Crystal structure of potassium orthoselenate(IV), K₂SeO₃

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Crystal structure data for potassium orthoselenate(IV), K₂SeO₃, are reported for the first time. Colorless, block-shaped crystals were grown in a potassium hydroflux, i.e. under ultra-alkaline conditions, within 10 h. K₂SeO₃ crystallizes isostructural with Na₂SO₃ and K₂TeO₃ in the trigonal space group \( \text{P}\overline{3} \) with lattice parameters \( a = 6.1063 \) (4) Å and \( c = 6.9242 \) (4) Å at 100 (1) K. In the trigonal-pyramidal, \( C_3v \)-symmetric \([\text{SeO}_3]^{2-}\) anion, the bond length is 1.687 (1) Å, and the bond angle is 103.0 (1). Two of the three unique potassium cations exhibit a coordination number of six, and the third a coordination number of nine.

1. Chemical context

Ternary alkali metal selenates(IV) are a long-known but poorly studied class of compounds. After the discovery of the first salts of selenic acid by Berzelius, comprehensive studies on these salts were not carried out until the beginning of the 1930s, when Janitzki reported the syntheses of sodium and potassium salts of selenic acid (Janitzki, 1932). Moreover, the composition and solubility of hydrates and anhydrates of these selenates(IV) were determined. However, only two crystal structures of ternary alkali metal selenates(IV) are known to date, viz. K₂Se₂O₅ (Rider et al., 1985) and Na₂SeO₃ (Helmholdt et al., 1999; Wickleder, 2002). The latter compound was synthesized by annealing a mixture of Na₂O and SeO₂ at 773 K.

In this communication, we report on the synthesis and crystal structure of potassium orthoselenate(IV), K₂SeO₃. The title compound was synthesized using the hydroflux approach, an ultra-alkaline reaction medium consisting of an approximately equimolar mixture of water and alkali metal hydroxide (Bugaris et al., 2013; Chance et al., 2013). Advantages of the hydroflux method are the good solubility of oxides and hydroxides, the fast and simple reaction at moderate temperatures, and the formation of single-crystals suitable for X-ray diffraction. Moreover, the high hydroxide concentration within the hydroflux reduces the activity of water, leading to the unexpected fact that water-sensitive products can be isolated, e.g. K₂[Fe₂O₆(OH)₂] (Albrecht et al., 2019), Tl₁IO (Albrecht et al., 2020), or K₂Te₃ (Albrecht & Ruck, 2021).

2. Structural commentary

Five atoms represent the asymmetric unit of K₂SeO₃, one selenium atom (site symmetry \( 3\ldots \), Wyckoff position 2d), three potassium atoms (K₁: \( 3\ldots \), 1a; K₂: \( 3\ldots \), 1b; K₃: 3., 2d) and one
The selenium atom is bound to three oxygen atoms with a Se—O bond length of 1.687 (1) Å and a bond angle O—Se—O of 103.0 (1)°. The pyramidal shape of the $C_{3v}$-symmetric $[\text{SeO}_3]^{2-}$ anion can be attributed to the electron lone pair of the selenium(IV) atom. This oxidation state is supported by the bond-valence sum calculation (Brese & O’Keeffe, 1991) for selenium $v(\text{Se}) = \sum \exp \left[ \left( R_{\text{SeO}} - d_{\text{SeO}} \right) / b \right] = 3 \cdot \exp \left[ (1.811 \text{ Å} - 1.687 (1) \text{ Å}) / 0.37 \text{ Å} \right] = 4.2$ valence units.

It is noted that the X-ray powder diffraction pattern of ground K$_2$SeO$_3$ crystals (Fig. 3) differs significantly from previously published data (Hanawalt et al., 1938; Klushina et al., 1968).

K$_2$SeO$_3$ crystallizes isostructural with Na$_2$SO$_3$ (Zachariasen & Buckley, 1931; Larsson & Kierkegaard, 1969) and K$_2$TeO$_3$ (Andersen et al., 1989). On a more general level, the structure of K$_2$SeO$_3$ can be related to the Ni$_2$In type in space group $P6_3/mmc$ (Laves & Wallbaum, 1942), with the K$^+$ ions on the Ni positions and $[\text{SeO}_3]^{2-}$ anions occupying the positions of the In atoms. The orientation of the selenate(IV) groups is responsible for the symmetry reduction to $P3_1$; the higher pseudosymmetry is mirrored in the respective twin laws.

Potassium orthoselenate(IV), K$_2$SeO$_3$, was synthesized in a potassium hydroxide hydroflux with a molar water-base ratio of 1.7. The reaction was carried out in a PTFE-lined 50 mL Berghof-type DAB-2 stainless steel autoclave to prevent evaporation of water. The starting material SeO$_2$ (4 mmol, Merck, 99.8%) was dissolved in 3 ml of water before adding 6.3 g of KOH (Fischer Scientific, 86%). After closing the autoclave, the reaction mixture was heated to 473 K at a rate of 2 K min$^{-1}$ and, after 8 h, cooled to room temperature at a rate of $-1$ K min$^{-1}$. The solid reaction product was washed twice with 2 ml of methanol on a Schlenk frit under inert conditions to remove adherent hydroflux. The colorless, block-shaped crystals of K$_2$SeO$_3$ (Fig. 4) dissolve readily in water, but dissolve in methanol a little slower than the hydroflux. Scanning electron microscopy showed that the surface of the crystals was etched by the washing process (Fig. 5). Due to its hygroscopicity, the product was dried in dynamic vacuum and stored under argon. Pure K$_2$SeO$_3$ was obtained with a yield of about 50%. Energy-dispersive X-ray spectroscopy on selected crystals confirmed the chemical composition within the limits of the method.

For the Rietveld refinement, the program JANA2006 was used (Petříček et al., 2014). Scanning electron microscopy was
performed using a SU8020 (Hitachi) with a triple detector system for secondary and low-energy backscattered electrons ($U_a = 5$ kV). The composition of selected single crystals was determined by semi-quantitative energy dispersive X-ray analysis ($U_a = 15$ kV) using a Silicon Drift Detector X–MaxN (Oxford Instruments). The data were processed applying the AZtec software package (Oxford Instruments, 2013).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The investigated crystal was found to be a fourfold twin: twinning by merohedry plus twofold rotation along [001]. The crystal, thus, partially conserves the hexagonal (pseudo-)symmetry of the Ni$_2$In type.

Funding information

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Table 1

| Crystal data | Experimental details. |
|--------------|------------------------|
| Chemical formula | K$_2$SeO$_3$ |
| $M_r$ | 205.2 |
| Crystal system, space group | Trigonal, $P\bar{3}$ |
| Temperature (K) | 100 |
| $a$, $c$ (Å) | 6.1063 (2), 6.9242 (4) |
| $V$ (Å$^3$) | 223.59 (2) |
| $Z$ | 2 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 10.11 |
| Crystal size (mm) | 0.05 $\times$ 0.05 $\times$ 0.02 |

| Data collection | Diffraetometer |
|-----------------|----------------|
| Absorption correction | Bruker APEXII CCD |
| $T_{min}$, $T_{max}$ | 0.539, 0.747 |
| No. of measured, independent and observed $|F > 3\sigma(F)$| reflections | 12526, 790, 785 |
| $R_{int}$ | 0.021 |
| $\sin \theta/\lambda_{max}$ (Å$^{-1}$) | 0.858 |

| Refinement | |
|-----------------|-----------------|
| $R[F > 3\sigma(F)]$, $wR(F)$, $S$ | 0.009, 0.033, 1.05 |
| No. of reflections | 790 |
| No. of parameters | 24 |
| $\Delta_{F_{max}} - \Delta_{F_{min}}$ (e Å$^{-3}$) | 0.77, $-1.51$ |

Computer programs: APEX2 (Bruker, 2016), SAINT (Bruker, 2016), SUPERFLIP (Palatinus & Chapuis, 2007), JANA2006 (Petříček et al., 2014), DIAMOND (Brandenburg, 2021), and publCIF (Westrip 2010).

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Figure 4

Photograph of K$_2$SeO$_3$ crystals.

Figure 5

Scanning electron microscopy image after the washing process.

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Computing details

Data collection: APEX2 (Bruker, 2016); cell refinement: SAINT (Bruker, 2016); data reduction: SAINT (Bruker, 2016); program(s) used to solve structure: Superflip (Palatinus & Chapuis, 2007); program(s) used to refine structure: JANA2006 (Petříček et al., 2014); molecular graphics: DIAMOND (Brandenburg, 2021); software used to prepare material for publication: publCIF (Westrip 2010).

Dipotassium orthoselenate(IV)

Crystal data

\( \text{K}_2\text{SeO}_3 \)

\( M_r = 205.2 \)

Trigonal, \( P\overline{3} \)

Hall symbol: -\( P\overline{3} \)

\( a = 6.1063 (2) \, \text{Å} \)

\( c = 6.9242 (4) \, \text{Å} \)

\( V = 223.59 (2) \, \text{Å}^3 \)

\( Z = 2 \)

\( F(000) = 192 \)

\( D_a = 3.047 \, \text{Mg} \, \text{m}^{-3} \)

Mo \( K\alpha \) radiation, \( \lambda = 0.71073 \, \text{Å} \)

Cell parameters from 7032 reflections

\( \theta = 2.9\text{–}37.6^\circ \)

\( \mu = 10.11 \, \text{mm}^{-1} \)

\( T = 100 \, \text{K} \)

Block, colourless

0.05 \times 0.05 \times 0.02 \, \text{mm}

Data collection

Bruker APEXII CCD diffractometer

Radiation source: X-ray tube

Graphite monochromator

\( \omega \)– and \( \varphi \)–scans

Absorption correction: multi-scan

(\text{SADABS}; Krause et al., 2015)

\( T_{\text{min}} = 0.539, \, T_{\text{max}} = 0.747 \)

12526 measured reflections

790 independent reflections

785 reflections with \( I > 3\sigma(I) \)

\( R_{\text{int}} = 0.021 \)

\( \theta_{\text{max}} = 37.6^\circ, \, \theta_{\text{min}} = 2.9^\circ \)

\( h = -10\rightarrow10 \)

\( k = -10\rightarrow10 \)

\( l = -11\rightarrow11 \)

Refinement

Refinement on \( F^2 \)

\( R[F > 3\sigma(F)] = 0.009 \)

\( wR(F) = 0.033 \)

\( S = 1.05 \)

790 reflections

24 parameters

0 restraints

0 constraints

Primary atom site location: chargeflipping

Secondary atom site location: difference Fourier map

Weighting scheme based on measured s.u.'s \( w = 1/(\sigma^2(I) + 0.000576F^2) \)

\( (\Delta\sigma)_{\text{max}} = 0.001 \)

\( \Delta\rho_{\text{max}} = 0.77 \, \text{e} \, \text{Å}^{-3} \)

\( \Delta\rho_{\text{min}} = -1.51 \, \text{e} \, \text{Å}^{-3} \)

Extinction correction: B-C type 1 Gaussian

isotropic (Becker & Coppens, 1974)

Extinction coefficient: 570 (40)
Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|   | x         | y         | z            | U(eq)   |
|---|-----------|-----------|--------------|---------|
| Se | 0.666667  | 0.333333  | 0.338432 (15)| 0.00495 (4) |
| K1 | 0         | 0         | 0            | 0.00741 (8)  |
| K2 | 0         | 0         | 0.5          | 0.00764 (8)  |
| K3 | 0.333333  | 0.666667  | 0.14233 (5)  | 0.01091 (6)  |
| O  | 0.38608 (13)| 0.25027 (14)| 0.23422 (10)| 0.0135 (2)  |

Atomic displacement parameters (Å²)

|   | U₁₁   | U₂₂   | U₃₃   | U₁₂   | U₁₃   | U₂₃   |
|---|-------|-------|-------|-------|-------|-------|
| Se | 0.00527 (5) | 0.00527 (5) | 0.00432 (6) | 0.00263 (3) | 0 | 0 |
| K1 | 0.00743 (9)  | 0.00743 (9)  | 0.00735 (14) | 0.00372 (5) | 0 | 0 |
| K2 | 0.00816 (9)  | 0.00816 (9)  | 0.00658 (13) | 0.00408 (5) | 0 | 0 |
| K3 | 0.01248 (8)  | 0.01248 (8)  | 0.00778 (10) | 0.00624 (4) | 0 | 0 |
| O  | 0.0064 (3)   | 0.0208 (4)   | 0.0126 (3)   | 0.0062 (2)  | −0.0022 (2) | 0.0004 (2) |

Geometric parameters (Å, °)

|   |       |       |       |       |       |
|---|-------|-------|-------|-------|-------|
| Se—O | 1.6865 (8) | K2—K3 | 4.3084 (4) |
| Se—Oi | 1.6865 (12) | K2—K3 ⊙ | 4.3084 (4) |
| Se—Oii | 1.6865 (7) | K2—K3 ⊙v | 4.3084 (3) |
| K1—K2 ⊙ii | 3.4621 (4) | K2—O | 2.7708 (7) |
| K1—K2 | 3.4621 (4) | K2—Ox | 2.7708 (10) |
| K1—K3 ⊙iv | 3.6606 (3) | K2—Oxi | 2.7708 (10) |
| K1—K3v | 3.6606 (1) | K2—Oxii | 2.7708 (7) |
| K1—K3v | 3.6606 (3) | K2—Oxvi | 2.7708 (10) |
| K1—K3v | 3.6606 (1) | K2—Oxvii | 2.7708 (8) |
| K1—K3viii | 3.6606 (3) | K3—K3viii | 4.0391 (4) |
| K1—O | 2.6307 (7) | K3—K3vii | 4.0391 (3) |
| K1—Ox | 2.6307 (10) | K3—K3viii | 4.0391 (4) |
| K1—Ox | 2.6307 (8) | K3—O | 2.7915 (10) |
| K1—Ox | 2.6307 (7) | K3—Oxix | 2.7915 (8) |
| K1—Ox | 2.6307 (10) | K3—Ox | 2.7915 (12) |
| K1—Ox | 2.6307 (8) | K3—Oxixi | 3.0203 (8) |
| K2—K3v | 4.3084 (4) | K3—Oxi | 3.0203 (10) |
| K2—K3v | 4.3084 (3) | K3—Oxii | 3.0203 (8) |
| O—Se—Oi | 103.03 (4) | O—K2—Ox | 80.69 (2) |
| O—Se—Oii | 103.03 (4) | O—K2—Oxii | 180 |
| O—Se—Oii | 103.03 (5) | O—K2—Oxvii | 99.31 (2) |
| O—K1—Ox | 85.98 (3) | O—K2—Oxvii | 99.31 (2) |
| O—K1—Ox | 85.98 (2) | Ox—K2—Ox | 80.69 (3) |
| O—K1—Ox | 180 | Ox—K2—Oxvii | 99.31 (2) |
| O—K1—Ox | 94.02 (3) | Ox—K2—Oxvii | 180 |
| O—K1—Ox | 94.02 (2) | Ox—K2—Oxvii | 99.31 (3) |
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|----------------------|--------------|----------------------|--------------|
| OⅧ—K1—OⅩ           | 85.98 (3)    | OⅩ—K2—OⅩⅢ          | 99.31 (2)    |
| OⅩ—K1—OⅥ           | 94.02 (3)    | OⅩ—K2—OⅩⅥ          | 99.31 (3)    |
| OⅩ—K1—OⅪ           | 180          | OⅩ—K2—OⅩⅦ          | 180          |
| OⅩ—K1—OⅪⅡ          | 94.02 (3)    | OⅩⅢ—K2—OⅩⅥ         | 80.69 (2)    |
| OⅩ—K1—OⅢ           | 94.02 (2)    | OⅩⅢ—K2—OⅩⅦ         | 80.69 (2)    |
| OⅩ—K1—OⅩⅦ          | 180          | OⅩ—K3—OⅩⅩ          | 114.97 (3)   |
| OⅩⅢ—K1—OⅩⅦ         | 85.98 (3)    | OⅩ—K3—OⅩⅦ          | 114.97 (2)   |
| OⅩⅢ—K1—OⅩⅧ          | 85.98 (2)    | OⅩ—K3—OⅩⅪ         | 92.04 (2)    |
| OⅩⅢ—K1—OⅩⅨ         | 85.98 (3)    | OⅩ—K3—OⅩⅪⅡ        | 132.80 (3)   |
| OⅩⅢ—K2—OⅩ           | 80.69 (2)    | OⅩ—K3—OⅩⅧ         | 82.84 (2)    |

Symmetry codes: (i) −y+1, x−y, z; (ii) −x−y+1, x+1, z; (iii) x, y, z−1; (iv) x−1, y−1, z; (v) x, y−1, z; (vi) −x, −y, −z; (vii) −x, y+1, −z; (viii) −x+1, −y+1, −z; (ix) −y, x+1, −z; (x) −x+y, −x, z; (xi) −x+y, −y, −z; (xii) x−y, x, −z; (xiii) −x, −y, −z+1; (xiv) −x, y+1, −z+1; (xv) −x+1, −y+1, −z+1; (xvi) y, −x+y, −z+1; (xvii) x−y, x, −z+1; (xviii) −x+1, −y+2, −z; (xix) −y+1, x−y+1, z; (xx) −x+y, −x+1, z; (xxi) y, −x+y+1, −z.