Tetrakis(tetramethylammonium) tricarbonatodioxidouranate octa-hydrate

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The environment of the U atom in the title compound, $(C_4H_{12}N)_4[UO_2(CO_3)_3]\cdot 8H_2O$, presents a typical hexagonal bipyramidal geometry found in many actinide complexes. It is a model for actinide species and consists of common environmental moieties (carbonate, water and ammonia species). The structure displays a sheet-like hydrogen-bonding network formed from crystallization water molecules and carbonate ligands. The compound is isomorphous with a previously described Np isolog [Grigorev *et al.* (1997). *Radiokhimiya (Russ. Radiochem.)*, **39**, 325–329].

Comment

The total amount of uranium resource in seawater is about 4.5 billion tons ([U] 3 µg l^{-1}, ocean volume 1.37×10^9 km^3), 1000 times the amount of uranium in terrestrial ores (Davies *et al.*, 1964). Therefore, the ocean would virtually be a limitless reservoir as a source of uranium if the uranium could be extracted from seawater at an economically competitive cost. Because the dioxouranium(VI) tricarbonate anion, $[UO_2(CO_3)_3]^{4-}$, is considered to be the dominant uranium species in seawater, there is great interest in revealing its structure and stability. Single crystals of the title compound, tetrakis(tetramethylammonium) tricarbonatodioxidouranate octahydrate, (I), were obtained from alkaline solutions in the presence of 1-hydroxyethane-1,1-diphosphonic acid (HEDPA), a ligand that forms a number of strong complexes with UO_2^{2+} (uranyl) in acid and basic solutions (Reed *et al.*, 2007). The results indicate that the carbonate anions, having formed when CO_2 was absorbed in the hydroxide solution, could effectively compete with HEDPA to complex UO_2^{2+}. The structure of the title compound is compared with that of an isomorphous Np[VI] analog reported previously (Grigorev *et al.*, 1997).

The U atom adopts a typical distorted hexagonal bipyramidal geometry with the UO_2 moiety acting as the axis (Fig. 1). Predictably, the angles formed by the O atoms of each

carbonate coordinating the U atom are more acute than the O—U—O angle formed between O atoms on adjacent carbonates. However, these angles do not deviate excessively from the ideal angle of 60°. The structure of the uranyl tricarbonate anion is otherwise comparable with the previously reported Np[VI] complex. The An—O (An = actinide) equatorial distance and the O=An=O angle are very similar in the two compounds (Table 1). The shorter Np=O distance reflects the higher charge density of Np compared with U owing to the contraction along the actinide series.

(I)
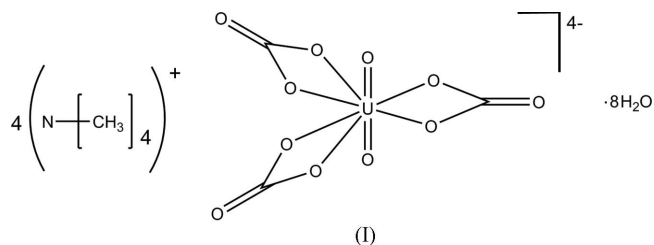
Of particular interest, with regard to the premise that this compound could be formed from aqueous media (*e.g.* seawater), is the extensive hydrogen bonding displayed within the structure (Fig. 2). All eight water molecules of crystallization are involved in the network, as are all but two of the carbonate O atoms (O3 and O6). The uranyl O atoms are not involved in the hydrogen-bond network, thus restricting the geometry to a planar arrangement. The tetramethylammonium cations are located between the layers formed by the
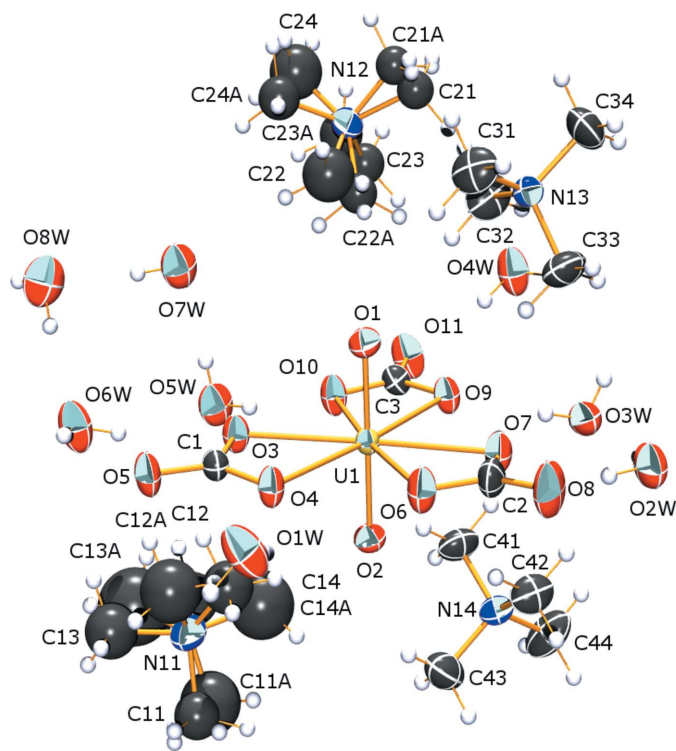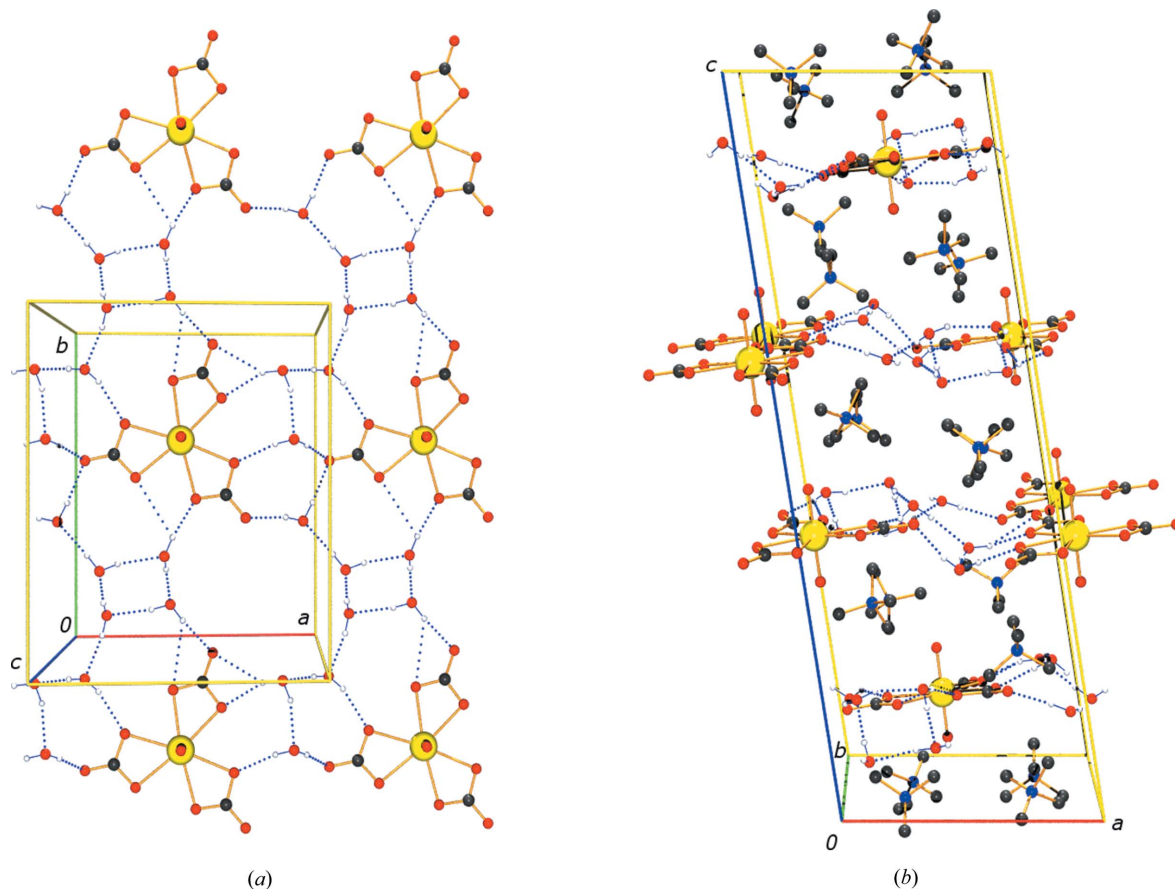

Figure 1
The molecular structure of the title compound, shown with 50% probability displacement ellipsoids. Suffix 'A' denotes the second component of the disordered tetramethylammonium cations.

Figure 2
Hydrogen-bonding network depiction viewed (*a*) along the *c* axis, showing an individual [$UO_2(CO_3)_3$]·$8H_2O$ layer of hydrogen-bonded molecules and (*b*) along the *b* axis, including tetramethylammonium cations depicting the layering. Dotted lines (blue in the electronic version of the paper) represent hydrogen-bond interactions. Disordered components have been removed for clarity and atoms are depicted as spheres of arbitrary radius. (Colour key in the electronic version of the paper: U atoms yellow, O red, N Blue, C grey and H white.)

water/cation hydrogen-bonding network, further bounding the hydrogen bonding to two dimensions. This cation/anion layering is observed in the Np^{VI} complex.

Two of the water molecules are involved in hydrogen bonding exclusively to other water molecules. O6*W* forms hydrogen bonds to O4*W* and O5*W* and accepts one hydrogen bond from O8*W*, and O8*W* donates hydrogen bonds to O1*W* and O6*W* as well as accepting a hydrogen bond from O7*W*. O3*W* and O4*W* form hydrogen bonds with carbonates on adjacent uranyl complexes, forming a hydrogen-bonded bridge. O1*W*, in concert with O2*W*, also forms a bridge between carbonate ligands of the same uranyl complexes as O3*W* and O4*W*. This hydrogen bonding extends the network along the *a* direction. In a similar concerted hydrogen-bonding scheme, O7*W* and O5*W* also form a hydrogen-bonded bridge between carbonates on adjacent uranyl complexes. However, this acts to extend the network along the *b* direction. The result of these hydrogen-bonding interactions is a two-dimensional sheet of uranyl tricarbonate anions and water molecules which extends through the lattice parallel to the *ab* plane. This too is observed in the Np^{VI} complex.

We have demonstrated that uranyl carbonate can form under mildly basic conditions in the presence of CO_2, resulting in a crystalline compound that has a very similar geometry to that of a previously characterized Np^{VI} tricarbonate complex.

Experimental

Crystals of the title compound were obtained by slow evaporation in air (six weeks), at room temperature and under ambient pressure, from an aqueous solution (25 ml) containing uranyl 1-hydroxy-ethane-1,1-diphosphonate (dissolved as 0.3 g yellow solid) and tetramethylammonium hydroxide (0.2 *M*). Transparent yellow crystals were mounted on a glass fiber using Paratone N hydrocarbon oil for data collection.

Crystal data

$(C_4H_{12}N)_4[UO_2(CO_3)_3]$·$8H_2O$	$V = 3666.5$ (11) Å^3
$M_r = 890.77$	$Z = 4$
Monoclinic, $P2_1/n$	Synchrotron radiation
$a = 10.5377$ (18) Å	$\lambda = 0.7750$ Å
$b = 12.358$ (2) Å	$\mu = 2.46$ mm^{-1}
$c = 28.533$ (5) Å	$T = 173$ K
$\beta = 99.343$ (4)°	$0.07 \times 0.05 \times 0.05$ mm

Data collection

Bruker Platinum 200 diffractometer	26534 measured reflections
Absorption correction: multi-scan	7499 independent reflections
(*SADABS*; Sheldrick, 2003)	6587 reflections with $I > 2\sigma(I)$
$T_{min} = 0.847$, $T_{max} = 0.887$	$R_{int} = 0.039$

Table 1
Comparison of selected interatomic distances (Å) and angles (°) between the isomorphous compounds of tricarbonate U^{VI} (this work) and Np^{VI} (Grigorev *et al.*, 1997) (An = actinide).

	$[N(CH_3)_4]_4[UO_2(CO_3)_3]\cdot 8H_2O$	$[N(CH_3)_4]_4[NpO_2(CO_3)_3]\cdot 8H_2O$
Axial An—O	1.803 (3), 1.814 (3)	1.774 (3), 1.773 (3)
Carbonate/equatorial	2.418 (3), 2.423 (3)	2.429 (3), 2.442 (3)
An—O	2.424 (3), 2.450 (3)	2.400 (3), 2.419 (3)
	2.435 (3), 2.444 (3)	2.442 (3), 2.413 (3)
O≡An≡O angle	179.63 (11)	179.8 (1)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1O$A\cdots$O4	0.85 (2)	2.03 (3)	2.778 (4)	146 (5)
O1W—H1O$B\cdots$O2W^i	0.86 (2)	1.96 (2)	2.824 (6)	174 (5)
O2W—H2O$A\cdots$O3W	0.86 (2)	1.99 (2)	2.810 (5)	158 (5)
O2W—H2O$B\cdots$O7	0.86 (2)	2.05 (3)	2.838 (4)	152 (5)
O3W—H3O$A\cdots$O5^{ii}	0.83 (2)	1.94 (2)	2.758 (4)	169 (5)
O3W—H3O$B\cdots$O9	0.84 (2)	1.95 (2)	2.774 (4)	170 (5)
O4W—H4O$A\cdots$O5^{ii}	0.85 (2)	1.89 (2)	2.738 (5)	172 (5)
O4W—H4O$B\cdots$O11	0.86 (2)	1.89 (2)	2.733 (4)	169 (5)
O5W—H5O$A\cdots$O7W	0.83 (2)	1.97 (2)	2.799 (5)	173 (5)
O5W—H5O$B\cdots$O10	0.84 (2)	1.93 (2)	2.751 (4)	169 (5)
O6W—H6O$A\cdots$O4W^i	0.84 (2)	1.87 (2)	2.705 (5)	176 (5)
O6W—H6O$B\cdots$O5W	0.84 (2)	2.00 (3)	2.794 (5)	157 (5)
O7W—H7O$A\cdots$O8^{iii}	0.84 (2)	1.83 (2)	2.666 (5)	172 (5)
O7W—H7O$B\cdots$O8W	0.83 (2)	1.93 (2)	2.752 (6)	169 (5)
O8W—H8O$A\cdots$O1W^{iii}	0.86 (2)	1.91 (2)	2.760 (5)	170 (6)
O8W—H8O$B\cdots$O6W	0.85 (2)	1.96 (2)	2.806 (6)	173 (6)

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	H atoms treated by a mixture of
$wR(F^2) = 0.072$	independent and constrained
$S = 1.06$	refinement
7499 reflections	$\Delta\rho_{max} = 1.70$ e Å^{-3}
429 parameters	$\Delta\rho_{min} = -0.79$ e Å^{-3}
24 restraints	

X-ray intensity data were collected at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory, Berkeley, USA, Beamline 11.3.1. An otherwise routine data collection was undertaken at standard settings for this instrument (wavelength, temperature *etc.*).

Methyl H atoms were included in geometrically calculated positions, with C—H bond distances restrained to 0.98 Å. Water H atoms were included in their observed positions, but were subsequently refined with an O—H bond-distance restraint of 0.85 (1) Å. All water H atoms were found to form good hydrogen bonds to nearby hydrogen-bond acceptor atoms. Displacement parameters of the H atoms were tied to that of the atom to which they are bonded, *viz.* $1.5U_{eq}$(C) for methyl H atoms and $1.2U_{eq}$(O) for water H atoms.

Two of the four tetramethylammonium cations were found to exhibit positional disorder. For one cation, the disorder was a simple 50:50 split over two sites. The other cation, upon investigation, showed that there was some preference for one site over the other. Subsequently this cation was refined with site occupancies for the major and minor component summing to unity; the final occupancy ratio is 0.646 (13):0.354 (13). The disordered C atoms were refined with isotropic displacement parameters.

One reflection, *viz.* 002, was omitted from the refinement. The F_{obs} for this reflection is significantly smaller than F_{calc}, though non-zero. Presumably, this reflection was partially eclipsed by the beam-stop during data collection.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Sheldrick, 2008), *POV-Ray* (Cason, 2003) and *DIAMOND* (Brandenburg, 2009); software used to prepare material for publication: *XCIF* (Sheldrick, 2008), *enCIFer* (Allen *et al.*, 2004) and *publCIF* (Westrip, 2010).

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