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One-dimensional uranium–organic framework in *catena*-poly[[di-μ_2-hydroxido-bis[dioxouranium(VI)]]-di-μ_2-2-pyridylacetato-$\kappa^3O,N:O'$;-$\kappa^3O:O',N$]

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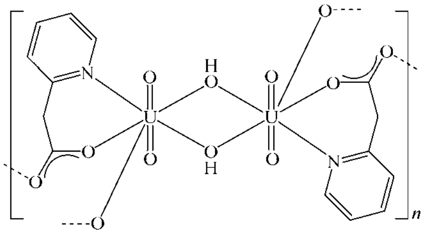
In the title compound, $\{[UO_2(C_7H_6NO_2)(OH)]\}_n$, the U atom is in a seven-coordinated pentagonal–bipyramidal environment. Each uranyl ion is bound to the N and one of the O atoms of a 2-pyridylacetate ligand, to one O atom from a second ligand and to two bridging hydroxide groups, all located in the equatorial plane. Hydroxide bridging gives uranyl dimers, which are assembled into planar and rectilinear ribbons by carboxylate bridges. 12-Membered rings are defined by proximal dimers in the ribbons, with two intra-ring hydrogen bonds involving the hydroxide groups and two carboxylate O atoms.

Comment

The carboxylic acid derivatives of pyridine are useful ligands for the synthesis of uranyl complexes and uranyl–organic frameworks. In particular, several complexes involving pyridine-2,6-dicarboxylate have been described, which are either molecular (Masci & Thuéry, 2005) or polymeric species (Immirzi *et al.*, 1975; Harrowfield *et al.*, 2006; Cahill *et al.*, 2007, and references therein). This ligand chelates the uranyl ion through its O,N,O'-donor atoms, and it appeared interesting to investigate the possible chelation by pyridine ligands bearing longer and more flexible acid chains. The monoacid used in this work, *viz*. 2-pyridylacetic acid, has seldom been used as a ligand in structural studies, and never with *f* element ions. The Cambridge Structural Database (CSD; Version 5.28; Allen, 2002) contains only eight structures of complexes formed by this ligand or its 6-methyl derivative with *d* transition metal atoms (Ni, Cu, Zn, Pd and Pt) or with Sb; in these complexes, the ligand is generally *O,N*-chelating, with the exceptions of one *N*-bonded Pt complex (Ma *et al.*, 2005) and one *O*-bonded Sb complex (Domagala *et al.*, 1990). The present title uranyl complex, (I), has been obtained under hydrothermal conditions and is polymeric, as expected.

The asymmetric unit in (I) comprises one uranyl ion, one deprotonated 2-pyridylacetate ligand and one hydroxide ion



(I)

(Fig. 1). The linear uranyl group is *O,N*-chelated by 2-pyridylacetate, and is also bound to one carboxylate O atom from a neighbouring complex unit and two bridging hydroxide groups. The five equatorial donor atoms [N1, O3, O5, O4^i and O5^{ii}; symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 1, -y + 1, -z + 1$] define a mean plane with an r.m.s. deviation of 0.13 Å, atom U1 being displaced by 0.0250 (12) Å. The uranium coordination geometry is thus the usual pentagonal–bipyramidal one. The N1—U1—O3 (Table 1) angle is rather large and precludes the equatorial six-coordinate environment that is the most frequent with pyridine-2,6-dicarboxylates. The U1—N1 and U1—O3 bond lengths are very close to their average counterparts in the *O,N,O*-chelated complexes with pyridine-2,6-dicarboxylate reported in the CSD (12 hits) [2.59 (6) and 2.42 (4) Å, respectively], although the latter are often six-coordinate. The lower coordination number in (I) is not associated with shorter bond lengths, which is probably a result of the less suitable ligand geometry. The chelating ligand and the metal atom form a six-membered ring which is in the boat conformation. Atoms N1, C5, C7 and O3 define a mean plane with an r.m.s. deviation of 0.017 Å, with atoms U1 and

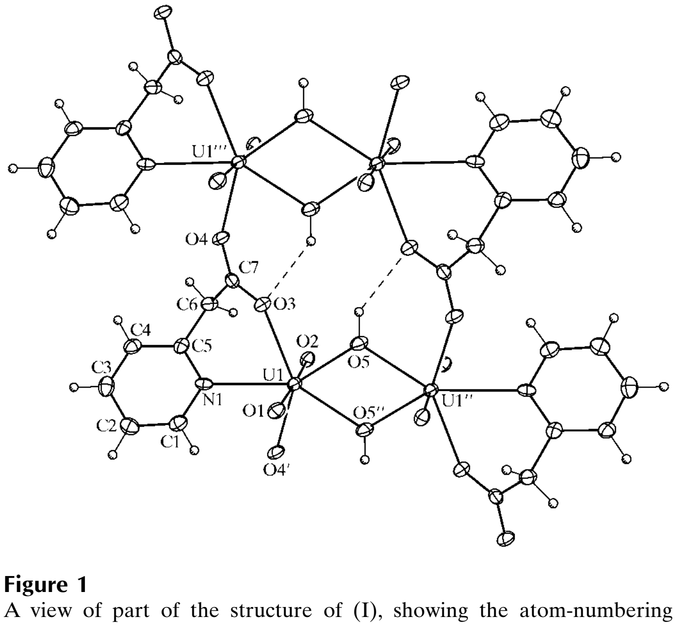


Figure 1
A view of part of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (′) $x + 1, y, z$; (″) $1 - x, 1 - y, 1 - z$; (‴) $x - 1, y, z$.]

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C6 located on the same side, at distances of 0.977 (8) and 0.668 (7) Å from the plane. The dihedral angles between the uranyl equatorial plane and the aromatic ring and O3/O4/C7 planes are 42.86 (10) and 32.3 (8)°, respectively, and that between the last two planes is 59.0 (5)°. The N1—C5—C6—C7 torsion angle of 65.4 (5)° indicates that the carboxylate group is tilted out of the plane of the aromatic ring, as in the previous chelate complexes with this ligand. Uranyl centrosymmetric dimers are formed by the hydroxide double bridges, the pentagonal–bipyramidal polyhedra of the two metal atoms sharing a common edge defined by the double bridge. Such an occurrence is quite frequent in uranyl complexes, either in molecular complexes, as in some dinuclear species with nitrate (Alcock & Flanders, 1987; Evans *et al.*, 2002; Thuéry & Masci, 2002; Fischer & Palladino, 2005; Spencer *et al.*, 2006) and pyridine-2,6-dicarboxylate ligands (Masci & Thuéry, 2005), or in polymeric complexes obtained under hydrothermal conditions (Thuéry, 2007). The average U1—O(hydroxide) bond length [2.33 (2) Å], the U1—O5—U1$^{\mathrm{ii}}$ angle (Table 1) and the U1$\cdots$U1$^{\mathrm{ii}}$ separation [3.8713 (6) Å] are in perfect agreement with the average values for the analogous complexes in the CSD (20 hits), which are 2.33 (2) Å, 112 (2)° and 3.85 (6) Å, respectively.

The hydroxide-bridged uranyl dimers are connected to one another along the *a* axis through two carboxylate bridges, thus defining a central centrosymmetric 12-membered ring which is occupied by two hydrogen bonds involving the hydroxide groups and carboxylate O atoms [O5$\cdots$O3$^{\mathrm{iii}}$ = 3.027 (5) Å, O5—H5 = 0.89 Å, H5$\cdots$O3$^{\mathrm{iii}}$ = 2.27 Å and O5—H5$\cdots$O3$^{\mathrm{iii}}$ = 143°; symmetry code: (iii) $-x, -y+1, -z+1$]. Planar ribbons running along the *a* axis are thus generated, as represented in Fig. 2, in which the central row of uranyl dimers is surrounded by two lateral rows of aromatic rings. When viewed down the *a* axis (Fig. 3), the packing displays ribbons stacked so as to form double C—H$\cdots\pi$ interactions around inversion centres, which link the aromatic rings to the methylene groups of neighbouring molecules [H6$B\cdots Cg^{\mathrm{iv}}$ = 2.77 Å and C6—H6$B\cdots Cg^{\mathrm{iv}}$ = 128°; symmetry code: (iv) $-x, -y, -z$]. No π stacking interactions are present. These weak C—H$\cdots\pi$ interactions result in the formation of loosely bound sheets parallel to $(01\overline{1})$, which interact with one another by van der Waals interactions only.

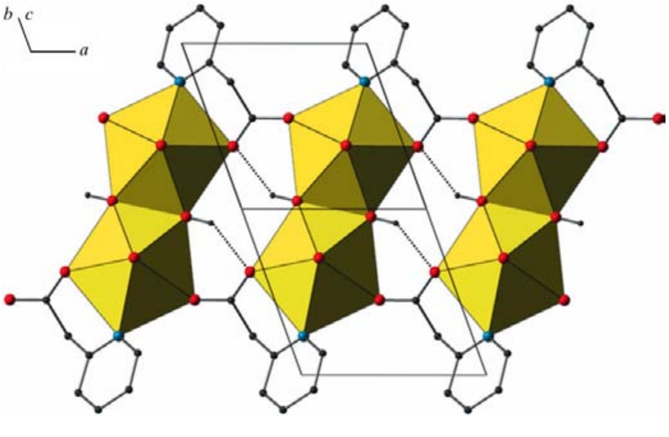

Figure 2
A view of the ribbon arrangement. The uranium coordination polyhedra are shown and the other atoms are shown as spheres of arbitrary radii. H atoms not involved in hydrogen bonds have been omitted. Hydrogen bonds are shown as dotted lines.

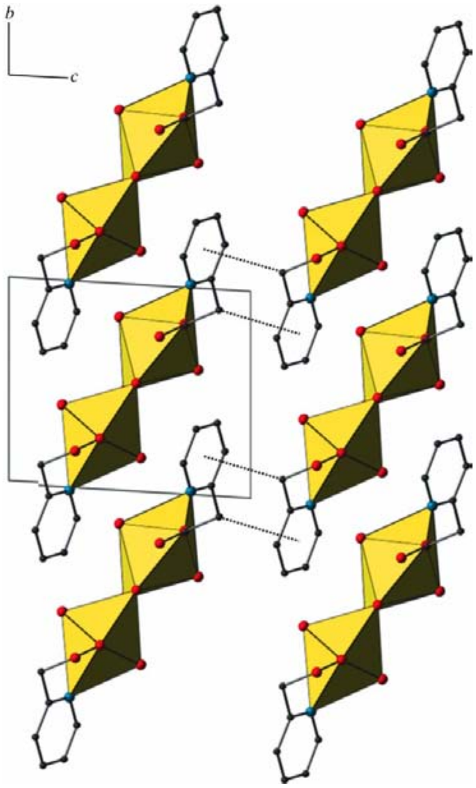

Figure 3
A view of the packing down the *a* axis, with ribbons viewed end-on. The uranium coordination polyhedra are shown and the other atoms are shown as spheres of arbitrary radii. H atoms have been omitted. C—H$\cdots\pi$ interactions are shown as dotted lines.

Experimental

Uranyl nitrate hexahydrate (155 mg, 0.309 mmol) and 2-pyridylacetic acid hydrochloride (54 mg, 0.311 mmol) were dissolved in demineralized water (3 ml) and a slight excess of $\mathrm{NEt_3}$ (45 mg, 0.44 mmol) was added. The solution was placed in a tightly closed glass vessel and heated at 453 K under autogenous pressure (*ca* 1.1 MPa), yielding crystals of (I) suitable for X-ray crystallography in 24 h. Compound (I) was then recovered and washed with water (22 mg, 0.052 mmol, 17% yield). Elemental analysis calculated for $\mathrm{C_7H_7NO_5U}$: C 19.87, H 1.67, N 3.31%; found: C 19.63, H 1.54, N 3.22%.

Crystal data

$[\mathrm{U(C_7H_6NO_2)O_2(OH)}]$
$M_r = 423.17$
Triclinic, $P\overline{1}$
$a = 6.4056$ (8) Å
$b = 8.2220$ (6) Å
$c = 9.0916$ (12) Å
$\alpha = 90.946$ (8)°
$\beta = 96.487$ (6)°
$\gamma = 110.425$ (8)°
$V = 445.04$ (9) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 18.23$ mm^{-1}
$T = 100$ (2) K
0.12 × 0.08 × 0.06 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.208$, $T_{\max} = 0.335$
17254 measured reflections
1674 independent reflections
1595 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.062$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.039$
$S = 1.04$
1674 reflections
127 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.78$ e Å^{-3}
$\Delta\rho_{\min} = -1.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

U1—O1	1.775 (4)	U1—O5	2.308 (4)
U1—O2	1.778 (3)	U1—O5$^{\rm ii}$	2.348 (3)
U1—O3	2.438 (3)	U1—N1	2.612 (4)
U1—O4$^{\rm i}$	2.374 (3)		
O1—U1—O2	176.08 (14)	O5$^{\rm ii}$—U1—O4$^{\rm i}$	74.80 (11)
N1—U1—O3	71.53 (12)	O4$^{\rm i}$—U1—N1	71.53 (11)
O3—U1—O5	75.56 (10)	U1—O5—U1$^{\rm ii}$	112.51 (12)
O5—U1—O5$^{\rm ii}$	67.49 (12)		

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

The H atom bound to atom O5 was found in a difference Fourier map and introduced as a riding atom, with a $U_{\rm iso}$(H) value of $1.2U_{\rm eq}$(O5). All other H atoms were introduced at calculated positions as riding atoms, with C—H bond lengths of 0.93 (CH) or 0.97 Å (CH_2) and $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL-2000* (Otwinowski & Minor, 1997); data reduction: *HKL-2000*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999) and *Balls & Sticks* (Ozawa & Kang, 2004); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3075). Services for accessing these data are described at the back of the journal.

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