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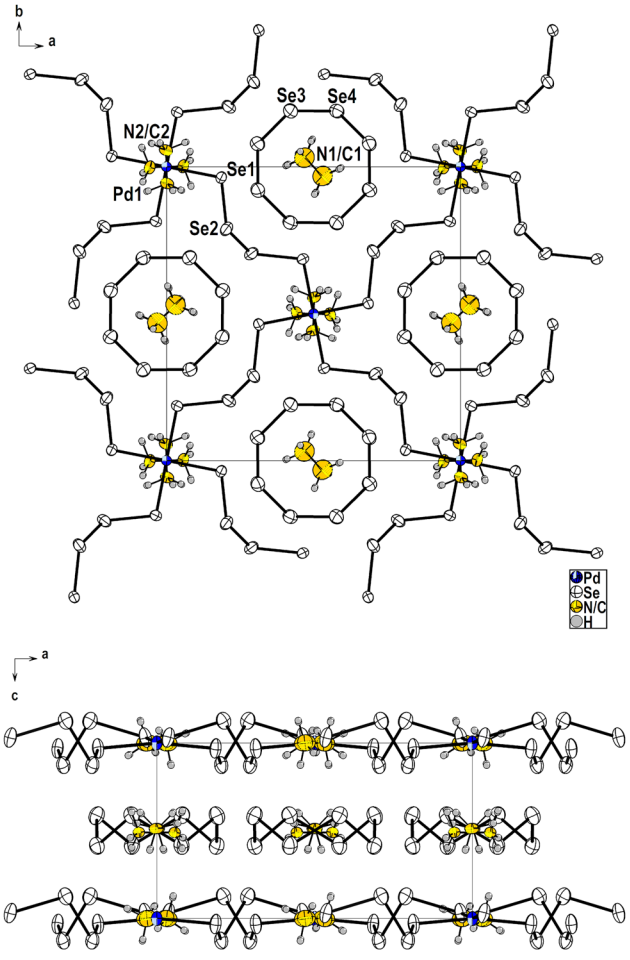
Crystal structure of bis(methylammonium) hexadecaselenidopalladate(II), $(CH_3NH_3)_2PdSe_{16}$



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Abstract

$(CH_3NH_3)_2PdSe_{16}$, tetragonal, $P\bar{4}b2$ (no. 117), a = 12.7821(4) Å, c = 7.1123(2) Å, V = 1162.02(8) Å^3, Z = 2, $R_{gt}(F)$ = 0.0306, w$R_{ref}(F^2)$ = 0.0841, T = 223 K.

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Table 1: Data collection and handling.

Crystal:	Black chunk
Size:	0.18 × 0.15 × 0.12 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	25.9 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}:	40,693, 1457, 0.099
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 $\sigma(I_{obs})$, 1377
$N(param)_{refined}$:	54
Programs:	Bruker [1], SHELX [2], WinGX/ORTEP [3], Diamond [4]

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

1 Source of material

K_2PdCl_4 (0.020 g, 0.061 mmol), K_2Se_4 (0.096 g, 0.24 mmol) and CH_3NH_3Cl (0.008 g, 0.12 mmol) were charged to a Pyrex tube with diameter of 9 mm under an argon atmosphere and about 0.5 mL methanol 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 80 °C for 3 days, then cooled to room temperature. Black chunky crystals were isolated by filtration and washed with methanol and diethyl ether several times. Crystals of $(CH_3NH_3)_2PdSe_{16}$ were obtained in 11 % yield, based on the Pd metal used.

2 Experimental details

H atoms were positioned geometrically and treated as riding, with N–H = 0.90 Å and C–H = 0.97 Å; U_{iso}(H) = 1.2U_{eq}(N) and 1.5U_{eq}(C). H atoms of NH_3 and CH_3 were positioned to be staggered with respect to the shortest other bond to the atom to which NH_3 and CH_3 is attached.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Pd1	1.000000	1.000000	1.000000	0.0246 (2)
Se1	0.96361 (6)	0.81405 (6)	0.96910 (16)	0.0383 (2)
Se2	0.78848 (8)	0.79594 (7)	0.87366 (14)	0.0390 (2)
Se3	0.57833 (8)	0.80950 (8)	0.58501 (16)	0.0457 (3)
Se4	0.42052 (8)	0.81025 (7)	0.41248 (16)	0.0433 (3)
N1[a]	0.5309 (17)	0.9691 (17)	1.000000	0.156 (15)
H1A[b]	0.586293	0.991373	1.067024	0.234*
H1B[b]	0.550881	0.955961	0.881013	0.234*
H1C[b]	0.505206	0.910286	1.051963	0.234*
C1[a]	0.5309 (17)	0.9691(17)	1.000000	0.156 (15)
H1D[b]	0.590771	0.993270	1.071608	0.234*
H1E[b]	0.552140	0.954639	0.871705	0.234*
H1F[b]	0.503341	0.905839	1.056687	0.234*
N2[b]	0.502 (4)	0.5567 (14)	0.489 (4)	0.060 (5)
H2A[b]	0.438078	0.582056	0.459337	0.090*
H2B[b]	0.548755	0.578798	0.403637	0.090*
H2C[b]	0.520246	0.579637	0.603819	0.090*
C2[b]	0.502 (4)	0.5567 (14)	0.489 (4)	0.060 (5)
H2D[b]	0.433056	0.584030	0.457575	0.090*
H2E[b]	0.552195	0.580523	0.396614	0.090*
H2F[b]	0.521989	0.581412	0.612604	0.090*

[a]Occupancy: 0.5, [b]Occupancy: 0.25.

3 Comment

The structures of Pd polyselenide anions have proven to be highly sensitive to the size and shape of their counterions [5, 6]. As one of Pd polyselenide compounds, A_2PdSe_{16} (A = Rb, Cs) is featured to possess a 2D layered Pd polyselenide anion, $[Pd(Se_4)_2]_n^{2n-}$ with encapsulated Se_8 rings [7–9]. Smaller alkali metal ion such as K^+ has been found to be inappropriate for the A_2PdSe_{16} (A = Rb, Cs) compound, instead, to stabilize $K_4[Pd(Se_4)_2][Pd(Se_6)_2]$ with two independent interpenetrating 3D frameworks of $[Pd(Se_x)_2]_n^{2n-}$ (x = 4, 6), $K_6[Pd(Se_5)_4]$ with a discrete anion of $[Pd(Se_5)_4]^{6-}$, and $K_2[Pd(Se_5)_2]$ with a 1D polymeric $[Pd(Se_5)_2]^{2-}$ anion [5, 10, 11]. Compared to the alkali metal cations, organic ammonium cations have the advantage of being removed with less damage to the chalcogenidometallate anion framework by thermal treatment at lower temperatures. Among organic ammonium cations, the smallest cation, $CH_3NH^+_3$ is known to be in possession of a close ionic radius to those of Cs^+ and Rb^+. Successful replacement of Cs^+ or Rb^+ with $CH_3NH^+_3$ has already been demonstrated for the preparation of organic–inorganic hybrid perovskite material such as $CH_3NH_3PbI_3$ [12, 13].

$(CH_3NH_3)_2PdSe_{16}$ was prepared by the methanothermal reaction of K_2PdCl_4, K_2Se_4 and CH_3NH_3Cl in a molar ratio of 1:4:2. In the case of A_2PdSe_{16} (A = Rb, Cs), the mixture of A_2Se (A = Na, Cs) and elemental Se served as the source of Se_4^{2-} ligands and Se_8 rings, but K_2Se_4 was used instead for the preparation of $(CH_3NH_3)_2PdSe_{16}$.

The structure of $(CH_3NH_3)_2PdSe_{16}$ is isostructural to those of A_2PdSe_{16} (A = Rb, Cs), as all three compounds are crystallized in the same space group $P\bar{4}b2$. As with the A_2PdSe_{16} (A = Rb, Cs) analogues, the structure of $[PdSe_{16}]^{2-}$ in $(CH_3NH_3)_2PdSe_{16}$ consists of an array of Se_8 rings and $[Pd(Se_4)_2]_n^{2n-}$ layers running through the *ab* plane. The unit cell volume of $(CH_3NH_3)_2PdSe_{16}$ is 1162.02(8) Å^3, which is considerably larger than that of A_2PdSe_{16} (A = Rb, Cs) with values of 1112.9(2) and 1118.5(3) Å^3, respectively. The increase in the unit cell volume of $(CH_3NH_3)_2PdSe_{16}$, compared to A_2PdSe_{16} (A = Rb, Cs), is attributed not only to the increase in the *c* parameter but also to changes in both the *a* and *c* unit cell parameters. The Pd–Se bond length is 2.4319(8) Å and the Se–Se bond lengths are in the range of 2.350(2)–2.361(2) Å, which are similar values to those of the A_2PdSe_{16} (A = Rb, Cs) analogues. Bond angles around Se atoms are in the range of 103.86(6)–107.73(4)°, noticeably greater than those values, 102.56(3)–106.3(3)° and 103.15(14)–105.90(12)° of A_2PdSe_{16} (A = Rb, Cs). To accommodate a slightly larger cation, Se–Se chains in the $[Pd(Se_4)_2]_n^{2n-}$ networks and Se_8 rings were expanded by increasing the bond angles around Se atoms. In the structure of 2D $[Pd(Se_4)_2]_n^{2n-}$ anion, there is a little distortion from the ideal square geometry around Pd, with Se1–Pd–Se1 angles of 90.468(6)° and 169.63(6)° for *cis* and *trans* Se atoms, respectively. A similar distortion around Pd was observed in the A_2PdSe_{16} (A = Rb, Cs) analogues to a nearly identical extent. In the Rb_2PdSe_{16}, the distance between Rb(2) and Pd was found to be 3.464 Å, suggesting an interaction between the electron density of the Pd d^2_z orbital and the Rb^+ *s* orbital. As $CH_3NH^+_3$ cations are unable to participate in the interaction observed between Pd and heavy alkali metal cations, such interaction is not considered indispensable for the stabilization of the $[Pd(Se_4)_2]_n^{2n-}$ frameworks. There are two crystallographically independent $CH_3NH_3^+$ cations in the structure of $(CH_3NH_3)_2PdSe_{16}$. Both $CH_3NH_3^+$ cations occupy the sites where Rb^+ and Cs^+ cations are located in the A_2PdSe_{16} (A = Rb, Cs) analogues. The C and N atoms of $CH_3NH_3^+$ exhibit complete disorder and the midpoints of C–N bonds in $CH_3NH_3^+$ cations are positioned at the sites where the centres of Rb^+ and Cs^+ cations are positioned. For the one $CH_3NH_3^+$ cation, C1 and N1 atoms are simultaneously sitting at a site with coordinates (0.5 + *x*, 0.5 + *y*, 0.5 – *z*) near to the special position (0.5, 0.5, 0.5) with 4-fold symmetry, generating four symmetrically equivalent sites which are assigned for disordered C and N atoms with 25 % occupancy. For the other $CH_3NH_3^+$ cation, C2 and N2 atoms are

also simultaneously sitting at a site with coordinates $(0.5 + x, 1.0 - y, 1.0)$, generating two symmetrically equivalent sites, which are assigned for disordered C and N atoms with 50 % occupancy.

Thermal stability and decomposition behaviour of $(CH_3NH_3)_2PdSe_{16}$ was examined by the TGA experiments. TGA results show that there are three decomposition steps upon heating to 900 °C under N_2 flow. Based on the amount of weight loss during the periods of decomposition steps, $CH_3NH_3^+$ cations were lost in the first step and seleniums were lost in the following two steps to leave PdSe as a final residue. The first decomposition step begins at about 150 °C and ends at about 200 °C. The other two steps occur between 300 and 420 °C and between 460 and 870 °C, respectively. While decomposition of both Rb_2PdSe_{16} and Cs_2PdSe_{16} analogues did not occur up to around 300 °C, $(CH_3NH_3)_2PdSe_{16}$ can lose its organic cation below 200 °C, and start its second decomposition at about 300 °C. When crystals of $(CH_3NH_3)_2PdSe_{16}$ were calcined at 250 °C under N_2 flow for a day, the shape and morphology of the crystals remained intact, but numerous holes formed on the surface. The XRD pattern of the calcined crystals indicates a loss of crystallinity in $(CH_3NH_3)_2PdSe_{16}$ with no prominent crystalline peaks.

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