Crystal Engineering

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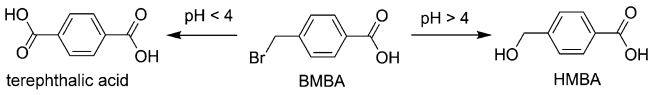
Uranyl Hybrid Material Derived from In Situ Ligand Synthesis: Formation, Structure, and an Unusual Phase Transformation**

*Michael B. Andrews and Christopher L. Cahill**

Interest in the synthesis of uranyl (UO_2^{2+}) organic hybrid materials has resulted in a family of compounds with a broad range of structural topologies which have been studied for their interesting luminescent properties as well as potential applications in the fields of photocatalysis and photoelectric conversion.[1] In an effort to expand the structural chemistry of uranyl hybrid materials we have explored the use of in situ ligand synthesis (ISLS). In these systems the ligands are formed during the hydro- or solvothermal synthesis of the hybrid material. While ISLS was initially observed as a serendipitous phenomenon,[2] recent efforts to harness these reactions have emerged. As such, many well-known organic reactions have been explored with the intention of promoting an organic reaction in the presence of inorganic building units.[3] A common theme of ISLS is the conversion of poorly coordinating compounds into ligands with greater affinities for the particular metal being used. For instance, carboxylic acids have been formed by a variety of reactions.[4]

An organic reaction that appears to be underutilized is the oxidation of alkyl halides to form carboxylic acids. In an effort to assess the potential applications of this reaction in the development of metal–organic hybrid materials, we have studied the behavior of 4-(bromomethyl)benzoic acid (BMBA) with the uranyl cation under hydrothermal conditions. The oxidation of the alkyl halide to a carboxylic acid was found to have a strong pH dependence (Scheme 1), and



Scheme 1. In situ reactivity of BMBA in solutions at different pH values.

occurred only in strongly acidic conditions and without coordination to the metal (see the Supporting Information). At higher pH the alkyl halide was hydrolyzed to 4-(hydroxymethyl)benzoic acid (HMBA), which was observed coordinating to the uranyl cation in product **1**, $NH_4[(UO_2)(C_8H_7O_3)_3]$.

The hydrothermal reaction of BMBA and $UO_2(NO_3)_2.6H_2O$ in a 1:1 ratio (pH_i 5–6, adjusted with NH_4OH) resulted in yellow, fluorescent rodlike crystals which were identified by single-crystal X-ray diffraction (XRD) to be $NH_4[UO_2(HMBA)_3]$ (**1**). **1** is formed from a single unique UO_2^{2+} unit that is bound in the equatorial plane to three crystallographically identical HMBA ligands through bidentate coordination of the carboxylate groups (Figure 1). These

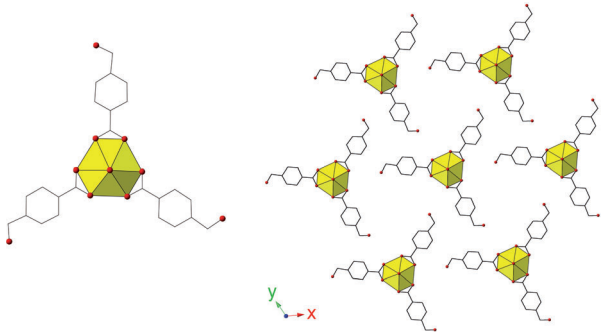


Figure 1. Monomeric unit of **1** (left) and the triangular tiling arrangement of these units (right).

monoanionic molecular units lie in the (001) plane in a triangular tiling arrangement with the NH_4^+ counterion occupying the void space (Figure 1). These layers stack to form hexagonal channels that propagate along [001].

After washing **1** with water and ethanol and allowing it to dry in air, a color change from pale yellow to dull orange was observed, along with a loss of fluorescence. Inspection of the bulk sample revealed that the crystallinity and the general rodlike morphology had been preserved, yet the majority of the crystals showed lateral cracks. Single-crystal XRD on an intact crystal resulted in the structure $[UO_2(HMBA)_2]$ (**2**). The structure of **2** is formed from a single and unique UO_2^{2+} unit which is bound to two pairs of crystallographically identical HMBA ligands (Figure 2). Two ligands bind trans to each other through bidentate coordination of the carboxylate group while the remaining two bind in a monodentate fashion through the hydroxy oxygen (Figure 2). The dual binding mode of the ligand allows it to act as a linker between the uranyl units to form a "stepped-sheet" topology which stacks along [001] with vacant interlayer spaces (Figure 3).

Although low pH conditions resulted in the predicted in situ reactivity it appears likely that they also caused the product, terephthalic acid, to remain protonated and thus

[*] Dr. M. B. Andrews, Prof. C. L. Cahill
Department of Chemistry, The George Washington University
Washington, DC 20052 (USA)
E-mail: cahill@gwu.edu

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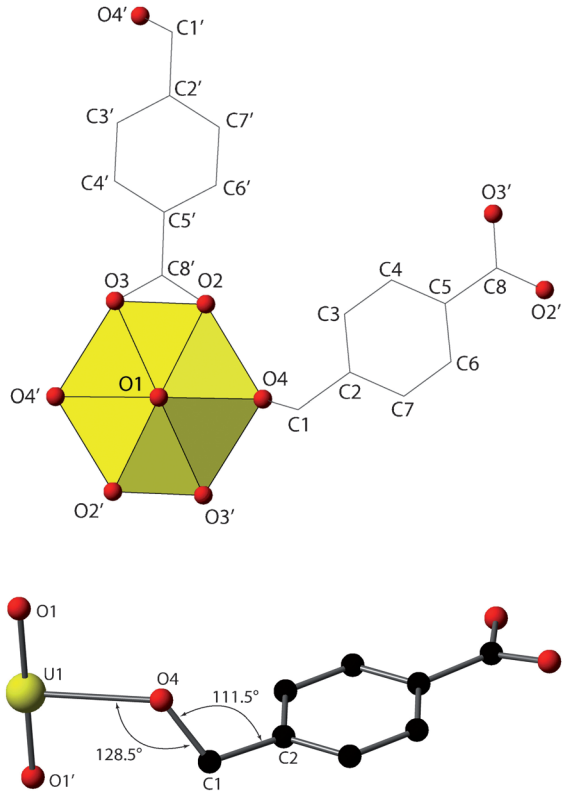


Figure 2. Local structure of **2** showing arrangement of ligands (left) and hydroxy coordination with respect to the uranyl cation (right).

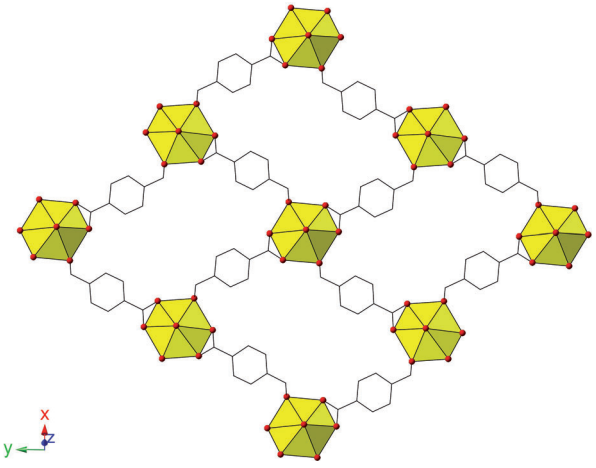


Figure 3. A view of a single two-dimensional sheet present in the structure of **2**.

precluded coordination to the uranyl cation. At higher pH, however, an alternative reaction was observed—the hydrolysis of the alkyl bromide to an alkyl alcohol. When HMBA was presynthesized hydrothermally prior to reactions with uranium salts (see the Supporting Information) the results were the same as those in the in situ method. It is possible that an organic reaction that can occur in the absence of a metal salt may occur before coordination to the metal. Alternatively, since the reactive site is both sterically and electronically removed from the site of coordination, the metal may play some role in directing the structure of the product. In fact, previous studies have shown that reactions at the 3-position of a substituted benzoic acid can result in different structures relative to the ones obtained when the preformed ligands are reacted directly with a metal, whereas those at the 4-position do not.[5] While this is admittedly speculative, it suggests that further work is needed to assess the potential benefits of the reaction in question, specifically in pre-ligands which show a greater affinity for binding metal ions in positions where they may influence the sterics or electronics of the in situ reaction.

While the crystal engineering of uranium hybrid materials uses many of the same methods as the development of d-block hybrid materials, it is with a decidedly different emphasis as the coordination chemistry of the uranyl cation with environmentally relevant functional groups[6] is of significant importance to waste stewardship. It is with this in mind that the postsynthetic behavior of **1** is of particular interest. On washing **1** with ethanol and allowing it to dry in air, the bulk sample undergoes a change in general appearance as well as fluorescent properties. Only a small fraction of the sample (Figure 4), however, remained suitable for analysis by XRD, thereby revealing the structure of the second phase to be **2** and thus suggesting that a phase transformation from **1** to **2** is responsible for the changes observed in the bulk sample. An alternative explanation for this, however, would be the synthesis of a mixed-phase product and the subsequent selective decomposition of **1**, thus resulting in a bulk sample containing only the amorphous or poorly crystalline remains of **1** along with the more robust single crystals of **2**. Powder XRD (PXRD) studies, however, suggest that this is not the case.

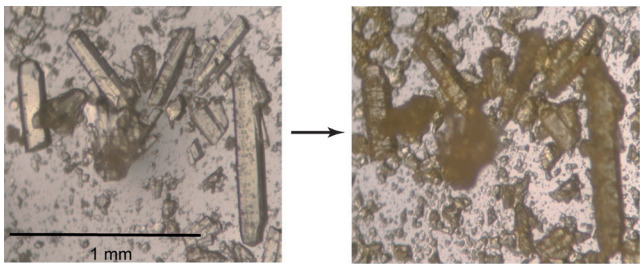


Figure 4. Example of crystals before and after phase transformation.

A sample of **1** was isolated by vacuum filtration and the PXRD pattern of this sample was compared to the calculated pattern to confirm purity. If the sample was repeatedly moistened with ethanol the PXRD pattern of the sample showed a gradual weakening of peaks associated with **1** and the appearance of peaks assigned to **2** over the course of approximately 9 hours (Figure 5). Weakening of the PXRD peaks associated with **1** is consistent with a selective decomposition mechanism. While this is indeed observed, the fact that peaks associated with **2** grew in intensity over this time period is not consistent with selective decomposition. This data instead suggests that the changes in the bulk properties

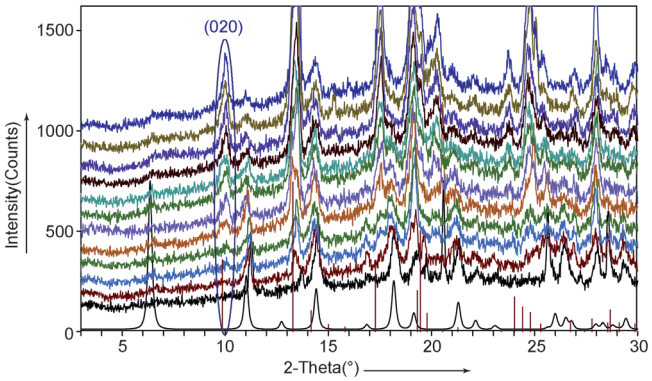
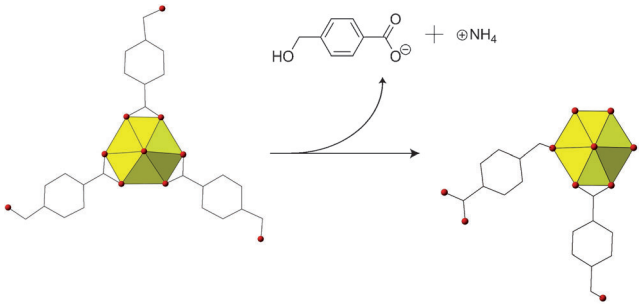


Figure 5. The time-resolved PXRD, showing a change in the bulk sample from **1** (simulated pattern) to **2** (calculated pattern). Highlighted is the (020) peak of **2**, which is completely absent from the initial sample. *t* (in min) from lower to upper trace: 0, 30, 75, 120, 165, 210, 255, 300, 345, 390, 435, 480.



Scheme 2. A possible mechanism for the solid-state transformation from **1** into **2**.

are due to a solid-state phase transformation as shown in Scheme 2.

Both **1** and **2** may be considered layered structures (Figure 6). In **1** the layers are formed by intermolecular forces and in **2** by covalent bonding (Figures 2 and 3). The relative orientation of the structures within the crystal must be taken into account, however, if a mechanism for the phase change is to be proposed. The rod-shaped morphology of the crystals allow a facile comparison between the two structures (see the Supporting Information). As would be predicted from crystal formation considerations the short "a" axis of **1** is aligned with

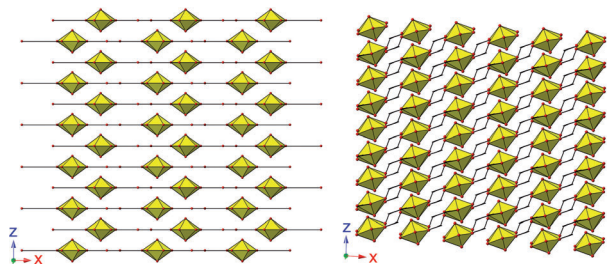


Figure 6. The layered structures of **1** (left) and **2** (right). In each case the z axis corresponds to the long dimension of the rod-shaped crystals.

the longest dimension of the crystal. The covalent layers in **2**, however, propagate in a stepwise fashion through the crystal. This difference in orientation suggests that rather than a direct conversion of the hydrogen-bonded sheets of **1** into the covalently bonded sheets of **2**, the ligands of the $[UO_2(HMBA)_3]^-$ unit present in **1** interact with units in the adjacent layers to form the stepped-sheet morphology present in **2**, a reaction that is likely facilitated by free rotation of the alcohol about the sp^3-hybridized alkyl carbon atom.

When considering the mechanism of the phase transformation another factor must be taken into account. The change in formula from $NH_4[UO_2(HMBA)_3]$ (**1**) to $[UO_2(HMBA)_2]$ (**2**) implies the loss of an anionic ligand and an associated counterion (Scheme 2), and it is only possible if the structure contains sufficient void space to accommodate this loss. The structure of **1** was calculated[7] to have a solvent-accessible void space of approximately 400 $Å^3$ per unit cell and inspection of the crystal structure shows this exists as continuous channels which run in the [001] direction (Figure 7). Small aromatic molecules take up approximately

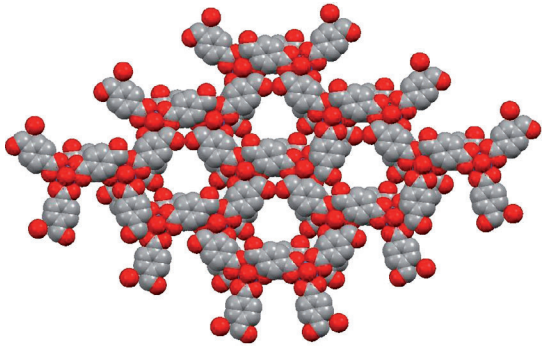


Figure 7. The channels present in **1**. The solvent molecules were removed for clarity.

100–300 $Å^3$,[8] thus suggesting that these channels are of sufficient size to allow the escape of the lost ligand and counterion. It seems likely that washing **1** with ethanol induces the phase change by solubilizing the lost ligand and counter ion. Finally, the phase change from $NH_4[UO_2(HMBA)_3]$ to $[UO_2(HMBA)_2]$ may also explain the loss in fluorescence, as compound **2** displays coordination of a protonated alcohol to the uranyl cation, which may provide a nonradiative decay mechanism through the oscillation of the OH bonds.

In summary, the oxidation/hydrolysis of alkyl halides has been shown to occur under hydrothermal conditions. In this case these in situ reactions did not result in different products relative to those obtained from reacting the preformed products directly with the metal. Further work is needed to access the potential of these reactions to yield compounds that are inaccessible by other methods. Additionally, the product of reacting HMBA with a uranyl salt was shown to undergo a solid-state phase transformation accompanied by the loss of a ligand and counterion. Phase transformations involving uranyl are known,[9] as are those involving the loss of aromatic guest molecules,[10] as well as phase changes

involving the loss of a ligand.[11] Typically however, the ligands lost are water or small alcohols, whereas the loss or exchange of larger aromatic ligands is much less common. It seems likely that the reaction of the nonbonded alcohol groups present in **1** with uranium atoms in adjacent layers causes the loss of one ligand per uranyl unit which is accommodated by the lability of equatorial ligands and the large pores present in **1**.

Experimental Section

1: BMBA (100 mg), uranyl nitrate hexahydrate (233 mg), and distilled water (2 mL) were placed in a 23 mL Teflon-lined Parr vessel and the pH of the mixture was adjusted to between 4 and 5 (by addition of NH_4OH). The mixture was then heated statically at 150 °C for three days. Upon cooling to room temperature the mixture was filtered over vacuum to give pure **1** (91 mg, 16% based on U) as pale yellow, fluorescent, rodlike crystals that were identified by single-crystal XRD. Full discussion of the data collection and refinement methods can be found in the Supporting Information.

2: On washing compound **1** with ethanol and allowing it to dry under ambient conditions the bulk sample was observed to undergo the solid-state change described above, without dissolution. Single-crystal XRD on an intact crystal resulted in the structure of compound **2**.

1: $C_{24}H_{21}N_1O_{11}U_1$, $M = 737.45$, hexagonal, space group P-62/c, $a = 16.0576(8)$, $b = 16.0576(8)$, $c = 6.8530(4)$ Å, $V = 1530.29(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.600\ mg\,m^{-13}$, $T = 100(1)$ K, $F(000) = 704$, $\mu(Mo_{K\alpha}) = 5.354\ mm^{-1}$, yellow rod-like crystal, 29936 reflections measured, 1609 unique ($R_{int} = 0.0843$), 75 parameters, $R_1 = 0.0419$ ($I > 2\sigma(I)$), $wR_2 = 0.1134$ (all data), GOF = 1.101.

2: $C_{16}H_{14}O_8U_1$, $M = 572.30$, monoclinic, space group $P21/c$, $a = 6.2490(16)$, $b = 17.934(5)$, $c = 7.1757(19)$ Å, $\beta = 93.599(4)°$, $V = 802.6(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.368\ mg\,m^{-13}$, $T = 293(1)$ K, $F(000) = 532$, $\mu(Mo_{K\alpha}) = 10.155\ mm^{-1}$, yellow rod-like crystal, 13025 reflections measured, 1666 unique ($R_{int} = 0.0434$), 143 parameters, $R_1 = 0.0356$ ($I > 2\sigma(I)$), $wR_2 = 0.0406$ (all data), GOF = 1.074.

Supporting information for this article is available on the WWW. References numbers CCDC 859073 (**1**) and 859074 (**2**) 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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