

Structure of Calcium Selenite(IV) Monohydrate, $\text{CaSeO}_3 \cdot \text{H}_2\text{O}$

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Abstract. $M_r = 185.05$, monoclinic, $P2_1/c$, $a = 7.622(3)$, $b = 6.745(2)$, $c = 7.922(3)$ Å, $\beta = 108.46(3)^\circ$, $V = 386.4(3)$ Å³, $Z = 4$, $D_x = 3.18$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 107.74$ cm⁻¹, $F(000) = 352$, $T = 295$ K, $R = 0.04$ for 1251 observed reflections. The polyhedron around calcium is pentagonal bipyramidal and the selenite group forms a trigonal pyramid with selenium and oxygen atoms at the apices. These pyramids form layers parallel to the bc plane which are connected by hydrogen bonds involving crystal water. The selenite group acts as a bidentate ligand.

Introduction. Although the number of known structures of beryllium-group metals is very large, the only known structure of beryllium-group metals with selenite is magnesium selenite hexahydrate (Weiss, Wendling & Grandjean, 1966). We are confining our study of selenites by turning now to the systematic investigation of beryllium-group selenites.

Experimental. Crystals prepared from selenous acid and calcium nitrate solutions using gel growth technique in sodium silicate gel. The synthesis, analyses, thermal behaviour and IR spectrum of the title compound have been published elsewhere (Losoi & Valkonen, 1985). Experimental details of the structure determination are given in Table 1. Semi-empirical absorption corrections made on the basis of a φ scan with five different 2θ values. The largest measured relative reduction in intensity was from 1.00 to 0.194 indicating a very large absorption. Lp correction applied. Sites of calcium and selenium atoms calculated from the Patterson function and the sites of oxygen atoms from difference Fourier map after refinement of calcium and selenium atoms. Hydrogen atoms could not be found. Max. peak height in final difference Fourier synthesis $1.9 \text{ e } \text{Å}^{-3}$, found in neighbourhood of selenium atom. Calculations made with XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) using scattering factors for neutral atoms (Cromer & Mann, 1968). Refinement based on structure factors and unit weights. Diagrams drawn with ORTEP (part of XRAY system).

Table 1. Conditions of data collection and structure refinement

Crystal size	0.25 × 0.25 × 0.1 mm
Diffractometer	Syntex P2 ₁
Number of reflections in unit-cell determination	15
Range of 2θ in unit-cell determination	5.64–23.01°
Method of data collection	$\theta/2\theta$
Scan speed	2.93° min ⁻¹
Range of 2θ in data collection	5–70°
Min. and max. indices	0,0,–12; 12,10,12
Standard reflection	12 $\bar{1}$, after every 100 th intensity, no significant variation
Number of reflections measured	1841
Number of unique reflections	1841
Number of observed reflections	1251 [$I > 4\sigma(I)$]
Refinement type (on F)	Full-matrix
R (isotropic)	4.8%
R (anisotropic)	4.0%
wR (anisotropic)	5.2%
S	1.92
Max. shift/error in positional parameters after last cycle	0.07

Discussion. Fractional coordinates of atoms in the asymmetric unit are listed in Table 2 and Ca–O and Se–O distances in Table 3.* The coordination polyhedron around calcium is distorted pentagonal bipyramidal with bond distances in agreement with literature values. The ranges of Ca–O distances reported for compounds with pentagonal-bipyramidal structure around calcium are 2.225–3.008 Å for $\text{Ca}_3(\text{PO}_4)_2$ (Mathew, Schroeder, Dickens & Brown, 1977) and 2.285–2.668 Å for $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (Mandel, 1975).

Oxygen atoms O(2), O(2^{II}), O(3^{III}), O(3^{II}) and O(4) (symmetry codes are given in Table 3) form the equatorial plane of the pentagonal bipyramid. The edge lengths of this plane and the central angles and deviations from the least-squares plane are given in Fig. 1. The angle involving capping atoms O(1) and O(3^{IV}) and Ca(1) is 154.58(5)°. Although these results indicate that the polyhedron around calcium is distorted, it can be confirmed to be pentagonal bipyramidal.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42006 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional coordinates with e.s.d.'s in parentheses and equivalent isotropic temperature factors ($\times 10^2$)

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}(\text{\AA}^2)$
Ca(1)	0.9909 (4)	0.13729 (5)	0.34147 (4)	1.01
Se(1)	0.26220 (2)	0.65768 (2)	0.50896 (2)	0.90
O(1)	0.26389 (19)	0.55875 (23)	0.70248 (16)	1.74
O(2)	0.18481 (18)	0.47527 (19)	0.35437 (16)	1.35
O(3)	0.06520 (17)	0.79892 (19)	0.45154 (16)	1.30
O(4)	0.35940 (20)	0.09769 (25)	0.60582 (19)	2.19

Table 3. Interatomic distances (\AA) and angles ($^\circ$) around Se(1)

Ca(1)—O(1 ⁱ)	2.327 (2)	Se(1)—O(1)	1.668 (1)
O(2)	2.365 (2)	O(2)	1.704 (1)
O(2 ⁱⁱ)	2.481 (1)	O(3)	1.714 (1)
O(3 ⁱⁱⁱ)	2.486 (2)		
O(3 ^{iv})	2.396 (2)		
O(3 ^v)	2.511 (1)		
O(4)	2.401 (1)		

O(1)—Se(1)—O(2) 105.77 (7)

O(1)—Se(1)—O(3) 102.56 (7)

O(2)—Se(1)—O(3) 97.80 (6)

Symmetry code: (i) $x, \frac{1}{2} - y, -\frac{1}{2} + z$; (ii) $-x, -\frac{1}{2} + y, \frac{1}{2} - z$; (iii) $x, -1 + y, z$; (iv) $-x, 1 - y, 1 - z$.

The selenite groups form a trigonal pyramid with selenium and oxygen atoms at the apices. Distances and angles as shown in Table 3 are in good agreement with the literature. [See, for example, Valkonen & Leskelä (1978).]

All oxygen atoms of the selenite group are connected to calcium atoms: O(1) is connected to one calcium atom, O(2) to two calcium atoms and O(3) to three. O(2) and O(3) are connected to the same calcium, so that the selenite group acts as a bidentate ligand. That explains the shortest oxygen—oxygen distance (2.575 \AA) in the equatorial plane of the pentagonal bipyramid around Ca(1) in Fig. 1 as well as the smallest angle (62.1 $^\circ$).

The selenite group and CaO_7 group form a layer structure parallel to the *bc* plane as shown in Fig. 2. The oxygen atom O(3) plays a special role in the structure by connecting three calcium atoms and the selenium atom together. The selenite group and CaO_7 group share a common edge, and also two CaO_7 groups are connected through a common edge or common apex.

The layers formed by SeO_3 and CaO_7 groups are connected by hydrogen bonds involving crystal water (Fig. 3). There is one hydrogen bond of 2.803 (2) \AA between O(4) and O(1), and possibly a second hydrogen bond between O(4) and O(2) of length 2.748 (2) \AA . This latter bond is between two CaO_7 polyhedra in the same layer, however. There are no other O(4)⋯O distances less than 3.3 \AA between the layers.

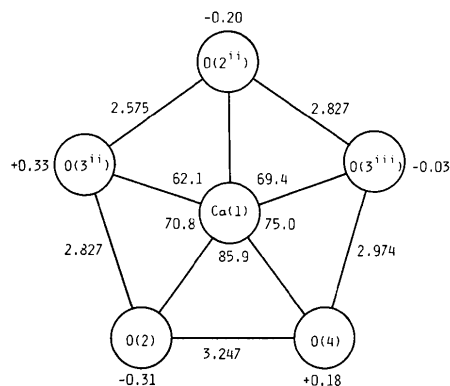


Fig. 1. The equatorial plane of the pentagonal bipyramid around the calcium atom. The O—O distances are in \AA and the e.s.d.'s are less than 0.002 \AA . The O—Ca—O angles are in $^\circ$ and the e.s.d.'s are less than 0.06 $^\circ$. The deviations from the least-squares plane are in \AA and the e.s.d.'s are 0.24 \AA . The calcium atom is 0.02 \AA above the plane.

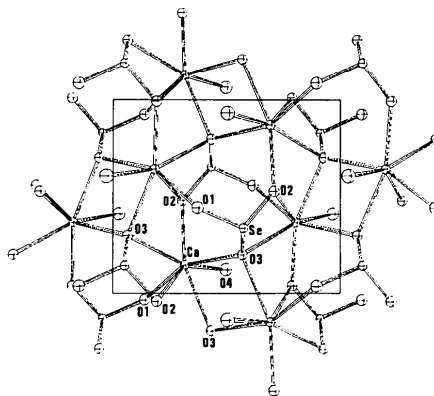


Fig. 2. The layer structure of calcium selenite monohydrate along the *x* axis.

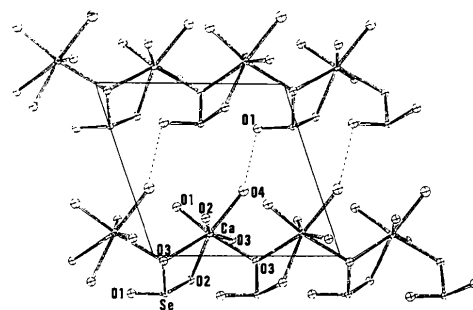


Fig. 3. The layer structure of calcium selenite monohydrate along the *y* axis. For clarity, only one chain of the layer is included in the picture. Broken lines indicate hydrogen bonds.

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Structure de la Roubaultite, $\text{Cu}_2(\text{UO}_2)_3(\text{CO}_3)_2\text{O}_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$

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Abstract. $M_r = 1195$, triclinic, $P\bar{1}$, $a = 7.767$ (3), $b = 6.924$ (3), $c = 7.850$ (3) Å, $\alpha = 92.16$ (4), $\beta = 90.89$ (4), $\gamma = 93.48$ (4)°, $V = 421$ Å³, $Z = 1$, $D_x = 4.71$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 29.85$ mm⁻¹, $F(000) = 534$, $T = 295$ K, final $R = 0.041$ for 2246 reflections. The crystal structure consists of alternate chains of $[\text{Cu}(\text{O},\text{OH},\text{H}_2\text{O})_6]$ distorted octahedra and $[\text{UO}_8]$ and $[\text{UO}_6(\text{OH})]$ hexagonal and pentagonal dipyramids, all parallel to $[010]$ and linked together by hydrogen bonds to form planes parallel to $(10\bar{1})$. Within both types of dipyramid there are two short U–O bonds with the other U–O approximately equal, mean values 2.44 $[\text{UO}_8]$ and 2.35 Å $[\text{UO}_6(\text{OH})]$.

Introduction. La roubaultite, qui provient de la zone d'oxydation du gisement uranifère de Shinkolobwe, Province du Shaba, Zaïre, avait été décrite originellement comme un uranate de cuivre hydraté de formule $\text{Cu}_2(\text{UO}_2)_3(\text{OH})_{10} \cdot 5\text{H}_2\text{O}$ (Cesbron, Pierrot & Verbeek, 1970). L'extrême rareté de ce minéral n'avait permis à l'époque qu'une analyse à la microsonde électronique ainsi qu'une analyse thermogravimétrique effectuée seulement sur 4,72 mg: la perte de poids avait alors été attribuée en totalité au départ de molécules d'eau.

La détermination de la structure atomique, effectuée sur le cristal original, a révélé qu'il s'agissait en fait d'un uranyl carbonate hydraté de cuivre de formule $\text{Cu}_2(\text{UO}_2)_3(\text{CO}_3)_2\text{O}_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. Les deux départs majeurs observés sur le thermogramme (perte totale: 15,04 %) correspondent donc au départ de cinq molécules d'eau puis de deux CO_2 (perte totale: 7,54 + 7,36 = 14,90 %).

Cette modification de formule a été approuvée par la Commission des Nouveaux Minéraux et des noms de minéraux de l'Association Internationale de Minéralogie.

Partie expérimentale. Les paramètres trouvés par Cesbron, Pierrot & Verbeek (1970) étaient: $a = 7,73$, $b = 6,87$, $c = 10,87$ Å; $\alpha = 86,29$, $\beta = 134,12$ et $\gamma = 93,10^\circ$; la matrice de passage aux nouveaux indices est donc

$$\begin{vmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 1 & 0 & 1 \end{vmatrix}$$

Les paramètres de maille du cristal, de dimensions $0,050 \times 0,070 \times 0,164$ mm, affinés sur diffractomètre Philips PW 1100 (anticathode au Mo) à partir de 25 réflexions. Angle $\theta \leq 32^\circ$ ($-11 \leq h \leq 11$, $-10 \leq k \leq 10$, $0 \leq l \leq 11$) avec trois raies de référence ($\bar{3}03$, $\bar{1}\bar{3}\bar{2}$, $30\bar{3}$) mesurées toutes les heures (sans variation); corrections de Lorentz–polarisation, ainsi que celles dues à l'absorption, faites en suivant la méthode analytique de de Meulenaer & Tompa (1965). Sur 3115 réflexions indépendantes, 2246 retenues ($F_o \geq 22,4$ et $\theta \geq 4,2^\circ$). Méthode de l'atome lourd: la fonction de Patterson tridimensionnelle a placé les atomes U(1), U(2) et Cu; autres atomes positionnés par des synthèses de Fourier successives. Affinement des coordonnées atomiques et des coefficients de température effectué par la méthode des moindres carrés (matrice complète) en minimisant la fonction $\sum w(\Delta F)^2$. Les facteurs de