Growth and Structure Refinement of CaSeO₄.2H₂O

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Abstract. CaSeO₄.2H₂O, $M_r = 219\cdot07$, monoclinic, $I2/a$, $a = 5\cdot8377$ (8), $b = 15\cdot521$ (2), $c = 6\cdot595$ (1) Å, $\beta = 116\cdot837$ (9)°, $V = 533\cdot2$ Å³, $Z = 4$, $D_x = 2\cdot729$ g cm⁻³, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 78\cdot57$ cm⁻¹, $F(000) = 424$, $T = 293$ K, $R = 0\cdot0171$ for 468 reflections $(F > 3\sigma F)$. A diffusion-controlled crystal-growth method with subsequent ultrasound twin-crystal cleavage was applied. The gypsum-type structure was confirmed.

Experimental. Precipitated from concentrated solutions, CaSeO₄.2H₂O generally forms small twinned crystals not suitable for single-crystal diffraction techniques (Snyman & Pistorius, 1963). In order to obtain high-quality single crystals gel-growth techniques (Henisch, 1970) were first tried. Owing to the high oxidation power of the selenate(VI) ion agar gels could not be used. The rather high solubility of CaSeO₄.2H₂O in water (70 g l⁻¹) also prevents the application of silica gels (Ca silicates are formed). With bentonite gels and with polyacrylamide gels, which are stable in air, no improvement of the crystal quality could be obtained. Finally, a controlled diffusion process with a diaphragm technique was successful. Common dialysis hoses were used (modified cellulose acetate ester, Visking tubing size 2-18/32″, 13 mm diameter, from Medicell International Ltd, London). The hoses were filled with a half-concentrated aqueous solution of Na₂SeO₄ and placed into a half-concentrated aqueous solution of CaCl₂. After four weeks the crystals growing at the exterior side of the hose were removed and washed with ethanol. The well formed crystals showed typical 'swallow-tail' twinning. The crystals were layered with ethanol and treated with ultra sound for some 30 min. After this procedure single crystals could be selected.

The crystal used for the data collection was mounted on top of a glass thread. A summary of data and structure refinement is given in Table 1.

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Table 1. *Summary of data collection and structure refinement*

Crystal shape	Faces {010}, {110}, (12$\bar{1}$), ($\bar{1}$21), (12$\bar{1}$), ($\bar{1}$21)
Crystal volume (mm³)	7·4492 × 10⁻⁴
Diffractometer	Siemens AED2, graphite-monochromated Mo $K\alpha$ radiation
Determination of cell parameters	
number of reflections used	24
θ range (°)	25–30
Intensity data collection	
max. $\sin\theta/\lambda$ (Å⁻¹)	0·5943
range of h, k, l	$\bar{7}$,0,$\bar{8}$ to 7,18,8
scan mode	ω, variable learnt profile method Clegg (1981)
standard reflections	1,10,1, 20$\bar{4}$, $\bar{2}$6$\bar{2}$
intensity variation (%)	< 1
measured reflections	965
unique reflections	468
observed reflections	468 with $F > 3\sigma_F$
R_{int}	0·0206
Numercial absorption correction	
min./max. transmission	0·497/0·66
Structure refinement (on F)	
$R, wR, w = 0\cdot5747/\sigma^2(F_o)$	0·0171, 0·0145
S	1·54
number of parameters	47
max. final shift/e.s.d.	0·044 for U of atom H(1)
min./max. final $\Delta\rho$ (e Å⁻³)	$-0\cdot39 \leq \Delta \leq 0\cdot28$

Table 2. *Positional and equivalent isotropic displacement parameters for atoms in* CaSeO₄.2H₂O

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	Site	x	y	z	U_{eq}(Å²)
Ca	4(e)	0·75	0·16970 (5)	0	0·0145 (3)
Se	4(e)	0·25	0·32914 (2)	0	0·0121 (2)
O(1)	8(f)	0·2874 (3)	0·3873 (1)	0·2195 (3)	0·0202 (7)
O(2)	8(f)	0·5093 (3)	0·2700 (1)	0·0957 (3)	0·0194 (6)
O(W)	8(f)	0·6449 (4)	0·0684 (2)	0·2113 (4)	0·028 (1)
H(1)	8(f)	−0·051 (6)	0·418 (2)	0·245 (5)	0·04 (1)†
H(2)	8(f)	0·656 (7)	0·022 (2)	0·231 (6)	0·05 (1)†

† Isotropically refined.

The initial positions of Ca and Se were obtained from the structure model of gypsum CaSO₄.2H₂O (Cole & Lancucki, 1974) after shifting the origin $-\frac{1}{4}$, $-\frac{1}{4}$, $-\frac{1}{4}$ in order to achieve the special position 4(e) in the setting given in *International Tables for*

Crystallography (Hahn, 1983). Subsequent ΔF synthesis yielded the positions of the O and H atoms. The positions of the latter could be refined isotropically without any constraints. Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The program used was *SHELX*76 (Sheldrick, 1978). Atomic parameters are given in Table 2,* bond lengths and some important bond angles in Table 3. A projection plot of the isotypic gypsum-type structure is given elsewhere (Cole & Lancucki, 1974).

Related literature. A discussion of the structural relationships between some phases with gypsum-type structure like $CaSO_4.2H_2O$ (Cole & Lancucki, 1974), $CaSeO_4.2H_2O$ (present work) and $Y_{1-x}(Gd,Dy,Er)_xPO_4.2H_2O$ (Seidel, Sowa, Reithmayer, Schulz, Krüger & Abriel, 1991) will be published in due course (Krüger & Abriel, 1991).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54045 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond lengths (Å) and bond angles (°)*

Ca—O(W)	2× 2·358 (2)		O(2)–O(1)	2·573 (2)
—O(2)	2× 2·365 (2)		—O(2)	2·695 (2)
—O(2)	2× 2·565 (2)		—O(2)	2·703 (2)
—O(1)	2× 2·643 (1)		—O(1)	2·718 (2)
Se–O(2)	2× 1·634 (1)		O(W)–H(2)	0·73 (4)
—O(1)	2× 1·635 (2)		—H(1)	0·75 (2)
O(1)—O(2)	2·573 (2)		H(1)—H(2)	1·16 (4)
—O(2)	2·718 (2)		—O(1)	2·11 (2)
—O(1)	2·727 (2)			
—O(W)	2·844 (2)		H(2)—O(1)	2·12 (4)
—O(W)	2·846 (3)			
O(2)—Se—O(2)	111·59 (8)		H(2)—O(W)—H(1)	103 (3)
O(2)—Se—O(1)	2× 112·49 (6)			
O(2)—Se—O(1)	2× 103·79 (7)			
O(1)—Se—O(1)	112·96 (9)			

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Structure of Tripotassium Hexahydrogenhexamolybdoaluminate(III) Heptahydrate

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Abstract. $K_3H_6[AlMo_6O_{24}].7H_2O$, $M_r = 1236.06$, monoclinic, $P2_1/a$, $a = 11.392$ (1), $b = 11.273$ (1), $c = 22.354$ (2) Å, $\beta = 94.69$ (1)°, $V = 2861.0$ (8) Å^3, $Z = 4$, $D_x = 2.87$ g cm^{-3}, Mo $K\alpha$ radation (graphite monochromator, $\lambda = 0.71069$ Å), $\mu = 30.7$ m^{-1}, $F(000) = 2360$, $T = 296$ K, $R = 0.068$ ($wR = 0.068$) for 3642 reflections with $I_o > 4.00\sigma(I_o)$. The $H_6[AlMo_6O_{24}]^{3-}$ polyanion is a typical Anderson-type heteropolyanion. The Mo—O distances range from 1.67 to 2.32 Å. The AlO_6 octahedron is almost regular and mean Al—O bond distances range from 1.89 to 1.92 Å.

Experimental. Colorless, monoclinic crystals of $K_3H_6[AlMo_6O_{24}].7H_2O$ were obtained by mixing $AlCl_3$ and K_2MoO_4 solution in the molar ratio Al:Mo = 1:6, by adjusting the pH to 3–4 with dilute HCl solution (Hall, 1907; Baker, Foster, Tan,