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Structures and luminescent properties of new uranyl-based hybrid materials

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ABSTRACT

Six uranyl coordination compounds, $UO_2(OH)(PYCA)$ (**1**), $UO_2(PYCA)_2(H_2O)\cdot 2H_2O$ (**2**), $UO_2(PIC)_2$ (**3**), $UO_2(H_2O)_2(NIC)_2$ (**4**), $UO_2(OH)(HINIC)(INIC)$ (**5**), and $UO_2(PYTAC)_2(H_2O)_2$ (**6**) were grown as single crystals via hydrothermal synthesis (PYCA = pyrazine-2-carboxylate, PIC = picolinate, NIC = nicotinate, INIC = isonicotinate, and PYTAC = 2-(pyridin-4-yl)thiazole-5-carboxylate) to study their optical properties. All six compounds have been identified via single crystal X-ray diffraction and fully characterized via powder X-ray diffraction, infrared spectroscopy, UV–Vis spectroscopy, and fluorescence spectroscopy. Three of the complexes, **1**, **3**, and **6**, represent new structures, and their synthesis and structural characterization is detailed within. The structures of **2**, **4**, and **5** have previously been reported in the literature. Coordination polymer **1** crystallizes in the orthorhombic space group *Pca*21 ($a = 13.5476(5)$ Å, $b = 6.6047(2)$ Å, $c = 8.3458(3)$ Å), and forms infinite 1-D chains of corner-sharing uranium polyhedra connected into 2-D layers by bridging ligands. Coordination polymer **3** crystallizes in the monoclinic space group *Cc* ($a = 8.4646(8)$ Å, $b = 13.0357(11)$ Å, $c = 11.8955(10)$ Å, $\beta = 96.815(2)^\circ$), and forms ligand-bridged 1-D chains. Complex **6** crystallizes in the triclinic space group *P*-1 ($a = 5.6272(7)$ Å, $b = 8.9568(10)$ Å, $c = 10.4673(12)$ Å, $\alpha = 90.508(2)^\circ$, $\beta = 104.194(2)^\circ$, $\gamma = 91.891(2)^\circ$), and consists of isolated uranyl complexes connected via hydrogen bonds. The structures and luminescent properties of $UO_2(OH)(PYCA)$ (**1**), $UO_2(PYCA)_2(H_2O)\cdot 2H_2O$ (**2**), $UO_2(PIC)_2$ (**3**), $UO_2(H_2O)_2(NIC)_2$ (**4**), $UO_2(OH)(HINIC)(INIC)$ (**5**), and $UO_2(PYTAC)_2(H_2O)_2$ (**6**) are discussed.

1. Introduction

Organic-inorganic hybrid materials contain two notable features: (1) positively or neutrally charged metal ions or metal-oxo clusters, and (2) negatively or neutrally charged organic ligands [1]. These two are infinitely linked via dative bonds in 0-, 1-, 2-, or 3-dimensions, and are further held together via intermolecular and packing forces to create a fully crystalline motif. Depending on the metal cations and organic anions chosen, these hybrid materials have a wide variety of applications [2,3].

The use of the uranyl (UO_2^{2+}) cation as a metal-oxo cluster in place of the more traditional transition metals can allow for increased stability due to the strong U–O bond [4]. Additionally, as a hard acidic species, the uranyl cation is known for binding both to oxygen and nitrogen atoms, allowing for a wide variety of coordination chemistry involving carboxylate, phosphonate, and heterocyclic groups [5–10]. It is a highly luminescent species, and among the most studied ions of the actinide series [11–16]. Furthermore, several uranyl-containing systems have been found useful for photocatalytic properties, as the excited uranyl ion is a strong oxidant [2,17,18].

Choosing small, rigid ligands similar to the pyridine and pyrazine carboxylate series as the organic anion has several compelling benefits. Due to their multiple classes of hard and soft basic binding sites, each with its own metal preferences, they are able to accommodate a variety of metals and mixed-metal systems [19]. These ligands also have great flexibility within a three-dimensional motif without compromising their luminescent potential, allowing for sensitized emission of the coordinated-uranyl cation via the antenna effect [20]. This phenomenon has been well-demonstrated in similar ligand series, such as the pyridine and pyrazole dicarboxylates [21–23], although it was concluded not to play a role in this particular series of coordination compounds.

Combining the inorganic cation and the organic anion under hydrothermal reaction conditions provides the energy and pressure necessary for the high-yield crystallization of millimeter-sized single crystals. In addition, it allows for high reproducibility and

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Abbreviations: HPYCA, pyrazine-2-carboxylic acid; HPIC, picolinic acid; HNIC, nicotinic acid; HINIC, isonicotinic acid; HPYTAC, 2-(pyridin-4-yl)thiazole-5-carboxylic acid; PYCA, pyrazine-2-carboxylate; PIC, picolinate; NIC, nicotinate; INIC, isonicotinate; PYTAC, 2-(pyridin-4-yl)thiazole-5-carboxylate; PXRD, powder X-ray diffraction.

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consistency of conditions essential for temperature- and pH-dependent studies of structural motifs. The use of this methodology has resulted in the synthesis of a number of organic-uranyl hybrid materials, six of which are included here. Three of the complexes, **1**, **3**, and **6**, represent new structures and their synthesis and structural characterization is detailed within. The structures of **2**, **4**, and **5** have been reported in the literature. The luminescent properties of all six complexes were investigated and the results are reported herein.

2. Experimental details

2.1. Materials and methods

All solvents and reagents were purchased from commercial sources and used without further purification. All heating and cooling was performed in a Fisher Scientific Isotemp programmable oven, at a rate of 1 °C per minute and 0.1 °C per minute, respectively. Caution: Uranyl acetate contains depleted uranium, but standard precautions for handling radioactive and highly toxic substances should be followed.

2.2. Hydrothermal synthesis

2.2.1. Synthesis of $UO_2(OH)(PYCA)$ (**1**)

Uranyl acetate (0.25 mmol, 106 mg), pyrazine-2-carboxylic acid (HPYCA) (0.50 mmol, 62 mg), and 0.5 mL aqueous sodium bicarbonate (pH 8.5) were combined in a 9 mm glass tube and flame sealed under vacuum. The tube was heated to 80 °C, held for 12 h, heated to 160 °C, held for three days, cooled to 80 °C, held for 12 h, and finally cooled to room temperature. Crystals of **1** formed under autogenous pressure as yellow plates in 100% yield based on stoichiometric ratios.

2.2.2. Synthesis of $UO_2(PYCA)_2(H_2O)\cdot 2H_2O$ (**2**)

Uranyl acetate (0.25 mmol, 106 mg), pyrazine-2-carboxylic acid (HPYCA) (0.50 mmol, 62 mg), and 0.5 mL aqueous sodium bicarbonate (pH 8.5) were combined in a 9 mm glass tube and flame sealed under vacuum. The tube was heated to 80 °C, held for 12 h, heated to 130 °C, held for three days, cooled to 80 °C, held for 12 h, and finally cooled to room temperature. Crystals of **2** formed under autogenous pressure as yellow plates in 100% yield based on stoichiometric ratios.

2.2.3. Synthesis of $UO_2(PIC)_2$ (**3**)

Uranyl acetate (0.25 mmol, 106 mg), picolinic acid (HPIC) (0.50 mmol, 62 mg), and 0.5 mL aqueous sodium bicarbonate (pH 8.5) were combined in a 9 mm glass tube and flame sealed under vacuum. The tube was heated to 80 °C, held for 12 h, heated to 160 °C, held for three days, cooled to 80 °C, held for 12 h, and finally cooled to room temperature. Crystals of **3** formed under autogenous pressure as yellow blocks in 25% yield based on stoichiometric ratios.

2.2.4. Synthesis of $UO_2(H_2O)_2(NIC)_2$ (**4**)

Uranyl acetate (0.25 mmol, 106 mg), nicotinic acid (HNIC) (0.50 mmol, 62 mg), and 0.5 mL aqueous sodium bicarbonate (pH 8.5) were combined in a 9 mm glass tube and flame sealed under vacuum. The tube was heated to 80 °C, held for 12 h, heated to 130 °C, held for three days, cooled to 80 °C, held for 12 h, and finally cooled to room temperature. Crystals of **4** formed under autogenous pressure as yellow blocks in 100% yield based on stoichiometric ratios.

2.2.5. Synthesis of $UO_2(OH)(HINIC)(INIC)$ (**5**)

Uranyl acetate (0.25 mmol, 106 mg), isonicotinic acid (HINIC) (0.50 mmol, 62 mg), and 0.5 mL aqueous sodium bicarbonate (pH 8.5) were combined in a 9 mm glass tube and flame sealed under vacuum. The tube was heated to 80 °C, held for 12 h, heated to 130 °C, held for three days, cooled to 80 °C, held for 12 h, and finally cooled to room temperature. Crystals of **5** formed under

Table 1
Crystal data and structure refinements for compounds **1**, **3**, and **6**.

	1	**3**	**6**
Empirical formula	$C_5H_4N_2O_5U$	$C_{12}H_8N_2O_6U$	$C_{18}H_{14}N_4O_8S_2U$
Formula weight	410.13	514.23	716.48
Temperature	100(2) K	295(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Pca*21	*Cc*	*P*−1
Unit cell dimensions	a = 13.5476(5) Å	a = 8.4646(8) Å	a = 5.6272(7) Å
	b = 6.6047(2) Å	*b* = 13.0357(11) Å	*b* = 8.9568(10) Å
	c = 8.3458(3) Å	*c* = 11.8955(10) Å	*c* = 10.4673(12) Å
	α = 90°	〈 = 90°	α = 90.508(2)°
	β = 90°	® = 96.815(2)°	β = 104.194(2)°
	γ = 90°	© = 90°	γ = 91.891(2)°
Volume	746.76(4) Å^3	1303.3(2) Å^3	511.11(10) Å^3
Z	4	4	1
Density (calculated)	3.648 Mg/m^3	2.621 Mg/m^3	2.328 Mg/m^3
Absorption coefficient	21.727 mm^{-1}	12.484 mm^{-1}	8.201 mm^{-1}
F(000)	720	936	338
Crystal size	0.14 × 0.08 × 0.04 mm^3	0.08 × 0.06 × 0.04 mm^3	0.08 × 0.06 × 0.05 mm^3
Theta range for data collection	3.01–.34°	2.88–27.72°	2.01–26.05°
Index ranges	$-18 \le h \le 18, -8 \le k \le 8, -11 \le l \le 11$	$-11 \le h \le 11, -16 \le k \le 16, -15 \le l \le 15$	$-6 \le h \le 6, -11 \le k \le 11, -12 \le l \le 12$
Reflections collected	15876	12550	5685
Independent reflections	1848 [R(int) = 0.0307]	3036 [R(int) = 0.0474]	1999 [R(int) = 0.0504]
Completeness to theta = 28.34°	99.8%	99.8%	99.7%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.3713	1.0000 and 0.7168	0.6846 and 0.5599
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1848/2/123	3036/2/190	1999/2/157
Goodness-of-fit on F^2	1.076	1.009	1.066
Final *R* indices [I > 2sigma(I)]	*R*1 = 0.0133, w*R*2 = 0.0322	*R*1 = 0.0263, w*R*2 = 0.0501	*R*1 = 0.0358, wR2 = 0.0790
R indices (all data)	*R*1 = 0.0142, w*R*2 = 0.0325	*R*1 = 0.0305, w*R*2 = 0.0520	*R*1 = 0.0360, wR2 = 0.0791
Largest diff. peak and hole	0.747 and −0.518 e.Å^{-3}	1.095 and −0.443 e.Å^{-3}	1.843 and −0.977 e.Å^{-3}