LETTER TO THE EDITOR

Cs$_2$PdSe$_8$: A Unique Open Framework Structure with Double Helical Assemblies of [Pd(Se$_4$)$_2$]$^{2-}$

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Cs$_2$PdSe$_8$(1), a novel palladium polyselenide with a three-dimensional open framework structure, has been synthesized via a solvothermal reaction using ethylenediamine as solvent. Its crystal structure has been determined by single crystal X-ray diffraction. The structure belongs to the tetragonal space group $I4_1/acd$ (No. 142), $a=14.935(2)$, $c=12.907(3)$ Å, $V=2897.0(8)$ Å^3, $Z=8$, $R_1=0.044$, and $wR_2=0.063$, for 640 unique reflections. The unique three-dimensional network is composed of two $^3_\infty$[Pd(Se$_4$)$_2$]$^{2-}$ frameworks that are topologically identical and mutually insertional. Each framework is built upon by connecting the neighboring square-planar [Pd(Se$_4$)$_2$]$^{2-}$ units to generate an infinite assembly resembling alternating right- and left-handed helices running along the c-axis. Thermal analysis (TGA) showed that compound 1 is stable up to 320 °C. Optical studies performed on the powder sample of 1 suggested that the compound is a semiconductor and a band gap of 1.5 eV was estimated from the diffuse reflectance data. © 1998 Academic Press

Recently, we have shown that ethylenediamine(en) serves as an excellent organic medium for the crystal growth of metal chalcogenides under mild solvothermal conditions. A number of new compounds, most of which are metastable, have been synthesized at temperatures below 180°C (1). While ethylenediamine incorporates into many of these compounds by forming a coordination complex with a metal center to give a complex cation, the size of such a metal complex can be crucial in the geometric arrangement of the overall structural framework. The resultant structures are typically molecular or one-dimensional. Alkali-metal counterions ($A^+ = $ K$^+$, Rb$^+$, and Cs$^+$), on the other hand, can influence the structural reorganization in such a way as to allow the formation of extended 2D and 3D networks, often with open channels and cavities, especially under mild synthetic conditions (2). Such compounds are

attractive to us due to their potential for preparation of nanoporous chalcogenide materials. In an effort to make new compounds of this sort, we have used alkali-metal polychalcogenides as reactive reagents in our synthesis and have succeeded in obtaining copper-, silver-, mercury-, and antimony-based alkali-metal chalcogenides containing 2D and 3D networks (3). The Pd/Pt systems are particularly interesting due to the catalytic functions (4) of these metals and their ability to form polychalcogenide complexes and framework structures (5) in solution media. Here we report the solvothermal synthesis and crystal structure of Cs$_2$PdSe$_8$ (1), a novel palladium polyselenide with a three-dimensional open framework structure built upon a double helical arrangement of the [Pd(Se$_4$)$_2$]$^{2-}$ building blocks.

Solvothermal reactions of Cs$_2$Se, Se, and PdCl$_2$ in ethylenediamine at 160°C afforded black prism-like crystals of **1** (6). Subsequent direct reactions of Cs$_2$Se, Pd, and Se at 250°C produced **1** in high yield (approx. 90%).

Compound **1** represents the first ternary alkali-metal palladium chalcogenide synthesized using ethylenediame as a solvent. It contains a unique three-dimensional $^3_\infty$[(PdSe$_8$)$^{2-}$] open framework structure constructed from [Pd(Se$_4$)$_2$]$^{2-}$ building blocks (7). The Pd atom lies on the Wyckoff 8a position and possesses a $\bar{4}$ symmetry. It has a square-planar coordination with four terminal Se atoms from the four polyselenide (Se$_4$)$^{2-}$ ligands, as shown in Fig. 1. The Se–Pd–Se angles are close to 90° (90.125°) and 180° (174.65°). The three-dimensional framework results by the bridging of the neighboring Pd atoms with the chelating (Se$_4$)$^{2-}$ ligands. Figure 2 gives two projections of the structure along the c- and a-axis, respectively. The Cs$^+$ counterions fill in the open spaces around each Pd(Se)$_4$ unit (see Fig. 2a) with Cs$\cdots$Se(1) distances of 3.575 Å $\times$ 2, 3.649 Å $\times$ 2, and 3.862 Å $\times$ 2 and a Cs$\cdots$Se(2) distance of 3.803 Å $\times$ 2.

One of the intriguing features in this remarkable structure is that it is composed of two 3D $^3_\infty$[Pd(Se$_4$)$_2$]$^{2-}$ frameworks (**A** and **B** in Fig. 3) that are topologically identical and mutually insertional. The Pd atoms in the two frameworks

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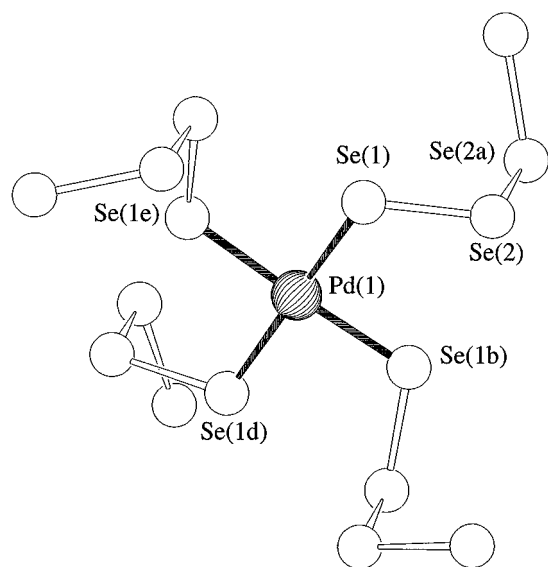**FIG. 1.** The $[Pd(Se_4)_2]^{2-}$ building block. The Pd atom has a square planar coordination to the four polyselenide Se_4 ligands via the terminal Se atoms

are derived from the single crystallographic site. Each framework (**A** or **B**) can be constructed by connecting the neighboring $[Pd(Se_4)_2]^{2-}$ units which generates an infinite assembly that resembles alternating right- and left-handed helices running along the *c*-axis, as illustrated in Fig. 4. The overall 3D structure results upon insertion of the two sub-

frameworks in which the Pd(**A**) and Pd(**B**) atoms merge at a distance of 6.453 Å (along the *c*-axis). The square-planar $Pd(Se_4)$ motifs in the two sub frameworks give rise to a "staggered" configuration (see Figs. 2a and 3c). The overall structure can also be thought of as an infinite assembly of alternating left- and right-handed double helices running down the *c*-axis that is formed by mutual insertion of **A** and **B** at a distance of $1/2c$. Each double helix contains an **A** and a **B** with the same handedness.

As far as we are aware, the only other three-dimensional alkali-metal palladium chalcogenide structure that is built upon the $[Pd(Se_4)_2]^{2-}$ motif is K_2PdSe_{10} (8). The latter is composed of two interpenetrating 3D frameworks, $_\infty^3[Pd(Se_4)_2]^{2-}$ and $_\infty^3[Pd(Se_6)_2]^{2-}$. The $[Pd(Se_4)_2]^{2-}$ sublattice in K_2PdSe_{10} is very similar to the sublattice **B** in **1**. The Pd–Se bond length in **1**, 2.428(1) Å, is slightly shorter than the average distance of 2.465(9) Å in K_2PdSe_{10} (the $_\infty^3[Pd(Se_4)_2]^{2-}$ framework). The average Se–Se distances in the $(Se_4)^{2-}$ ligands are similar in the two structures, 2.356(2) Å and 2.34(1) Å, respectively. The Se–Se–Se (104.58°) and Se–Se–Pd (113.25°) angles in **1** are, however, significantly different from those in K_2PdSe_{10}, 106.3° and 108.6°, respectively. While the two structures are closely related, **1** is unique in that its two sublattices (**A** and **B**) are derived from a single Pd crystallographic site, they are topologically identical, and the perfect insertion of the two helical assemblies generates an extended yet open structural framework.
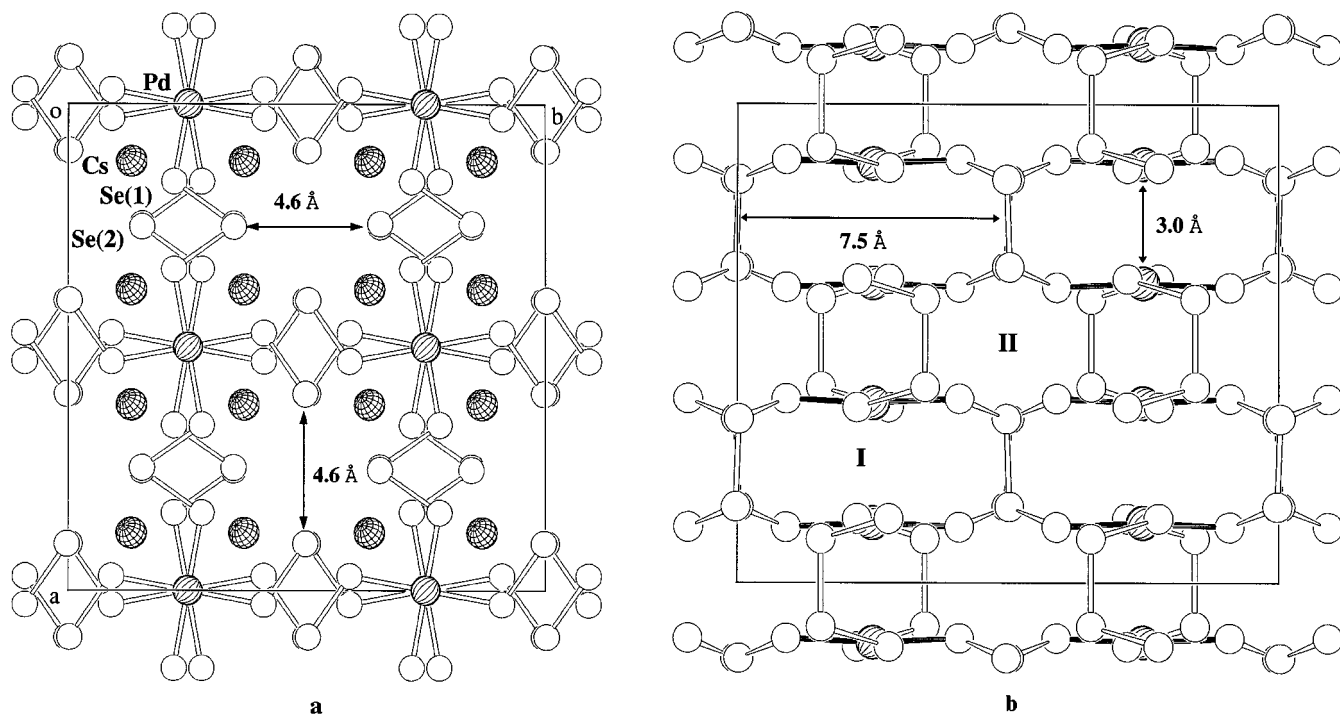

FIG. 2. Crystal structure of Cs_2PdSe_8 (**1**) projected along (a) the *c*-axis and (b) the *a*-axis. The shaded circles are Pd atoms, the open circles Se, and the doubly shaded circles Cs. The approximate dimensions of the open channels are indicated in the structure.
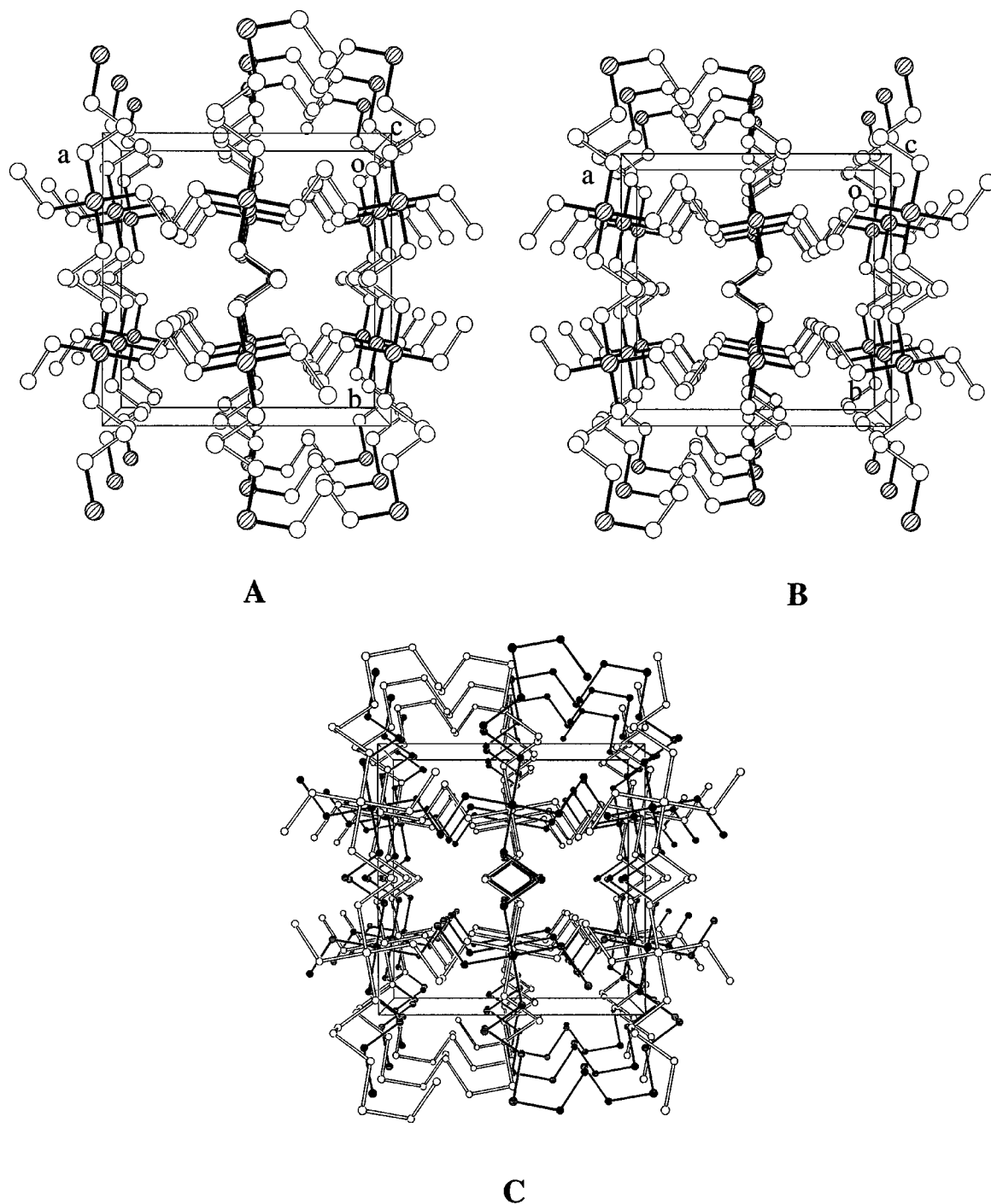
FIG. 3. Perspective views showing the two sub frameworks (**A** and **B**) and the overall three-dimensional $^3_\infty[Pd(Se_4)_2]^{2-}$ network upon insertion of the two sub-lattices (**C**). Framework **A** is shown in black in **C**. The approximate dimensions of the open channels in **A** and **B** are 6.4×4.6 Å.

Compound **1** contains several mutually perpendicular open channels running parallel to the three crystallographic axes. These channels are depicted in Fig. 2. Parallel to the *c*-axis are the one-dimensional channels with a four-fold symmetry. The approximate dimensions of these open channels are 4.6×4.6 Å. The channels running parallel to *a*- and *b*-axes are identical due to the tetragonal symmetry. When considered separately, each **A** or **B** framework is perforated with channels as large as 10.1×9.6 Å. Upon insertion of **A** and **B**, channels of smaller size result. The actual dimensions are 7.5×3 Å (the larger one, **I**) and 4×3 Å (the smaller one, **II**).
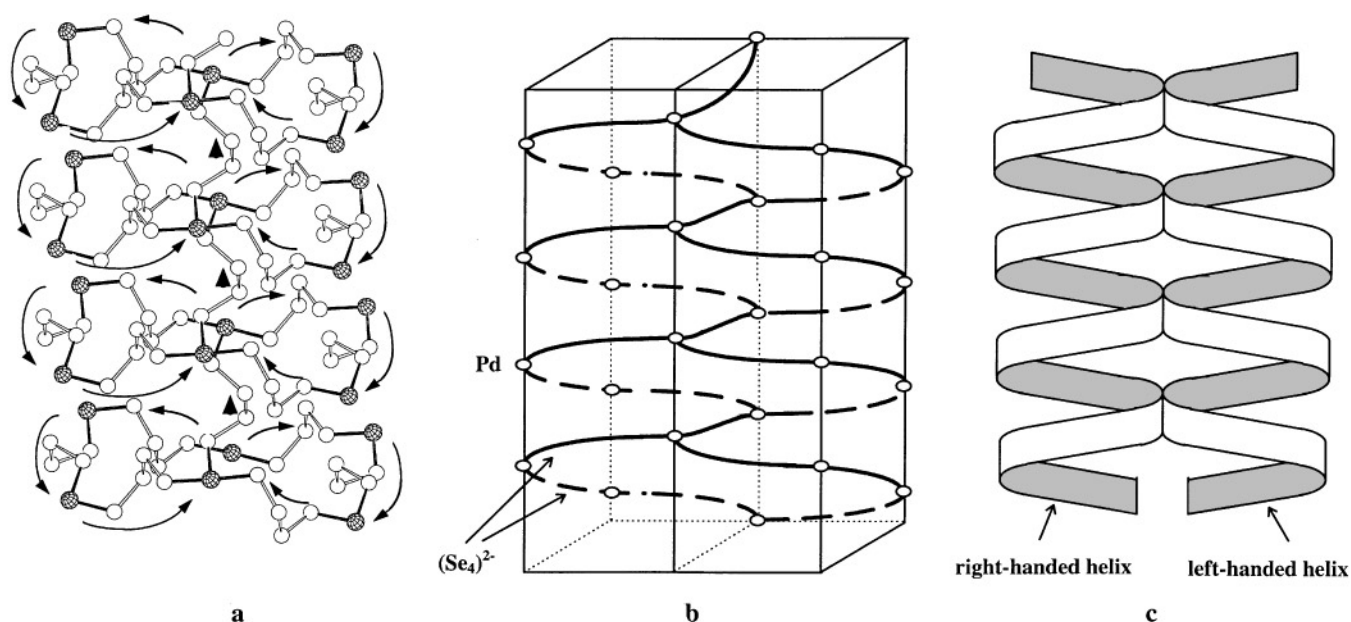
FIG. 4. Topological drawings illustrating, (a) The side view of left- and right-handed helical arrangements of one of the $\frac{3}{\infty}[Pd(Se_4)_2]^{2-}$ sub frameworks (**A** or **B**) in Cs_2PdSe_8, (b) A schematic drawing of (a) to show the propagation direction of the helical assemblies. Notice that some of the Pd atoms are shared by the two helices. The dimensions of each of the two boxes are $\frac{1}{2}a \times \frac{1}{2}b \times 4c$. (c) The relation of such an arrangement to the left- and right-handed helices.

Compound **1** is stable in air indefinitely but unstable at high temperatures. Upon being heated to 320°C, it decomposes to produce $PdSe_2$, Cs_2Se_3, and Se (9). The optical properties of **1** were assessed from the diffuse reflectance data. A band gap energy of 1.5 eV was estimated, which confirms the semiconducting nature of this compound (10).

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6. $PdCl_2$ (99.9%, Strem Chemical Co.) and Se (99.5%, Strem Chemical Co.) powders and Cs_2Se were used as starting materials. Cs_2Se was prepared by reaction of cesium metal and elemental selenium in a 2 : 1 ratio in liquid ammonia. Ethylenediamine (99%, anhydrous, Fisher Scientific) was used as solvent. Single crystals of **1** were obtained from a solvothermal reaction containing 0.25 mmol (0.086 g) of Cs_2Se, 0.75 mmol (0.059 g) of Se, and 0.25 mmol (0.044 g) of $PdCl_2$. The reagents were weighed and mixed under inert atmosphere. The mixture was then transferred to a thick-walled Pyrex tube and approximately 0.4 ml

of solvent (en) was added to the sample. After the liquid was condensed by liquid nitrogen, the tube was sealed with a torch under vacuum. The sample was heated at 160°C for 7 days. After being cooled to room temperature, the mixture was washed with 30% and 95% ethanol followed by drying with anhydrous diethyl ether. Black prism-like crystals of **1** were isolated from the final product. The approximate composition of Cs/Pd/Se was established with the microprobe of a JEOL JXA-8600 Superprobe. Subsequent reactions by stoichiometric combination of Cs_2Se (0.088 g), Pd (0.053 g) and Se (0.140 g) at 250°C produced **1** in high yield (approx. 90%).

7. Crystal size: $0.2 \times 0.3 \times 0.4$ mm, tetragonal space group $I4_1/acd$ (No. 142), $a = 14.935(2)$, $c = 12.907(3)$ Å, $V = 2879.0(8)$ Å^3, $Z = 8$, ρ(calc) = 4.632 g cm^{-3}, $\mu = 26.454$ mm^{-1}, $R_1 = 0.044$, and $wR_2 = 0.063$ for 640 unique reflections. The room temperature ($294 \pm 1°$K) single-crystal X-ray diffraction experiments were performed on an Enraf–Nonius CAD4 diffractometer wing graphite monochromatized Mo$K\alpha$ radiation. Data were collected by the ω-scan method within the limits $6° < 2\theta < 50°$. An empirical absorption correction based on ψ-scans was applied to all data. The structure was solved by direct methods and refined by full-matrix least-squares on F_o^2. Anisotropic thermal displacements were assigned to all atoms. All calculations were performed using SHELX97 (G. M. Sheldrick, "SHELX-97: Program for Crystal Structure Refinement," University of Goettingen; 1997). Crystal draw-ings were produced with SCHAKAL 92 (E. Keller, "SCHAKAL 92, a Computer Program for the Graphical Representation of Crystallographic Models," University of Freiburg, 1992).

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9. Differential scanning calorimetry (DSC) analysis of **1** was performed with a TA Instruments 2920 DSC analyzer. A powder sample from ground single crystals (total mass = 10.1640 mg) was loaded into an aluminium hermetic pan and heated from room temperature to 600°C with a ramp rate of 10°C/min. A larger endothermic peak was observed at ~ 320°C, indicative of a thermal decomposition of **1** into the elemental Se and binary phases $PdSe_2$ and Cs_2Se_3, which were later confirmed by powder X-ray diffraction analysis.

10. A Shimadzu UV-3101PC double beam double monochromator spectrophotometer was used to measure the optical diffuse reflectance of **1**. $BaSO_4$ powder was used as reference (100% reflectance). The absorption coefficients were computed using the Kubelka–Munk or remission function (11) and an estimated band-gap energy was obtained (12).

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