

THE CRYSTAL STRUCTURE OF SYNTHETIC GRIMSELITE, $K_3Na[(UO_2)(CO_3)_3](H_2O)$

YAPING LI AND PETER C. BURNS[§]

*Department of Civil Engineering and Geological Sciences, University of Notre Dame, 156 Fitzpatrick Hall,
Notre Dame, Indiana 46556-0767, U.S.A.*

ABSTRACT

Crystals of grimselite, $K_3Na[(UO_2)(CO_3)_3](H_2O)$, were synthesized by room-temperature evaporation of an aqueous solution. The structure of grimselite is hexagonal, a 9.302(2), c 8.260(3) Å, V 618.9(3) Å³, space group $P\bar{6}2c$, $Z = 2$. The crystal structure was refined on the basis of F^2 for all 546 unique reflections measured using MoK α X-radiation and a CCD-based detector to an $R1$ of 2.55%, calculated using the 459 unique observed reflections with $F_o \geq 4\sigma_F$. Consistent with other uranyl carbonates with a U : C ratio of 1 : 3, the structure of grimselite contains the uranyl tricarbonate cluster $[(UO_2)(CO_3)_3]$, which consists of a uranyl hexagonal bipyramid that shares three equatorial edges with (CO_3) triangles. The uranyl tricarbonate clusters are oriented perpendicular to $[001]$ and are interconnected through bonds to Na and K polyhedra.

Keywords: uranyl carbonate, grimselite, crystal structure.

SOMMAIRE

Nous avons synthétisé des cristaux de grimselite, $K_3Na[(UO_2)(CO_3)_3](H_2O)$, par évaporation à température ambiante d'une solution aqueuse. La structure de la grimselite possède une symétrie hexagonale, a 9.302(2), c 8.260(3) Å, V 618.9(3) Å³, groupe spatial $P\bar{6}2c$, $Z = 2$. Nous avons affiné cette structure en utilisant les facteurs F^2 pour les 546 réflexions uniques, mesurées avec rayonnement MoK α et un détecteur de type CCD jusqu'à un résidu $R1$ de 2.55%, calculé en utilisant les 459 réflexions uniques observées ayant $F_o \geq 4\sigma_F$. Comme c'est le cas avec les autres carbonates d'uranyle ayant un rapport U : C de 1 : 3, la structure de la grimselite contient un groupement d'uranyle tricarbonate $[(UO_2)(CO_3)_3]$ fait d'une dipyramide hexagonale d'uranyle qui partage trois de ses arêtes dipyramidales avec des triangles (CO_3) . Ces groupements d'uranyle tricarbonate sont orientés perpendiculairement à $[001]$ et interconnecté grâce à des liaisons avec des polyèdres contenant Na et K.

(Traduit par la Rédaction)

Mots-clés: carbonate d'uranyle, grimselite, structure cristalline.

INTRODUCTION

We are interested in the crystal structures of uranyl carbonates owing to their crystal-chemical complexity and importance to the environment (Li *et al.* 2000, 2001). As part of our ongoing research concerning uranyl carbonates, we have synthesized grimselite, $K_3Na[(UO_2)(CO_3)_3](H_2O)$, and provide a modern refinement of the crystal structure. Grimselite was originally discovered in a cable tunnel between Gerstenegg and Sommerloch in the Grimsel area, Aarmassif, Switzerland (Walenta 1972), where it is associated with schrockingerite, monohydrocalcite and other unnamed carbonate minerals.

A partial structure was reported for synthetic material with composition $K_3Na[(UO_2)(CO_3)_3]$ by Mazzi & Rinaldi (1960) on the basis of Weissenberg film techniques. The structure was not refined, and complete atom coordinates were not given in the brief published report. The structure was given in space group $P\bar{6}2c$, with cell dimensions a 9.29, c 8.26 Å. In his study of grimselite, Walenta (1972) concluded that it is very similar to the material studied by Mazzi & Rinaldi (1960), with the same space-group and cell dimensions. Analyses of synthetic and natural material given by Walenta (1972) indicate that grimselite contains H_2O , although none was reported in the crystal structure of the synthetic material.

[§] E-mail address: pburns@nd.edu

EXPERIMENTAL

Synthesis of crystals

Crystals of grimselite were synthesized by evaporation of an aqueous solution containing 0.50 g $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa), 10 mL deionized water, 0.60 g KNO_3 (Aldrich), and 0.30 g Na_2CO_3 (Fisher). The reactants were added to a test tube in the order stated, and then were transferred to a 50 mL beaker followed by 2 minutes of stirring. The solution was left undisturbed at room temperature for 10 days, at which time hexagonal prisms of grimselite were recovered. The crystals are soluble in water.

Single-crystal X-ray diffraction

A single crystal of synthetic grimselite with dimensions $0.03 \times 0.04 \times 0.11$ mm was selected and mounted on a glass fiber, and diffraction data were collected using a Bruker 1K SMART CCD diffractometer with a crystal-to-detector distance of 5.0 cm and $\text{MoK}\alpha$ X-radiation. More than a hemisphere of three-dimensional data was collected using frame widths of 0.6° in ω , with 60 seconds spent counting per frame. The unit-cell dimensions (Table 1) were refined from 1312 reflections using least-squares techniques. The data were reduced and corrected for Lorentz, polarization and background effects using the Bruker program SAINT. An empirical correction for absorption was applied on the basis of equivalent reflections by modeling the crystal as an ellipsoid, which reduced R_{int} of 866 intense reflections from 10.8% to 6.1%. A total of 3521 reflections were collected, of which 546 reflections were independent, with 459 classed as observed ($F_o \geq 4\sigma_F$).

Structure solution and refinement

The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of

the crystal structure. The structure was solved and refined in space group $P\bar{6}2c$. The refinement converged rapidly, and the location of the H_2O group, which was not reported by Mazzi & Rinaldi (1960), was inserted into the model. Refinement resulted in an abnormally large isotropic displacement parameter for the OW(5) site, and we noted that symmetrically related OW(5) sites were separated by $\sim 2 \text{ \AA}$. Refinement of the occupancy of the OW(5) site showed that it is $\sim 50\%$ occupied, an observation that is consistent with the short separation of equivalent sites. We reduced the symmetry to $P31c$, but this did not result in an improvement of the refinement and did not result in better behavior of the OW(5) site. Although the site no longer has a symmetry equivalent at $\sim 2 \text{ \AA}$, a peak in the difference-Fourier map calculated following refinement of the model indicated the presence of two H_2O sites separated by $\sim 2 \text{ \AA}$, consistent with results for space group $P\bar{6}2c$.

The structure was refined on the basis of all 546 unique F^2 in space group $P\bar{6}2c$. The final refinement included all atomic positional parameters, allowed for anisotropic displacement of all atoms, and included a weighting scheme of the structure factors. It converged to an $R1$ of 2.55%, calculated for the 459 unique observed reflections ($|F_o| \geq 4\sigma_F$), and a goodness-of-fit (S) of 0.95. In the final cycle of refinement, the mean parameter shift/esd was 0.000, and the maximum peaks in

TABLE 1. CRYSTALLOGRAPHIC DATA FOR SYNTHETIC GRIMSELITE

a (Å)	9.302(2)	Crystal size (mm)	$0.03 \times 0.04 \times 0.11$
c (Å)	8.260(3)	Total ref.	3521
V (Å ³)	618.9(3)	Unique ref.	546
Space group	$P\bar{6}2c$	R_{int} (%)	7.8
$I(000)$	552	Unique $ F_o \geq 4\sigma_F$	459
μ (mm ⁻¹)	14.215	Final $R1$ (%)	2.55
D_{calc} (g/cm ³)	3.264	S	0.95

Unit cell contents: $2\{\text{K}_2\text{Na}[(\text{UO}_2)(\text{CO}_3)_3](\text{H}_2\text{O})\}$ $R1 = \Sigma(|F_o| - |F_c|) / \Sigma |F_o|$ $S = [\Sigma w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$, for m observations and n parameters

TABLE 2. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR SYNTHETIC GRIMSELITE

	x	y	z	$U^*(\text{eq})$	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
U	2/3	1/3	3/4	0.018(1)	0.018(1)	0.018(1)	0.017(1)	0	0	0.009(1)
K	0.2921(2)	0	0	0.037(1)	0.042(1)	0.037(1)	0.031(1)	0.008(1)	0.004(1)	0.019(1)
Na	1/3	2/3	3/4	0.031(1)	0.037(2)	0.037(2)	0.019(2)	0	0	0.018(1)
O(1)	0.9694(6)	0.4797(15)	3/4	0.029(1)	0.025(3)	0.026(6)	0.041(3)	0	0	0.017(6)
O(2)	0.8485(7)	0.6315(7)	3/4	0.030(2)	0.022(5)	0.028(4)	0.038(3)	0	0	0.012(3)
O(3)	2/3	1/3	0.9673(6)	0.031(1)	0.038(2)	0.038(2)	0.016(2)	0	0	0.019(1)
O(4)	0.1274(7)	0.7571(8)	3/4	0.036(2)	0.024(3)	0.025(3)	0.048(4)	0	0	0.005(3)
OW(5)**	0	0	0.1277(18)	0.063(4)	0.057(6)	0.057(6)	0.075(10)	0	0	0.028(3)
C	0.9883(10)	0.6282(11)	3/4	0.023(2)	0.016(5)	0.027(6)	0.017(4)	0	0	0.004(4)

* $U^*(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor; **Site occupancy for OW(5) = 0.5

the final difference-Fourier maps were 0.71 and $-1.19 e/\text{\AA}^3$. The final atomic coordinates and anisotropic-displacement parameters are listed in Table 2, selected interatomic distances are in Table 3, and a bond-valence analysis is given in Table 4. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

STRUCTURE DESCRIPTION

Cation coordination

The structure of grimselite contains a single symmetrically unique U^{6+} cation, which is part of an approximately linear $(UO_2)^{2+}$ uranyl ion (designated *Ur*) with a $\langle U-O_{Ur} \rangle$ bond length of 1.795(5) Å. The uranyl ion is further coordinated by six O atoms arranged at the equatorial positions of a hexagonal bipyramid. The $\langle U^{6+}-O_{eq} \rangle$ bond length is 2.430 Å, which compares well with the $\langle [^{18}U]-O_{eq} \rangle$ bond length of 2.47(12) Å that was derived from numerous well-refined structures (Burns *et al.* 1997). Grimselite contains one symmetrically unique C^{4+} cation in the usual triangular coordination, with a $\langle C-O \rangle$ bond length of 1.29 Å (Table 3).

Grimselite contains two symmetrically distinct low-valence cation sites that are occupied by K and Na. The K cations are coordinated by eight O atoms and one H_2O group; only one of the two OW(5) sites is occupied locally in each K polyhedron (Fig. 1a). The $K-\phi$ ($\phi: O^{2-}, H_2O$) bond lengths range from 2.722(4) to 3.320(2)

Å, with a $\langle K-\phi \rangle$ of 2.929 Å (Table 3). The Na site is coordinated by eight O atoms arranged at the vertices of a hexagonal bipyramid. The Na-O bonds range from 2.335(5) to 2.932(5) Å, with a $\langle Na-O \rangle$ of 2.601 Å (Table 3).

Structural connectivity

The structure of grimselite contains uranyl tricarbonate clusters with composition $[(UO_2)(CO_3)_3]$, as is the case for other uranyl carbonates with a U : C

TABLE 3. BOND LENGTHS (Å) AND ANGLES (°) FOR SYNTHETIC GRIMSELITE

U-O(3), a	1.795(5)×2	C-O(1)	1.30(2)
U-O(2), b, c	2.421(6)×3	C-O(2)	1.32(1)
U-O(1), b, c	2.439(5)×3	C-O(4)d	1.249(9)
O(3)-U-O(3)a	180	O(4)d-C-O(1)	123.0(8)
$\langle U-O_{ur} \rangle$	1.795	O(4)d-C-O(2)	122.6(8)
$\langle U-O_{eq} \rangle$	2.430	O(1)-C-O(2)	114.4(7)
		$\langle C-O \rangle$	1.29
		$\langle O-C-O \rangle$	120.0
K-O(2)e, f	2.722(4)×2	Na-O(3)m, n	2.335(5)×2
K-O(1)g, h	2.809(8)×2	Na-O(4), o, p	2.447(7)×3
K-O(4)i, j	2.873(4)×2	Na-O(1)c, q, r	2.932(5)×3
K-OW(5), k	2.914(6)×2	$\langle Na-O \rangle$	2.601
K-O(3)g, l	3.320(2)×2		
$\langle K-\phi \rangle$	2.929		

Symmetry transformations used to generate equivalent atoms: a: x, y, z +3/2; b: -x + y + 1, -x + 1, z; c: -y + 1, x - y, z; d: x + 1, y, z; e: -y + 1, x - y, z - 1; f: -x + 1, x + y, z + 1; g: y, x - 1, z + 1; h: -x + y - 1, -x + 1, z - 1; i: x, y - 1, z - 1; j: x - y + 1, -y + 1, z + 1; k: y, x, z - 1; l: x, y, z - 1; m: y, x, z - 1/2; n: y, x, z + 2; o: -x + y, -x + 1, z; p: -y + 1, x - y + 1, z; q: -x + y + 1, -x + 2, z; r: x - 1, y, z

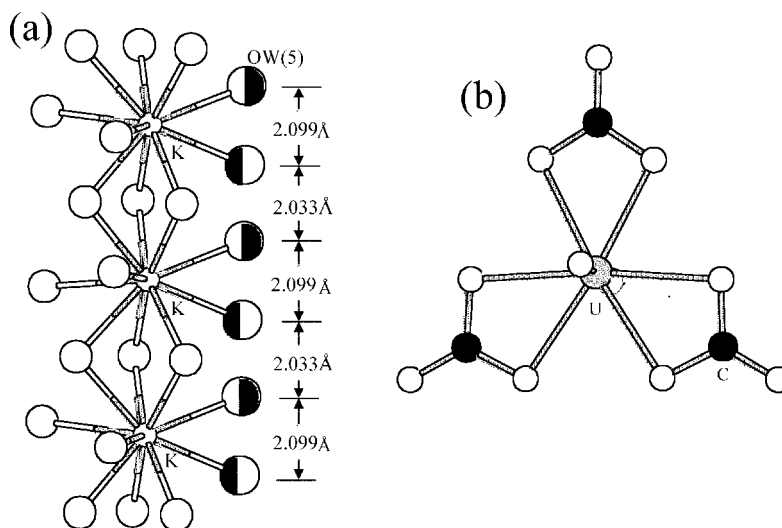


FIG. 1. (a) Ball-and-stick representation of the relationship among K polyhedra in the structure of grimselite, showing the coordination environment of K cations in the structure, and distribution of H_2O groups that are bonded to K cations. (b) The uranyl tricarbonate cluster in the structure of grimselite.

TABLE 4. BOND VALENCE ANALYSIS FOR SYNTHETIC GRIMSELITE

	O(1)	O(2)	O(3)	O(4)	OW(5)	Σ
U	0.46 \times 3 \rightarrow	0.47 \times 3 \rightarrow	1.63 \times 2 \rightarrow			6.05
K	0.16 \times 2 \downarrow \rightarrow	0.20 \times 2 \downarrow \rightarrow	0.04 \times 2 \rightarrow , \times 3 \downarrow	0.13 \times 2 \downarrow	0.12 \times 3 \downarrow	1.18
Na	0.05 \times 3 \rightarrow		0.24 \times 2 \rightarrow	0.17 \times 3 \rightarrow		1.14
C	1.27	1.22		1.47		3.96
Σ	2.10	2.09	1.99	1.90	0.36	

*bond-valence parameters for U^{6+} from Burns *et al.* (1997) and for other cations from Brese & O'Keefe (1991)

ratio of 1 : 3. The cluster consists of a uranyl hexagonal bipyramid that shares three of its equatorial edges with (CO_3) triangles (Fig. 1b). In grimselite, the clusters are linked by bonds to low-valence cations only. Thus according to Burns *et al.* (1996), the structure may be classified as containing isolated clusters of polyhedra of higher bond-valence.

The uranyl tricarbonate clusters in grimselite are linked into layers parallel to (100) by sharing polyhedral elements with NaO_8 hexagonal bipyramids (Fig. 2a). Each NaO_8 polyhedron shares three equatorial edges with (CO_3) groups, as well as three equatorial vertices with three different UrO_6 hexagonal bipyramids. The resulting heteropolyhedral layers are stacked along [001], with the layers offset, facilitating linkage between the layers by sharing of apical vertices between UrO_6 and NaO_8 hexagonal bipyramids (Fig. 2b). Voids in the resulting heteropolyhedral framework contain K cations and H_2O groups (Fig. 2b).

Structural formula

The crystal-structure analysis provides the structural formula for grimselite. The single unique U^{6+} and Na^+ cations are located on Wyckoff positions *s* in space group $P6_2c$, giving two atoms of each per unit cell. The

K^+ cations are on position *g*; thus there are six K^+ cations per cell. The O(1), O(2), O(4) and C sites are on positions *h*, giving six of each of these cations per cell. The O(3) site is on position *f*, resulting in four O(3) atoms per cell. Finally, the OW(5) site is on position *e*, but it is only 50% occupied, resulting in two atoms per cell. The resulting formula is $K_3Na[(UO_2)(CO_3)_3](H_2O)$, $Z = 2$, which is in agreement with that given by Walenta (1972).

Comparison with other uranyl carbonate minerals with $U : C = 1 : 3$

The common building unit of the structures of uranyl carbonate minerals with $U : C = 1 : 3$ is the uranyl tricarbonate cluster, but the details of how these clusters are connected vary from mineral to mineral, depending upon the ratios of both $M : U$ (M : low-valence cations) and $H_2O : U$ in the structures. The structure of grimselite is unique in that it involves edge-sharing of carbonate groups with NaO_8 polyhedra, whereas in other structures, only corner-sharing of carbonate groups with low-valence cation polyhedra is commonly observed. The structures of grimselite, schröckingerite $\{NaCa_3[(UO_2)(CO_3)_3](SO_4F(H_2O)_{10})\}$ and $Na_4(UO_2)(CO_3)_3$ are quite similar and involve the same $M : U$ ratio. Grimselite has the smallest quantity of H_2O of the hydrated uranyl carbonates with $U : C = 1 : 3$, and like $Na_4(UO_2)(CO_3)_3$, has Na – uranyl carbonate layers that are linked directly rather than through H_2O groups in the interlayer.

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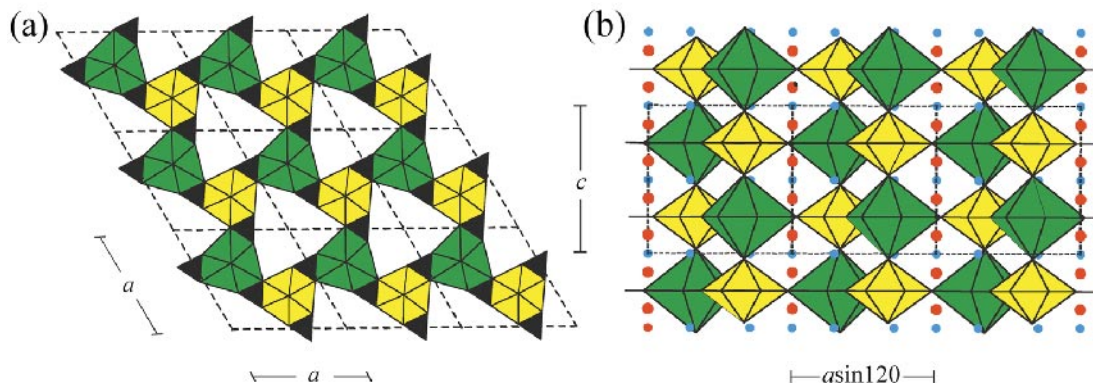


FIG. 2. Polyhedral representations of the structure of grimselite. (a) Heteropolyhedral layer composed of edge-sharing of uranyl hexagonal bipyramids (yellow), carbonate triangles (black), and NaO_8 hexagonal bipyramids (green), projected along [001]. (b) The structure projected along [100], showing the connection of NaO_8 hexagonal bipyramids with uranyl hexagonal bipyramids in adjacent sheets, with blue and red circles representing K cations and H_2O groups, respectively.

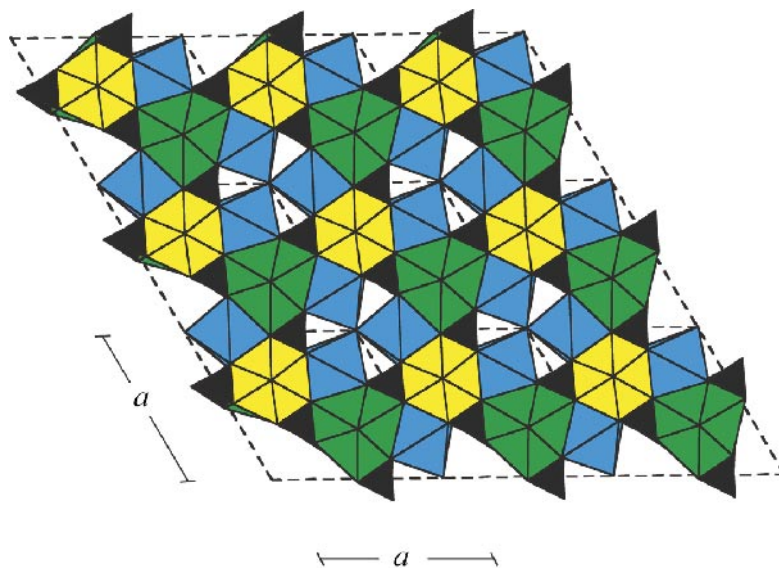


FIG. 3. The heteropolyhedral framework structure of grimselite, projected along [001].

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