A neutron diffraction study of potassium trihydrogen selenite, KH3(SeO3)2. By B. Prelesnik and R. Herak,

Solid State Laboratory, Institute of Nuclear Sciences 'Boris Kidrich', Vincha, Belgrade, P.O. Box 522, *Yugoslavia,* and
Lj. Manojlović-Muir and K. W. Muir, *Chemistry Department, University of Glasgow, Glasgow G* 12, 8 *QQ, Scotland*

Neutron-diffraction analysis of the title compound, based on 509 reflexions, led to a conventional *R*
of 0·124. The hydrogen bonding network derived from X-ray analysis was confirmed.

Potassium trihydrogen selenite, $KH_3(SeO_3)_2$, undergoes a phase transition involving a change in dielectric properties at $-61.6°C$ (Shuvalov, Ivanov & Sitnik, 1967). The crystal structure of its room-temperature phase was determined by X-ray methods (Hansen, Hazell & Rasmussen, 1969). It was found that the selenite ions are held together by two OHO bonds and a hydrogen-bonding network was proposed. The shorter bond involves oxygen atoms related by a twofold symmetry axis and at an O···O distance of 2·567 Å. Since it is believed that the longest O···O distance in a symmetric O···H···O bond is about 2·55 Å (Hamilton & Ibers, 1968), it was assumed that the hydrogen atom participating in this bond is statistically distributed in two symmetry-related positions, and it was suggested that the dielectric anomalies of the salt at low temperatures may result from an ordering of this atom. To determine structural parameters of the hydrogen atoms with a higher precision we have undertaken a neutron-diffraction study of the same phase of the compound.

The crystals were prepared by slow evaporation of an equimolar aqueous solution of SeO_2 and K_2CO_3. The dimensions of the orthorhombic unit cell, $a=16.152$ (5), $b=6.249$ (2) and $c=6.307$ (2) Å, and the space group *Pbcn*, were those determined by Hansen *et al.* (1969). The intensity measurements were made on a MAN diffractometer, operated manually at the RA reactor at Vincha. The crystal used was of approximate dimensions $0.3 \times 0.4 \times 0.6$ cm. The neutron wavelength was 1·020 Å. The integrated intensities of all independent reflexions with $\sin \theta < 0.7$ were measured by the $\theta-2\theta$ scan technique. The 509 intensities, which were significantly above background, were reduced to structure amplitudes in the usual way. Absorption and extinction corrections were not applied. The coherent neutron-scattering amplitudes employed were those of the Neutron Diffraction Commission, IUCr (1969).

The structural model refined initially, and based on non-hydrogen atoms only, was that determined by X-ray analysis. Positions of the two crystallographically non-equivalent hydrogen atoms were revealed by a subsequent Fourier synthesis of nuclear density. Although the map showed only one negative peak, at $0,y,\frac{1}{4}$, for the hydrogen atom participating in the shorter OHO bond [atom H(2)], two structural models were further considered. In the ordered model the atom H(2) was placed at the twofold axis, and in the disordered model it was statistically distributed in two positions slightly displaced from this axis. Each model was refined by full-matrix least-squares calculations, first with isotropic and later with anisotropic thermal parameters for all atoms. As in the other neutron-diffraction studies of strong and possibly symmetric hydrogen bonds (McGaw & Ibers, 1963), the two refinements converged with practically the same *R* index: 0·124 and 0·123 for ordered and disordered models respectively. The thermal-motion parameters of the H(2) atom are physically reasonable in each model. For all other atoms, the final

structural parameters are the same, the differences being within one standard deviation. Hence the atomic parameters presented in Table 1, with the exception of those involving the H(2) atom, refer to one model only (ordered).

Table 1. *Final atomic parameters with corresponding standard deviations*

The temperature factor was of the form:

$$\exp\left[-10^{-4}(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})\right].$$

(*a*) Fractional coordinates

	x	y	z
K	$\frac{1}{2}$	0·1889 (16)	$\frac{1}{4}$
Se	0·1516 (2)	0·1883 (4)	0·2125 (5)
O(1)	0·1113 (3)	0·3881 (7)	0·0711 (9)
O(2)	0·0670 (3)	0·1119 (8)	0·3581 (9)
O(3)	0·2070 (3)	0·3235 (9)	0·4067 (9)
H(1)	0·1723 (7)	0·4388 (18)	0·4667 (20)
H(2)	0	0·1292 (23)	$\frac{1}{4}$
H(2)¹*	0·011 (3)	0·129 (3)	0·280 (9)

(*b*) Vibrational parameters

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	22 (4)	114 (25)	49 (27)	0	11 (8)	0
Se	9 (1)	69 (7)	50 (9)	7 (2)	3 (2)	2 (5)
O(1)	16 (1)	104 (12)	68 (14)	−2 (3)	−4 (3)	35 (8)
O(2)	13 (2)	154 (13)	71 (15)	−7 (3)	8 (3)	23 (9)
O(3)	16 (1)	155 (14)	118 (15)	3 (3)	−27 (4)	−33 (11)
H(1)	35 (4)	212 (26)	165 (32)	−29 (8)	−33 (9)	44 (21)
H(2)	71 (12)	123 (32)	328 (65)	0	119 (25)	0
H(2)¹	35 (27)	136 (33)	72 (146)	−3 (13)	18 (31)	4 (36)

* H(2) and H(2)¹ refer to the same atom in ordered and disordered models respectively.

We have recently become aware of another, and more accurate, neutron-diffraction study of this compound, carried out by Lehmann & Larsen (1971). The results of the two analyses are in very good agreement. They confirm the crystal structure of the compound, the environment of the potassium ion, the geometry of the selenite group, and the proposed hydrogen bonding network of Hansen *et al.* The geometry of the OHO bonds has been elaborated by Lehmann & Larsen and will not be discussed here.

The calculations were carried out on Vincha CDC 3600 and Chilton Atlas computers.

References

Hamilton, W. C. & Ibers, J. A. (1968). *Hydrogen Bonding in Solids*. New York: Benjamin.
Hansen, F., Hazell, R. G. & Rasmussen, S. E. (1969). *Acta Chem. Scand.* **23**, 2561.
Lehmann, M. S. & Larsen, F. K. (1971). *Acta Chem. Scand.* **25**, 3859.
McGaw, B. L. & Ibers, J. A. (1963). *J. Chem. Phys.* **39**, 2677.
Neutron Diffraction Commission, IUCr. (1969). *Acta Cryst.* A**25**, 391.
Shuvalov, L. A., Ivanov, N. R. & Sitnik, T. K. (1967). *Kristallografiya,* **12**, 366.