and are stacked alternately at a half period of the c axis. These diameters are considerably larger than those of one-dimensional tunnels in the other compounds, *e.g.* beryl (~5·2 Å), K_xWO_3 (~5·5 Å) and priderites (~5·3 Å) (Watanabe, Fujiki, Kanazawa & Tsukimura, 1986). If one assumes 1·40 Å for the oxygen radius, the net diameter of the present tunnels is 3·4 Å, comparable to the effective size of the eight-coordinated Cs ion (Shannon, 1976). It is suggested that such ions as K and Rb have no virtual bottlenecks for their translation in the tunnels, which is very interesting from the viewpoint of one-dimensional ion conduction phenomena. This subject will be described elsewhere in comparison with the hollandite-type tunnels in priderites (Watanabe, Sasaki, Kitami & Fujiki, 1986).

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References

BURSILL, L. A. (1979). *Acta Cryst.* B**35**, 530–538.
FINGER, L. W. & PRINCE, E. (1975). *Natl Bur. Stand. (US) Tech. Note* No. 854.
GELLER, S. (1960). *J. Chem. Phys.* **33**, 676–684.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
LLOYD, D. J., GREY, I. E. & BURSILL, L. A. (1976). *Acta Cryst.* B**32**, 1756–1761.
SAKURAI, T. (1967). *Universal Computation Program System (UNICS)*. Tokyo: The Crystallographic Society of Japan.
SASAKI, S. (1982). *RADY*. Programs derived from *ORFLS* and *RADIEL*. State Univ. New York, Stony Brook.
SHANNON, R. D. (1976). *Acta Cryst.* A**32**, 751–767.
WADSLEY, A. D. (1964). *Non-Stoichiometric Compounds*, edited by L. MANDELCORN, pp. 98–209. New York: Academic Press.
WATANABE, M., FUJIKI, Y., KANAZAWA, Y. & TSUKIMURA, K. (1986). *J. Solid State Chem.* In the press.
WATANABE, M., SASAKI, T., KITAMI, Y. & FUJIKI, Y. (1986). *J. Solid State Chem.* In the press.
WUENSCH, B. J. & PREWITT, C. T. (1965). *Z. Kristallogr.* **1**, 24–59.
YOSHIKADO, S. (1987). In preparation.
YOSHIKADO, S., OHACHI, T., TANIGUCHI, I., ONODA, Y., WATANABE, M. & FUJIKI, Y. (1983). *Solid State Ionics*, **9/10**, 1305–1310.

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Single-Crystal Neutron Diffraction Study of Hydrogen Bonding in Selenic Acid

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Abstract. H_2SeO_4, $M_r = 144{\cdot}98$, orthorhombic, $P2_12_12_1$, $Z = 4$, $F(000) = 94{\cdot}8 \times 10^{-15}$ m, λ(neutron) $= 1{\cdot}1757\,(1)$ Å, $\mu = 0{\cdot}11$ mm^{-1}. $T = 243$ K: $a = 8{\cdot}476\,(5)$, $b = 8{\cdot}123\,(5)$, $c = 4{\cdot}585\,(4)$ Å, $V = 315{\cdot}7$ Å^3, $D_x = 3{\cdot}05$ Mg m^{-3}. $T = 80$ K: $a = 8{\cdot}449\,(5)$, $b = 8{\cdot}118\,(5)$, $c = 4{\cdot}588\,(4)$ Å, $V = 314{\cdot}7$ Å^3, $D_x = 3{\cdot}06$ Mg m^{-3}. 519 ($T = 243$ K) and 308 ($T = 80$ K) diffractometer data; final $R = 0{\cdot}052$, $wR = 0{\cdot}051$ (243 K) and $R = 0{\cdot}032$, $wR = 0{\cdot}041$ (80 K). Hydrogen atoms were located and well ordered at both temperatures. Tetrahedral SeO_4 groups are connected by hydrogen bonds with O···O distances of 2·615 (5) and 2·621 (4) Å at 243 K to four neighbouring groups and form layers parallel to (100).

Introduction. The crystal structure of selenic acid was determined by Bailey & Wells (1951) from X-ray data. A neutron diffraction study on polycrystalline H_2SeO_4 (Moodenbaugh, Hartt, Hurst, Youngblood, Cox & Frazer, 1983) reported hydrogen positions determined by profile analysis at 330 and 10 K. Our investigation was already in progress when the results of Moodenbaugh *et al.* became available. The aim of our study was essentially the same as that of the previous one: determination of hydrogen positions and search for a possible order–disorder transition.

Experimental. Single crystals of selenic acid were obtained following a procedure described by Gilbertson & King (1936). Selenic acid with some water (Merck) was used as starting material and dried for several days by pumping dry air over the liquid. Final crystallization was achieved by seeding the liquid at room temperature in a dry glove-box. The crystal used for data collection was deliquescent and of irregular shape with dimensions 3 × 2 × 2 mm. It was sealed in a glass capillary and mounted in a closed-loop Displex cryostat. Data collection was performed on the four-circle $P32$ diffractometer at the reactor Siloë of the CENG, wavelength $\lambda = 1{\cdot}1757\,(1)$ Å from Cu(200),

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cell parameters refined from setting angles of 15 reflections in the range $15 < \theta < 40°$ at both temperatures. An $\omega/2\theta$ scan technique was used and data were collected up to $\sin\theta/\lambda = 0{\cdot}69$ Å^{-1} (about 0·60 Å^{-1} at 80 K); range in hkl: 0→11, 0→11, −6→0; the absorption coefficient was calculated ($\mu = 0{\cdot}11$ mm^{-1}) but no correction was applied; Lorentz correction. The standard reflection was $\bar{2}2\bar{2}$ at 243 K and $22\bar{2}$ at 80 K, measured every 50 reflections; no intensity fluctuations exceeding 2σ were observed. 569 measured reflections (243 K) and 337 (80 K) yielded 519 and 308 unique reflections; weights were assigned to individual reflections according to $w(I) = 1/\sigma(I)^2$ where $\sigma(I)$ is from counting statistics, all reflections used in refinement. The *XRAY* package of computer programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used for all calculations with neutron scattering lengths (units of 10^{-15} m): $b_{Se} = 7{\cdot}95$, $b_O = 5{\cdot}803$, $b_H = 3{\cdot}7409$ (Koester, 1977). The hydrogen positions were derived from difference Fourier maps and refined anisotropically. Final shift/e.s.d. was 0·01. 243 K: $R = 0{\cdot}052$, $wR = 0{\cdot}051$, $S = 2{\cdot}1$; 80 K: $R = 0{\cdot}032$, $wR = 0{\cdot}041$, $S = 1{\cdot}5$. 65 parameters refined in each case. Positional and thermal parameters are listed in Table 1.*

Discussion. No structural phase transition was detected between 80 and 243 K. According to the neutron powder data of Moodenbaugh *et al.* (1983) the structure remains unchanged down to 10 K. The crystal structure and the hydrogen bonds are presented in Fig. 1. The structure consists of SeO_4 tetrahedra which are linked together by relatively strong hydrogen bonds within layers perpendicular to [100]. Our results confirm the basic structure proposed by Bailey & Wells (1951) and Moodenbaugh *et al.* (1983) but detailed inspection of distances and angles (Table 2) reveals considerable differences in all interatomic distances compared with the two previous determinations. The Se—OH bonds are about 0·1 Å longer than the Se—O bonds, whereas they were almost equal in the previous determinations. The difference is, however, in agreement with selenium–oxygen distances in the $HSeO_4^-$ anion in oxonium hydrogen selenate (Lundgren & Taesler, 1979).

The unit-cell volume changes only slightly between 243 and 80 K; only the decrease in a is appreciable. It is remarkable that the distances are somewhat longer at low temperature. We therefore performed a librational analysis of rigid-molecule motion using the method of

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43478 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters (estimated standard deviations in parentheses) and equivalent isotropic thermal parameters* (Å^2)

$U_{eq} = \frac{1}{3}$ trace **U**.

First row 243 K, second row 80 K.

	x	y	z	U_{eq}
Se	0·3675 (2)	0·2110 (2)	0·5669 (3)	1·59
	0·3675 (2)	0·2109 (2)	0·5655 (3)	1·33
O(1)	0·5161 (3)	0·1291 (4)	0·7192 (7)	3·03
	0·5179 (3)	0·1283 (3)	0·7201 (6)	2·02
O(2)	0·2867 (3)	0·1118 (3)	0·3092 (5)	2·39
	0·2864 (3)	0·1110 (3)	0·3054 (5)	1·73
O(3)	0·2333 (4)	0·2663 (4)	0·8174 (5)	2·75
	0·2317 (3)	0·2665 (3)	0·8170 (4)	1·82
O(4)	0·4152 (4)	0·3918 (3)	0·4168 (6)	2·74
	0·4145 (3)	0·3921 (3)	0·4120 (5)	1·86
H(1)	0·2512 (6)	0·2060 (7)	0·0047 (9)	3·48
	0·2509 (5)	0·2065 (6)	0·0062 (7)	2·88
H(2)	0·4527 (7)	0·4737 (7)	0·5612 (15)	4·18
	0·4527 (5)	0·4752 (6)	0·5587 (10)	3·24

Table 2. *Bond distances with corrections for thermal vibration* (Å) *and angles* (°) *for* H_2SeO_4

	243 K		80 K	
	uncorr.	corr.	uncorr.	corr.
Se—O(1)	1·587 (3)	1·594	1·603 (3)	1·608
Se—O(2)	1·585 (3)	1·595	1·597 (3)	1·603
Se—O(3)	1·678 (3)	1·686	1·688 (3)	1·695
Se—O(4)	1·672 (2)	1·678	1·679 (3)	1·684
O(1)—O(2)	2·708 (4)		2·732 (2)	
O(1)—O(3)	2·682 (4)		2·703 (3)	
O(1)—O(4)	2·685 (5)		2·710 (4)	
O(2)—O(3)	2·685 (4)		2·705 (3)	
O(2)—O(4)	2·570 (4)		2·572 (4)	
O(3)—O(4)	2·606 (4)		2·622 (3)	
O(3)—H(1)	1·001 (5)	1·004	1·008 (4)	1·011
O(4)—H(2)	0·991 (7)	0·996	1·004 (5)	1·009
O(1)—Se—O(2)	117·2 (2)		117·3 (2)	
O(1)—Se—O(3)	110·5 (2)		110·4 (1)	
O(1)—Se—O(4)	110·9 (2)		111·4 (2)	
O(2)—Se—O(3)	110·7 (2)		110·8 (2)	
O(2)—Se—O(4)	104·2 (2)		103·5 (1)	
O(3)—Se—O(4)	102·1 (2)		102·3 (1)	
Se—O(3)—H(1)	110·7 (3)		110·5 (3)	
Se—O(4)—H(2)	113·1 (4)		112·6 (1)	

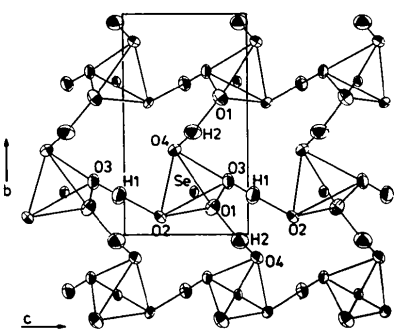

Fig. 1. The crystal structure of H_2SeO_4 at 80 K projected on the *bc* plane.

Table 3. *Hydrogen-bonding scheme* (*first row* 243 K, *second row* 80 K)

D—H···*A*	*D*···*A*	*D*—H	H···*A*	∠*D*—H···*A*
O(3)—H(1)···O(2)	2·621 (4) Å	1·001 (5) Å	1·620 (6) Å	177·8 (5)°
	2·613 (3)	1·008 (4)	1·605 (4)	178·4 (5)
O(4)—H(2)···O(1)	2·615 (5)	0·991 (7)	1·636 (7)	168·8 (5)
	2·617 (4)	1·004 (5)	1·623 (5)	168·6 (5)

Schomaker & Trueblood (1968). Although the difference in bond lengths is reduced (Table 2) the higher-temperature structure still has the shorter bond lengths. An oxygen–oxygen correction could not be carried out because the structure becomes 'polymeric' if sufficiently large atomic radii are included. This indicates that H_2SeO_4 is not 'rigid' enough to be treated as a discrete molecule.

The hydrogen-bonding scheme (Table 3) indicates medium to strong hydrogen bonds according to the criteria proposed by Ferraris and co-workers (Chiari & Ferraris, 1982; Ferraris, Fuess & Joswig, 1986). The basic features of the hydrogen-bonding scheme confirm the results of Moodenbaugh *et al.* (1983). The donor–hydrogen–acceptor angle is near to 180° [177·8 (5) and 168·8 (5)°] and the H···O distances are 1·620 (6) and 1·636 (7) Å at 243 K. The shortest interlayer contact is between O(1) and O(3) and is 2·936 (3) Å, which indicates van der Waals contact.

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References

BAILEY, M. & WELLS, A. F. (1951). *J. Chem. Soc.* **217**, 968–973.

CHIARI, G. & FERRARIS, G. (1982). *Acta Cryst.* B**38**, 2331–2341.

FERRARIS, G., FUESS, H. & JOSWIG, W. (1986). *Acta Cryst.* B**43**, 253–258.

GILBERTSON, L. I. & KING, G. B. (1936). *J. Am. Chem. Soc.* **58**, 180.

KOESTER, L. (1977). *Neutron Physics. Springer Tracts in Modern Physics*, Vol. 80, edited by G. HÖHLER. Berlin: Springer-Verlag.

LUNDGREN, J. O. & TAESLER, I. (1979). *Acta Cryst.* B**35**, 2384–2386.

MOODENBAUGH, A. R., HARTT, J. E., HURST, J. J., YOUNGBLOOD, R. W., COX, D. E. & FRAZER, B. C. (1983). *Phys. Rev. B*, **28**, 3501–3505.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The *XRAY72* system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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Structure de $Li_3In_2P_3O_{12}$

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Abstract. Lithium indium phosphate, $M_r = 535{\cdot}4$, monoclinic, $P2_1/n$, $a = 8{\cdot}592$ (2), $b = 8{\cdot}908$ (2), $c = 12{\cdot}290$ (3) Å, $\beta = 90{\cdot}0$ (2)°, $V = 940{\cdot}65$ (4) Å^3, $Z = 4$, $D_x = 3{\cdot}78$ Mg m^{-3}, Ag $K\bar{\alpha}$, $\lambda = 0{\cdot}5608$ Å, $\mu = 2{\cdot}06$ mm^{-1}, $F(000) = 992$, room temperature, R factor 2·3% for 1582 reflections. The structure of $Li_3In_2P_3O_{12}$ consists of InO_6 octahedra and PO_4 tetrahedra. Two octahedra groups, $In(1)O_6$ and $In(2)O_6$, are linked together by sharing oxygen corners with three PO_4 tetrahedra forming, *via* In—O—P bonds, an infinite three-dimensional framework $[In_2P_3O_{12}]$. The three lithium ions are found in highly distorted tetrahedra, one LiO_4 tetrahedron sharing corners with two different InO_6 groups and two other LiO_4 groups sharing edges with the same InO_6 octahedra.

Introduction. L'étude de la variation de la conductivité ionique des composés de formule générale $Li_{1+x}Ti_{2-x}In_xP_3O_{12}$ en fonction de x (Li Shi-Chun & Lin Zu-Xiang, 1983) a montré l'existence d'une phase de faible concentration en indium, $x \simeq 0{,}3$, présentant une conductivité comparable à celle du Nasicon [$Na_3Zr_2Si_2PO_{12}$, $\sigma T \simeq 10^{-3}$ $(\Omega\,\text{cm})^{-1}$ à 573 K]. L'étude cristallographique (Hamdoune, Gondrand & Tran Qui, 1986) a montré que les diagrammes de poudres de ces phases peuvent être indexés dans le système rhomboédrique pour $0 \le x \le 0{,}4$ (en fait les résultats récents de nos études structurales ont clairement indiqué que la phase avec $x = 0{,}1$ a la symétrie monoclinique, $C2/c$). En poursuivant la caracterisation (par la technique des monocristaux) des phases plus riches en indium nous avons montré que ces composés deviennent orthorhombiques, *Pbca*, pour $0{,}4 \le x \le 1{,}0$ et pour une plus grande concentration en indium, $x > 1$, ils adoptent la symétrie monoclinique $P2_1/n$ (Hamdoune, Tran Qui & Schouler, 1986). Dans le cadre d'une étude générale sur

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