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Incorporation of U(IV) into Metal-Organic Framework Solids, $[\text{UO}_2(\text{C}_4\text{H}_4\text{O}_4)] \cdot \text{H}_2\text{O}$, $[\text{UO}_2\text{F}(\text{C}_5\text{H}_6\text{O}_4)] \cdot 2\text{H}_2\text{O}$, and $[(\text{UO}_2)_{1.5}(\text{C}_8\text{H}_4\text{O}_4)_2]_2 [(\text{CH}_3)_2\text{NCOH}_2] \cdot \text{H}_2\text{O}$

Jong-Young Kim

Alexander J. Norquist
Haverford College, anorquis@haverford.edu

Dermot O'Hare

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Incorporation of uranium(VI) into metal–organic framework solids, $[\text{UO}_2(\text{C}_4\text{H}_4\text{O}_4)] \cdot \text{H}_2\text{O}$, $[\text{UO}_2\text{F}(\text{C}_5\text{H}_6\text{O}_4)] \cdot 2\text{H}_2\text{O}$, and $[(\text{UO}_2)_{1.5}(\text{C}_8\text{H}_4\text{O}_4)_2]_2[(\text{CH}_3)_2\text{NCOH}_2] \cdot \text{H}_2\text{O}$

Jong-Young Kim, Alexander J. Norquist and Dermot O'Hare*

Inorganic Chemistry Laboratory, South Parks Road University of Oxford, Oxford, UK OX1 3QR. E-mail: dermot.ohare@chem.ox.ac.uk

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Uranium–organic framework solids, in which uranium building units are connected by bidentate dicarboxylate anions such as succinate, glutarate, and isophthalate, were synthesized; the glutarate and isophthalate compounds contain cavities, in which occluded water and organic templates reside.

The preparation of microporous solids involving the co-ordination of metal centers to organic linker moieties with the aim of yielding open framework structures is the subject of considerable effort. Dicarboxylate ligands have been exploited recently to form a variety of metal–organic frameworks to produce zeolitic host–guest behavior. For example, Yaghi and co-workers have shown that the construction of metal–organic frameworks using dicarboxylate groups with variable sizes and shapes can provide an effective strategy to tailor the functionality and pore-size.^{1,2} Recently, Zheng and co-workers reported thermally robust terephthalate and isophthalate polymers containing a Zn_6SiO_4 core.^{3,4} Despite the importance of uranium-containing materials in catalysis,⁵ there are currently few examples of uranium–organic framework solids.⁶ We have recently synthesized a series of new organically templated actinide materials such as uranium fluorides,⁷ phosphites,^{8a} phosphates,^{8b} molybdates,⁹ and thorium fluorides¹⁰ by hydrothermal reaction. In this work, we report the synthesis, structure, and characterization of new uranium–organic framework solids incorporating succinate (**I**), $[\text{UO}_2(\text{C}_4\text{H}_4\text{O}_4)] \cdot \text{H}_2\text{O}$, glutarate (**II**), $[\text{UO}_2\text{F}(\text{C}_5\text{H}_6\text{O}_4)] \cdot 2\text{H}_2\text{O}$, and isophthalate (**III**), $[(\text{UO}_2)_{1.5}(\text{C}_8\text{H}_4\text{O}_4)_2]_2[(\text{CH}_3)_2\text{NCOH}_2] \cdot \text{H}_2\text{O}$.

I and **III** are synthesized in a one-step process by the reaction of $\text{UO}_2(\text{NO}_2)_2 \cdot 6\text{H}_2\text{O}$ with succinic acid (1,4-butanedioic acid) or isophthalic acid (1,3-benzenedicarboxylic acid) in the presence of DMF (*N,N*-dimethylformamide) and 40% HF under hydrothermal conditions at 180 °C. The materials are isolated in phase purity as octahedral- and rod-shaped yellow crystals, respectively. **II** is synthesized as rod-shaped yellow crystals by allowing the post heating solution to evaporate slowly for four weeks at room temperature. † ‡

The structure of **I** is composed of uranium pentagonal bipyramid (PBs) and succinate anions connected in a three-dimensional network. (Fig. 1) Each uranium center contains a uranyl unit ($\text{O}=\text{U}=\text{O}$ angle: 178.4(4)°; $\text{U}(1)-\text{O}(1)$: 1.73(1) Å; $\text{U}(1)-\text{O}(4)$: 1.750(9) Å) and is equatorially coordinated to four

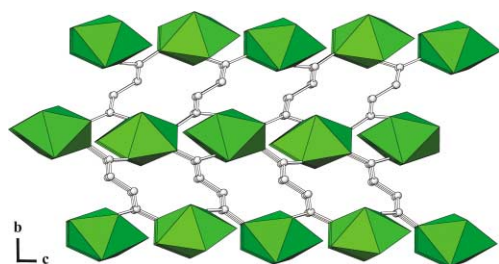


Fig. 1 View of **I** along [100] direction. Inorganic layers built up from uranium pentagonal bipyramids (green polyhedra) are linked by the organic group of succinate.

oxides from succinate groups and one from a bound water molecule. The uranium polyhedra form a layer in the *ac* plane, which is constructed by uranium PBs and dicarboxylate group linking each PBs (Fig. 1). The three dimensional architecture of **I** is completed by the bridging of the 2D-uranium layer by bidentate succinate units. The alkyl chains act as spacers between the layers.

II exhibits a one-dimensional chain structure consisting of uranium oxyfluoride dimers and cross-linking glutarate units. Each uranium is coordinated by six oxide and two fluoride ligands in a hexagonal bipyramid arrangement, which shares an edge with each of the adjacent polyhedra to form dimers. Each uranium center is bound axially to two oxides forming a uranyl group ($\text{O}=\text{U}=\text{O}$ angle: 179.6(5)°; $\text{U}(1)-\text{O}(1)$: 1.779(8) Å). The six equatorial coordination sites around each uranium centre are occupied by four dicarboxylate and two fluoride ligands. The neutral $[\text{UO}_2\text{F}][\text{C}_5\text{O}_4\text{H}_6]$ chain, which runs along [100] direction and the occluded water molecule in the cavity within the chain are shown in Fig. 2. Hydrogen bonding interactions are observed between the waters and the oxides of uranium dimer, ($\text{O}(4)-\text{H} \cdots \text{O}(3)$: 2.86 Å). As shown in Fig. 3, the linkages between the anionic glutarates and the uranium oxyfluoride dimers create a channel of width 3.4×2.0 Å along [001] direction (shortest atom–atom contact distance considering the van der Waals radii).

The thermal behavior of **II** was studied using thermogravimetric analysis and X-ray powder diffraction. Around

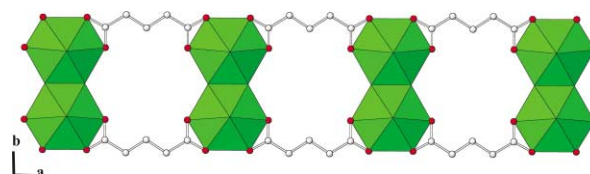


Fig. 2 Uranium glutarate chain of **II** running along [100] direction. Red and white spheres represent oxygen and carbon atoms, respectively.

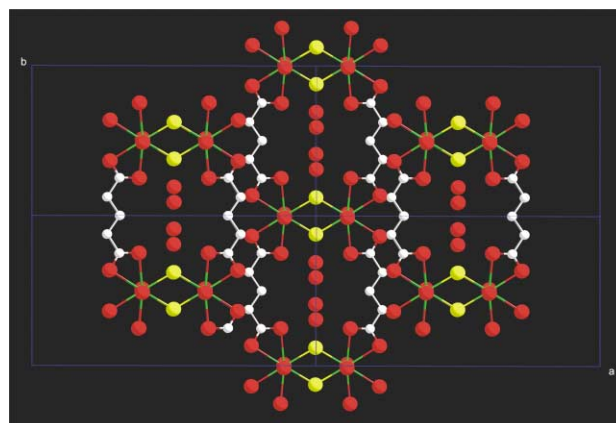


Fig. 3 Ball and stick representation of **II** along [001] direction showing channels, in which occluded water molecules reside. Green, yellow, red, and white spheres correspond to uranium, fluorine, oxygen, and carbon atoms, respectively.

100 °C, a mass loss owing to the removal of the occluded water is observed (obs. 4.5, calcd. 4%). Beyond 200 °C, further mass losses corresponding to the decomposition of organic component were observed (obs. 37.5, calcd. 35.8%). Porosity experiment was unsuccessful owing to collapse of the structure upon removal of occluded water molecules.

III has a one-dimensional chain structure consisting of uranium hexagonal bipyramids (HPs) and anionic bridges of 1,3-benzenedicarboxylate (BDC). The uranium HPs are composed of uranyl units and six equatorial oxide ligands from the BDC bridges or bound water. The uranium–BDC chain running along [100] direction is shown in Fig. 4(a). The connectivity creates cavities within the chain, in which the protonated DMF molecules reside. In the cavity of width 4.2×4.0 Å (shortest atom–atom contact distance considering the van der Waals radii), the DMF forms hydrogen bonding interactions with the oxides of the uranium HPs (O(13)–H \cdots O(5): 2.79 Å; O(14)–H \cdots O(11): 2.93 Å; N(1)–H \cdots O(3): 2.94 Å). The uranium–BDC chains stack along the *b* axis as shown in Fig. 4(b).

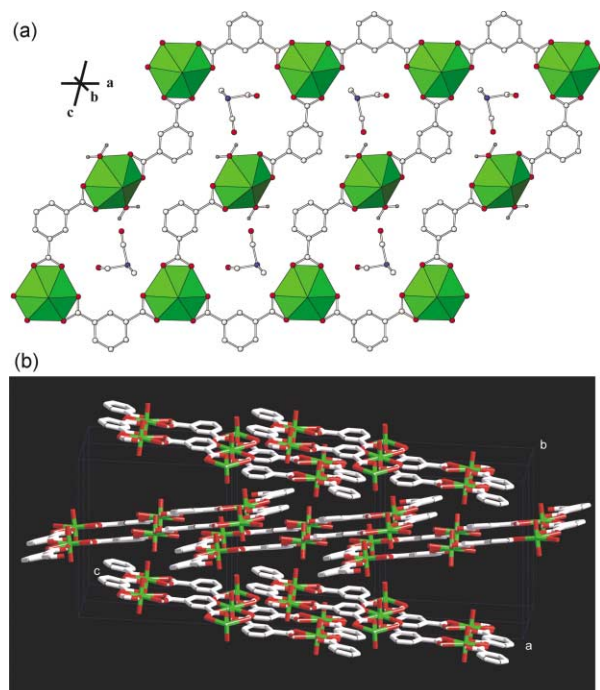


Fig. 4 (a) Uranium–BDC chain of **III** running along [100] direction. The protonated DMF cations in the cavity are disordered over two orientations. (b) Packing of uranium–BDC chain of **III**. The DMF cations and hydrogen atoms are omitted for clarity. Green, red, white colours represent uranium, oxygen, carbon atoms, respectively.

In summary, we have reported the syntheses and crystal structures of a series of uranium–organic frameworks crosslinked by three bidentate dicarboxylate anions; succinate, glutarate, and isophthalate. These results give us encouragement that we may be able to form stable porous actinide–organic frameworks.

Notes and references

† **I** and **III** were synthesized by combining $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.502 g), HF (0.120 g), H_2O (5.00 g), and $\text{C}_4\text{H}_6\text{O}_4$ (0.0945 g)/DMF (0.0146 g) or $\text{C}_8\text{H}_6\text{O}_4$ (0.166 g)/DMF (0.584 g) at room temperature. The respective mixtures were heated to 180 °C for 24 h and cooled to room temperature at 3 °C h^{-1} . Monophasic crystalline products were recovered for **I** and **III** in ~46 and ~65% yield based on uranium. For **II**, a mixture of $\text{UO}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (0.502 g), HF (0.120 g), H_2O (5.00 g), $\text{C}_5\text{H}_8\text{O}_4$ (0.396 g), and DMF (0.439 g) were heated to 180 °C for 24 h and cooled slowly to room temperature. The resultant solution was kept standing for four weeks and the crystalline product was filtrated and recovered with ~15% yield.

Elemental analyses: **I**: obsd. (calcd.): C 11.97 (11.89), H 1.49 (1.47), U 57.64 (58.90); **II**: obsd. (calcd.): C 13.83 (13.74), H 1.88 (1.85), U 53.46 (54.45); **III**: obsd. (calcd.): C 30.08 (27.65), H 2.35 (2.20), N 1.97 (1.70), U 40.97 (43.26).

‡ *Crystallographic data*: Single crystals of dimension $0.04 \times 0.04 \times 0.08$ mm for **I**, $0.08 \times 0.08 \times 0.2$ mm for **II**, and $0.08 \times 0.08 \times 0.2$ mm for **III** were used for structural determination. Data were collected using an Enraf Nonius FR 590 Kappa CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Crystals were mounted on a glass fibre using N-Paratone oil and cooled *in situ* using an Oxford Cryostream 600 Series to 150 K for data collection. Frames were collected, indexed and processed using Denzo SMN and the files scaled together using HKL GUI within Denzo SMN.¹¹ The heavy atom positions were determined using SIR97¹² and SHELXL-97.¹³ All other non-hydrogen atoms were located from Fourier difference maps and refined with anisotropic thermal parameters using full matrix least squares procedures on F_o^2 . Hydrogen atoms were placed in geometrically idealized positions. All calculations were performed using CRYSTALS,¹⁴ CAMERON,¹⁵ or WINGX¹⁶ software packages.

For **I**: monoclinic, space group $P2_1/n$ (No. 14), $a = 7.5720(5)$ Å, $b = 10.7786(8)$ Å, $c = 9.5090(6)$ Å, $\beta = 90.773(5)^\circ$, $V = 776.01(9)$ Å³, $Z = 4$, $D_c = 3.442$ g cm^{-3} , 3481 reflections collected of which 1768 were independent and 1201 were observed [$I > 3\sigma(I)$]. Refinement converged with $R = 0.0389$, $wR = 0.0830$.

For **II**: orthorhombic, space group $C2/m$ (No. 12), $a = 11.3572(4)$ Å, $b = 18.1700(8)$ Å, $c = 7.1855(3)$ Å, $\beta = 119.577(2)^\circ$, $V = 1289.58(9)$ Å³, $Z = 4$, $D_c = 2.324$ g cm^{-3} , 5396 reflections collected of which 1533 were independent and 1382 were observed [$I > 2\sigma(I)$]. Refinement converged with $R = 0.0539$, $wR = 0.1277$.

For **III**: monoclinic, space group $P2_1/n$ (No. 14), $a = 9.9344(2)$ Å, $b = 15.6519(3)$ Å, $c = 14.7961(3)$ Å, $\beta = 104.4136(7)^\circ$, $V = 2228.26(8)$ Å³, $Z = 8$, $D_c = 2.400$ g cm^{-3} , 9840 reflections collected of which 5039 were independent and 3491 were observed [$I > 3\sigma(I)$]. Refinement converged with $R = 0.0234$, $wR = 0.0532$.

CCDC reference numbers 210317–210319. See <http://www.rsc.org/suppdata/dt/b3/b306733p/> for crystallographic data in CIF or other electronic format.

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