A new adamantanecarboxylate coordination polymer: poly[[(μ3-adamantane-1,3-dicarboxylato)aqua-dioxidouranium(VI)] monohydrate]

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The title compound, $\{[U(C_{12}H_{14}O_4)O_2(H_2O)]\cdot H_2O\}_n$, is the first actinide complex featuring adamantanecarboxylate ligands. The metal ion possesses a pentagonal–bipyramidal UO_7 coordination involving two axial oxide ligands [U—O = 1.732 (5) and 1.764 (5) Å] and five equatorial O atoms [U—O = 2.259 (5)–2.494 (4) Å] of aqua and carboxylate ligands. The latter display pseudo-chelating and bridging coordination modes of the carboxylate groups that are responsible for the generation of the centrosymmetric discrete uranium–carboxylate $[UO_2(\mu\text{-}R\text{COO})_2UO_2]$ dimers [U···U = 5.5130 (5) Å] and their connection into one-dimensional chains. Hydrogen bonding involving two coordinated and two solvent water molecules [O···O = 2.719 (7)–2.872 (7) Å] yields centrosymmetric $(H_2O)_4$ ensembles and provides noncovalent linkage between the coordination chains to generate a three-dimensional network structure.

Comment

Adamantane carboxylate ligands are receiving growing attention as versatile molecular building blocks for sustaining the structure of coordination solids, in particular focusing upon the construction of framework coordination polymers. This interest is largely predetermined by the geometrically rigid structure of the adamantane skeleton and the ease of its multiple functionalization at the four available bridgehead positions. The defined and proper multiple binding directions, which are supported by such species, were especially relevant for the sophisticated coordination framework architecture involving adamantane-1,3-dicarboxylate (Nielsen et al., 2008; Tang et al., 2009) and adamantane-1,3,5,7-tetracarboxylate in combination with a series of transition metal cations, viz. Cu^{2+} (Chen et al., 2000), Zn^{2+} (Rosi et al., 2005), and Ni^{2+} and Cd^{2+} (Kim et al., 2001). The second important feature of such

molecular building blocks originates in a relatively high density of donor centres adopted around the adamantane scaffold. That is a prerequisite for a high connection of the framework nodes and it commonly favours the assembly of complex multiply connected 'secondary building units', for example, binuclear paddle-wheel Cu–carboxylate motifs (Chen et al., 2000). An alternative possibility may be found with the exploitation of rather high coordination numbers, which are typical of the metal ions of the lanthanide and actinide families. However, this particular issue for the coordination chemistry of adamantane carboxylate ligands remains practically unexplored. Ninefold coordination of Eu^{3+} ions was essential for sustaining the three-dimensional framework structure of the thermally stable luminescent adamantane-1,3-dicarboxylate (ADC) complex (Millange et al., 2004) and some recently characterized mixed-ligand 1,10-phenanthroline–ADC lanthanide coordination polymers (Li et al., 2009). We report herein the synthesis and structure of the first actinide adamantane carboxylate complex adopted by dioxouranium(VI) cations and ADC dianions. In addition to the very specific inherent coordination geometries of the UO_2^{2+} ions in the carboxylate coordination frameworks (Borkowski & Cahill, 2006), such species may attract interest for their photoluminescent properties and photocatalytic activity (Chen et al., 2003).

(I)
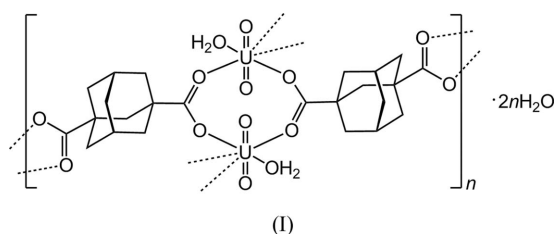
In the title compound, (I), the polymeric array is organized by interconnection of metal ions by bitopic carboxylate
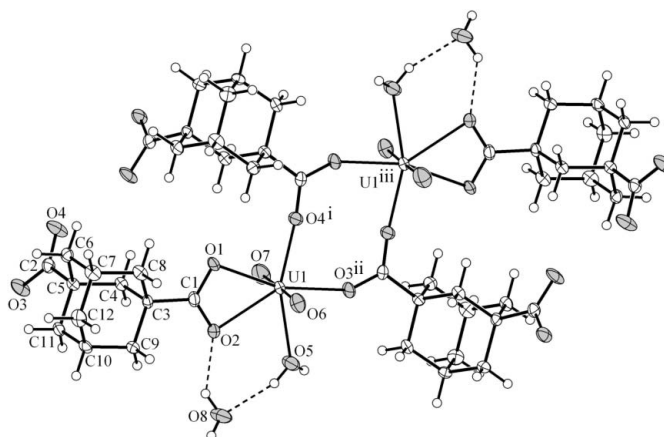

Figure 1
The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed lines indicate O—H···O interactions. [Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $x, 1 - y, \frac{1}{2} + z$; (iii) $-x, 1 - y, 1 - z$.]

ligands. The asymmetric unit includes the dioxouranium(VI) cation, the carboxylate dianion, and one coordinated and one solvent water molecule.

The carboxylate groups of the organic linker display two different coordination modes, *viz.* bidentate pseudo-chelating (C1/O1/O2) and bidentate bridging (C2/O3/O4) (Fig. 1). Thus, the organic ligand is responsible for the connection of three metal ions and the generation of the one-dimensional coordination polymer based upon dinuclear uranium–carboxylate motifs. The bridging carboxylate groups sustain the centrosymmetric dimers [U1···U1^{iii} = 5.5130 (5) Å; symmetry code: (iii) $-x, 1 - y, 1 - z$], in which the characteristic pentagonal–bipyramidal sevenfold coordination (Katz *et al.*, 1986) around two U^{VI} ions is completed by equatorial chelate carboxylate and aqua ligands, and also includes two typically short axial bonds within the essentially linear uranyl moiety (Table 1).

Such carboxylate dimers are characteristic of molecular dioxouranium(VI) species, which commonly accommodate additional single O-atom donors (*L*), for example, *L* = DMF (*N,N*-dimethylformamide) (Navaza *et al.*, 1993; Spitsin *et al.*, 1982) and Ph$_3$PO (Panattoni *et al.*, 1969). Therefore, the dimeric motif may be considered as a special kind of supramolecular synthon for the modular assembly of the uranium–carboxylate frameworks. However, the number of derived polymeric solids as yet is very small and limited to a one-dimensional polymer with the trimesic acid dianion (*L* = H$_2$O; Borkowski & Cahill, 2004) and two-dimensional square grid polymers with camphorate (*L* = MeOH; Thuery, 2006) and succinate [*L* = DMSO (dimethyl sulfoxide); Shchelokov *et al.*, 1985] anions. In the latter two examples, the dimers represent four-connected nodes of the framework. Rather long aliphatic α,ω-dicarboxylate linkers (C$_3$ to C$_8$) typically demonstrate subtle evolution of the pattern. This includes elimination of the neutral O-atom donors and subsequent polymerization of the dimers through a set of additional U–carboxylate bonds

(Borkowski & Cahill, 2005, 2006). Therefore, the steric environment of the tertiary carboxylate groups at the adamantane matrix is essential for sustaining the discrete dimers in (I) [similar to the camphorate prototype reported by Thuery (2006)].

The bridging function of the ADC ligands affords one-dimensional double chains running in the *c* direction (Fig. 2), in which neighbouring dimers along the chain (symmetry code: $-x, y, \frac{1}{2} - z$) are linked by a 'double adamantane bridge'. Such organization of the polymer and the specific coordination mode of the organic ligand bear close resemblance to the one-dimensional structures of [*M*(ADC)(HADC)(phen)-(H$_2$O)] complexes (*M* = Sm, Eu; Li *et al.*, 2009). In particular, the angular orientation of the carboxyl groups installed at the 1,3-positions of the adamantane skeleton is favourable for a double linkage between the coordination dimers and assembly of one-dimensional chains, instead of a four-connected planar network with the single links between the nodes. The same function was observed for the benzene-1,3,5-tricarboxylate dianion, as a bifunctional angular linker between the uranium ions (Borkowski & Cahill, 2004).

The interchain interactions occur by means of relatively strong hydrogen bonding, which involves two coordinated (O5 and O5^{iv}, double donors) and two solvent (O8 and O8^{iv}, double acceptors) [symmetry code: (iv) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$] water molecules supporting flat (H$_2$O)$_4$ tetramers with very characteristic hydrogen-bonding parameters (Fig. 3 and Table 2). An additional hydrogen bond (O8—H3*W*···O2) to a coordinated carboxylate group is also important. These interactions connect the uranium–carboxylate dimers into ribbons along the *a* direction, while weaker hydrogen bonds with UO$_2^{2+}$ oxide ligands [O8—H4*W*···O6^v; symmetry code: (v) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$] unite the ribbons into flat hydrogen-bonded layers parallel to the *ab* plane. Topologically, each
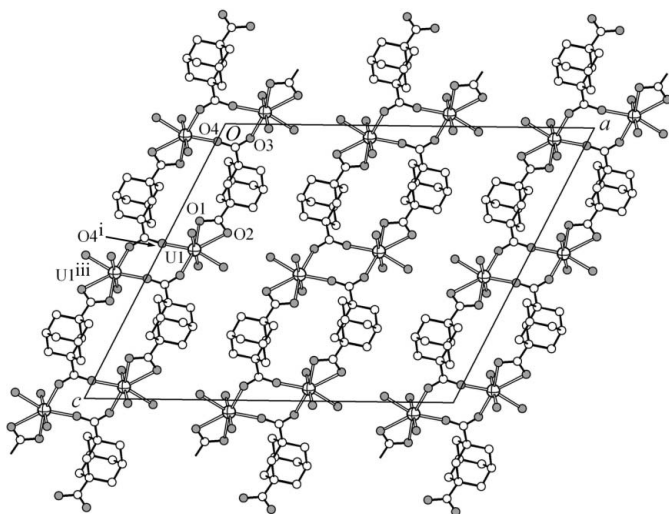

Figure 2
Projection of the structure of (I) on to the *ac* plane, showing a set of coordination chains along the *c* direction. Hydrogen bonds have been omitted for clarity. [Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (iii) $-x, 1 - y, 1 - z$.]
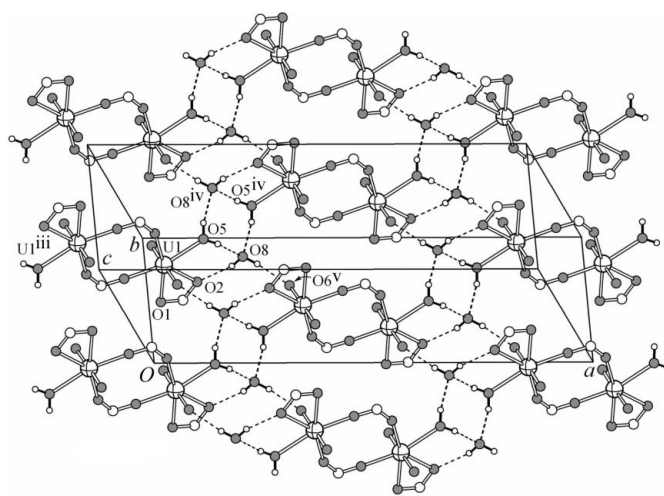

Figure 3
The hydrogen-bonded layer constituted by aquauranium–carboxylate dimers (indicated with open bonds) and solvent water molecules. The adamantanediyl groups have been omitted for clarity (they connect the layers in the direction that is nearly orthogonal to the drawing plane). [Symmetry codes: (iii) $-x, 1 - y, 1 - z$; (iv) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$; (v) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.]

layer represents a planar four-connected net in which the above-mentioned coordination dimers and water tetramers constitute the nodes (Fig. 3). Successive layers, which are related by half-translation along the *c* direction, are separated by 9.061 (2) Å and are linked together by adamantane spacers. In this way, the covalent 'double adamantane links' between the dimers extend this array in a third direction leading to a three-dimensional four- and six-connected hybrid framework formed via coordination bonds and hydrogen bonding.

In brief, the title structure is important as a prototype for the construction of actinide and adamantane carboxylate coordination frameworks, which could be anticipated especially for the typical MO_2^{2+} cations and a wide range of 1,3-bi-, 1,3,5-tri- and 1,3,5,7-tetrafunctional adamantane tectons and the related functionalized 'nanodiamond' molecules.

Experimental

Adamantane-1,3-dicarboxylic acid (H$_2$ADC) was synthesized by the Koch–Haaf carboxylation of adamantane-1,3-diol (Stetter & Wulff, 1960). For the preparation of the title compound, a mixture of H$_2$ADC (11.5 mg, 0.051 mmol), UO$_2$(OAc)$_2$·2H$_2$O (Ac is acetyl; 24.5 mg, 0.058 mmol) and NH$_4$OAc (5.5 mg, 0.071 mmol) in water (2 ml) was sealed in a 15 ml Pyrex tube, heated at 453 K for 48 h and then cooled to room temperature at a rate of 3 K h^{-1}. Yellow–orange crystals of the product, (I), were collected by filtration, yielding 17.5 mg (65%, based on the ligand).

Crystal data

[U(C$_{12}$H$_{14}$O$_4$)O$_2$(H$_2$O)]·H$_2$O
$M_r = 528.29$
Monoclinic, $C2/c$
$a = 24.254$ (2) Å
$b = 6.7855$ (6) Å
$c = 20.2586$ (16) Å
$\beta = 116.549$ (4)°

$V = 2982.5$ (4) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 10.92$ mm^{-1}
$T = 296$ K
$0.19 \times 0.09 \times 0.08$ mm

Data collection

Bruker APEXII area-detector diffractometer
Absorption correction: numerical, face indexed (*SADABS*; Bruker, 2008)
$T_{min} = 0.264$, $T_{max} = 0.464$

9437 measured reflections
3151 independent reflections
2525 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.074$
$S = 1.05$
3151 reflections

190 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 1.87$ e Å^{-3}
$\Delta\rho_{min} = -1.30$ e Å^{-3}

All H atoms were located from difference maps and then refined as riding, with O—H distances constrained to 0.85 Å, methylene C—H distances constrained to 0.97 Å and methine C—H distances constrained to 0.98 Å, and with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(O).

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); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Table 1
Selected geometric parameters (Å, °).

U1—O1	2.407 (4)	U1—O5	2.475 (5)
U1—O2	2.494 (4)	U1—O6	1.764 (5)
U1—O3^{ii}	2.317 (4)	U1—O7	1.732 (5)
U1—O4^{i}	2.259 (5)		
O1—U1—O2	52.46 (14)	O3^{ii}—U1—O4^{i}	83.80 (16)
O1—U1—O3^{ii}	163.17 (16)	O3^{ii}—U1—O5	74.89 (15)
O1—U1—O4^{i}	79.39 (15)	O3^{ii}—U1—O6	90.58 (19)
O1—U1—O5	121.85 (14)	O3^{ii}—U1—O7	89.9 (2)
O1—U1—O6	88.9 (2)	O4^{i}—U1—O5	158.49 (15)
O1—U1—O7	91.2 (2)	O4^{i}—U1—O6	90.6 (2)
O2—U1—O3^{ii}	144.32 (16)	O4^{i}—U1—O7	91.1 (2)
O2—U1—O4^{i}	131.85 (15)	O5—U1—O6	86.7 (2)
O2—U1—O5	69.44 (14)	O5—U1—O7	91.7 (2)
O2—U1—O6	87.95 (17)	O6—U1—O7	178.2 (2)
O2—U1—O7	90.66 (19)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H1W···O8	0.85	1.96	2.772 (6)	160
O5—H2W···O8^{iv}	0.85	1.96	2.753 (7)	154
O8—H3W···O2	0.85	2.02	2.719 (7)	139
O8—H4W···O6^{v}	0.85	2.03	2.872 (7)	170

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

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