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Hydrothermal Synthesis of a Novel Uranium Oxalate/Glycolate via In-Situ Ligand Formation

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A novel templated uranium oxalate/glycolate, $(UO_2)_4(O)_2(C_2O_4)(H_2C_2O_3)_2 \cdot 2[(C_8H_{20})N]$ ($a = 7.9230(8)$ Å, $b = 13.3793(13)$ Å, $c = 17.4141(18)$ Å, $\beta = 96.006(2)°$, monoclinic, $P2_1/n$, $Z = 2$), has been synthesized under hydrothermal conditions via in-situ ligand synthesis. The oxalate and glycolate anions have been formed through the oxidation of 1,4-diazabicyclo[2.2.2]octane, which proceeds through intermediates such as piperazine and ethylene glycol. Reported herein is the synthesis of this compound, crystal structure, and mechanistic information regarding the oxidation pathway.

Introduction

Inorganic/organic coordination polymers, hybrid materials that consist of metal centers connected through organic linker molecules to form extended structures, have become an extensive area of research, owing to their structural diversity and noteworthy physical properties.[1−10] Unlike the synthesis of transition metal coordination polymers, that of uranium(VI)-containing coordination polymers is considerably less developed. These materials are of particular interest due to their physical−chemical properties and potential application in optical, magnetic, ion exchange, and catalytic materials.[11−31] More specifically, uranyl-containing materials are being explored for their photoluminescent properties, as well as their photocatalytic activity. Photoexcited uranyl cations have been shown to oxidize organic molecules[32−34] and most

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recently have been used to cleave DNA and RNA.[35] Moreover, the syntheses of uranium(VI)-containing coordination polymers under hydrothermal conditions is of general importance not only in materials synthesis but also in environmental settings such as nuclear fuel stewardship.[36,37]

In-situ ligand synthesis has become an increasingly popular route to new hybrid materials. This approach offers the advantages of simplified synthesis, slow ligand formation to promote single-crystal growth, environmental friendliness, and in some cases a novel pathway to new materials.[38] Several in-situ ligand syntheses have been observed in hydrothermal systems.[39−47] Under these conditions, the in-situ formation of organic linkers often relies on the rearrangement or cleavage of organic compounds. The rearranged organic species are then observed in the crystalline reaction products. Whereas the frequency of in-situ ligand syntheses reported has increased, mechanisms remain poorly understood and occurrences are largely serendipitous. Oxalate anion formation under hydrothermal conditions is one such example. This phenomenon has been observed by several researchers and is typically attributed to one of three different pathways including decarboxylation or oxidation of a carboxylate functionalized organic species,[48−51] the reductive coupling of adventitious CO_2,[49,52−56] and oxidative degradation of L-ascorbic acid.[57−59] Additionally, instances of the oxidative coupling of methanol and ethanol to yield oxalate have been reported.[60]

The investigation reported herein began with the unexpected formation of $[(UO_2)_2(OH)_2(C_2O_4)(H_2O)_2]$ from the hydrothermal treatment of $UO_2(NO_3)_2\cdot 6H_2O$ and DABCO (1,4-diazabicyclo[2.2.2]octane). The direct synthesis of this material from oxalic acid has been reported previously,[61] yet in an effort to capitalize on the notion of generating ligands in situ, we explored the use of organic structure-directing agents (templates) to promote the formation of novel uranium−oxalate compounds with occluded guests. In other words, we attempted to direct the self-assembly of the in-situ-generated oxalate ligands with uranyl cations using a “template”. Tetraalkylammonium salts were chosen for this role on the basis of their robustness or resistance to oxidation as compared to DABCO. Whereas oxalate linkages formed in situ and subsequent observation in crystalline reaction products have previously been reported, efforts to elucidate the mechanism of in-situ ligand formation have been scarce and to a large part disregarded. Furthermore, oxidation of an organic that is not functionalized with carboxylic groups or carboxylate precursors (such as aldehydes, lactones)[50,57−59,62] to yield oxalate ligands has not yet, to our knowledge, been reported. Consequently, our system provides a suitable forum to examine the reactions of uranium and DABCO under hydrothermal conditions in the presence of a structure-directing agent, as well as the assembly of in-situ-generated oxalate ligands with the uranyl cation. We herein report the synthesis of $(UO_2)_4(O)_2(C_2O_4)(H_2C_2O_3)_2\cdot 2[(C_8H_{20})N]$ via oxidation of DABCO, as well as mechanistic information regarding the formation and assembly of this compound.

Experimental Section

Caution: *Whereas the uranium oxynitrate* $(UO_2)(NO_3)_2\cdot 6H_2O$ *used in this investigation contains depleted U, standard precautions for handling radioactive substances should be followed.*

Synthesis. $(UO_2)_4(O)_2(C_2O_4)(H_2C_2O_3)_2\cdot 2[(C_8H_{20})N]$ (1). Uranium oxynitrate hexahydrate (0.141 g, 0.28 mmol), tetraethylammonium hydroxide, 20 wt % solution in water (0.164 g, 0.22 mmol), 1,4-diazabicyclo[2.2.2]octane (0.066 g, 0.59 mmol), and distilled water (5 g, 278 mmol) were placed into a 23 mL Teflon-lined Parr bomb in the molar ratio of 1.0:0.8:2.1:992. The pH was adjusted to 1.4 using concentrated HNO_3. The reaction vessel was then sealed and heated statically at 120 °C for 14 days. Upon cooling to room temperature, a clear yellow solution (pH 3.0) was decanted and yellow-orange plates were obtained. The crystals were washed with distilled water followed by ethanol and then allowed to air-dry at room temperature. Yield: 84% (based on uranium). A single crystal of the sample was isolated from the bulk for single-crystal analysis.

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Table 1. Crystallographic Data and Structure Refinement for **1**

empirical formula	$C_{11}H_{22}NO_{10}U_2$
fw	804.36
T	295(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	$P2_1/n$
unit cell dimens	$a = 7.9230(8)$ Å
	$b = 13.3793(13)$ Å
	$c = 17.4141(18)$ Å
	$\alpha = 90°$
	$\beta = 96.006(2)°$
	$\gamma = 90°$
V	1835.8(3) Å^3
Z	4
density (calcd)	2.910 g/cm^3
abs coeff	17.667 mm^{-1}
$F(000)$	1436
cryst size	$0.06 \times 0.03 \times 0.02$ mm^3
θ range for data collection	1.92−30.35°
index ranges	$-9 \le h \le 11$,
	$-18 \le k \le 19$,
	$-24 \le l \le 24$
reflns collected	35 659
independent reflns	5228 [R(int) = 0.0357]
completeness to $\theta = 25.00°$	99.9%
abs correction	empirical
max. and min. transmission	0.702 and 0.535
refinement method	full-matrix least-squares on F^2
data/restraints/params	5228/0/217
GOF on F^2	1.054
final R indices [$I > 2\sigma(I)$][a]	R1 = 0.0227, wR2 = 0.0475
R indices (all data)	R1 = 0.0291, wR2 = 0.0498
largest diff. peak and hole	1.878 and −1.275 e.Å^{-3}

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Powder X-ray diffraction data were collected using a Rigaku Miniflex diffractometer (Cu Kα, 3−60°). The observed pattern was compared to the calculated pattern to confirm phase purity, and both were in agreement. Elemental analysis (Galbraith Laboratories, Knoxville, TN), observed (calcd): C 16.30% (16.4%); N 1.78% (1.74%); H 2.76% (2.76%). Reaction time seemingly affects only the yield of **1**, in that it was synthesized under the same reaction conditions at 5, 7, and 10 days with increasing yield.

Single-Crystal X-ray Diffraction. A single crystal was selected from the bulk and mounted on a glass fiber. Reflections were collected at room temperature using a Bruker SMART diffractometer equipped with an APEX II CCD detector using Mo Kα radiation ($\lambda = 0.7103$ Å) and both φ and ω scans. The data were integrated with the SAINT software package,[63] and an empirical absorption correction was performed by modeling the crystal as a (001) plate. The structure was solved in a monoclinic space group $P2_1/n$ using direct methods and was refined using SHELX-97[64] within the WinGX software suite.[65] Tests for missing symmetry using Platon[66] indicated that $P2_1/n$ was the correct space group. The heavy atoms and all non-hydrogen atoms in the structure were found using Fourier difference maps and ultimately refined anisotropically. Hydrogen atoms were calculated and allowed to ride on their respective C atoms. Details of the data collection and refinement can be found in Table 1, and CIF data are available as Supporting Information. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) and may be obtained at http://www.ccdc.cam.ac.uk/ by citing reference no. 643463.

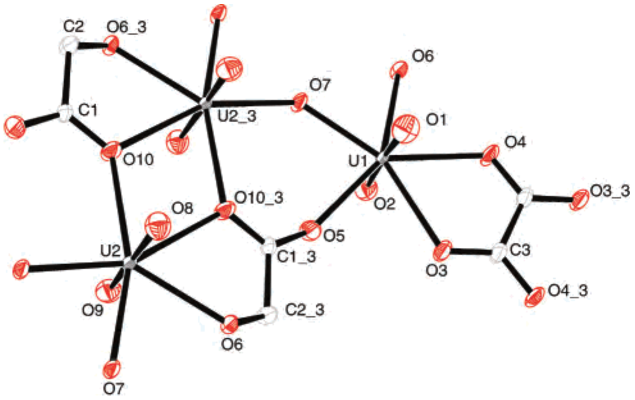

Figure 1. ORTEP of **1**, $(UO_2)_4(O)_2(C_2O_4)(H_2C_2O_3)_2 \cdot 2[(C_2H_5)N]$. Ellipsoids are shown at the 50% level. Both tetraethylammonium molecules and hydrogen atoms are omitted for clarity.

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

U(1)−O(1)	1.771(3)	U(2)−O(8)	1.785(3)
U(1)−O(2)	1.780(3)	U(2)−O(9)	1.780(3)
U(1)−O(3)	2.222(2)	U(2)−O(7)	2.282(2)
U(1)−O(4)	2.341(2)	U(2)−O(7)[1]	2.247(2)
U(1)−O(5)	2.398(3)	U(2)−O(6)	2.388(2)
U(1)−O(6)	2.474(3)	U(2)−O(10)	2.528(2)
U(1)−O(7)	2.491(2)	U(2)−O(10)[2]	2.607(2)
C(1)−C(2)	1.507(5)	C(3)−C(3)[3]	1.526(8)
C(1)−O(5)[1]	1.247(4)	C(3)−O(3)	1.251(4)
C(2)−O(6)[2]	1.401(4)	C(3)−O(4)	1.248(4)
O(2)−U(1)−O(1)	175.13(15)	O(8)−U(2)−O(9)	173.58(14)

[a] Symmetry transformations: (1) $-x + 1, -y, -z$; (2) $-x + z, -y, -z$; (3) $-x + 1, -y + 1, -z$.

Structural Description. The structure of **1** (Figure 1) consists of two crystallographically unique uranium metal centers, each of which contains a near-linear UO_2^{2+} cation equatorially coordinated to five oxygen atoms. The coordination sphere of U1 consists of the uranyl oxygens (O1 and O2) at an average distance of 1.776 Å (Table 2) and five oxygen atoms (O3−O7), two (O3 and O4) from a bidentate oxalate ligand, two from glycolate molecules (O5 and O6), and a tricoordinated O7 in the equatorial plane forming a pentagonal bipyramid coordination geometry. U2 is also found in a pentagonal bipyramid geometry with the uranyl oxygens (O8 and O9) at an average distance of 1.783 Å. Furthermore, U2 is equatorially coordinated to five oxygen atoms, three (O6, O10 and its symmetry equivalent) from glycolate anions and two tricoordinated oxygen atoms (O7 and its symmetry equivalent). U1 and U2 coordination polyhedra edge-share through a glycolate oxygen (O6) and O7 to form dimers. These dimers are then connected to an additional dimer through O7 and its symmetry equivalent to form "pseudo" tetramers. The tetramers are further connected by edge-sharing to form 1D chains through O10 of two glycolate molecules. The 1D chains are further connected to form a 2D sheet through oxalate linkages (Figure 2). Viewing down the [100], tetraethylammonium (TEA) cations charge balance the anionic sheets (Figure 3).

Discussion

The mechanism by which this material was synthesized is of particular interest, considering that neither oxalate or glycolate materials were present as reactants. As mentioned

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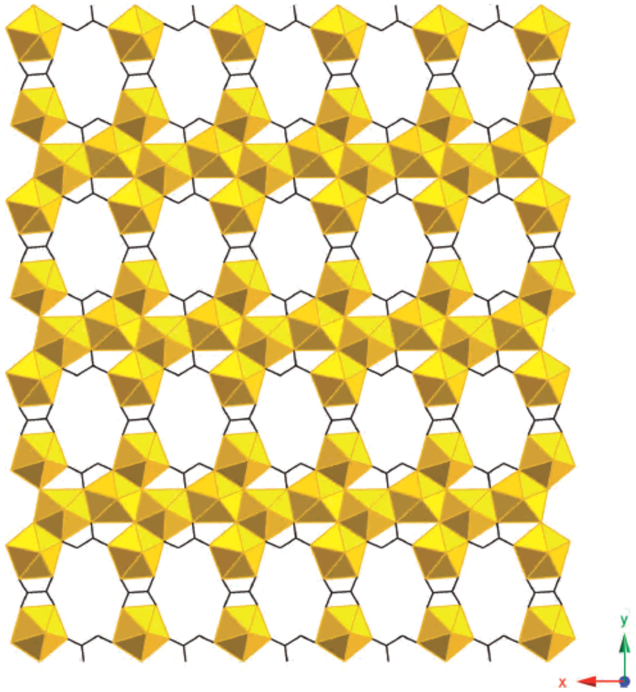

Figure 2. Polyhedral representation of **1** viewed down the [001] direction. Yellow polyhedra are uranium(VI) atoms in pentagonal bipyramid geometry. The black lines represent the oxalate and glycolate linkages.

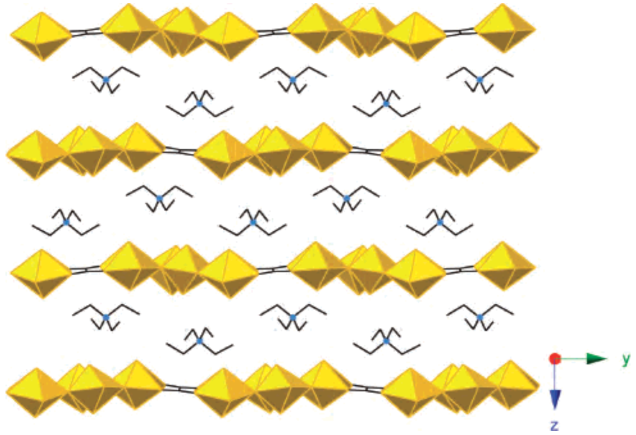

Figure 3. View of **1** down the [100] direction illustrating the 2D sheets of $(UO_2)_4(O)_2(C_2O_4)(H_2C_2O_3)_2$. Charge balancing the anionic sheets are the tetraethylammonium molecules, which are shown between the layers.

previously, a number of routes to oxalate anion formation have been proposed for other systems, including decarboxylation of a carboxylate-functionalized organic species,[48−50] the reductive coupling of adventitious CO_2,[49,52−56] and oxidative degradation of L-ascorbic acid.[57−59] With regard to CO_2 fixation, the yield of compound **1** (0.096 g) indicates that this material (or rather the oxalate and glycolate ligands) does not result from this route, as has been observed previously.[49,53−56,67] Glycolate oxidation to yield oxalate is fairly common in biological systems;[68,69] however, we have found only one reported occurrence of this redox process in materials synthesis. Castineiras et al. reported the formation of $\{Cu(GLYO)_{0.44}(ox)_{0.56}(bipy)]\cdot 2H_2O\}$ from Cu_2CO_3, glycolic acid, and 2,2′-bipyridine under reflux conditions.[70] Important to note is that in the absence of DABCO, neither an oxalate- or glycolate-containing material is formed. Furthermore, DABCO does not have any carboxylate-functionalized groups that could cleave to form CO_2 and subsequently couple to form oxalate or glycolate anions, a process that has been proposed in other systems. Therefore, in this system, we propose that DABCO is oxidized to first yield piperazine, ethylene glycol, and ethylenediamine (Scheme 1), a mechanism supported by observations from other researchers.[71−73] The formation of these intermediates is achieved through the activation of the DABCO C−N bond, either through protonation of the DABCO nitrogen or coordination of this N to the uranium metal center, followed by nucleophilic attack of a water oxygen on the two C−N bonds of DABCO.[72] Further oxidation of ethylene glycol then yields the glycolate and oxalate anions, as outlined in Scheme 2. Supportive of this mechanism was the isolation of single crystals of *N*,*N*′-dinitrosopiperazine through the evaporation of the reaction solution, confirming the presence of piperazine in the solution.[74,75]

The oxidation or decomposition of DABCO is not believed to be solely a hydrothermal process but rather a metal-mediated oxidation, although the specific role of the metal is not entirely clear. Reactions of DABCO in water were studied, and it was found that upon heating DABCO under hydrothermal conditions, a clear brown solution is obtained. Upon evaporation, this solution yields a hydrated form of DABCO, $(C_6H_{12}N_2)\cdot H_2O$, suggesting that DABCO is not oxidized simply as a result of temperature and pressure. Furthermore, under conditions analogous to those under which **1** was synthesized, DABCO in the presence of nitrate groups does not undergo oxidation but rather can be observed in the crystalline reaction product as $(C_6H_{14}N_2)(NO_3)_2$. See Supporting Information for the syntheses, crystal data, and structure refinements of $(C_6H_{12}N_2)\cdot H_2O$ and $(C_6H_{14}N_2)(NO_3)_2$.

We propose that the oxalate and glycolate ligands ultimately result from the oxidation of DABCO; however, at this time it is not apparent what species is being reduced, as no $U^{(IV)}O_2$ or otherwise reduced uranium species are observed. It has been hypothesized that nitrate groups may

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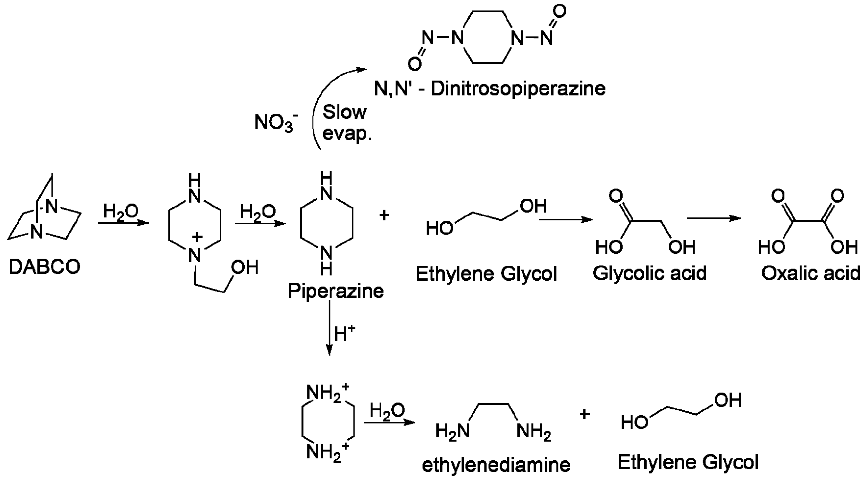
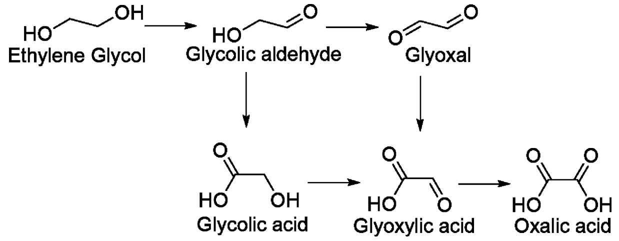
Scheme 1. Proposed Mechanism for DABCO Oxidation to Yield Glycolate and Oxalate Ligands.



Scheme 2. Glycolate and Oxalate Ligand Formation via Oxidation of Ethylene Glycol.[76,77]



act as oxidants; however, no species evident of this (such as NO_2, N_2, or N_2O) have been observed. Evans and Lin reported the oxidative coupling of methanol to form oxalate in the presence of nitrate groups. In addition, attempts to synthesize the oxalate-containing material using perchlorate in place of the nitrate salts did not yield an oxalate.[60] Barrett Adams et al. also found that the nitrate groups were critical to the formation of oxalate linkages via the reductive coupling of atmospheric CO_2 and that in the absence of these species, no oxalate containing products were formed.[53] Similarly, in our investigation efforts to synthesize oxalate- and glycolate-containing materials in the absence of nitrate groups by using uranium oxyacetate were unsuccessful, thus suggesting that nitrate groups do play a mechanistic role in the formation of oxalate containing materials. Alternatively, atmospheric O_2 may act as an oxidant. It is indeed plausible that the oxidation of DABCO first utilizes the dissolved oxygen in the system and that further decomposition proceeds with the reduction of NO_3^-.[78]

Additional support for the proposed DABCO oxidation mechanism and the promise of in-situ ligand synthesis in general is found in the following observations: (i) Attempts were made to synthesize **1** using oxalic acid and sodium oxalate (with and without glycolic acid), effectively the oxidation products of DABCO, as oxalate sources. Compound **1** was not obtained via this route. (ii) Compound **1** was not able to be produced via direct combination of stoichiometric amounts of glycolic and oxalic acids. (iii) Compound **1** can be produced from glycolic acid, as suggested by Scheme 2.[79] (iv) Compound **1** can be produced from ethylene glycol, also suggested in Scheme 2.[80]

Conclusion

As interest in coordination polymers and metal−organic frameworks has grown, so has the frequency of materials synthesized via in-situ ligand synthesis. Many compounds obtained through this route are largely unexpected, and therefore, the challenge will be to elucidate mechanistic information and harness these reactions to produce new compounds. This present contribution is a step in this direction, in that we have directed an otherwise serendipitous result toward a desired structure type. We have synthesized a novel uranium oxalate/glycolate from the oxidation of DABCO and are in the process of producing a series of these compounds through this route.

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(79) Synthesis of **1** using glycolic acid. Uranium oxynitrate hexahydrate (0.141 g, 0.28 mmol), tetraethylammonium hydroxide, 20 wt % solution in water (0.164 g, 0.22 mmol), glycolic acid (0.043g, 0.57 mmol), and distilled water (5 g, 278 mmol) were placed into a 23 mL Teflon-lined Parr bomb in the molar ratio of 1.0:0.8:2.0:992, pH 2.0. The reaction vessel was sealed and heated statically at 120 °C for 7 days. Upon cooling to room temperature, a clear yellow solution (pH 2.0) was decanted and yellow-orange plates were obtained. The crystals were washed with distilled water followed by ethanol and then allowed to air dry at room temperature. Yield: 52% (based on uranium). Product was characterized by single-crystal x-ray diffraction, and phase purity was confirmed by powder x-ray diffraction.

(80) Synthesis of **1** from ethylene glycol. Uranium oxynitrate hexahydrate (0.141 g, 0.28 mmol), tetraethylammonium hydroxide, 20 wt % solution in water (0.164 g, 0.22 mmol), ethylene glycol (330 uL, 2.5 mmol), and distilled water (5 g, 278 mmol) were placed into a 23 mL Teflon-lined Parr bomb in the molar ratio of 1.0:0.8:9.0:992, pH 3.15. The reaction vessel was sealed and heated statically at 120 °C for 14 days. Upon cooling to room temperature, a clear yellow solution (pH 2.4) was decanted and yellow-orange plates were obtained. The crystals were washed with distilled water followed by ethanol and then allowed to air dry at room temperature. Yield: 81% (based on uranium). Product was characterized by single-crystal x-ray diffraction, and phase purity was confirmed by powder x-ray diffraction.

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Supporting Information Available: Crystallographic data for **1** in CIF format, syntheses of DABCO salts, and supplemental figures of $[(UO_2)_2(OH)_2(C_2O_4)(H_2O)_2]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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