

Fig. 2. Configuration of the non-framework constituents Na, O(2), D(1) and D(2) within the sodalite cage of the structure of $(\text{Na}_3\text{Q})_2[\text{AlSiO}_4]_6 \cdot 8\text{D}_2\text{O}$. Only two six-membered rings of the aluminosilicate framework are shown, Si and Al atoms omitted for clarity. Dashed lines show the hydrogen bonding between one of the H atoms of the hydrate water [D(1)—O(1) = 1.94 (4) Å] and the framework O atoms. It is this hydrogen bond which makes this structure different from the hydrates of the basic hydrosodalite phases $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_x \cdot n\text{H}_2\text{O}$ ($0 \leq x \leq 2$; $0 < n \leq 4$), which give no evidence for hydrogen bonding from corresponding diffraction studies. Dashed circles indicate positional disorder of symmetry-equivalent D(1) and D(2) atoms.

Because of the large value of the temperature factor of the D(2) atom, the enlarged angle D(1)—O(2)—D(2) = 113 (2)° and the contact distances of the H atoms and the Na ions, there is some evidence for

positional disorder or considerable dynamical behaviour of the D(2) atoms with respect to the remaining non-framework constituents. For verification of these findings special NMR and quasielastic neutron scattering experiments are now being carried out.

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Structure of Caesium Hydrogenselenate

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Abstract. CsHSeO_4 , $M_r = 276.9$, monoclinic, $P2_1/c$, $a = 7.977(4)$, $b = 8.409(4)$, $c = 7.803(6)$ Å, $\beta = 111.37(5)^\circ$, $V = 487.4$ Å³, $Z = 4$, $D_x = 3.77$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 15.6$ mm⁻¹, $F(000) =$

488, $T = 299(1)$ K, final $R = 0.047$ and $wR = 0.062$ for 1020 non-zero reflexions. The crystal is not isomorphous with any other MHSeO_4 or MHSO_4 crystal. The separated chains of asymmetric hydrogen bonds run parallel to the c axis. The O...O distance utilized in the hydrogen bonding is 2.603 (15) Å.

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Introduction. CsHSeO₄ belongs to a family of MXO₄-type crystals ($X = S$ or Se , $M = NH_4^+$, K^+ , Rb^+ , Cs^+) exhibiting interesting properties and phase transitions. The first report on phase transitions of CsHSeO₄ indicates DTA anomalies at 400, 521 and 673–743 K (Foose & Mitra, 1977). The phase transition at the lowest temperature is accompanied by a large entropy change, which is comparable with that associated with the phase transition of CsHSO₄ at 413 K (Yokota, Takanoashi, Osaka & Makita, 1982; Komukae, Osaka, Makita, Ozaki, Itoh & Nakamura, 1981). Optical and X-ray examinations of CsHSeO₄ (Yokota & Makita, 1982; Yokota, 1982) showed that this crystal undergoes an improper ferroelastic phase transition at 401 K (T_c). It was also found (Yokota, 1982) that CsHSeO₄ is tetragonal above T_c and monoclinic (space group $P2_1/c$) below T_c . The CsHSeO₄ crystal is not isomorphous with CsHSO₄ which is also monoclinic, but belongs to another space group, $P2_1/m$ (Itoh, Ozaki & Nakamura, 1981). Thus, a knowledge of the crystal structure of CsHSeO₄ at room temperature is very desirable in order to explain its interesting physical properties.

Experimental. Single crystals of CsHSeO₄ were grown at 303 K by slow evaporation from an aqueous solution containing Cs₂SeO₄ and H₂SeO₄ in equimolar ratio (Yokota, 1982). The crystals were transparent and formed polygonal plates parallel to the (100) cleavage plane. D_m was not measured. Systematic absences on Weissenberg photographs uniquely indicated the space group $P2_1/c$, as was reported by Wolak & Czaplá (1981), but contrary to Yokota, Takanoashi, *et al.* (1982) who reported the space group as $P2/c$.

A small specimen was cut from a large single crystal and shaped into an ellipsoid ($0.15 < 2R < 0.25$ mm) by polishing using water. The sample thus prepared was sealed in a glass capillary. Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation for lattice parameters (14 reflexions in range $22 < 2\theta < 29^\circ$) and intensity measurements; 2θ - ω scan technique, 2905 reflexions measured below $\theta = 30^\circ$ (h 0→11, k -11→11, l -10→10); after each group of 50 reflexions two standards measured, variation 15%; most of the calculations performed on a Nova 1200 computer with locally modified XTL/XTLE programs (Syntex, 1976); neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); real and imaginary components of anomalous dispersion included for all atoms; structure solved by direct methods; O atoms from difference map; an absorption correction following the DIFABS procedure (Walker & Stuart, 1983) applied on isotropically refined data; min. and max. absorption correction 0.588 and 1.312; the symmetry-related reflexions were averaged after DIFABS; $R_{int} = 0.025$. Full-matrix refinement based on F (Se, Cs and O anisotropic) for 1020 reflexions with $I \geq 3.0\sigma(I)$,

Table 1. *The final atom coordinates and equivalent isotropic thermal parameters of caesium hydrogen-selenate*

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

	x	y	z	$B_{eq}(\text{\AA}^2)$
Cs	0.2099 (1)	0.1285 (2)	0.2062 (2)	1.55
Se	0.7452 (2)	0.1261 (2)	0.2786 (2)	1.15
O(1)	0.5689 (13)	0.2182 (14)	0.1125 (16)	2.67
O(2)	0.8965 (14)	0.2599 (13)	0.3653 (15)	2.48
O(3)	0.6505 (13)	0.0644 (12)	0.4186 (14)	2.13
O(4)	0.8112 (16)	-0.0191 (13)	0.1876 (16)	3.20

$w = 1/\sigma^2(F_o)$, gave $R = 0.047$ and $wR = 0.062$; maximum least-squares Δ/σ 0.01 (six strongest reflexions suffered from strong extinction and were omitted from the calculations). Highest peaks in final difference synthesis $2.5 e \text{\AA}^{-3}$ around Cs and $1.5 e \text{\AA}^{-3}$ around Se, but the H atom was not determined.

The final atomic parameters are given in Table 1.*

Discussion. Some interatomic distances and angles are presented in Table 2. As depicted in Fig. 1, the crystal is built up from separate chains of hydrogen-bonded selenate ions. These chains run parallel to the c axis, the O(1)···O(3^b) distance being 2.603 (15) Å. The structure is not isomorphous with those of ferroelectric RbHSeO₄ (Wařkowska, Olejnik, Łukaszewicz & Głowiak, 1978; Wařkowska, Olejnik, Łukaszewicz & Czaplá, 1980; Roziere, Brach & Jones, 1983) and NH₄HSeO₄ (Kruglik, Misjul & Aleksandrov, 1980; Aleksandrov, Kruglik, Misjul & Simonov, 1980) nor with that of nonferroelectric KHSeO₄ (Baran & Lis, 1986). The structure of CsHSeO₄ is different from that of CsHSO₄ (Itoh *et al.*, 1981) where the chains of centrosymmetric hydrogen bonds [O···O = 2.572 (7) Å] run along the monoclinic b axis. The hydrogen bonds in CsHSeO₄ are asymmetric. This follows from a comparison of the Se–O bonds. The Se–O(3) bond [1.623 (10) Å] is significantly shorter than the Se–O(1) bond [1.711 (11) Å] and longer than Se–O(2) [1.608 (11) Å] and Se–O(4) [1.595 (11) Å]. The Se–O distances correspond to those in RbHSeO₄ (Wařkowska *et al.*, 1978; Roziere *et al.*, 1983), NH₄HSeO₄ (Kruglik *et al.*, 1980) and KHSeO₄ (Baran & Lis, 1986).

The Cs atoms are surrounded by nine O atoms at distances of 3.06 (1)–3.37 (1) Å which correspond to those in CsHSO₄ (Itoh *et al.*, 1981). The three further distances are 3.647 (11), 3.899 (11) and 4.052 (10) Å.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43608 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Principal interatomic distances (Å) and bond angles (°) for CsHSeO₄*

Se—O(1)	1.711 (11)	O(1)—Se—O(2)	106.6 (6)
Se—O(2)	1.608 (11)	O(1)—Se—O(3)	101.5 (6)
Se—O(3)	1.623 (10)	O(1)—Se—O(4)	108.8 (6)
Se—O(4)	1.595 (11)	O(2)—Se—O(3)	113.7 (6)
O(1)···O(3 ^{iv})	2.603 (15)	O(2)—Se—O(4)	113.8 (6)
		O(3)—Se—O(4)	111.4 (6)

Symmetry code: (i) $x, 0.5-y, z-0.5$.

Cs—O(1)	3.291 (11)	Cs—O(1 ⁱ)	3.899 (11)
—O(1 ⁱⁱ)	3.647 (11)	—O(2 ⁱⁱⁱ)	3.358 (11)
—O(2 ^{iv})	3.208 (10)	—O(2 ^v)	3.059 (11)
—O(3)	3.339 (11)	—O(3 ^v)	4.052 (10)
—O(3 ^{vi})	3.173 (10)	—O(4 ⁱⁱⁱ)	3.368 (13)
—O(4 ^v)	3.099 (10)	—O(4 ⁱⁱⁱ)	3.152 (12)

Symmetry code: (i) $1-x, y-0.5, 0.5-z$; (ii) $x, 0.5-y, 0.5+z$; (iii) $x-1, y, z$; (iv) $x-1, 0.5-y, z-0.5$; (v) $1-x, 0.5+y, 0.5-z$; (vi) $1-x, -y, 1-z$; (vii) $1-x, -y, -z$.

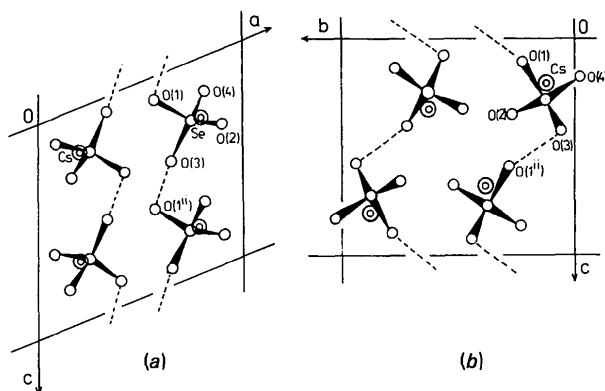


Fig. 1. Projections of the CsHSeO₄ crystal structure on (a) the *ac* plane and (b) the *bc* plane. [Symmetry code: (ii) $x, 0.5-y, 0.5+z$.]

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KGdNb₆Cl₁₈: Nouveau Chlorure Quaternaire de Niobium à Cluster Octaédrique Nb₆

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Abstract. $M_r = 1391.9$, trigonal, $R\bar{3}$, $a = 10.0494$ (8) Å, $\alpha = 54.950$ (5)°, $V = 633.30$ (9) Å³, $Z = 1$, $D_x = 3.65$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 71.83$ cm⁻¹, $F(000) = 635$, room temperature. The structure was solved by direct methods and refined by least squares to $R = 0.024$ for 1089 independent reflections. The structure is built up with

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Note added in proof: The recently published structure of CsDSO₄ (Merinov, Baranov, Maximov & Shuvalov, 1986) appears to be isomorphous with that of CsHSeO₄ and different from that of CsHSO₄ (Itoh *et al.*, 1981).

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(Nb₆Cl₆)Cl₆ units, linked to each other by Gd atoms lying in an almost regular chlorine octahedron. The K atoms surrounded by twelve Cl atoms are in statistical occupancy (0.5).

Introduction. La chimie des halogénures de niobium et de tantale de basse valence comporte de nombreux