Structure of Ferroelastic $K_3H(SeO_4)_2$

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Abstract. Tripotassium hydrogenbis(selenate), $K_3H(SeO_4)_2$, $M_r = 404.2$, monoclinic, $A2/a$, $a = 10.1291$ (8), $b = 5.9038$ (5), $c = 14.961$ (1) Å, $\beta = 103.640$ (8)°, $V = 869.5$ (1) Å^3, $Z = 4$, $D_x = 3.086$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0.71073$ Å, $\mu = 9.86$ mm^{-1}, $F(000) = 760$, $T = 299$ K, $R(F) = 0.0294$ for 1670 unique reflections. $K_3H(SeO_4)_2$ is isomorphous with most $M_3H(XO_4)_2$-type crystals ($M = $ K, Rb and Cs; $X = $ S and Se); two SeO_4 groups are connected by a crystallographically symmetric hydrogen bond into a dimer. The bond distances and angles in the SeO_4 group are similar to those in $Rb_3H(SeO_4)_2$ and $Rb_3D(SeO_4)_2$. The hydrogen-bond length, 2.524 (5) Å, is the shortest among the members of the $M_3H(SeO_4)_2$ family exhibiting the low-temperature phase transition.

Introduction. $K_3H(SeO_4)_2$ (abbreviated TKHSe) belongs to a family of hydrogen-bonded crystals with general formula $M_3H(XO_4)_2$. At room temperature all the members are ferroelastic and isomorphous with space group $A2/a$, except for $Cs_3H(SeO_4)_2$ (TCHSe) and $Cs_3D(SeO_4)_2$ (TCDSe) with space group $C2/m$ [see references in Ichikawa, Gustafsson & Olovsson (1991)]. Above room temperature they undergo a ferroelastic transition at 339–456 K to the same trigonal ($R\bar{3}m$) paraelastic and superionic phase [see, for example, Baranov, Tregubchenko, Shuvalov & Shchagina (1987); Merinov, Baranov & Shuvalov (1990)]. Below room temperature where our present interest lies, $K_3H(SO_4)_2$, $Rb_3H(SO_4)_2$ and $Rb_3H(SeO_4)_2$ (TRHSe) do not exhibit any phase transition down to 4.2 K, whereas other members apparently do, ranging from 20 K in $K_3H(SeO_4)_2$ (Endo, Kaneko, Osaka & Makita, 1983) to 180 K in

$Cs_3D(SeO_4)_2$ (Ichikawa *et al.*, 1991). These characteristics make the $M_3H(XO_4)_2$-type crystals suitable for systematic studies of the structure and phase transitions. Especially, because of the lowest transition temperature, $K_3H(SeO_4)_2$ occupies an important position for studies of the correlation between the transition temperature and hydrogen bonding. In this context, as part of our systematic structural studies of $M_3H(XO_4)_2$-type crystals, the structure of $K_3H(SeO_4)_2$ has been investigated by X-rays at 299 K.

Experimental. The preparation of crystals has been described by Endo *et al.* (1983). A spherically shaped crystal of diameter 0.29 (4) mm with a ferroelastic single domain was used. Intensity data were collected on a Rigaku AFC-3 automatic four-circle X-ray diffractometer at the Institute of Solid State Physics, the University of Tokyo. Graphite monochromator; ω–2θ scan; $\Delta\omega = (1.5 + 0.5\tan\theta)°$; $4 < 2\theta < 70°$ (h $-16 \to 15$, k $0 \to 9$, l $0 \to 24$); $(\sin\theta/\lambda)_{max} = 0.807$ Å^{-1}. 1970 measured reflections were averaged to 1670 unique observed reflections $[|F_o| > 3\sigma(|F_o|)]$; $wR_{int} = 0.009$. Five standard reflections were monitored every 50 reflections. The data were corrected for Lp and absorption effects (transmission factors 0.16–0.19) and for stability by least squares from the variations of the standard reflections [McCandlish, Stout & Andrews (1975) correction factors 1.0–1.0014]. An examination of the diffraction symmetry and systematic absences confirmed the same space group $A2/a$ as most of the $M_3H(XO_4)_2$-type crystals. The unit-cell parameters were determined by least-squares fit of the θ values of 40 reflections in the range $9.3 < \theta < 11.2°$.

The least-squares refinement was started with the room-temperature structure of $Rb_3D(SeO_4)_2$ (Ichikawa, Gustafsson & Olovsson, 1992a). The

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Table 1. *Fractional coordinates* ($\times 10^5$) *and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j U_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
K(1)	25000	75538 (18)	0	2.02 (1)
K(2)	65190 (7)	73701 (13)	19654 (5)	2.78 (1)
Se	46014 (3)	23210 (5)	11609 (2)	1.53 (1)
O(1)	39881 (25)	1293 (38)	15747 (16)	2.73 (3)
O(2)	43475 (24)	18139 (41)	184 (14)	2.86 (3)
O(3)	62361 (19)	24982 (46)	15443 (15)	1.97 (3)
O(4)	38256 (26)	46412 (40)	12910 (17)	3.70 (3)
H	50000	0	0	9.8 (26)

Table 2. *Bond distances* (Å) *and angles* (°)

Bond distances have not been corrected for thermal motion, except for Se—O distances where the riding-model corrected values are also given in the second row. Symmetry operations: (i) x, $1 + y$, z; (ii) $1 - x$, $-y$, $-z$; (iii) $1 - x$, $1 - y$, $-z$; (iv) $1 - x$, $\frac{1}{2} - y$, $\frac{1}{2} - z$; (v) $1 - x$, $\frac{3}{2} - y$, $\frac{1}{2} - z$; (vi) $\frac{1}{2} + x$, $1 - y$, z; (vii) $\frac{3}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$.

K-atom coordination

K(1)—O(1^i)	×2	2.909 (2)	K(2)—O(1^i)	2.977 (3)
—O(2^i)	×2	3.131 (3)	—O(1^{iv})	3.077 (3)
—O(2^{iii})	×2	3.222 (2)	—O(1^{iv})	2.782 (3)
—O(3^{iii})	×2	2.894 (2)	—O(2^{iii})	2.930 (2)
—O(4)	×2	2.696 (3)	—O(3)	2.944 (3)
Average		2.970 (93)*	—O(3^i)	3.092 (3)
			—O(3^{vii})	2.785 (2)
			—O(4)	3.124 (3)
			—O(4^{vi})	3.000 (3)
			—O(4^v)	3.236 (3)
			Average	2.995 (46)

SeO$_4$ ion

Se—O(1)	1.620 (2)	O(1)—Se—O(2)	105.3 (1)
	1.632	—Se—O(3)	111.6 (1)
—O(2)	1.694 (2)	—Se—O(4)	113.0 (1)
	1.707	O(2)—Se—O(3)	105.5 (1)
—O(3)	1.623 (2)	—Se—O(4)	108.0 (1)
	1.636	O(3)—Se—O(4)	112.8 (1)
—O(4)	1.614 (2)	Average	109.4 (1.5)
	1.627		
Average	1.638 (19)		
	1.651 (19)		

		Hydrogen bond	
O(1)—O(2)	2.635 (3)	O(2)···O(2^{ii})	2.524 (5)
—O(3)	2.682 (3)		
—O(4)	2.696 (3)		
O(2)—O(3)	2.641 (3)		
—O(4)	2.677 (3)		
O(3)—O(4)	2.696 (3)		
Average	2.671 (11)		

$$* \ \sigma(\bar{d}) = \{[\Sigma(d - \bar{d})^2]/n(n - 1)\}^{1/2}.$$

function minimized was $\Sigma w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(|F_o|)$. Anisotropic displacement parameters were used for non-H atoms and an isotropic parameter for the H atom. 62 parameters were refined. A type-I isotropic extinction parameter (0.13×10^4) with Gaussian distribution resulted in the best agreement between observed and calculated data (maximum correction factor 1.27 for $\overline{2}04$). In the final refinement, eight reflections were omitted because of large differences between calculated and observed intensities, probably owing to instrument

trouble. Refinement converged at $R(F) = 0.0294$, $wR(F) = 0.0275$, $S = 3.17$ for 1719 non-zero reflections; maximum $(\Delta/\sigma) = 0.002$, and maximum and minimum heights in the final $\Delta\rho$ map $= 0.73$ and -0.93 e Å^{-3}. The calculations were performed using a program system described by Lundgren (1983) and *ORTEP*II (Johnson, 1976) on a MicroVAX computer. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Final positional and displacement parameters are given in Table 1.* Interatomic distances and angles are given in Table 2; a riding-model correction for thermal motion has also been made for SeO$_4$ and is given in Table 2. The projection of the structure along **b** is shown in Fig. 1.

Discussion. The structure of $K_3H(SeO_4)_2$ is built up of hydrogen-bonded SeO$_4$ dimers and K cations (Fig. 1). There are two kinds of K atoms: K(1)
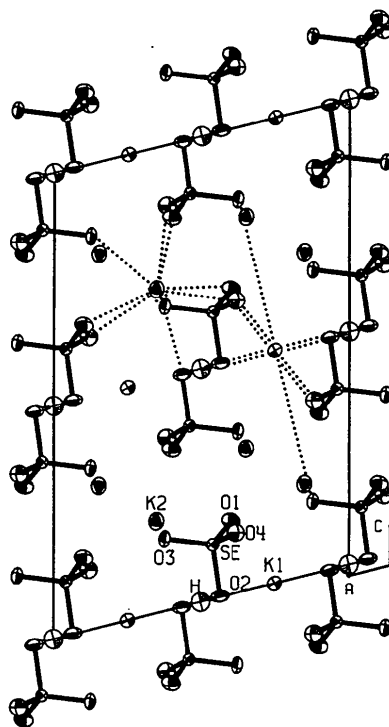

Fig. 1. The *b*-axis projection of the structure of $K_3H(SeO_4)_2$. Dotted lines indicate short K···O distances (doubled ones denote that the K···O distances are superposed).

occupies a special position on a twofold axis; K(2) is at a general position. Both types of K atoms are surrounded by ten O atoms. The K—O distances in each coordination polyhedron are shown by dotted lines in Fig. 1. The K—O distances in each KO_{10} polyhedron in TKHSe are more scattered than those in TRHSe and TRDSe.

The two SeO_4 groups in the dimer are related by a centre of symmetry, at which the H atom is located or positionally disordered. The large B value of the H atom appears to favour the disordering (Table 2). The dimensions and systematic trends in distortion from a regular tetrahedron of the SeO_4 anion, as shown from the bond lengths and angles, are close to those in TRHSe and TRDSe [for detailed discussion consult Ichikawa *et al.* (1992*a*)]. Furthermore, a trend among the values of the equivalent isotropic displacement parameters and the disk-like anisotropy in the O(2)(H) and O(3) atoms are similarly observed in the Rb and Cs analogues [see the deposited list of anisotropic displacement parameters and Ichikawa, Gustafsson & Olovsson (1992*b*)].

The hydrogen-bond distance $O(2) \cdots O(2^{ii})$ is 2.524 (5) Å. This value is the shortest among the members of the $M_3H(SeO_4)_2$ family exhibiting a low-temperature phase transition. That also means that $K_3H(SeO_4)_2$ with the shortest hydrogen bond has the lowest transition temperature. We thus expect that a linear relation between the transition temperature and hydrogen-bond distance at T_c is also valid for the $M_3H(SeO_4)_2$ family (Ichikawa, Motida & Yamada, 1987). Structure analysis at 30 K is now in progress, which will give us the definite conclusion to the validity of the linear correlation.

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A Neutron Powder Diffraction Study of HIO₃ and DIO₃

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Abstract. The crystal structures of hydrogen iodate, HIO_3, and its deuterated form, DIO_3, have been refined using the Rietveld method from neutron powder-diffraction data; $\lambda = 1.470$ (1) Å, $T = 295$ K, $P2_12_12_1$, $Z = 4$; HIO_3: $M_r = 175.91$, $a = 5.5448$ (3), $b = 5.8829$ (3), $c = 7.7434$ (4) Å, $V = 252.59$ (4) Å^3, $D_x = 4.64$ g cm^{-3}, $\mu = 0.72$ cm^{-1}, $9 \le 2\theta \le 118.7°$ in 1372 steps, $R_p = 1.51\%$, $R_{wp} = 1.92\%$, GOF = 1.38, $R_F = 0.32\%$ (274 Bragg reflections) and 36 refined parameters; DIO_3: $M_r = 176.91$, $a = 5.5408$ (4), $b =$