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THE CRYSTAL STRUCTURE OF A NOVEL URANYL TRICARBONATE, $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$

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ABSTRACT

Crystals of a novel uranyl carbonate, $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$, were synthesized from an aqueous solution at room temperature. The crystal structure of $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$, orthorhombic, space group *Pnnm*, *a* 17.015(2), *b* 18.048(2), *c* 18.394(2), *V* 5684.3(1), $Z = 8$, was solved by direct methods and refined by least-squares techniques on the basis of F^2 for all unique reflections ($|F_o| > 4s_F$) to an agreement index (R_1) of 4.17% and a goodness-of-fit (S) of 0.882. The structure consists of uranyl hexagonal bipyramids that share three equatorial edges with carbonate triangles, resulting in uranyl tricarbonate clusters of composition $[(UO_2)(CO_3)_3]^{4-}$. As with all known uranyl tricarbonate phases, these clusters are not directly linked; rather, they are connected through bonds to lower-valence cations. The uranyl tricarbonate clusters in the structure of $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$ are connected through bonds to K and Ca polyhedra. We contend that $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$ could occur in nature on the basis of its ease and extent of formation under laboratory conditions.

Keywords: synthesis, uranyl carbonate, uranium, crystal chemistry, crystal structure.

SOMMAIRE

Nous avons synthétisé des cristaux d'un carbonate uranylé insoupçonné, $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$, à partir d'une solution aqueuse à température ambiante. La structure cristalline de $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$, orthorhombique, groupe spatial *Pnnm*, *a* 17.015(2), *b* 18.048(2), *c* 18.394(2), *V* 5684.3(1), $Z = 8$, a été résolue par méthodes directes et affinée par moindres carrés en utilisant les facteurs F^2 pour toutes les réflexions uniques ($|F_o| > 4s_F$) jusqu'à une concordance (R_1) de 4.17% et un indice de concordance (S) de 0.882. La structure est faite de bipyramides hexagonales à uranyle qui partagent trois arêtes équatoriales avec des groupes triangulaires de carbonate, menant à des groupements tricarbonatés uranylés de composition $[(UO_2)(CO_3)_3]^{4-}$. Comme avec toutes les phases connues contenant de tels groupements, ils ne sont pas connectés directement, mais plutôt grâce à des liaisons à des cations de faible valence. Dans ce cas, les groupements tricarbonatés uranylés de la structure de $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$ sont connectés *via* des liaisons avec les polyèdres contenant K et Ca. A notre avis, le $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$ pourrait exister dans la nature, compte tenu de la facilité de le synthétiser en grande quantité au laboratoire.

(Traduit par la Rédaction)

Mots-clés: synthèse, carbonate uranylé, uranium, chimie cristalline, structure cristalline.

INTRODUCTION

The structures and chemical composition of uranyl carbonate phases formed from aqueous species are of particular interest for uranium isolation in long-term repositories of high-level nuclear waste. Uranyl carbonate minerals generally form as a coating on other uranium minerals, and often as efflorescences on mine walls or in deposits in arid climates. Most uranyl carbonates are soluble in water and may crystallize from fluid migrating away from the primary source of uranium. The stability, solubility and crystal chemistry of uranyl carbonate phases may well have an impact on the long-distance transport of uranium.

The uranyl tricarbonate complex, $[(UO_2)(CO_3)_3]^{4-}$, is the dominant aqueous species in slightly to strongly alkaline water (Langmuir 1997). Whereas grimselite, $K_3Na[(UO_2)(CO_3)_3](H_2O)$, readily precipitates from uranyl carbonate solutions containing both K^+ and Na^+, the novel uranyl tricarbonate $K_2Ca_3[(UO_2)(CO_3)_3]_2$

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$(H_2O)_6$ precipitates from solutions containing Ca^{2+} rather than Na^+. The phase $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$ may occur in nature, and could coexist with grimselite.

The crystal structure and crystal chemistry of $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$ are reported here. This compound is similar to $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_{9-10}$, for which powder-diffraction data and optical properties were given by Meyrowitz *et al.* (1964). These compounds have similar unit-cell dimensions and composition; however, they differ in hydration state.

EXPERIMENTAL

Synthesis of crystals

A solution was prepared containing 0.622 g K_2CO_3 (J.T. Baker), 0.357 g $Ca(NO_3)_2(H_2O)_4$ (J.T. Baker), and 9 mL water. A second solution was prepared containing 0.753 g $UO_2(NO_3)(H_2O)_6$ (Alfa Aesar) in 1 mL water. The uranyl nitrate solution was added dropwise to the first solution at room temperature while continuously stirring. The resulting solution was sealed and left at room temperature and room pressure for two weeks. The products consist of translucent yellow prismatic crystals of $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$ with maximum dimensions attaining 4 mm.

Single-crystal X-ray diffraction

A single crystal of $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$ measuring 150 3 150 3 140 mm was selected for study and mounted on the end of a tapered glass fiber. Diffraction data were collected using a Bruker PLATFORM three-circle X-ray diffractometer equipped with a 4K APEX CCD detector and a crystal-to-detector distance of 4.67 cm. A sphere of three-dimensional data was collected using graphite-monochromatized Mo*K*a radiation, frame widths of 0.3° in v, and 10 seconds spent counting per frame. Unit-cell parameters (Table 1) were refined from 6349 unique reflections ($|F_o| > 4s_F$) using least-squares techniques. Intensity data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semi-empirical correction for adsorption was applied by modeling the crystal as an ellipsoid; it reduced R_{INT} of 4586 reflections from 22.7 to 13.4%. A total of 117,247 reflections were collected, of which 12,221 are classified as unique, and of these 6349 were classified as observed ($|F_o| > 4s_F$).

Structure solution and refinement

The Bruker SHELXTL Version 5 system of programs was used for the solution and refinement of the crystal structure. Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from International Tables for Crystallography, Vol. IV (Ibers & Hamilton 1974). The structure was solved by direct methods and refined in space group *Pnnm*. During the course of the refinement, atomic displacement parameters for the C(7) and O(25) positions, which are located on sites with Wyckoff symmetry 4*g*, were found to be strongly asymmetrical. These sites were subsequently replaced by sites designated C(7A), C(7B) and O(25A), O(25B), respectively, which are displaced from their corresponding special positions. Attempts were made to solve the structure in space group *Pnn2*, but this did not result in an improved refinement and did not result in better behavior of the C(7) and O(25) sites. Refinement of the occupancy of the K(1), K(2), K(3), K(4), K(5), and K(6) sites show that they are 83, 80, 45, 50, 25 and 17% occupied, respectively. Refinement of anisotropic displacement parameters for O(23) through O(33) resulted in physically unrealistic shapes; each site was assigned an isotropic displacement parameter during the final stages of refinement.

The final structural model included refined coordinates of the atoms, refined displacement parameters, and a weighting scheme for the structure factors. The model was refined on the basis of F^2 for all unique reflections and gave a final agreement index (R_1) of 4.17%, which was calculated for the 6349 unique observed reflections ($|F_o| > 4s_F$). The final value of wR_2 was 11.12% for all data, and the goodness-of-fit (*S*) was 0.882. Final coordinates of the atoms and displacement parameters are given in Table 2. Selected interatomic distances and angles are given in Table 3. Bond-valence sums at the cation and anion sites are provided 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.

TABLE 1. CRYSTAL DATA AND STRUCTURE REFINEMENT FOR $K_2Ca_3(UO_2)_2(CO_3)_6(H_2O)_6$

a (Å)	17.015(2)
b (Å)	18.048(2)
c (Å)	18.394(2)
V (Å^3)	5684.3(1)
Space group	*Pnnm*
Z	8
Formula	$K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$
F(000)	4432
μ (mm^{-1})	12.4
D_{calc} (g/cm^3)	2.84
Crystal size (μm)	150 x 150 x 140
Reflections collected	117247
Independent reflections	12221
R_{int} (%)	10.30
Unique $\|F_o\| \geq 4\sigma_F$	6349
Refinement method	Full-matrix least-squares on F^2
Parameters varied	392
R_1 (%)	4.17
wR_2 (%)	11.12
S	0.882
Largest diff. peak and hole (e/Å^{-3})	3.29 and -1.42

RESULTS AND DISCUSSION

Coordination of the cations

The structure of $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$ contains three symmetrically independent U^{6+} positions, each of which is part of an approximately linear uranyl ion, $(UO_2)^{2+}$, with average <U–O_{Ur}> (O_{Ur}: uranyl oxygen) bond-lengths of 1.79, 1.80, and 1.79 Å, respectively. These values are consistent with the average value 1.81 Å obtained by Burns *et al.* (1997) for numerous uranyl hexagonal bipyramids in well-refined structures. Each uranyl ion is further coordinated by six anions arranged at the equatorial edges of hexagonal

TABLE 2. ATOM COORDINATES (Å² ·10⁴) AND ANISOTROPIC DISPLACEMENT PARAMETERS (Å² ·10³) FOR $K_2Ca_3(UO_2)_2(CO_3)_6(H_2O)_6$

	x	y	z	U(eq)	U11	U22	U33	U23	U13	U12
U(1)	0.23291(2)	0.01077(2)	0	0.02196(9)	0.0263(2)	0.0241(2)	0.0154(2)	0	0	0.0064(1)
U(2)	0.23301(2)	-0.52808(2)	0	0.02249(9)	0.0250(2)	0.0273(2)	0.0152(2)	0	0	-0.0081(1)
U(3)	0.20784(1)	-0.26067(1)	-0.22558(1)	0.01988(6)	0.0206(1)	0.0168(1)	0.0223(1)	0.00081(1)	-0.00429(9)	0.00022(9)
Ca(1)	0.32298(8)	-0.07042(7)	-0.18713(7)	0.0184(3)	0.0201(7)	0.0179(6)	0.0170(6)	-0.0005(5)	-0.0010(5)	0.0017(5)
Ca(2)	0.32528(8)	-0.45012(7)	-0.18652(7)	0.0182(3)	0.0209(7)	0.0178(6)	0.0158(6)	-0.0002(5)	-0.0011(5)	-0.0011(5)
Ca(3)	0.4675(1)	-0.2592(1)	0	0.0248(4)	0.032(1)	0.0222(9)	0.0204(9)	0	0	0.0012(8)
Ca(4)	0.0645(1)	-0.6835(1)	0	0.0283(5)	0.028(1)	0.031(1)	0.026(1)	0	0	-0.0076(8)
K(1)	0	0	0	0.066(2)	0.033(3)	0.110(5)	0.054(4)	0	0	0.001(3)
K(2)	-0.2199(4)	-0.2704(2)	-0.2147(2)	0.065(1)	0.043(2)	0.106(3)	0.045(2)	0.019(2)	0.005(1)	-0.009(2)
K(3)	0.2200(4)	-0.2245(4)	0	0.044(2)	0.044(4)	0.054(4)	0.035(3)	0	0	0
K(4)	0	-0.5	-0.1643(5)	0.086(4)	0.070(6)	0.107(7)	0.080(7)	0	0	0.018(4)
K(5)	0.716(1)	-0.242(1)	0	0.11(1)	0.07(1)	0.12(2)	0.17(3)	0	0	-0.01(1)
K(6)	0.5372(6)	-0.4707(6)	-0.0375(7)	0.042(4)	0.031(6)	0.036(6)	0.060(7)	-0.018(5)	-0.018(5)	0.025(4)
C(1)	0.3599(4)	-0.2600(4)	0.1544(4)	0.022(1)	0.024(3)	0.019(3)	0.022(3)	0.001(3)	0.003(2)	0.001(3)
C(2)	0.1379(4)	-0.1233(4)	-0.2663(4)	0.026(2)	0.023(4)	0.019(3)	0.036(4)	0.004(3)	-0.004(3)	0.004(3)
C(3)	0.1387(4)	-0.3995(4)	-0.2636(4)	0.027(2)	0.023(4)	0.026(4)	0.033(4)	-0.005(3)	-0.005(3)	0
C(4)	0.1704(4)	-0.5837(4)	-0.1360(4)	0.023(1)	0.027(4)	0.024(4)	0.020(4)	0.002(3)	-0.002(3)	-0.003(3)
C(5)	0.3576(8)	-0.0962(6)	0	0.042(3)	0.059(9)	0.037(7)	0.029(7)	0	0	0.029(6)
C(6)	0.1665(4)	0.0559(4)	0.1362(4)	0.027(2)	0.026(4)	0.036(4)	0.018(4)	0.001(3)	0.005(3)	0.005(3)
C(7A)	0.359(1)	-0.422(1)	0	0.019(4)	0.02(1)	0.02(1)	0.017(9)	0	0	-0.016(8)
C(7B)	0.329(2)	-0.393(1)	0	0.029(5)	0.05(2)	0.02(1)	0.02(1)	0	0	0
O(1)	0.2025(3)	-0.1254(3)	-0.2291(3)	0.029(1)	0.023(3)	0.025(3)	0.040(3)	0	-0.011(2)	0.002(2)
O(2)	0.4268(3)	-0.2603(3)	0.1277(3)	0.027(1)	0.025(2)	0.024(2)	0.032(3)	0.001(2)	0.010(2)	-0.002(2)
O(3)	0.2066(3)	-0.3961(3)	-0.2316(3)	0.030(1)	0.027(3)	0.020(2)	0.042(3)	0.001(2)	-0.012(2)	0.002(2)
O(4)	0.1018(3)	-0.1864(3)	-0.2749(3)	0.034(1)	0.022(3)	0.022(3)	0.059(4)	0.007(2)	-0.016(3)	-0.004(2)
O(5)	0.2273(3)	0.0125(3)	-0.1342(3)	0.031(1)	0.036(3)	0.038(3)	0.021(3)	0.001(2)	0.003(2)	0.015(2)
O(6)	0.1420(3)	0.0794(3)	0.0730(3)	0.033(1)	0.037(3)	0.043(3)	0.018(3)	0	0.002(2)	0.019(2)
O(7)	0.2557(3)	-0.2601(3)	-0.3115(3)	0.034(1)	0.039(3)	0.037(3)	0.027(3)	-0.004(2)	0.003(2)	-0.003(2)
O(8)	0.1040(3)	-0.3376(3)	-0.2716(3)	0.038(1)	0.030(3)	0.023(3)	0.062(4)	-0.005(3)	-0.025(3)	0.005(2)
O(9)	0.1585(3)	-0.2618(3)	-0.1392(3)	0.037(1)	0.040(3)	0.039(3)	0.031(3)	0.003(2)	0.007(2)	-0.005(2)
O(10)	0.1642(5)	-0.0646(4)	0	0.040(2)	0.044(5)	0.038(5)	0.039(5)	0	0	-0.008(4)
O(11)	0.1577(5)	-0.4585(4)	0	0.039(2)	0.044(5)	0.035(4)	0.037(5)	0	0	0.004(4)
O(12)	0.3006(5)	0.0868(4)	0	0.037(2)	0.038(5)	0.036(4)	0.037(5)	0	0	-0.008(3)
O(13)	0.3098(5)	-0.5971(4)	0	0.040(2)	0.033(5)	0.048(5)	0.038(5)	0	0	0.004(4)
O(14)	0.2270(3)	-0.5346(3)	-0.1326(3)	0.031(1)	0.037(3)	0.038(3)	0.020(3)	0.005(2)	0	-0.014(2)
O(15)	0.3197(3)	-0.2001(3)	0.1675(3)	0.039(1)	0.041(3)	0.017(3)	0.058(4)	-0.004(2)	0.030(3)	-0.003(2)
O(16)	0.1384(3)	-0.6037(3)	-0.1931(3)	0.030(1)	0.030(3)	0.042(3)	0.017(3)	-0.002(2)	-0.003(2)	-0.006(2)
O(17)	0.3228(3)	-0.3195(3)	0.1735(3)	0.039(1)	0.033(3)	0.018(3)	0.064(4)	-0.001(2)	0.028(3)	0
O(18)	0.1501(3)	-0.6083(3)	-0.0719(3)	0.031(1)	0.038(3)	0.035(3)	0.019(3)	0.001(2)	0.003(2)	-0.018(2)
O(19)	0.1093(3)	-0.4599(3)	-0.2862(3)	0.035(1)	0.032(3)	0.019(2)	0.054(4)	-0.006(2)	-0.010(3)	-0.002(2)
O(20)	0.3289(3)	-0.0685(3)	-0.0593(3)	0.0381(1)	0.050(4)	0.054(4)	0.010(2)	-0.002(2)	0	0.022(3)
O(21)	0.1101(3)	-0.0635(3)	-0.2902(3)	0.038(1)	0.028(3)	0.023(3)	0.063(4)	0.009(3)	-0.013(3)	0
O(22)	0.1339(3)	0.0751(3)	-0.1932(3)	0.038(1)	0.047(4)	0.050(4)	0.017(3)	-0.002(2)	0.004(3)	0.013(2)
O(23)	0.3211(4)	-0.4413(3)	-0.0588(3)	0.046(2)						
O(24)	0.4116(7)	-0.1437(6)	0	0.079(4)						
O(25A)	0.420(1)	-0.3783(9)	0	0.040(4)						
O(25B)	0.352(1)	-0.3298(8)	0	0.034(4)						
OW(26)	0.4617(3)	-0.4169(3)	-0.1582(3)	0.038(1)						
OW(27)	0.4604(4)	-0.1003(3)	-0.1639(3)	0.045(1)						
OW(28)	0.1191(4)	-0.7694(3)	0.0872(4)	0.052(2)						
OW(29)	-0.0375(6)	-0.7828(6)	0	0.072(3)						
OW(30)	-0.0253(5)	-0.6382(4)	-0.0929(5)	0.083(3)						
OW(31)	0.5409(9)	-0.0427(8)	-0.0574(8)	0.069(4)						
OW(32)	0.581(1)	-0.2515(8)	-0.0767(9)	0.080(5)						
OW(33)	-0.0299(8)	-0.8900(7)	0.1248(7)	0.053(3)						

TABLE 3. BOND LENGTHS (Å) AND ANGLES (°) FOR $K_2Ca_3(UO_2)_2(CO_3)_6(H_2O)_6$

U(1)-O(12)	1.792(7)	Ca(2)-O(23)	2.356(6)	K(2)-O(8)	2.755(6)	C(1)-O(2)	1.241(8)
U(1)-O(10)	1.794(8)	Ca(2)-O(21c)	2.362(5)	K(2)-O(4)	2.894(6)	C(1)-O(17)	1.294(8)
U(1)-O(6)	2.394(5)	Ca(2)-O(22d)	2.363(5)	K(2)-OW(28g)	2.902(7)	C(1)-O(15)	1.301(8)
U(1)-O(6a)	2.394(5)	Ca(2)-O(17a)	2.370(5)	K(2)-OW(30f)	2.928(9)		
U(1)-O(20)	2.431(5)	Ca(2)-O(3)	2.391(5)	K(2)-O(16f)	2.978(6)	C(2)-O(21)	1.258(8)
U(1)-O(20a)	2.431(5)	Ca(2)-OW(26)	2.454(5)	K(2)-O(2k)	3.052(6)	C(2)-O(1)	1.296(8)
U(1)-O(5)	2.470(5)	Ca(2)-O(14)	2.471(5)			C(2)-O(4)	1.303(8)
U(1)-O(5a)	2.470(5)			K(3)-O(9)	2.846(6)		
O(12)-U(1)-O(10)	179.4(4)	Ca(3)-O(24)	2.292(12)	K(3)-O(9a)	2.846(6)	C(3)-O(19)	1.271(8)
		Ca(3)-O(25A)	2.297(16)	K(3)-O(25B)	2.94(2)	C(3)-O(8)	1.272(8)
U(2)-O(11)	1.794(8)	Ca(3)-O(25B)	2.347(17)	K(3)-O(10)	3.04(1)	C(3)-O(3)	1.297(8)
U(2)-O(13)	1.805(8)	Ca(3)-OW(32)	2.389(17)	K(3)-OW(29g)	3.11(1)		
U(2)-O(18)	2.416(5)	Ca(3)-OW(32a)	2.389(5)			C(4)-O(16)	1.237(8)
U(2)-O(18a)	2.416(5)	Ca(3)-O(2)	2.448(5)	K(4)-OW(30)	2.851(9)	C(4)-O(18)	1.306(8)
U(2)-O(23)	2.423(6)	Ca(3)-O(2a)	2.448(5)	K(4)-OW(30f)	2.851(9)	C(4)-O(14)	1.310(8)
U(2)-O(23a)	2.423(6)			K(4)-O(19)	3.002(9)		
U(2)-O(14)	2.443(5)	Ca(4)-O(18)	2.391(5)	K(4)-O(19f)	3.002(9)	C(5)-O(27)	1.26(1)
U(2)-O(14a)	2.443(5)	Ca(4)-O(18a)	2.391(5)	K(4)-O(16)	3.054(6)	C(5)-O(20)	1.295(7)
O(11)-U(2)-O(13)	179.2(4)	Ca(4)-OW(28)	2.418(7)	K(4)-O(16f)	3.054(6)	C(5)-O(20a)	1.295(7)
		Ca(4)-OW(28a)	2.418(7)				
U(3)-O(7)	1.778(5)	Ca(4)-OW(30)	2.435(9)	K(5)-OW(32)	2.712(23)	C(6)-O(22)	1.235(8)
U(3)-O(9)	1.797(5)	Ca(4)-OW(30a)	2.435(9)	K(5)-OW(32a)	2.712(23)	C(6)-O(5a)	1.298(8)
U(3)-O(8)	2.402(5)	Ca(4)-OW(29)	2.49(1)	K(5)-O(12l)	2.819(20)	C(6)-O(6)	1.307(8)
U(3)-O(4)	2.424(5)			K(5)-O(13m)	2.935(20)		
U(3)-O(17a)	2.423(5)	K(1)-O(10)	3.028(8)	K(5)-OW(28n)	3.237(17)	C(7A)-O(23)	1.30(1)
U(3)-O(15a)	2.441(5)	K(1)-O(10e)	3.028(8)	K(5)-OW(28m)	3.237(17)	C(7A)-O(23a)	1.30(1)
U(3)-O(1)	2.444(5)	K(1)-OW(33f)	3.08(1)			C(7A)-O(25A)	1.31(2)
U(3)-O(3)	2.446(4)	K(1)-OW(33g)	3.08(1)	K(6)-O(25A)	2.69(2)		
O(7)-U(3)-O(9)	179.4(3)	K(1)-OW(33h)	3.08(1)	K(6)-OW(26)	2.74(1)	C(7B)-O(25B)	1.21(3)
		K(1)-OW(33i)	3.08(1)	K(6)-O(25Am)	2.90(2)	C(7B)-O(23)	1.39(2)
Ca(1)-O(20)	2.353(5)	K(1)-O(6)	3.113(6)	K(6)-O(23n)	2.91(1)	C(7B)-O(23a)	1.39(2)
Ca(1)-O(19b)	2.355(5)	K(1)-O(6a)	3.113(6)	K(6)-O(13m)	2.96(1)		
Ca(1)-O(15a)	2.369(5)	K(1)-O(6e)	3.113(6)	K(6)-OW(26n)	3.01(1)		
Ca(1)-O(16b)	2.375(5)	K(1)-O(6j)	3.113(6)				
Ca(1)-O(1)	2.404(5)						
Ca(1)-O(5)	2.417(5)						
Ca(1)-OW(27)	2.437(6)						

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

bipyramids, with <U– w_{eq}> (w_{eq}: equatorial O anion or H_2O group) bond lengths in the range of 2.39 to 2.47 Å (Table 3). The structure contains seven symmetrically unique C^{4+} ions, all in triangular coordination, with <C–O> bond lengths ranging from 1.28 to 1.33 Å.

The structure of $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$ contains ten symmetrically distinct low-valence cation sites that are occupied by K and Ca. Of the four distinct Ca sites, Ca(1), Ca(2), and Ca(4) are coordinated by seven anions, with <Ca–w> bond lengths of 2.39, 2.39 and 2.43 Å, respectively; Ca(3) is coordinated by six anions with a <Ca–w> bond length of 2.38 Å (Table 3).

K(1) is coordinated by ten anions, with a <K(1)–w> bond length of 2.92 Å. K(2), K(4), K(5) and K(6) are each octahedrally coordinated with <K–w> bond lengths of 2.95, 2.97, 2.99, and 2.88 Å, respectively. K(3) is coordinated by five anions with a <K(3)–w> bond length of 2.97 Å.

TABLE 4. BOND-VALENCE* (*vu*) ANALYSIS FOR THE STRUCTURE OF $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$

U(1)	6.06	C(2)	3.98	O(8)	2.02	O(22)	1.87
U(2)	6.03	C(3)	4.04	O(9)	1.69	O(23)	1.97
U(3)	6.09	C(4)	4.01	O(10)	1.75	O(24)	1.86
Ca(1)	2.25	C(5)	4.02	O(11)	1.63	O(25A)	1.77
Ca(2)	2.22	C(6)	4.06	O(12)	1.67	O(25B)	2.02
Ca(3)	1.66	C(7A)	3.78	O(13)	1.66	OW(26)	0.32
Ca(4)	2.04	C(7B)	3.61	O(14)	1.95	OW(27)	0.28
K(1)	0.61	O(1)	2.05	O(15)	2.07	OW(28)	0.41
K(2)	0.74	O(2)	1.84	O(16)	1.96	OW(29)	0.28
K(3)	0.56	O(3)	2.05	O(17)	2.11	OW(30)	0.45
K(4)	0.64	O(4)	1.84	O(18)	2.05	OW(31)	0.00
K(5)	0.58	O(5)	2.01	O(19)	1.78	OW(32)	0.36
K(6)	0.85	O(6)	1.81	O(20)	2.10	OW(33)	0.06
C(1)	4.07	O(7)	1.68	O(21)	1.78		

* Bond-valence parameters for uranium are taken from Burns *et al.* (1999), and those for calcium, potassium, and carbon, from Brese & O'Keefe (1991).

Structural connectivity

The structure of $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$ contains uranyl tricarbonate clusters of composition $[(UO_2)(CO_3)_3]^{4-}$. Each cluster consists of a uranyl hexagonal bipyramid that shares three non-adjacent equatorial edges with CO_3 triangles. The uranyl tricarbonate clusters are not directly connected; rather they are connected through bonds to Ca and K.

The U(2) cation is coordinated by apical anions O(11) and O(13), and equatorial anions O(14)a, b, O(18)a, b, and O(23)a, b. The symmetrically equivalent O(23) positions correspond to the equatorial edge of the uranyl hexagonal bipyramid that is shared with the C(7) triangle. The C(7) position is split, with either the C(7A) or C(7B) position occupied locally, and adjacent C(7) positions are separated by 0.73(3) Å. The apical oxygen of the $C(7)O_3$ triangle, O(25), also is split and occupies either O(25A) or O(25B), where C(7A) or C(7B) is occupied, respectively (Fig. 1). The O(25) positions are separated by 1.46(2) Å.

The U(1) and U(2) hexagonal bipyramids in $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$ are connected parallel to [001] through bonds to Caw_7 polyhedra. The Caw_7 polyhedra share one equatorial edge with a uranyl hexagonal bipyramid and one equatorial vertex with a CO_3 triangle of an adjacent $[(UO_2)(CO_3)_3]^{4-}$ group (Fig. 2). The chains are linked by bonds to Caw_7, Kw_{10}, and Kw_6 polyhedra (Fig. 3).

The uranyl tricarbonate clusters in $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$ corresponding to the U(3) position are linked into layers parallel to (001) by sharing polyhedron elements with two Caw_7 and one Kw_6 polyhedra (Fig. 4). Each Caw_7 polyhedron shares one equatorial edge with a uranyl hexagonal bipyramid and one vertex with a CO_3 triangle of an adjacent $[(UO_2)(CO_3)_3]^{4-}$

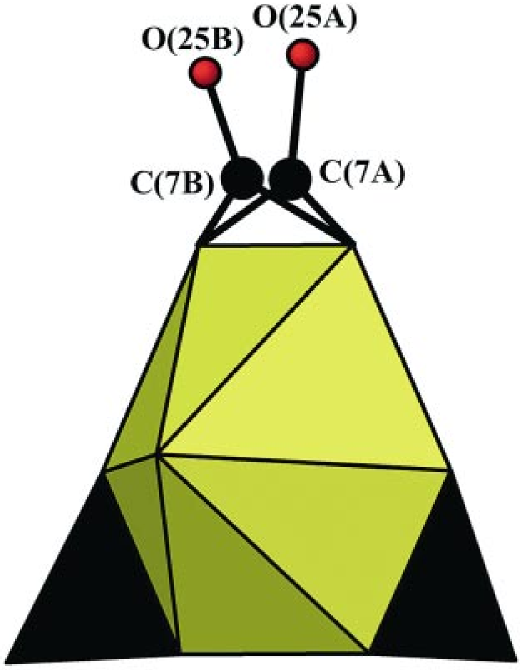

FIG. 1. The U(2) site in the structure of $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$. The C(7) position is split, with either C(7A) or C(7B) occupied locally. Consequently, the apical oxygen atom of this carbonate triangle, O(25), is split with either O(25A) or O(25B) occupied locally where C(7A) or C(7B) is occupied, respectively. The uranyl hexagonal bipyramid is shown in yellow, CO_3 as black triangles, C(7) sites as black spheres, and O(25) sites as red spheres.

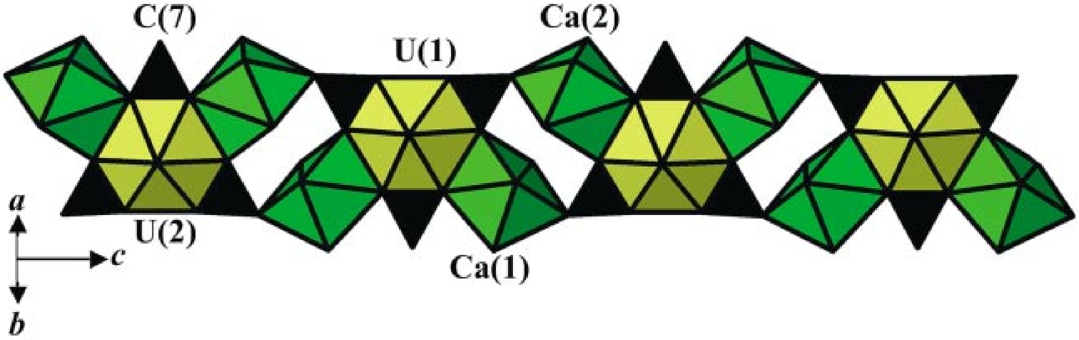

FIG. 2. Polyhedron representation of the connectivity of the U(1) and U(2) polyhedra in the structure of $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$, parallel to (110). The Caw_7 polyhedra (green) share one equatorial edge with a UO_8 hexagonal bipyramid (yellow) and one equatorial vertex with a CO_3 triangle (black) of an adjacent $[(UO_2)(CO_3)_3]$ group. Both the *a* and *b* axes are inclined to the diagram.

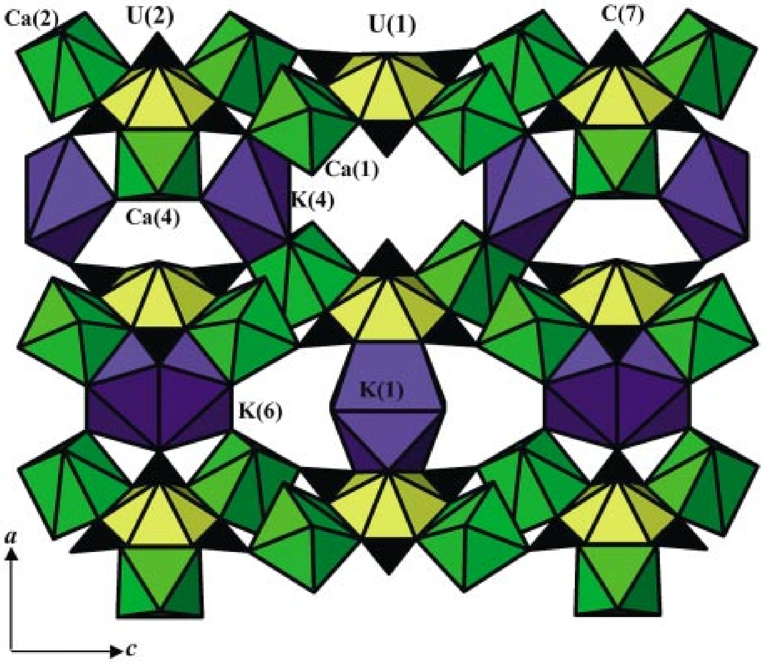

FIG. 3. The framework of the U(1) and U(2) polyhedra in the structure of $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$, projected parallel to [010]. Chains of alternating (Caw_7) polyhedra and $[(UO_2)(CO_3)_3]^{4-}$ clusters are linked by bonds to Kw_{10} and Kw_6 polyhedra (blue).

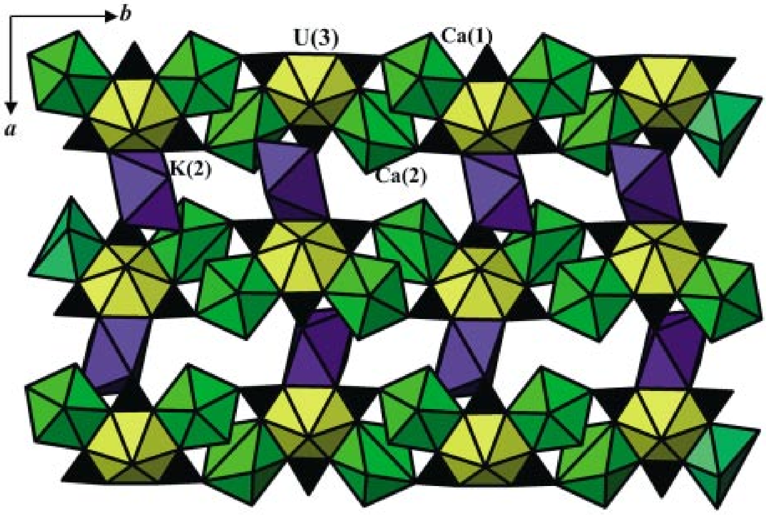

FIG. 4. Polyhedron representation of the connectivity of the $U(3)O_8$ polyhedra in the structure of $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$. The U(3) uranyl tricarbonate clusters are linked parallel to (001) by sharing polyhedral elements with two Caw_7 and one Kw_6 polyhedra. Each Caw_7 polyhedron shares one equatorial edge with a UO_8 hexagonal bipyramid and one vertex with a CO_3 triangle of an adjacent $[(UO_2)(CO_3)_3]^{4-}$ group, linking adjacent $[(UO_2)(CO_3)_3]^{4-}$ groups into chains parallel to (100). The Kw_6 polyhedra share an equatorial edge with one UO_8 hexagonal bipyramid and a vertex with a CO_3 triangle of an adjacent $[(UO_2)(CO_3)_3]$ cluster, linking the chains parallel to (010).

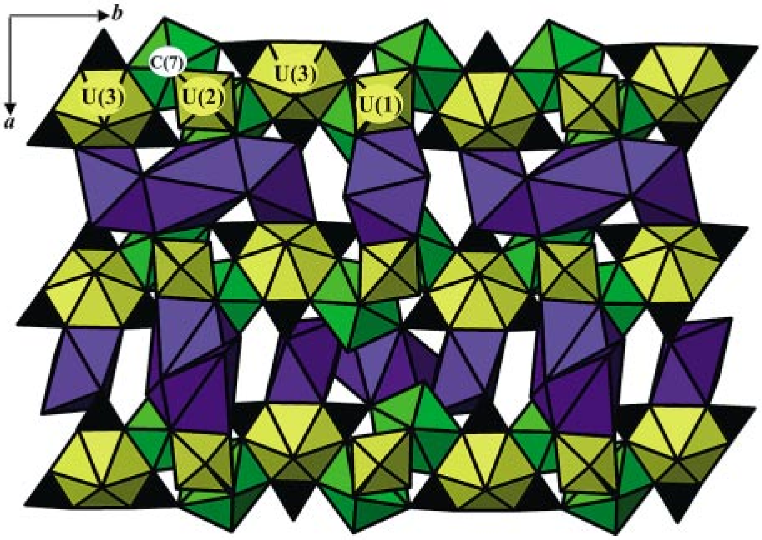

FIG. 5. The crystal structure of $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$ projected parallel to [001].

group, linking adjacent $[(UO_2)(CO_3)_3]^{4-}$ groups into chains parallel to (100). The Kw_6 polyhedra share an equatorial edge with one uranyl hexagonal bipyramid and a vertex with a CO_3 triangle of an adjacent $[(UO_2)(CO_3)_3]^{4-}$ cluster, linking the chains parallel to (010). Sheets containing U(3) are connected with sheets containing U(1) and U(2) through vertices sharing with Caw_7, Caw_6, Kw_{10}, Kw_6, and Kw_5 polyhedra (Fig. 5).

Related structures

A review of uranyl mineral structures, including uranyl carbonates, was given by Burns (1999). All known structures involving a uranium-to-carbon ratio of 1:3 are based on isolated uranyl tricarbonate clusters of composition $[(UO_2)(CO_3)_3]^{4-}$. These clusters are connected through bonds to low-valence cations, such as K and Na in the structure of grimselite (O'Brien & Williams 1983). The nature of the bonds between the uranyl tricarbonate clusters and lower-valence cations vary, with corner-sharing between the carbonate groups and lower-valence cations being most common. However, as in the structure of grimselite, the structure of $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$ also involves the sharing of edges of polyhedra of lower-valence cations. We contend that $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$ is likely to occur in nature, given that it is readily synthesized under aqueous conditions where Na^+ is not sufficient to form grimselite.

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