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Trigonal $Na_4[UO_2(CO_3)_3]$

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Tetrasodium tricarbonatodioxouranate(VI), $Na_4[UO_2(CO_3)_3]$, crystallizes in the trigonal space group $P\bar{3}c1$. Though the symmetry differs from other similar compounds (*e.g.* the NH_4^+, K^+ and Tl^+ salts) which are monoclinic, there is a common structure motif consisting of $UO_2(CO_3)_3$ groups with a trigonal outline when viewed along the shortest O—U—O bond pair. In $Na_4[UO_2(CO_3)_3]$, there are three non-equivalent Na atoms; Na1 (site symmetry $\bar{3}$) and Na2 (site symmetry 3) are in centres of face-sharing octahedra, which form a chain running parallel to the *c* axis at each unit-cell corner, whereas the Na3 atom is surrounded by a deformed square pyramid of O atoms, forming edge-sharing triplets. The title compound has also a natural dimorph, namely the recently approved triclinic mineral čejkaite.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(O–C) = 0.006 Å
R factor = 0.024
wR factor = 0.062
Data-to-parameter ratio = 12.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Recently, we have found a natural triclinic compound of $Na_4[UO_2(CO_3)_3]$ composition in Jáchymov, the Czech Republic. This natural triclinic material does not form crystals suitable for single-crystal study. We recognized that a compound of the same chemistry but with trigonal symmetry had been described by Douglass (1956), who determined the extinction symbol, unit-cell dimensions and also additional physical parameters. An attempt to prepare a synthetic analogue of our natural triclinic compound failed; instead, we synthesized a trigonal dimorph equivalent to the material of Douglass for which we report a complete structure.

There are chemically similar compounds – $NH_4[UO_2(CO_3)_3]$, $K_4[UO_2(CO_3)_3]$ and $Tl_4[UO_2(CO_3)_3]$ – for which the crystal structures are known (Graziani *et al.*, 1972; Anderson *et al.*, 1980; Mereiter, 1986; respectively). All these materials crystallize in the monoclinic space group *C*2/*c*. They share the common basic structural motif of $UO_2(CO_3)_3$ groups with the compound we synthesized. This group is, in our case, built up from the asymmetric unit (Fig. 1) due to the threefold axis and contains three planar CO_3 triangles sharing one of their edges with the UO_2O_6 polyhedron. The lengths of the U—O bonds oriented along the direction of the *c* axis (U1—O1 and U1—O2) are significantly shorter compared to the U—O distances in the medial plane of the UO_2O_6 polyhedron (U1—O11 and U1—O12) in the compound $Na_4[UO_2(CO_3)_3]$. The planes of the CO_3 triangles attached to the UO_2O_6 polyhedron are inclined from the 001 plane. Atoms Na1 and Na2 are octahedrally coordinated by O13 atoms. The octahedra share a common face and form a chain of alternating polyhedra around Na1 and Na2 running parallel to the *c* axis and situated at each unit-cell corner. The octahedron around Na1 is fairly regular, with quadratic elongation of 1.012 and bond-angle s.u. of 6.87°. On the contrary, the polyhedron

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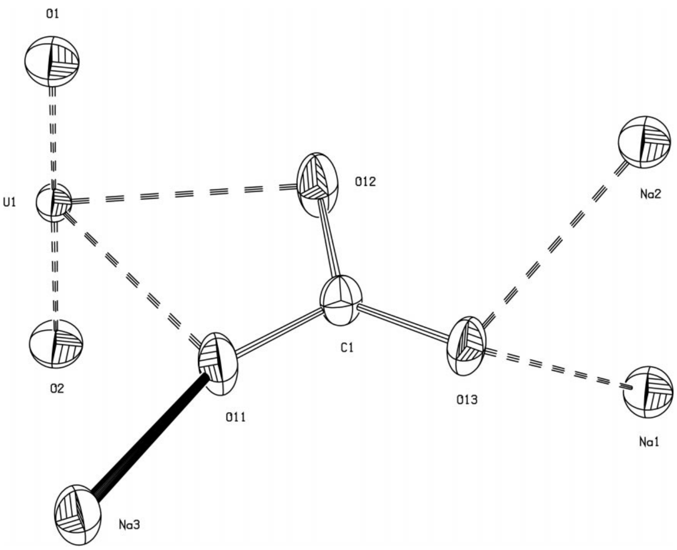

Figure 1
View of the asymmetric unit of $Na_4[UO_2(CO_3)_3]$ with the atom-numbering scheme. Displacement ellipsoids are at the 50% probability (*PLATON*; Spek, 1999).

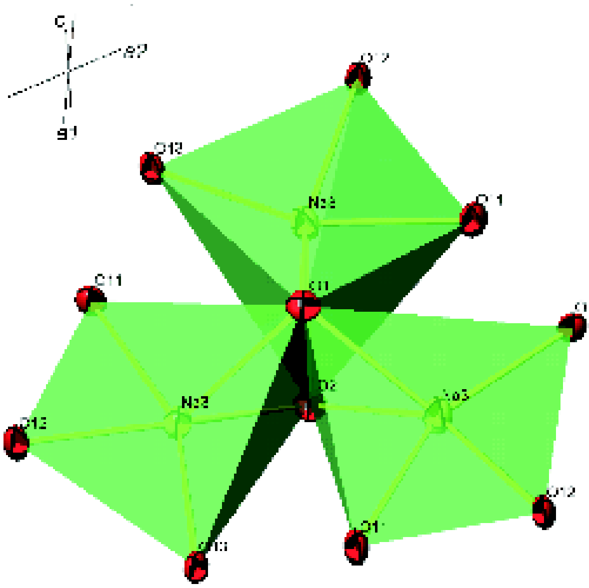

Figure 2
Polyhedral presentation of an edge-sharing triplet of NaO_5 polyhedra.

around Na2 departs significantly from ideal geometry, which results in quadratic elongation of 1.121 and bond-angle s.u. of 18.78°. The volumes of both octahedra are comparable; the polyhedron around Na1 has a volume of 19.02 $Å^3$ and that around Na2 17.40 $Å^3$. Atom Na3 has a coordination number of 5; the polyhedron around it can be described as square pyramidal as $\tau = 0.15$ (Addison & Reedijk, 1984). Three of these polyhedra build up edge-sharing triplets (Fig. 4). The shared edge is defined by the atoms O1—O2 and it runs parallel to the *c* axis (Fig. 2). The overall structure motif is apparent from Fig. 3. Triplets of polyhedra around Na3 atoms share vertices of their common edges with vertices of $UO_2(CO_3)_3$ complexes adjacent to them in the [001] direction. These complexes, in turn, share edges O11—O12 with laterally neighbouring square pyramids around Na3 atoms, building up

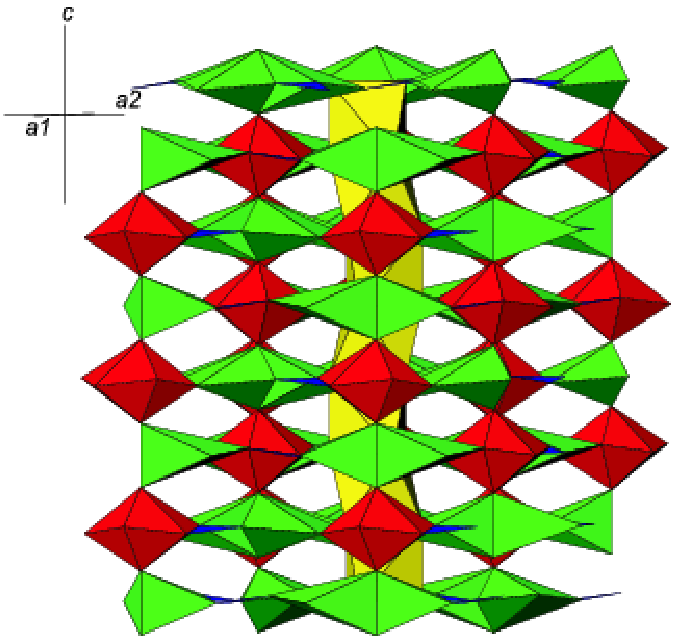

Figure 3
Projection of the crystal structure of $Na_4[UO_2(CO_3)_3]$ onto the 100 plane. Note the chain of alternating octahedra around the Na1 and Na2 atoms parallel to [001] at the unit-cell edge. Colour-coding of polyhedra, red: UO_2O_6 polyhedron; blue: planar CO_3 triangles; yellow: NaO_6 octahedra; green: NaO_5 irregular square pyramid.

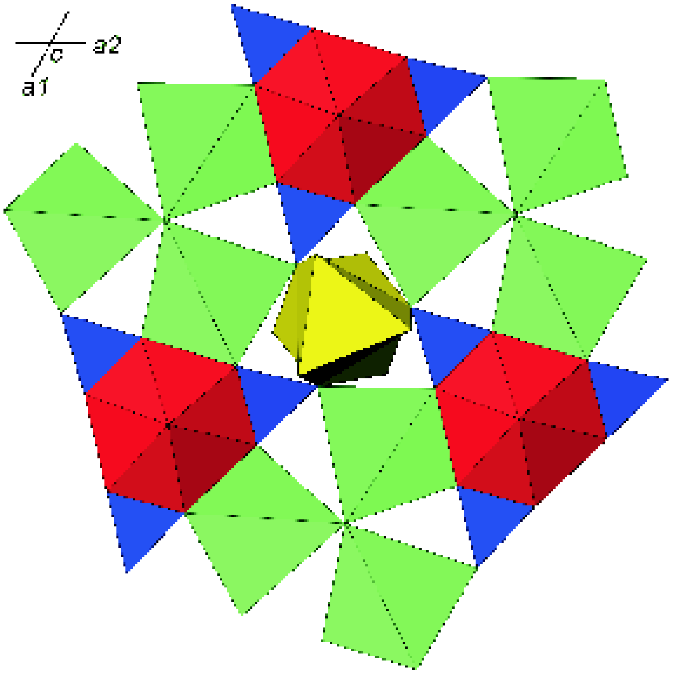

Figure 4
Polyhedral presentation of a single layer consisting of the $UO_2(CO_3)_3$ complex, triplets of polyhedra around Na3 and octahedra around Na1 or Na2 found in the $Na_4[UO_2(CO_3)_3]$ viewed down [001]. Colour-coding of polyhedra, red: UO_2O_6 polyhedron; blue: planar CO_3 triangles; yellow: NaO_6 octahedra; green: NaO_5 irregular square pyramid.

two-dimensional sheets parallel to 001 typical for this structure. The sheets are stacked along [001] so that the next sheet is rotated by 60° around [001] with respect to the adjacent one. Finally, each of three apical carbonate O13 atoms from any $UO_2(CO_3)_3$ complex is shared by the octahedron around either Na1 or Na2 (depending on the height of the sheet along [001] in the unit cell) and also makes a vertex of laterally adjacent triplet of polyhedra around Na3 (Fig. 4). Using the approach of effective coordination numbers (Hoppe, 1979) and the program of Rieder (1993), we calculated effective coordination numbers (ECoNs) for central atoms as U1 = 2.24, Na1 = 6.00, Na2 = 6.12, Na3 = 4.76 and C1 = 2.94; for U1 and Na3 polyhedra, these ECoNs depart significantly from their ideal values. This could be ascribed to substantial irregularity of individual polyhedra. Their irregularity results also in bond-valence sums departing from ideal values. Using the data of Brown & Altermatt (1985) and the program of Wills & Brown (1999), we calculated bond-valence sums as [central atom, bond valence sum in vu (valance units) and departure in percent from the ideal oxidation state] U1 6.59 [10], Na1 1.074 [7], Na2 1.02 [2], Na3 1.127 [13], C1 4.033 [1].

Experimental

Clear yellow hexagonal prismatic crystals up to 1 mm long of the title compound have been synthesized from synthetic triclinic $Na_4[(UO)_2(CO_3)_3]$ powder by recrystallization in sealed silica glass tubes under hydrothermal conditions at a pressure of about 20 MPa and a temperature of 408 K for 3 d. In addition to the crystals of the title compound, we recovered from the tube an orange powdered material which we identified as containing sodium di- and heptauranates.

Crystal data

$Na_4[UO_2(CO_3)_3]$
$M_r = 542.02$
Trigonal, $P\bar{3}c1$
$a = 9.3380$ (2) Å
$c = 12.8170$ (3) Å
$V = 967.89$ (4) Å^3
$Z = 4$
$D_x = 3.720$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10 249 reflections
$\theta = 1$–27.5°
$\mu = 17.01$ mm^{-1}
$T = 293$ (2) K
Bar, yellow
0.11 × 0.05 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans to fill the Ewald sphere
Absorption correction: Gaussian (Coppens, 1970)
$T_{min} = 0.208$, $T_{max} = 0.617$
22 328 measured reflections
746 independent reflections
615 reflections with $I > 2\sigma(I)$
$R_{int} = 0.090$
$\theta_{max} = 27.5°$
$h = -12 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.062$
$S = 1.07$
746 reflections
60 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0358P)^2 + 2.8258P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.33$ e Å^{-3}
$\Delta\rho_{min} = -1.73$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0074 (5)

Table 1
Selected geometric parameters (Å, °).

U1—O1	1.809 (8)	Na3—O13^{ii}	2.320 (4)
U1—O2	1.810 (7)	Na3—O11	2.338 (4)
U1—O12	2.379 (4)	Na3—O1^{iii}	2.486 (5)
U1—O11	2.422 (4)	Na3—O2^{iv}	2.541 (5)
Na1—O13	2.440 (3)	C1—O13	1.242 (5)
Na2—O13	2.492 (4)	C1—O12	1.303 (7)
Na3—O12^{i}	2.287 (4)	C1—O11	1.304 (6)
O1—U1—O2	180.000 (1)	O12^{i}—Na3—O11	70.15 (16)
O1—U1—O12	85.88 (10)	O13^{ii}—Na3—O11	155.48 (16)
O1—U1—O11	93.52 (9)	O12^{i}—Na3—O1^{iii}	136.50 (19)
O12—U1—O11	53.67 (12)	O13^{ii}—Na3—O1^{iii}	110.46 (13)
O12^{i}—U1—O11	67.22 (12)	O11—Na3—O1^{iii}	91.08 (11)
O12^{v}—U1—O11	173.15 (12)	O12^{i}—Na3—O2^{iv}	146.30 (18)
O13^{vi}—Na1—O13	96.58 (12)	O13^{ii}—Na3—O2^{iv}	109.34 (14)
O13^{vii}—Na2—O13^{viii}	83.99 (15)	O11—Na3—O2^{iv}	89.31 (11)
O13^{ix}—Na2—O13^{viii}	148.55 (15)	O1^{iii}—Na3—O2^{iv}	67.4 (2)
O13^{vii}—Na2—O13	81.30 (12)	O13—C1—O12	124.0 (4)
O13^{viii}—Na2—O13	123.64 (16)	O13—C1—O11	123.5 (5)
O13^{x}—Na2—O13	148.55 (15)	O12—C1—O11	112.5 (4)
O12^{i}—Na3—O13^{ii}	85.84 (15)		

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

Data collection: *COLLECT* (Hooft, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Shape Software, 1999).

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