Crystal structure of bis(*N*,*N*,*N*-triethylammonium) bis(tetraselenido-$\kappa^2 Se^1$,Se^4)palladate(II), $C_{12}H_{32}N_2PdSe_8$

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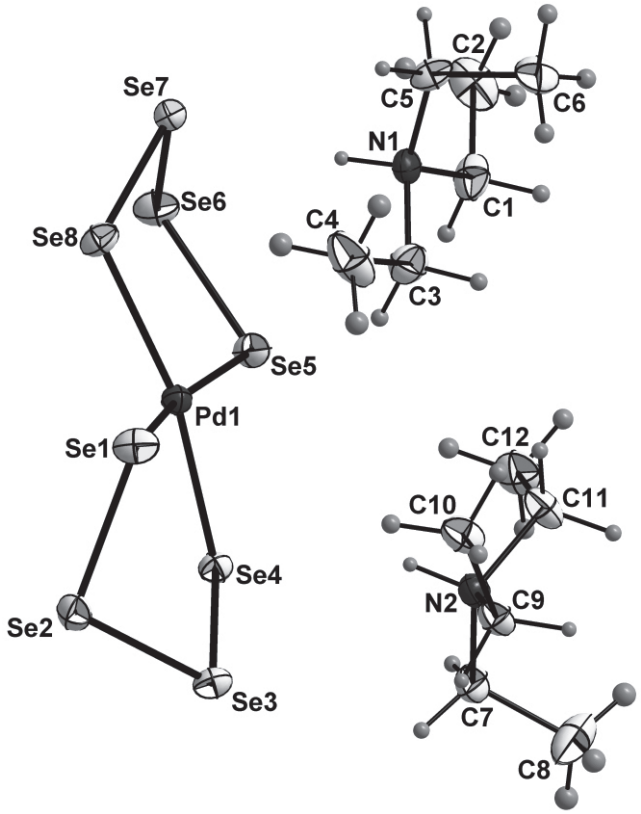

Abstract

$C_{12}H_{32}N_2PdSe_8$, orthorhombic, *Pca*2$_1$ (no. 29), a = 17.493(3) Å, b = 8.109(1) Å, c = 17.326(2) Å, V = 2457.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.0270, $wR_{ref}(F^2)$ = 0.0565, T = 173 K.

Table 1. Data collection and handling.

Crystal:	black blocks, size 0.168×0.183×0.202 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	126.04 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56.78°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12967, 5562
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4938
$N(param)_{refined}$:	208
Programs:	SHELX, WinGX, DIAMOND [12–14]

Source of material

Na_2PdCl_4 (0.035 g, 0.12 mmol), Na_2Se_4 (0.130 g, 0.36 mmol) and Et_3NHCl (0.033 g, 0.24 mmol) were charged to a Pyrex tube with diameter of 9 mm under an argon atmosphere and about 0.5 ml MeOH was added as a solvent. While the solvent was being frozen, the Pyrex tube was evacuated under vacuum and sealed. The sealed tube was placed in an oven and heated at 80 °C for 3 days, then cooled to room temperature. Black crystals were isolated by filtration and washed with MeOH and diethyl ether several times. These crystals are soluble in DMF, but insoluble in water and MeOH. Black blocks of $[Et_3NH]_2[Pd(Se_4)_2]$ were obtained in 31% yield.

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Experimental details

H atoms were positioned geometrically and treated as riding, with N–H = 0.91, C–H = 0.97 (CH_2) and 0.96 (CH_3) Å with U_{iso}(H) = 1.2U_{eq}(N) and 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.

Discussion

The title compound, $(Et_3NH)_2[Pd(Se_4)_2]$, which has been prepared by the solvothermal reaction of Na_2PdCl_4, Na_2Se_4 and Et_3NHCl with MeOH as a solvent, is composed of a complex $[Pd(Se_4)_2]^{2-}$ anion and two charge-balancing Et_3NH^+ cations. The $[Pd(Se_4)_2]^{2-}$ anion features to be a member of the well-known family of bis(tetrachalcogenido)metallates, $[M(Q_4)_2]^{2-}$ (Q = S, Se, Te) [1–3]. There exist two previously known $[Pd(Se_4)_2]^{2-}$ complexes, $(Ph_4P)_2[Pd(Se_4)_2]$ and $(Et_4N)_5[2Pd(Se_4)_2{\cdot}2Pd(Se_5)_2]$, which were structurally characterized [4,5]. Both $(Ph_4P)_2[Pd(Se_4)_2]$ and $(Et_4N)_5[2Pd(Se_4)_2{\cdot}2Pd(Se_5)_2]$ were prepared by the solution method using DMF as a solvent. $(Et_3NH)_2[Pd(Se_4)_2]$ is a rare example of a $[M(Q_4)_2]^{2-}$ complex prepared by either a hydrothermal or a solvothermal method. In the structure of $[Pd(Se_4)_2]^{2-}$, the square planar geometry around Pd(II) coordinated by two chelating tetraselenide ligands is quite distorted as the Se–Pd–Se angles are in the range of 80.47-100.19°. The Pd–Se and Se–Se distances are typical, ranging from 2.425(1) to 2.431(1) Å, and from 2.326(1) to 2.382(1) Å, respectively, similar to those found in the other $[Pd(Se_4)_2]^{2-}$ complexes. There is a small but distinct variation in the Se–Se bond lengths in the $PdSe_4$ rings. The outer Sel–Se2, Se3–Se4, Se5–Se6, and Se7–Se8 bonds have an average length of 2.359(20) Å, which is 0.032 Å longer than the average length of central Se2–Se3 and Se6–Se7 bonds. Similar alternations in Se–Se bond lengths have been observed previously in the other isolated $[Pd(Se_4)_2]^{2-}$ complexes [4, 5]. Interestingly, such alternations are not present in 3D connected $[Pd(Se_4)_2]^{2-}$ complexes of K_2PdSe_{10}, $Cs_2[Pd(Se_4)_2]$, and $K_2(enH_2)_2[Pd(Se_4)_2{\cdot}2Se_4]$ [6–8], and 2D connected $[Pd(Se_4)_2]^{2-}$ complexes of $A_2[Pd(Se_4)_2]{\cdot}Se_8$ (A = Rb, Cs) [9, 10]. In addition, distorted square planar geometry around the Pd(II) metal center in molecular $[Pd(Se_4)_2]^{2-}$ complexes is not distorted anymore in 3D and 2D $[Pd(Se_4)_2]^{2-}$ complexes. The closest intermolecular Se···Se distance between $[Pd(Se_4)_2]$, is 3.5306(9) Å between Se2 and Se7. This value is a little longer but comparable to 3.415 Å of the $(EtMe_3N)_2[Hg(Se_4)_2]$, the shortest intermolecular Se···Se distance among the reported molecular

$[M(Se_4)_2]^{2-}$ compounds [11]. Intermolecular hydrogen bonds between H of N–H and Se occur through N1–H1···Se7 and N2–H2···Se4 with H···Se distances of 2.5795(6) and 2.5607(6) Å, respectively. The angles around N1–H1···Se7 and N2–H2···Se4 hydrogen bonds are 170.1(3) and 156.6(3)°, respectively. Based on the fact that both terminal Se (Se4) and internal Se (Se7) participated in the hydrogen bonding, packing consideration and factors other than the nature of Se seem to be more important for the formation of hydrogen bonds in this compound.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*a*	0.7690	1.0079	0.7669	0.026
H(2)	4*a*	0.9966	1.2047	0.9659	0.026
H(1A)	4*a*	0.8220	1.3178	0.7310	0.039
H(1B)	4*a*	0.8738	1.1635	0.7458	0.039
H(2A)	4*a*	0.8652	1.2136	0.6157	0.060
H(2B)	4*a*	0.7760	1.1973	0.6194	0.060
H(2C)	4*a*	0.8277	1.0426	0.6342	0.060
H(3A)	4*a*	0.8153	1.1212	0.8734	0.039
H(3B)	4*a*	0.7681	1.2821	0.8584	0.039
H(4A)	4*a*	0.7109	1.1323	0.9549	0.069
H(4B)	4*a*	0.7039	0.9788	0.9003	0.069
H(4C)	4*a*	0.6558	1.1379	0.8836	0.069
H(5A)	4*a*	0.6465	1.0843	0.7648	0.029
H(5B)	4*a*	0.6834	1.1101	0.6833	0.029
H(6A)	4*a*	0.6097	1.3368	0.7153	0.049
H(6B)	4*a*	0.6954	1.3909	0.7082	0.049

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(6C)	4*a*	0.6587	1.3652	0.7899	0.049
H(7A)	4*a*	1.1222	1.2630	0.9617	0.034
H(7B)	4*a*	1.0932	1.2570	1.0472	0.034
H(8A)	4*a*	1.1725	1.4837	1.0306	0.070
H(8B)	4*a*	1.0899	1.5455	1.0503	0.070
H(8C)	4*a*	1.1194	1.5510	0.9649	0.070
H(9A)	4*a*	0.9705	1.3503	1.0817	0.028
H(9B)	4*a*	0.9564	1.5035	1.0283	0.028
H(10A)	4*a*	0.8403	1.3748	1.0555	0.045
H(10B)	4*a*	0.8708	1.2095	1.0201	0.045
H(10C)	4*a*	0.8567	1.3626	0.9667	0.045
H(11A)	4*a*	1.0096	1.5069	0.8967	0.034
H(11B)	4*a*	0.9439	1.3808	0.8792	0.034
H(12A)	4*a*	1.0354	1.3642	0.7830	0.053
H(12B)	4*a*	1.0339	1.1967	0.8282	0.053
H(12C)	4*a*	1.0989	1.3255	0.8443	0.053

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd(1)	4*a*	0.88624(2)	0.80653(4)	0.92998(2)	0.0176(2)	0.0164(2)	0.0154(2)	–0.0005(1)	–0.0001(2)	–0.0004(2)
Se(1)	4*a*	0.79943(3)	0.80030(7)	1.03904(3)	0.0179(3)	0.0374(3)	0.0215(3)	–0.0025(2)	0.0030(2)	–0.0029(3)
Se(2)	4*a*	0.88126(3)	0.74309(7)	1.14215(3)	0.0300(3)	0.0229(3)	0.0183(3)	–0.0016(2)	0.0033(2)	0.0017(2)
Se(3)	4*a*	0.96762(3)	0.95801(7)	1.12478(3)	0.0230(3)	0.0248(3)	0.0201(3)	–0.0012(2)	–0.0014(2)	–0.0044(2)
Se(4)	4*a*	1.00224(3)	0.89539(6)	0.99512(3)	0.0165(2)	0.0202(2)	0.0202(3)	–0.0002(2)	0.0000(2)	–0.0003(2)
Se(5)	4*a*	0.96490(3)	0.86983(7)	0.81829(3)	0.0234(3)	0.0295(3)	0.0190(3)	–0.0076(2)	0.0008(2)	0.0026(2)
Se(6)	4*a*	0.92990(3)	0.66782(7)	0.72815(3)	0.0283(3)	0.0356(3)	0.0198(3)	–0.0004(2)	0.0034(2)	–0.0049(3)
Se(7)	4*a*	0.79800(3)	0.70404(6)	0.73399(3)	0.0274(3)	0.0180(2)	0.0243(3)	–0.0011(2)	–0.0082(2)	0.0000(3)
Se(8)	4*a*	0.78326(3)	0.65493(7)	0.86835(3)	0.0210(3)	0.0247(3)	0.0254(3)	–0.0063(2)	0.0006(2)	–0.0031(3)
N(1)	4*a*	0.7609(3)	1.1186(5)	0.7699(3)	0.024(3)	0.015(2)	0.026(2)	0.002(2)	–0.003(2)	0.000(2)
N(2)	4*a*	1.0090(3)	1.3131(5)	0.9711(3)	0.024(2)	0.019(2)	0.021(2)	0.003(2)	–0.001(2)	0.002(2)
C(1)	4*a*	0.8252(3)	1.1992(7)	0.7246(4)	0.020(3)	0.025(3)	0.053(4)	–0.004(2)	–0.001(3)	0.005(3)
C(2)	4*a*	0.8234(4)	1.1597(8)	0.6411(4)	0.033(4)	0.049(4)	0.038(4)	0.012(3)	0.009(3)	0.010(3)
C(3)	4*a*	0.7672(4)	1.1629(7)	0.8537(4)	0.038(4)	0.027(3)	0.032(3)	0.003(3)	–0.004(3)	–0.007(3)
C(4)	4*a*	0.7038(4)	1.0971(9)	0.9025(4)	0.063(5)	0.047(4)	0.028(3)	0.020(4)	0.010(3)	0.008(3)
C(5)	4*a*	0.6837(3)	1.1487(7)	0.7363(3)	0.017(3)	0.030(3)	0.026(3)	–0.005(2)	0.001(2)	–0.006(3)
C(6)	4*a*	0.6597(3)	1.3264(7)	0.7375(4)	0.019(3)	0.036(3)	0.043(4)	0.003(2)	–0.010(3)	0.005(3)
C(7)	4*a*	1.0900(3)	1.3182(6)	0.9992(4)	0.027(3)	0.022(3)	0.036(4)	0.004(2)	–0.006(3)	0.001(3)
C(8)	4*a*	1.1207(4)	1.4904(7)	1.0124(5)	0.030(4)	0.028(3)	0.082(6)	0.000(3)	–0.008(4)	–0.016(4)
C(9)	4*a*	0.9544(3)	1.3841(6)	1.0305(3)	0.027(3)	0.027(3)	0.016(3)	0.004(2)	0.003(2)	0.002(2)
C(10)	4*a*	0.8731(3)	1.3276(7)	1.0170(4)	0.027(3)	0.034(3)	0.029(3)	0.006(2)	–0.003(3)	0.002(3)
C(11)	4*a*	0.9973(3)	1.3904(7)	0.8935(3)	0.033(4)	0.032(3)	0.020(3)	0.009(3)	0.001(3)	0.007(3)
C(12)	4*a*	1.0458(4)	1.3121(8)	0.8316(4)	0.044(4)	0.039(4)	0.024(3)	0.002(3)	0.005(3)	0.001(3)

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