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Note

Structure and luminescence of a one-dimensional uranium coordination polymer assembled through benzophenone-4,4′-dicarboxylate

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ABSTRACT

Uranyl nitrate reacts under hydrothermal conditions with benzophenone-4,4′-dicarboxylic acid to produce a one-dimensional coordination polymer constructed through a double-chain motif. Upon excitation of the organic component in the near-UV, sensitized uranyl emission is observed. Thermogravimetric analysis demonstrates that this material is stable until 245 °C.

1. Introduction

Inorganic–organic hybrid materials have been of considerable interest of late, in part owing to their highly crystalline nature and interesting physical properties [1–7]. Uranium containing hybrid materials have been studied with a variety of organic molecules under hydrothermal conditions [8–12]. Mimicking geothermal environments, the overall goal is to understand these metal–organic interactions in terms of the long-term stewardship of nuclear waste [13–15]. Through the use of multi-functional organic molecules, or “linkers” extended structures can be attained. The linear uranyl cation (UO_2^{2+}) results in compounds that are primarily limited to one or two dimensions owing to the typical “non-bonding” behavior of the axial oxygen atoms and allowing coordination of the organic component through equatorial positions only [10]. Furthermore, the uranyl ion will adapt but one of three bipyramidal coordination geometries in solution: tetragonal, pentagonal, or hexagonal bipyramidal. These primary building units ($(UO_2)X_n$; X = organic/ligand donor atoms, $n = 4$, 5, or 6) can be extended to form interesting secondary building units through clustering of metal centers, and include such motifs as dimers, tetramers, sheets, etc. Fundamentally, we are interested in how metal speciation in solution can be used to predict final structural topologies when reacted with small organic moieties. Here we report the synthesis, structure, and emission properties of a one-dimensional coordination polymer constructed through $(UO_2)O_5$ monomers extended through benzophenone-4,4′-dicarboxylate ions.

2. Experimental

Caution! Whereas the uranyl nitrate hexahydrate $[UO_2(NO_3)_2]\cdot 6H_2O$ used in these experiments contained depleted uranium, standard precautions for the handling and disposal of radioactive materials should be observed. The title compound, $[(UO_2)(C_{15}H_8O_5)(H_2O)]_n$ was synthesized through the hydrothermal reaction of benzophenone-4,4′-dicarboxylic acid (BPDC) with uranyl nitrate. In a typical synthesis, uranyl nitrate hexahydrate (75 mg, 0.15 mmol) and benzophenone-4,4′-dicarboxylic acid (40 mg, 0.15 mmol) were combined with 5 mL of distilled water into a 23 mL Teflon-lined Parr steel autoclave with an initial pH 3.0. After heating statically for five days at 180 °C, the autoclave was cooled naturally to room temperature and opened. A clear, yellow solution of pH 1.8 was decanted from the solid material. Upon visual inspection of the product, some clear, colorless crystals were observed amongst the yellow crystals of the title compound. These crystals were most likely from the organic linker as they dissolved in ethanol and were completely removed through several ethanol washes assisted with sonication. The purified yield was typically ~35% depending on sample. A powder X-ray diffraction pattern of the bulk material demonstrated its phase purity as compared to the single crystal structural model, with no indication of a second (organic) crystalline phase. Elemental analyses conducted by

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Table 1
Crystallographic details.

$[(UO_2)(C_{15}H_8O_5)(H_2O)]_n$	
Formula weight	556.26
Crystal class	monoclinic
Space group	$P2_1/c$
a (Å)	16.3958(6)
b (Å)	8.6857(3)
c (Å)	10.6190(4)
α (°)	90
β (°)	102.96
γ (°)	90
V (Å^3)	1473.74(9)
Z	4
T (K)	100(2)
μ (mm^{-1})	11.058
Reflections collected	16845
R_{int} (independent reflections)	0.0332
wR_2[a]	0.0264
R_1[a] [$I > 2\sigma I$]	0.0465
Goodness-of-fit (GOF) on F^2	1.039

[a] $R_1 = \sum \frac{||F_o|-|F_c||}{|F_o|}$; $wR_2 = \left(\frac{\sum[w(F_o^2-F_c^2)^2]}{\sum[w(F_o^2)^2]}\right)^{\frac{1}{2}}$.

Galbraith Laboratories in Knoxville, TN, USA further supports phase purity (theoretical/experimental): C (32.37%/32.99%) and H (1.81%/1.92%). Single crystal X-ray diffraction data were collected [16]. The compound crystallizes in the monoclinic space group $P2_1/c$, and crystallographic details can be found in Table 1.

3. Results and discussion

3.1. Structural description

In general, the structure consists of one-dimensional chains of uranyl monomers proliferated down [100] through the organic linker. The uranium center is in pentagonal bipyramidal geometry, as can be seen in Fig. 1 and is bound to three distinct BPDC ions. One end of the BPDC ion connects to two neighboring uranium centers in a monodentate fashion through O1 and O2, with the other end connecting to a third U center through a bidentate mode with oxygen atoms O4 and O5. Two uranyl monomers stitch together through O1 and O2 (Fig. 1) forming a double-chain motif, and are related by inversion centers between both the uranyl centers and between neighboring BPDC ions. This double-chain propagates down [100] (Fig. 2) in an alternating zig-zag fashion through coordination of O4 and O5. A bound water (O3) ligand fulfills the equatorial coordination sphere, with O6 and O7 bonding in the expected axial positions and bind only to the U center. Selected bond lengths and angles can be found in Table 2. Two relatively strong hydrogen bonds between O3 (bound water hydrogens) and the uranyl O1 on a neighboring chain are present, and details can be found in Table 3. Neighboring chains further interact through a weak σ–π interaction between C6–H6···Cg2 (Cg2 = the center of the phenyl ring C10–C15) at a donor–acceptor distance of 3.602(3) Å. The shortest intra-chain phenyl–phenyl interaction is ~4.4 Å, reducing any π–π interactions effectively null. A thermal ellipsoid plot of the crystallographically unique atoms is in Fig. 3.

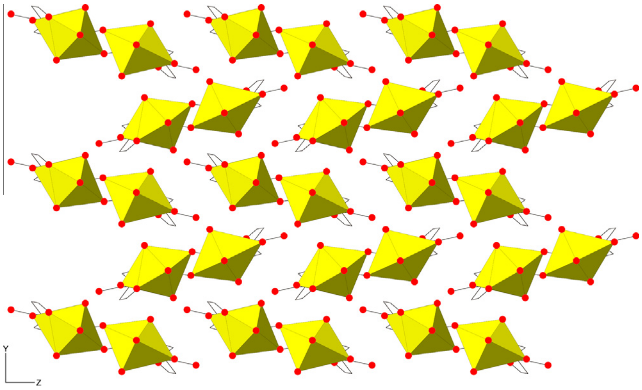

Fig. 2. View down [100] depicting how the 1D chains stack in an alternating zig-zag fashion to form the overall structure. Yellow polyhedra are UO_7, red spheres are oxygen atoms, and black lines are carbon atoms. Hydrogen atoms are omitted. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2
Selected bond lengths (Å) and angles (°).

U1–O6	1.774(2)	O6–U1–O7	177.29(11)
U1–O7	1.769(2)	O4–U1–O5	54.11(8)
U1–O1	2.320(2)	O1–U1–O5	80.01(8)
U1–O2	2.359(2)	O1–U1–O2	82.75(8)
U1–O3	2.473(2)	O2–U1–O3	74.99(9)
U1–O4	2.410(2)	O3–U1–O4	68.58(9)
U1–O5	2.429(2)		

Table 3
Hydrogen bond geometry (Å, °).

D–H···A	D–H	H···A	D···A	D–H···A
O3–H3A···O8	0.72(5)	2.29(4)	2.946(4)	152(4)
O3–H3B···O8	0.85(5)	2.12(5)	2.919(4)	157(5)

Within the organic linker, the two phenyl rings are nonplanar with a torsion angle of ~30° between them. This in combination with the restriction to equatorial bonding is arguably the reason the material's dimensionality is limited to one. However, upon

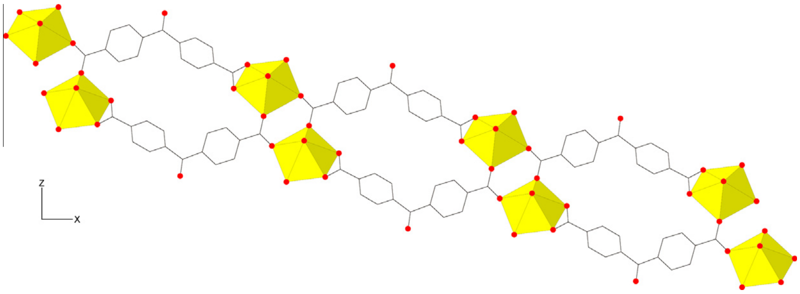

Fig. 1. A view of the one-dimensional chains that run down [100] to construct this material. Yellow polyhedra represent the UO_7 moiety, with oxygen atoms denoted as red spheres. The black lines represent carbon atoms. Hydrogen atoms are omitted. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)