The Crystal Structure of K₂SeO₄

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Potassium selenate crystallizes in the orthorhombic space group *Pnam* with $a=7.661\pm0.004$, $b=10.466\pm0.008$, $c=6.003\pm0.003$ Å. Refinement of the structure, which is isomorphous with β -K₂SO₄, has been carried out by the method of least squares with anisotropic vibrational parameters. *R* decreased to 4.8% for 334 independent reflexions measured on an automatic diffractometer. The structure is built of fairly regular SeO₄²⁻ tetrahedra, with a mean vibrationally-corrected Se-O bond length of 1.648 ± 0.010 Å, and K⁺ cations in two different oxygen environments.

Introduction

The crystal structure studies of the orthoselenates in the literature are mostly limited to the determination of the crystal data, which indicate, however, the important fact that their structures are generally isomorphous with those of the corresponding sulphates (Aurivillius & Malmros, 1961; Gattow, 1960, 1962; Kokkoros, 1938; Madar, 1960; Pistorius, 1966; Pistorius & Pistorius, 1962). Only a few structure analyses have been completed: H_2SeO_4 (Bailey & Wells, 1951), Na₂SeO₄ (Náray-Szabó & Argay, 1963) and Cu(NH₃)₂SeO₄ (Morosin, 1969). There is also the structure determination of Se₄O₁₂ (Mijlhoff, 1965). These results, limited in number and accuracy, indicate the need for further determinations of selenate structures in order to improve the understanding of bonding in tetrahedral oxyanions.

The lattice parameters of K₂SeO₄ were originally determined by Koch-Holm & Schönfeldt (1927). In their description of the orthorhombic K₂CrO₄, Zachariasen & Ziegler (1931) listed K₂SeO₄ as one of several crystals isomorphous with β -K₂SO₄. This was confirmed by Gattow (1962) who deduced the space group *Pnam*, in agreement with that of β -K₂SO₄ (Robinson, 1958).

Experimental

The crystals of K_2SeO_4 obtained from the aqueous solution of a BDH‡ product evaporated slowly at room temperature were thin, but rather large plates. From one of these plates an almost cylindrical needle, 0.8 mm long with an average diameter of 0.1 mm was carefully shaped. In terms of the axes chosen by Gattow (1962) the needle axis is *a*. K_2SeO_4 crystals, similarly to others which have a β -K₂SO₄ type of structure (Sasvári, 1963), show an almost hexagonal pseudo-symmetry, with $b:c=1.7437 \simeq 1/3$. Thus care was needed to get the correct crystal orientation on the four-circle goniometer. For the correct orientation, according to the 0kl Weissenberg diagram, the intensity of the 080 reflexion should be considerably higher than that of 044, which corresponds to 080 in the pseudo-unit cell.

Data were collected on a Hilger & Watts automatic four-circle diffractometer in the equi-inclination arrangement. Integrated intensities were measured for $\theta \le 56^{\circ}$ by the $\theta - 2\theta$ scanning method using Cu Ka radiation and a scintillation counter with an Ni filter and pulse height discrimination. Each reflexion was integrated in eighty steps of 0.01°. In consequence of a slight, but systematic error in the geometry of the four-circle goniometer, which could not be completely eliminated, the hk0 reflexions had to be remeasured with a revised orientation matrix. The observed structure factors were derived from the integrated intensities in a data reduction program, which also corrected for the variation in the integrated intensity of a standard reflexion (111) measured at frequent intervals during the data collection. Correction was made for absorption ($\mu R = 1.3$) by the method described for cylindrical crystals in International Tables for X-ray Crystallography (1962). 362 independent reflexions were measured, of which 14 were below threshold and have not been included in the refinement. The lattice parameters given by Gattow (1962) were refined from measurement of diffraction angles on the diffractometer.

Crystal data

- K₂SeO₄. $M = 221 \cdot 15$. Orthorhombic $a = 7.661 \pm 0.004$, $b = 10.466 \pm 0.008$, $c = 6.003 \pm 0.003$ Å; $V = 481 \cdot 32$ Å³, Z = 4, $D_c = 3.052$ g. cm⁻³, $D_x = 3.032$ g. cm⁻³, F(000) = 416.
 - Space group Pnam (no. 62).
 - μ for Cu Ka ($\lambda = 1.5418$ Å) 263.7 cm⁻¹.

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Structure determination and refinement

A model of the structure set up on the basis of that for β-K₂SO₄ (Robinson, 1958) and for K₂CrO₄ (Zachariasen & Ziegler, 1931) was refined by a full-matrix least-squares program written by J. S. Stephens for the ATLAS computer. The form factors for neutral selenium and oxygen atoms and for K⁺ were taken from International Tables for X-ray Crystallography (1962). Three cycles of refinement of coordinates and individual isotropic vibrational parameters together with two scale factors, one for hkl and another for hk0, reduced the residual $R = (\sum \Delta)/(\sum |kF_o|)$ to 9.0%. At this stage 12 of the hk1 reflexions with indices $h \ge 5$, $k \ge 4$, together with the reflexions 752 and 742, had to be rejected as unreliable. The intensities of these reflexions were evidently affected by the error in the geometry of the four-circle goniometer.

The refinement was then continued with anisotropic vibration parameters for all atoms. A correction parameter for secondary extinction was also refined. Four cycles reduced R to 4.9% and $R' = [\sum w \Delta^2)/(\sum w |kF_o|^2)]^{1/2}$ to 6.4%. Complex scattering factors were then introduced for the correction of the anomalous dispersion, which was expected to be significant for the Se $(\Delta f' = -1.0, \Delta f'' = 1.1)$ and K $(\Delta f' = 0.0, \Delta f'' = 1.1)$ atoms. Two further cycles, with a weighting scheme

$w = (3 \cdot 0 - 0 \cdot 167 |F_o| + 0 \cdot 005 |F_o|^2)^{-1}$

reduced the residuals to the final R = 4.8 and R' = 6.2%. The $|F_o|$ and final $|F_c|$ values are given in Table

1, and the final parameters in Tables 2 and 3.

Table 1. Observed and calculated structure factors

The last two columns show $10|F_0|$ and $10|F_c|$. An asterisk indicates an unreliable reflexion omitted from the refinement.

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Table 2. Coordinates with their e.s.d.'s

	x/a	y/b	z/c
Se	0.2242 (2)	0.4200 (1)	*
K(1)	0.1705 (5)	0.0843 (3)	14
K(2)	-0.0057 (4)	-0.2905(3)	1
D(1)	0.2931 (10)	0.3471 (6)	0.0271 (10)
D(2)	0.3024 (16)	-0.4356 (8)	1 4
D(3)	0.0126 (21)	0.4251 (10)	1

Owing to the large thermal vibration of the oxygen atoms (Table 3) a rigid-body vibration analysis and coordinate corrections were carried out on the SeO_4 tetrahedron by the method of Cruickshank (1956,



Fig. 1. Projection of the structure along [001]. Potassium atoms are shown by large circles, oxygen atoms by smaller open circles, and selenium atoms by small full circles. For numbering of atoms see Table 5. Tetrahedra are labelled by capital letters and may be identified also in Fig.2. Pairs of dashed lines indicate contacts to a pair of atoms in the same tetrahedron. A dashed line paired with a dash-dot line indicates that the pair of superposed atoms are in different tetrahedra.

Table 3. Vibration parameters with their e.s.d.'s $(Å^2)$

	U_{11}	U ₂₂	U_{33}	U_{12}	U_{13}	U_{23}
Se	0.0125 (11)	0.0160 (10)	0.0172 (10)	-0.0006(4)	0	0
K(1)	0.0164 (19)	0.0295 (17)	0.0283 (16)	0.0032(11)	0	0
K(2)	0.0135 (15)	0.0198 (15)	0.0264 (16)	0.0002 (11)	0	0
O(1)	0.0474 (43)	0.0417 (36)	0.0239 (35)	0.0132(31)	0.0060 (31)	-0.0107(31)
O(2)	0.0373 (70)	0.0213 (49)	0.0465 (60)	-0.0090(41)	0	0 ` ´
O(3)	0.0389 (83)	0.0583 (75)	0.0584 (72)	-0.0088(52)	0	0

Table 4. Interatomic distances and bond angles for the SeO₄ group

Se-O(1) Se-O(1') Se-O(2) Se-O(3)	Uncorrected 1.628 Å 1.628 1.625 1.622	Corrected 1.649 (6) Å 1.649 (6) 1.644 (9) 1.648 (16)	
Se-O(1)	1.628 A	1.649 (6) A	
Se-O(T)	1.079	1.049 (0)	
Se-O(2)	1.625	1.644 (9)	
Se-O(3)	1.622	1.648 (16)	
$O(1) \cdots O(1') \qquad 2.676 (9) Å$	ι ο	O(1) - Se - O(1')	110.50 (0.37)
$O(1) \cdots O(2)$ 2.640 (10)	0	(1) - Se - O(2)	108.43 (0.33)
$O(1) \cdots O(3)$ 2.660 (15)	0	(1) - Se - O(3)	109.84 (0.34)
$O(1') \cdots O(2)$ 2.640 (10)	0	(1')-Se-O(2)	108.43 (0.33)
$O(1') \cdots O(3)$ 2.660 (15)	0	(1')-Se-O(3)	109.84 (0.34)
$O(2) \cdots O(3)$ 2.656 (19)	0	(2) - Se - O(3)	109.76 (0.59)

1961). The calculations were performed on the ATLAS computer using a program written by J. S. Stephens. The corrections to the bond lengths are quite considerable, ranging from 0.019 to 0.026 Å. Table 4 gives the uncorrected and corrected bond lengths, the oxygenoxygen distances and the bond angles with their estimated standard deviations. The uncorrected potassium-oxygen distances are given in Table 5.

Table 5. Potassium-oxygen interatomic distances

The coordinates are given in accordance with the parameters shown in Table 2 and Figs. 1 and 2.

K(1)(x, y, z)				
O[1]	O(1)	(<i>x</i> ,	y, z	3·20 Å
O[II]	O(1)	(<i>x</i> ,	$y, \frac{1}{2} - z$	3.20
O[III]	O(1)	$(-\frac{1}{2}+x, \frac{1}{2})$	$-y, \frac{1}{2}-z$	3.26
O[IV]	O(1)	$(-\frac{1}{2}+x, \frac{1}{2})$	-y, z	3.26
O[V]	O(1)	$(\frac{1}{2}-x, -\frac{1}{2})$	$+y, \frac{1}{2}+z$	3.00
O[VI]	O(1)	$(\frac{1}{2}-x,-\frac{1}{2})$	+y, -z)	3.00
O[VII]	O(2)	$(-\frac{1}{2}+x, -\frac{1}{2})$	$-y, \frac{1}{2}-z$	3.23
O[VIII]	O(2)	$(\frac{1}{2}-x, \frac{1}{2}-x)$	$+y, \frac{1}{2}+z)$	3.02
O[IX]	O(2)	$(\frac{1}{2}-x, \frac{1}{2}-x)$	+y, -z	3.02
O[X]	O(3)	$(\frac{1}{2}+x, \frac{1}{2}-$	$-y, \frac{1}{2}-z)$	2.64
0[XI]	O(3)	(<i>x</i> ,	y, z)	3.76
K(2)(x, 1+y,	z)			
O[XII]	O(1)	(-x, -x)	$-v_{\cdot}$ $-z)$	2·83 Å
οίχιιίι	OÌÌ	(-x, -x)	$-v, \frac{1}{2}+z)$	2.83
0[V']	O(1)	$(\frac{1}{2} - x, \frac{1}{2} - x)$	$+y, \frac{1}{2}+z$	2.73
O[VI′]	O(1)	$(\tilde{1}_2 - x, \tilde{1}_2 - x)$	+y, -z	2.73
O[XIV]	O(2)	$(x, \hat{1} -$	+y, z)	2.80
O[VII′]	O(2)	$(-\frac{1}{2}+x, \frac{1}{2}-$	$-y, \frac{1}{2}-z)$	2.79
O[XI]	O(3)	(<i>x</i> ,	y, z)	2.98
O[XV]	O(3)	(-x, -x)	-y, -z	3.32
O[XVI]	O(3)	(-x, -x)	$-y, \frac{1}{2}+z$	3.32

Discussion

The two kinds of potassium ion have different environments (Table 5 and Figs. 1 and 2). K(1) is surrounded by 11 oxygen atoms. One of them is at a

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rather long distance (3.76 Å) but geometrically it seems to belong to the environment of K(1). This oxygen atom, O[XI], and two others, O[VII] and O[X], form an almost regular triangle (O[VII]–O[X] = 5.44, O[VII]– O[XI] = 5.47, O[X] - O[XI] = 5.30 Å) around the potassium ion on the common mirror plane at $z = \frac{1}{4}$. The other eight oxygen atoms form two mirror-related irregular tetrahedra surrounding the potassium ion. The planes formed by O[II], O[III] and O[V] and by O[I], O[IV] and O[VI] are almost parallel to the mirror plane $(\varepsilon = 4.5^{\circ})$, while the fourth members of these tetrahedra, O[IX] and O[VIII], are almost above and under the potassium ion at distances of $z = \pm 0.5$. Thus the 11 oxygen atoms form a nearly spherical environment for K(1). The other potassium ion K(2) has only 9 oxygen atoms in its neighbourhood. Three oxygen atoms, O[VII'], O[XI] and O[XIV], share the mirror plane with K(2), while three, O[V'], O[XIII] and O[XV], are above and three, O[VI'], O[XII] and O[XVI] are below in a rather irregular arrangement. The average potassium-oxygen distance of 2.93 Å for K(2) is significantly shorter than the average of 3.14 Å for K(1).

The SeO₄²⁻ anion is an almost regular tetrahedron within e.s.d.'s. The mean value of the vibrationally corrected Se-O bond lengths is 1.648 ± 0.010 Å. This is in a good agreement with the mean value in Cu(NH₃)₂SeO₄, which was originally given by Morosin (1969) as 1.635 ± 0.008 Å but increases to 1.643 Å on vibrational correction. A similar but less accurate value of 1.654 ± 0.021 Å was found in Na₂SeO₄ (Kálmán & Cruickshank, 1969; Náray–Szabó & Argay, 1963). In Se₄O₁₂ (Mijlhoff, 1965) the Se-O distances involving the bridging oxygen atoms are 1.75 and 1.80, and for the non-bridging oxygen atoms 1.54 and 1.56 Å (e.s.d.'s. $\simeq 0.013$ Å); however the mean value of 1.66 Å is similar to those in the orthoselenates. The hypo-



Fig.2. Projection of the structure along [100]. See caption to Fig.1 for explanations.

thetical Se–O single bond is presumably about 1.85 Å, which indicates that in the orthoselenates the Se–O bond has multiple-bond character.

In each orthoselenate the O-Se-O angles are close to the regular tetrahedral value, especially in $Cu(NH_3)_2SeO_4$, where the root-mean-square deviation is only 0.13°.

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