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The Rb analogue of grimselite, $Rb_6Na_2[(UO_2)(CO_3)_3]_2(H_2O)$

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The crystal structure of the Rb analogue of grimselite, rubidium sodium uranyl tricarbonate hydrate, $Rb_6Na_2[(UO_2)(CO_3)_3]_2(H_2O)$, consists of a uranyl hexagonal bipyramid that shares three non-adjacent equatorial edges with carbonate triangles, resulting in a uranyl tricarbonate cluster of composition $[(UO_2)(CO_3)_3)]$. These uranyl tricarbonate clusters form layers perpendicular to [001] and are interconnected by NaO_8 polyhedra. The title compound is isostructural with grimselite, with a reduced occupancy of the H_2O site (25% *versus* 50% in grimselite).

Comment

The compound $Rb_6Na_2[(UO_2)(CO_3)_3]_2(H_2O)$ was obtained by evaporation of a solution containing $UO_2(NO_3)_2(H_2O)_6$, $RbNO_3$ and Na_2CO_3 at ambient temperature and pressure. $Rb_6Na_2[(UO_2)(CO_3)_3]_2(H_2O)$ is structurally analogous to the mineral grimselite, $K_3Na[(UO_2)(CO_3)_3](H_2O)$ (Li & Burns, 2001). Each contains the uranyl tricarbonate cluster, $[(UO_2)(CO_3)_3]$, and crystallizes in space group $P\overline{6}2c$. However, these two compounds differ in their hydration state.

There is one symmetrically distinct U^{VI} atom in the structure of $Rb_6Na_2[(UO_2)(CO_3)_3]_2(H_2O)$. This atom is part of a linear uranyl ion, $(UO_2)^{2+}$, which is coordinated by six equatorial O atoms, forming a uranyl hexagonal bipyramid. Three non-adjacent equatorial edges of the uranyl hexagonal bipyramid share edges with CO_3 groups, giving the uranyl tricarbonate cluster, $[(UO_2)(CO_3)_3]$ (Fig. 1). These clusters share edges with NaO_8 hexagonal bipyramids, to form heteropolyhedral sheets parallel to (001) (Fig. 2). These sheets are stacked along [001], with voids in the resulting framework containing Rb cations and H_2O molecules. The H_2O sites are 25% occupied in the structure of $Rb_6Na_2[(UO_2)(CO_3)_3]_2(H_2O)$, whereas they are 50% occupied in the structure of grimselite. This difference in H_2O content may be attributable to the larger size of the Rb^+ cation.

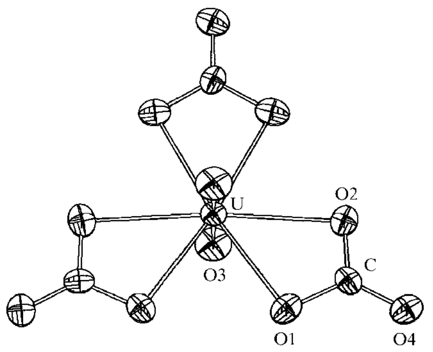

Figure 1
A view of the $[(UO_2)(CO_3)_3]$ clusters in $Rb_6Na_2[(UO_2)(CO_3)_3]_2(H_2O)$, shown with 50% probability displacement ellipsoids.

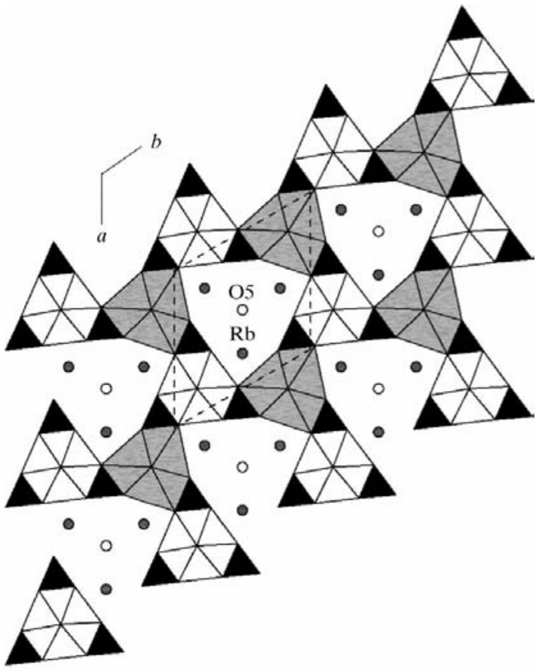

Figure 2
The heteropolyhedral layer of NaO_8 hexagonal bipyramids (grey) and $[(UO_2)(CO_3)_3]$ clusters (UO_8 shown in white, CO_3 shown in black), projected along [001] (unit cell shown as dashed lines).

Bond-valence sums were calculated for each ion using the parameters of Brese & O'Keeffe (1991), giving the following values: 6.18 for U, 4.15 for C, 1.29 for Rb and 1.15 for Na (Burns *et al.*, 1997). The bond-valence sum for Rb is based on its coordination environment when the O5 site is occupied, and the partial occupancy of this site may, therefore, represent a way to limit the overbonding of the Rb site. For atoms O1, O2, O3 and O4, the bond-valence sums are within the normal range (1.88–2.25). The bond-valence sum for atom O5 (0.32) is consistent with a water molecule.

Experimental

Transparent yellow crystals of $Rb_6Na_2[(UO_2)(CO_3)_3]_2(H_2O)$, up to 1 mm in maximum dimension, were synthesized from a solution containing Na_2CO_3 (0.026 g), $RbNO_3$ (0.111 g) and $UO_2(NO_3)_2(H_2O)_6$ (0.123 g) in ultra-pure water (25 ml). Following evaporation

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in an open beaker for 28 d at 293 K under ambient pressure, crystals were recovered from the beaker walls.

Crystal data

$Rb_6Na_2[(UO_2)(CO_3)_3]_2(H_2O)$
$M_r = 1476.94$
Hexagonal, $P\overline{6}2c$
$a = 9.4316$ (7) Å
$c = 8.3595$ (8) Å
$V = 643.99$ (9) Å^3
$Z = 1$
$D_x = 3.808$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 1623 reflections
$\theta = 3.3$–$33.8°$
$\mu = 23.95$ mm^{-1}
$T = 297$ (2) K
Anhedral, yellow
$0.15 \times 0.12 \times 0.12$ mm

Data collection

Bruker APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical *via* ψ scan (*SHELXTL-NT*; Bruker, 1998)
$T_{min} = 0.044$, $T_{max} = 0.056$
12 787 measured reflections

958 independent reflections
787 reflections with $I > 2\sigma(I)$
$R_{int} = 0.073$
$\theta_{max} = 34.6°$
$h = -14 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.085$
$S = 0.97$
958 reflections
40 parameters
$w = 1/[\sigma^2(F_o^2) + (0.052P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 2.04$ e Å^{-3}
$\Delta\rho_{min} = -1.69$ e Å^{-3}
Extinction correction: *SHELXTL-NT* (Bruker, 1998)
Extinction coefficient: 0.044 (8)
Absolute structure: Flack (1983), with 407 Friedel pairs
Flack parameter = −0.02 (4)

The positions of the U, Rb, Na and C atoms, and of most of the O atoms, were determined by direct methods. The remaining O atoms were located by subsequent difference Fourier syntheses. The locations of the highest peak and deepest hole in the difference Fourier map are 0.75 Å from U and 0.51 Å from Rb, respectively. H-atom positions were not determined in the refinement. However, atom O2 is a possible hydrogen-bond acceptor, as it is the nearest O atom to O5 [O2···O5 = 3.122 (9) Å].

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2000); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXTL-NT* (Bruker, 1998); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *SHELXTL-NT* and *WinGX* (Farrugia, 1999).

Table 1
Selected bond lengths (Å).

U—O3^{i}	1.779 (8)	Na—O4^{ix}	2.368 (9)
U—O2^{ii}	2.418 (8)	Na—O3^{vii}	2.401 (8)
U—O1	2.433 (6)	Na—O1^{viii}	3.018 (6)
Rb—O2^{iii}	2.822 (6)	C—O4	1.237 (14)
Rb—O1^{iv}	2.897 (9)	C—O2	1.281 (14)
Rb—O4^{v}	2.992 (7)	C—O1	1.295 (17)
Rb—O5^{vi}	3.086 (19)		

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1032). Services for accessing these data are described at the back of the journal.

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