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Synthesis, structure and fluorescent studies of novel uranium coordination polymers in the pyridinedicarboxylic acid system†

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Received 8th June 2006, Accepted 13th July 2006
First published as an Advance Article on the web 9th August 2006
DOI: 10.1039/b608187h

Self-assembly under hydrothermal conditions has been employed to synthesize several novel uranium-containing polymeric materials in the pyridinedicarboxylic acid (pydc) system. Uranium containing coordination polymers were synthesized utilizing 2,3-pyridinedicarboxylic acid (2,3-pydc), 2,4-pyridinedicarboxylic acid (2,4-pydc) and 2,6-pyridinedicarboxylic acid (2,6-pydc) as the organic linker. Furthermore, several bimetallic compounds were also synthesized, U–M–2,6-pydc (M = Cu, Ag, Pb). A new secondary building unit for uranium(VI) compounds has also been realized in compound **4** $[(UO_2)_2(C_7H_3NO_4)(O)(H_2O)]$ through tetramer building units edge shared to form one-dimensional chains. Presented herein will be the syntheses, crystal structures and fluorescent properties of these uranium-containing compounds.

Introduction

The crystal engineering of inorganic–organic hybrid materials has become an increasingly popular field of research over the past few decades owing to the potential for the synthesis of technologically important compounds with tailored topologies. Hybrid materials have shown promise in a vast array of applications such as catalysis, gas storage, ion exchange, magnetic materials, optics and separations.[1–15] Much effort has been geared towards the design of multi-dimensional hybrid architectures by taking advantage of the favored geometry of the local metal center in addition to utilizing the functionalities and sterics of the organic components through which the metal centers are linked.[16]

Although the efforts to produce transition metal-based coordination polymers have been quite extensive,[16–33] the synthesis of actinide-based coordination polymers has been a less examined area.[34–49] Our current interests lie within the under explored area of synthesizing uranium(VI) based compounds. From a crystal engineering perspective, uranium(VI) coordination polymers are distinctive in that these materials are built upon the linear, triatomic UO_2^{2+} moiety (often referred to as the uranyl ion). Since the uranyl oxygen atoms are almost exclusively non-bonding, the uranium metal center binds to organic linkers through equatorial positions to produce geometries such as square-, pentagonal- and hexagonal-bipyramids. These geometries typically (yet not exclusively) promote one- or two-dimensional structures as seen in the previously cited examples. Furthermore, higher dimensional uranium(VI) coordination polymeric materials have demonstrated potential in applications similar to those mentioned previously mentioned for hybrid materials.[36,43,44,50–52]

An expansion of these earlier efforts has been to synthesize heterometallic compounds by employing heterofunctional ligands, that is, ligands with multiple, yet distinct functional groups. The addition of a second metal center in bimetallic compounds has many advantages. From a structural point of view, this additional metal center has the possibility of altering the local geometry of the structure and thus influences the overall topology potentially leading to higher dimensional structures. Bimetallic systems, in general, have also demonstrated promise in areas such as magnetism, catalysis and adsorption.[53–58] Previously, we utilized 3,5-pyrazoledicarboxylic acid (H_3pdc) to synthesize a novel uranium–copper coordination polymer.[59] Hard/soft acid/base considerations (HSAB)[60,61] successfully predicted the binding positions of the uranium(VI) and copper(II) metal centers to the H_3pdc organic linker: the hard uranium metal center was exclusively coordinated to the carboxylate groups while the softer copper metal center was coordinated to the (softer) pyrazole ring, along with an oxygen atom from the carboxylate group. Following this approach, we have chosen a series of pyridinedicarboxylic acids (pydc) as the organic linker based on the terminal (harder) carboxylic acid and the (softer) pyridine functional groups. Specifically, three ligands have been chosen for this study with the only structural difference occurring in the position of the second carboxylic acid: 2,3-pyridinedicarboxylic acid (2,3-pydc), 2,4-pyridinedicarboxylic acid (2,4-pydc) and 2,6-pyridinedicarboxylic acid (2,6-pydc). HSAB distinctions were our initial inspiration for this work, yet we will see that this has failed to predict the binding positions of the metals to the ligand. There are clearly more complex considerations (sterics, *etc*) that dictate the local geometries of the metal centers. Recently, the pyridinedicarboxylic acids have produced transition metal-based and lanthanide-based coordination polymers that have demonstrated properties in areas such as magnetism, photoluminescence, adsorption and nonlinear optics.[62–77] Whereas there have been a few reported uranium–pydc compounds,[52,78–81] Harrowfield *et al.*[82] recently reported five

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† Electronic supplementary information (ESI) available: Powder XRD patterns for compounds **1–3**, higher resolution emission spectra for compounds **1–3**, absorbance spectrum for compound **3**, emission spectra for compound **3** at various wavelengths and additional figures for compounds **1**, **4**, **6** and **8**. See DOI: 10.1039/b608187h

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uranium containing bimetallic coordination polymers, U–M–2,6-pydc (M = Li, Na, K, Rb, Cs), although the only structures solved *via* single-crystal X-ray diffraction were the three-dimensional Rb and Cs compounds. Furthermore, the bifunctional pyridinedicarboxylic acids are optimal ligands to enhance uranium fluorescence through sensitized emission (the "antenna effect")[83] which can occur *via* an energy transfer from excited π orbitals of the pyridine ring to the uranium metal center.

Reported herein are the syntheses, crystal structures and fluorescent properties of four novel U–pydc and four bimetallic 2,6-pydc coordination polymers.

Experimental

CAUTION: While uranium(IV) oxide, UO_2 and uranium(VI) nitrate hexahydrate, $UO_2(NO_3)_2\cdot 6H_2O$, contain depleted uranium, standard precautions for handling radioactive substances should be followed.

Uranium(IV) oxide (UO_2) was obtained from Strem Chemicals while 2,4-pyridinedicarboxylic acid and 2,6-pryidinedicarboxylic acid were obtained from Acros Organics. 2,3-Pyridinedicarboxylic acid, copper(II) nitrate hemipentahydrate [$Cu(NO_3)_2\cdot 2.5H_2O$] and lead(II) nitrate $Pb(NO_3)_2$ were obtained from Aldrich Chemicals Inc. Silver nitrate $Ag(NO_3)$ was obtained from Alfa Products. All reagents were used without further purification.

The uranium precursor for all the uranium containing compounds, uranyl nitrate hexahydrate [$UO_2(NO_3)_2\cdot 6H_2O$], was synthesized by adding excess concentrated HNO_3 to uranium(IV) oxide. This solution was stirred for about 2 h under low heat, after which the acid was evaporated until a precipitate became visible. At this point, the heat was removed and the solution was allowed to cool to room temperature resulting in the formation of the yellow powder precipitate of $UO_2(NO_3)_2\cdot 6H_2O$ as verified by powder X-ray diffraction.

All of the reactants, in their appropriate molar ratios, were dissolved in distilled water and placed in a 23 mL Teflon-lined stainless steel Parr bomb and heated. Upon completion of the reaction, the Parr bombs were allowed to cool to room temperature. The crystals were obtained after decanting the mother-liquor, washed with both distilled water and ethanol and dried in air at room temperature. The molar ratios of the reactants and the reaction conditions along with the percent yields of pure samples and the initial and final pH of the reactions for compounds **1–8** are summarized in Table 1. Elemental analyses were performed on pure samples by Galbraith Laboratories, Inc., Knoxville, TN.

Characterization

Instrumentation. The crystal structures of compounds **1–8** were determined *via* single-crystal X-ray diffraction and the crystallographic data are summarized in Table 2. The single crystals were either mounted on a cryoloop with oil or on a glass fiber using epoxy gel. Intensity data were collected on a Bruker SMART diffractometer equipped with an APEX II CCD detector. Data processing was performed using SAINT[84] and the structures were solved using direct methods. Refinements were carried out using SHELXL-97[85] within the WINGX software suite.[86] Powder X-ray diffraction (PXRD) data were collected on a ScintagXDS

Table 1 Synthesis conditions for compounds **1–8**

	1 $(UO_2)(C_7H_3NO_4)$	**2** $(UO_2)(C_7H_3NO_4)$	**3** $(UO_2)(C_7H_3NO_4)$	**4** $(UO_2)_2(C_7H_3NO_4)$-$(O)(H_2O)$	**5** $(UO_2)(C_7H_3NO_4)_2$-$Cu(H_2O)_4\cdot 4H_2O$	**6** (UO_2)-$(C_7H_3NO_4)_2Ag_2$	**7** $(UO_2)(C_7H_3NO_4)_2$-$Pb_2(C_2O_4)(H_2O)_2$	**8** $(UO_2)(C_7H_3NO_4)_2$-$Pb\cdot 2H_2O$
$UO_2(NO_3)_2$ (molar ratio)	1	1	1	1/2	1/2	1/2	1/2	1/2
Acid (molar ratio)	23PDCA (1)	24PDCA (1)	26PDCA (1)	26PDCA (1)	26PDCA (1)	26PDCA (1)	26PDCA (1)	26PDCA (1)
H_2O (molar ratio)	151	151	151	555	555	555	555	555
Metal (molar ratio)				$Zn(NO_3)_2$ (2)	$Cu(NO_3)_2$ (2)	$AgNO_3$ (2)	$Pb(NO_3)_2$ (2)	$Pb(NO_3)_2$ (2)
T/°C	120	120	120	180	180	180	180	180
t/days	3	3	3	3	3	3	3	2
Pure? yield (%)	Yes 22 mg, 10.1	Yes 157 mg, 72.2	Yes 201 mg, 92.4	No, along with **3**	No, along with **3**	No, along with unidentified gray phase	No, along with unidentified red phase	No, and Immirzi *et al.*[79]
pH (init./final)	1.76/1.80	1.66/1.08	1.34/1.09	1.37/4.99	1.56/1.09	1.94/4.94	1.58/3.56	1.51/1.56
Topology	2D Sheets	3D	3D	1D Chains	1D Chains	1D Chains	3D	3D
U coordination	Pentagonal bipyramids	Pentagonal bipyramids	Pentagonal bipyramids	Pentagonal bipyramids	Hexagonal bipyramids	Hexagonal bipyramids	Hexagonal bipyramids	Hexagonal bipyramids
EA[a] found (calc.)	C: 19.3 (19.4); H: 0.7 (0.9); N: 3.2 (3.4)	C: 19.3 (19.3); H: 0.7 (0.7); N: 3.2 (3.3)	C: 19.3 (19.2); H: 0.7 (0.8); N: 3.2 (3.3)	N/A	N/A	N/A	N/A	N/A

[a] Elemental analysis on pure samples (%).

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Table 2 Crystallographic data for compounds **1–8**

	(**1**) (UO_2)-$(C_7H_3NO_4)$	(**2**) (UO_2)-$(C_7H_3NO_4)$	(**3**) (UO_2)-$(C_7H_3NO_4)$	(**4**) $(UO_2)_2(C_7H_3NO_4)$-$(O)(H_2O)$	(**5**) $(UO_2)(C_7H_3NO_4)_2$-$Cu(H_2O)_4{\cdot}4H_2O$	(**6**) (UO_2)-$(C_7H_3NO_4)_2Ag_2$	(**7**) $(UO_2)(C_7H_3NO_4)_2$-$Pb_2(C_2O_4)(H_2O)_2$	(**8**) $(UO_2)(C_7H_3NO_4)_2$-$Pb{\cdot}2H_2O$
M_r	1740.54	435.13	1740.54	1474.33	1615.68	1631.96	2269.28	1678.86
T/K	298	298	298	100	100	100	100	100
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$Pca2_1$ (no. 29)	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)	$C2/m$ (no. 12)	$P\bar{1}$ (no. 2)	Cc (no. 9)	$C2/c$ (no. 15)
a/Å	6.5288(7)	13.4877(10)	5.5685(4)	7.7478(10)	14.888(3)	8.4579(3)	8.7087(4)	13.9437(9)
b/Å	15.4692(15)	6.9699(5)	8.4635(5)	9.1757(11)	7.0906(17)	9.4393(4)	19.9618(10)	16.0610(9)
c/Å	9.5211(10)	9.4739(7)	19.7227(12)	9.3460(12)	10.944(3)	11.8454(4)	12.8850(7)	8.8145(5)
α/°	90	90	90	86.151(2)	90	72.7230(10)	90	90
β/°	95.512(2)	90	90	71.627(2)	96.525(3)	69.3170(10)	106.8420(10)	116.9670(10)
γ/°	90	90	90	77.395(2)	90	66.6810(10)	90	90
V/Å^3	957.14(17)	890.62(11)	929.51(10)	615.35(13)	1147.8(5)	798.76(5)	2143.87(19)	1759.37(18)
Z	1	4	1	1	1	1	2	2
D_c/Mg m^{-3}	3.020	3.245	3.109	3.978	2.314	3.393	3.515	3.169
μ(Mo-Kα)/mm^{-1}	16.966	18.233	17.470	26.335	8.065	12.607	23.294	18.824
Absorption correction	Semi-empirical	Semi-empirical	Semi-empirical	Semi-empirical	Semi-empirical	Semi-empirical	Semi-empirical	Semi-empirical
F(000)	768	768	768	632	746	740	2000	1496
Crystal size/mm	0.16 × 0.04 × 0.02	0.08 × 0.06 × 0.04	0.24 × 0.06 × 0.04	0.12 × 0.08 × 0.02	0.10 × 0.06 × 0.04	0.04 × 0.02 × 0.02	0.14 × 0.08 × 0.08	0.08 × 0.06 × 0.04
θ Range for data collection/°	2.52–28.01°	3.02–28.01°	2.07–27.92°	2.27–30.11°	1.87–28.01°	1.87–28.08°	1.65–30.31°	2.07–30.27°
Index ranges, hkl	−8 to 8, −19 to 19, −12 to 12	−17 to 17, −9 to 7, −12 to 12	−4 to 7, −11 to 11, −25 to 25	−10 to 10, −12 to 11, −12 to 13	−18 to 19, −9 to 8, −14 to 14	−10 to 11, −11 to 12, −15 to 9	−12 to 11, −24 to 27, −17 to 18	−18 to 19, −21 to 22, −12 to 12
Reflections collected	7207	6335	7093	11904	4436	7549	10742	8601
R_{int} (ind. refl.)	0.0611 (2102)	0.0348 (1994)	0.0255 (2037)	0.0940 (3336)	0.0714 (1399)	0.0263 (3453)	0.0298 (5637)	0.0290 (2439)
Flack parameter		0.015(11)	0.00(6)				0.000(18)	
GOF on F^2	1.044	0.920	0.948	0.967	1.065	1.042	1.021	1.035
R^a [$I > 2\sigma(I)$]	0.0409	0.0222	0.0215	0.0471	0.0470	0.0278	0.0233	0.0186
$wR2^a$	0.0686	0.0367	0.0534	0.0762	0.0782	0.0520	0.0521	0.0405

[a] $R = \sum\|F_o| - |F_c\|/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

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2000 diffractometer (Cu-Kα, 3–60°, 0.05° step, 1.0 s step^{-1}) and manipulated using the JADE software package.[87] Phase purity of the bulk sample was determined by the comparison of the observed and calculated PXRD patters. UV-Vis studies were performed on a Shimadzu UV-2401PC UV-Vis Recording Spectrophotometer. Fluorescent studies were performed on a Shimadzu RF-5301 PC Spectrofluorophotometer (ligand excitation wavelength: 300 (2,3-pydc), 306 (2,4-pydc) and 301 nm (2,6-pydc); uranium excitation wavelength: 365 and 424 nm;[88,89] emission wavelength: 400–800 nm; slit width: 1.5 (excitation) and 5.0 (emission); sensitivity: low (**1**, **3**) or high (**2**) with a UV-35 filter).

CCDC reference numbers 610438–610445.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b608187h

Results and discussion

Structure description

Crystal structure of [$(UO_2)(C_7H_3NO_4)$] (1). The crystal structures of compounds **1–3** are all similarly formed from a central uranium(VI) atom bound to two axial oxygen atoms at an average distance of 1.750 and 1.758 Å to form an average angle of 177.6°, thus creating the familiar UO_2^{2+} cation. The uranyl bond distances are characteristic for a UO_2^{2+} metal center.[90] The uranium metal center in **1** (Fig. 1) is bound to three distinct 2,3-pyridinedicarboxylic acid (2,3-pydc) units through the equatorial positions to form an overall pentagonal bipyramidal geometry. The uranium is bound to one 2,3-pydc through a carboxylate oxygen atom, O1, at a distance of 2.375(6) Å. The uranium metal center is further bound to two additional 2,3-pydc units in a bidentate fashion. One of the 2,3-pydc units is bound to the uranium through an oxygen atom from each carboxylate group, O4 and O5, at distances of 2.346(7) and 2.362(6) Å, respectively. The other acid unit is bound through the nitrogen of the pyridine ring, N1, at a distance of 2.621(7) Å and through a carboxylate oxygen, O6, at a distance of 2.385(7) Å to form an O6–U1–N1 angle of 63.1(2)°. The uranium metal centers are linked *via* the bridging bidentate carboxylate groups to form an overall two-dimensional sheet structure with a vacant interlayer region (Fig. 2). The stacking of the sheets is realized along [010].

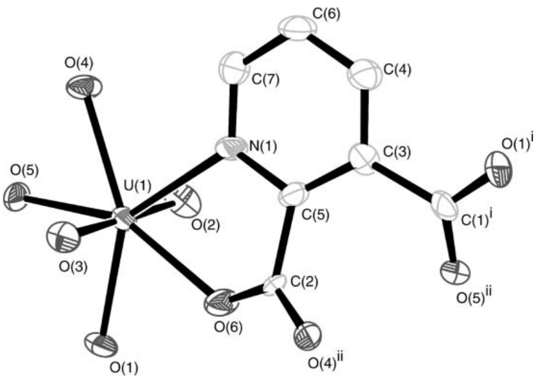

Fig. 1 The ORTEP of compound **1** [$(UO_2)(C_7H_3NO_4)$]. The ellipsoids are shown at the 50% level and the hydrogen atoms are omitted for clarity. Symmetry equivalents: (i) $-x + 1/2, y + 1/2, -z + 1/2$; (ii) $x + 1/2, -y + 1/2, z + 1/2$.

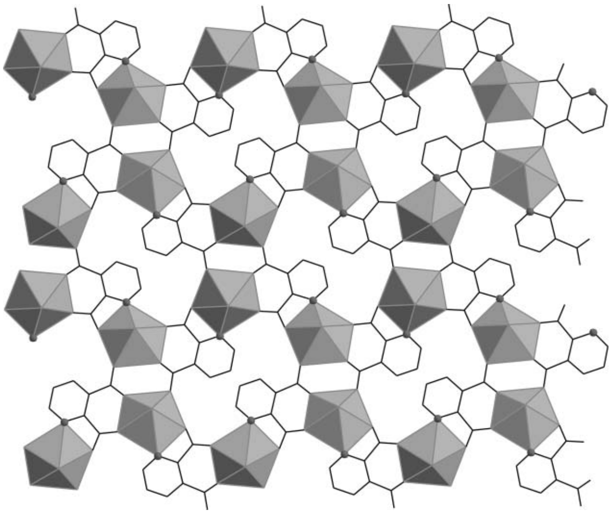

Fig. 2 Two-dimensional sheet of compound **1**. The polyhedra are the uranium pentagonal bipyramids whereas the black lines are the 2,3-pydc linkers.

Crystal structure of [$(UO_2)(C_7H_3NO_4)$] (2). The crystal structure of compound **2** (Fig. 3) has the UO_2^{2+} cation bound to four distinct 2,4-pyridinedicarboxylic acid (2,4-pydc) units in the equatorial positions to form an overall pentagonal bipyramidal geometry, similar to the geometry seen in compound **1**. One 2,4-pydc unit is bound to the uranium center in a bidentate fashion through N1 of the pyridine ring at a distance of 2.641(6) Å and O5 from a carboxylate group at a distance of 2.385(5) Å resulting in a O5–U1–N1 angle of 63.53(17)°. The other three 2,4-pydc units are all similarly bound in a monodentate fashion to the uranium metal center through an oxygen atom from a carboxylate group, O3, O4 and O6, at distances of 2.358(5), 2.334(6) and 2.395(4) Å, respectively, to complete the pentagonal bipyramidal coordination.

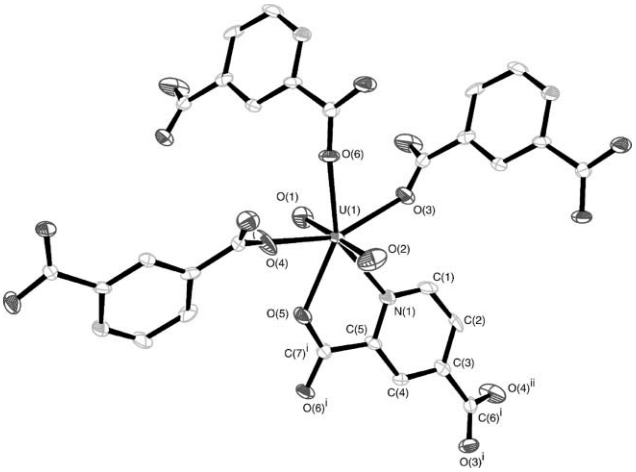

Fig. 3 The ORTEP of compound **2** [$(UO_2)(C_7H_3NO_4)$]. The ellipsoids are shown at the 50% level and the hydrogen atoms are omitted for clarity. Symmetry equivalents: (i) $x + 1/2, -y, z + 1/2$; (ii) $-x + 1/2, y, z + 1/2$.

With the change in position of the second carboxylate group (with respect to **1**), compound **2** displays an overall three-dimensional structure. The uranium metal centers are linked in two

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directions by the carboxylic acid groups. The carboxylate oxygen atoms, O5 and O6, bridge the uranium metal centers along the [100] direction (Fig. 4), this can be seen along [010] (Fig. 5). The uranium(VI) is further connected by a second carboxylic acid, O3 and O4, to complete the three-dimensional structure.

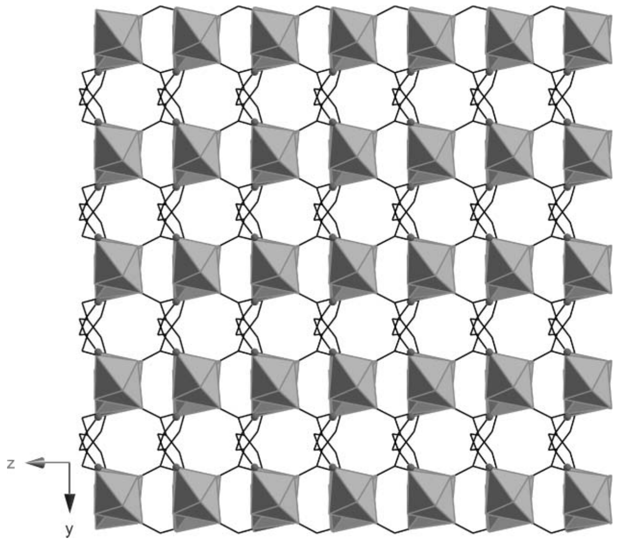

Fig. 4 A view of compound **2** down the [100] direction. The polyhedra are the uranium pentagonal bipyramids whereas the black lines are the 2,4-pydc linkers.

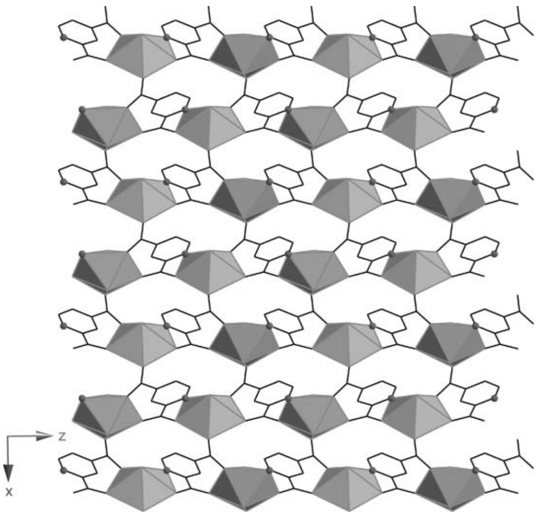

Fig. 5 Compound **2** as viewed down the *y*-axis.

Crystal structure of [$(UO_2)(C_7H_3NO_4)$] (3). The structure of compound **3** (Fig. 6) has the UO_2^{2+} cation bound to three distinct 2,6-pyridinedicarboxylic acid (2,6-pydc) units. Two 2,6-pydc units are bound to the uranium metal center *via* a single oxygen atom from a carboxylate group, O4 and O6, at a distance of 2.332(5) and 2.429(5) Å, respectively. To complete the pentagonal bipyramidal coordination of the uranium metal center, the third 2,6-pydc is bound in a tridentate fashion thought N1 of the pyridine ring at a distance of 2.528(6) Å and through one oxygen atom from each carboxylate group, O3 and O5, at a distance of 2.423(5) and 2.379(5) Å, respectively. The angles formed from this tridentate bonding of O5–U1–N1, 62.84(18)° and O3–U1–N1, 63.41(19)°, are similar to the equivalent angles reported in compounds **1** and **2** from the bidentate coordination of the uranium metal center to pydc.

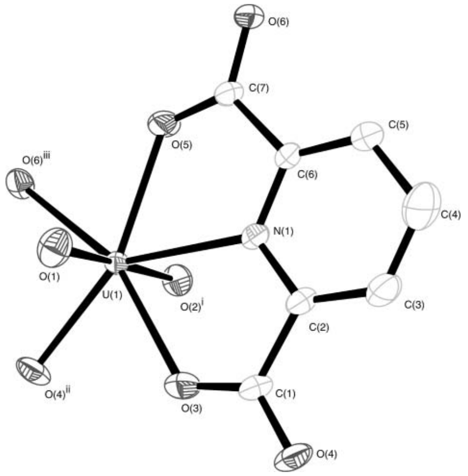

Fig. 6 The ORTEP of compound **3** [$(UO_2)(C_7H_3NO_4)$]. The ellipsoids are shown at the 50% level and the hydrogen atoms are omitted for clarity. Symmetry equivalents: (i) $-x + 1/2, -y, z + 1/2$; (ii) $-x, y + 1/2, -z + 1/2$; (iii) $x + 1/2, -y + 1/2, -z$.

A view down [100] (Fig. 7) seems to suggest a two-dimensional structure. Within the *yz*-plane, the uranium metal centers are bound to one 2,6-pydc unit in a tridentate fashion. However, viewing down [010] (Fig. 8) direction reveals additional bonding to the second and third acid units through a single carboxylate oxygen atom, O4 and O6, in the *x*-direction promoting an overall three-dimensional structure.

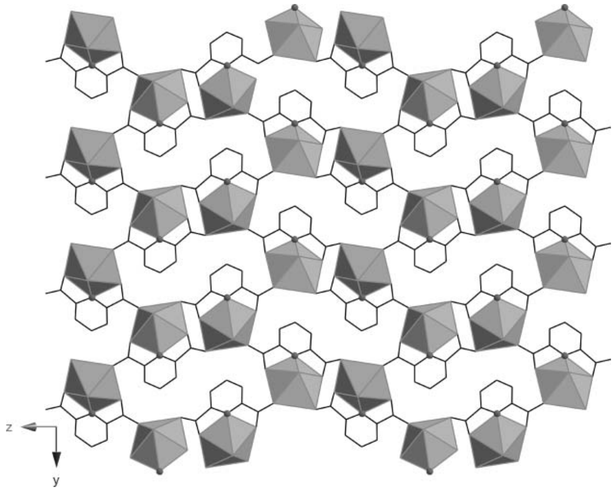

Fig. 7 Compound **3** viewed down the *x*-axis. The black lines are the 2,6-pydc linkers and the polyhedra are the uranium pentagonal bipyramids.

Crystal structure of $(UO_2)_2(C_7H_3NO_4)(O)(H_2O)$ (4). The crystal structure of compound **4** (Fig. 9) consists of two crystallographically distinct UO_2^{2+} metal centers. The first UO_2^{2+} cation is formed from two uranyl oxygen atoms bound to U1 at distances of 1.760(9) and 1.766(9) Å forming an O7–U1–O9 angle of 174.5(4)°. The second uranyl ion is similarly formed by O6 and O3 bound to

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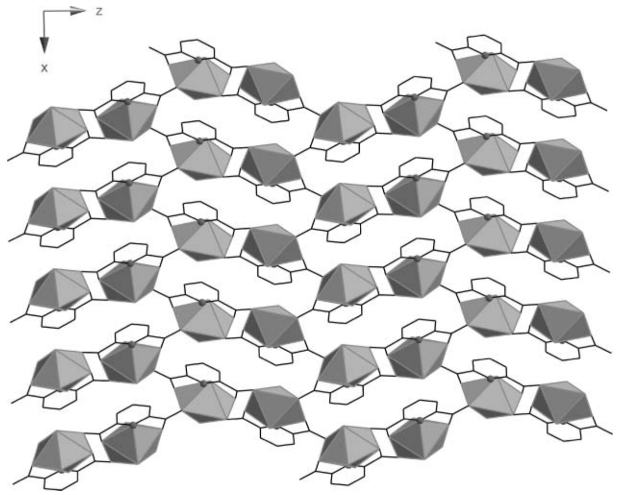

Fig. 8 A view of compound **3** down the [010] direction.

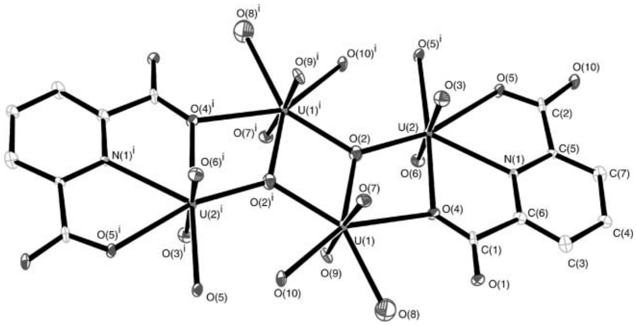

Fig. 9 The ORTEP of compound **4** [$(UO_2)_2(C_7H_3NO_4)(O)(H_2O)$]. The ellipsoids are shown at the 50% level and the hydrogen atoms are omitted for clarity. Symmetry equivalent: (i) $-x$, $-y$, $-z$.

U2 at a distance of 1.783(8) and 1.794(9) Å, respectively, to form an angle of 174.7(4)°.

There are two 2,6-pydc units bound to U1 through a carboxylate oxygen atom, O4 and O10, at a distance of 2.544(8) and 2.434(9) Å. Additionally, there is one bound water molecule, O8, at a distance of 2.150(8) Å. U2 is bound to a 2,6-pydc in a tridentate fashion similar to compound **3**. The 2,6-pydc is bound to U2 through the pyridine ring at a distance of 2.575(9) Å and through an oxygen atom from both carboxylate groups, O4 and O5, at a distance of 2.544(8) and 2.521(8) Å. This tridentate coordination results in O4–U1–N1 and O5–U1–N1 angles of 63.0(3) and 61.6(3)°. A second 2,6-pydc unit is bound to U2 through a single carboxylate oxygen atom, O5, at a distance of 2.456(8) Å. The presence of a three coordinate bridging oxygen atom, O2, completes the pentagonal bipyramidal geometry on both U1 and U2. Each O2 bridges one U2 at a distance of 2.181(8) Å and two U1 metal centers at distances of 2.284(9) and 2.286(9) Å, respectively. Both charge balance and bond valence summations[91] (2.03 v.u.) confirm O2 as a bridging oxygen atom as opposed to a bridging hydroxyl group or water molecule. With the bridging oxygen atom, a tetrameric secondary building unit (SBU) is realized (Fig. 9). The U2 metal centers within the tetramer SBUs are further edge shared through the bridging carboxylate oxygen atom, O5, to form overall one-dimensional chains (Fig. 10).

Crystal structure of [$(UO_2)(C_7H_3NO_4)_2(Cu(H_2O)_4)\cdot 4H_2O$] (5). The crystal structures of the bimetallic compounds, **5**–**8**, are all similarly formed from the triatomic UO_2^{2+} cation, as seen in **1**–**4**, resulting from the central uranium(VI) atom bound to two axial oxygen atoms at an average distance of 1.767 and 1.769 Å to form an average angle of 179.2°. Furthermore, in all the bimetallic compounds, the uranyl ion is bound in a tridentate fashion to two distinct 2,6-pydc units through the pyridine ring at an average distance of 2.635 Å and through an oxygen atom from each carboxylate group at an average distance of 2.468 Å to complete the hexagonal bipyramidal geometry around the uranium metal center.

The structure of compound **5** (Fig. 11) consists of two distinct metal centers: a UO_2^{2+} site and a Cu^{2+} site, each of which lies on an independent inversion center. The copper(II) is bound to two distinct 2,6-pydc units through a carboxylate oxygen atom, O5, at a distance of 1.979(8) Å resulting in a O5–Cu1–O5 angle of 180°. The copper metal center is further bound to four water molecules orthogonal to the pydc plane at a distance of 2.202(11) Å to yield an overall distorted octahedral geometry. The copper metal centers connect the uranium complexes through O4 and O5 of the bridging carboxylate group to form one-dimensional chains (Fig. 12).

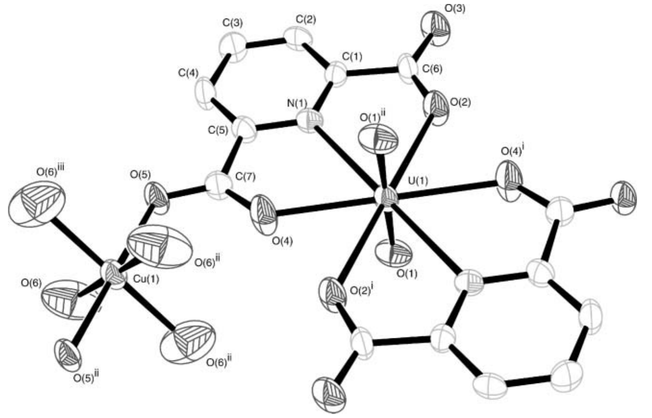

Fig. 11 The ORTEP of compound **5** [$(UO_2)(C_7H_3NO_4)_2(Cu(H_2O)_4)\cdot 4H_2O$]. The ellipsoids are shown at the 50% level and the hydrogen atoms are omitted for clarity. Symmetry equivalents: (i) $-x$, y, $-z$; (ii) $-x$, $-y$, $-z$; (iii) x, $-y$, z.

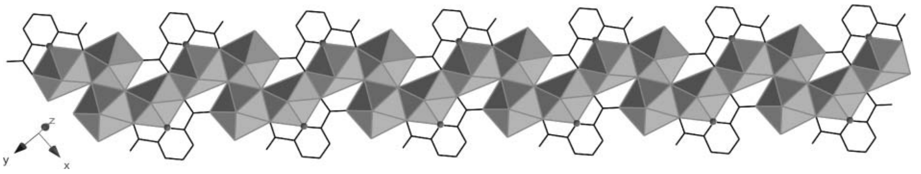

Fig. 10 The one-dimensional chains of compound **4**. The polyhedra are the uranium pentagonal bipyramids whereas the black lines are the 2,6-pydc linkers.

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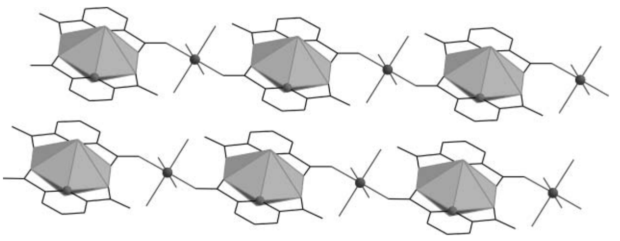

Fig. 12 The one-dimensional chains of compound **5**. The polyhedra are the uranium hexagonal bipyramids. The copper(II) sites in distorted octahedral geometry are shown as spheres.

Crystal structure of [(UO$_2$)(C$_7$H$_3$NO$_4$)$_2$Ag$_2$] (6). The structure of compound **6** (Fig. 13) contains three distinct metal centers: a UO$_2^{2+}$ site and two Ag$^+$ sites. Each silver metal center is bound to four distinct 2,6-pydc units. Both silver metal centers are bound to three oxygen atoms from carboxylate groups at an average distance of 2.346 Å to Ag1 and 2.345 Å to Ag2. The coordination of the silver metal centers to the 2,6-pydc units results in the formation of chains similar to the one-dimensional chains seen in **5**. Finally, each silver metal center is point shared through an additional bond to the carboxylate oxygen atom, O1, to complete the distorted tetrahedral geometry around the silver metal centers. These bonds, Ag1–O1 and Ag2–O1 at a distance of 2.436(4) and 2.613 Å, respectively, dimerize two individual chains into a larger one-dimensional chain (Fig. 14).

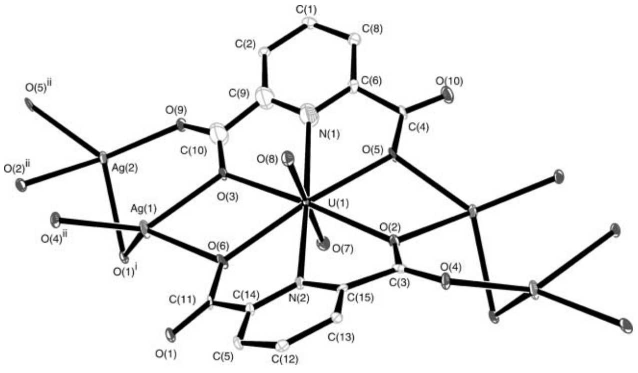

Fig. 13 The ORTEP of compound **6** [(UO$_2$)(C$_7$H$_3$NO$_4$)$_2$Ag$_2$]. The ellipsoids are shown at the 50% level and the hydrogen atoms are omitted for clarity. Symmetry equivalents: (i) $-x$, $-y$, $-z$; (ii) $x + 1$, $y + 1$, $z + 1$.

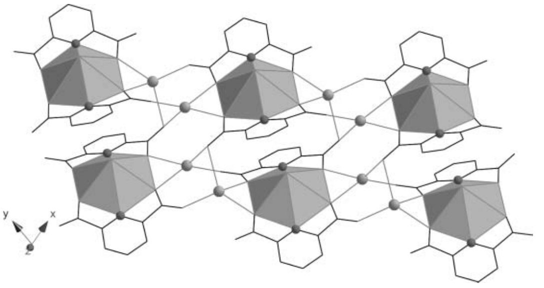

Fig. 14 A view of the one-dimensional chains of compound **6**. The silver(I) sites are shown as spheres. The polyhedra are the uranium hexagonal bipyramids.

Crystal structure of [(UO$_2$)(C$_7$H$_3$NO$_4$)$_2$Pb$_2$(C$_2$O$_4$)(H$_2$O)$_2$] (7). The crystal structure of compound **7** (Fig. 15) consists of three distinct metal centers: a UO$_2^{2+}$ site and two Pb^{2+} sites. The first lead metal center, Pb1, is bound to four distinct 2,6-pydc units though carboxylate oxygen atoms. Two of the oxygen atoms, O3 and O4, are bound to Pb1 at a distance of 2.571(5) and 2.481(5) Å, respectively, and bridge the uranium metal centers to Pb1. These bridging oxygen atoms form U1–O3–Pb1 and U1–O4–Pb1 angles of 118.7(2) and 123.6(2)°, respectively. The other two carboxylate oxygen atoms, O7 and O10, are bound to Pb1 at an average distance of 2.865 Å. A water molecule is additionally bound to Pb1 at a distance of 2.766 Å. The second lead metal center, Pb2, is bound to three distinct acid units through carboxylate oxygen atoms. Similar to Pb1, there are two oxygen atoms, O1 and O2, which are bound to Pb2 at a distance of 2.555(5) and 2.496(5) Å, respectively, and bridge U1 to Pb2. These bridging atoms result in the subsequent formation of U1–O1–Pb2 and U1–O2–Pb2 angles of 118.7(2) and 122.1(2)°. Also similar to Pb1, Pb2 has one bound water molecule at a distance of 2.838 Å. The bridging of the metal centers by the carboxylate oxygen atoms results in a two-dimensional sheet structure (Fig. 16). The lead metal centers are further connected through oxalate linkages to create an overall three-dimensional structure (Fig. 17). It is proposed that the source of the oxalate anions results from either the reductive coupling of ambient CO$_2$(g) or from a possible decarboxylation of the 2,6-pydc as will be discussed later. Each lead(II) is coordinated to an oxalate linkage in a bidentate fashion through an oxygen atom from each carboxylate group. Pb1 is bound to O11 and O12 at a

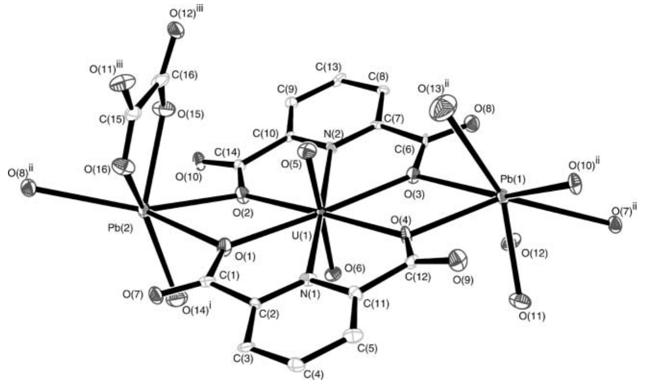

Fig. 15 The ORTEP of compound **7** [(UO$_2$)(C$_7$H$_3$NO$_4$)$_2$Pb$_2$(C$_2$O$_4$)(H$_2$O)$_2$]. The ellipsoids are shown at the 50% level and the hydrogen atoms are omitted for clarity. Symmetry equivalents: (i) x, $-y$, $z + 1/2$; (ii) $x + 1/2$, $y + 1/2$, z; (iii) $x + 1/2$, $-y + 1/2$, $z + 1/2$.

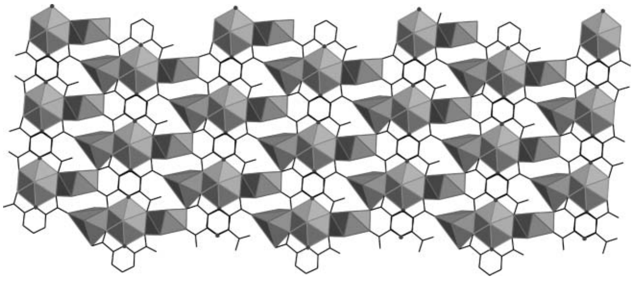

Fig. 16 A view of the two-dimensional sheets of compound **7**. The uranium polyhedra are hexagonal bipyramids. The lead(II) polyhedra edge share with the uranium metal centers.

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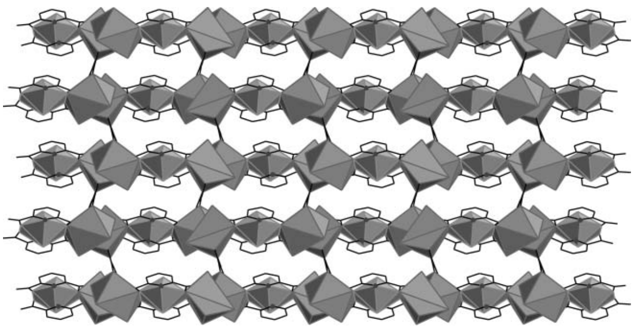

Fig. 17 A view of the oxalate linkages connecting the two-dimensional sheets to form the overall three-dimensional structure of compound **7**.

distance of 2.445(5) and 2.516(5) Å, respectively, forming a O11–Pb1–O12 angle of 67.1(2)°. Likewise, O15 and O16 are bound to Pb2 at a distance of 2.485(5) and 2.504(5) Å, respectively, to form the O15–Pb2–O16 angle of 65.8(2)°.

Crystal structure of [$(UO_2)(C_7H_3NO_4)_2Pb\cdot 2H_2O$] (8). The crystal structure of compound **8** (Fig. 18) consists of two distinct metal centers: a UO_2^{2+} site on an inversion center and a Pb^{2+} site. The lead metal center is bound to six distinct 2,6-pydc units by a single carboxylate oxygen atom. Pb(II) is bound to two 2,6-pydc units though O5 at a distance of 2.733(2) Å. Completing the six-coordinate local geometry, the Pb(II) is bound to two symmetry equivalent O2 and O5 atoms at a distance of 2.627(3) and 2.467(2) Å, respectively. A view down [001] reveals the uranium and lead metal centers are edge shared through O2 and O3 (Fig. 19). Additionally, the lead metal centers are linked by a bridging carboxylate group, O2 and O5, of the 2,6-pydc creating a O2–Pb1–O5 angle of 108.82(8)° resulting in an overall three-dimensional framework. This linkage can be demonstrated viewing down [100]. Moreover, there are two symmetry equivalent water molecules located within the pore space as can be seen in Fig. 19.

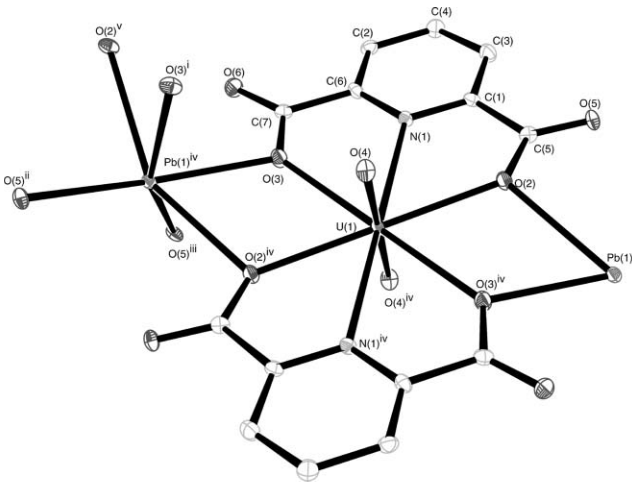

Fig. 18 The ORTEP of compound **8** [$(UO_2)(C_7H_3NO_4)_2Pb\cdot 2H_2O$]. The ellipsoids are shown at the 50% level and the hydrogen atoms are omitted for clarity. Symmetry equivalents: (i) $-x, y, -z + 1/2$; (ii) $x + 1/2, y + 1/2, z$; (iii) $-x + 1/2, y + 1/2, -z + 1/2$; (iv) $-x + 1/2, -y + 1/2, -z$; (v) $x + 1/2, -y + 1/2, z + 1/2$.

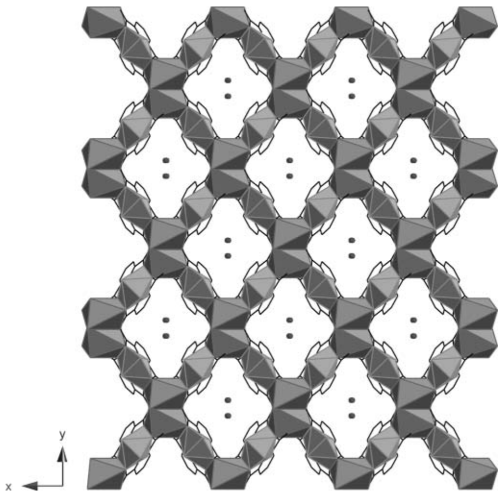

Fig. 19 A view of compound **8** down the [001] direction. The uranium and lead metal centers are edge shared and there are two unbound water molecules within the pores.

Discussion

Efforts to combine pyridinedicarboxylic acid (pydc) and uranium(VI) to synthesize coordination polymers have been seen previously in a few reports.[52,78–81] Our current efforts take this a step further to produce novel U–M–pydc polymeric materials. The synthesis of heterometallic compounds is promoted by the use of a series of pyridinedicarboxylic acids as the organic linkers due to their multiple functional groups. The two functional groups, the pyridine ring and the carboxylate groups, have the potential to aid in producing heterometallic compounds. The pyridinedicarboxylates are also advantageous for the potential to enhance uranium fluorescence through sensitized emission. Uranium containing heterometallic compounds in the pydc system were previously reported by Harrowfield *et al.* and comparisons will be made below.[82]

The properties of hard/soft acid/base (HSAB) theory can help in predicting the binding positions of each metal center. HSAB considerations would expect a hard metal center such as uranium(VI) to bind to a hard functional group such as a carboxylic acid and a softer transition metal center like copper(II) to bind with the softer pyridine ring. Reviewing the binding positions of the metal centers in the bimetallic compounds (**5–8**), one notices that the softer transition metals are predominantly bound to the harder carboxylic functional groups. In all of these compounds, the hard uranium(VI) is bound in a tridentate fashion to two distinct 2,6-pydc units through the pyridine ring and through an oxygen atom from each carboxylate group. These results appear to conflict with the HSAB predictions indicating that more complex considerations such as sterics could be essential in determining the binding positions of the metal centers. Taking a closer look, one mode of connectivity for the uranium to the 2,6-pydc is in a tridentate fashion (**3**), when there are no other competing metal centers, similarly seen in the bimetallic compounds. The uranium has a higher affinity to coordinate to the organic linker through both the pyridine ring and the carboxylate groups resulting with the uranium and 2,6-pydc forming two five-membered rings (Scheme 1).

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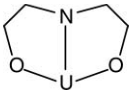
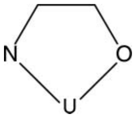


Scheme 1

Looking at compounds **1** and **2**, the five-membered ring (Scheme 2) is also present.



Scheme 2

This ring formation has been seen previously in our studies in the 3,5-pyrazoledicarboxylic acid system[59] and is possibly the result of a chelating effect to increase the overall stability of the compound. As a result of the ring formation, the remaining carboxylate oxygen atoms are the only open binding positions available for the softer transition metals which is what we observe in **5–8**.

A recent search on the Cambridge Structural Database (CSD, Version 5.27)[92] for structures containing 2,3-pyridinedicarboxylic acid as the organic linker resulted in zero structures suggesting that **1** is the first such synthesized compound. A literature search also revealed one 2,4-pyridinedicarboxylic acid and uranium(VI) compound synthesized by Zheng *et al.*[52] However, a search for uranium containing compounds with 2,6-pyridinedicarboxylic acid as the organic linker resulted in six unique structures of which two were polymeric (LEWFEY and PYDCUO).[52,78,79,93]

A recently published article by Harrowfield *et al.* reported uranium containing bimetallic coordination polymers, U–M–2,6-pydc (M = Li, Na, K, Rb, Cs), although the only structures solved *via* single-crystal X-ray diffraction were the Rb and Cs compounds.[82] Comparisons can be made with the bimetallic compounds reported herein with the U–Rb/Cs-2,6-pydc polymeric materials. Each of the compounds have the UO_2^{2+} cation coordinated to two distinct 2,6-pydc units in a tridentate fashion through the pyridine ring and through an oxygen atom from each carboxylate group to complete the overall hexagonal bipyramidal geometry. The average U–N bond distance of 2.663 Å as reported by Harrowfield *et al.* is comparable to the distance of 2.635 Å reported for **5–8**. The average bond distance for the uranium to be coordinated to the carboxylate groups is also comparable, 2.440 and 2.466 Å as reported by Harrowfield *et al. vs.* 2.447 and 2.488 Å for **5–8**.

Along with synthesizing several novel bimetallic compounds in the pydc system, we have also demonstrated a new secondary building unit for uranium(VI) as seen in compound **4**. The majority of synthetic uranium(VI) compounds prefer to adopt a structure based on either dimeric or monomeric building units while there have been a few examples of the tetramer building unit seen previously in literature.[48,94–100] As far as we know, **4** is the first uranium(VI) compound comprised of pentagonal bipyramids forming tetramer building units which are further edge shared to form infinite one-dimensional chains. These tetramers can be compared to those seen in $[(C_6H_{14}N_2)(UO_2)_2F_6]$.[101] Cahill and Burns observed point sharing between the tetramer building units to promote two-dimensional sheets. The difference in dimensionality between the two compounds is likely due to the number of tetramers which are connected. In $[(C_6H_{14}N_2)(UO_2)_2F_6]$, each tetramer is point shared to four distinct building units to form sheets while in **4** each tetramer is edge shared to only two building units to form chains.

Compound **7**, $(UO_2)(C_7H_3NO_4)_2Pb_2(C_2O_4)(H_2O)_2$, consists of two-dimensional sheets connected through oxalate linkages to form an overall three-dimensional structure. Oxalic acid was not one of the starting materials indicating that the formation of the oxalate linkages resulted from an alternative source. One suggestion for the formation of the oxalate linkages is through *in situ* ligand synthesis. In a recent review article,[102] various examples of *in situ* ligand syntheses under hydro(solvo)thermal conditions were described, one of which being decarboxylation of the starting material.[36,73,103] The oxalate linkages could be formed in a two step process, wherein first decarboxylation occurs followed by subsequent coupling to form the anions. An alternative rationale is the reduction of ambient $CO_2(g)$ to form radicals which are further coupled to produce the oxalate linkages. The reduction of ambient $CO_2(g)$ has been seen in other systems all of which suggest the reductive coupling of $CO_2(g)$.[104–108] A third possible explanation is the degradation/oxidation of the starting organic material to an oxalate linkage or an oxalate precursor. For example, it is known that L-ascorbic acid will undergo oxidative degradation to form dehydroascorbic acid (DHA) which will further decompose to produce oxalic acid.[109] This decomposition has been seen previously wherein Unaleroglu *et al.* synthesized Co(II) and Gd(III) oxalates using L-ascorbic acid as the starting organic.[110] Efforts are currently underway to modify the hydrothermal conditions (including inert atmosphere techniques) in order to understand which of these proposed pathways results in the formation of oxalate anions.

Fluorescence studies

The pyridinedicarboxylates are attractive ligands for studies of energy transfer because of its conjugation within the pyridine ring which can aid in this phenomenon *via* the "antenna effect". The antenna effect is a specific type of energy transfer which occurs through an interaction between a donor and an acceptor whereby the emission spectrum of the donor (pydc) overlaps the absorption spectrum of the acceptor (uranium).[83,111] As such, fluorescence studies were carried out on compounds **1–3**. For these efforts **1–3** were used as synthesized. Fluorescence studies were not performed on compounds **4–8** because these samples could not be obtained as pure phases. Various excitation wavelengths were utilized in this study: two uranyl ion excitation wavelengths of 365 and 424 nm,[88,89] and the ligand excitation wavelength of 2,3-pydc (300 nm), 2,4-pydc (306 nm) and 2,6-pydc (301 nm) (the maximum absorption as determined by UV-Vis). The emission spectra (Fig. 20–22) for all the compounds tested in this study produced the characteristic vibronic structure of the UO_2^{2+} moiety.[44,112–117] The five characteristic peaks of each spectrum ranged from *ca.* 480–575 nm with the only difference between the various excitation wavelengths being the relative intensities of the corresponding emission spectra. Furthermore, when the uranyl ion is excited directly, the emission spectra are on the same order of magnitude of intensity as compared to the spectrum resulting from direct

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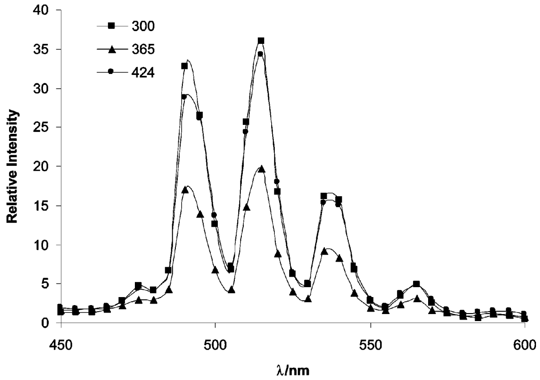

Fig. 20 Emission spectra for compound **1** at different excitation wavelengths: ligand (300 nm) and uranium (365 and 424 nm).

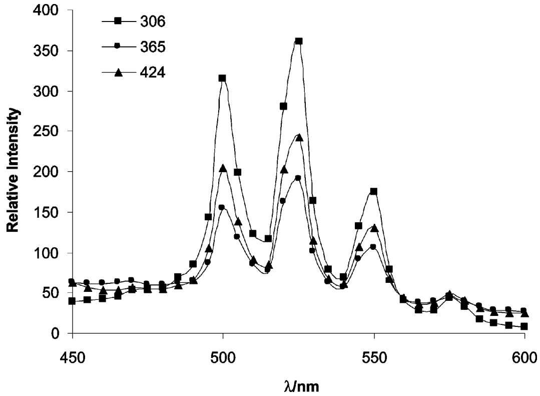

Fig. 21 Emission spectra for compound **2** at different excitation wavelengths: ligand (306 nm) and uranium (365 and 424 nm).

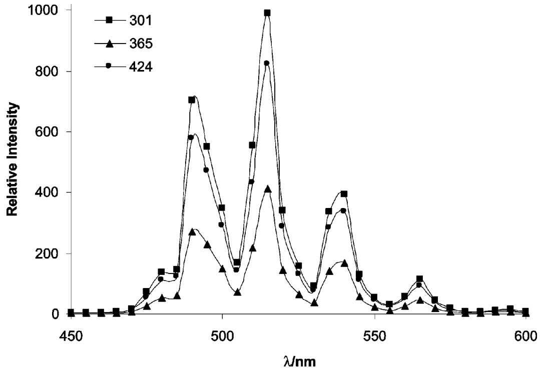

Fig. 22 Emission spectra for compound **3** at different excitation wavelengths: ligand (301 nm) and uranium (365 and 424 nm).

ligand excitation. This possibly indicates that there is little energy loss from radiationless decay.

The uranium emission spectra of compounds **1–3** differ from those seen previously in that each displays some degree of peak asymmetry.[44,59,88,89,118] This asymmetry is fully realized by the presence of shouldering of peaks in compound **3**. These secondary peaks become more pronounced in **1–3** when a higher resolution spectrum is obtained (see ESI†). These shoulder peaks in the uranium emission are possibly due to ligand-to-metal charge transfer and these "additional" peaks are the vibrational fine structure. Further experiments are necessary (and in progress) to fully understand and offer a more thorough explanation of this phenomenon.

Conclusion

In summary, compounds **1–8** represent novel U or U–M coordination polymers synthesized under by hydrothermal conditions. Uranium-containing compounds were produced using 2,3-pyridinedicarboxylic acid (**1**) and 2,4-pyridinedicarboxylic acid (**2**) as the organic linker. A novel secondary building unit for uranium(VI) compounds has been realized in compound **4**, $[(UO_2)_2(C_7H_3NO_4)(O)(H_2O)]$, where linear tetrameric building units edge share to form one-dimensional chains. Furthermore, several bimetallic compounds, U–M–2,6-pydc (M = Cu, Ag, Pb), have been synthesized. Compound **7**, $(UO_2)(C_7H_3NO_4)_2Pb_2(C_2O_4)(H_2O)_2$, contains oxalate linkages connecting two-dimensional sheets to form an overall three-dimensional structure. The fluorescent properties of these materials have also been investigated and an antenna effect is realized by observing uranyl ion emission upon direct excitation of the organic linker. Further experiments are necessary to fully understand and explain the occurrence of the features present in the fluorescence spectra.

Acknowledgements

The authors gratefully acknowledge the National Science Foundation for funding (DMR-0348982, CAREER Award to C. L. C.) and for the acquisition of the single-crystal diffractometer (DMR-0419754), as well as the US Department of Energy (DE-FG02–05ER15736).

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