

Tetrapotassium dicarbonatodioxo- peroxouranium(VI) 2.5-hydrate, $K_4[U(CO_3)_2O_2(O_2)] \cdot 2.5H_2O$

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Received 15 September 2004

Accepted 1 November 2004

Online 18 December 2004

The title compound was obtained by reacting UO_2 powder in 2 M K_2CO_3 with hydrogen peroxide. The compound contains individual $[U(CO_3)_2O_2(O_2)]^{4-}$ ions, which are linked *via* an extended network of K atoms and hydrogen bonding. The U atom is coordinated to two *trans*-axial O atoms and six O atoms in the equatorial plane, forming distorted hexagonal bipyramids. The carbonate ligands are bound to the U center in a bidentate manner, with U–O bond distances ranging from 2.438 (5) to 2.488 (5) Å. The peroxo group forms a three-membered ring with the U atom, with U–O bond distances of 2.256 (6) and 2.240 (6) Å. The U=O bond distances of 1.806 (5) and 1.817 (5) Å, and an O–U–O angle of 175.3 (3)° are characteristic of the linear uranyl(VI) unit.

Comment

The use of oxidizing alkaline solutions for the successful dissolution of metals has been recognized for many decades. The interaction of oxidizing agents, such as peroxide, with actinide elements has been of great importance due to the multiple uses of peroxide in plutonium reprocessing (Cleveland, 1979). Several research groups have investigated the complexation and precipitation of uranium by peroxide in alkaline media. However, the characterization and identification of major solution species and solid structures remains relatively unexplored.

Gurevich and co-workers suggested about a dozen uranium(VI) peroxo compounds that form under different carbonate or peroxide concentrations, studying both their compositions and solubilities (Gurevich, 1961; Gurevich & Polozhenskaya, 1960, 1961). Most of the reported compounds were obtained as solid phases and characterized by classical gravimetric and vibrational spectroscopic techniques; only a few structural characterizations of single crystals have been reported, which reveal a more detailed picture of coordination geometries and bond lengths in U^{VI} peroxo complexes. Burns & Hughes (2003) reported a one-dimensional peroxide mineral, $[UO_2(O_2)(H_2O)_2](H_2O)_2$, with bridging peroxo

groups. In addition, Alcock (1968) reported the crystal structure of the layered compound $Na_4[UO_2(O_2)_3] \cdot 9H_2O$, where the U atom is coordinated to three peroxo groups, while Mikhailov *et al.* (1981) determined the crystal structure of $(CN_3H_6)_4[U(CO_3)_2O_2(O_2)] \cdot 2H_2O$, which to date is the only molecular structure of a mixed U^{VI} peroxo–carbonate complex. We report here the synthesis and structural characterization of the title compound, (I), a structurally different mixed uranyl(VI) peroxo–carbonate compound, $K_4[U(CO_3)_2O_2(O_2)] \cdot 2.5H_2O$.

The structure of (I) consists of $[UO_8]$ polyhedra staggered down the crystallographic *b* axis and linked by a network of K^+ ions and interstitial water molecules. These polyhedra are comprised of two axial *trans*-O atoms [mean $U=O = 1.81$ (1) Å, with an $O=U=O$ angle of 175.3 (3)°], and six O atoms in the equatorial plane, to complete a slightly distorted hexagonal–bipyramidal coordination (Fig. 1). Four O atoms originate from two bidentate carbonate ligands, with U–O bond lengths between 2.438 (5) (U1–O3) and 2.488 (5) Å (U1–O6) (Table 1). The peroxo ligand is coordinated through both O atoms, with slightly shorter U–O bond distances of

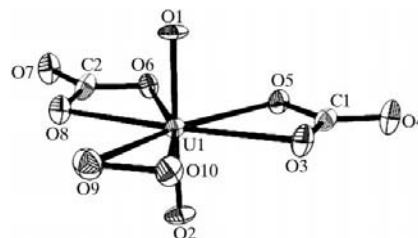


Figure 1
A view of the anionic $[U(CO_3)_2O_2(O_2)]^{4-}$ unit in the molecular structure of $K_4[U(CO_3)_2O_2(O_2)] \cdot 2.5H_2O$, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

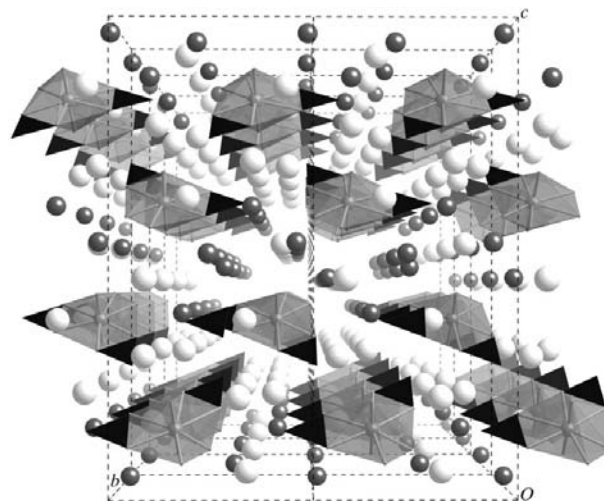
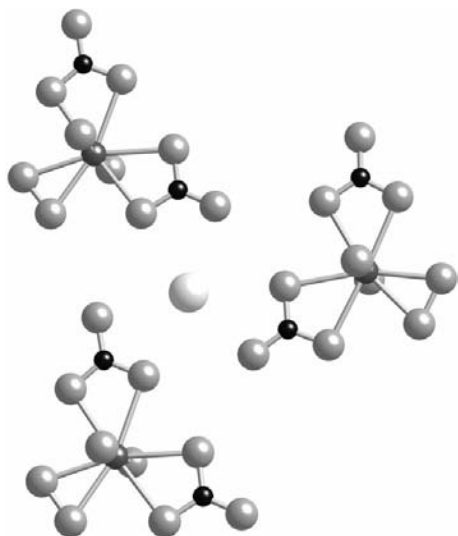


Figure 2
The packing of the $[U(CO_3)_2O_2(O_2)]^{4-}$ units in $K_4[U(CO_3)_2O_2(O_2)] \cdot 2.5H_2O$, with interstitial K^+ ions and water molecules, viewed along the *a* axis. Light-grey spheres denote K^+ ions, dark-grey spheres water molecules, light grey polyhedra $[UO_8]$ groups and black triangles $[CO_3]$ groups.


Figure 3

The arrangement of the K1 atom in the equatorial planes of three adjacent $[\text{U}(\text{CO}_3)_2\text{O}_2(\text{O}_2)]^{4-}$ units. The light-grey sphere denotes the K⁺ ion, mid-grey spheres denote O atoms, dark-grey U atoms and black C atoms.

2.256 (6) Å for U1—O9 and 2.240 (6) Å for U1—O10. These distances are very similar to those in $(\text{CN}_3\text{H}_6)_4[\text{U}(\text{CO}_3)_2\text{O}_2(\text{O}_2)] \cdot 2\text{H}_2\text{O}$ (2.23 Å; Mikhailov *et al.*, 1981) and $\text{Na}_4[\text{UO}_2(\text{O}_2)_3] \cdot 9\text{H}_2\text{O}$ (mean 2.28 Å; Alcock, 1968). The distance of 1.495 (8) Å between the two peroxo O atoms agrees well with the O—O distances found in $(\text{CN}_3\text{H}_6)_4[\text{U}(\text{CO}_3)_2\text{O}_2(\text{O}_2)] \cdot 2\text{H}_2\text{O}$ (1.52 Å; Mikhailov *et al.*, 1981), $\text{Na}_4[\text{UO}_2(\text{O}_2)_3] \cdot 9\text{H}_2\text{O}$ (1.51 Å; Alcock, 1968) and sodium peroxide (1.49 Å; Tallman *et al.*, 1957).

The $[\text{UO}_8]$ polyhedra extend along the *b* axis, with the equatorial planes parallel to one another (Fig. 2). In contrast, the $[\text{UO}_8]$ polyhedra in the previously reported compound $(\text{CN}_3\text{H}_6)_4[\text{U}(\text{CO}_3)_2\text{O}_2(\text{O}_2)] \cdot 2\text{H}_2\text{O}$ (Mikhailov *et al.*, 1981) are angled towards each other. Interestingly, one of the three crystallographically distinct K atoms, K1, lies within the equatorial planes of adjacent $[\text{UO}_8]$ polyhedra and is surrounded by six O atoms from three carbonate groups of three different $[\text{U}(\text{CO}_3)_2\text{O}_2(\text{O}_2)]^{4-}$ molecules (Fig. 3). The distances between atom K1 and the nearest O atoms range between 2.72 and 2.91 Å.

Experimental

UO_2 powder (591 mg, 2.2 mmol in U) was suspended in a 2 M K_2CO_3 solution (30 ml) and 35% H_2O_2 (1.8 ml) was added. After vigorous stirring for 15 min, the reaction was stopped by filtering the solution through a 45 mm polyamide syringe filter. Subsequently, the resulting deep-red solution (4 ml) was layered with methanol (6 ml). Single crystals of (I), in the form of red rectangular plates, grew overnight at the interface of these two layers. After 4 d, some of these crystals reached a size of 1.0 × 0.6 mm. Evaporating the solvent over a period of weeks resulted in the subsequent crystallization of $\text{K}_4[\text{U}(\text{CO}_3)_2\text{O}_2]$, which has been reported previously by Anderson *et al.* (1980). This is caused by the degradation of peroxide.

Crystal data

$\text{K}_4[\text{U}(\text{CO}_3)_2\text{O}_2(\text{O}_2)] \cdot 2.5\text{H}_2\text{O}$
 $M_r = 623.49$
 Monoclinic, $P2_1/n$
 $a = 6.9077$ (14) Å
 $b = 9.2332$ (18) Å
 $c = 21.809$ (4) Å
 $\beta = 91.310$ (4)°
 $V = 1390.6$ (5) Å³
 $Z = 4$

$D_x = 2.978$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 9687 reflections
 $\theta = 1.9$ – 28.3 °
 $\mu = 12.92$ mm⁻¹
 $T = 293$ (2) K
 Plate, red
 0.10 × 0.10 × 0.08 mm

Data collection

Bruker *P4* diffractometer with a SMART 1K CCD area-detector
 φ scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.300$, $T_{\max} = 0.356$
 9687 measured reflections

3046 independent reflections
 2616 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\text{max}} = 28.3$ °
 $h = -8 \rightarrow 8$
 $k = -11 \rightarrow 11$
 $l = -28 \rightarrow 28$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.095$
 $S = 1.56$
 3046 reflections
 176 parameters

H-atom parameters not defined
 $w = 1/[\sigma^2(F_o^2) + (0.0388P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 4.38$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.93$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

U1—O2	1.806 (5)	U1—O8	2.443 (5)
U1—O1	1.817 (5)	U1—O6	2.488 (5)
U1—O10	2.240 (6)	U1—C1	2.878 (9)
U1—O9	2.256 (6)	U1—C2	2.888 (8)
U1—O3	2.438 (5)	O9—O10	1.496 (8)
U1—O5	2.445 (6)		
O2—U1—O1	175.3 (3)	O10—U1—O9	38.9 (2)

Water atom O3W was refined as one-half occupancy, based on a comparison of its displacement parameters with those of other water O atoms in the structure. H-atom positions were not assigned to any of the water O atoms. Water atom O3W is at one-half occupancy, while for atoms O1W and O2W, the displacement parameters and the presence of more than one set of hydrogen-bond donors at meaningful hydrogen-bonding distances strongly suggest that these water molecules are disordered. This disorder, when combined with a difference map that suggested too few H-atom positions, precluded including the H-atom positions in the model. The highest residual electron-density peak was near U1 and the largest hole was near C2 (2 Å from U1). Both of these peaks are most likely to be a combination of uncompensated electron density (from premature truncation of the Fourier map in a heavy-atom structure) and the inability to perform an ideal absorption correction for this highly absorbing crystal.

Data collection: SMART (Siemens, 1996); cell refinement: SMART; data reduction: SAINT (Siemens, 1996); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: CrystalMaker (CrystalMaker Software, 2004); software used to prepare material for publication: SHELXTL (Bruker, 1997)

The authors thank the Advanced Fuel Cycle Initiative (AFCI) for financial support. SMP is a Director's Postdoctoral Fellow, funded through the Los Alamos National Laboratory's

Laboratory-Directed Research and Development (LDRD) Program.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1480). Services for accessing these data are described at the back of the journal.

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