Crystal structure of potassium orthoselenate(IV), K_2SeO_3

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Crystal structure data for potassium orthoselenate(IV), K_2SeO_3, 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. K_2SeO_3 crystallizes isostructural with Na_2SO_3 and K_2TeO_3 in the trigonal space group $P\overline{3}$ 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 $[SeO_3]^{2-}$ 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.
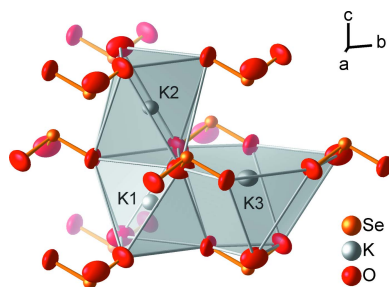
1. Chemical context

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.* $K_2Se_2O_5$ (Rider *et al.*, 1985) and Na_2SeO_3 (Helmholdt *et al.*, 1999; Wickleder, 2002). The latter compound was synthesized by annealing a mixture of Na_2O and SeO_2 at 773 K.

In this communication, we report on the synthesis and crystal structure of potassium orthoselenate(IV), K_2SeO_3. 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.* $K_2[Fe_2O_3(OH)_2]$ (Albrecht *et al.*, 2019), Tl_3IO (Albrecht *et al.*, 2020), or K_2Te_3 (Albrecht & Ruck, 2021).

2. Structural commentary

Five atoms represent the asymmetric unit of K_2SeO_3, one selenium atom (site symmetry 3.., Wyckoff position 2d), three potassium atoms (K1: $\overline{3}$.., 1a; K2: $\overline{3}$.., 1b; K3: 3.., 2d) and one
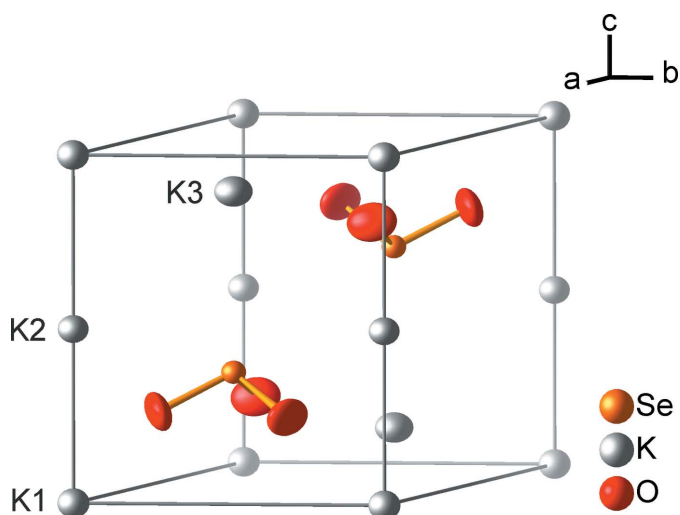
Figure 1
Crystal structure of K_2SeO_3 at 100 K, with displacement ellipsoids drawn at the 99% probability level; the unit cell is outlined.

oxygen atom (1, 6g). The unit cell of K_2SeO_3 is depicted in Fig. 1. 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 $[SeO_3]^{2-}$ 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 $v(Se) = \sum\exp[(R_{SeO} - d_{SeO})/b)] = 3 \cdot \exp[(1.811 \text{ Å} - 1.687 (1) \text{ Å}) / 0.37 \text{ Å})] = 4.2$ valence units. The potassium cations K1 and K2 are octahedrally coordinated by oxygen atoms with K—O distances of 2.631 (1) and 2.771 (1) Å, respectively. K3 has nine oxygen neighbors at distances of 2.792 (1), 3.020 (1) Å, and 3.474 (1) Å (Fig. 2).

It is noted that the X-ray powder diffraction pattern of ground K_2SeO_3 crystals (Fig. 3) differs significantly from previously published data (Hanawalt *et al.*, 1938; Klushina *et al.*, 1968).
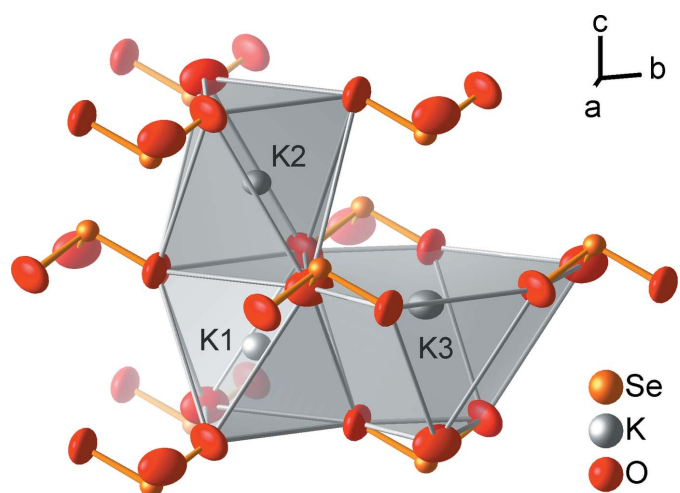

Figure 2
Coordination polyhedra of the potassium atoms, with displacement ellipsoids drawn at the 99% probability level.
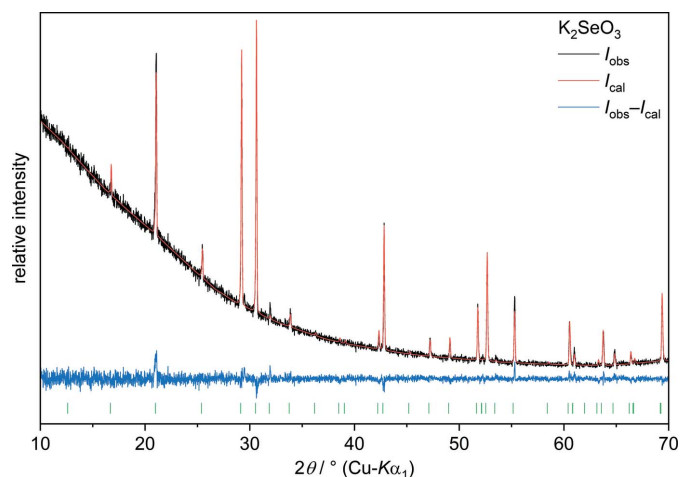

Figure 3
Powder X-ray diffractogram and Rietveld refinement of ground K_2SeO_3 crystals measured in a capillary at room temperature [a = 6.1114 (1) Å, c = 6.9938 (1) Å; R_p = 0.056, wR_p = 0.057, gof = 1.21].

3. Database survey

K_2SeO_3 crystallizes isostructural with Na_2SO_3 (Zachariasen & Buckley, 1931; Larsson & Kierkegaard, 1969) and K_2TeO_3 (Andersen *et al.*, 1989). On a more general level, the structure of K_2SeO_3 can be related to the Ni_2In type in space group $P6_3/mmc$ (Laves & Wallbaum, 1942), with the K^+ ions on the Ni positions and $[SeO_3]^{2-}$ anions occupying the positions of the In atoms. The orientation of the selenate(IV) groups is responsible for the symmetry reduction to $P\bar{3}$; the higher pseudo-symmetry is mirrored in the respective twin laws.

4. Synthesis and crystallization

Potassium orthoselenate(IV), K_2SeO_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, abcr, 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_2SeO_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_2SeO_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
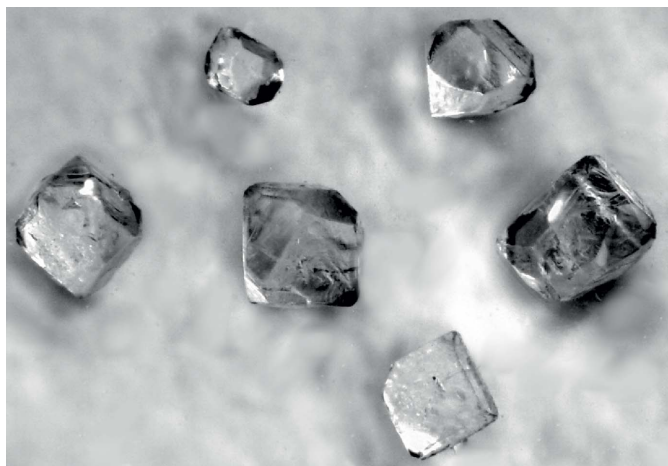
Figure 4
Photograph of K_2SeO_3 crystals.

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_2In type.

Funding information
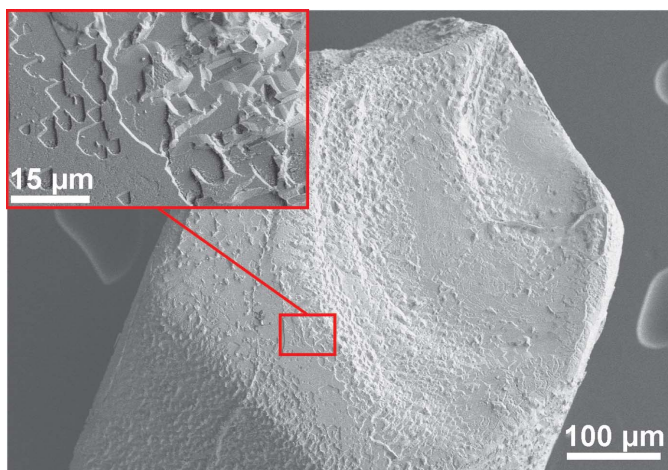
Figure 5
Scanning electron microscopy image after the washing process.

Table 1
Experimental details.

Crystal data	
Chemical formula	K_2SeO_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 (Å³)	223.59 (2)
Z	2
Radiation type	Mo $K\alpha$
μ (mm⁻¹)	10.11
Crystal size (mm)	$0.05 \times 0.05 \times 0.02$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.539, 0.747
No. of measured, independent and observed [$I > 3\sigma(I)$] 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
$\Delta\rho_{max}, \Delta\rho_{min}$ (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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Crystal structure of potassium orthoselenate(IV), K₂SeO₃

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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

K_2SeO_3	$D_x = 3.047$ Mg m^{-3}
$M_r = 205.2$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Trigonal, $P\bar{3}$	Cell parameters from 7032 reflections
Hall symbol: -P 3	$\theta = 2.9$–37.6°
$a = 6.1063$ (2) Å	$\mu = 10.11$ mm^{-1}
$c = 6.9242$ (4) Å	$T = 100$ K
$V = 223.59$ (2) Å^3	Block, colourless
$Z = 2$	$0.05 \times 0.05 \times 0.02$ mm
$F(000) = 192$	

Data collection

Bruker APEXII CCD diffractometer	12526 measured reflections
Radiation source: X-ray tube	790 independent reflections
Graphite monochromator	785 reflections with $I > 3\sigma(I)$
ω– and φ–scans	$R_{int} = 0.021$
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)	$\theta_{max} = 37.6°$, $\theta_{min} = 2.9°$
	$h = -10\rightarrow10$
	$k = -10\rightarrow10$
$T_{min} = 0.539$, $T_{max} = 0.747$	$l = -11\rightarrow11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
$R[F > 3\sigma(F)] = 0.009$	
$wR(F) = 0.033$	Weighting scheme based on measured s.u.'s $w = 1/(\sigma^2(I) + 0.000576I^2)$
$S = 1.05$	
790 reflections	$(\Delta/\sigma)_{max} = 0.001$
24 parameters	$\Delta\rho_{max} = 0.77$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -1.51$ e Å^{-3}
0 constraints	Extinction correction: B-C type 1 Gaussian isotropic (Becker & Coppens, 1974)
Primary atom site location: chargeflipping	Extinction coefficient: 570 (40)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/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)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
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, º)

Se—O	1.6865 (8)	K2—K3	4.3084 (4)
Se—O[i]	1.6865 (12)	K2—K3[xiii]	4.3084 (4)
Se—O[ii]	1.6865 (7)	K2—K3[xiv]	4.3084 (3)
K1—K2[iii]	3.4621 (4)	K2—K3[xv]	4.3084 (4)
K1—K2	3.4621 (4)	K2—O	2.7708 (7)
K1—K3[iv]	3.6606 (3)	K2—O[ix]	2.7708 (10)
K1—K3[v]	3.6606 (1)	K2—O[x]	2.7708 (8)
K1—K3	3.6606 (3)	K2—O[xiii]	2.7708 (7)
K1—K3[vi]	3.6606 (3)	K2—O[xvi]	2.7708 (10)
K1—K3[vii]	3.6606 (1)	K2—O[xvii]	2.7708 (8)
K1—K3[viii]	3.6606 (3)	K3—K3[vii]	4.0391 (4)
K1—O	2.6307 (7)	K3—K3[viii]	4.0391 (3)
K1—O[ix]	2.6307 (10)	K3—K3[xviii]	4.0391 (4)
K1—O[x]	2.6307 (8)	K3—O	2.7915 (10)
K1—O[vi]	2.6307 (7)	K3—O[xix]	2.7915 (8)
K1—O[xi]	2.6307 (10)	K3—O[xx]	2.7915 (12)
K1—O[xii]	2.6307 (8)	K3—O[viii]	3.0203 (8)
K2—K3[iv]	4.3084 (4)	K3—O[xxi]	3.0203 (10)
K2—K3[v]	4.3084 (3)	K3—O[xii]	3.0203 (8)
O—Se—O[i]	103.03 (4)	O—K2—O[x]	80.69 (2)
O—Se—O[ii]	103.03 (4)	O—K2—O[xiii]	180
O[i]—Se—O[ii]	103.03 (5)	O—K2—O[xvi]	99.31 (2)
O—K1—O[ix]	85.98 (3)	O—K2—O[xvii]	99.31 (2)
O—K1—O[x]	85.98 (2)	O[ix]—K2—O[x]	80.69 (3)
O—K1—O[vi]	180	O[ix]—K2—O[xiii]	99.31 (2)
O—K1—O[xi]	94.02 (3)	O[ix]—K2—O[xvi]	180
O—K1—O[xii]	94.02 (2)	O[ix]—K2—O[xvii]	99.31 (3)

O^{ix}—K1—O^{x}	85.98 (3)	O^{x}—K2—O^{xiii}	99.31 (2)
O^{ix}—K1—O^{vi}	94.02 (3)	O^{x}—K2—O^{xvi}	99.31 (3)
O^{ix}—K1—O^{xi}	180	O^{x}—K2—O^{xvii}	180
O^{ix}—K1—O^{xii}	94.02 (3)	O^{xiii}—K2—O^{xvi}	80.69 (2)
O^{x}—K1—O^{vi}	94.02 (2)	O^{xiii}—K2—O^{xvii}	80.69 (2)
O^{x}—K1—O^{xi}	94.02 (3)	O^{xvi}—K2—O^{xvii}	80.69 (3)
O^{x}—K1—O^{xii}	180	O—K3—O^{xix}	114.97 (3)
O^{vi}—K1—O^{xi}	85.98 (3)	O—K3—O^{xx}	114.97 (2)
O^{vi}—K1—O^{xii}	85.98 (2)	O—K3—O^{viii}	92.04 (2)
O^{xi}—K1—O^{xii}	85.98 (3)	O—K3—O^{xxi}	132.80 (3)
O—K2—O^{ix}	80.69 (2)	O—K3—O^{xii}	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*−*y*, *z*; (x) −*x*+*y*, −*x*, *z*; (xi) *y*, −*x*+*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*.