inorganic papers

Barium palladium selenostannate perselenostannate diselenide, $Ba_8Pd(SnSe_4)_{3.75}(SnSe_5)_{0.25}(Se_2)$

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(Pd–Se) = 0.002 Å
Disorder in solvent or counterion
R factor = 0.037
wR factor = 0.077
Data-to-parameter ratio = 31.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The quaternary selenostannate $Ba_8Pd(SnSe_4)_{3.75}(SnSe_5)_{0.25}$-$(Se_2)$ adopts a new structure type composed of $SnSe_4$ tetrahedra in a distorted cubic close-packing arrangement. $Pd_2(Se_2)_2$ hexagons containing two Pd atoms and two Se_2 dumb-bells fill one-eighth of the octahedral voids. Two Se atoms from the diselenide groups and the neighbouring $SnSe_4$ units, respectively, form a distorted square-planar coordination around palladium. Eight or nine Se atoms surround the Ba^{2+} cations. One $SnSe_4^{4-}$ tetrahedron is substituted statistically by a perselenostannate ion $SnSe_5^{4-}$ to an extent of approximately 25%.

Comment

The remarkably varied crystal chemistry of selenogermanate and -stannate compounds emerges mainly from the co-existence and balance of different types of bonding interactions. Sn—Se bonds are essentially covalent and the tetrahedral $SnSe_4^{4-}$ anions may be regarded as quasi-molecular entities in the solid. On the other hand, metal—Se bonds range from purely ionic for alkali or alkaline earth metals to perceptibly covalent for transition metals. Thus, the combination of tetrahedral chalcogenoanions with different metal components leads to many new structure types. Recently, we reported the first palladium thiogermanate, $PdGeS_3$, which forms a novel quasi-one-dimensional structure (Johrendt & Tampier, 1998). Motivated by this, we continued our investigations on palladium compounds with tetrahedral chalcogenoanions of group 14 elements. In the present paper,
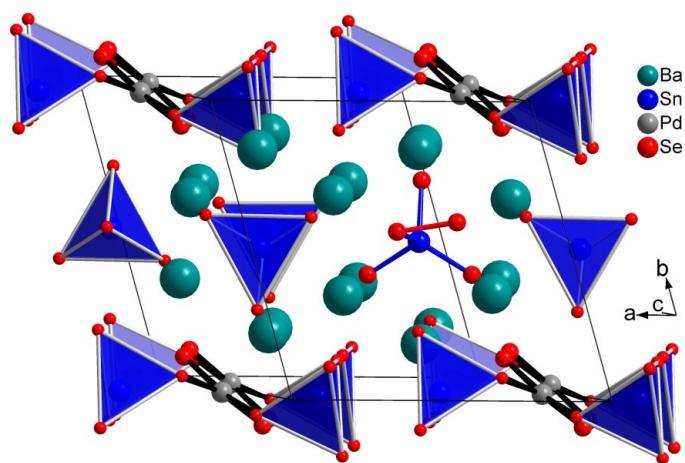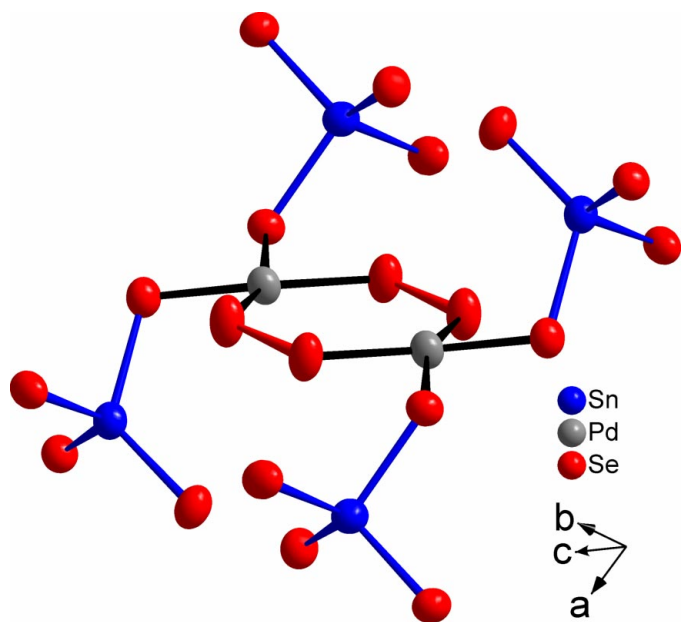

Figure 1
The unit-cell contents of $Ba_8PdSn_4Se_{18.25}$. The perselenostannate group $SnSe_5$ shown substitutes for 25% of $SnSe_4$ tetrahedra in this position.

Figure 2
The $Pd_2(Se_2)_2$ hexagon, connected to $SnSe_4$ tetrahedra in $Ba_8PdSn_4Se_{18.25}$. Displacement ellipsoids are drawn at the 90% probability level.

we report the crystal structure of the first quaternary barium palladium selenostannate.

The crystal structure of $Ba_8PdSn_4Se_{18.25}$ is presented in Fig. 1. Slightly distorted $SnSe_4$ tetrahedra [Se—Sn—Se angles range from 95.8 (1) to 126.6 (2)°] are arranged in slabs parallel to (010) at $y \sim 0$ and $\sim 1/2$. Pd atoms connect pairs of tetrahedra in the $y \sim 0$ slab. Seven or eight of the terminal Se atoms of the $SnSe_4$ units coordinate the Ba atoms between them, mainly forming capped trigonal prisms. Fig. 2 shows the surrounding of the Pd atoms. Their distorted square-planar coordination consists of two Se atoms from two $SnSe_4$ tetrahedra and two from Se_2 dumb-bells, which are not connected to tin. Two Pd atoms and two diselenide groups form a formally uncharged centrosymmetric $Pd_2(Se_2)_2$ hexagon, which is surrounded by $SnSe_4$ tetrahedra (Fig. 2). An additional Se atom in the structure is not connected to tin, but to an Se atom of the $Sn4Se_4$ tetrahedron, thus forming a per-selenostannate anion, $Sn4Se_5^{4-}$ (Fig. 1). This group replaces statistically 25% of the $Sn4Se_4$ tetrahedra, leading to the non-integer formula coefficients. An ordered distribution requires the space group $P1$, but since the $SnSe_4$:$SnSe_5$ ratio is 3:1, even this would not resolve the statistical occupation. In the present case, we cannot distinguish between three possible arrangements in a single unit cell: two $Sn4Se_4$ or two $Sn4Se_5$ groups (both cases with space group $P\bar{1}$) or one of each (with space group $P1$). Depending on the particular domain structures, different amounts of $SnSe_5$ groups may occur in different crystals. Consequently, we can assume a composition range from $Ba_8PdSn_4Se_{18}$ to $Ba_8PdSn_4Se_{19}$.

The insertion of the additional Se atom appears to be plausible from chemical reasons. Fig. 3 is a cut-out of the structure, showing the barium environment of the Se18 atoms,
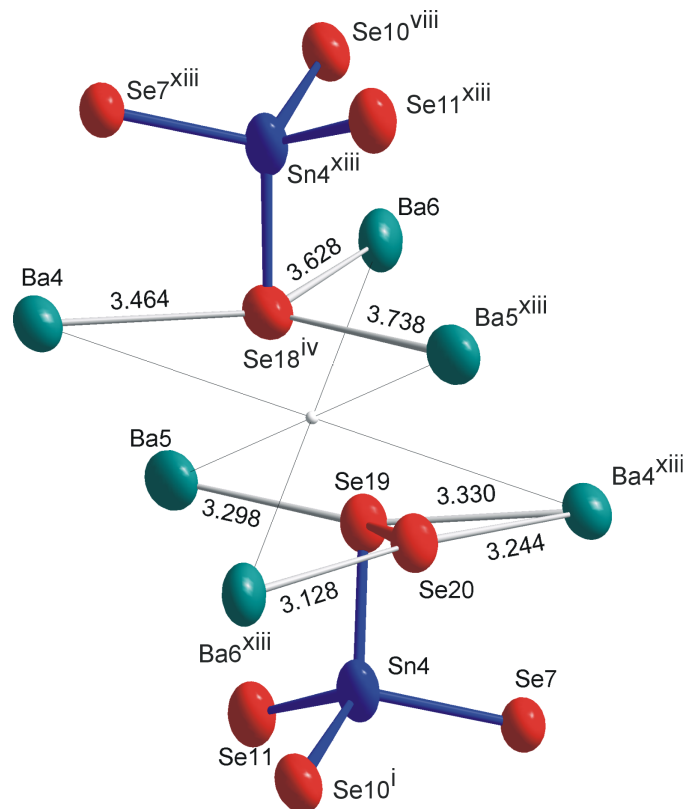
Figure 3
Cut-out of the $Ba_8PdSn_4Se_{18.25}$ structure, showing the environments of the statistically distributed $SnSe_5$ and $SnSe_4$ groups. The small white sphere marks the inversion centre. Displacement ellipsoids are drawn at the 90% probability level.

partially replaced by the Se19—Se20 dumb-bell on the other side of the inversion centre (indicated as a small white sphere). The Ba5—Se18 and Ba6—Se18 distances are 3.737 (3) and 3.628 (3) Å, respectively, significantly longer than the usual range of 3.1–3.4 Å; *i.e.* near the sum of the ionic radii, 3.40 Å. The coordination of Ba5 and Ba6 is significantly improved when Se18 is replaced by the Se19—Se20 dumb-bell, because now the Ba5—Se19 and Ba6—Se20 distances are 3.298 (7) and 3.128 (5) Å, respectively. However, the question, why the substitution of $Sn4Se_4$ groups by $Sn4Se_5$ occurs only partially, must remain open here.

$Ba_8PdSn_4Se_{18.25}$ crystallizes in its own structure type, which has no direct relation to a known one at first glance. As proposed recently (Tampier & Johrendt, 2001), we can trace the structures of compounds with isolated tetrahedral anions back to well-known principles of closest packing. For this, we consider the $SnSe_4$ tetrahedra as molecular entities, which is also reasonable from the view of chemical bonding. The space needed for such a 'molecule' is a sphere with an approximate radius ($d_{Sn-Se} + r_{Se}$) of 3.7 Å. These pseudo-spheres are arranged in a distorted cubic close packing in $Ba_8PdSn_4Se_{18.25}$, as depicted in Fig. 4 (smaller spheres with radii of 2.7 Å are shown for clarity). The $Pd_2(Se_2)_2$ hexagons are located in one eight of the octahedral voids of this packing, whereas the Ba^{2+} ions occupy the tetrahedral voids. From this viewpoint, we can derive this complex selenostannate structure from a filled anti-
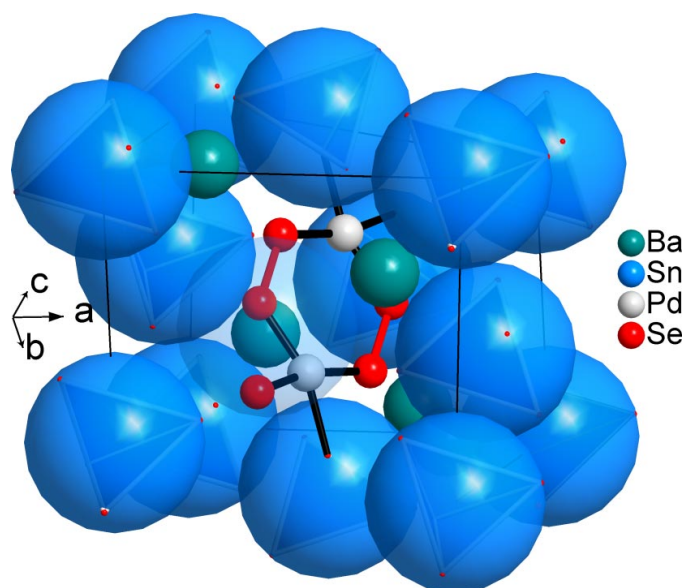
Figure 4
The motif of a distorted cubic close-packing arrangement, formed by $SnSe_4$ tetrahedra in $Ba_8PdSn_4Se_{18.25}$. $Pd_2(Se_2)_2$ hexagons occupy the octahedral and Ba^{2+} ions the tetrahedral voids.

CaF_2 structure according to the formulation $Ba_{16}{}^t(Pd_2Se_4)^{1/8o}$-$(SnSe_4)_8{}^{fcc}$.

Experimental

The title compound was synthesized by heating mixtures of the elements with the nominal composition $Ba_8PdSn_4Se_{18.5}$ in corundum crucibles, sealed in quartz ampoules under an argon atmosphere. The samples were first heated slowly ($20\ K\ h^{-1}$) to 973 K for 15 h and then cooled to room temperature. The inhomogeneous product was ground under argon and heated again to 1073 K for 2 d. This yielded a black crystalline powder, which is stable in air for several weeks. Single crystals appeared deep red when crushed to transparent pieces. X-ray powder diagrams could be completely indexed by using the crystallographic data obtained from the single-crystal experiment.

Crystal data

$Ba_8Pd(SnSe_2)_{3.75}(SnSe_5)_{0.25}(Se_2)$
$M_r = 3120.90$
Triclinic, $P\bar{1}$
$a = 12.604\ (1)$ Å
$b = 12.614\ (1)$ Å
$c = 14.782\ (2)$ Å
$\alpha = 67.85\ (1)°$
$\beta = 66.02\ (1)°$
$\gamma = 74.08\ (1)°$
$V = 1968.4\ (4)$ Å^3

$Z = 2$
$D_x = 5.266$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6409
reflections
$\theta = 2.6–27.9°$
$\mu = 27.66$ mm^{-1}
$T = 293\ (2)$ K
Plate, black
$0.07 \times 0.03 \times 0.01$ mm

Data collection

Stoe IPDS diffractometer
ω scans
Absorption correction: Gaussian
(X-RED; Stoe & Cie, 1996)
$T_{min} = 0.19$, $T_{max} = 0.51$
17825 measured reflections
9142 independent reflections
4504 reflections with $I > 2\sigma(I)$

$R_{int} = 0.043$
$\theta_{max} = 28.0°$
$h = -16 \rightarrow 15$
$k = -16 \rightarrow 16$
$l = -19 \rightarrow 19$
50 standard reflections
frequency: 12.0 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.077$
$S = 0.67$
9142 reflections
293 parameters

$w = 1/[\sigma^2(F_o{}^2) + (0.0313P)^2]$
where $P = (F_o{}^2 + 2F_c{}^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.95$ e Å^{-3}
$\Delta\rho_{min} = -2.04$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

Ba1—Se3	3.2360 (18)	Ba6—Se1	3.264 (2)
Ba1—Se9	3.3586 (16)	Ba6—Se16^i	3.3071 (18)
Ba1—Se11	3.4082 (16)	Ba6—Se2^{iv}	3.434 (2)
Ba1—Se13	3.4419 (19)	Ba6—Se15	3.4358 (19)
Ba1—Se17	3.462 (2)	Ba6—Se5	3.4468 (15)
Ba1—Se7	3.524 (2)	Ba6—Se10	3.4510 (19)
Ba1—Se6	3.5358 (18)	Ba6—Se13^{ix}	3.598 (2)
Ba1—Se11^i	3.653 (2)	Ba6—Se18	3.628 (3)
Ba2—Se10	3.4115 (19)	Ba7—Se17	3.3407 (16)
Ba2—Se12^{ii}	3.4124 (17)	Ba7—Se12	3.3886 (19)
Ba2—Se9^{iii}	3.4300 (16)	Ba7—Se9^i	3.3960 (19)
Ba2—Se11^i	3.4522 (17)	Ba7—Se2^i	3.4392 (19)
Ba2—Se15	3.5985 (19)	Ba7—Se8^{xiv}	3.475 (2)
Ba2—Se9	3.5985 (19)	Ba7—Se7^i	3.5687 (18)
Ba2—Se3	3.6114 (19)	Ba7—Se15^{xiv}	3.575 (2)
Ba2—Se8	3.6456 (19)	Ba7—Se15^x	3.6480 (18)
Ba2—Se12^i	3.648 (2)	Ba8—Se3^{xv}	3.224 (2)
Ba3—Se16^{iv}	3.349 (2)	Ba8—Se10^i	3.3459 (18)
Ba3—Se4^v	3.4085 (19)	Ba8—Se16	3.420 (2)
Ba3—Se13	3.4114 (17)	Ba8—Se14^i	3.4646 (16)
Ba3—Se14^{vi}	3.4592 (18)	Ba8—Se8^{xv}	3.4703 (17)
Ba3—Se4^{ii}	3.4689 (15)	Ba8—Se17^{xv}	3.5147 (19)
Ba3—Se6	3.4728 (19)	Ba8—Se10^{xv}	3.519 (2)
Ba3—Se2^{vii}	3.4915 (18)	Ba8—Se7	3.582 (2)
Ba3—Se3	3.5517 (19)	Sn1—Se12^{ii}	2.5044 (17)
Ba3—Se5^{viii}	3.5776 (19)	Sn1—Se3	2.5173 (16)
Ba4—Se20^i	3.244 (5)	Sn1—Se4^{ii}	2.5208 (19)
Ba4—Se6^i	3.3275 (19)	Sn1—Se14^{xiv}	2.612 (2)
Ba4—Se19^i	3.330 (6)	Sn2—Se9^x	2.5070 (18)
Ba4—Se4^{ix}	3.3681 (19)	Sn2—Se6^x	2.5216 (17)
Ba4—Se7^i	3.3722 (19)	Sn2—Se1^i	2.5296 (16)
Ba4—Se5^x	3.4445 (16)	Sn2—Se5^i	2.6194 (19)
Ba4—Se18	3.464 (2)	Sn3—Se17^{ii}	2.535 (2)
Ba4—Se6^{xi}	3.4809 (17)	Sn3—Se16^{xvi}	2.549 (2)
Ba4—Se1^{xii}	3.4931 (19)	Sn3—Se2^{iii}	2.5503 (16)
Ba5—Se1^i	3.2847 (18)	Sn3—Se13^{ii}	2.553 (2)
Ba5—Se19	3.298 (7)	Sn4—Se19	2.486 (7)
Ba5—Se20^{xiii}	3.330 (6)	Sn4—Se10^i	2.5400 (19)
Ba5—Se13	3.3471 (15)	Sn4—Se7	2.5421 (16)
Ba5—Se12	3.3531 (19)	Sn4—Se11	2.545 (2)
Ba5—Se4	3.4617 (17)	Sn4—Se18^i	2.603 (3)
Ba5—Se2^i	3.482 (2)	Pd—Se8^{xiv}	2.4292 (18)
Ba5—Se11	3.677 (2)	Pd—Se15^x	2.4342 (17)
Ba5—Se16^{xiii}	3.683 (2)	Pd—Se14	2.4385 (18)
Ba5—Se18^i	3.737 (3)	Pd—Se5^x	2.4468 (19)
Ba6—Se20^i	3.128 (5)	Se19—Se20	2.416 (10)

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x, 1 + y, z$; (iii) $1 - x, 2 - y, 1 - z$; (iv) $1 + x, y, z$; (v) $2 - x, 1 - y, -z$; (vi) $x, 1 + y, z - 1$; (vii) $1 + x, y, z - 1$; (viii) $x, y, z - 1$; (ix) $x, y, 1 + z$; (x) $x, y - 1, z$; (xi) $x, y - 1, 1 + z$; (xii) $1 - x, 1 - y, 2 - z$; (xiii) $1 - x, 1 - y, -z$; (xiv) $2 - x, 1 - y, 1 - z$; (xv) $x - 1, y, z$; (xvi) $1 + x, 1 + y, z$.

Refinements on a first model in $P\bar{1}$ gave a residual $wR2 = 0.15$, with large displacement parameters for the Se18 atom and two residual electron-density peaks in its vicinity. Their positions correspond to a Se_2-dumb-bell $[d_{(Se-Se)} = 2.41$ Å$]$ connected to an Sn4 atom and thus forming a perselenostannate ion, $SnSe_5{}^{4-}$. Further refinements of the occupation factors resulted in a statistical distribution of 75% $Sn4Se_4$ and 25% $Sn4Se_5$ groups. Attempts to refine an ordered arrangement in the space group $P1$ resulted in nearly the same statistical distribution with larger s.u.'s. Therefore, we decided to keep the space group $P\bar{1}$ for the final refinement.

Data collection: *IPDS Software* (Stoe & Cie, 1998); cell refinement: *IPDS Software*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998).

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