*Inorg. Chem.* **2003**, *42*, 7041–7045

Inorganic Chemistry

Article

# Topological Evolution in Uranyl Dicarboxylates: Synthesis and Structures of One-Dimensional $UO_2(C_6H_8O_4)(H_2O)_2$ and Three-Dimensional $UO_2(C_6H_8O_4)$

**Lauren A. Borkowski**[†] **and Christopher L. Cahill***[,†,‡]

*Department of Chemistry, The George Washington University, Washington, DC 20052, and Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015*

Received June 16, 2003

Two novel uranyl adipates are reported as synthesized via hydrothermal treatment of uranium oxynitrate and adipic acid. One-dimensional $UO_2(C_6H_8O_4)(H_2O)_2$ (**1**) [$a = 9.6306(6)$ Å, $c = 11.8125(10)$ Å, tetragonal, $P4_32_12$ (No. 96), $Z = 4$] consists of chains of $(UO_2)O_4(H_2O)_2$ hexagonal bipyramids tethered through a linear adipic acid backbone. Three-dimensional $UO_2(C_6H_8O_4)$ (**2**) [$a = 5.5835(12)$ Å, $b = 8.791(2)$ Å, $c = 9.2976(17)$ Å, $\alpha = 87.769(9)°$, $\beta = 78.957(8)°$, $\gamma = 81.365(11)°$, triclinic, $P\bar{1}$ (No. 2), $Z = 2$] is produced by decreasing the hydration level of the reaction conditions. This structure contains a previously unreported $[(UO_2)_2O_8]$ building unit cross-linked into a neutral metal–organic framework topology with vacant channels.

## Introduction

A number of research groups have been exploring the hydrothermal synthesis and crystal chemistry of novel uranium oxide and oxyfluoride materials. Generally speaking, these efforts follow a theme of polymerizing well-known U−O (or U−O−F and U−F) polyhedra either to each other or through transition-metal centers and/or complex anions in the presence of organic or alkali-metal structure-directing agents. Using this approach, a host of novel one-, two-, and three- dimensional uranyl oxides,[1] molybdates,[2−10] iodates,[11−18] phosphates,[19−23] (oxy)fluorides,[24−35] phosphites,[36] sulfates,[37−40] selenites,[41,42] and tellurites[43,44] have been produced in the past few years and thus demonstrate the remarkable structural diversity within these systems.

---

* Author to whom correspondence should be addressed. E-mail: cahill@gwu.edu.

[†] The George Washington University.

[‡] Carnegie Institution of Washington.

(1) Li, Y.; Cahill, C. L.; Burns, P. C. *Chem. Mater.* **2001**, *13*, 4026−4031.
(2) Krivovichev, S. V.; Cahill, C. L.; Burns, P. C. *Inorg. Chem.* **2002**, *41*, 34−39.
(3) Krivovichev, S. V.; Burns, P. C. *Can. Mineral.* **2002**, *40*, 201−209.
(4) Krivovichev, S. V.; Burns, P. C. *J. Solid State Chem.* **2002**, *168*, 245−258.
(5) Krivovichev, S. V.; Burns, P. C. *Can. Mineral.* **2002**, *40*, 1571−1577.
(6) Krivovichev, S. V.; Burns, P. C. *Can. Mineral.* **2001**, *39*, 197−206.
(7) Krivovichev, S. V.; Burns, P. C. *Can. Mineral.* **2001**, *39*, 207−214.
(8) Krivovichev, S. V.; Burns, P. C. *Can. Mineral.* **2000**, *38*, 717−726.
(9) Krivovichev, S. V.; Burns, P. C. *Can. Mineral.* **2000**, *38*, 847−851.
(10) Halasyamani, P. S.; Francis, R. J.; Walker, S. M.; O'Hare, D. *Inorg. Chem.* **1999**, *38*, 271−279.
(11) Bean, A. C.; Albrecht-Schmitt, T. E. *J. Solid State Chem.* **2001**, *161*, 416−423.
(12) Bean, A. C.; Campana, C. F.; Kwon, O.; Albrecht-Schmitt, T. E. *J. Am. Chem. Soc.* **2001**, *123*, 8806−8810.
(13) Bean, A. C.; Ruf, M.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2001**, *40*, 3959−3963.
(14) Bean, A. C.; Peper, S. M.; Albrecht-Schmitt, T. E. *Chem. Mater.* **2001**, *13*, 1266−1272.
(15) Sykora, R. E.; McDaniel, S. M.; Wells, D. M.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2002**, *41*, 5126−5132.
(16) Sykora, R. E.; Wells, D. M.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2002**, *41*, 2697−2703.
(17) Sykora, R. E.; Wells, D. M.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2002**, *41*, 2304−2306.
(18) Sykora, R. E.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2003**, *42*, 2179−2181.
(19) Danis, J. A.; Runde, W. H.; Scott, B.; Fettinger, J.; Eichhorn, B. *Chem. Commun.* **2001**, 2378−2379.
(20) Francis, R. J.; Drewitt, M. J.; Halasyamani, P. S.; Ranganathachar, C.; O'Hare, D.; Clegg, W.; Teat, S. J. *Chem. Commun.* **1998**, 279−280.
(21) Locock, A. J.; Burns, P. C. *J. Solid State Chem.* **2002**, *167*, 226−236.
(22) Locock, A. J.; Burns, P. C. *J. Solid State Chem.* **2002**, *163*, 275−280.
(23) Locock, A. J.; Burns, P. C. *Am. Mineral.* **2003**, *88*, 240−244.
(24) Francis, R. J.; Halasyamani, P. S.; O'Hare, D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2214−2217.
(25) Francis, R. J.; Halasyamani, P. S.; O'Hare, D. *Chem. Mater.* **1998**, *10*, 3131−3139.
(26) Francis, R. J.; Halasyamani, P. S.; Bee, J. S.; O'Hare, D. *J. Am. Chem. Soc.* **1999**, *121*, 1609−1610.
(27) Halasyamani, P. S.; Walker, S. M.; O'Hare, D. *J. Am. Chem. Soc.* **1999**, *121*, 7415−7416.
(28) Halasyamani, P. S.; Francis, R. J.; Bee, J. S.; O'Hare, D. *Mater. Res. Soc. Symp. Proc.* **1999**, *547*, 383−388.

10.1021/ic030196e CCC: $25.00

Inspired by these efforts and the well-established crystal chemistry of U−O polyhedra, our group has begun to focus on the design of U-framework materials assembled using organic linking agents, particularly difunctional carboxylic acids. This represents a departure from some of our recent synthetic investigations in that the organic components of these materials serve as integral structural components of the extended topologies themselves, as opposed to space-filling and/or charge-balancing roles in the oxides and oxyfluorides. This approach is not entirely novel, as there has been an explosion of metal−organic framework (MOF) chemistry in recent years, driven in part by their potential applications in optoelectronics, magnetics, separations, ion exchange, gas storage, and catalysis.[45−55] Briefly, MOFs exploit directional, covalent interactions between metal centers (or clusters) and functional groups on organic backbones or "linkers" to direct the assembly of expanded and often porous architectures. At the foundation of this approach is the use of multifunctional linkers to promote *polymerization* of metal centers, as opposed to formation of zero-dimensional complexes expected from monofunctional ligands. The metal−carboxylate system (among others) is representative of this philosophy, as it exhibits a wide range of structure types and compositions that present new opportunities for structural design and hence tailored functionality.[49−51,54−60]

Relevant to our current efforts is the observation that the local crystal chemistry of uranyl carboxylates is relatively well established. Recent reviews[61] and searches of the Cambridge Structural Database (CSD; V5.24) yielded 176 compounds, yet only 31 have polymeric topologies, only 5 of which are three-dimensional frameworks. A fundamental structural component of these materials is the linear $UO_2^{2+}$ cation, a species that when coordinated to carboxylate groups forms square, pentagonal, or hexagonal bipyramids with polymerization occurring solely through the equatorial positions. The apical oxygen atoms (often referred to as the "uranyl oxygens") are bound to the central uranium atom only and show no tendency to bridge to other species. The maturity of uranyl carboxylate chemistry actually makes this system ideal for exploring structures of higher dimensionality (i.e., MOFs) as synthetic investigations can harness the local structural features and thus focus on polymerization efforts by employing multifunctional ligands. In this paper, we present the results of a synthetic investigation into the uranium−adipic acid−$H_2O$ system. Efforts to polymerize $UO_2^{2+}$ through this difunctional carboxylic acid ($C_6H_{10}O_4$ or $HO_2C(CH_2)_4CO_2H$) have resulted in a novel one-dimensional chain compound, $(C_6H_8O_4)UO_2(H_2O)_2$. Modification of reaction conditions (decreasing $H_2O$ content) is shown to direct formation of a novel three-dimensional MOF material, $UO_2(C_6H_8O_4)$, constructed from tethered $[(UO_2)_2O_8]$ dimers, a previously unreported coordination in the uranyl carboxylate system.

## Experimental Section

**Synthesis.** *Caution: While the uranium oxynitrate $(UO_2)(NO_3)_2\cdot 6H_2O$ contains depleted U, standard precautions for handling radioactive substances should be followed!*

Compound **1**, $UO_2(C_6H_8O_4)(H_2O)_2$, was prepared by dissolving 0.15 g of uranium oxynitrate hexahydrate (Alfa), 0.0146 g of adipic acid (Aldrich), and 0.0223 g of potassium chloride (Aldrich) in 3.5 g of water (molar ratio 1:1:1:2223). The solution (pH 1.76) was prepared in a 23 mL Teflon-lined Parr bomb and then heated statically at 180 °C for 3 days. The resulting liquid (pH 2.59) was then allowed to crystallize over 3 days at room temperature and pressure in an uncovered Petri dish. Efforts to produce the same crystals without the use of potassium chloride resulted only in recrystallization of the adipic acid (below). Further characterization of the sample was not attempted due to the inability to completely separate the crystals from the mother liquor.

---

(29) Walker, S. M.; Halasyamani, P. S.; Allen, S.; O'Hare, D. *J. Am. Chem. Soc.* **1999**, *121*, 10513−10521.
(30) Allen, S.; Barlow, S.; Halasyamani, P. S.; Mosselmans, J. F. W.; O'Hare, D.; Walker, S. M.; Walton, R. I. *Inorg. Chem.* **2000**, *39*, 3791−3798.
(31) Cahill, C. L.; Burns, P. C. *Inorg. Chem.* **2001**, *40*, 1347−1351.
(32) Almond, P. M.; Talley, C. E.; Bean, A. C.; Peper, S. M.; Albrecht-Schmitt, T. E. *J. Solid State Chem.* **2000**, *154*, 635−641.
(33) Almond, P. M.; Deakin, L.; Porter, M. J.; Mar, A.; Albrecht-Schmitt, T. E. *Chem. Mater.* **2000**, *12*, 3208−3213.
(34) Talley, C. E.; Bean, A. C.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2000**, *39*, 5174−5175.
(35) Almond, P. M.; Deakin, L.; Mar, A.; Albrecht-Schmitt, T. E. *J. Solid State Chem.* **2001**, *158*, 87−93.
(36) Doran, M.; Walker, S. M.; O'Hare, D. *Chem. Commun.* **2001**, 1988−1989.
(37) Thomas, P. M.; Norquist, A. J.; Doran, M. B.; O'Hare, D. *J. Mater. Chem.* **2003**, *13*, 88−92.
(38) Norquist, A. J.; Doran, M. B.; Thomas, P. M.; O'Hare, D. *J. Chem. Soc., Dalton Trans.* **2003**, 1168−1175.
(39) Norquist, A. J.; Thomas, P. M.; Doran, M. B.; O'Hare, D. *Chem. Mater.* **2002**, *14*, 5179−5184.
(40) Doran, M.; Norquist, A. J.; O'Hare, D. *Chem. Commun.* **2002**, 2946−2947.
(41) Almond, P. M.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2002**, *41*, 1177−1183.
(42) Almond, P. M.; Peper, S. M.; Bakker, E.; Albrecht-Schmitt, T. E. *J. Solid State Chem.* **2002**, *168*, 358−366.
(43) Almond, P. M.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2002**, *41*, 5495−5501.
(44) Almond, P. M.; McKee, M. L.; Albrecht-Schmitt, T. E. *Angew. Chem., Int. Ed.* **2002**, *41*, 3426−3429.
(45) Evans, O. R.; Lin, W. *Acc. Chem. Res.* **2002**, *35*, 511−522.
(46) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319−330.
(47) Rosi, N. L.; Eddaoudi, M.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Cryst. Eng. Commun.* **2002**, *4*, 401−404.
(48) Reineke, T. M.; Eddaoudi, M.; Fehr, M.; Kelley, D.; Yaghi, O. M. *J. Am. Chem. Soc.* **1999**, *121*, 1651−1657.
(49) Pan, L.; Woodlock, E. B.; Wang, X.; Zheng, C. *Inorg. Chem.* **2000**, *39*, 4174−4178.
(50) Pan, L.; Liu, H.; Lei, X.; Huang, X.; Olson, D. H.; Turro, N. J.; Li, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 542−546.
(51) Pan, L.; Adams, K. M.; Hernandez, H. E.; Wang, X.; Zheng, C.; Hattori, Y.; Kaneko, K. *J. Am. Chem. Soc.* **2003**, *125*, 3062−3067.
(52) Lawandy, M. A.; Pan, L.; Huang, X.; Li, J.; Yuen, T.; Lin, C. L. *Mater. Res. Soc. Symp. Proc.* **2001**, *658*, GG6.12.11−GG16.12.16.
(53) Rather, B.; Moulton, B.; Bailey Walsh, R. D.; Zaworotko, M. J. *Chem. Commun.* **2002**, 694−695.
(54) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629−1658.
(55) Ferey, G. *Chem. Mater.* **2001**, *13*, 3084−3098.
(56) Li, H.; Eddaoudi, M.; Groy, T. L.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 8571−8572.
(57) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, M. *Nature (London)* **1999**, *402*, 276−279.
(58) Mori, W.; Takamizawa, S. *J. Solid State Chem.* **2000**, *152*, 120−129.
(59) Forster, P. M.; Cheetham, A. K. *Angew. Chem., Int. Ed.* **2002**, *41*, 457−459.
(60) Pan, L.; Huang, X.; Li, J. *J. Solid State Chem.* **2000**, *152*, 236−246.
(61) Leciejewicz, J.; Alcock, N. W.; Kemp, T. J. *Struct. Bonding* **1995**, *82*, 43−84.

Compound **2**, $UO_2(C_6H_8O_4)$, was prepared by dissolving 0.251 g of uranium oxynitrate hexahydrate and 0.073 g of adipic acid in 1.4 g of water (molar ratio 1:1:151). Once again the solution (pH 1.07) was placed in a Parr bomb and heated statically at 180 °C for 3 days. The crystals were formed in situ and washed with water and ethanol (yield 40.5% based on U). The amount of water contained in the reaction was systematically altered, and it was found that pure **2** does not form above a water molar ratio of 250. The effect of pH was examined by adjustment with ammonium hydroxide over a range of 1−7 (∼1.0 unit increments); products from these syntheses were found to be isomorphous with **2** as indicated by powder X-ray diffraction (below). The sample was further characterized by IR, thermogravimetric analysis (TGA), and elemental analysis. The TGA (Perkin-Elmer Pyris1, 30−600 °C; 10 deg/min; flowing $N_2(g)$) revealed a single weight loss (presumably decomposition) at approximately 335 °C, suggesting a relatively robust framework when compared to several other MOF materials.[57,62−66] The IR spectrum revealed peaks associated with alkane and carboxylate bonds and none from nitrogen-containing species. The elemental analysis (Galbraith Laboratories, Knoxville, TN) data supported the absence of nitrogen in the material [obsd (calcd)]: C, 16.86% (17.40%); H, 1.77% (1.95%); N, <0.5% (0%).

**X-ray Diffraction.** A single crystal of each of the samples was selected from the bulk and mounted on a glass fiber. Reflections were collected on a Bruker P4 diffractometer equipped with an Apex CCD detector using 0.3° and 1.0° $\omega$ scans, and data were integrated with the SMART/SAINT software packages.[67] Structure **1** was solved in space group $P4_32_12$ with SIR97[68] and refined with SHELXL-97[69] using the WINGX software suite.[70] As $P4_32_12$ is an enantiomorphic space group with $P4_12_12$, solution and refinement were tested using this model, yet this yielded an unsatisfactory Flack parameter, indicating that the original assignment of $P4_32_12$ was indeed correct. Hydrogen atom positions for those bound to the carbon chain were calculated, whereas those associated with water molecules (O3) were observed and refined isotropically. No residual electron density >0.5 e/Å³ was observed in the interchain region, indicating that no other components were present in the structure. This is noted since KCl was required for crystallization yet is not observed in the final product. Further, neither $K^+$ nor $Cl^-$ is required for charge balance.

**Table 1.** Crystallographic Information for **1** and **2**

| | 1 | 2 |
|---|---|---|
| emprical formula | $C_6H_{12}O_8U$ | $C_6H_8O_6U$ |
| fw | 450.19 | 414.15 |
| temp (K) | 293(2) | 293(2) |
| system | tetragonal | triclinic |
| space group | $P4_32_12$ (No. 96) | $P\bar{1}$ (No. 2) |
| $a$ (Å) | 9.6306(6) | 5.5835(12) |
| $b$ (Å) | 9.6306(6) | 8.791(2) |
| $c$ (Å) | 11.8125(10) | 9.2976(17) |
| $\alpha$ (deg) | 90 | 87.769(9) |
| $\beta$ (deg) | 90 | 78.957(8) |
| $\gamma$ (deg) | 90 | 81.365(11) |
| $V$ (Å³) | 1095.59(13) | 442.83(16) |
| Z | 4 | 2 |
| $\lambda$(Mo K$\alpha$) | 0.71073 | 0.71073 |
| $D_{calcd}$ (g cm$^{-1}$) | 2.729 | 3.106 |
| $\mu$ (cm$^{-1}$) | 14.836 | 18.323 |
| R1 (on $F_o^2$, $I > 2\sigma(I)$)[a] | 0.0194 | 0.0369 |
| wR2 (on $F_o^2$, $I > 2\sigma(I)$)[b] | 0.0430[c] | 0.1390[d] |

[a] $R1(F_o^2) = \sum[(F_o^2 - F_o^2)]/\sum(F_o)$. [b] $wR2(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (0.0207P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$. [d] $w = 1/[\sigma^2(F_o^2) + (0.1000P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$.

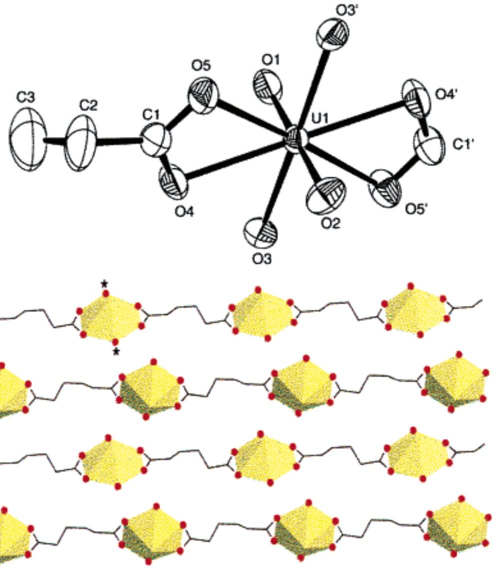

**Figure 1.** Top: ORTEP of **1**. Ellipsoids are shown at the 50% level. H-atoms have been omitted for clarity. O1 and O2 are the uranyl oxygen positions. Bottom: Polyhedral representation of **1**. Yellow hexagonal bipyramids are $UO_2(O_6)$ units connected through adipic acid backbones along [001]. The equatorial positions marked with an asterisk are $H_2O$ groups (O3 in ORTEP).

Structure **2** was solved readily with direct methods (SHELXS)[71] in both $P1$ and $P\bar{1}$, with $P\bar{1}$ giving a lower initial $R$ factor. Refinement with SHELXL-97 within WINGX proceeded for both models, yet tests for missing symmetry using Platon clearly indicated $P\bar{1}$ to be the correct assignment. Details of the data collection and refinement for both structures can be found in Table 1, and Supporting Information in CIF format is available. Powder X-ray diffraction data were collected on a Scintag XDS 2000 diffractometer (Cu K$\alpha$, 3−60°, 0.05° step, 1.0 s/step) and manipulated using the JADE software package.[72] Comparison of observed and calculated patterns confirmed the samples to be single phase.

## Structural Descriptions

The structure of **1** consists of chains of dihydrated $UO_2^{2+}$ cations tethered through an adipic acid backbone (Figure 1; Table 2). Within the hexagonal bipyramidal coordination sphere of the uranium, there are three distinct types of oxygens. The uranyl oxygens are bonded to the central uranium atom at an average distance of 1.74 Å (Table 2) to form the linear $UO_2^{2+}$ cation. Six equatorial positions contain

---

(62) Benetollo, F.; Bombieri, G.; Herrero, J. A.; Rojas, R. M. *J. Inorg. Nucl. Chem.* **1979**, *41*, 195−199.
(63) Dimos, A.; Tsaousis, D.; Michaelides, A.; Skoulika, S.; Golhen, S.; Ouahab, L.; Didierjean, C.; Aubry, A. *Chem. Mater.* **2002**, *14*, 2616−2622.
(64) Chen, B.; Eddaoudi, M.; Hyde, S. T.; O'Keeffe, M.; Yaghi, O. M. *Science* **2001**, *291*, 1021−1023.
(65) Tabares, L. C.; Navarro, J. A. R.; Salas, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 383−387.
(66) Vaidhyanathan, R.; Natarajan, S.; Rao, C. N. R. *Chem. Mater.* **2001**, *13*, 185−191.
(67) Bruker Analytical X-ray Systems, Madison, WI, 1998.
(68) Altomare, A.; Burla, M. C.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori., G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*.
(69) Sheldrick, G. M., Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
(70) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.
(71) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.
(72) JADE, V6.1, Materials Data Inc., Livermore, CA.

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for **1**[a]

| | | | |
|---|---|---|---|
| U(1)−O(1) | 1.749(6) | U(1)−O(5) (×2) | 2.524(4) |
| U(1)−O(2) | 1.739(6) | O(4)−C(1) | 1.265(7) |
| U(1)−O(3) (×2) | 2.440(5) | O(5)−C(1) | 1.273(8) |
| U(1)−O(4) (×2) | 2.526(4) | ⟨C−C⟩ | 1.467 |
| O(1)−U(1)−O(2) | 180.0(2) | O(3)−U(1)−O(4) (×2) | 63.9(2) |
| O(3)$^{\#1}$−U(1)−O(5) (×2) | 65.5(2) | O(5)−U(1)−O(4) (×2) | 50.8(2) |

[a] Symmetry transformation: #1, $y$, $x$, $-z + 2$.

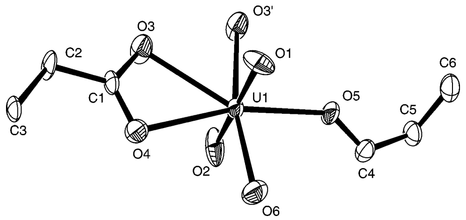

**Figure 2.** ORTEP of **2**. Ellipsoids are shown at the 50% level. H-atoms have been omitted for clarity. O1 and O2 are the uranyl oxygen positions.

two water molecules (U−O ⟨2.44 Å⟩) and four carboxylate oxygens (U−O ⟨2.52 Å⟩). The equatorial hexagon is slightly distorted with O−U−O angles that range from 50.8° to 65.5°. Similar chain structures have been previously reported, specifically uranyl fumarate, $UO_2(C_4H_2O_4)(H_2O)_2$,[73] and $(C_{20}H_{28}O_{24}U_3)(C_6H_{16}N_2)\cdot 4H_2O$.[74] Both contain dihydrated hexagonal bipyramidal uranium coordination spheres connected through dibasic carboxylic acid groups.

The structure of **2** (Figures 2−4; Table 3) consists of $[(UO_2)_2O_8]$ dimers cross-linked through adipic acid groups to form a neutral three-dimensional framework. Each dimer contains two edge-shared U pentagonal bipyramids constructed from linear $UO_2^{2+}$ cations coordinated to five equatorial carboxylate oxygens donated from four unique adipic acid molecules. The dimers are linked through bridging carboxylate groups to form chains running along [001], which are then cross-linked by additional adipic acid groups to form channels parallel to the chain direction (Figure 4). The adipic acid groups occur in two distinct environments, and thus, there are two modes of cross-linking the dimer chains. Figures 3 and 4 offer roughly orthogonal views of the framework topology. The region marked A in Figure 3 represents a flat adipic acid molecule cross-linked to a parallel "in plane" dimer chain. Region B, on the other hand, shows a "kinked" backbone cross-linked to chains above and below those shown. The carboxylic group in region A is connected to a single dimer edge, whereas region B bridges the $[(UO_2)_2O_8]$ dimers into chains along [001]. Note that each adipic acid molecule exhibits a *single* type of coordination; i.e., those that bridge dimers do so at each end of the molecule, as do those coordinated to dimer edges. This distance between the cross-linked chains is approximately 3.3 Å as measured from the center position of uranyl oxygen atoms on parallel chains (Figure 4).

Looking at the local structure of the dimers, the equatorial regions of the pentagonal bipyramids are distorted slightly

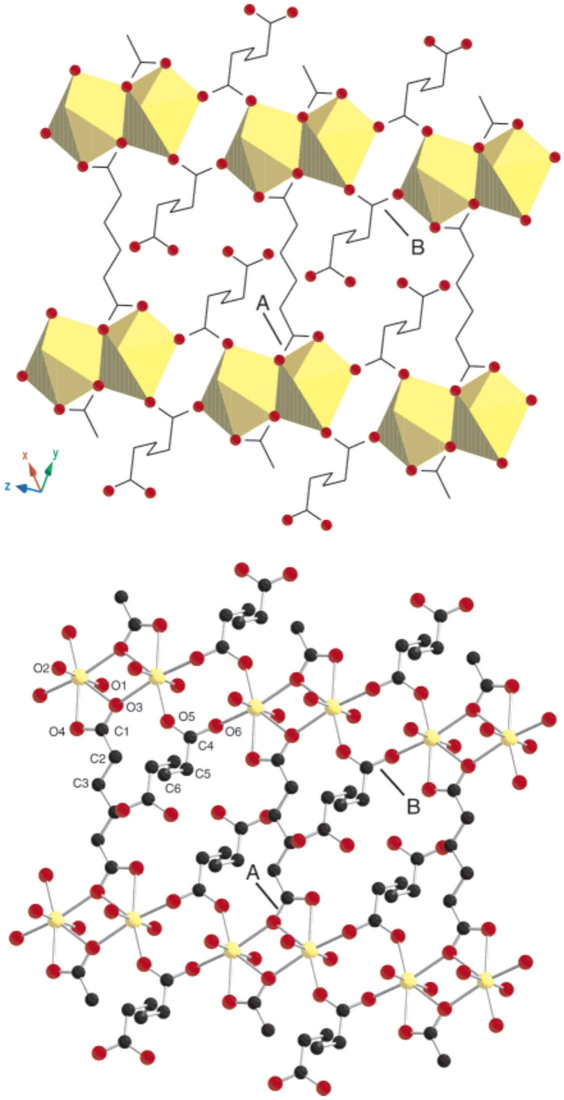

**Figure 3.** Polyhedral (top) and ball-and-stick (bottom) representations of **2**. Red spheres are oxygen atoms, yellow are uranium, and black are carbon. H-atoms are omitted for clarity. Chains of edge-shared $[(UO_2)_2O_8]$ dimers run along [001] and are cross-linked through two different adipic acid environments, A and B. Acid group A links the chains in an "edge-to-edge" fashion, whereas B links "bridging site-to-bridging site". A is an in-plane connectivity, whereas B links to chains above and below those shown.

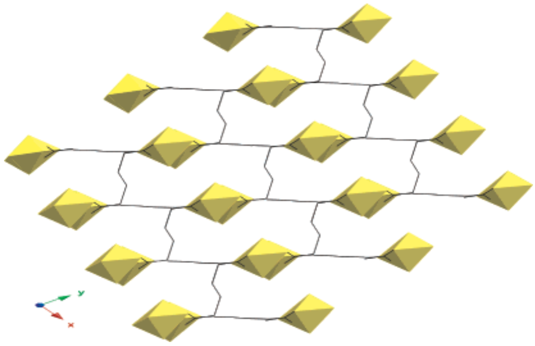

**Figure 4.** Polyhedral representation of **2** shown down [001] to emphasize channel direction. The narrowest aperture is between uranyl oxygens on parallel chains (∼ 3.3 Å).

with O−U−O angles ranging from 51.4° to 87.0°; the smallest angles (51.4° and 63.9°) are involved with the shared edge of the bipyramid. The uranyl oxygens of **2** are at a

---

(73) Bombieri, G.; Benetollo, F.; Rojas, R. M.; De Paz, M. L.; Del Pra, A. *Inorg. Chim. Acta* **1982**, *61*, 149−154.

(74) Zhang, Y.; Livens, F. R.; Collison, D.; Helliwell, M.; Heatley, F.; Powell, A. K.; Wocadlo, S.; Eccles, H. *Polyhedron* **2002**, *21*, 69−79.

**Table 3.** Selected Bond Distances (Å) and Angles (deg) for **2**[a]

| | | | |
|---|---|---|---|
| U(1)−O(1) | 1.753(8) | U(1)−O(6) | 2.261(9) |
| U(1)−O(2) | 1.707(9) | O(3)−C(1) | 1.273(13) |
| U(1)−O(3) | 2.531(8) | O(4)−C(1) | 1.260(13) |
| U(1)−O(3)$^{\#1}$ | 2.385(8) | O(5)−C(4) | 1.266(13) |
| U(1)−O(4) | 2.455(8) | O(6)−C(4)$^{\#2}$ | 1.247(14) |
| U(1)−O(5) | 2.314(8) | ⟨C−C⟩ | 1.499 |
| O(1)−U(1)−O(2) | 176.8(4) | O(4)−U(1)−O(6) | 76.6(3) |
| O(3)−U(1)−O(3)$^{\#1}$ | 63.9(3) | O(5)−U(1)−O(3)$^{\#1}$ | 81.3(3) |
| O(3)−U(1)−O(4) | 51.4(3) | O(5)−U(1)−O(6) | 87.0(3) |

[a] Symmetry transformations: #1, $-x + 1, -y + 2, -z + 1$; #2, $-x + 1, -y + 2, -z + 2$.

comparable distance from the uranium center compared to **1** (⟨1.73 Å⟩), yet unlike **1**, all of the equatorial positions are occupied by oxygen atoms associated with an adipic acid chain. These oxygen atoms are held closer to the uranium center with the bond distance, non-edge-sharing oxygens, being 2.34 Å on average. The oxygen atoms involved with the shared edge are slightly farther away at ⟨2.46 Å⟩.

## Discussion

Inspection of the U hexagonal bipyramids of **1** suggests that the $UO_2^{2+}$ cation is undersaturated with respect to carboxylate oxygens; i.e., the two water groups could conceivably be replaced by one carboxylic acid group and increase the dimensionality. Indeed, there are several examples (e.g., uranium oxyacetate[75]) where the equatorial positions of the hexagonal bipyramids are fully occupied by oxygen atoms not associated with bound water molecules. This observation prompted us to increase the U:$H_2O$ ratio in the preparation of **2**. Interestingly, however, rather than an increased degree of polymerization of the hexagonal bipyramids, we see a coordination change to a novel building unit, the $[(UO_2)_2O_8]$ dimers. This is intriguing since there are several examples of materials in which the uranyl cation is equatorially bound to three carboxylic groups,[61,76−78] and full equatorial occupation is the norm in uranyl carbonate minerals.[79] Further, $(C_{20}H_{28}O_{24}U_3)(C_6H_{16}N_2)\cdot 4H_2O$[74] is a material with two different hexagonal bipyramidal polyhedra exhibiting two different hydration levels: one uranium is bound to six carboxylate oxygens and no water molecules, while the other is bound to four carboxylate oxygens and two water molecules, thus demonstrating the range of variability within this building unit. In light of this, it is not entirely clear why the U coordination changes from hexagonal bipyramidal to pentagonal bipyramidal in going from the structure of **1** to **2**, yet one could speculate that the resulting increase in concentration of $U^{6+}$ leads to the formation of higher order polyhedra ($[(UO_2)_2O_8]$ dimers) and the simultaneous increase in acid concentration leads to a greater degree of polymerization in **2** compared with that in **1**.

The ability of the adipic acid backbone to rotate about single C−C bonds likely contributes to the diversity of structure types in not only this system, but also lanthanum adipate materials.[63,80,81] This lack of rigidity is especially apparent in the structure of **2**, where two different acid groups are flat and kinked (regions A and B, respectively), and thus give rise to two types of interchain linkages and ultimately a three-dimensional topology. It may be suggested by examining previously prepared uranyl aliphatic carboxylates that a sufficient chain length is required for three-dimensional topologies; no frameworks are observed for dicarboxylate chains shorter than four carbons.[61] A similar argument could be made about longer chain species as there are no reports in the literature, nor have our efforts succeeded in producing a framework structure from a chain containing more than six carbon atoms. Presumably these could become unstable under hydrothermal conditions or lack the rigidity required to support a framework.

## Conclusion

We have reported two novel uranyl adipates: **1** consists of hexagonal bipyramids connected through adipic acid groups to form a one-dimensional structure; **2** consists of chains of previously unreported $[(UO_2)_2O_8]$ dimers connected by adipic acid in three directions to form a thermally robust three-dimensional MOF. Despite the number of known uranyl carboxylate compounds, the formation of this new coordination suggests that there is still room for discovery in this system.[82] Efforts continue to explore the relationships outlined in this investigation and also to examine the effect of rigidity (unsaturation) in the carboxylate backbones.

**Acknowledgment.** We are grateful for financial support from George Washington University's University Facilitating Fund and the Junior Scholar Incentive Award program.

**Supporting Information Available:** Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC030196E

---

(75) Zachariasen, W. H.; Plettinger, H. A. *Acta Crystallogr.* **1959**, *12*, 526−530.

(76) Le Roux, S. D.; Van Tets, A.; Adrian, H. W. W. *Acta Crystallogr., Sect. B* **1979**, *B35*, 3056−3057.

(77) Viossat, B.; Nguyen Huy, D.; Soye, C. *Acta Crystallogr., Sect. C* **1983**, *C39*, 573−576.

(78) Burns, C. J.; Sattelberger, A. P. *Inorg. Chem.* **1988**, *27*, 3692−3693.

(79) Burns, P. C. *Rev. Mineral.* **1999**, *38*, 23−90.

(80) Kiritsis, V.; Michaelides, A.; Skoulika, S.; Golhen, S.; Ouahab, L. *Inorg. Chem.* **1998**, *37*, 3407−3410.

(81) Borkowski, L. A.; Cahill, C. L. Manuscript in preparation.

(82) During review of this paper, the following manuscript appeared in press, further demonstrating the interest and structural diversity in these types of materials: Kim, J.-Y.; Norquist, A. J.; O'Hare, D. *J. Chem. Soc., Dalton Trans.* **2003**, 2813−2814.