Hydrogen-bonded network structures in dipyridinium, bis(2-methyl-pyridinium), bis(3-methylpyridinium) and bis(4-methylpyridinium) dioxido-bis(oxydiacetato)uranate(VI)

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Four complexes containing the $[UO_2(oda)_2]^{2-}$ anion (oda is oxydiacetate) are reported, namely dipyridinium dioxidobis-(oxydiacetato)uranate(VI), $(C_5H_6N)_2[U(C_4H_4O_5)_2O_2]$, (I), bis(2-methylpyridinium) dioxidobis(oxydiacetato)uranate(VI), $(C_8H_8N)_2[U(C_4H_4O_5)_2O_2]$, (II), bis(3-methylpyridinium) di-oxidobis(oxydiacetato)uranate(VI), $(C_8H_8N)_2[U(C_4H_4O_5)_2O_2]$, (III), and bis(4-methylpyridinium) dioxidobis(oxydiacet-ato)uranate(VI), $(C_8H_8N)_2[U(C_4H_4O_5)_2O_2]$, (IV). The anions are achiral and are located on a mirror plane in (I) and on inversion centres in (II)–(IV). The four complexes are assembled into three-dimensional structures via N—H···O and C—H···O interactions. Compounds (III) and (IV) are isomorphous; the $[UO_2(oda)_2]^{2-}$ anions form a porous matrix which is nearly identical in the two structures, and the cations are located in channels formed in this matrix. Compounds (I) and (II) are very different from (III) and (IV): (I) forms a layered structure, while (II) forms ribbons.

Comment

We recently published a study of complexes featuring the nine-coordinate chiral $[Ln(oda)_3]^{3-}$ anion (where Ln = Pr, Eu, Gd or Dy, and oda = oxydiacetate) (Lennartson & Håkansson, 2009a). In the case of $Na_5[Er(oda)_3](H_2O)_6(BF_4)_2$, which crystallizes in the Sohncke space group (Flack, 2003) R32, it was possible to crystallize a whole sample as one enantio-merically pure single crystal. This represents the first example of the preparation of enantiomerically pure bulk quantities of a nine-coordinate complex displaying only achiral ligands. Since all precursors [diglycolic acid, erbium(III) chloride hexahydrate, sodium hydroxide, sodium bicarbonate, sodium tetrafluoroborate and water] were achiral, the overall synth-esis may be regarded as a case of absolute asymmetric

synthesis (Feringa & van Delden, 1999; Mislow, 2003). Progressing from the oxydiacetate lanthanide complexes we have examined the corresponding actinide complexes, and four complexes containing the dioxidobis(oxydiacetato)uran-ate(VI) anion, $[UO_2(oda)_2]^{2-}$, are presented in this paper.

Only six crystal structures of uranyl complexes containing the oxydiacetate ligand are listed in the Cambridge Structural Database (CSD, Version 5.30 of May 2009; Allen, 2002). In the absence of coordinating ligands, uranyl oxydiacetate forms a coordination polymer (Bombieri et al., 1974), which undergoes spontaneous resolution (Jacques et al., 1984; Perez-Garcia & Amabilino, 2007) on crystallization. The other structures pub-lished are oxodiacetatodi(pyridine oxide)dioxouranium(VI) (Bombieri et al., 1973), di(1,3,5,7-tetraazaadamant-1-ium)-di(μ_2-hydroxo)di(oxodiacetato)tetraoxodiuranium(VI) dihy-drate (Jiang et al., 2002) and three structures containing the $[UO_2(oda)_2]^{2-}$ anion (Bombieri et al., 1973; Jiang et al., 2002).

(I) $X = Y = Z = $ H
(II) $X = $ Me, $Y = Z = $ H
(III) $X = Z = $ H, $Y = $ Me
(IV) $X = Y = $ H, $Z = $ Me
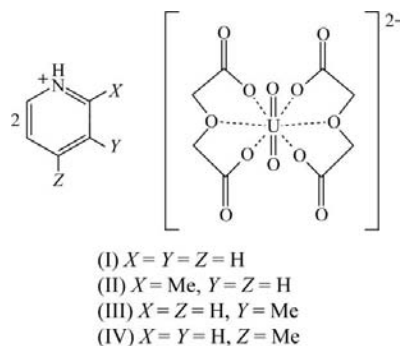
Dipyridinium dioxidobis(oxydiacetato)uranate(VI), (I), bis-(2-methylpyridinium) dioxidobis(oxydiacetato)uranate(VI), (II), bis(3-methylpyridinium) dioxidobis(oxydiacetato)uran-ate(VI), (III), and bis(4-methylpyridinium) dioxidobis(oxy-diacetato)uranate(VI), (IV), all form yellow crystals from aqueous solution. None of the crystal structures includes water, neither coordinated to the U atom nor as co-crystal-lized water.
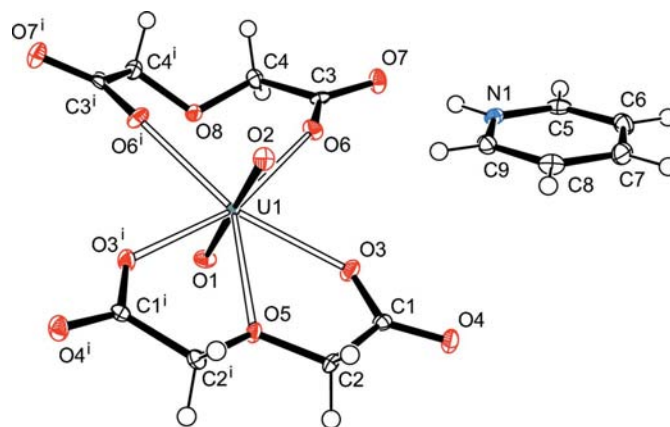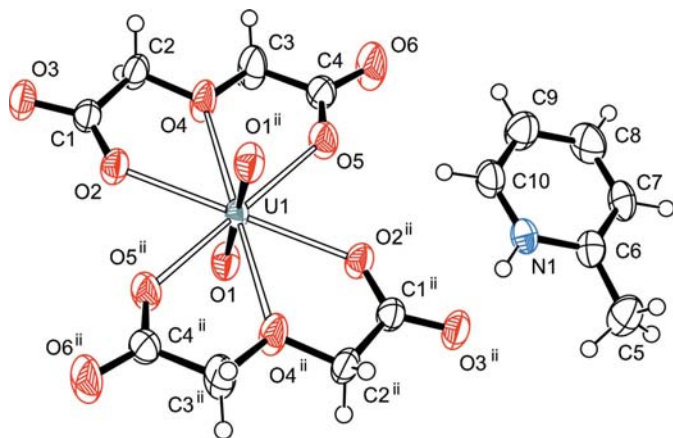

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) x, $\frac{1}{2} - y$, z.]

metal-organic compounds

Figure 2
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (ii) $-x$, $-y$, $-z$.]
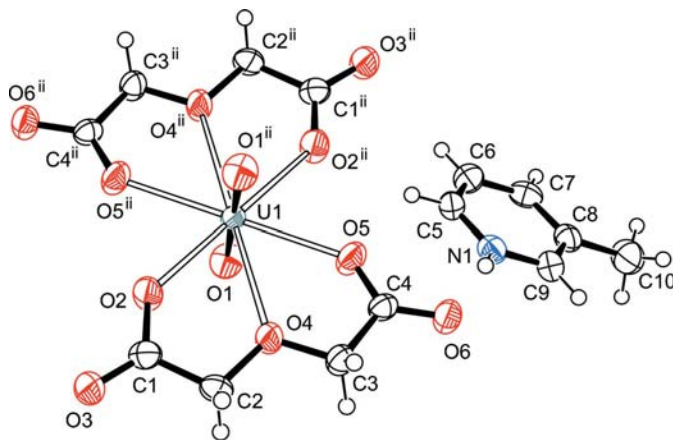

Figure 3
The molecular structure of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (ii) $-x$, $-y$, $-z$.]
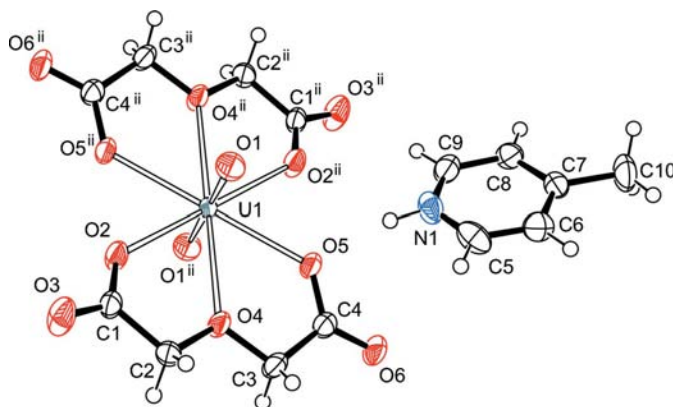

Figure 4
The molecular structure of (IV), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (ii) $-x$, $-y$, $-z$.]
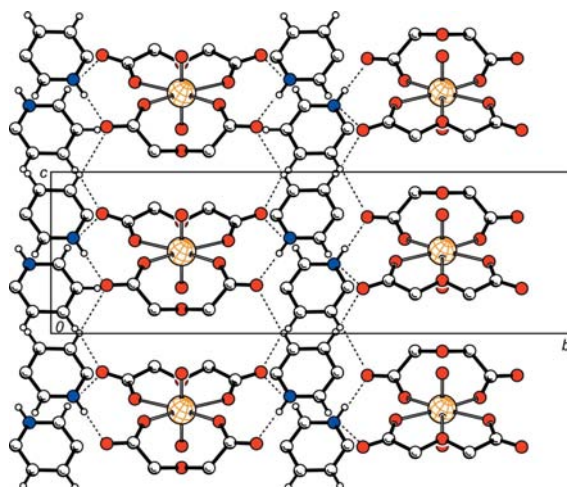

Figure 5
The N—H⋯O and C—H⋯O bonded layer in (I). Hydrogen bonds are shown as dashed lines. All H atoms not involved in these interactions have been omitted for clarity.
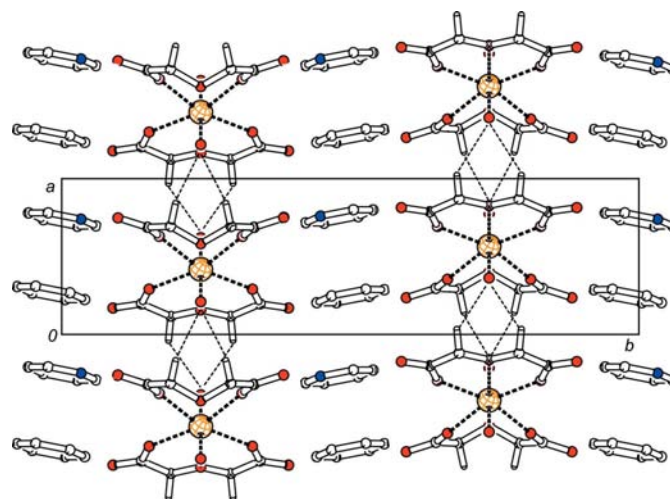

Figure 6
Diagram showing how the layers in (I) are assembled into a network structure by C—H⋯O interactions (dashed lines). Three layers are depicted and run horizontally in the figure. All H atoms not involved in these interactions have been omitted for clarity.

The uranyl moieties in compounds (I)–(IV) are linear, as expected, and are coordinated by two oxydiacetate ligands, giving rise to complex $[UO_2(oda)_2]^{2-}$ anions. The anions differ somewhat between the four compounds. In (I), the $[UO_2(oda)_2]^{2-}$ anion is located on a mirror plane bisecting both oxydiacetate ligands (Fig. 1). The two oxydiacetate ligands are coordinated differently to the central U atom. One is virtually planar, and atoms O3 and O5 are both coordinated to the central U atom. The other ligand deviates considerably from planarity and, since the U1—O8 distance is probably too long to be considered a U—O bond, it is best described as a bidentate ligand. The $[UO_2(oda)_2]^{2-}$ anions in (II), (III) and (IV) are very similar (Figs. 2–4), with the central U atoms located on crystallographic inversion centres and with the oxydiacetate ligands virtually planar. Both types of coordi-
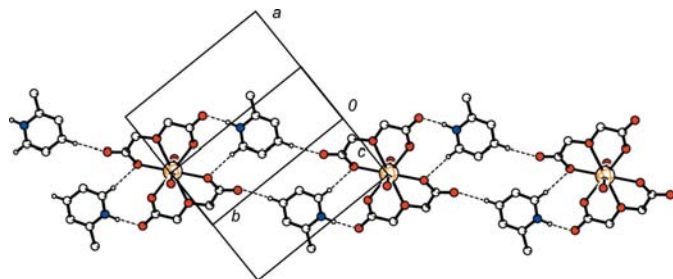
Figure 7
Diagram showing how the N—H···O and C—H···O interactions in (II) (dashed lines) give rise to ribbons. All H atoms not involved in these interactions have been omitted for clarity.

Figure 9
The C—H···O interactions in (III) (dashed lines), involving the cation (top) and the anion (bottom).
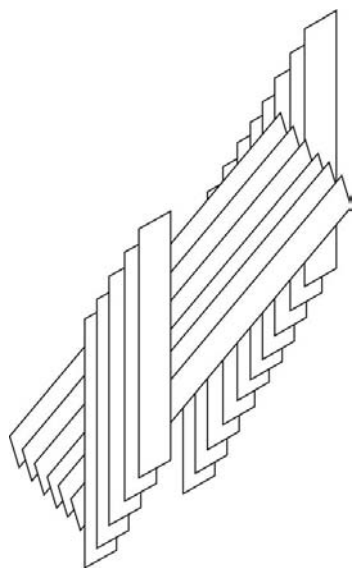

Figure 8
Schematic drawing of the ribbons in the structure of (II). The ribbons form layers which are stacked into a three-dimensional structure; three such layers are depicted.

Figure 10
Diagram showing how the cations in (III) are located in channels running through the unit cell. All H atoms have been omitted.

nation mode have been reported previously (Jiang *et al.*, 2002). Selected geometric parameters for (I)–(IV) are compared in Table 1. The $[UO_2(oda)_2]^{2-}$ anions are achiral, in contrast with the propeller-shaped $[Ln(oda)_3]^{3-}$ anions, but this does not exclude the possibility of a chiral crystal structure, since achiral molecules may assemble into chiral supramolecular structures (Matsuura & Koshima, 2005; Lennartson & Håkansson, 2009*b*). However, compounds (I)–(IV) form centrosymmetric crystals.

The ions in (I) are associated by N—H···O and C—H···O interactions (Table 2). Classical N—H···O interactions form a short contact between atoms H1 and O7 within the asymmetric unit. Due to symmetry, each $[UO_2(oda)_2]^{2-}$ anion will interact with two pyridinium cations. The C—H···O interactions involving H5···O4(1 − x, −y, 1 − z), H7···O4(1 − x, −y, 2 − z) and H8···O7(x, y, 1 + z) give rise to layers in the *bc* plane (Fig. 5). These layers are further associated into a network structure (Fig. 6) by two sets of C—H···O interactions, *viz.* H2A···O2(−1 + x, y, z) and H4A···O1(1 + x, y, z).

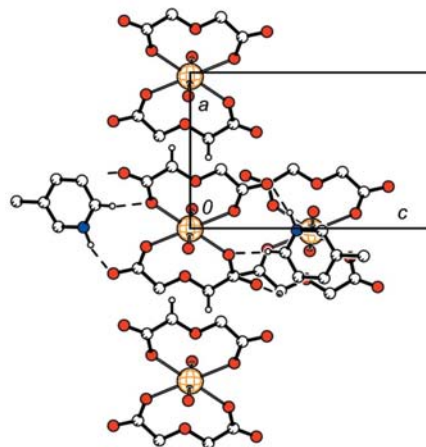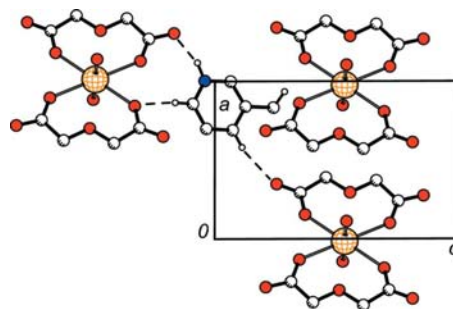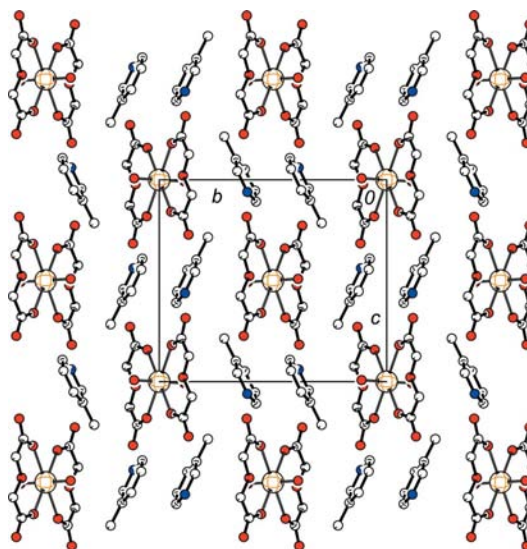Introducing a methyl group in the 2-position on the pyridinium cation, *i.e.* on going from (I) to (II), dramatically alters the crystal packing (Table 3). The 2-picolinium cation in (II) binds two $[UO_2(oda)_2]^{2-}$ anions through N—H···O and C—H···O interactions. Two sets of interactions, *viz.* H1···O3(−x, −y, −z) and H10···O5, connect the 2-picolinium cation to one anion, and a third interaction, H8···O6-(1 − x, 1 − y, −z), introduces connections to a second anion. As seen in Fig. 7, these interactions give rise to infinite ribbons.
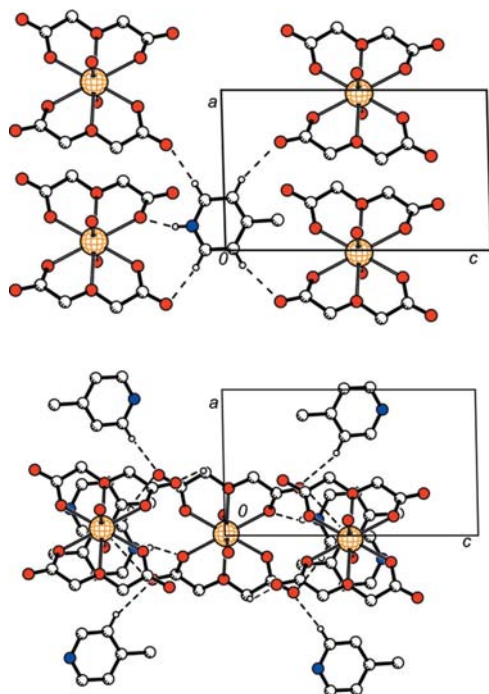
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Figure 11
C—H···O interactions in (IV) (dashed lines), involving the cation (top) and the anion (bottom).

Sets of ribbons are partly stacked in a similar fashion to the strakes in a ship's hull, giving rise to layers. The layers are stacked into a three-dimensional structure, where ribbons in adjacent layers are orthogonal; a schematic drawing is presented in Fig. 8.

The crystal structure of the analogous 3-picolinium complex, (III), is different from both (I) and (II) (Table 4). N—H···O and C—H···O interactions in (III) give rise to a three-dimensional network structure (Fig. 9). The [UO$_2$-(oda)$_2$]$^{2-}$ anions in (III) form a porous matrix with channels running parallel to the crystallographic *a* and *c* axes. These channels are occupied by the 3-picolinium cations. A view along the *a* axis is presented in Fig. 10.

Compound (IV) is isomorphous with (III). The matrices formed by the anions are almost identical, forming the same type of channels. The orientations of the cations occupying these channels differ between the two structures, and the intermolecular interactions in (IV) (Table 5) are of course different from those in (III), as depicted in Fig. 11.

In the case of the [Ln(oda)$_3$]$^{3-}$ complexes, spontaneous resolution did not occur for Na$_3$[Ln(oda)$_3$](H$_2$O)$_6$, which crystallized in the polar space group *Cc*. Addition of certain salts led to more complex structures, of which Na$_3$NH$_4$[Ln-(oda)$_3$](SCN)(H$_2$O)$_4$ is racemic and Na$_5$[Ln(oda)$_3$](H$_2$O)$_6$-(BF$_4$)$_2$ undergoes spontaneous resolution. It appears that the presence of BF$_4^-$ is essential for spontaneous resolution to occur in this system. Preliminary studies show that recrystallization of (I) from water in the presence of inorganic salts leads to cocrystallization in certain cases, and the formation of a chiral supramolecular structure may be observed at a future date.

Experimental

For the preparation of uranyl oxydiacetate, diglycolic acid (0.13 g, 1.0 mmol) and sodium bicarbonate (0.17 g, 2.0 mmol) were dissolved in water (5 ml). A solution of uranyl nitrate hexahydrate (0.50 g, 1 mmol) in water (5 ml) was added. The solution was heated to reflux and a yellow precipitate formed. The mixture was cooled to ambient temperature and the precipitate collected by filtration, washed with water (3 × 5 ml) and acetone (3 × 5 ml), and dried by suction (yield 0.35 g, 87%). For the preparation of (I), pyridine (0.3 ml) and water (1.0 ml) were added to a mixture of uranyl oxydiacetate (0.35 g, 0.82 mmol) and diglycolic acid (0.11 g, 0.82 mmol). The mixture was heated until a clear solution was obtained. Yellow crystals of (I) formed on cooling to ambient temperature (yield 0.33 g, 54%). Compounds (II)–(IV) were prepared in an analogous manner, substituting pyridine by 2-, 3- and 4-picoline, respectively.

Compound (I)

Crystal data

(C$_5$H$_6$N)$_2$[U(C$_4$H$_4$O$_5$)$_2$O$_2$]	$V = 1076.5$ (5) Å^3
$M_r = 694.39$	$Z = 2$
Monoclinic, $P2_1/m$	Mo $K\alpha$ radiation
$a = 6.675$ (2) Å	$\mu = 7.61$ mm^{-1}
$b = 23.025$ (5) Å	$T = 100$ K
$c = 7.500$ (2) Å	$0.2 \times 0.2 \times 0.1$ mm
$\beta = 110.946$ (11)°	

Data collection

Rigaku R-AXIS IIC image-plate diffractometer	5883 measured reflections
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000)	1853 independent reflections
$T_{min} = 0.240$, $T_{max} = 0.470$	1763 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.032$

Table 1
Selected geometric parameters (Å, °) for (I)–(IV).

	(I)	(II)	(III)	(IV)
U1—O1	1.781 (3)	1.760 (3)	1.756 (4)	1.760 (4)
U1—O2	1.777 (3)	2.443 (3)	2.364 (4)	2.414 (4)
U1—O4	2.348 (2)	2.690 (3)	2.716 (4)	2.653 (3)
U1—O5	2.561 (3)	2.391 (3)	2.426 (4)	2.445 (4)
U1—O6	2.357 (2)			
O1—U1—O2	178.59 (12)	92.63 (13)	90.1 (2)	87.66 (17)
O1—U1—O3	89.38 (7)			
O1—U1—O5	94.06 (11)	92.24 (14)	89.33 (18)	88.15 (18)
O1—U1—O6	96.12 (8)			
O2—U1—O4		57.89 (10)	57.79 (13)	58.72 (11)
O2—U1—O5		114.84 (10)	114.65 (14)	116.69 (12)
O3—U1—O5	61.48 (5)			
O3—U1—O6	73.72 (7)			
O4—U1—O5		57.73 (10)	56.95 (12)	58.24 (12)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O7	0.87 (3)	1.82 (3)	2.688 (3)	179 (6)
C2—H2A···O2^i	0.97	2.61	3.446 (5)	144
C4—H4A···O1^{ii}	0.97	2.55	3.482 (5)	161
C5—H5···O4^{iii}	0.93	2.28	3.168 (4)	161
C7—H7···O4^{iv}	0.93	2.28	3.195 (4)	167
C8—H8···O7^v	0.93	2.47	3.354 (4)	159

Symmetry codes: (i) $x - 1, y, z$; (ii) $x + 1, y, z$; (iii) $-x + 1, -y, -z + 1$; (iv) $-x + 1, -y, -z + 2$; (v) $x, y, z + 1$.

Table 3
Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1···O3^i	0.90 (6)	1.77 (6)	2.666 (5)	170 (6)
C7—H7···O1^{ii}	0.93	2.63	3.409 (6)	141
C8—H8···O6^{iii}	0.93	2.32	3.242 (7)	171
C10—H10···O5	0.93	2.41	3.328 (6)	170

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y + 1, -z$; (iii) $-x + 1, -y + 1, -z$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.016$
$wR(F^2) = 0.038$
$S = 1.06$
1853 reflections
161 parameters
1 restraint

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.81$ e Å^{-3}
$\Delta\rho_{min} = -0.96$ e Å^{-3}

Compound (II)

Crystal data

$(C_6H_8N)_2[U(C_4H_4O_5)_2O_2]$
$M_r = 722.44$
Monoclinic, $P2_1/c$
$a = 9.183$ (2) Å
$b = 11.104$ (3) Å
$c = 12.826$ (4) Å
$\beta = 111.490$ (7)°

$V = 1217.0$ (6) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 6.73$ mm^{-1}
$T = 295$ K
$0.2 \times 0.2 \times 0.1$ mm

Data collection

Rigaku R-AXIS IIC image-plate diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000)
$T_{min} = 0.304, T_{max} = 0.510$

7415 measured reflections
2106 independent reflections
1694 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.059$
$S = 0.92$
2106 reflections
165 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 1.15$ e Å^{-3}
$\Delta\rho_{min} = -1.38$ e Å^{-3}

Compound (III)

Crystal data

$(C_6H_8N)_2[U(C_4H_4O_5)_2O_2]$
$M_r = 722.44$
Monoclinic, $P2_1/c$
$a = 7.415$ (2) Å
$b = 13.312$ (5) Å
$c = 11.806$ (4) Å
$\beta = 91.224$ (15)°

$V = 1165.1$ (7) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 7.03$ mm^{-1}
$T = 295$ K
$0.4 \times 0.2 \times 0.1$ mm

Data collection

Rigaku R-AXIS IIC image-plate diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000)
$T_{min} = 0.088, T_{max} = 0.500$

7099 measured reflections
1885 independent reflections
1544 reflections with $I > 2\sigma(I)$
$R_{int} = 0.104$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.130$
$S = 1.03$
1885 reflections
165 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 2.20$ e Å^{-3}
$\Delta\rho_{min} = -3.34$ e Å^{-3}

Table 4
Hydrogen-bond geometry (Å, °) for (III).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1···O6	0.94 (7)	1.79 (7)	2.682 (7)	157 (6)
C3—H3A···O3^i	0.97	2.57	3.441 (8)	150
C5—H5···O2^{ii}	0.93	2.32	3.233 (8)	169
C6—H6···O6^{iii}	0.93	2.55	3.309 (7)	139
C7—H7···O3^{iv}	0.93	2.38	3.291 (7)	165

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

Table 5
Hydrogen-bond geometry (Å, °) for (IV).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1···O5	0.90 (6)	1.97 (6)	2.835 (6)	165 (7)
C2—H2B···O6^i	0.97	2.59	3.451 (6)	147
C5—H5···O3^{ii}	0.93	2.27	3.115 (6)	152
C6—H6···O6^{iii}	0.93	2.50	3.387 (7)	160
C8—H8···O6^{iv}	0.93	2.49	3.279 (7)	143
C9—H9···O3^v	0.93	2.18	3.099 (7)	169

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

Compound (IV)

Crystal data

$(C_6H_8N)_2[U(C_4H_4O_5)_2O_2]$
$M_r = 722.24$
Monoclinic, $P2_1/c$
$a = 7.3439$ (13) Å
$b = 12.999$ (2) Å
$c = 12.194$ (2) Å
$\beta = 92.438$ (9)°

$V = 1163.0$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 7.05$ mm^{-1}
$T = 295$ K
$0.2 \times 0.2 \times 0.1$ mm

Data collection

Rigaku R-AXIS IIC image-plate diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000)
$T_{min} = 0.231, T_{max} = 0.490$

6992 measured reflections
2002 independent reflections
1752 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.086$
$S = 1.14$
2002 reflections
165 parameters
1 restraint

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 2.28$ e Å^{-3}
$\Delta\rho_{min} = -1.99$ e Å^{-3}

The N-bound H atoms were located in difference Fourier maps and refined isotropically, with the N—H distances in (I) and (IV) restrained to 0.90 (2) Å. The C-bound H atoms were included in calculated positions, with C—H = 0.93 (aromatic), 0.96 (methyl) or 0.97 Å (methylene), and refined using a riding model, with $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl groups and $1.5U_{eq}(C)$ for the remainder. A few strong low-angle reflections were excluded since these caused saturation of the image plate.

For all compounds, data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLUTON* (Spek,

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