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: $((C_4H_{12}N_2)[(UO_2)_2(C_4H_3O_5)_2] \cdot 4 H_2O$ (**UMal1**), $(C_4H_{12}N_2)[(UO_2)_2(C_4H_3O_5)_2]$ (**UMal1-b**), $[(UO_2)(C_4H_3O_5)Cu(C_{10}H_8N_2)Cl(H_2O)] \cdot 2 H_2O$ (**UCuMal1**), $[(UO_2)_2(C_4H_3O_5)_2Cu(C_5H_5N)_2(H_2O)_2] \cdot 2 H_2O$ (**UCuMal2**), $[(UO_2)_2(C_4H_3O_5)_2Cu(C_5H_5N)_2(H_2O)_2] \cdot 2 H_2O$ (**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.

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 $(\text{UO}_2)^{2+}$ 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

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4 approaches to structural design in uranyl compounds and focus significant attention to additional
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7 supramolecular approaches towards rational design of materials. In both reviews, the importance
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9 of metal hydrolysis is noted in the formation oligomers and their contribution to secondary
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11 building unit evolution [7, 8].
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15 Even with the variability in ligand denticity, chelation, and intramolecular interaction, there
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17 is still a propensity of U(VI) materials to be controlled by the passivation of the uranyl oxo
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19 groups,[17] resulting in the formation of 1-D chains and 2-D sheet topologies and limiting
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21 extended 3D frameworks [6, 8]. One strategy to increase dimensionality of uranyl materials is to
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23 include a second metal cation, but in creating these heterometallic systems, additional
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25 complexity is introduced to the overall design. First-row transition metals and lanthanide cations
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27 are the most common secondary metal to be added to uranyl compounds and do result in the
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29 formation of a larger fraction of extended 3D networks [8]. This is specifically true for the
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31 incorporation of Cu(II) into hybrid uranyl compounds, where sixteen of the thirty reported
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33 structures contain framework topologies [18-30]. In addition, Thuery [31] detailed the
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35 importance of the Cu(II) cation to induce the formation of dodeca- and hexadecanuclear cluster
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37 compounds at the expense of more traditional 1- and 2-D topologies. Some variability within the
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39 structure is added through the role of the transition metal as either just a charge balancing species
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41 in the crystalline lattice or as a linker between the uranyl secondary building units [8].
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43 Additional flexibility is also gained through the presence of the Cu(II) cation because of
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45 variation of coordination geometry; however, important structural design features for controlling
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47 dimensionality are still difficult to discern.
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57 Our research group is specifically interested in designing uranyl hybrid materials with
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59 macrocyclic and nanotubular features [32], thus understanding the design principles that control
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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 ((C₄H₁₂N₂)[(UO₂)₂(C₄H₃O₅)₂] • 4 H₂O (**UMal1**), (C₄H₁₂N₂)[(UO₂)₂(C₄H₃O₅)₂] (**UMal1-b**), [(UO₂)(C₄H₃O₅)Cu(C₁₀H₈N₂)Cl(H₂O)] • 2 H₂O (**UCuMal1**), [(UO₂)₂(C₄H₃O₅)₂Cu(C₅H₅N)₂(H₂O)₂] • 2 H₂O (**UCuMal2**), [(UO₂)₂(C₄H₃O₅)₂Cu(C₅H₅N)₂(H₂O)₂] • 2 H₂O (**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 Millipore water (18.2 MΩ) and chemicals purchased were used directly without further purification. CAUTION: (UO₂)(NO₃)₂•6H₂O *contains radioactive* ²³⁸U, 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

UMal1 (C₄H₁₂N₂)[(UO₂)₂(C₄H₃O₅)₂] • 4 H₂O and **UMal1-b**

(C₄H₁₂N₂)[(UO₂)₂(C₄H₃O₅)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 (C₄H₆O₅) 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 20-40%.

UCuMal1 and **UCuMal2** $[(UO_2)(C_4H_3O_5)Cu(C_{10}H_8N_2)Cl(H_2O)] \cdot 2 H_2O$: 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:H₂O 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 μ L 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.

UCuMal3 $[(UO_2)_2(C_4H_3O_5)_2Cu(C_5H_5N)_2(H_2O)_2] \cdot 2 H_2O$: 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 μ L pyridine. Two mL 0.1 M DL-malic acid was added to the vial and the solution stirred for 20 minutes. At this point a colloidal phase was detected due to the translucent teal color of the liquid, so 550 μ L 1.0 M HNO₃ 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 MoK α radiation ($\lambda = 0.7107$ 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 $P-1$ with $a = 7.9421(6)$ Å, $b = 8.4226(6)$ Å, $c = 9.1852(6)$ Å, $\alpha = 75.067(2)^\circ$, $\beta = 73.037(2)^\circ$, and $\gamma = 79.497(2)^\circ$. A related compound for **UMal1** (**UMal1-b**) crystallizes in the triclinic space group $P-1$ with $a = 7.8529(19)$ Å, $b = 8.2762(19)$ Å, $c = 8.895(2)$ Å, $\alpha = 106.530(7)^\circ$, $\beta = 115.225(7)^\circ$, and $\gamma = 91.534(7)^\circ$. 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 noncentrosymmetric 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 Tables 1. Selected bond distances and angles for each compound can be found in the supporting information section.

Table 1. Selected crystallographic information for $(C_4H_{12}N_2)[(UO_2)_2(C_4H_3O_5)_2] \cdot 4 H_2O$ (**UMal1**), $(C_4H_{12}N_2)[(UO_2)_2(C_4H_3O_5)_2]$ (**UMal1-b**), $[(UO_2)(C_4H_3O_5)Cu(C_{10}H_8N_2)Cl(H_2O)] \cdot 2 H_2O$ (**UCuMal1**), $[(UO_2)_2(C_4H_3O_5)_2Cu(C_5H_5N)_2(H_2O)_2] \cdot 2 H_2O$ (**UCuMal2**), $[(UO_2)_2(C_4H_3O_5)_2Cu(C_5H_5N)_2(H_2O)_2] \cdot 2 H_2O$ (**UCuMal3**)

	UMal1	UMal1-b	UCuMal1	UCuMal2	UCuMal3
FW (g/mol)	962.21	890.14	710.32	710.32	1095.64
Space Group	$P-1$	$P-1$	$P2_1/n$	$P2_1$	$P-1$
a (Å)	7.9421(6)	7.853(2)	8.2649(9)	8.2614(6)	7.7476(4)
b (Å)	8.4226(6)	8.276(2)	16.9591(18)	16.9977(13)	8.3366(4)
c (Å)	9.1852(6)	8.895(2)	13.9972(15)	14.0497(11)	11.5285(6)
α (°)	75.067(2)	106.530(7)	90	90	71.460(2)
β (°)	73.037(2)	115.225(7)	96.735(4)	97.334(3)	80.146(2)
γ (°)	79.497(2)	91.534(7)	90	90	74.765(2)
V (g/cm ³)	564.02(7)	494.0(2)	1948.4(4)	1956.8(3)	678.03(6)
Z	2	1	4	4	2
ρ_{calc} (g/cm ³)	2.810	2.61	2.422	2.391	2.684
μ (mm ⁻¹)	14.427	16.445	9.586	9.544	12.776
F(000)	432	400	1332	1308	503
Crystal size (mm)	0.18 x 0.17 x 0.08	0.17 x 0.05 x 0.04	0.20 x 0.18 x 0.06	0.20 x 0.10 x 0.10	0.20 x 0.18 x 0.10
Theta range (°)	2.70 to 27.02	2.61 to 27.04	1.894 to 27.446	1.46 to 25.29	1.87 to 25.34
Limiting	$-10 < h < 10$	$-9 < h < 9$	$-10 < h < 10$	$-9 < h < 9$	$-9 < h < 9$
Indices	$-10 < k < 10$	$-10 < k < 10$	$-21 < k < 21$	$-20 < k < 20$	$-10 < k < 10$
	$-9 < l < 11$	$-11 < l < 10$	$-18 < l < 18$	$-16 < l < 16$	$-13 < l < 13$
Refl. collect/uniq.	9545 / 2451	7282/2148	33845 / 4449	33959/ 7087	11950 / 2473
R_{int}	0.0283	0.0323	0.0243	0.0242	0.0169
GOF	1.089	1.075	1.141	1.043	1.041
Final R [$I > 2\sigma(I)$]	$R_1 = 0.0268,$ $wR_2 = 0.0704$	$R_1 = 0.0198,$ $wR_2 = 0.0451$	$R_1 = 0.0288,$ $wR_2 = 0.0638$	$R_1 = 0.0186,$ $wR_2 = 0.0434$	$R_1 = 0.0140,$ $wR_2 = 0.0369$
Final R (all data)	$R_1 = 0.0276,$ $wR_2 = 0.0710$	$R_1 = 0.0214,$ $wR_2 = 0.0457$	$R_1 = 0.0318,$ $wR_2 = 0.0649$	$R_1 = 0.0197,$ $wR_2 = 0.0437$	$R_1 = 0.0140,$ $wR_2 = 0.0371$

2.3 Chemical Characterization

Powder X-ray diffractograms of bulk crystalline products were collected from 5-60° 2 θ with a step size of 0.05 and a count time of 1 sec/step on a Bruker D-5000 diffractometer (Cu K α) equipped with a LynxEye solid state detector. After determining purity of the samples,

thermogravimetric analysis of samples were performed using a TA instruments TGA Q500. Approximately 15-20 mg of each sample was placed onto an aluminium pan and heated from 25-600 °C in air at a ramp rate of 2 °C/minute. A powder X-ray diffraction pattern was also collected after the heat cycle to determine the identity of the residual product. Raman spectroscopy was performed on single crystal samples using a Nicolet Almega XR High Performance Dispersive spectrometer with a 785 nm excitation laser.

3. Results and Discussion

Structural Characterization

The common structural feature across all five compounds is dinuclear uranyl malate secondary building unit that forms an extended coordination polymer throughout the crystalline lattice. Each U(VI) cations form two strong bonds with oxygen atoms to create the nearly linear uranyl cation, $(\text{UO}_2)^{2+}$, with average bond length and angle of 1.773(4) Å and 178.5(2)°, respectively. The uranyl moiety is further coordinated about the equatorial plane by five O atoms with bond lengths ranging from 2.319(4) – 2.443(4) Å forming a pentagonal bipyramidal coordination geometry about the metal center. Each, malate ligand is fully deprotonated and shared between two U(VI) polyhedra, with the carboxylate end members bonded to separate UO_2^{2+} cations and the deprotonated alcohol group bridging the metal atoms into a dinuclear secondary building unit. Deprotonation of the alcohol upon complexation of the malate ligand to the uranyl cation has been previously observed for coordination complexes and confirmed by NMR spectroscopy [41]. The resulting building block is further linked via the carboxylate functional groups to create a one-dimensional infinite chain topology.

In **UMal1** and **UMal1-b**, the uranyl malate chain is the dominant feature and extends down the [010] direction of the lattice (Fig.1a). Overall the chains are negatively charged and piperazinium cations are located in the interstitial regions, where the molecules participate in H-bonding interactions with the uranyl oxo groups and the free carboxylate O atom within the neighboring chains (Fig. 1b). Hydrogen bonding interactions within these compounds can be considered quite strong, with H donor to acceptor distances of 2.70 and 2.87 Å. Interstitial water molecule are also observed in the lattice, resulting in an overall formula for **UMal1** of $(C_4H_{12}N_2)[(UO_2)_2(C_4H_3O_5)_2](H_2O)_4$. **UMal1-b** contains identical uranyl malate chains, but lacks the interstitial water molecules, leading to unit cell variations and an overall formula of $(C_4H_{12}N_2)[(UO_2)_2(C_4H_3O_5)_2]$.

Figure 1. a) Dinuclear uranyl building units in **UMal1** and **UMal1-b** are linked into a chain topology through the malate ligands. b) Piperazinium cations participate in hydrogen bonding interactions with the uranyl malate chains to create the extended crystallographic network. U polyhedra are depicted in yellow and the O, C, N, and H atoms are represented by red, black, light blue and pink sphere, respectively.

Loiseau et al.[8] determined that the dinuclear secondary building unit is a relatively common motif, with forty-seven structures reported in the literature. A dinuclear secondary building unit composed of two uranyl pentagonal bipyramids with two bridging groups (i.e. a shared edge) is the most common configuration, with twenty-five reported compounds. The identity of the bridging groups has typically been μ_3 -O atoms from the carboxylate group of the ligand or an independent μ_2 -OH group, whereas no μ_2 -O complexes have been reported [8]. **UMal1** and **UMal1-b** also contain an μ_3 -O atom, but instead of the carboxylate functional group it is part of a deprotonated alcohol.

Nine of the twenty-five compounds with the shared edge dinuclear motif also contain polymerization of the secondary building unit into a 1-D chain topology [8, 42-46]. Structures of particular note include $[(\text{UO}_2)(\text{HCit})]^-$ and $[(\text{UO}_2)(\text{Citml})]^-$ (Cit = Citrate, Citml = D-citramalate) synthesized under hydrothermal conditions and crystalized in the presence of DABCO and bipyridine [43]. Malate belongs in the same family of these ligands, with variation dependent on the substitution of the proton on the central carbon atom by either a methyl or carboxylate group to create the citramalate or citrate molecules, respectively. All three ligands chelate to the uranyl secondary building unit in an identical fashion, with μ_3 -O bridges forming the shared edge and polymerization taking place through free carboxylate O atoms to form an extend chain topology [43].

In **UCuMal1** and **UCuMal2**, Cu(II) atoms have been added to the exterior of the uranyl malate chains (Fig. 2). The Cu(II) cations are complexed in a bidentate fashion to the N atoms of the bipyridine molecule and bond to the exterior of the uranyl chain via the free carboxylate O atom of the malate ligand. The first shell coordination about the Cu(II) cation is completed

through the interaction of the metal center with one chlorine atom and one water molecule.

Average bond lengths for Cu-N, Cu-O, Cu-Cl, and Cu-OH₂ are 1.998(5), 1.972(4), 2.271(3), and 2.278(5) Å, respectively. Elongation of the Cu-OH₂ bond suggests a Jahn-Teller type distortion and leads to the formation of a distorted square pyramidal coordination geometry. The racemic mixture of the malate (D,L-malic acid) was utilized for **UCuMal1** (Fig. 2a) and the single enantiomer (L-malic) for **UCuMal2** (Fig. 2b), leading subtle differences in the chirality, but identical topological features.

Figure 2. a) The dinuclear secondary building units are preserved in **UCuMal1** (a) and **UCuMal2** (b) and Cu(II) cations complexed by bipyridine, chlorine atoms and water molecules decorate the exterior of the chain. The racemic D,L-malate ligand is also observed in **UCuMal1** whereas **UCuMal2** crystallize with the L-malate enantiomer. U polyhedra are depicted in yellow and the Cu, Cl, O, C, N, and H atoms are represented by dark blue, green, red, black, light blue and pink sphere, respectively.

Due to the addition of the bipyridine ligand, additional intermolecular interactions occur between the neighboring chains, resulting in the crystallization of the material (Fig. 3). As shown in Figure 3 for the **UCuMal1** compound, overlap of the bipyridine rings leads to π - π interactions down the [001] direction. This interaction is also observed in **UCuMal2** with average intermolecular distance between the bipyridine molecules of 4.47 Å. Interstitial water molecules are also observed in the lattice of both structures leading to the overall formula of $[(\text{UO}_2)(\text{D,L-C}_4\text{H}_3\text{O}_5)\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)\text{Cl}(\text{H}_2\text{O})](\text{H}_2\text{O})_2$ and $[(\text{UO}_2)(\text{L-C}_4\text{H}_3\text{O}_5)\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)\text{Cl}(\text{H}_2\text{O})](\text{H}_2\text{O})_2$ for **UCuMal1** and **UCuMal2**, respectively.

Figure 3. The uranyl copper malate coordination polymers in **UCuMal1** and **UCuMal2** interact through π - π interactions between neighboring bipyridine molecules along the [001] direction.

Replacing the bipyridine ligand with pyridine molecules leads to a uranyl copper malate 2-D sheet topology for **UCuMal3** (Fig 4a). The uranyl malate chain topology is conserved within this compound, but additional polymerization occurs Cu(II) cation and the free carboxylate O atom of the neighboring chains, effectively serving serves as a bridge for the secondary building units. Interactions between the Cu(II) cation and the neighboring chains

occurs in a *trans*-configuration with two additional pyridine molecules bonding to the metal center through the equatorial plane. The octahedral geometry about the Cu(II) cation is created upon bonding of two additional water molecules in the axial positions. Average Cu-N and Cu-O bond distances within the equatorial plane are 2.014(3) and 1.976(2) Å, respectively, but Jahn-Teller distortion causes elongation of the Cu-OH₂ bonds at 2.438(3) Å. Due to steric constraints, the pyridine are not planar in relationship to the two-dimensional sheet and instead are canted 110° from the plane and observed on the top and bottom of the sheet structure.

Figure 4. a) The bipyridine ligands are replaced by pyridine molecules in **UCuMal3**, resulting in the extension of the copper uranyl malate chain into a sheet topology. b) Ligated water molecules coordinated to the Cu(II) cation interact with neighboring interstitial water molecules through hydrogen bonding. U polyhedra are depicted in yellow and the Cu, Cl, O, C, N, and H atoms are represented by dark blue, green, red, black, light blue and pink sphere, respectively.

UCuMal3 contains a two-dimensional topology that run parallel to the [202] plane and pack into a crystalline lattice through intermolecular interactions with intercalated solvent molecules (Fig. 4b). An additional water molecule (OW1) is located within the interstitial region and interacts through strong hydrogen bonds with the ligated water molecule with donor to acceptor distances of 2.86 Å. Addition of the solvent molecules leads to $[(\text{UO}_2)_2(\text{C}_4\text{H}_3\text{O}_5)_2\text{Cu}(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})](\text{H}_2\text{O})$ as the overall formula of the **UCuMal3** compound.

The coordination sphere of the Cu(II) cation has been shown to vary in hybrid bimetallic uranyl materials with either four, five, or six ligands bonding to the metal center to create square planar, square bipyramidal, or octahedral geometries. While square planar Cu(II) complexes are widely observed in coordination complexes, within hybrid bimetallic uranyl compounds, it has only been reported in $[(\text{UO}_2)(\text{H}_2\text{O})_2(\text{C}_7\text{H}_3\text{NO}_4)_2\text{Cu}]$ [28]. The square pyramidal coordination geometry observed in **UCuMal1** and **UCuMal2** is widely observed for both for compounds synthesized at room temperature and under hydrothermal conditions, but typically occurs in the presence of amines. Octahedral coordination spheres have also been observed, but significant elongation of the axial positions, resulting from 4+2 Jahn-Teller distortions are observed, as is the case for both $(\text{Cu}(\text{H}_2\text{O})_2)(\text{UO}_2)_4[\text{C}_5\text{H}_4\text{PO}_3](\text{C}_6\text{H}_4\text{PO}_3\text{H})_4(\text{C}_8\text{H}_6\text{N}_4)$ [35] and $[(\text{UO}_2)_2\text{Cu}(\text{C}_{10}\text{H}_{16}\text{O}_4)_3(\text{C}_5\text{H}_9\text{NO})_2]$ [29].

Presence of transition metals can extend the dimensionality of uranyl hybrid materials, but choice of ligand is still the defining factor in determining the overall structural topology achieved in these systems. Without complexing ligands, the transition metal typically plays the role as a charge balancing cation intercalated between uranyl sheets [8]. Such is the case for the hexaqua- complexes of Fe(II), Co(II), Ni(II) and Zn(II) and hexamminecobalt(II) that have been incorporated into uranyl hybrid materials [16, 47-49]. Increasing the dimensionality for this system is more often achieved through additional coordination of the transition metal cation with free carboxylate groups. This interaction tends to favor the formation of framework topologies, particularly in when Cu(II), Co(II), Mn(II) cations are present in the uranyl-based compounds.

Direct interactions between the transition metal cation and the uranyl oxo group, also referred to in the actinide literature as a cation-cation interaction, is also observed in the formation of extended networks [20, 21, 25]. In some cases, these cation-cation interactions

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4 seem to be mediated by the organic ligands, as they provide additional chelation to stabilize the
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6 metal in this configuration [8]. In other cases, the metal itself seems to have a relatively strong
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8 interaction with the uranyl oxo group as evidenced by lengthening of the uranyl bond. This
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10 phenomenon can be observed in $[(\text{UO}_2)_2\text{O}(\text{OH})_2\text{Cu}(\text{H}_2\text{O})_2(\text{C}_7\text{H}_4\text{O}_4) \cdot \text{H}_2\text{O}]$, which displays
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12 elongation of the uranyl bond length (1.805(3) Å) and a smaller Cu-O bond length (2.350(3))
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14 compared to other copper uranyl hybrid materials that also display 4+2 Jahn-Teller distortion
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16 (bond lengths range from 2.43-2.74(5) Å) [25]. The ability of the Cu(II) cation to undergo Jahn-
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18 Teller distortions is an important feature that provides additional interaction with the uranyl oxo
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20 and promotes dimensionality in the system.
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26 27 *Thermogravimetric Analysis* 28 29

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31 A small, initial weight loss occurred between 25 and 50 °C for **UMal1**, followed by more
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33 significant decomposition of the material at 300 °C (Fig. 5). Dehydration of the solvent water
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35 molecules resulted in a weight loss of 5.27%, which corresponds to 2.75 water molecules. This
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37 was slightly less than the four molecules predicted using single-crystal X-ray diffraction for
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39 **UMal1**, but the powder diffractogram suggested a small amount of the anhydrous **UMal1-b**
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41 compound that would account for the difference in hydration state (Fig. S1). Complete
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43 breakdown of the malate ligand and piperazinium cations resulted in a residual weight loss of
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45 68.55%. The PXRD diffractogram of the material after analysis, depicted a few broad peaks
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47 (Fig. S5), suggesting the formation of a poorly crystalline uranyl oxide or oxyhydroxide phase.
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Figure 5. Thermogravimetric analysis of the **UMal1**, **UCuMal1**, **UCuMal2**, and **UCuMal3** compounds.

The isostructural nature of **UCuMal1** and **UCuMal2** resulted in similar weight losses, with initial dehydration followed by removal of the organic components (Fig. 5). Dehydration was more gradual than the **UMal** compound because complete removal of the water occurs by 90 °C. The dehydration step resulted in a 7.28% weight loss for both compounds, corresponding to the release of three water molecules per formula unit. This corresponds to removal of both the interstitial and ligated water molecules within the crystalline lattice, suggesting a weak Cu-OH₂ bond. A weak interaction between the Cu(II) cation and the axial H₂O molecule is supported by the long average bond length of 2.278(5) Å. Breakdown of the organic components was initiated at 245 °C and occurs in three distinct steps. A final residual weight of 50% was observed for both compounds and identified as a mixture of CuU₄O₁₀ (PDF 00-044-0979), CuUO₄ (PDF 97-003-6071), and U₃O₈ (PDF 97-019-1130) by PXRD.

Removal of the water in **UCuMal3** occurred between 25 and 95 °C and was followed by a significant weight loss at 250 °C (Fig. 5). The initial weight loss was 2.53% and corresponds

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4 to 1.5 water molecules per formula unit. This could indicate the presence of some additional
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6 interstitial water molecules that were not observed with structural analysis or partial removal of
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8 the ligated water molecules attached to the Cu(II) cation. The large weight loss corresponds to
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10 the decomposition of the organic components and resulted in a residual weight of 63.5%. Again
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12 the diffractogram identifies the decomposition product is a mixture of $\text{CuU}_4\text{O}_{10}$ (PDF 00-044-
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14 0979), CuUO_4 (PDF 97-003-6071), and U_3O_8 (PDF 97-019-1130) by PXRD.
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23 *Vibrational Spectroscopy*

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26 Major features of the Raman spectra for the uranyl malate and uranyl copper malate
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28 compounds were found between 700 and 1100 cm^{-1} . Figure 6 provides the combined spectra for
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30 this region for **UMal1**, **UCuMal1**, and **UCuMal3**. Spectra for **UCuMal1** and **UCuMal2** were
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32 identical; thus, only one spectrum is shown for clarity. The uranyl symmetric stretch (ν_1) is the
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34 strongest band in the spectra and occurs at 826, 841, and 833 cm^{-1} for **UMal1**, **UCuMal1**, and
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36 **UCuMal3**, respectively. The position of the symmetric stretching vibration is dependent on the
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38 variability of the orbital overlap for the ligands bonded through the equatorial plane to the UO_2^{2+}
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40 cation. Addition of strong sigma donors lead to a red shift from the uranyl pentaaqua complex
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42 ($[(\text{UO}_2)(\text{H}_2\text{O})_5]^{2+}$) band located at 870 cm^{-1} and the carboxylate groups of the malate ligand
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44 functions in this capacity [17]. All bands are blue shifted from the previously reported uranyl
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46 malate compounds, which observed a ν_1 stretch at 816 cm^{-1} [41]. In these molecular species,
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48 hydrolysis of the uranyl moiety leads to the formation of a trimer which has an additional $\text{u}_3\text{-O}$
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50 group, leading to additional red shift of the symmetric stretching vibration [41].
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Other strong bands observed in the Raman spectra corresponded to the malate ligand and the pyridine or 2,2-bipyridine molecules. Weaker secondary peaks in **UMal1** are located at 785, 967, and 1030 cm^{-1} and correspond to the malate ligand and piperazinium cations packed within the crystal structure. The peak positioned at approximately 790 cm^{-1} was also observed as a major band in the previously reported uranyl malate compounds [41]. Malate peaks are also apparent in the spectra for **UCuMal3**, with additional bands at 1011 and 986 cm^{-1} corresponding to the pyridine ligand. Peaks at 767, 806, 1030, and 1060 cm^{-1} are observed for **UCuMal2** that represent the 2,2-bipyridine ligand complexed to the Cu(II) cation and the malate ligand.

Figure 6. The Raman spectra for **UMal1**, **UCuMal2**, and **UCuMal3**.

4. Conclusion

Five uranyl malate compounds were synthesized, and characterized by single crystal X-ray diffraction, thermogravimetric analysis and Raman spectroscopy. The dinuclear uranyl malate secondary building unit was a dominate structural motif in all compounds, with additional

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4 variability observed through the addition of the Cu(II) cation. The presence of pyridine and
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6 bipyridine controlled the ability of the Cu(II) cation to complex to the neighboring uranyl malate
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8 chain, thus impacting the dimensionality of the system. Previously reported hybrid uranyl
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10 copper compounds exhibited additional extension in dimensionality through the presence of
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12 cation-cation interactions between the uranyl oxo group and the Cu(II) cation. Chemical
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15 characterization confirmed the structural model for these compounds and overall this system
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17 demonstrates the important structural features in the design of dimensionality within uranyl
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50 Raman spectrophotometer.
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