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Directing dimensionality in uranyl malate and copper uranyl malate compounds

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ABSTRACT

Uranyl hybrid compounds are complex materials due to variability in coordination geometry, flexibility in ligand chelation, and metal hydrolysis, which leads to difficulty in controlling the secondary building units. The presence of transition metals in uranyl hybrid materials adds to the complexity, but also leads to an increase in the dimensionality of the topology from infinite chains and 2-D sheets, to 3-D framework lattices. In this study, five uranyl malate compounds were synthesized at room temperature: $((C_4H_{12}N_2)[(UO_2)_2(C_4H_3O_5)_2]\cdot 4H_2O$ (**UMal1**), $(C_4H_{12}N_2)[(UO_2)_2(C_4H_3O_5)_2]$ (**UMal1-b**), $[(UO_2)(C_4H_3O_5)Cu(C_{10}H_8N_2)Cl(H_2O)]\cdot 2H_2O$ (**UCuMal1**), $[(UO_2)_2(C_4H_3O_5)_2Cu(C_5H_5N)_2(H_2O)_2]\cdot 2H_2O$ (**UCuMal2**), $[(UO_2)_2(C_4H_3O_5)_2Cu(C_5H_5N)_2(H_2O)_2]\cdot 2H_2O$ (**UCuMal3**)). These compounds were characterized using single-crystal X-ray diffraction, thermogravimetric analysis and Raman spectroscopy. All five compounds contain an identical uranyl malate secondary building unit that could be further linked through the Cu (II) cation. In this system, the identity of the ligands bonded to the Cu(II) cation impacted dimensionality and could be the key to designing materials with a known uranyl building unit.

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1. Introduction

Developing hybrid materials with specific structural connectivity and controlled physical properties is the overall goal of crystal engineering, but in practice, manipulating the individual building units to achieve the overall structural goal can be difficult [1–5]. This is particularly true for complex coordination geometries observed in hexavalent uranium, which forms strong covalent interactions to two O atoms to create the nearly linear uranyl cation $(UO_2)^{2+}$ as a fundamental building unit [6–10]. Flexibility for the uranyl moiety occurs with additional coordination about the equatorial plane, resulting three possible geometries: square, pentagonal, or hexagonal bipyramids [6,9]. Plasticity in the molecular geometry for the uranyl cation combined with variability in the chelation of the metal center by multidentate organic linkers results in limited predictability in structural features of the individual building units [7,9]. An additional design feature to consider in U(VI) hybrid materials is metal hydrolysis, which can further change the coordination of the ligand and provide additional variability of the individual building units [7,10,11].

There are several excellent reviews and journal articles that highlights the crystal engineering principles in uranyl hybrid materials and the difficult nature of controlling the design features for these compounds [7–9,12–16]. An extensive review by Loiseau et al. [8], focuses on the vast body of literature of uranyl carboxylate materials and highlights the distinct secondary building units that can arise from the carboxylate chelation. This detailed report emphasized the significant number of uranyl carboxylate compounds arising from the ability of the ligand to bond to the uranyl cation in either a mono- or bidentate fashion and form unpredictable extended arrays through free carboxylate oxygen atoms [8,10]. Andrews and Cahill [7] discuss several approaches to structural design in uranyl compounds and focus significant attention to additional supramolecular approaches towards rational design of materials. In both reviews, the importance of metal hydrolysis is noted in the formation oligomers and their contribution to secondary building unit evolution [7,8].

Even with the variability in ligand denticity, chelation, and intramolecular interaction, there is still a propensity of U(VI) materials to be controlled by the passivation of the uranyl oxo groups [17], resulting in the formation of 1-D chains and 2-D sheet topologies and limiting extended 3D frameworks [6,8]. One strategy to increase dimensionality of uranyl materials is to include a second metal cation, but in creating these heterometallic systems,

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additional complexity is introduced to the overall design. First-row transition metals and lanthanide cations are the most common secondary metal to be added to uranyl compounds and do result in the formation of a larger fraction of extended 3D networks [8]. This is specifically true for the incorporation of Cu(II) into hybrid uranyl compounds, where sixteen of the thirty reported structures contain framework topologies [18–30]. In addition, Thuery [31] detailed the importance of the Cu(II) cation to induce the formation of dodeca- and hexadecanuclear cluster compounds at the expense of more traditional 1- and 2-D topologies. Some variability within the structure is added through the role of the transition metal as either just a charge balancing species in the crystalline lattice or as a linker between the uranyl secondary building units [8]. Additional flexibility is also gained through the presence of the Cu(II) cation because of variation of coordination geometry; however, important structural design features for controlling dimensionality are still difficult to discern.

Our research group is specifically interested in designing uranyl hybrid materials with macrocyclic and nanotubular features [32], thus understanding the design principles that control dimensionality is of great interest. A majority of our work focuses on ligand sterics as the major design principle, but U(VI) nanotubular motifs [33–35] and nanoclusters [31,36] have been formed using transition metal cations. Herein, we provide the structural and chemical characterization of five uranyl malate structures ($(C_4H_{12}N_2)[(UO_2)_2(C_4H_3O_5)_2]\cdot 4H_2O$ (**UMal1**), $(C_4H_{12}N_2)[(UO_2)_2(C_4H_3O_5)_2]$ (**UMal1-b**), $[(UO_2)(C_4H_3O_5)Cu(C_{10}H_8N_2)Cl(H_2O)]\cdot 2H_2O$ (**UCuMal1**), $[(UO_2)_2(C_4H_3O_5)_2Cu(C_5H_5N)_2(H_2O)_2]\cdot 2H_2O$ (**UCuMal2**), $[(UO_2)_2(C_4H_3O_5)_2Cu(C_5H_5N)_2(H_2O)_2]\cdot 2H_2O$ (**UCuMal3**)) and the importance of ligand denticity is discussed in relationship to controlling dimensionality of the overall system.

2. Experimental

All solutions were prepared using Millipure water (18.2 M Ω) and chemicals purchased were used directly without further purification. CAUTION: $(UO_2)(NO_3)_2\cdot 6H_2O$ *contains radioactive ^{238}U, which is an alpha emitter, and like all radioactive materials must be handled with care. These experiments were conducted by trained personnel in a licensed research facility with special precautions taken towards the handling, monitoring, and disposal of radioactive materials.*

2.1. Synthesis

2.1.1. ***UMal1*** *$(C_4H_{12}N_2)[(UO_2)_2(C_4H_3O_5)_2]\cdot 4H_2O$ and* ***UMal1-b*** *$(C_4H_{12}N_2)[(UO_2)_2(C_4H_3O_5)_2]$*

A solution containing 1 mL of 0.2 M aqueous uranyl nitrate, one mL of 0.2 M aqueous nickel chloride and two mL of 0.2 M aqueous DL-malic ($C_4H_6O_5$) acid was prepared and the pH adjusted to 3.0 by 1.0 M piperazine. A 500 μL aliquot of the final solution was then transferred to a two mL glass vial and layered with one mL of toluene. After two weeks, yellow platelets of **UMal1** were discovered on the side of the vial. Several crystals associated with a minor secondary phase (**UMal1-b**) were also observed upon further aging and isolated based upon a variations in the morphology (blade versus plate). Multiple reactions produced yields ranging from 20% to 40%.

2.1.2. ***UCuMal1*** *and* ***UCuMal2*** *$[(UO_2)(C_4H_3O_5)Cu(C_{10}H_8N_2)Cl(H_2O)]\cdot 2H_2O$*

One mL of 0.2 M aqueous uranyl nitrate hexahydrate, one mL of 0.2 M copper chloride, one mL of 0.2 M aqueous D,L-malic acid or L-malic acid, and two mL of 0.1 M 2,2-bipyridine that had been dissolved in a 1:1 EtOH:H_2O solvent mixture were combined in a glass vial. The resulting clear teal solution was stirred for two minutes and the pH adjusted to 2.11 with 400 μL 1.0 M piperazine. After one week in a sealed vial under ambient conditions, lime green crystals formed on the bottom of the vessel. The crystals were isolated through vacuum filtration with yields of 56% and 82% for **UCuMal1** and **UCuMal2**, respectively.

2.1.3. ***UCuMal3*** *$[(UO_2)_2(C_4H_3O_5)_2Cu(C_5H_5N)_2(H_2O)_2]\cdot 2H_2O$*

An initial solution containing one mL 0.2 M aqueous uranyl nitrate hexahydrate and one mL of 0.2 M aqueous copper chloride was placed in a glass vial and the pH was adjusted to 3.72 with 150 μL pyridine. Two mL 0.1 M DL-malic acid was added to the vial and the solution stirred for 20 min. At this point a colloidal phase was detected due to the translucent teal color of the liquid, so 550 μL 1.0 M HNO_3 was added to the vial and the final solution was transparent. After one week in a sealed vial under ambient conditions, crystals had formed with yields of 35%.

2.2. Structural characterization

In all cases, crystals were taken from the mother liquor, coated in Infinium oil and mounted on a Nonius Kappa CCD single crystal X-ray diffractometer equipped with Mo Kα radiation (λ = 0.7107 Å) and a low temperature cryostat set at 100 K. Data were collected with the Nonius Collect software package [37] and peak intensities were corrected for Lorentz, polarization, and background effects using the Bruker APEX II software [38]. An empirical correction for adsorption was applied using the program SADABS within the Bruker Suite of software [38]. The structure solution was determined by direct methods and refined on the basis of F^2 for all unique data using the SHELXTL version 5 series of programs [39]. The primary sites of U, Cu, O, C, and N atoms were initially determined by intrinsic phasing with any disordered locations being determined from the difference Fourier maps. Hydrogen atoms associated with organic components were constrained using a riding model, whereas the H atoms on bound and interstitial water molecules (where possible) were determined from the difference Fourier maps following subsequent least-squares refinement of the partial structure models and restrained using the DFIX and DANG commands.

UMal1 crystallizes in the triclinic space group $P\bar{1}$ with a = 7.9421(6) Å, b = 8.4226(6) Å, c = 9.1852(6) Å, α = 75.067(2)°, β = 73.037(2)°, and γ = 79.497(2)°. A related compound for **UMal1** (**UMal1-b**) crystallizes in the triclinic space group $P\bar{1}$ with a = 7.8529(19) Å, b = 8.2762(19) Å, c = 8.895(2) Å, α = 106.530(7)°, β = 115.225(7)°, and γ = 91.534(7)°. Significant disorder was observed for the **UMal** and **UMal-b** structures and the U, O, and C atoms had to be modeled as split sites. For the compound **UCuMal1**, the U1 is modeled as three partially occupied sites due to positional disorder. Before modeling the partially occupied sites, multiple centro- and noncentrosymetric space groups were investigated. Doubling the unit cell axis in the [100] direction was also attempted to resolve the disorder, but that did not result in significant improvement in the structural model. Similar issues were initially observed for **UCuMal2**, but higher quality crystals were synthesized, which solved the positional disorder in the crystal. Additional synthesis attempts did not result in improvement in the crystallinity of the **UCuMal1** compound. **UCuMal2** was modeled in the space group $P2_1$ and additional symmetry within the structure was considered using the ADDSYM function of PLATON [40], but a center of symmetry could not located. Additional crystallographic information regarding the structural models for the uranyl and copper uranyl compounds can be found in Table 1. Selected bond distances and angles for each compound can be found in Supporting information section.

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