

Synthesis and Structure of Pr₃InSe₆

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Single crystals of the new compound Pr₃InSe₆ have been obtained by direct reaction among Pr, Se, and In₂Se₃ powders at 950°C. The material crystallizes with four formula units in space group $C_{2h}^2 - P2_1/c$ of the monoclinic system in a cell (at 123 K) of dimensions $a = 4.109(1)$, $b = 14.275(1)$, $c = 17.891(2)$ Å, $\beta = 103.27(1)^\circ$. The structure has been solved and refined from single-crystal X-ray data. The asymmetric unit contains three independent Pr atoms, two independent In atoms, and six independent Se atoms. Two of the crystallographically unique Pr atoms are in distorted bicapped trigonal prisms or distorted square antiprisms of Se atoms with Pr-Se interactions ranging from 2.970(2) to 3.281(2) Å while the other Pr atom is 7-coordinate in a greatly distorted monocapped octahedral environment with Pr-Se interactions ranging from 2.911(2) to 3.079(2) Å. Both independent In atoms are in distorted octahedra of Se atoms with In-Se interactions ranging from 2.537(2) to 2.856(2) Å. © 1989 Academic Press, Inc.

Introduction

Our work in ternary transition-metal chalcogenide systems has shown that structures can be analyzed and in some cases predicted in terms of the metal coordination polyhedra (1). Novel structure types can also be isolated by the incorporation of different coordination polyhedra derived from nontransition metals, with Eu_{0.59}Nb₅Se₈ (2) providing an example. Exploration of ternary main-group metal rare-earth chalcogenide systems has led to the preparation and characterization of a new praseodymium indium selenide Pr₃InSe₆ reported here.

Experimental

Synthesis. The title compound Pr₃InSe₆ was isolated in the product of a reaction consisting of Pr powder (ALFA, 99.9%), Se

powder (ATOMERGIC 99.999%), and In₂Se₃ powder in a 2:3:3 ratio. (In₂Se₃ was prepared by firing a stoichiometric mixture of In metal (ALFA, 99.9995%) and Se powder, sealed in an evacuated quartz tube at 600°C for 4 days.) The rare-earth reactant mixture was ground together under a blanket of Ar in a dry box, loaded into a carbon crucible, and subsequently sealed under vacuum (10⁻⁴ Torr) within a quartz jacket. The mixture was heated at a rate of approximately 50°/hr to 950°C, held at this temperature for 2 weeks, and then cooled to room temperature over a period of 24 hr. Black needles were found in the product. Analyses of these crystals with the microprobe of an EDAX-equipped Hitachi S570 scanning electron microscope indicated the presence of Pr, In, and Se.

Structure determination. A needle-shaped crystal measuring approximately 0.014 by 0.017 by 0.45 mm was mounted.

TABLE I
CRYSTAL DATA AND INTENSITY COLLECTION FOR
Pr₃InSe₆

Mol wt. (amu)	1011.3
Space group	$C_{2h}^5 - P2_1/c$
a (Å)	4.109(1)
b (Å)	14.275(1)
c (Å)	17.891(2)
β° (deg)	103.27(1)
V (Å ³)	1021.4
Z	4
ρ_c (g/cm ³)	6.575
T of data collection (K)	123 ^b
Radiation	Graphite monochromated CuK α ($\lambda(K\alpha_1) = 1.54056$ Å)
Crystal shape	Needle, bound by {001}, {010}, {0 $\bar{1}2$ }, { $\bar{1}01$ }, {02 $\bar{1}$ }
Crystal vol. (mm ³)	1.02×10^{-4}
Linear abs. coeff. (cm ⁻¹)	1541
Transmission factors ^c	0.011–0.252
Detector aperture (mm)	Horizontal slit 3, vertical slit 2.5, 20 cm from crystal
Take-off angle (deg)	3.5
Scan type	$\theta-2\theta$
Scan speed (deg/min)	2.74 with rescans up to 100 sec for initial $F_o^2 < 3\sigma(F_o^2)$
Scan range (deg)	-0.8 to +0.8° in 2θ
Background	$\frac{1}{4}$ of scan range on each side of reflection
2θ limits	$5^\circ \leq 2\theta \leq 153^\circ$
Data collected	$+h, +k, \pm l$
p for $\sigma(F^2)$	0.04
No. of unique data (including $F_o^2 < 0$)	2202
No. of unique data with $F_o^2 > 3\sigma(F_o^2)$	1867
$R(F^2)$	0.134
$R_w(F^2)$	0.154
R (on F for $F_o^2 > 3\sigma(F_o^2)$)	0.065
Error in observation of unit wt. (e ²)	2.3

^a α and γ were constrained to be 90° in the refinement of cell constants.

^b The low-temperature system is from a design by J. J. Bonnet and S. Askenazy and is commercially available from Sotorem, Z. I. de Vic, 31320 Castanet-Tolosan, France.

^c The analytical method as employed in the Northwestern absorption program AGNOST was used for the absorption correction (11).

The lattice constants were determined by a least-squares analysis of the setting angles of 25 reflections in the range $56^\circ \leq 2\theta$ ($\text{CuK}\alpha_1$) $\leq 65^\circ$ that had been automatically centered on an Enraf-Nonius CAD4 diffractometer. The refined cell constants and additional relevant crystal data are given in Table I. Six standard reflections measured every 3 hr throughout data collection showed no significant variations in intensity.

All calculations were carried out on a Harris 1000 computer with programs and methods standard in this laboratory (3). Conventional atomic scattering factors (4) were used and anomalous dispersion corrections (5) were applied. An examination of the intensity data showed the systematic absences characteristic of space group $P2_1/c$: $l = 2n + 1$ for $h0l$ reflections and $k = 2n + 1$ for $0k0$ reflections. Initial positions for Pr, In, and Se atoms were determined by the direct method program SHELX86 (6). The scale factor and atomic positions were subsequently refined to an R index of 0.162. From a difference electron density synthesis we verified that all atoms had

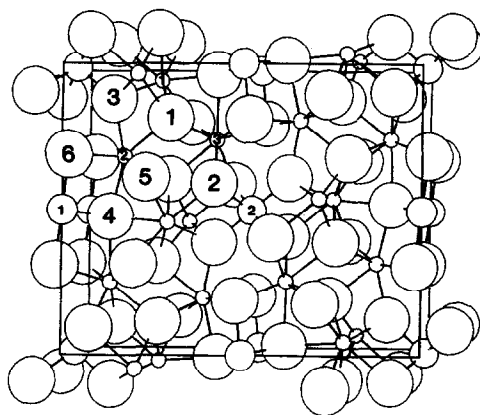


FIG. 1. View down the a -axis of the unit cell of Pr₃InSe₆. The origin is in the upper left, with the b -axis going from top to bottom and the c -axis from left to right. The small circles represent Pr atoms, the medium circles In atoms, and the large circles Se atoms. The numbering scheme is shown.

TABLE II
POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL
PARAMETERS FOR Pr_3InSe_6

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Pr(1)	0.22211(27)	0.041623(69)	0.222056(54)	0.04(2) ^a
Pr(2)	0.35433(29)	-0.186803(67)	0.354592(55)	0.08(2)
Pr(3)	-0.60564(29)	0.252454(69)	0.394274(56)	0.12(2)
In(1)	0	0	$\frac{1}{2}$	0.18(3)
In(2)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.77(3)
Se(1)	-0.21458(54)	0.18177(13)	0.28552(11)	0.20(3)
Se(2)	0.08400(56)	-0.09375(13)	0.08412(11)	0.20(3)
Se(3)	0.61200(57)	0.11326(14)	0.11233(11)	0.29(3)
Se(4)	0.39664(54)	0.02261(13)	0.39697(11)	0.15(3)
Se(5)	-0.24930(56)	-0.11038(14)	0.25143(11)	0.19(3)
Se(6)	-0.01848(55)	-0.18960(13)	0.48108(11)	0.14(3)

^a In view of the very significant absorption correction the standard deviations on *B* are probably greatly underestimated.

been located and we then corrected the data for absorption. Refinement of the model with use of the corrected data led to an *R* index of 0.099. The final cycle of refinement on F_o^2 , which included isotropic thermal parameters and an extinction factor, resulted in final values of *R* and *R_w* on F_o^2 of 0.134 and 0.154, respectively. The value of the conventional *R* index on *F* for those 1864 reflections having $F_o^2 > 3\sigma(F_o^2)$ is 0.065. A final difference electron density map contains no features greater than 5% the height of a Pr atom. No unusual trends were found in an analysis of F_o^2 versus F_c^2 as a function of F_o^2 , setting angles, and Miller indices. Final values of the atomic parameters appear in Table II. Final structure amplitudes are given in Table III.¹

Results

Description of the structure. Selected interatomic distances and bond angles for Pr_3InSe_6 are given in Table IV. Figure 1

shows a view of the unit cell down the *a*-axis. The structure contains two unique indium atoms, In(1) and In(2). Each shows a distorted octahedral coordination to neighboring Se atoms, with the In(1) octahedron (In(1)–Se, 2.726(1) to 2.747(2) Å) being more regular than the In(2) octahedron (In(2)–Se, 2.537(2) to 2.856(2) Å). The observed In–Se interatomic distances correspond well to the sum, 2.78 Å, of the effective radii for a 6-coordinate In^{3+} (0.80 Å) and Se^{2-} (1.98 Å) (7). The In–Se octahedra form chains along the *a*-axis with each chain derived solely from either In(1) or In(2) centered units.

There are three crystallographically unique Pr atoms in the structure. Atoms Pr(1) and Pr(3) are each surrounded by eight Se anions. Their coordination geometry can be described as a distorted bicapped trigonal prism or as a distorted square antiprism. The remaining Pr atom, Pr(2), is surrounded by only seven Se atoms. The geometry about this cation is derived from an octahedron where two neighboring equatorial atoms distort toward an axial position and a capping atom is placed at the opened triangular face. This type of metal anion polyhedron is observed in the structure of $\text{La}_{10}\text{Er}_9\text{S}_{27}$ (8). The Pr–Se distances

¹ See NAPS Document No. 04646 for 9 pages of supplementary materials. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or \$7.75 for photocopy.

TABLE IV
SELECTED INTERATOMIC DISTANCES (Å) and Angles (deg) for Pr₃InSe₆

Pr(1)–Se(3)	2.985(2)	Se(3)–Pr(1)–Se(3)	86.94(5)
Pr(1)–Se(3)	2.987(2)	Se(3)–Pr(1)–Se(5)	145.02(6)
Pr(1)–Se(5)	3.029(2)	Se(3)–Pr(1)–Se(5)	145.00(6)
Pr(1)–Se(5)	3.033(2)	Se(5)–Pr(1)–Se(5)	85.33(5)
Pr(1)–Se(1)	3.072(2)	Se(5)–Pr(1)–Se(1)	149.11(6)
Pr(1)–Se(1)	3.073(2)	Se(5)–Pr(1)–Se(1)	149.13(6)
Pr(1)–Se(2)	3.082(2)	Se(1)–Pr(1)–Se(1)	83.90(5)
Pr(1)–Se(4)	3.058(2)	Se(1)–Pr(1)–Se(3)	117.83(6)
		Se(1)–Pr(1)–Se(3)	117.85(6)
		Se(2)–Pr(1)–Se(4)	136.09(6)
Pr(2)–Se(3)	2.911(2)	Se(3)–Pr(2)–Se(4)	154.72(6)
Pr(2)–Se(4)	3.079(2)	Se(3)–Pr(2)–Se(5)	118.97(4)
Pr(2)–Se(5)	2.937(2)	Se(3)–Pr(2)–Se(5)	119.01(6)
Pr(2)–Se(5)	2.940(2)	Se(3)–Pr(2)–Se(6)	80.95(6)
Pr(2)–Se(6)	3.010(2)	Se(3)–Pr(2)–Se(6)	80.90(6)
Pr(2)–Se(6)	3.014(2)	Se(4)–Pr(2)–Se(5)	77.64(5)
Pr(2)–Se(1)	3.077(2)	Se(4)–Pr(2)–Se(5)	77.65(5)
		Se(4)–Pr(2)–Se(6)	80.64(5)
		Se(4)–Pr(2)–Se(6)	80.66(5)
		Se(5)–Pr(2)–Se(5)	88.70(5)
		Se(6)–Pr(2)–Se(6)	86.00(5)
		Se(5)–Pr(2)–Se(6)	88.55(6)
		Se(5)–Pr(2)–Se(6)	88.58(6)
		Se(1)–Pr(2)–Se(3)	63.85(5)
		Se(1)–Pr(2)–Se(5)	75.00(5)
		Se(1)–Pr(2)–Se(5)	75.05(5)
Pr(3)–Se(1)	2.970(2)	Se(1)–Pr(3)–Se(1)	87.51(5)
Pr(3)–Se(1)	2.971(2)	Se(1)–Pr(3)–Se(2)	142.56(6)
Pr(3)–Se(2)	3.030(2)	Se(1)–Pr(3)–Se(2)	142.57(6)
Pr(3)–Se(2)	3.030(2)	Se(2)–Pr(3)–Se(2)	85.38(5)
Pr(3)–Se(6)	3.119(2)	Se(2)–Pr(3)–Se(6)	124.62(5)
Pr(3)–Se(6)	3.121(2)	Se(2)–Pr(3)–Se(6)	124.65(5)
Pr(3)–Se(5)	3.204(2)	Se(6)–Pr(3)–Se(6)	82.35(5)
Pr(3)–Se(4)	3.281(2)	Se(6)–Pr(3)–Se(1)	143.24(6)
		Se(6)–Pr(3)–Se(1)	143.22(6)
		Se(4)–Pr(3)–Se(5)	128.47(6)
In(1)–2Se(4)	2.745(2)	Se(4)–In(1)–Se(4)	180.00(9)
In(1)–2Se(4)	2.747(2)	Se(4)–In(1)–Se(4)	83.15(5)
In(1)–2Se(6)	2.726(2)	Se(4)–In(1)–Se(4)	96.84(5)
		Se(6)–In(1)–Se(6)	180.00(0)
		Se(4)–In(1)–Se(6)	87.81(5)
		Se(4)–In(1)–Se(6)	87.86(6)
		Se(4)–In(1)–Se(6)	92.13(6)
		Se(4)–In(1)–Se(6)	92.18(5)
In(2)–4Se(2)	2.856(2)	Se(2)–In(2)–Se(2)	180.00(0)
In(2)–2Se(3)	2.537(2)	Se(2)–In(2)–Se(2)	91.99(5)
		Se(2)–In(2)–Se(2)	88.00(5)
		Se(3)–In(2)–Se(3)	180.00(0)
		Se(2)–In(2)–Se(3)	84.42(6)
		Se(2)–In(2)–Se(3)	84.46(6)
		Se(2)–In(2)–Se(3)	95.53(6)
		Se(2)–In(2)–Se(3)	95.57(6)

(2.911(2) to 3.082(2) Å) are in reasonable agreement with the value, 3.11 Å, calculated from the sum of effective ionic radii for Se^{2-} and 8-coordinate Pr^{3+} (1.13 Å).

Each of the Se anions is coordinated to five metal atoms, except for Se(3) which shows an interaction with Se(1) of 3.170(2) Å. All other Se ··· Se distances are greater than 3.571 Å.

The structure of Pr_3InSe_6 is similar to those of Sm_3InS_6 (9) and La_3InS_6 (10). These sulfides show 8- and 7-coordinated rare-earth cations while the Sm_3InS_6 structure has octahedral In metal sites and the La_3InS_6 structure possesses octahedral and tetrahedral In sites. An interaction between specific sulfur anions is also observed. In contrast to Pr_3InSe_6 , both of the sulfides crystallize in orthorhombic cells and show more regular coordination geometries about the metal atoms. This difference may be due to the larger size of the selenium anion over the sulfur anion, leading to distortions about the metal-anion polyhedra and subsequent packing of these polyhedra.

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