Supramolecular architectures of two novel organic–inorganic hybrid materials containing identical monomeric uranyl units

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Two isostructural uranyl complexes have been crystallized with different bipyridyl cations to yield the compounds hemi(4,4′-bipyridinium) tris(5-chlorothiophene-2-carboxylato)-dioxidouranate(VI) monohydrate, $(C_{10}H_{10}N_2)_{0.5}[U(C_5H_2ClO_2S)_3O_2]\cdot H_2O$, (I), and hemi[4,4′-(ethane-1,2-diyl)dipyridinium] tris(5-chlorothiophene-2-carboxylato)dioxidouranate(VI) monohydrate, $(C_{12}H_{14}N_2)_{0.5}[U(C_5H_2ClO_2S)_3O_2]\cdot H_2O$, (II). In the $[UO_2X_3]^-$ complexes (X is 5-chlorothiophene-2-carboxylate), the uranyl O atoms occupy the two axial positions and the equatorial positions are occupied by six O atoms of the three X ions so that each U atom is eight coordinated in a puckered hexagonal–bipyramidal structure. In both compounds, the metal centres are linked by classical O—H···O and N—H···O hydrogen bonds involving the coordinated ligands, the diprotonated organic linker cation (which rests on a centre of inversion at the mid-point of the central C—C bond) and water molecules. The crystal structures are further stabilized by weak C—H···O and π–π stacking interactions, forming similar three-dimensional supramolecular architectures, forming a two-dimensional network parallel to the (100) plane in (I) and a three-dimensional network in (II).

Comment

Uranium chelation has been an ongoing area of study (Szigethy & Raymond, 2009), in large part due to the role of the metal as the feedstock material for most nuclear power sources. Simple ligands that can effectively chelate and remove actinides from the environment or *in vivo* are of interest in this context. Systematic pairing of aromatic pyridyl-functionalized linkers with carboxylic and polycarboxylic acids of varying lengths and their influence on the three-dimensional architecture of uranyl-containing polymers have been extensively studied (Borkowski & Cahill, 2006). The uranyl ion (UO_2^{2+}), a particularly stable form of oxidized uranium

that is involved in nuclear fuel processing, has a high affinity for O-atom donors and a wide variety of resulting architectures are obtained in so-called uranyl–organic frameworks (UOFs) (Thuery & Masci, 2008). The uranyl cation maintains its linearity to within a couple of degrees in all of its coordination complexes, relegating coordinative variation to a square, pentagonal or hexagonal equatorial plane of coordinated carboxylate groups perpendicular to the O=U=O unit (Frisch & Cahill, 2005; Szigethy & Raymond, 2009). The combination of 5-chlorothiophene-2-carboxylic acid, a bipyridyl species and UO_2^{2+} has resulted in the synthesis of two

(I)

(II)
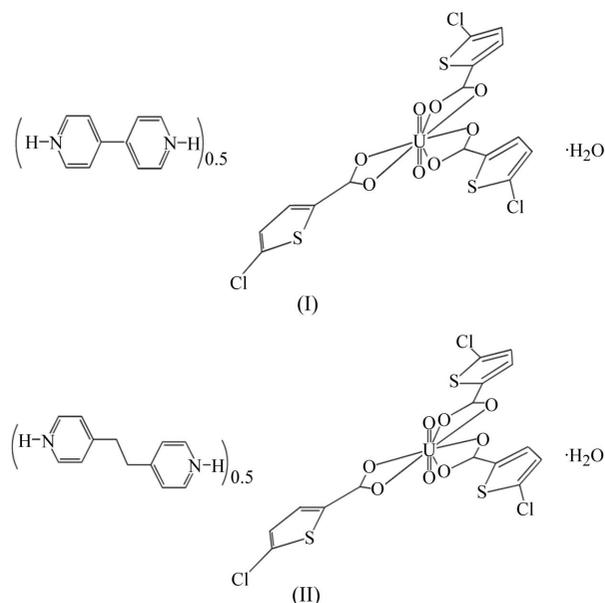
new compounds containing the same uranyl complex with different organic linker cations, namely hemi(4,4′-bipyridinium) tris(5-chlorothiophene-2-carboxylato)dioxidouranate(VI) monohydrate, (I), and hemi[4,4′-(ethane-1,2-diyl)dipyridinium] tris(5-chlorothiophene-2-carboxylato)dioxidouranate(VI) monohydrate, (II).
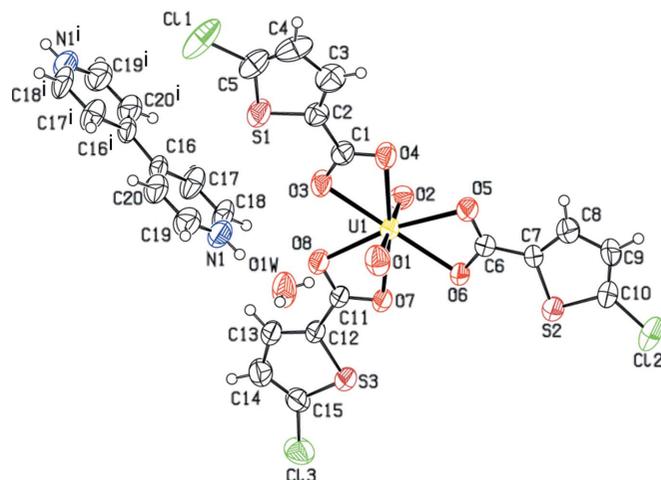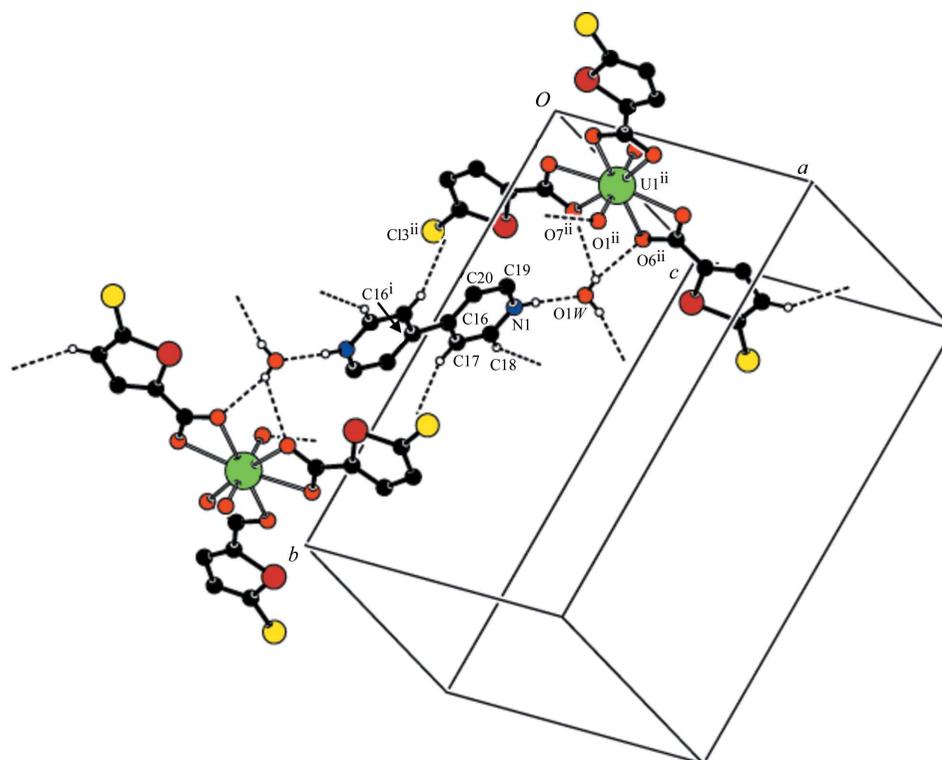

Figure 1
A view of the components of (I), showing displacement ellipsoids at the 50% probability level. [Symmetry code: (i) −x, −y + 1, −z.]
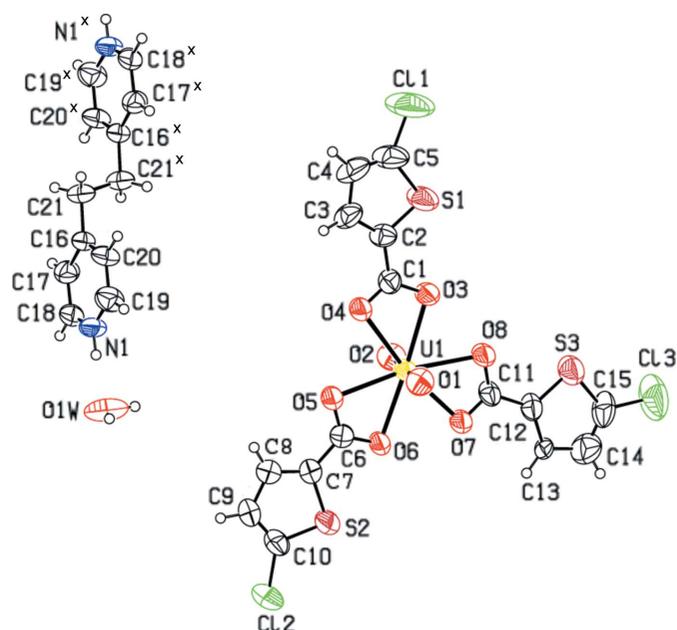
metal-organic compounds

Figure 2
The diprotonated 4,4′-bipyridinium cation and a pair of water molecules bridging two metal centres *via* hydrogen bonds (dashed lines) in (I). [Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.]

Both (I) and (II) contain the same anionic coordination complex with essentially identical geometries. The coordination of the single crystallographically unique U-atom site consists of a central near-linear UO_2^{2+} cation [O=U=O angle = 178.81 (17)° for (I)] with six O atoms from three bidentate 5-chlorothiophene-2-carboxylate (X) ions in the equatorial plane, leading to an overall hexagonal–bipyramidal coordination (Fig. 1). The short U—O axial bond lengths [1.756 (3) and 1.754 (3) Å] in (I) are in good agreement with the reported average uranyl bond length of 1.759 (4) Å (Thuery & Masci, 2008; Sasikumar & Muthiah, 2010; Thuéry, 2008; Masci & Thuéry, 2008). The U—O equatorial bond distances [2.437 (3)–2.515 (3) Å for (I)] are longer than the axial distances and the O—U—O bite angles of the bidentate carboxylate groups in the equatorial plane range from 51.87 (11) to 53.22 (10)°, compared with the ideal value of 60° for a regular hexagonal arrangement. The bipyridinium cation is relatively flat with a C20—C16—C16^i—C17^i torsion angle of 1.6 (7)° [symmetry code: (i) $-x, -y + 1, -z$].

In (I), two anionic $[UO_2X_3]^-$ units are linked by a protonated 4,4′-bipyridinium cation (located on a centre of inversion), as well as by water molecules, *via* N—H···O and O—H···O hydrogen bonds (Fig. 2). The water molecule acts as a hydrogen-bond acceptor from the protonated N atom of 4,4′-bipyridinium (O1W···H1—N1), while one H atom is involved in a bifurcated hydrogen bond with O atoms from two different coordinated carboxylates [O1W—H1W···O6^{ii} and O1W—H1W···O7^{ii}; symmetry code: (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$]

and the other is hydrogen bonded to a uranyl O atom (O1W—H2W···O1) (Fig. 2). π–π stacking is observed between nearly parallel coordinated thiophene rings of adjacent complexes [S1/C2/C3/C4/C5 and S2^{viii}/C7^{viii}/C8^{viii}/C9^{viii}/C10^{viii}; symmetry

Figure 3
A view of the components of (II), showing displacement ellipsoids at the 50% probability level. [Symmetry code: (x) $-x + 2, -y + 1, -z + 2$.]
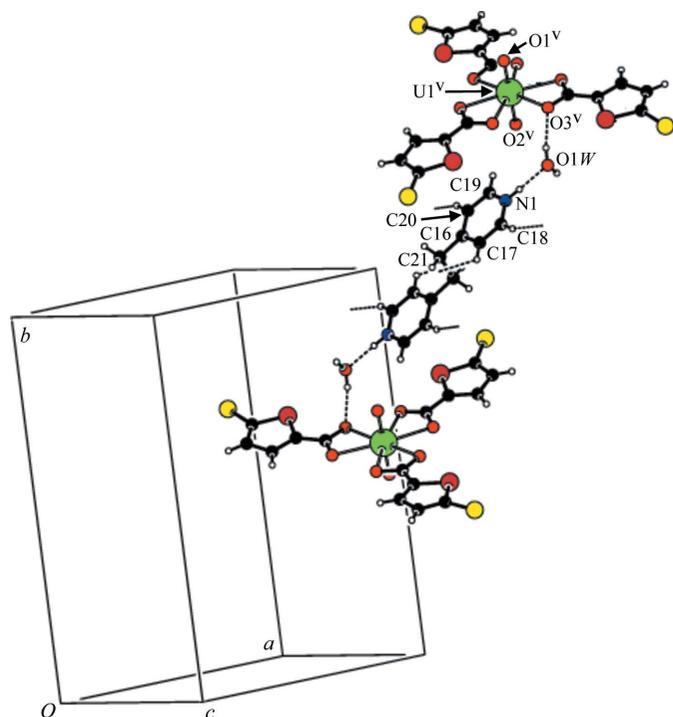
Figure 4
The diprotonated 4,4′-(ethane-1,2-diyl)dipyridinium cation and a pair of water molecules bridging two metal centres *via* hydrogen bonds (dashed lines) in (II). [Symmetry code: (v) $-x + 1$, $y + \frac{1}{2}$, $-z + \frac{3}{2}$.]

code: (viii) x, y, $z - 1$], with a centroid–centroid distance of 3.841 (3) Å. Intermolecular interactions are found between the C9—H9 group of an anionic unit and atom O4^{iii} [symmetry code: (iii) $-x + 1$, $-y + 1$, $-z + 2$] of an adjacent anionic unit, leading to the formation of a centrosymmetric ring which can be described by a graph-set motif of $R_2^2(16)$ (Bernstein *et al.*, 1995). In addition, there are C—H···O interactions involving bipyridine cations and the carboxylate O atoms (Table 1), generating a three-dimensional network.

In (II), the same anionic uranyl complexes are paired with protonated 4,4′-(ethane-1,2-diyl)dipyridinium cations that are also situated on inversion centres with a noncoordinated water molecule present as well (Fig. 3). As in (I), the metal complexes are linked by N1—H1···O1W and O1W—H2W···O3^v hydrogen bonds [symmetry code: (v) $-x + 1$, $y + \frac{1}{2}$, $-z + \frac{3}{2}$] involving the protonated 4,4′-(ethane-1,2-diyl)dipyridinium cation, water molecules and carboxylate O atoms (Fig. 4). Unlike the case in (I), only one of the water H atoms is involved in a hydrogen bond in (II). C—H···O interactions [C18—H18···O7^{vii} and C20—H20···O8^{iii}; symmetry code: (vii) $-x + 1$, $-y + 1$, $-z + 1$] connect the bipyridinium cations and the anionic centres. The oxide ion O1^{vi} [symmetry code: (vi) $x + 1$, y, z] interacts with the bipyridine moiety *via* C17 and H17. As in (I), π–π stacking interactions occur between nearly parallel thiophene rings [S1/C2/C3/C4/C5 and S2^{ix}/C7^{ix}/C8^{ix}/C9^{ix}/C10^{ix}; symmetry code: (ix) x, y, $z + 1$], with a centroid–centroid distance of 3.928 (4) Å.

We have crystallized the tris(5-chlorothiophene-2-carboxylato)uranyl(VI) complex using two different bipyridinium

cations. Although there are reports of several similar $[(UO_2^{2+})(RCOO^-)_3]$ complexes showing the puckered hexagonal–bipyramidal geometry (Borkowski & Cahill, 2006), this is the first pair of uranium complexes with the 5-chlorothiophene-2-carboxylate ligand. In both salts, there are alternating layers of anionic complexes and cations that are parallel to the *ac* plane and stack along the *b* axis. The bipyridinium cation of (I) contains two pyridine rings connected directly by a C—C bond, while in the 4,4′-(ethane-1,2-diyl)dipyridinium cation in (II) the pyridine rings are connected by a small alkyl chain which extends the distance between the rings. This leads to small elongations in the *a* and *b* unit-cell axes of the otherwise quite similar unit cells, which is important from a crystal engineering point of view. In (I), the classic interactions build a two-dimensional network parallel to (100) and this is extended into a three-dimensional network by a C—H···O interaction.

Experimental

Caution! With uranium being a radioactive and chemically toxic element, uranium-containing samples must be handled with suitable care and protection. All starting materials used in these synthetic reactions are available commercially and were used as obtained from the supplier.

For the preparation of (I), dioxouranium (VI) nitrate hexahydrate {[UO2(NO3)2]·6H2O; 0.1505 g, Loba Chemie} was dissolved in a methanol–water solution (1:1 *v/v*, 20 ml) and 5-chlorothiophene-2-carboxylic acid (0.0850 g, Hoechst Aktiengesellschaft) was dissolved in acetonitrile (20 ml). Both solutions were stirred separately for 30 min at 313 K. On mixing the two solutions, a pale-yellow solution was obtained. Then 4,4′-bipyridine (0.0442 g, Aldrich) was added directly to the warm solution with stirring and heating was continued for 30 min. The resulting clear pale-yellow solution was left undisturbed at room temperature for crystallization. After 30 d, clear yellow plate-shaped crystals formed on the surface of the mother liquor. The crystals were isolated, washed with small portions of methanol and dried in air.

For the preparation of (II), the same procedure was used with 1,2-bis(4-pyridyl)ethane in place of 4,4′-bipyridine. Yellow plate-shaped crystals were obtained. The approximate yield of the crystals for both (I) and (II) was about 52%.

Compound (I)

Crystal data

(C₁₀H₁₀N₂)₀.₅[U(C₅H₂ClO₂S)₃O₂]·H₂O	$\beta = 104.595\ (2)°$
$M_r = 851.90$	$V = 2720.34\ (16)$ Å³
Monoclinic, $P2_1/c$	$Z = 4$
$a = 14.1630\ (5)$ Å	Mo $K\alpha$ radiation
$b = 17.5777\ (6)$ Å	$\mu = 6.54$ mm⁻¹
$c = 11.2915\ (4)$ Å	$T = 296$ K
	$0.08 \times 0.06 \times 0.05$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	33776 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)	8824 independent reflections
$T_{min} = 0.577$, $T_{max} = 0.698$	5253 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.042$

metal-organic compounds

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.087$
$S = 0.99$
8747 reflections
313 parameters
3 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 1.16$ e Å^{-3}
$\Delta\rho_{min} = -1.03$ e Å^{-3}

Compound (II)

Crystal data

$(C_{12}H_{14}N_2)_{0.5}[U(C_5H_2ClO_2S)_3$-$O_2]\cdot H_2O$
$M_r = 865.92$
Monoclinic, $P2_1/c$
$a = 14.5189$ (2) Å
$b = 18.1169$ (3) Å
$c = 11.1399$ (2) Å

$\beta = 97.123$ (1)°
$V = 2907.60$ (8) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 6.12$ mm^{-1}
$T = 296$ K
$0.10 \times 0.08 \times 0.05$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min} = 0.531$, $T_{max} = 0.713$

32147 measured reflections
7244 independent reflections
4711 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.098$
$S = 1.01$
7244 reflections
328 parameters
3 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 1.32$ e Å^{-3}
$\Delta\rho_{min} = -0.68$ e Å^{-3}

All C- and N-bound H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å and N—H = 0.86 Å and with $U_{iso}(H) = 1.2U_{eq}(C$ or $N)$. The water H atoms of (I) and (II) were located in difference Fourier maps and refined using O—H distance restraints of 0.82 (2) Å and H···H restraints of 1.40 (2) [for (I)] and 1.38 (2) Å [for (II)] *via* DFIX commands with fixed $U_{iso}(H) = 1.2U_{eq}(O)$.

In (II), the atomic displacement ellipsoid for atom S3 is larger than normal, while that for atom C13 is quite small. This suggests that the thiophene ring is disordered through a 180° rotation of the ring, a feature that is common in structures involving such rings. The thiophene ring containing atoms S1 and C3 also shows this feature, but to a significantly lesser extent. No attempt was made to model the disorder.

For both compounds, data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008);

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1W	0.86	1.83	2.683 (6)	169
O1W—H1W···O6^{ii}	0.81 (4)	2.12 (4)	2.868 (5)	154 (5)
O1W—H1W···O7^{ii}	0.81 (4)	2.33 (5)	2.951 (5)	134 (5)
O1W—H2W···O1	0.82 (5)	2.10 (5)	2.903 (5)	166 (5)
C9—H9···O4^{iii}	0.93	2.52	3.318 (6)	144
C17—H17···O7^{iv}	0.93	2.48	3.379 (6)	162
C18—H18···O8	0.93	2.38	3.208 (6)	147

Symmetry codes: (ii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $-x+1, -y+1, -z+2$; (iv) $-x, -y+1, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1W	0.86	1.77	2.625 (7)	175
O1W—H2W···O3^{v}	0.82 (3)	1.92 (3)	2.731 (5)	171 (8)
C17—H17···O1^{vi}	0.93	2.57	3.238 (7)	129
C18—H18···O7^{vii}	0.93	2.28	3.173 (6)	161
C20—H20···O8^{iii}	0.93	2.47	3.362 (6)	160

Symmetry codes: (iii) $-x+1, -y+1, -z+2$; (v) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (vi) $x+1, y, z$; (vii) $-x+1, -y+1, -z+1$.

molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

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