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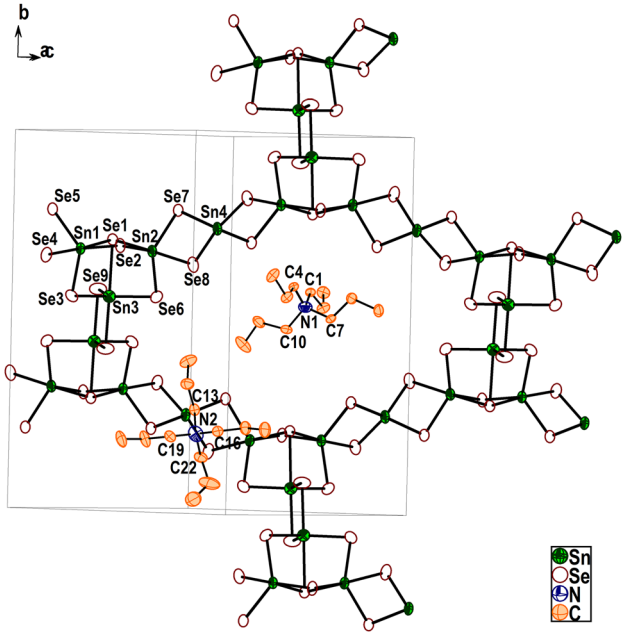
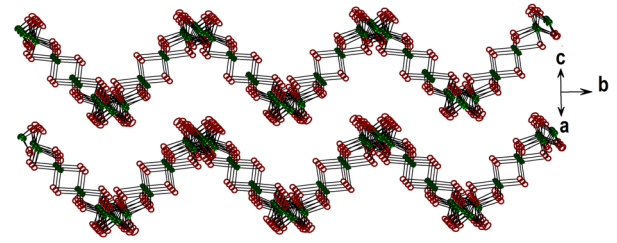
Crystal structure of bis(tetrapropylammonium) nonaselenidotetrastannate(IV), $(Pr_4N)_2[Sn_4Se_9]$





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Abstract

$C_{24}H_{56}N_2Sn_4Se_9$, monoclinic, $P2_1/n$ (no. 14), a = 15.3276(10) Å, b = 19.0577(15) Å, c = 15.3980(11) Å, β = 97.947(3)°, V = 4454.7(6) Å^3, Z = 4, $R_{gt}(F)$ = 0.0313, $wR_{ref}(F^2)$ = 0.0686, T = 223 K.

CCDC no.: 2157679

Table 1: Data collection and handling.

Crystal:	Orange rod
Size:	0.16 × 0.12 × 0.07 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	9.59 mm^{-1}
Diffractometer, scan mode:	PHOTON 100 CMOS, φ and ω
θ_{max}, completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	145688, 11105, 0.083
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 8204
$N(param)_{refined}$:	354
Programs:	Bruker [1], SHELX [2], WinGX/ ORTEP [3], Diamond [4]

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

Source of material

The starting materials $[CH_3COCHC(O)CH_3]_2SnCl_2$ (0.020 g, 0.052 mmol), K_2Se (0.016 g, 0.10 mmol) and Pr_4NBr (0.028 g, 0.10 mmol) were charged to a Pyrex tube with diameter of 9 mm under an argon atmosphere and about 0.5 mL 1:2 (v/v) H_2O/MeOH mixture was added as a solvent. While the solvent was 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 110 °C for a day, then cooled to room temperature. Orange red rectangular chunky crystals were isolated by filtration and washed with MeOH and diethyl ether several times. Crystals of $(Pr_4N)_2[Sn_4Se_9]$ were obtained in 65% yield, based on the Sn metal used.

Experimental details

H atoms were positioned geometrically and treated as riding, with C–H = 0.97 (CH_2) and 0.96 (CH_3) Å with U_{iso}(H) = 1.2 (1.5 for methyl) U_{eq}(C). H atoms of the CH_3 were positioned to be staggered with respect to the shortest other bond to the atom to which the CH_3 is attached.

Comment

The title compound, $(Pr_4N)_2[Sn_4Se_9]$, which has been prepared by the solvothermal reaction of $[CH_3COCHC(O)$

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

Atom	x	y	z	U_{iso}*/U_{eq}
Sn1	0.22839 (2)	0.18670 (2)	0.41491 (2)	0.02694 (7)
Sn2	0.04329 (2)	0.18337 (2)	0.24021 (2)	0.02988 (7)
Sn3	0.04474 (2)	0.06094 (2)	0.43074 (2)	0.03384 (8)
Sn4	0.41750 (2)	0.25281 (2)	0.54790 (2)	0.03220 (8)
Se1	0.05478 (3)	0.21112 (2)	0.41239 (3)	0.02886 (10)
Se2	−0.02049 (3)	0.06289 (3)	0.26825 (3)	0.04200 (12)
Se3	0.21224 (3)	0.06136 (3)	0.46428 (3)	0.03648 (11)
Se4	−0.04247 (4)	0.07812 (3)	0.55504 (4)	0.04611 (13)
Se5	−0.05257 (3)	0.29271 (3)	0.20429 (3)	0.03519 (11)
Se6	0.21039 (3)	0.19795 (3)	0.24849 (3)	0.03350 (11)
Se7	0.40742 (3)	0.16978 (3)	0.42266 (3)	0.03900 (12)
Se8	0.25685 (3)	0.28928 (3)	0.52333 (3)	0.03312 (10)
Se9	0.02744 (3)	0.15127 (3)	0.06473 (3)	0.04989 (14)
N1	0.1984 (3)	0.4546 (2)	0.3183 (3)	0.0406 (9)
N2	0.1718 (3)	0.2987 (2)	0.7996 (3)	0.0506 (11)
C1	0.1257 (3)	0.4162 (3)	0.3564 (4)	0.0463 (12)
H1A	0.1094	0.3752	0.3203	0.056*
H1B	0.1494	0.3996	0.4144	0.056*
C2	0.0436 (4)	0.4577 (4)	0.3636 (5)	0.0716 (19)
H2A	0.0133	0.4676	0.3054	0.086*
H2B	0.0595	0.5021	0.3924	0.086*
C3	−0.0170 (4)	0.4178 (4)	0.4151 (5)	0.0746 (19)
H3A	−0.0691	0.4451	0.4185	0.112*
H3B	0.0125	0.4089	0.4731	0.112*
H3C	−0.0331	0.3741	0.3863	0.112*
C4	0.2712 (3)	0.4014 (3)	0.3137 (3)	0.0444 (12)
H4A	0.2896	0.3834	0.3723	0.053*
H4B	0.2471	0.3624	0.2776	0.053*
C5	0.3512 (4)	0.4284 (3)	0.2778 (4)	0.0645 (17)
H5A	0.3737	0.4699	0.3100	0.077*
H5B	0.3356	0.4413	0.2166	0.077*
C6	0.4213 (4)	0.3716 (4)	0.2862 (5)	0.081 (2)
H6A	0.4724	0.3885	0.2630	0.121*
H6B	0.3987	0.3308	0.2541	0.121*
H6C	0.4371	0.3596	0.3469	0.121*
C7	0.1645 (4)	0.4838 (3)	0.2280 (3)	0.0495 (13)
H7A	0.1158	0.5154	0.2332	0.059*
H7B	0.2110	0.5111	0.2075	0.059*
C8	0.1339 (5)	0.4286 (4)	0.1602 (4)	0.0750 (19)
H8A	0.1848	0.4053	0.1424	0.090*
H8B	0.0995	0.3936	0.1862	0.090*
C9	0.0793 (5)	0.4591 (4)	0.0812 (5)	0.086 (2)
H9A	0.0618	0.4225	0.0396	0.129*
H9B	0.1133	0.4935	0.0549	0.129*
H9C	0.0279	0.4810	0.0983	0.129*
C10	0.2313 (4)	0.5155 (3)	0.3761 (4)	0.0608 (16)
H10A	0.1821	0.5467	0.3806	0.073*
H10B	0.2737	0.5414	0.3474	0.073*
C11	0.2739 (6)	0.4972 (4)	0.4680 (5)	0.097 (3)
H11A	0.2380	0.4622	0.4923	0.117*
H11B	0.3312	0.4765	0.4650	0.117*
C12	0.2850 (6)	0.5586 (5)	0.5279 (6)	0.121 (4)
H12A	0.3111	0.5437	0.5851	0.182*
H12B	0.2285	0.5793	0.5316	0.182*
H12C	0.3224	0.5926	0.5056	0.182*
C13	0.2108 (4)	0.2352 (3)	0.7590 (4)	0.0584 (15)
H13A	0.2137	0.2453	0.6977	0.070*
H13B	0.2707	0.2287	0.7876	0.070*
C14	0.1615 (5)	0.1673 (4)	0.7645 (5)	0.086 (2)
H14A	0.1554	0.1579	0.8252	0.103*
H14B	0.1029	0.1719	0.7320	0.103*
C15	0.2073 (6)	0.1077 (5)	0.7288 (7)	0.124 (3)
H15A	0.1868	0.1028	0.6673	0.186*
H15B	0.1950	0.0653	0.7586	0.186*
H15C	0.2696	0.1161	0.7372	0.186*
C16	0.1748 (4)	0.2900 (3)	0.8971 (4)	0.0570 (15)
H16A	0.1390	0.2497	0.9076	0.068*
H16B	0.1480	0.3310	0.9198	0.068*
C17	0.2652 (5)	0.2802 (4)	0.9486 (4)	0.081 (2)
H17A	0.2895	0.2354	0.9342	0.097*
H17B	0.3045	0.3170	0.9340	0.097*
C18	0.2570 (6)	0.2830 (5)	1.0449 (5)	0.107 (3)
H18A	0.3143	0.2784	1.0786	0.161*
H18B	0.2200	0.2452	1.0592	0.161*
H18C	0.2314	0.3270	1.0582	0.161*
C19	0.0760 (4)	0.3063 (3)	0.7616 (4)	0.0618 (16)
H19A	0.0449	0.2650	0.7780	0.074*
H19B	0.0522	0.3464	0.7892	0.074*
C20	0.0554 (4)	0.3152 (5)	0.6642 (5)	0.094 (3)
H20A	0.0810	0.3588	0.6471	0.113*
H20B	0.0816	0.2770	0.6352	0.113*
C21	−0.0418 (5)	0.3162 (5)	0.6354 (6)	0.113 (3)
H21A	−0.0536	0.3054	0.5740	0.169*
H21B	−0.0646	0.3619	0.6456	0.169*
H21C	−0.0697	0.2819	0.6681	0.169*
C22	0.2271 (4)	0.3611 (4)	0.7788 (5)	0.076 (2)
H22A	0.2885	0.3471	0.7889	0.091*
H22B	0.2128	0.3713	0.7167	0.091*
C23	0.2177 (7)	0.4281 (5)	0.8289 (9)	0.161 (5)
H23A	0.2257	0.4154	0.8905	0.193*
H23B	0.2676	0.4572	0.8201	0.193*
C24	0.1456 (6)	0.4703 (6)	0.8160 (9)	0.163 (5)
H24A	0.1534	0.5090	0.8563	0.244*
H24B	0.0944	0.4439	0.8257	0.244*
H24C	0.1379	0.4877	0.7570	0.244*

$CH_3]_2SnCl_2$, K_2Se and Pr_4NBr with 1:2 (*v*/*v*) H_2O/MeOH mixture as a solvent, is composed of a 2D polymeric, layered $[Sn_4Se_9]^{2-}$ anion and charge-balancing Pr_4N^+ cations (see upper part of the figure). $(Pr_4N)_2[Sn_4Se_9]$ features to be a new member of $A_2Sn_4Se_9$ (A = Rb, Cs, NH_4, $\{Fe(bipy)_3\}_{0.5}$, $(Bmmim)_{0.5}\{Ni(1,2\text{-}pda)_3\}_{0.25}$, $(Bmmim)_{0.375}(dienH)_{0.125}\{Ni(dien)_2\}_{0.25}$) family and the Se analogue of $(Pr_4N)_2[Sn_4S_9]$ [5–11]. In the $A_2Sn_4Se_9$ family, there exist three different structural types of the $[Sn_4Se_9]^{2-}$ anion. Small cations such as Rb^+, Cs^+, NH_4^+ stabilize a 2D layered structure of $[Sn_4Se_9]^{2-}$ containing two 5-coordinate trigonal bipyramidal Sn and two 4-coordinate tetrahedral Sn [5, 6]. In the

case including large transition metal complex cations such as $\{Fe(bipy)_3\}_{0.5}$, $(Bmmim)_{0.5}\{Ni(1,2\text{-}pda)_3\}_{0.25}$, $(Bmmim)_{0.375}(dienH)_{0.125}\{Ni(dien)_2\}_{0.25}$, a 3D framework structure of $[Sn_4Se_9]^{2-}$ with all four Sn of 5-coordinate trigonal bipyramidal geometry have been stabilized [7–9]. In the new member, $(Pr_4N)_2[Sn_4Se_9]$, a 2D layered structure of $[Sn_4Se_9]^{2-}$ with three 5-coordinate trigonal bipyramidal Sn and one 4-coordinate tetrahedral Sn has been stabilized.

$(Pr_4N)_2[Sn_4Se_9]$ crystallizes in the space group $P2_1/n$, which is the same space group as the sulfur analogue, $(Pr_4N)_2[Sn_4S_9]$ crystallizes in [10, 11]. As it can be seen from the top-view of the $[Sn_4Se_9]^{2-}$ layer of $(Pr_4N)_2[Sn_4Se_9]$ (see the upper part of the figure), building units of the $[Sn_4Se_9]^{2-}$ layer are edge-shared two Sn_3Se_4 broken cubes and $SnSe_4$ tetrahedra. The $SnSe_4$ tetrahedra connect the edge-shared two Sn_3Se_4 broken cubes, forming large elliptical 32-membered rings. A closer inspection of the edge-shared two Sn_3Se_4 cubes reveals that the edge-sharing of two Sn_3Se_4 cubes is accomplished through μ_2–Se (which is Se(9)) bridges. An asymmetric unit of Sn_4Se_9 is therefore composed of a Sn_3Se_4 broken cube, a Se bridge and a $SnSe_4$ tetrahedron. There are three $SnSe_5$ trigonal bipyramids in the edge-shared Sn_3Se_4 cube, with equatorial Sn–Se bond distances ranging from 2.5030(6) to 2.5687(6) Å and axial Sn–Se bond distances ranging from 2.6600(6) to 2.8822(6) Å. Sn–Se bond distances in the $SnSe_4$ tetrahedron range from 2.4753(6) to 2.5410(5) Å. Another feature of the $[Sn_4Se_9]^{2-}$ layers in $(Pr_4N)_2[Sn_4Se_9]$ is that they are quite corrugated running along the crystallographic *b* axis, as it can be seen from the side view of the layers (lower part of the figure).

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