Crystal structure of tetrapotassium hexaselenidohypodiphosphate, $K_4P_2Se_6$

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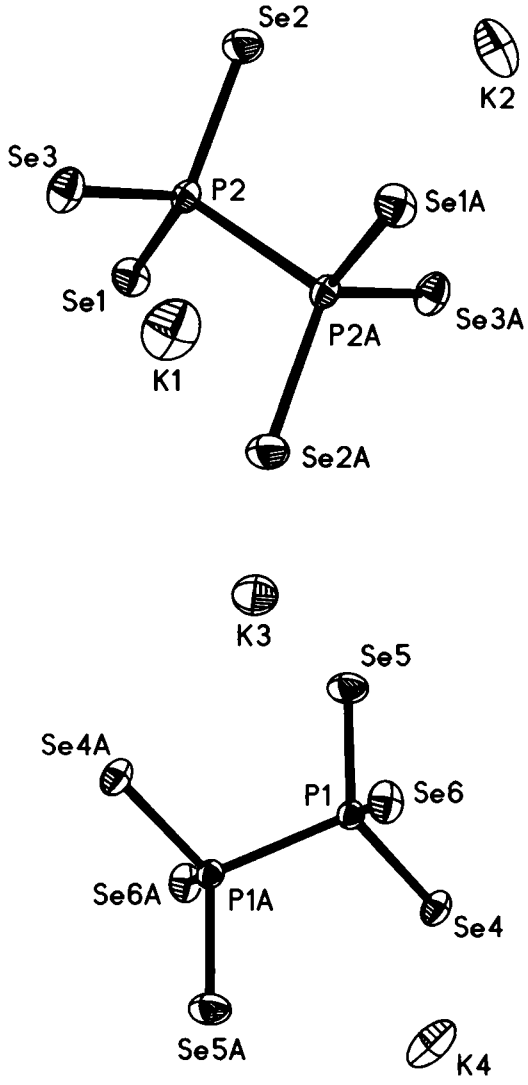

Abstract

$K_4P_2Se_6$, monoclinic, $P12_1/c1$ (no. 14), $a = 13.664(1)$ Å, $b = 12.3993(9)$ Å, $c = 8.7631(7)$ Å, $\beta = 91.267(1)°$, $V = 1484.3$ Å^3, $Z = 4$, $R_{gt}(F) = 0.047$, $wR_{ref}(F^2) = 0.083$, $T = 571$ K.

Source of material

Crystals of $K_4P_2Se_6$ were formed in a molten chalcogenide flux reaction of 21.8 mg P, 57 mg Se, and 170.2 mg K_2Se_2. The reactants were combined in a fused silica ampoule in an inert atmosphere glovebox, sealed under vacuum, and heated to 500 °C at a rate of 30 K/hour. After 150 hours of heating, the ampoule was cooled at 3 K/hour to room temperature. Dimethylformamide was added to dissolve remaining potassium selenide flux, resulting in well-formed block-like crystals of $K_4P_2Se_6$.

Discussion

The crystal structure of the title compound is isotypic to that of $Tl_4P_2Se_6$ [1]. It consists of isolated centrosymmetrical ethane-like units of $(P_2Se_6)^{4-}$ where the selenium atoms are staggered. The selenophosphate anions are surrounded by K^+ cations. In the asymmetric unit there are two crystallographically independent, similar units of these anions.

Table 1. Data collection and handling.

Crystal:	transparent green block, size 0.15 × 0.20 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	160.83 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	56.58°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13680, 3653
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3162
$N(param)_{refined}$:	110
Program:	SHELXTL [2]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Se(1)	4e	0.90323(4)	1.30791(4)	0.02115(6)	0.0284(3)	0.0188(3)	0.0283(3)	−0.0056(2)	0.0014(3)	0.0009(2)
Se(2)	4e	0.95962(4)	1.47051(4)	−0.30646(6)	0.0299(3)	0.0311(3)	0.0183(3)	−0.0021(3)	−0.0012(2)	−0.0012(2)
Se(3)	4e	0.81409(4)	1.58264(4)	−0.00130(7)	0.0190(3)	0.0273(3)	0.0325(3)	0.0039(2)	−0.0017(2)	−0.0054(2)
Se(4)	4e	0.67907(4)	0.90206(4)	0.03618(7)	0.0196(3)	0.0236(3)	0.0333(3)	0.0025(2)	−0.0045(2)	0.0040(2)
Se(5)	4e	0.53473(5)	0.96412(5)	−0.30458(7)	0.0403(4)	0.0333(3)	0.0197(3)	0.0056(3)	−0.0013(3)	−0.0036(2)
Se(6)	4e	0.60898(4)	1.17778(4)	−0.04700(7)	0.0249(3)	0.0176(3)	0.0394(4)	−0.0045(2)	0.0026(3)	0.0029(2)

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Table 2. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	4*e*	0.5688(1)	1.0079(1)	–0.0694(2)	0.0160(7)	0.0181(6)	0.0199(7)	–0.0011(5)	–0.0006(6)	0.0014(5)
P(2)	4*e*	0.9311(1)	1.4710(1)	–0.0625(2)	0.0141(7)	0.0176(6)	0.0191(7)	–0.0022(5)	–0.0024(5)	–0.0009(5)
K(1)	4*e*	0.9152(1)	1.7649(1)	0.2239(2)	0.0453(9)	0.0353(8)	0.0463(9)	–0.0010(7)	–0.0044(7)	–0.0187(7)
K(2)	4*e*	1.1855(1)	1.5678(1)	–0.3267(2)	0.0388(9)	0.0416(8)	0.0489(9)	–0.0042(7)	0.0214(7)	–0.0021(7)
K(3)	4*e*	0.4330(1)	1.2061(1)	–0.3404(2)	0.0427(9)	0.0318(7)	0.0411(8)	0.0014(6)	0.0006(7)	0.0121(6)
K(4)	4*e*	0.7060(1)	1.1083(1)	0.2865(2)	0.0396(9)	0.0379(8)	0.052(1)	0.0132(7)	–0.0232(7)	–0.0150(7)

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