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$APdCu(Se_2)(Se_3)$ (A = K and Rb): New Quaternary Copper Palladium Polyselenides with Unusual Metal–Selenium Coordination

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Two novel metal polyselenides, $KPdCu(Se_2)(Se_3)$ (**I**) and $RbPdCu(Se_2)(Se_3)$ (**II**), have been synthesized from solvothermal reactions in superheated ethylenediamine at 160 °C. The isostructural compounds crystallize in the monoclinic space group $P2_1/m$, $Z = 2$, with $a = 6.145(1)$ Å, $b = 7.268(1)$ Å, $c = 8.865(2)$ Å, $\beta = 102.41(3)°$ for **I**, and $a = 6.253(1)$ Å, $b = 7.267(1)$ Å, $c = 8.993(2)$ Å, $\beta = 102.28(3)°$ for **II**. Their crystal structures are two-dimensional networks with ${}^{2}_{\infty}[PdCu(Se_2)(Se_3)]^-$ anionic layers built from one-dimensional ${}^{1}_{\infty}[Pd(Se_2)(Se_3)]^{2-}$ "chains" that are "stitched" together by tetrahedrally coordinated Cu atoms. The DSC data show that **I** and **II** are stable up to 400 °C and decompose at ca. 436 and 424 °C, respectively. Both compounds are narrow band-gap semiconductors with estimated band gaps of about 0.7 eV (**I**) and 0.8 eV (**II**), respectively. They are the first structurally characterized quaternary copper palladium polychalcogenides with a $(Se_2)^{2-}$ and a $(Se_3)^{2-}$ fragment, both exhibiting interesting and unusual metal–selenium coordination.

Introduction

The Pd-containing compounds have attracted much attention due to the catalytic functions of the metal and its ability to form polychalcogenide complexes in solution media. In recent years, a number of ternary Pd polychalcogenides have been isolated and structurally characterized. These include $(Ph_4P)_2[Pd(Se_4)_2]$ with discrete $[Pd(Se_4)_2]^{2-}$ anions in which each Pd^{2+} is coordinated by two chelating $(Se_4)^{2-}$ ligands;[1] $\{(CH_3)N(CH_2CH_2)_3N\}_2[Pd(Se_6)_2]$ and $(enH)_2[Pd(Se_5)_2]$ featuring sheetlike, two-dimensional (2D) Pd polyselenide anionic frameworks;[2] $Rb_2[Pd(Se_4)_2]\cdot Se_8$ containing sheetlike polyanion $[Pd(Se_4)_2]^{2-}$ with "intercalated" crownlike Se_8 eight-membered rings;[3] and $K_4[Pd(Se_4)_2][Pd(Se_6)_2]$ ($=K_2PdSe_{10}$) and $Cs_2[Pd(Se_4)_2]$ ($=Cs_2PdSe_8$) having three-dimensional (3D) structures constructed from two interpenetrating $[Pd(Se_x)_2]^{2-}$ frameworks ($x = 4$ and 6 for the K^+ salt, $x = 4$ and 4 for the Cs^+ salt).[4,5] In contrast, the quaternary Pd transition metal chalcogenides are relatively unexplored. In the system of A−M−M′−Q (A = alkali metal, M = group I element, M′ = group VIII metal, Q = chalcogen), only several Fe compounds with the crystal formula of $AMFeQ_2$ (A = Li, Na, K, and Cs; M = Cu, Ag; Q = S, Se, Te) are known.[6−10] These monochalcogenides prepared by high-temperature solid state reactions or the molten alkali metal polychalcogenide flux method crystallize in two different space groups, $P\bar{3}m1$ (for Li and Na salts) and $I4/mmm$ ($ThCr_2Si_2$-type, for K and Cs salts), respectively. They are all layered compounds containing ${}^{2}_{\infty}[MFeQ_2]^-$ anionic layers of edge-sharing MQ_4 and FeQ_4 tetrahedra separated by A^+ counterions. In this paper, we reported the preparation, crystal structures, and optical and thermal properties of two novel compounds, $APdCu(Se_2)(Se_3)$ (A = K and Rb), which are the first quaternary copper palladium polychalcogenides obtained by solvothermal methods using ethylenediamine (en) as a reaction medium.

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Experimental Section

Materials. A_2Se (A = K, Rb) compounds were prepared by reactions of alkali metal and elemental Se in a 2:1 ratio in liquid ammonia. $PdSe_2$ was prepared by stoichiometric reactions of elements at 300 °C for 3 days. The other chemicals were used as purchased without further treatment: CuCl (99%, Aldrich), Se (99.5%, Strem Chemicals, Inc.), and ethylenediamine (99%, anhydrous, Aldrich).

Synthesis. $KPdCu(Se_2)(Se_3)$ (**I**) was prepared by weighing and mixing 0.039 g (0.25 mmol) of K_2Se, 0.066 g (0.25 mmol) of $PdSe_2$, 0.025 g (0.25 mmol) of CuCl, and 0.059 g (0.75 mmol) of Se in a glovebox under an inert atmosphere of argon. The mixture was then transferred to a thick-walled Pyrex tube, and 0.37 mL of en was added to it. After the liquid was condensed by liquid nitrogen, the tube was sealed with a torch under a vacuum of $\sim 10^{-3}$ Torr. The sample was placed in an oven and heated at 160 °C for one week, and then cooled to room temperature. The dark-red, columnlike crystals in about 80% yield were isolated by washing the reaction product with 20% and 80% ethanol followed by drying with anhydrous diethyl ether. $RbPdCu(Se_2)(Se_3)$ (**II**) was synthesized from a solvothermal reaction of 0.062 g (0.25 mmol) of Rb_2Se, 0.066 g (0.25 mmol) of $PdSe_2$, 0.025 g (0.25 mmol) of CuCl, and 0.059 g (0.75 mmol) of Se in en (0.37 mL). The same heating and isolation procedures as previously described for **I** were used. Dark-red, columnlike crystals of **II** were obtained in about 90% yield. Both **I** and **II** appeared to be relatively stable in air and water.

Crystal Structure Determination. Intensity data of the title compounds were collected at room temperature (293 ± 1 K) on an Enraf-Nonius CAD4 automatic four-circle diffractometer with graphite monochromated Mo Kα radiation. Cell dimensions were obtained from least-squares refinements with 20 (**I**) or 25 (**II**) automatically centered reflections in the range $7.89° \leq \theta \leq 12.36°$ (**I**), $6.58° \leq \theta \leq 13.59°$ (**II**). Three standard reflections were remeasured after every 2 h. No decay was observed except the statistic fluctuation in the ranges ±2.5% (**I**) and ±4.5% (**II**). Raw intensities were corrected for Lorentz and polarization effects, and for absorption by empirical method based on ψ-scan data. Direct phase determination and subsequent difference Fourier map synthesis yielded the positions of all atoms, all of which were eventually subjected to the anisotropic refinements. An extinction correction was applied to the calculated structure factors and refined to 0.0022(5) (**I**) and 0.0020(3) (**II**). For compound **I**, the final full-matrix least-squares refinements on F^2 led to R1 = 0.0316 and wR2 = 0.0770 for 649 observed reflections ($I > 2\sigma(I)$) and 47 variables. The reliability factors for compound **II** converged to R1 = 0.0502 and wR2 = 0.0841 for 529 observed reflections. The final difference electron density maps showed no features in both cases. Details of unit cell parameters, data collection, and structure refinements are given in Table 1. All computations were performed using the SHELX97 program package.[11] Crystal structure drawings were produced with SCHAKAL 92.[12] Final atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2.

Thermal Analysis. Differential scanning calorimetry (DSC) measurements were carried out on a computer-controlled TA Instrument DSC-2920 analyzer. Powder samples of **I** (25.830 mg) and **II** (19.580 mg) were sealed into two aluminum pans, respectively. An approximately equal mass of sealed empty aluminum pan was used as a reference. The samples were heated at a rate of 5 °C/min from room temperature to 550 °C under nitrogen and then cooled under nitrogen gas current. The residues were examined by powder X-ray diffraction immediately after the DSC experiments.

Table 1. Crystallographic Data for $KPdCu(Se_2)(Se_3)$ (**I**) and $RbPdCu(Se_2)(Se_3)$ (**II**)

	I	**II**
formula	$KPdCu(Se_2)(Se_3)$	$RbPdCu(Se_2)(Se_3)$
fw	603.84	650.21
space group	$P2_1/m$ (No. 11)	$P2_1/m$ (No. 11)
a, Å	6.145(1)	6.253(1)
b, Å	7.268(1)	7.267(1)
c, Å	8.865(2)	8.993(2)
β, deg	102.41(3)	102.28(3)
V, Å^3, Z	386.7(1), 2	399.3(1), 2
d_{calcd}, g/cm^3	5.186	5.408
λ, Å	0.71073	0.71073
μ, mm^{-1}	29.037	33.654
R indices [$I \geq 2\sigma(I)$],		
R1[b]	0.0316	0.0502
wR2[c]	0.0770	0.0841
R indices (all data),		
R1	0.0533	0.1038
wR2	0.0850	0.0961

[a] $R1 = (\Sigma||F_o| - |F_c||)/(\Sigma|F_o|)$. [b] $wR2 = \sqrt{\dfrac{\Sigma[w(F_o^2 - F_c^2)^2]}{\Sigma w(F_o^2)^2}}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Temperature Factors[a] (Å^2) for $KPdCu(Se_2)(Se_3)$ (**I**) and $RbPdCu(Se_2)(Se_3)$ (**II**)

atom	x	y	z	U_{eq}
		$KPdCu(Se_2)(Se_3)$ (**I**)		
Pd	0.5	0	0.5	0.013(1)
Cu	0.1188(3)	0.25	0.6075(2)	0.021(1)
Se(1)	0.7285(2)	0.25	0.6367(1)	0.013(1)
Se(2)	0.7201(2)	0.25	0.8991(2)	0.020(1)
Se(3)	0.0389(2)	−0.25	0.6662(1)	0.015(1)
Se(4)	0.3155(1)	−0.0139(1)	0.7198(1)	0.014(1)
K	0.2612(5)	0.25	1.0455(4)	0.029(1)
		$RbPdCu(Se_2)(Se_3)$ (**II**)		
Pd	0.5	0	0.5	0.016(1)
Cu	0.1108(5)	0.25	0.6099(4)	0.021(1)
Se(1)	0.7240(3)	0.25	0.6359(3)	0.014(1)
Se(2)	0.7088(4)	0.25	0.8933(3)	0.020(1)
Se(3)	0.0432(4)	−0.25	0.6597(3)	0.016(1)
Se(4)	0.3115(2)	−0.0126(3)	0.7129(2)	0.015(1)
Rb	0.2553(4)	0.25	1.0493(3)	0.025(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized **U** tensor.

Diffuse Reflectance Measurements. Optical diffuse reflectance spectra were measured at room temperature with a Shimadzu UV-3101PC double-beam, double-monochromator spectrophotometer. Data were collected in the wavelength range 250−2000 nm. $BaSO_4$ powder was used as a standard (100% reflectance). A similar procedure as previously described[13] was used to collect and convert the data using the Kubelka−Munk function.[14] The scattering coefficient (S) was treated as a constant since the average particle size of the samples used in the measurements was significantly larger than 5 μm.

Results and Discussion

Structure Description. Since **I** and **II** are isostructural, the discussion will refer mainly to **I**. $KPdCu(Se_2)(Se_3)$ (**I**)

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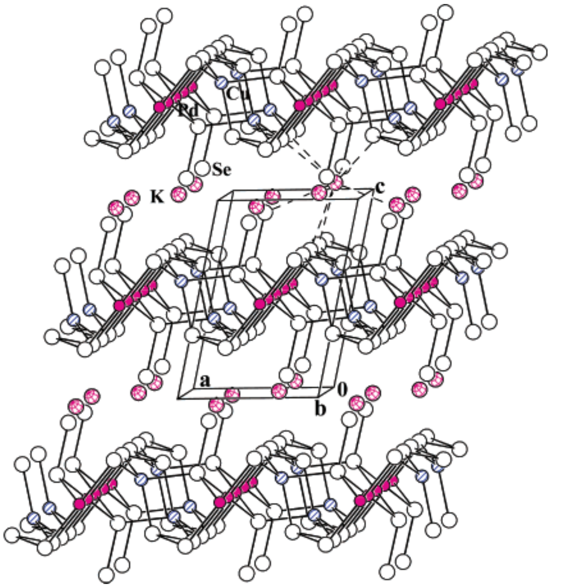

Figure 1. View of the $\mathrm{KPdCu(Se_2)(Se_3)}$ (**I**) structure approximately along the *b*-axis. Dashed lines show the coordination environment of the K^+ cations.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $\mathrm{KPdCu(Se_2)(Se_3)}$ (**I**) and $\mathrm{RbPdCu(Se_2)(Se_3)}$ (**II**)

	$\mathrm{KPdCu(Se_2)(Se_3)}$ (**I**)		
Pd−Se(1)	2.4515(9) ×2	Se(1)−Pd−Se(4)	87.20(4) ×2
Pd−Se(4)	2.458(1) ×2	Se(1)−Pd−Se(4)	92.80(4) ×2
Cu−Se(4)	2.369(1) ×2	Se(1)−Pd−Se(1)	180
Cu−Se(3)	2.411(2)	Se(4)−Pd−Se(4)	180
Cu−Se(1)	2.467(2)	Se(3)−Cu−Se(1)	85.19(7)
Se(1)−Se(2)	2.338(2)	Se(4)−Cu−Se(4)	108.08(8)
Se(3)−Se(4)	2.390(1) ×2	Se(4)−Cu−Se(1)	112.06(6) ×2
K−Se(2)	3.299(3)	Se(4)−Cu−Se(3)	118.77(5) ×2
K−Se(2)	3.349(4)	Se(4)−Se(3)−Se(4)	91.78(6)
K−Se(4)	3.423(3) ×2	Se(3)−Se(4)−Pd	107.53(5)
K−Se(3)	3.458(4)	Se(2)−Se(1)−Pd	111.05(4) ×2
K−Se(4)	3.541(3) ×2	Pd−Se(1)−Pd	95.67(5)
K−Se(2)	3.6656(7) ×2		
	$\mathrm{RbPdCu(Se_2)(Se_3)}$ (**II**)		
Pd−Se(4)	2.454(2) ×2	Se(4)−Pd−Se(1)	87.55(7) ×2
Pd−Se(1)	2.455(2) ×2	Se(4)−Pd−Se(1)	92.45(7) ×2
Cu−Se(4)	2.362(2) ×2	Se(1)−Pd−Se(1)	180
Cu−Se(3)	2.411(4)	Se(4)−Pd−Se(4)	180
Cu−Se(1)	2.479(3)	Se(3)−Cu−Se(1)	84.6(1)
Se(1)−Se(2)	2.337(4)	Se(4)−Cu−Se(4)	107.8(1)
Se(3)−Se(4)	2.383(2) ×2	Se(4)−Cu−Se(1)	114.2(1) ×2
Rb−Se(2)	3.407(3)	Se(4)−Cu−Se(3)	117.4(1) ×2
Rb−Se(2)	3.420(3)	Se(4)−Se(3)−Se(4)	92.8(1)
Rb−Se(3)	3.524(4)	Se(3)−Se(4)−Pd	107.74(9)
Rb−Se(4)	3.525(3) ×2	Se(2)−Se(1)−Pd	110.73(8) ×2
Rb−Se(4)	3.656(3) ×2	Pd−Se(1)−Pd	95.46(8)
Rb−Se(2)	3.6702(7) ×2		

consists of 2D $_{\infty}^{2}[\mathrm{PdCu(Se_2)(Se_3)}]^-$ anionic layers separated by K^+ cations (Figure 1). Each Pd^{2+} center is coordinated by two Se1 atoms from two $(Se_2)^{2-}$ and two Se4 atoms from two $(Se_3)^{2-}$ fragments in a slightly distorted square-planar geometry, typical for d^8-ions. Because the Pd atom resides on an inversion center, the $(Se_2)^{2-}$and $(Se_3)^{2-}$ pairs are arranged in a *trans* conformation. The Pd−Se distances of 2.4515(9)−2.458(1) Å (Table 3) compare well with those found in other polyselenides, e.g., $\mathrm{K_2PdSe_{10}}$ (average 2.462(5) Å),[4] $\mathrm{Rb_2[Pd(Se_4)_2]\cdot Se_8}$ (2.4339(6) Å),[3] and $\mathrm{Cs_2PdSe_8}$ (2.428(1) Å).[5] The Se−Pd−Se angles are 87.20(4)−92.80(4)° for *cis* and 180° for *trans* Se atoms, respectively.

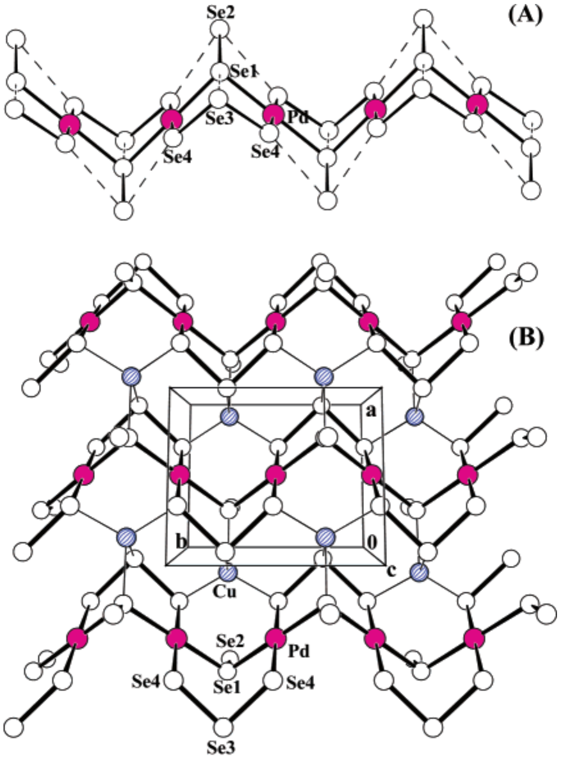

Figure 2. (A) Fragment of the undulating 1D $_{\infty}^{1}[\mathrm{Pd(Se_2)(Se_3)}]^{2-}$ "ribbons" found in $\mathrm{KPdCu(Se_2)(Se_3)}$ (**I**). The Se···Se nonbonding interactions (less than 3.31 Å) are denoted by dashed lines. (B) Perspective view of the 2D $_{\infty}^{2}[\mathrm{PdCu(Se_2)(Se_3)}]^-$ anionic layer along the [001] direction. Both Pd−Se and Se−Se bonds are drawn with thick solid lines, while the Cu−Se bonds are represent by thin solid lines.

Two neighboring Pd^{2+} centers are doubly bridged by one $(Se_2)^{2-}$ and one $(Se_3)^{2-}$ ligands to form the undulating 1D $_{\infty}^{1}[\mathrm{Pd(Se_2)(Se_3)}]^{2-}$ "ribbons", in which the bridging Se1 atoms of $(Se_2)^{2-}$ units and the central Se3 atoms of the $(Se_3)^{2-}$ units are positioned at the peaks of the wave with the unshared terminal Se2 atoms of $(Se_2)^{2-}$ units pointing away from the curve. The "ribbons" are closely related to those found in the one-dimensional chain compound $\mathrm{BaPdS_2}$ and can be viewed as substitutional variants of the $_{\infty}^{1}[\mathrm{PdS_2}]^{2-}$ type in which $(Se_2)^{2-}$ and $(Se_3)^{2-}$ occupy the S^{2-} sites.[15] These "ribbons" are propagated by a crystallographic screw axis resulting in the Se2 atoms appearing on opposite sides of the Se−Pd−Se linkage, as depicted in Figure 2A. Interestingly, the central Se3 atoms of the triselenide and the terminal Se2 atoms of the diselenide units are roughly coplanar with the central $\mathrm{PdSe_4}$ coordination plane, their deviations from this plane being 0.014(2) and 0.694(2) Å, respectively. As a consequence, short Se−Se nonbonding contacts are formed between Se1 and Se3 (3.302(2) Å) as well as Se2 and Se4 atoms (3.269(2) Å) (see dashed lines in Figure 2A). The values are definitely less than the sum (3.60 Å) of the Se···Se van der Waals radii and may be indicative of secondary bonding interactions. Similar weak interactions are also found in $\mathrm{Rb_2[Pd(Se_4)_2]\cdot Se_8}$, as revealed by the Se···Se distances of 3.287−3.465 Å.[3] The origin of this weak interaction is not clear but is probably associated with the well-known catenation capacity of the chalcogens. The Se−

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Se bond distances in the diselenide units (2.338(2) Å) are slightly shorter than those in the triselenide units (2.390(1) Å), and both are close to those of K_2Se_3[16] and K_3AuSe_{13},[17] in good agreement with the Se−Se covalent bond distance, 2.3 Å.[18] The Se−Se−Se angles of 91.78(6)° are smaller than the Pd−Se−Se angles (107.53(5)−111.05(4)°), which follows the general trend observed in other known Pd polyselenides.[3−5]

The ${}^{1}_{\infty}[Pd(Se_2)(Se_3)]^{2-}$ “chains” run parallel to the crystallographic *b*-axis and stack in phase along the [100] direction. They are “stitched” together by tetrahedrally coordinated Cu atoms leading to the formation of the 2D ${}^{2}_{\infty}[PdCu(Se_2)(Se_3)]^{-}$ anionic layers. Each Cu atom is bonded at two points to Se4 atoms of two $(Se_3)^{2-}$ species from one ${}^{1}_{\infty}[Pd(Se_2)(Se_3)]^{2-}$ “chain”, and at the remaining sites to one bridging Se1 atom of $(Se_2)^{2-}$ and one central Se3 atom of $(Se_3)^{2-}$ from the neighboring “chain”. This connection mode causes the adjacent $PdSe_4$ coordination planes to form an angle close to the tetrahedral value thereby giving rise to a unusual zigzag structural arrangement of the ${}^{1}_{\infty}[Pd(Se_2)(Se_3)]^{2-}$ “chain”. While the $CuSe_4$ tetrahedra and $PdSe_4$ square planes share common corners, the $CuSe_4$ tetrahedra themselves are linked together by joining the three Se corners to form four Se−Se bonds (Se3−Se4 bonds) with neighboring tetrahedra and the fourth corner occupied by a $(Se_2)^{2-}$ group. The distance of 4.216(2) Å between adjacent Cu centers is considerably longer than that in elemental Cu (2.56 Å), eliminating any $d^{10}\cdots d^{10}$ Cu(I) interactions. The tetrahedral environments around Cu atoms are severely distorted, with Cu−Se distances divided into two sets (2.369(1) × 2, 2.411(2), 2.467(2) Å). A set of two longest Cu−Se contacts has the smallest bond angle of 85.19(7)°, while other Se−Cu−Se angles are between 108.08(8)° and 118.77(5)°. A similar, highly distorted copper coordination geometry has also been observed in $Cs_2Cu_2Sb_2Se_5$ (Cu−Se distances 2.410(3)−2.637(3) Å; Se−Cu−Se angles 96.29(8)−128.2(1)°).[19]

As can be seen from Figure 1, the potassium cations are located between the anionic layers to balance the charge and stabilize the dangling end of the $(Se_2)^{2-}$ ligands. Each K^+ is coordinated to nine Se atoms, five of which are from the top layer, and the others are from the bottom layer. They are arranged in a monocapped square-antiprismatic geometry with the K−Se distances of 3.299(3)−3.6656(7) Å, which are in the same range as reported for the nine-coordinated K^+ in $K_{12}Mo_{12}Se_{56}$ (3.305−3.825 Å).[20] The ${}^{2}_{\infty}[PdCu(Se_2)(Se_3)]^{-}$ anionic framework is not subject to a cation effect as one moves from the smaller K^+ to the larger Rb^+ cation. This may arise from the fact that the size difference between K^+ and Rb^+ is not large enough to overcome the strong preference of the Pd^{2+} cations for square plane coordination. Attempts to prepare the isostructural cesium analogue “$CsPdCu(Se_2)(Se_3)$” have so far been unsuccessful, possibly because Cs^+ is too large to stabilize this structure type.

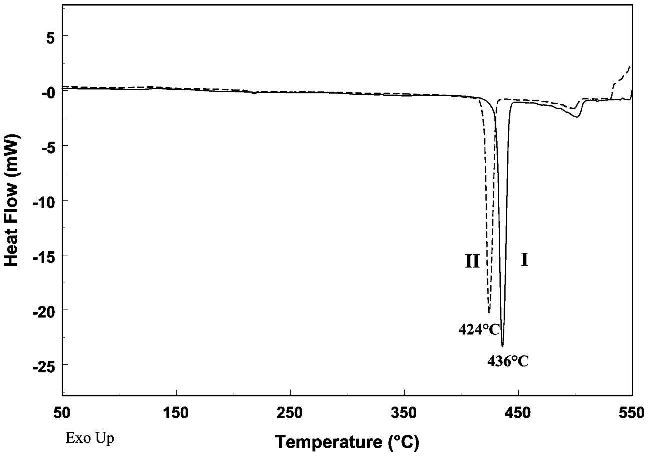

Figure 3. Differential scanning calorimetry (DSC) curves of $KPdCu(Se_2)(Se_3)$ (**I**) and $RbPdCu(Se_2)(Se_3)$ (**II**), respectively.

It is noted that both $(Se_2)^{2-}$ and $(Se_3)^{2-}$ polyanions found in the title compounds behave in a rather unusual manner. Each $(Se_2)^{2-}$ functions as a μ_3-bridging ligand bonded to two Pd atoms and one Cu atom via a single Se1 atom, with another Se of the diselenide unit (Se2) kept noninteracting, while each $(Se_3)^{2-}$ is 5-fold coordinate to two Cu atoms and two Pd atoms via its two terminal Se4 atoms and to the other Cu via its central Se3 atom. Chelating and bridging Q_n^{2-} ligands (Q = S, Se, Te), that are bound to metal centers through their terminal Q atoms, are common in polychalcogenide chemistry, while the tridentate $(Se_2)^{2-}$ dangling bond and the direct coordination of the central Se atom of the $(Se_3)^{2-}$ unit to a metal are quite rare. Limited examples of tellurides with bridging μ_2-$(Te_2)^2$ ligands in a dangling mode are $K_4Hf_3Te_{17}$[21] and $[K\text{-}2,2,2\text{-crypt}]_2[Mo_4(Te_2)_5(Te_3)_2(en)_4]$.[22] There are no corresponding examples mentioned in the literature for the analogous $(Se_2)^{2-}$ ligands, but several monodentate dangling ligands such as η^1-$(Se_3)^{2-}$ and η^1-$(Se_5)^{2-}$ were previously found in Na_3AuSe_8[23] and K_3AuSe_{13},[17] respectively. The unusual 5-fold coordinated μ_5-$(Se_3)^{2-}$ unit has been encountered in the structure of $CuAu(Se_3)Se$ whose crystals were grown from the molten K_2Se_x fluxes at 310 °C.[24]

Physical Properties. The DSC data of the title compounds (Figure 3) showed a single strong endotherm upon heating, with the peak position centered at ca. 436 °C for **I**, and ca. 424 °C for **II**, respectively. Examination of the DSC residue by powder XRD revealed that both compounds decomposed to give similar products: $PdSe_2$, Se, and an unknown amorphous material.

The title compounds are electron precise and are predicted to be semiconductors. The optical properties were examined by analyzing their diffuse reflectance data. The Kubelka−Munk functions[14] for **I** and **II** were converted from the

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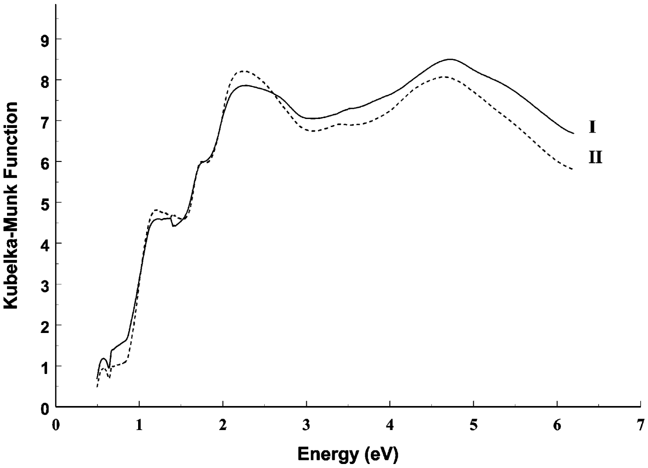

Figure 4. Optical absorption spectra of $KPdCu(Se_2)(Se_3)$ (**I**) and $RbPdCu(Se_2)(Se_3)$ (**II**).

diffuse reflectance data ($F = (1 - R_\infty)^2/2R_\infty$, where R_∞ is the relative diffuse reflectance of an infinitely thick layer. For practical purposes, this can be achieved at a layer depth of a few millimeters). Plotted in Figure 4 are remission functions versus the wavelength. The spectra of both compounds display steep absorption edges, from which an optical band gap of 0.7 eV is estimated for $KPdCu(Se_2)(Se_3)$ (**I**), while in the case of $RbPdCu(Se_2)(Se_3)$ (**II**) this band gap is shifted to higher energy by about 0.1 eV. The band gaps are significantly smaller than those observed for other 2D and 3D ternary Pd polyselenides (range 1.4−1.6 eV), indicating both compounds to be narrow-gap semiconductors.

So far, solvothermal reactions have produced many binary and ternary polychalcogenides containing long $(Q_n)^{2-}$ ($n \geq 2$) fragments;[25] however, the number of known quaternary polychalcogenides prepared via this route is very limited. $APdCu(Se_2)(Se_3)$ (A = K, Rb) represents a new structure type and the first example of a quaternary copper palladium polychalcogenide with a $(Se_2)^{2-}$ and a $(Se_3)^{2-}$ fragment, both exhibiting interesting and unusual bond modes. The successful syntheses of the title compounds confirmed that the mild solvothermal conditions stabilize the polychalcogen building blocks and allow $(Se_2)^{2-}$ and $(Se_3)^{2-}$ ions to incorporate and remain intact in the final structure. It is believed that the synthetic route is still promising for the preparation of more metal polychalcogenides with unusual structures and properties.

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Supporting Information Available: ORTEP plots (2) showing atoms in asymmetric unit as 50% thermal ellipsoids. Tables of atomic coordinates of all atoms, isotropic and anisotropic thermal parameters, bond distances and angles, crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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