

Poly[[[diaquadioxouranium(VI)]- μ_3 -nitrilotriacetato- κ^3 O:O':O''] trihydrate]

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The basic units in the structure of the title compound, $\{[\text{UO}_2(\text{C}_6\text{H}_7\text{NO}_6)(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}\}_n$, are ribbons in which every UO_2^{2+} cation is coordinated in a monodentate manner to three tridentate-bridging nitrilotriacetate dianions. Hydrogen bonds bind the ribbons into a three-dimensional structure.

Comment

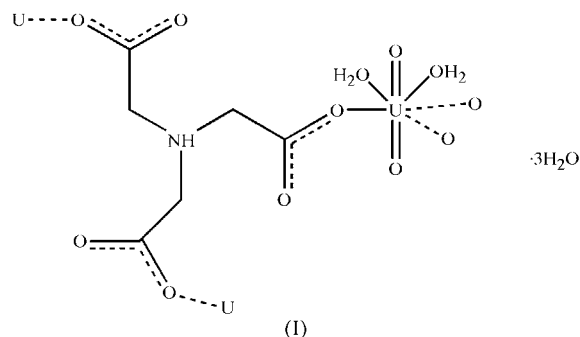
In the field of human toxicology, internal contamination with actinides under either acute or chronic conditions has the potential to induce both radiological and chemical toxicity. At the molecular level, our general understanding of the interactions present in actinide adducts, *i.e.* physical chemical mechanisms that drive the affinity of possible coordination sites for actinide cations, still needs to be deepened. As a result, the intramolecular interactions of actinide elements with either smart chelates designed for coordination and bioorganic chemistry or naturally occurring chelating agents are relatively unknown.

Nitrilotriacetic acid [H_3nta , $\text{N}(\text{CH}_2\text{COOH})_3$] is a derivative of glycine commonly used in biochemistry and medicine. It behaves as a tri- or tetradentate aminocarboxylate chelate that is well known to form complexes with transition metal cations. Lanthanides(III) can also form three-dimensional structures with nta^{3-} anions in various patterns (Wang *et al.*, 2004). In addition, H_3nta can be used as a protecting group for actinides(IV) (Np^{IV} and Pu^{IV}) against hydrolysis at physiological pH.

The present investigation of the complexation of uranium by nitrilotriacetic acid is aimed at obtaining a broader understanding of the interaction of actinides with biological ligands.

The U atom in the title compound, (I), is seven-coordinate, its coordination polyhedron being a distorted pentagonal

bipyramid with equatorial positions occupied by three O atoms of three Hnta^{2-} anions and two O atoms of coordinated water molecules (Fig. 1). Bond lengths in the U atom environment are given in Table 1. The Hnta^{2-} anions act as tridentate-bridging ligands, forming infinite ribbons with uranyl cations in the [010] direction (Fig. 2).



The central N atom in the Hnta^{2-} anion is protonated, preventing this atom from coordinating to U. This H atom forms three intramolecular hydrogen bonds, typical of nitrilotriacetate anions (Antsyshkina *et al.*, 1997; Davidovich *et al.*, 2002; Ilyukhin *et al.*, 1998, 1999; Oliver *et al.*, 1984), with the non-coordinated O atoms of the carboxylate groups acting as acceptors (Fig. 1 and Table 2). This hydrogen bonding gives

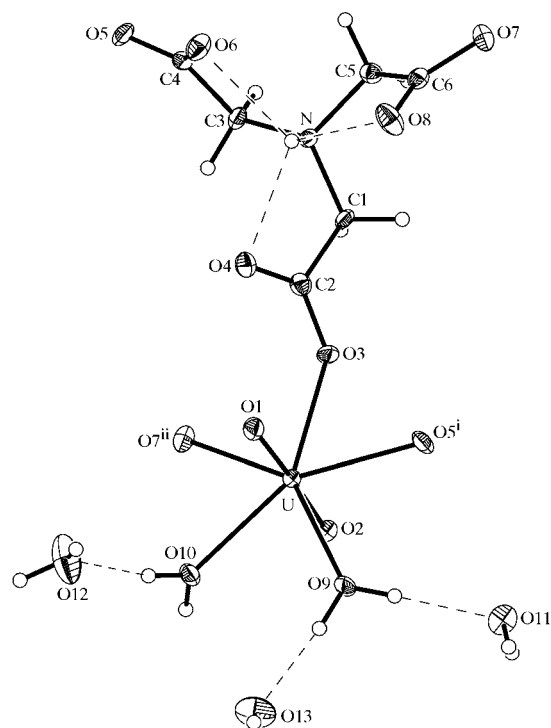


Figure 1

A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size. Dashed lines indicate the hydrogen-bonding interactions. [Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.]

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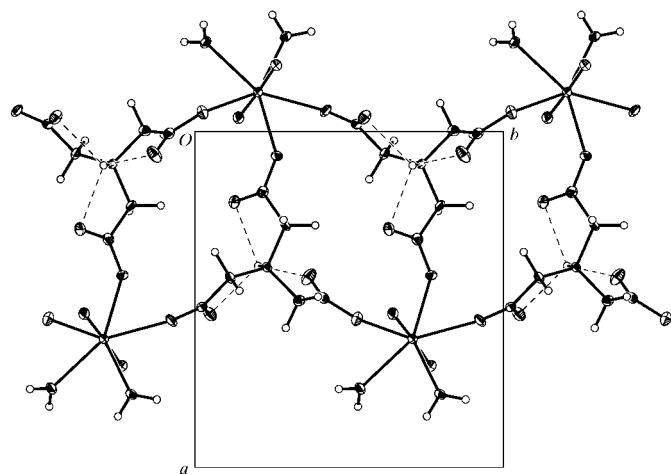


Figure 2
A [UO₂(Hnta)(H₂O)₂]_n ribbon in the structure of (I).

the anion nearly C₃ symmetry, as can be seen from the torsion angles given in Table 1. For this symmetric conformation of the anion the distances between the unligated O atoms of different carboxylate groups are greater than 3.5 Å; the shortest is O4···O8 [3.539 (5) Å]. Comparing this with the O···O distances in the equatorial plane of the uranyl cation [range 2.769 (5)–2.889 (5) Å, average 2.81 (2) Å], we infer that intramolecular hydrogen bonding could be a factor preventing the Hnta²⁻ anion from chelating uranium with the formation of an eight-membered ring. Nevertheless, single-carboxylate chelation with the formation of a four-membered ring still seems to be possible.

Coordinated and crystallization water molecules participate in a number of hydrogen bonds (Table 2). The O10–H10B···O6ⁱ hydrogen bonds link the ribbons into layers in the (002) planes. The hydrogen bonds in which the uncoordinated water molecules participate bind the layers into a three-dimensional structure. Only one hydrogen bond can be found in which the H₂O13 water molecule acts as a donor. This may be the reason why only one H atom of this molecule was located.

Experimental

For the preparation of (I), a 0.1 M solution of Na₂Hnta (pH ~5, 0.125 ml) was added to a 0.025 M UO₂(NO₃)₂ solution (pH ~2, 0.5 ml). After several days of storage at room temperature, agglomerates of yellow needles appeared.

Crystal data

[U(C ₆ H ₇ O ₆)O ₂ (H ₂ O) ₂] _n ·3H ₂ O	<i>D_x</i> = 2.536 Mg m ⁻³
<i>M_r</i> = 549.24	Mo Kα radiation
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Cell parameters from 16104 reflections
<i>a</i> = 10.8858 (3) Å	<i>θ</i> = 2.5–27.4°
<i>b</i> = 9.9530 (2) Å	<i>μ</i> = 11.35 mm ⁻¹
<i>c</i> = 13.3275 (3) Å	<i>T</i> = 120 (2) K
<i>β</i> = 95.0178 (15)°	Needle, yellow
<i>V</i> = 1438.45 (6) Å ³	0.10 × 0.06 × 0.04 mm
<i>Z</i> = 4	

Data collection

Nonius KappaCCD area-detector diffractometer	3240 independent reflections
<i>φ</i> and <i>ω</i> scans	2599 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (MULABS in PLATON; Spek, 2003)	<i>R</i> _{int} = 0.065
<i>T</i> _{min} = 0.487, <i>T</i> _{max} = 0.635	<i>θ</i> _{max} = 27.4°
16104 measured reflections	<i>h</i> = -14 → 13
	<i>k</i> = -12 → 12
	<i>l</i> = -16 → 17

Refinement

Refinement on <i>F</i> ²	H atoms treated by a mixture of independent and constrained refinement
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.029	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0254 <i>P</i>) ²]
<i>wR</i> (<i>F</i> ²) = 0.061	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>S</i> = 1.03	(Δ/σ) _{max} = 0.061
3240 reflections	Δρ _{max} = 2.02 e Å ⁻³
221 parameters	Δρ _{min} = -1.71 e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

U–O1	1.775 (3)	U–O10	2.367 (3)
U–O2	1.767 (3)	U–O5 ⁱ	2.372 (3)
U–O3	2.402 (4)	U–O7 ⁱⁱ	2.361 (3)
U–O9	2.443 (4)		
C1–N–C3–C4	152.3 (4)	N–C1–C2–O3	-179.9 (4)
C3–N–C5–C6	153.7 (4)	N–C3–C4–O5	174.2 (4)
C5–N–C1–C2	146.7 (4)	N–C5–C6–O7	167.7 (4)
C1–N–C5–C6	-77.4 (5)	N–C1–C2–O4	-2.0 (6)
C3–N–C1–C2	-84.9 (5)	N–C3–C4–O6	-7.8 (7)
C5–N–C3–C4	-79.8 (5)	N–C5–C6–O8	-14.3 (6)

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

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O9–H9A···O11	0.84 (2)	1.84 (2)	2.683 (5)	175 (6)
O9–H9B···O13	0.84 (4)	1.92 (4)	2.735 (6)	164 (6)
O10–H10A···O12	0.83 (3)	1.84 (4)	2.656 (5)	167 (5)
O10–H10B···O6 ⁱⁱⁱ	0.84 (4)	1.82 (4)	2.634 (5)	163 (6)
O11–H11A···O8 ^{iv}	0.85 (3)	1.85 (3)	2.673 (5)	163 (6)
O11–H11B···O7 ⁱⁱⁱ	0.85 (4)	2.07 (4)	2.819 (5)	148 (5)
O12–H12A···O11 ^v	0.85 (5)	2.10 (5)	2.932 (6)	166 (6)
O12–H12B···O4 ^{vi}	0.85 (3)	2.04 (3)	2.890 (5)	173 (6)
O13–H13A···O3 ^{vii}	0.83 (2)	2.27 (4)	2.953 (5)	140 (6)
N–H1···O4	0.84 (7)	2.24 (3)	2.655 (6)	111 (2)
N–H1···O6	0.84 (7)	2.22 (3)	2.614 (5)	109 (2)
N–H1···O8	0.84 (7)	2.19 (3)	2.599 (5)	110 (2)

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

H atoms were located in difference Fourier syntheses, except for one H atom of one of the three solvent water molecules. H atoms of CH₂ groups were refined as riding in idealized positions (C–H = 0.99 Å), with displacement parameters equal to 1.2 times the *U*_{eq} values of the attached C atoms. H atoms of water molecules were refined with restraints on the O–H distances and H–O–H angles, the displacement parameters being equal to 1.2 times the *U*_{eq} values of the attached O atoms. For the H atom attached to the N atom, only its orientation was fixed during refinement. The largest electron-density peaks in the final difference Fourier synthesis are 2.02 (1.06 Å from atom O5 and 1.73 Å from the U atom) and 1.69 e Å⁻³ (1.59 Å from H3B), and the deepest hole is 0.87 Å from the U atom.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL Package* (Otwinowski & Minor, 1997); data reduction: *HKL Package*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3002). Services for accessing these data are described at the back of the journal.

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