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Tetra(tetramethylammonium) Uranyltricarbonate octahydrate

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Tetra(tetramethylammonium) uranyltricarbonate octahydrate, $C_3O_{11}U.4(C_4H_{12}N).8(H_2O)$ adopts 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 the waters of crystallization and the carbonate ligands.

Comment

The total amount of uranium resource in seawater is about 4.5 billion tons ([U] ~ 3 ppb, ocean volume ~ 1.37×10^9 km^3), one thousand times of 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 economically compatitive cost. Because the dioxouranium(VI) tricarbonate anion, $UO_2(CO_3)^{4-}$, 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 were obtained in 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+} 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) analogue previously reported (Grigorev *et al.* 1997).

The uranium adopts a typical distorted hexagonal bipyramidal geometry with the UO_2 moiety acting as the axis (Figure 1). Predictably, the angles formed by the O atoms of each carbonate coordinating the uranium are more constrained 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 equatorial distance and the □ O=An=O are very similar in the two compounds (Table 3). The shorter Np–O_{ax} distance reflects the higher charge density of Np compared with U due to the contraction along the actinide series.

Of particular interest, with regards to the premise that this compound could be formed as a product from aqueous media (seawater), is the extensive hydrogen-bonding displayed within the structure (Figure 2). All eight waters of crystallization are invloved in the network and all but two of the carbonate oxygen atoms (O3 and O6). The uranyl O atoms are not involved in the H-bond network, thus restricting the geometry to a planar arrangement. The tetramethyl ammonium cations are located between the layers formed by the water/cation H-

bonding network, further bounding the H-bonding to two dimensions. This cation/anion layering is identical to that observed in the Np(VI) complex.

Two of the water molecules are involved in H-bonding exclusively to other water molecules. O6W forms H-bonds to O4W and O5W and accepts one H-bond from O8W, and O8W donates H-bonds to O1W and O6W as well as accepting on H-bond from O7W. O3W and O4W form H-bonds with carbonates on adjacent uranyl complexes, forming an H-bonded bridge. O1W, in concert with O2W, also forms a bridge between carbonates of the same uranyl complexes as O3W and O4W. This H-bonding extends the network along the *a*-direction. In a similar concerted H-bonding scheme, O7W and O5W also form an H-bonded bridge between carbonates on adjacent uranyl complexes. However, this acts to extend the network along the *b*-direction. The result of these H-bonding interactions is a two-dimensional sheet of uranyl tricarbonate anions and water molecules that extend through the lattice parallel to the *a/b*-plane. This too, is identical to that 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 geometry identical to that of a previously characterized Np(VI) tricarbonate complex.

Experimental

Crystals of the title compound were obtained, by slow evaporation in air (~ 6 weeks) at room temperature and under ambient pressure, from an aqueous solution (25 ml) containing uranyl 1-hydroxyethane-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

$C_3O_{11}U·4(C_4H_{12}N)·8(H_2O)$	$V = 3666.5$ (11) $Å^3$
$M_r = 890.77$	$Z = 4$
Monoclinic, $P2_1/n$	Synchrotron radiation, $\lambda = 0.77500$ Å
$a = 10.5377$ (18) Å	$\mu = 2.46$ mm^{-1}
$b = 12.358$ (2) Å	$T = 173$ K
$c = 28.533$ (5) Å	$0.07 \times 0.05 \times 0.05$ mm
$\beta = 99.343$ (4)°	

Data collection

Bruker Platinum 200 diffractometer	7499 independent reflections
Absorption correction: multi-scan *SADABS*, Sheldrick, 2008	6587 reflections with $I > 2\sigma(I)$
$T_{min} = 0.847$, $T_{max} = 0.887$	$R_{int} = 0.039$
26534 measured reflections	

Refinement

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

Table 1

Selected geometric parameters (Å, °)

U1—O1	1.803 (3)	U1—O3	2.424 (2)
U1—O2	1.814 (3)	U1—O10	2.435 (3)
U1—O6	2.418 (3)	U1—O9	2.444 (3)
U1—O7	2.423 (3)	U1—O4	2.450 (3)

O1—U1—O2	179.63 (11)	O10—U1—O9	52.97 (8)
O6—U1—O7	53.39 (10)	O6—U1—O4	67.04 (9)
O3—U1—O10	67.61 (8)	O3—U1—O4	53.19 (8)
O7—U1—O9	66.05 (9)		

Table 2

Hydrogen-bond geometry (Å, °)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1$OA\cdots$O4	0.85 (2)	2.03 (3)	2.778 (4)	146 (5)
O1W—H1$OB\cdots$O2W^i	0.86 (2)	1.96 (2)	2.824 (6)	174 (5)
O2W—H2$OA\cdots$O3W	0.86 (2)	1.99 (3)	2.810 (5)	158 (5)
O2W—H2$OB\cdots$O7	0.86 (2)	2.05 (3)	2.838 (4)	152 (5)
O3W—H3$OB\cdots$O9	0.84 (2)	1.95 (2)	2.774 (4)	170 (5)
O4W—H4$OA\cdots$O5^{ii}	0.85 (2)	1.89 (2)	2.738 (5)	172 (5)
O4W—H4$OB\cdots$O11	0.86 (2)	1.89 (2)	2.733 (4)	169 (5)
O5W—H5$OA\cdots$O7W	0.83 (2)	1.97 (2)	2.799 (5)	173 (5)
O5W—H5$OB\cdots$O10	0.84 (2)	1.93 (2)	2.751 (4)	169 (5)
O6W—H6$OA\cdots$O4W^i	0.84 (2)	1.87 (2)	2.705 (5)	176 (5)
O6W—H6$OB\cdots$O5W	0.84 (2)	2.00 (3)	2.794 (5)	157 (5)
O7W—H7$OA\cdots$O8^{iii}	0.84 (2)	1.83 (2)	2.666 (5)	172 (5)
O7W—H7$OB\cdots$O8W	0.83 (2)	1.93 (2)	2.752 (6)	169 (5)
O8W—H8$OA\cdots$O1W^{iii}	0.86 (2)	1.91 (2)	2.760 (5)	170 (6)
O8W—H8$OB\cdots$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) $x, y-1, z$.

Table 3

Comparison of selected interatomic distances (Å) and angles (°) between the isomorphous compounds of tricarbonato uranium(VI) (this work) and Np(VI)

	$[N(CH_3)_4]_4[UO_2(CO_3)_3](H_2O)_8$	$[N(CH_3)_4]_4[NpO_2(CO_3)_3](H_2O)_8$
An-O$_{axial}$	1.806 (3), 1.812 (3)	1.774 (3), 1.773 (3)
An-O$_{carbonate, equatorial}$	2.418 (3), 2.426 (3)	2.429 (3), 2.442 (3)
	2.426 (3), 2.453 (3)	2.400 (3), 2.419 (3)
	2.444 (3), 2.434 (3)	2.442 (3), 2.413 (3)
⟋ O=U=O	179.90 (13)	179.8 (1)

Data collection: Bruker *APEX* 2 v1.022; cell refinement: Bruker *APEX* 2 v1.022; data reduction: Bruker *APEX* 2 v1.022; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Sheldrick, 2008)/*POV-RAY* v3.6.2 (Cason, 2003)/Diamond v3.2c (Brandenburg, 2009); software used to prepare material for publication: XCIF (Sheldrick, 2008)/*enCIFer* (Allen *et al.*, 2004)/*publCIF* (Westrip, 2007).

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Figure 1

$[N(CH_3)_4]_4[UO_2(CO_3)_3](H_2O)_8$, shown with 50% probability displacement ellipsoids.

Figure 2

Hydrogen-bonding network depiction. (a) view along c-axis showing an individual $[UO_2(CO_3)_3](H_2O)_8$ layer of H-bonded molecules (b) view along b-axis, including $N(CH_3)_4$ molecules depicting the layering. Blue dotted lines represent H-bond interactions.
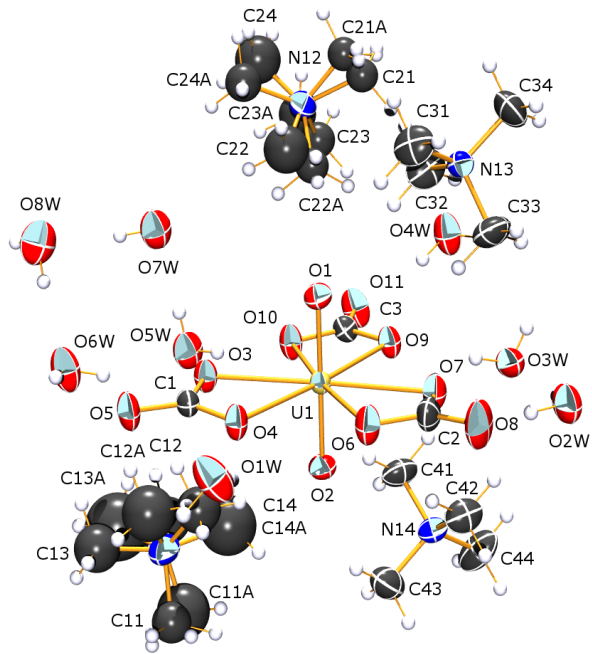
Figure 1

Figure 2

(a)   (b)