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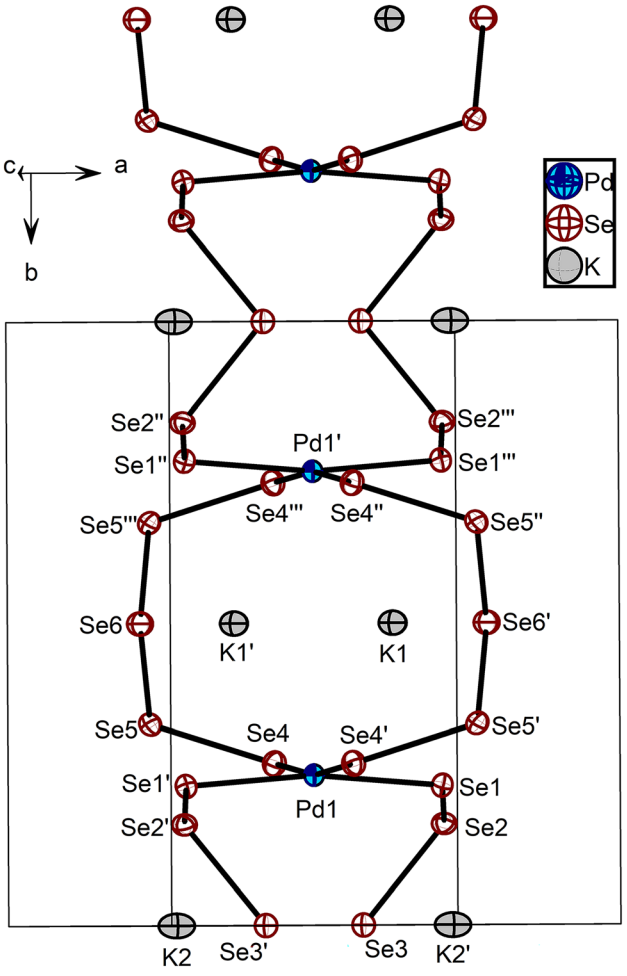
Crystal structure of potassium bis(pentaselenido-κ^2Se^1,Se^5)palladate(II), $K_2[Pd(Se_5)_2]$



https://doi.org/10.1515/ncrs-2023-0081
Received February 21, 2023; accepted March 9, 2023;
published online March 27, 2023

Abstract

K_2PdSe_{10}, orthorhombic, *Pcma* (no. 55), a = 8.293(3) Å, b = 10.987(3) Å, c = 16.432(5) Å, V = 1497.1(8) Å^3, Z = 4, $R_{gt}(F)$ = 0.0349, $wR_{ref}(F^2)$ = 0.0688, T = 173(2) K.

CCDC no.: 2247451

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Table 1: Data collection and handling.

Crystal:	Black block
Size:	0.17 × 0.10 × 0.10 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	6.0 mm^{-1}
Diffractometer, scan mode:	Bruker APEXII, φ and ω
θ_{max}, completeness:	56.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13239, 9148, 0.025
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 7183
$N(param)_{refined}$:	686
Programs:	Bruker [1], SHELX [2], WinGX [3], Diamond [4]

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of material

K_2PdCl_4 (0.040 g, 0.12 mmol), K_2Se_4 (0.190 g, 0.48 mmol) and Et_3NHCl (0.033 g, 0.24 mmol) were charged to a Pyrex tube with a diameter of 9 mm under an argon atmosphere and about 0.5 mL MeOH was added as a solvent. While the solvent being frozen, the Pyrex tube was evacuated under vacuum and sealed with the use of a flame. The sealed tube was placed in an oven and heated at 80 °C for 3 days, then cooled to room temperature. Black platelet crystals were isolated by filtration and washed with MeOH and diethyl ether several times. Crystals of $K_2[Pd(Se_5)_2]$ were obtained in 26% yield, based on the Pd metal used.

2 Experimental details

2.1 Comment

The title compound, $K_2[Pd(Se_5)_2]$, which has been prepared by the solvothermal reaction of K_2PdCl_4, K_2Se_4 and Et_3NHCl with methanol as a solvent, is composed of a 1D polymeric $[Pd(Se_5)_2]^{2-}$ anion and charge-balancing K^+ cations. The 1D structure of $[Pd(Se_5)_2]^{2-}$ is the first example among the members of Pd polyselenide family $[Pd(Se_x)_2]^{2-}$ (x = 2 – 7) [5–14]. Actually the chain structure of $[Pd(Se_5)_2]^{2-}$ is quite

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

Atom	*X*	*y*	*z*	U_{iso}*/U_{eq}
Pd1	0.000000	0.24848 (7)	0.000000	0.01540 (18)
Se1	−0.29166 (9)	0.23077 (7)	0.01754 (4)	0.01795 (18)
Se2	−0.34455 (9)	0.16713 (7)	0.15235 (4)	0.01867 (18)
Se3	−0.17289 (13)	0.000000	0.17631 (6)	0.0205 (3)
Se4	0.03532 (9)	0.26779 (7)	0.14648 (4)	0.01865 (18)
Se5	0.30080 (9)	0.33339 (7)	0.17514 (4)	0.01978 (18)
Se6	0.35360 (13)	0.500000	0.08944 (6)	0.0212 (3)
K1	−0.2224 (3)	0.500000	0.12557 (15)	0.0303 (6)
K2	0.2671 (3)	0.000000	0.11187 (15)	0.0318 (7)

unprecedented in the metal polyselenide chemistry [15, 16]. Two independent pairs of symmetrically equivalent Se_5^{2-} bridging ligands connect adjacent Pd(II) atoms alternatively in a helical screw mode to form a chain. So far, the bridging pentaselenide, Se_5^{2-} has been rarely found in compounds such as $(H_3NCH_2CH_2NH_2)_2[Pd(Se_5)_2]$, $(Ph_4P)_4[Cu_2(Se_4)(Se_5)_2]$, and $(R_4E)_4[\{In(Se_4)_2\}_2(\mu\text{–}Se_5)]$ (R = Ph, E = P; R = Et, Pr, E = N) [7, 17, 18].

The other two compounds containing $[Pd(Se_5)_2]^{2-}$ anions are $(H_3NCH_2CH_2NH_2)_2[Pd(Se_5)_2]$, which has a layered structure of $[Pd(Se_5)_2]^{2-}$, and $(Et_4N)_5[2Pd(Se_4)_2{\cdot}0.5Pd(Se_5)_2]$, which has a 0D molecular $[Pd(Se_5)_2]^{2-}$ [6, 7]. Compared to the synthetic condition of $K_2[Pd(Se_5)_2]$, use of $PdCl_2$ and water instead of K_2 $PdCl_4$ and methanol, respectively, had been reported to yield another K_2PdSe_{10}, which is better described as $K_4[Pd(Se_4)_2][Pd(Se_6)_2]$ [5]. The $K_4[Pd(Se_4)_2][Pd(Se_6)_2]$ is composed of interpenetrating 3D $[Pd(Se_4)_2]^{2-}$ and $[Pd(Se_6)_2]^{2-}$ frameworks. In addition, the methanothermal reaction of K_2PdCl_4 and K_2Se_5 in a 1:6 M ratio at 80 °C had been reported to produce $K_6[Pd(Se_5)_4]$ containing a molecular $[Pd(Se_5)_4]^{4-}$ anion, composed of a Pd(II) metal center and four dangling Se_5^{2-} ligands [7]. When K_2Se_4 was used in less amount instead of K_2Se_5, the title compound, $K_2[Pd(Se_5)_2]$ instead of $K_6[Pd(Se_5)_4]$ was produced. Dangling Se_5^{2-} ligands of molecular $[Pd(Se_5)_4]^{6-}$ anions are supposed to be connected additionally by Pd(II) atoms in excess to form a $[Pd(Se_5)_2]^{2-}$ chain. For the synthesis of $K_2[Pd(Se_5)_2]$, Et_3NH^+ organic cations seemed to be necessary at least to yield good enough crystals for single crystal X-ray diffraction study.

For the structure of $[Pd(Se_5)_2]^{2-}$ in $K_2[Pd(Se_5)_2]$, the square planar geometry around Pd(II), coordinated by four bridging pentaselenide ligands, is quite ideal as Se–Pd–Se angles are in the range of 90.26(2)–90.54(2)°. The Pd–Se and Se–Se distances are also typical, ranging from 2.4339(10) to 2.4435(10) Å, and from 2.3507(11) to 2.3640(12) Å, respectively, similar to those found in the other $[Pd(Se_x)_2]^{2-}$ complexes [5–14]. The distances between the adjacent Pd atom centers in the 1D chain structure of $[Pd(Se_5)_2]^{2-}$ are 5.4601(18) Å and 5.5269(19) Å, respectively. Considering the distances, 8.507 Å, between the Pd atom centers in the 2D layered structure of $[Pd(Se_5)_2]^{2-}$, the bridging Se_5^{2-} ligands need to be much more folded and twisted to fit in the shorter distances for the 1D chain structure of $[Pd(Se_5)_2]^{2-}$. Around each of the two K cations in $K_2[Pd(Se_5)_2]$, six Se atoms are present inside the range of 3.9 Å, and the closest Se atoms are Se4(3.346(2) Å) for K1 and Se1(3.315(2) Å) for K2, respectively.

Acknowledgements: This work was supported by the Incheon National University Research Grant in 2018.
Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: Incheon National University Research Grant in 2018.
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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