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Structure of a Cubic Sodium Strontium Magnesium Tricarbonatodioxouranate(VI) Hydrate

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Abstract. $Na_{0.87}Sr_{1.40}Mg_{0.17}[UO_2(CO_3)_3].4.66H_2O$, $M_r = 680.7$, cubic, $Pa3$, $a = 20.290 (3)$ Å, $V = 8353 (4)$ Å^3, $Z = 24$, $D_x = 3.25$ g cm^{-3}, $\lambda(Mo\,K\alpha) = 0.71069$ Å, $\mu = 163$ cm^{-1}, $F(000) = 7425$, $T = 295$ K, final $R = 0.041$ for 1588 observed reflections. Five different cation coordination polyhedra and a $[UO_2(CO_3)_3]$ unit build up a framework with the structural chemical formula $Na^{[6]}(Na,\square)_2^{[7]}Sr_6^{[8]}(Sr,Na,\square)_6^{[8]}Mg^{[6]}[U^{[2+6]}O_2(CO_3)_3]_6.28H_2O$. Disorder in cation site occupation affects to some extent also the rest of the structure.

Introduction. In a study of uranyl carbonate minerals and related synthetic compounds, the preparation of monoclinic $SrMg[UO_2(CO_3)_3].12H_2O$ (Mereiter, 1986a) was attempted from solutions which also contained Na. Instead of the expected prismatic crystals large isometric crystals of a novel uranyl carbonate were obtained. The structure of this salt is reported here.

Experimental. Yellow cubes with corners truncated by small $\{111\}$ faces, size ≤ 5 mm, stable in air, grown by room-temperature evaporation of solutions made from 3.18 g Na_2CO_3, 5.02 g $UO_2(NO_3)_2.6H_2O$, 1.06 g $Sr(NO_3)_2$ and 1.02 g $MgCl_2.6H_2O$ in 70 g H_2O. Bright yellow-green fluorescence, optically isotropic to weakly birefringent with sector zoning, refractive index n = 1.559 at $\lambda = 589$ nm. Optical anisotropy is probably connected to the observed disorder of two cation sites (see below). Chemical analysis gave on average 4% Na_2O, 21.2% SrO, 0.9% MgO, 42.2% UO_3, 19.5% CO_2 and 12.1% H_2O, sum 99.9%, and evidence for reciprocal variations in Na and Sr content; calculated values for the chemical formula given in the *Abstract* are 3.95, 21.31, 0.99, 42.02, 19.39 and 12.35%, respectively. Preliminary cell and space-group information from X-ray powder patterns and precession photographs. Further work on a Siemens AED2 diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. Unit-cell dimensions from 24 reflections, $16 \leq \theta \leq 18°$. Data collected with a crystal sphere of 0.18 mm diameter, θ–2θ scans, scan width 1.08 + 0.35tanθ, three standard reflections with ±2% variation. Two sets each of 2706 independent reflections measured in two different octants of the reciprocal lattice, θ: 2 to 25°, h: −24 to 24, k: 0 to 24, l: 0 to 18. Spherical absorption correction with transmission factors from 0.13 to 0.15; data merged to 1588 independent reflections with $F_o \geq 4\sigma(F_o)$ which were subsequently used, $R_{merge} = 0.033$ for these reflections.

The structure was solved by direct and Fourier methods in space group $Pa3$, which is unambiguously defined by the observed Laue symmetry and systematic extinctions. H atoms could not be located. Structure refinement with anisotropic temperature factors for all

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{8}{3}\pi^2(U_{11} + U_{22} + U_{33}).$$

		x	y	z	$B_{eq}(\text{Å}^2)$
Na(1)	4(a)	0·0000	0·0000	0·0000	1·9 (2)
Na(2)*	8(c)	0·2111 (4)	0·2111 (4)	0·2111 (4)	6·5 (8)
Sr(1)	24(d)	0·27630 (5)	0·02608 (5)	0·02281 (5)	1·28 (3)
Sr(2)†	24(d)	0·36660 (11)	0·37055 (10)	0·00207 (12)	1·81 (6)
Mg	4(b)	0·5000	0·5000	0·5000	1·3 (2)
U	24(d)	0·21864 (2)	0·22309 (2)	0·00805 (3)	2·07 (2)
O(1)	24(d)	0·2193 (5)	0·2139 (5)	0·0944 (5)	3·8 (3)
O(2)	24(d)	0·2169 (4)	0·2312 (4)	−0·0796 (5)	3·5 (3)
C(1)	24(d)	0·1211 (6)	0·1225 (6)	−0·0163 (7)	2·1 (3)
O(3)	24(d)	0·1833 (4)	0·1098 (4)	−0·0082 (5)	3·7 (3)
O(4)	24(d)	0·1065 (4)	0·1835 (4)	−0·0030 (5)	3·2 (3)
O(5)	24(d)	0·0799 (4)	0·0810 (4)	−0·0371 (4)	2·0 (2)
C(2)	24(d)	0·1832 (6)	0·3581 (6)	0·0276 (7)	2·4 (3)
O(6)	24(d)	0·1407 (4)	0·3096 (4)	0·0289 (5)	3·1 (3)
O(7)	24(d)	0·2429 (4)	0·3412 (4)	0·0149 (5)	3·2 (3)
O(8)	24(d)	0·1669 (4)	0·4168 (4)	0·0389 (5)	2·9 (2)
C(3)	24(d)	0·3553 (5)	0·1888 (5)	0·0010 (7)	1·8 (3)
O(9)	24(d)	0·3357 (4)	0·2491 (5)	0·0024 (6)	4·1 (3)
O(10)	24(d)	0·3088 (4)	0·1455 (4)	0·0036 (6)	3·7 (3)
O(11)	24(d)	0·4136 (4)	0·1733 (4)	−0·0051 (5)	3·2 (3)
W(1)	24(d)	0·4155 (4)	0·0488 (4)	0·0344 (4)	1·9 (2)
W(2)	24(d)	0·4629 (7)	0·3212 (5)	0·0362 (7)	8·4 (5)
W(3)	24(d)	0·3591 (8)	0·3290 (7)	0·1372 (7)	9·4 (5)
W(4)	24(d)	0·3386 (8)	0·1890 (9)	0·1629 (8)	11·0 (6)
W(5)	8(c)	0·2728 (13)	0·2728 (13)	0·2728 (13)	17·2 (18)
W(6)	8(c)	0·3489 (9)	0·3489 (9)	0·3489 (9)	11·4 (14)

* Occupation factor refined to 0·82 (4).
† Mixed occupation by 0·40 Sr (factor fixed in accordance with chemical composition) and by 0·35 (2) Na (factor allowed to vary).

positions showed partial and mixed occupation of two cation sites [Na(2), Sr(2)] and large thermal-vibration parameters for many O atoms. Different models were tried to account for these disorder phenomena. In the refinement model finally selected the anisotropic temperature factors of 14 C and O atoms [C(1) through C(3), O(1) through O(11)] were restricted to $U_{11} = U_{22}$ and $U_{23} = U_{13} = U_{12} = 0$ to account for the previously observed anisotropy, and occupation factors for the sites Na(2) and Sr(2) were allowed to vary. Final $R = 0·041$, $wR = 0·036$, $w = [\sigma^2(F_o) + 0·0001F_o^2]^{-1}$, $S = 1·12$, $(\Delta/\sigma)_{max} \le 0·01$, max. features in $\Delta\rho$ map $\pm 1·1\,e\,\text{Å}^{-3}$; isotropic extinction parameter $X = 0·00013$ according to the definition of program *SHELX*76 (Sheldrick, 1976). Neutral-atom scattering functions from *International Tables for X-ray Crystallography* (1974). Geometric calculations with program *PARST* (Nardelli, 1982).

Discussion. Final atomic parameters are given in Table 1, bond lengths and angles in Table 2.* The structure contains a $[UO_2(CO_3)_3]^{4-}$ unit, five different cation coordination polyhedra − Na(1)O_6, Na(2)O_3W_4, Sr(1)-

* Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44816 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected bond lengths (Å) and angles (°)*

Na(1)–O(5)	2·43 (1) (6×)	O(5)–Na(1)–O(5)	180 (3×),
			88·0 (5) (6×)
			and 92·0 (5) (6×)
Na(2)–O(1)	2·38 (2) (3×)	O(1)–Na(2)–O(1)	95·2 (6) (3×)
–W(4)	2·80 (3) (3×)	O(1)–Na(2)–W(4)	65·9 (6) (3×),
–W(5)	2·17 (5)		81·0 (6) (3×)
			and 160·0 (6) (3×)
		O(1)–Na(2)–W(5)	121·5 (6) (3×)
		W(4)–Na(2)–W(4)	114·5 (6) (3×)
		W(4)–Na(2)–W(5)	76·2 (4) (3×)
Sr(1)–O(3)	2·62 (1)	Sr(2)–O(5)	2·77 (1)
–O(4)	2·60 (1)	–O(5)	2·67 (1)
–O(6)	2·49 (1)	–O(7)	2·59 (1)
–O(8)	2·52 (1)	–O(9)	2·54 (1)
–O(10)	2·54 (1)	–W(2)	2·30 (2)
–O(11)	2·48 (1)	–W(2)	2·25 (2)
–W(1)	2·87 (1)	–W(3)	2·87 (2)
–W(2)	2·64 (2)	–W(3)	3·00 (2)
Mg–W(1)	2·10 (1) (6×)	W(1)–Mg–W(1)	180 (3×),
			87·5 (6) (6×)
			and 92·5 (6) (6×)
U–O(1)	1·76 (1)	O(1)–U–O(2)	178·9 (9)
–O(2)	1·79 (1)	O(1)–U–[O(3)–O(10)]	84·7 – 93·7 (8)
–O(3)	2·43 (1)	O(2)–U–[O(3)–O(10)]	85·4 – 95·4 (8)
–O(4)	2·42 (1)	O(3)–U–O(4)	52·9 (5)
–O(6)	2·40 (1)	O(4)–U–O(6)	68·9 (5)
–O(7)	2·45 (1)	O(6)–U–O(7)	53·6 (5)
–O(9)	2·43 (1)	O(7)–U–O(9)	66·1 (5)
–O(10)	2·42 (1)	O(9)–U–O(10)	53·2 (5)
		O(10)–U–O(3)	66·5 (5)
C(1)–O(3)	1·30 (2)	O(3)–C(1)–O(4)	113 (1·5)
–O(4)	1·30 (2)	O(3)–C(1)–O(5)	124 (1·5)
–O(5)	1·26 (2)	O(4)–C(1)–O(5)	124 (1·5)
C(2)–O(6)	1·31 (2)	O(6)–C(2)–O(7)	115 (1·5)
–O(7)	1·29 (2)	O(6)–C(2)–O(8)	122 (1·5)
–O(8)	1·26 (2)	O(7)–C(2)–O(8)	123 (1·5)
C(3)–O(9)	1·29 (2)	O(9)–C(3)–O(10)	115 (1·5)
–O(10)	1·29 (2)	O(9)–C(3)–O(11)	123 (1·5)
–O(11)	1·23 (2)	O(10)–C(3)–O(11)	122 (1·5)

Mean bond lengths with dispersion in parentheses

Na(1)–O	2·428 (0)	U–O(1), O(2)	1·774 (17)
Na(2)–O, W	2·528 (266)	U–[O(3)–O(10)]	2·426 (18)
Sr(1)–O, W	2·595 (127)	C–O(all)	1·279 (18)
Sr(2)–O, W	2·625 (261)	C–O(U-bonded)	1·295 (9)
Mg–O	2·100 (0)	C–O(terminal)	1·249 (16)

O_6W_2, Sr(2)O_4W_4 and MgW_6, where W denotes water molecules − and a lattice water molecule W(6). The $[UO_2(CO_3)_3]$ unit and the polyhedra Na(1)O_6, Sr(1)O_6W_2, Sr(2)O_4W_4 and MgW_6 can be regarded as building up sheets parallel to (100), (010) and (001), one of which is shown in Fig. 1. These sheets repeat at intervals of $a/2$ and intersect each other to produce a framework of which the characteristic box-like part comprising 1/8 of the unit cell is shown in Fig. 2. The corners of this box (a subcell with edge length $a/2$) are defined by four Na(1) and four Mg, and its faces by six $[UO_2(CO_3)_3]$ units, Sr(1) and Sr(2). Inside the box are three uranyl oxygens, O(1) and O(2), three Sr(2)-bonded W(3), one Na(2) with three W(4) and one W(5) as terminal ligands, and the water molecule W(6). The remaining molecules W(1) and W(2) bridge between cations on the walls of the box.

The formula of the compound may be written as $Na^{[6]}(Na,\square)_2^{[7]}Sr_6^{[8]}(Sr,Na,\square)_6^{[8]}Mg^{[6]}[UO_2(CO_3)_3]_6 \cdot 28$-$H_2O$. The squares indicate partial vacancies in the cation

sites Na(2) and Sr(2), the latter with mixed occupation by approximately equal amounts of Sr and Na. The vacancies are necessary because the number of cations per formula unit, shown by chemical analysis to be about $0.87Na + 1.40Sr + 0.17Mg = 2.45$, does not match the number of available cation sites, $0.17Na(1) + 0.33Na(2) + 1Sr(1) + 1Sr(2) + 0.17Mg = 2.67$. The consequent disorder in cation site occupation produces notable effects on the rest of the structure. First, all atoms of the $[UO_2(CO_3)_3]$ unit show thermal-vibration ellipsoids which are distinctly elongated perpendicular to the plane of projection of Fig. 1; second, the water molecules $W(2)$ through $W(6)$, most of which are bonded to Na(2) or Sr(2), exhibit strikingly large thermal-vibration parameters and partial occupation cannot be excluded for molecules $W(5)$ and $W(6)$.

Despite the pecularities of the structure the geometry of the $[UO_2(CO_3)_3]$ unit agrees well with previously

studied uranyl carbonates. Typical mean bond lengths of $\langle U{-}O \rangle = 1.783$ (13) Å for uranyl O atoms, $\langle U{-}O \rangle = 2.430$ (18) and $\langle C{-}O \rangle = 1.298$ (9) Å for uranium-bonded carbonate O atoms, and $\langle C{-}O \rangle = 1.251$ (11) Å for terminal carbonate O atoms have been reported (Mereiter, 1986b) and compare reasonably with the figures in Table 2. While the $U(CO_3)_3$ entity of such units is frequently almost flat, it shows a distinct wave-like deformation in the title compound (Fig. 2); the r.m.s. deviation of these atoms from the least-squares plane fitted through them is 0.15 (9) Å.* A similar deformation is known for the $[UO_2(CO_3)_3]$ unit of andersonite, $Na_2Ca[UO_2(CO_3)_3].5-6H_2O$ (Coda, Della Giusta & Tazzoli, 1981), a mineral with a framework structure related to that of the title compound.

The coordination polyhedra of Na(1), Mg and Sr(1) have normal bond lengths. Both $Na(1)O_6$ and MgW_6 octahedra have point symmetry $\bar{3}$ and are almost undistorted. Their links with other coordination polyhedra are outlined in Fig. 3. The $Sr(1)O_6W_2$ polyhedron is a distorted square antiprism comparable in shape and bond lengths with $Sr(O,W)_8$ polyhedra in $SrMg[UO_2(CO_3)_3].12H_2O$ and $Sr_2[UO_2(CO_3)_3].8H_2O$ (Mereiter, 1986a,b). The coordination figures of the partly vacant sites Na(2) and Sr(2) show besides a majority of normal bond distances three which are significantly affected by disorder and are too short by ~ 0.2 Å. This is the case for $Na{-}W(5)$ in the Na(2)-O_3W_4 polyhedron, a distorted monocapped trigonal antiprism, and the two independent $Sr{-}W(2)$ bonds in the $Sr(2)O_4W_4$ polyhedron, a distorted square antiprism. As shown in Fig. 3(a) six of the Sr(2) polyhedra are linked by shared faces into a ring around the Na(1) octahedron. It is not unlikely that the approximately equal amounts of Sr and Na which occupy the Sr(2) positions alternate within this ring.

Among the six independent water molecules only $W(1)$ forms obvious hydrogen bonds. They are directed to O(8) and O(11) at distances of 2.72 (1) and
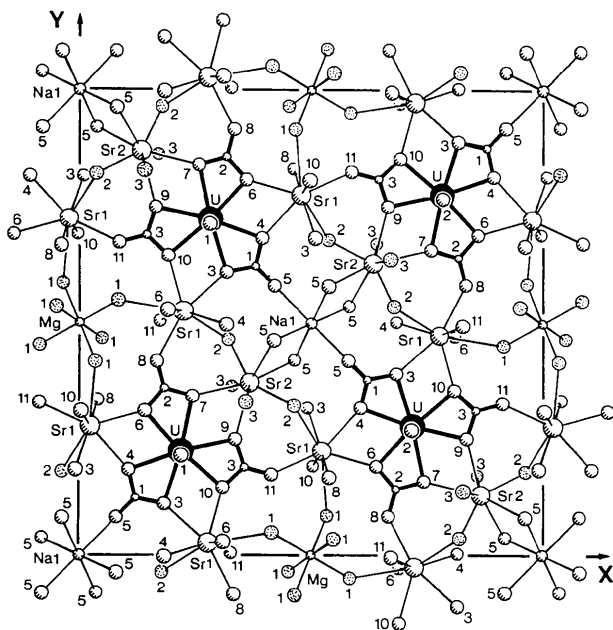

Fig. 1. Sheet-like part of the structure parallel to (001) at $z \sim 0$. Water molecules are dotted.
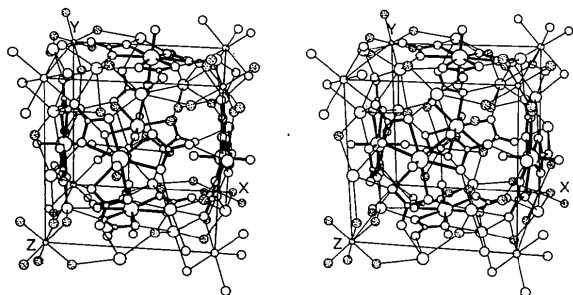
Fig. 2. Stereoscopic view of $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$ the unit cell. Water molecules are dotted.
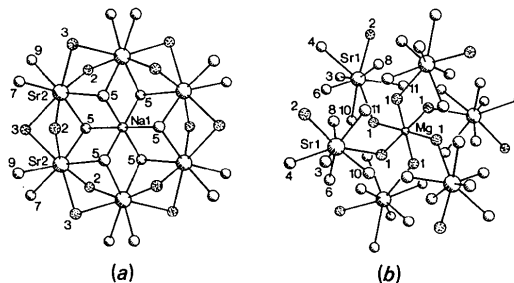

(a)   (b)

Fig. 3. (a) $Na(1)O_6$ octahedron with surrounding $Sr(2)O_4W_4$ polyhedra; (b) MgW_6 octahedron with surrounding $Sr(1)O_6W_2$ polyhedra. Both views along threefold axis, water molecules dotted.

2·65 (1) Å. With one Mg and one Sr(1) they provide the molecule with a tetrahedral coordination. The molecule $W(2)$ forms a bridge between one Sr(1) and two Sr(2), $W(3)$ a bridge between two Sr(2) and $W(4)$ and $W(5)$ are terminal to Na(2). The molecule $W(6)$ is enclosed in a cavity formed by three O(10), three O(11) and one $W(5)$.

The connections between polyhedra in the title compound follow closely those observed in other uranyl carbonates containing Mg, Ca and/or Sr. Typical in this respect are the edge-sharing links between the UO_2O_6 hexagonal bipyramid and the three surrounding $Sr(O,W)_8$ polyhedra (Fig. 1), which correspond to the situation for Ca in schröckingerite, $NaCa_3$-$[UO_2(CO_3)_3](SO_4)F.10H_2O$, or the presence of Mg in the form of MgW_6 octahedra as found for instance in $SrMg[UO_2(CO_3)_3].12H_2O$ (Mereiter, 1986a,c). Three-dimensional interconnections and the arrangement of $[UO_2(CO_3)_3]$ units in the title compound resemble the trigonal-rhombohedral framework structure of andersonite, $Na_2Ca[UO_2(CO_3)_3].5–6H_2O$ (Coda et al., 1981).

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Structure of Caesium Tricarbonatodioxouranate(VI) Hexahydrate

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Abstract. $Cs_4[UO_2(CO_3)_3].6H_2O$, $M_r = 1089·8$, monoclinic, $P2_1/n$, $a = 18·723 (3)$, $b = 9·647 (2)$, $c = 11·297 (2)$ Å, $\beta = 96·84 (1)°$, $V = 2026 (1)$ Å^3, $Z = 4$, $D_x = 3·573$ g cm^{-3}, $\lambda(Mo\,K\alpha) = 0·71069$ Å, $\mu = 147$ cm^{-1}, $F(000) = 1912$, $T = 295$ K, final $R = 0·041$ for 2267 observed reflections. The asymmetric unit contains four independent Cs ions with coordination numbers 9 and 11 (Cs–O < 3·75 Å), one $[UO_2(CO_3)_3]$ unit and six Cs-bonded water molecules. Cs ions and $[UO_2(CO_3)_3]$ units show a layer-like arrangement parallel to $(10\bar{1})$, but on the whole the structure is framework-like with dominating links parallel to (100).

Introduction. The uranyl carbonates $M_4[UO_2(CO_3)_3]$ with $M =$ Tl, NH_4, K, Rb and Cs form a series of isostructural anhydrous salts, the water solubility of which increases considerably in the given order. During attempts to grow the anhydrous Cs salt, analogous to the K and Rb compounds, by room-temperature evaporation of aqueous solutions, the title compound was obtained, recognized to be a hydrate and subjected to a structural study. The existence of this hydrate has not been mentioned in previous works (Bachelet, Cheylan, Douis & Goulette, 1954; Gmelin Handbook of Inorganic Chemistry, 1983). The intended anhydrous caesium uranyl carbonate could be obtained, however, by evaporation crystallization at elevated temperatures. With the Rb compound it will be the subject of a forthcoming publication (Mereiter, Preisinger & Mikenda, 1988).

Experimental. Rectangular plates flattened on (100) and stretched along z, typical dimensions $6 \times 4 \times 0·5$ mm, colour yellow, fluorescence bright yellow-green, stable in humid air, in dry air dehydrating to a whitish matter, readily dissolving in water, grown by room-temperature evaporation of solutions obtained by digesting 10 g $Ag_4[UO_2(CO_3)_3]$ in a solution of 6·7 g CsCl in 60 g H_2O and subsequent removal of the insoluble residue (AgCl) by filtration. X-ray data collection with a lacquer-coated sphere of 0·20 mm diameter on a Philips PW 1100 four-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. Unit-cell dimensions from 72 reflections, $7 < \theta < 23°$. 3585 independent reflections measured with θ–2θ scans, scan width $1 + 0·35\tan\theta$, θ range 2 to 25°,