Table 3. *Comparison of the distortion indices* (*Baur*, 1974) *in four chlorapatites*

| | $Ba_5Cl(PO_4)_3$ | $Sr_5Cl(PO_4)_3$ (1) | $Ca_5Cl(PO_4)_3$ (2) | $Cd_5Cl(PO_4)_3$ (3) |
|---|---|---|---|---|
| DI(PO) | 0·002 | 0·002 | 0·003 | 0·005 |
| DI(OO) | 0·014 | 0·018 | 0·020 | 0·024 |
| DI(OPO) | 0·011 | 0·012 | 0·013 | 0·013 |

References: (1) Sudarsanan & Young (1974); (2) Mackie *et al.* (1972); (3) Sudarsanan *et al.* (1973).

These values are given in Table 3 along with those of other chlorapatites for comparison. Among the metal ions which form the apatite structure, the ionic radius of $Ba^{2+}$ is the largest and gives the smallest distortion of the $PO_4$ tetrahedron.

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## References

BAUR, W. H. (1974). *Acta Cryst.* **B30**, 1195–1215.

COPPENS, S. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.

ENGEL, G., PRETZSCH, J., GRAMLICH, V. & BAUR, W. H. (1975). *Acta Cryst.* **B31**, 1854–1860.

HATA, M., OKADA, K., IWAI, S., AKAO, M. & AOKI, H. (1978). *Acta Cryst.* **B34**, 3062–3064.

*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.

MACKIE, P. E., ELLIOTT, J. C. & YOUNG, R. A. (1972). *Acta Cryst.* **B28**, 1840–1848.

SUDARSANAN, K. & YOUNG, R. A. (1969). *Acta Cryst.* **B25**, 1534–1543.

SUDARSANAN, K. & YOUNG, R. A. (1974). *Acta Cryst.* **B30**, 1381–1386.

SUDARSANAN, K., YOUNG, R. A. & DONNAY, J. D. H. (1973). *Acta Cryst.* **B29**, 808–814.

TOKONAMI, M. (1965). *Acta Cryst.* **19**, 486.

WUENSCH, B. J. & PREWITT, C. T. (1965). *Z. Kristallogr.* **122**, 24–59.

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*Acta Cryst.* (1979). B**35**, 2384–2386

# Orthorhombic Oxonium Hydrogenselenate*

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**Abstract.** $[H_3O]^+[HSeO_4]^-$, orthorhombic, *Pbca*, $Z = 8$, $a = 8{\cdot}4958$ (2), $b = 10{\cdot}4528$ (2), $c = 9{\cdot}1307$ (1) Å, m.p. 296·8 K. X-ray intensities were recorded at 223 K. Refinement with 780 observed data gave $R_w(F^2) = 0{\cdot}056$. The structure contains $HSeO_4^-$ ions hydrogen bonded to each other to form chains with $O-H\cdots O$ lengths of 2·751 (3) Å, and $H_3O^+$ ions hydrogen bonded to $HSeO_4^-$ ions. The $OH_3^+\cdots O$ bonds are 2·571 (3), 2·577 (3) and 2·632 (3) Å.

**Introduction.** The present investigation forms part of a series of systematic studies of crystalline hydrates of strong acids in progress at this Institute. One of our objectives is to study the geometry of the oxonium ion in different environments. Neutron diffraction studies of oxonium *p*-toluenesulphonate, where the $H_3O^+$ environment has virtually threefold symmetry, and oxonium trifluoromethanesulphonate, with an asymmetric environment around $H_3O^+$, have been reported by Lundgren & Williams (1973) and Lundgren, Tellgren & Olovsson (1978). A neutron diffraction study of the present compound is in progress.

Anhydrous selenic acid was prepared by the oxidation of selenous acid with hydrogen peroxide (Gilbertson & King, 1936). Crystals of the monohydrate grown from a selenic acid–water solution (molar ratio 1:1) were purified by recrystallization. The final product contained only 0·10% selenous acid. Crystals used for the X-ray work were grown in capillaries filled with an acid–water (1:1) solution. Crystallization could be induced in the capillaries only in the presence of seed crystals of the monohydrate. These were taken from a larger batch where crystallization was more readily attainable. At least two modifications of the monohydrate were found to exist: an orthorhombic form with a melting point of 296·8 K in agreement with literature values (297 K, Meyer &

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* Hydrogen Bond Studies. CXXXVII. Part CXXXVI: Lundgren (1979*a*).

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Aulich, 1928), and a triclinic form with a melting point of ~290 K. Seed crystals from the low-melting-point batch always gave triclinic crystals; the other batch always gave the orthorhombic modification. The structure of the orthorhombic form is presented here.

Cell dimensions and intensities were measured at 223 K on a Stoe–Philips semi-automatic two-circle diffractometer [graphite-monochromatized Cu $K\alpha$ radiation, $\lambda(\mathrm{Cu}\ K\alpha_1) = 1{\cdot}54051$ Å, $\lambda(\mathrm{Cu}\ K\alpha_2) = 1{\cdot}54433$ Å]. The cell dimensions were determined by least-squares refinement from the measured $2\theta$ values of 50 reflexions from two different crystals mounted around [100] and [010]. The intensities of 798 independent reflexions from a crystal mounted around [100] (layers $0kl$ to $8kl$) were recorded in the equi-inclination $\omega$-scan mode with a variable scan range. The crystal was cylindrical with a diameter of 0·15 mm and a length of 0·15 mm. Four test reflexions were monitored at regular intervals within each layer. No systematic variations were observed for their intensities, except for two very strong zero-layer reflexions where the intensities increased during the data collection. This was probably due to an increase in crystal mosaicity, with a consequent decrease in extinction.

A complementary set of 229 independent reflexions (layers $h0l$ to $h2l$) was similarly measured at 223 K from a crystal mounted around [010]. This set was used only to determine the relative scale factors between layers in the previous data set.

The data were corrected for Lorentz, polarization and absorption effects [$\mu$(calc.) = 12·17 mm$^{-1}$]. Standard deviations, $\sigma_c(I)$, of the intensities were estimated from Poisson counting statistics.

The structure was solved by Patterson techniques and refined by full-matrix least squares with *UPALS*. The function minimized was $\sum w(F_o^2 - F_c^2)^2$, where $w^{-1} = \sigma_c^2(F_o^2) + (0{\cdot}01F_o^2)^2$. After refinement with anisotropic temperature factors, the H atoms were located on a difference map calculated from data with $\sin\theta/\lambda < 0{\cdot}4$ Å$^{-1}$. In the final cycles, 72 parameters were varied; these included one overall scale factor, an isotropic extinction parameter, coordinates for all atoms, anisotropic thermal parameters for the non-hydrogen atoms and isotropic temperature factors for the H atoms. A refinement including 783 reflexions with $F_o^2 > 0$ gave $R(F^2) = \sum |F_o^2 - F_c^2|/\sum F_o^2 = 0{\cdot}045$, $R_w(F^2) = [\sum w(F_o^2 - F_c^2)/\sum wF_o^4]^{1/2} = 0{\cdot}056$ and $R(F) = \sum |F_o - F_c|/\sum F_o = 0{\cdot}025$. The standard deviation of an observation of unit weight was $s = 1{\cdot}94$. Five strong low-angle reflexions with extinction-correction factors $>2{\cdot}0$ were not included in the final refinements. The refined value of the isotropic extinction parameter $g$ was $0{\cdot}53\ (2) \times 10^4$ (Coppens & Hamilton, 1970).

Table 1. *Atomic coordinates for non-hydrogen atoms* ($\times 10^5$)

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| Se | 39114 (4) | 26578 (3) | 3874 (3) |
| O(1) | 24601 (26) | 34189 (19) | 11324 (22) |
| O(2) | 37008 (27) | 11268 (21) | 3966 (21) |
| O(3) | 43178 (27) | 32575 (19) | −12098 (21) |
| O(4) | 55531 (32) | 29927 (23) | 14014 (22) |
| O($w$) | 20448 (28) | 1472 (19) | 30827 (24) |

Scattering factors for Se$^0$ and O$^0$ were from Hanson, Herman, Lea & Skillman (1964). The spherical scattering factors of Stewart, Davidson & Simpson (1965) were used for H. Anomalous-dispersion corrections were included for the non-hydrogen atoms (Cromer & Liberman, 1970). The programs used for all computations with IBM 370/155, IBM 1800 and NORD-10 computers have been described by Lundgren (1979*b*). The final positional parameters for the non-hydrogen atoms are given in Table 1.*

**Discussion.** A stereoscopic illustration of the structure is shown in Fig. 1. Bond distances involving non-hydrogen atoms are included in Fig. 2 and are listed with angles in Table 2. The structure is composed of $H_3O^+$ and $HSeO_4^-$ ions linked together by hydrogen bonds to form puckered layers perpendicular to [100]. The shortest interatomic distance between different layers is the contact O(4)···O(1), 2·810 (3) Å. This might be regarded as a weak hydrogen bond, although the H···O(1) distance (2·58 Å) and the O(4)–H···O(1) angle (105°) do not satisfy the generally accepted geometrical requirements for hydrogen bonding

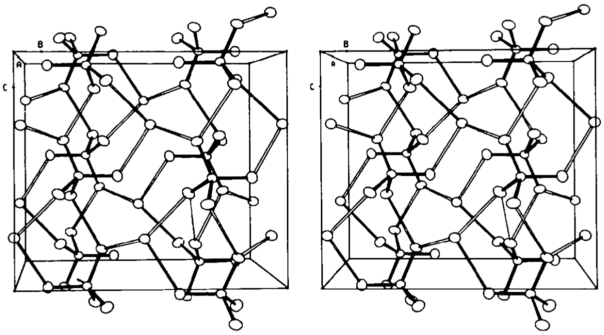

Fig. 1. Stereoscopic *ORTEP* (Johnson, 1965) illustration of the crystal structure of $[H_3O]^+[HSeO_4]^-$ (H atoms have been omitted). Covalent bonds are filled; hydrogen bonds open. The short contact O(4)···O(1) between different hydrogen-bonded layers, which is not considered to be a hydrogen bond, is indicated by a single line. The thermal ellipsoids are scaled to enclose 50% probability.

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* Lists of structure factors, thermal parameters and H-atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34578 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

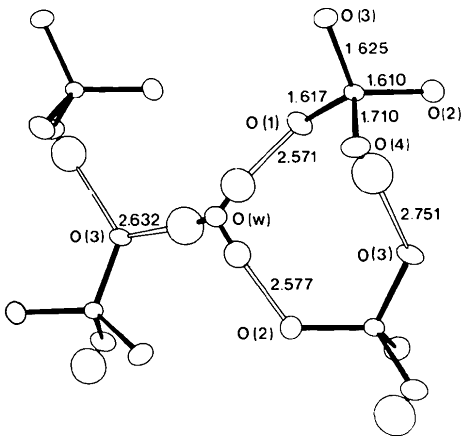

Fig. 2. Bond distances (Å) and hydrogen-bonding scheme. H-atom positions and thermal parameters are as obtained from the refinement. The distances refer to non-hydrogen atoms. Thermal ellipsoids enclose 50% probability.

Table 2. *Interatomic distances* (Å) *and angles* (°) *involving non-hydrogen atoms*

(*a*) Covalent bonds

| | | | |
|---|---|---|---|
| Se—O(1) | 1·617 (2) | O(1)—Se—O(2) | 113·7 (1) |
| Se—O(2) | 1·610 (2) | Se—O(3) | 110·5 (1) |
| Se—O(3) | 1·625 (2) | Se—O(4) | 107·1 (1) |
| Se—O(4) | 1·710 (3) | O(2)—Se—O(3) | 114·3 (1) |
| | | Se—O(4) | 106·9 (1) |
| | | O(3)—Se—O(4) | 103·5 (1) |

(*b*) Hydrogen bonds

| | | | |
|---|---|---|---|
| O(*w*)···O(1) | 2·571 (3) | O(1)···O(*w*)···O(2) | 104·2 (1) |
| ···O(2) | 2·577 (3) | O(*w*)···O(3) | 119·7 (1) |
| ···O(3) | 2·632 (3) | O(2)···O(*w*)···O(3) | 107·9 (1) |
| O(4)···O(3) | 2·751 (3) | O(4)···O(3)···O(*w*) | 112·7 (1) |
| [O(4)···O(1) | 2·810 (3)] | Se—O(1)···O(*w*) | 120·8 (1) |
| | | Se—O(2)···O(*w*) | 122·5 (1) |
| | | Se—O(3)···O(*w*) | 108·0 (1) |
| | | Se—O(3)···O(4) | 127·6 (1) |
| | | Se—O(4)···O(3) | 91·2 (1) |
| | | [Se—O(4)···O(1) | 159·5 (1)] |
| | | [Se—O(1)···O(4) | 134·3 (1)] |

(H···O ≤ 2·4 Å, ∠O—H···O ≳ 130°). The corresponding values for the hydrogen bond within the layer [2·751 (3) Å] are H···O(3) 2·14 Å, O(4)—H···O(3) 164°.

In the $HSeO_4^-$ ion the Se—OH bond, 1·710 (3) Å, is 0·1 Å longer than the Se—O bonds. The Se—O bonds are not exactly equal: the longest bond, 1·625 Å, is to O(3), which is the only O atom to accept two hydrogen bonds. The HO—Se—O angles are smaller than the O—Se—O angles; the average values are 105·8 and 112·8° respectively.

The oxonium ion is hydrogen bonded to three different $HSeO_4^-$ ions in a pyramidal arrangement, with an average O···O(*w*)···O angle of 110·6°. The mean O(*w*)···O distance, 2·59 Å, is near the average value of 2·57 Å found in a number of oxonium salts (Lundgren & Olovsson, 1976).

Distances and angles involving H atoms, though inaccurately measured, are reasonable. The O—H distances and H—O—H angles within $H_3O^+$ are 0·77, 0·84, 0·90 (5) Å and 100, 114 and 117 (5)° respectively. The O—H distance in $HSeO_4^-$ is 0·64 (6) Å. The hydrogen bonds appear to be almost linear in most cases: the O—H···O angles are all >170°, except for O(4)—H···O(3) (164°).

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## References

Coppens, P. & Hamilton, W. C. (1970). *Acta Cryst.* A**26**, 71–83.
Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
Gilbertson, L. I. & King, G. B. (1936). *J. Am. Chem. Soc.* **58**, 180.
Hanson, H. P., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* **17**, 1040–1044.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
Lundgren, J.-O. (1979*a*). *Acta Cryst.* B**35**, 780–783.
Lundgren, J.-O. (1979*b*). *Crystallographic Computer Programs*. Report UUIC-B13-4-04. Institute of Chemistry, Univ. of Uppsala.
Lundgren, J.-O. & Olovsson, I. (1976). *The Hydrogen Bond*, edited by P. Schuster, G. Zundel & C. Sandorfy. Amsterdam: North-Holland.
Lundgren, J.-O., Tellgren, R. & Olovsson, I. (1978). *Acta Cryst.* B**34**, 2945–2947.
Lundgren, J.-O. & Williams, J. M. (1973). *J. Chem. Phys.* **58**, 788–796.
Meyer, J. & Aulich, W. (1928). *Z. Anorg. Allg. Chem.* **172**, 321–343.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.