with that of the uncomplexed ligand H_2L^2. Crystal data and struc-

Table 2. Crystal data and structure refinement details.

	1	2	3
Empirical formula	$C_{22}H_{24}N_4O_{18}U_2$	$C_{25}H_{29}N_3O_6U$	$C_{12}H_{22}O_8U$
Formula mass	1108.51	705.54	532.33
Crystal system	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_1$
a [Å]	8.5930(4)	9.6288(4)	8.9042(4)
b [Å]	8.8937(5)	14.7667(8)	18.4850(11)
c [Å]	11.4899(7)	19.1379(11)	9.8137(5)
α [°]	96.053(3)	90	90
β [°]	107.979(3)	90	91.599(4)
γ [°]	113.464(3)	90	90
V [Å^3]	739.45(8)	2721.1(2)	1614.65(15)
Z	1	4	4
$D_{calcd.}$ [Mg·m^{-3}]	2.489	1.722	2.190
μ (Mo-K_α) [mm^{-1}]	11.026	6.006	10.086
F(000)	512	1360	1000
Reflections collected	31496	56216	71395
Independent reflections	2797	5139	6083
Observed reflections [$I > 2\sigma(I)$]	2684	4761	5880
R_{int}	0.071	0.067	0.033
Parameters	208	307	390
R_1	0.023	0.039	0.036
wR_2 (all data)	0.049	0.106	0.104
S	1.031	1.064	1.045
Flack parameter	–	0.006(14)	0.003(13)
$\Delta\rho_{min.}$ [e·Å^{-3}]	–1.91	–1.09	–0.84
$\Delta\rho_{max.}$ [e·Å^{-3}]	1.37	1.20	1.36

ture refinement details are given in Table 2. The molecular plots were drawn with SHELXTL.[16] CCDC-604884 to -604886 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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