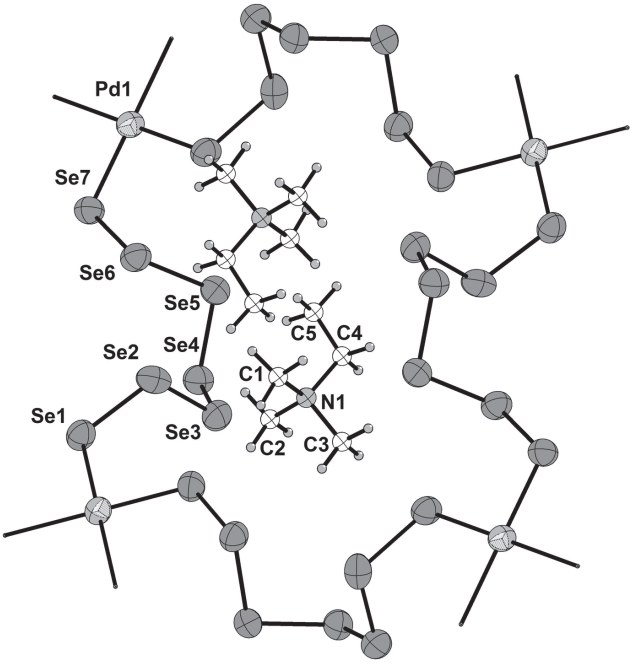
Di Wang, Hoseop Yun and Kang-Woo Kim*

Crystal structure of bis(*N*,*N*,*N*-trimethylethanaminium) poly[bis(μ$_2$-heptaselenido-κ^{2}Se^1,Se^7) palladate(II)], $C_{10}H_{28}N_2PdSe_{14}$



https://doi.org/10.1515/ncrs-2017-0126
Received May 13, 2017; accepted September 13, 2017; available online September 29, 2017

Abstract

$C_{10}H_{28}N_2PdSe_{14}$, monoclinic, $P2_1/c$ (no. 14), $a = 9.4146(7)$ Å, $b = 14.3446(11)$ Å, $c = 12.4731(9)$ Å, $\beta = 113.403(2)°$, $V = 1545.9(2)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0510$, $wR_{ref}(F^2) = 0.1446$, $T = 293$ K.

CCDC no.: 1574233

The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Polyhedron, black
Size:	0.20 × 0.14 × 0.12 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	17.1 mm^{-1}
Diffractometer, scan mode:	Rigaku R-axis Rapid S, ω-scans
$2\theta_{max}$, completeness:	27.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	14982, 3526, 0.099
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1710
$N(param)_{refined}$:	136
Programs:	Rigaku/MSC [1], SHELX [2], WinGX, ORTEP [3], Diamond [4]

Source of material

Na_2PdCl_4 (0.035 g, 0.12 mmol), Na_2Se_4 (0.129 g, 0.36 mmol) and $EtMe_3NI$ (0.102 g, 0.48 mmol) were charged to a Pyrex tube with diameter of 9 mm under an argon atmosphere and about 0.5 mL MeOH was added. While the solvent was being frozen, the Pyrex tube was evacuated and sealed with the use of a flame. The sealed tube heated at 80 °C for 3 days, then cooled to room temperature. Reddish black polyhedral crystals were isolated by filtration and washed with MeOH and diethyl ether. Crystals of $[EtMe_3N]_2[Pd(Se_7)_2]$ were obtained in 27% yield, based on the Pd metal used.

Experimental details

One ethyl group and two methyl groups in the $EtMe_3N^+$ cation were refined to be disordered 0.64(3)/0.36(3). 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) $U_{eq}(C)$.

Discussion

Recently $(Et_2Me_2N)_2[Pd(Se_7)_2]$ has been reported as a new metal polyselenide compound possessing the longest bridging polyselenide anion, Se_7^{2-} ligand [5]. The title compound $(EtMe_3N)_2[Pd(Se_7)_2]$ is another metal polyselenide compound with the bridging Se_7^{2-} ligand. Actually both

***Corresponding author: Kang-Woo Kim,** Department of Chemistry and Research Institute for Natural Sciences, Incheon National University, Incheon 22012, Korea, e-mail: kimkw@inu.ac.kr
Di Wang: Department of Chemistry and Research Institute for Natural Sciences, Incheon National University, Incheon 22012, Korea
Hoseop Yun: Department of Chemistry, Ajou University, Suwon 16499, Korea

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

Atom	x	y	z	U_{iso}*/U_{eq}
Pd1	1.0000	0.0000	1.0000	0.0560(4)
Se1	0.25052(13)	0.43317(9)	0.62469(10)	0.0680(4)
Se2	0.24434(16)	0.27134(9)	0.61734(12)	0.0780(4)
Se3	0.26159(16)	0.21996(9)	0.44441(12)	0.0829(5)
Se4	0.52638(16)	0.19721(9)	0.49111(11)	0.0731(4)
Se5	0.59337(15)	0.07442(9)	0.62466(10)	0.0721(4)
Se6	0.64013(14)	0.14936(9)	0.80493(10)	0.0681(4)
Se7	0.90510(14)	0.15372(8)	0.91797(11)	0.0672(4)
N1	0.7835(13)	0.0536(8)	0.2355(9)	0.082(3)
C1	0.729(2)	0.0734(12)	0.3312(14)	0.130(6)
H1A	0.6632	0.0235	0.3355	0.195*
H1B	0.6714	0.1308	0.3148	0.195*
H1C	0.8162	0.0786	0.4044	0.195*
C2	0.885(4)	0.124(2)	0.232(3)	0.115(11)*
H2A	0.9731	0.1265	0.3055	0.172*
H2B	0.8327	0.1832	0.2176	0.172*
H2C	0.9195	0.1113	0.1706	0.172*
C3	0.650(3)	0.056(2)	0.1200(18)	0.099(9)
H3A	0.5779	0.0075	0.1173	0.149*
H3B	0.6864	0.0456	0.0591	0.149*
H3C	0.5998	0.1152	0.1092	0.149*
C4	0.850(4)	−0.044(2)	0.246(2)	0.118(12)
H4A	0.7696	−0.0895	0.2348	0.142*
H4B	0.8885	−0.0534	0.1848	0.142*
C5	0.968(5)	−0.056(3)	0.353(4)	0.19(2)
H5A	1.0090	−0.1180	0.3583	0.291*
H5B	0.9300	−0.0469	0.4128	0.291*
H5C	1.0488	−0.0116	0.3626	0.291*
C2X	0.839(7)	0.153(4)	0.197(5)	0.104(17)*
H2X1	0.8743	0.1416	0.1356	0.156*
H2X2	0.9211	0.1798	0.2628	0.156*
H2X3	0.7528	0.1954	0.1690	0.156*
C3X	0.684(6)	−0.021(4)	0.163(5)	0.13(2)*
H3X1	0.7161	−0.0363	0.1006	0.198*
H3X2	0.5784	−0.0010	0.1305	0.198*
H3X3	0.6936	−0.0758	0.2100	0.198*
C4X	0.958(5)	0.014(3)	0.292(3)	0.069(12)*
H4X1	1.0005	0.0199	0.2331	0.083*
H4X2	1.0169	0.0556	0.3553	0.083*
C5X	0.995(5)	−0.086(3)	0.341(4)	0.068(13)*
H5X1	1.1049	−0.0959	0.3733	0.103*
H5X2	0.9466	−0.1304	0.2790	0.103*
H5X3	0.9562	−0.0952	0.4007	0.103*

Atoms C2-H5C and the atoms C2X-H5X3 are included with an occupancy of 0.63(3) and 0.36(3), respectively.

$(EtMe_3N)_2[Pd(Se_7)_2]$ and $(Et_2Me_2N)_2[Pd(Se_7)_2]$ are structural analogs containing the $[Pd(Se_7)_2]^{2-}$ coordination polymer. $EtMe_3N^+$ is another unsymmetric alkyl ammonium cation, but smaller than $Et_2Me_2N^+$. The size difference between $EtMe_3N^+$ and $Et_2Me_2N^+$ does not seem to be large enough to show the counterion effects well manifested in Pd polyselenide compounds [6–9]. Other ammonium cations of similar size, including Et_3MeN^+ have been also adopted to stabilize the $[Pd(Se_7)_2]^{2-}$ anion without success. In the title structure $(EtMe_3N)_2[Pd(Se_7)_2]$, the Pd atom is sitting on the special position with the site symmetry $\bar{1}$ and the square planar geometry around Pd, coordinated by four bridging heptaselenide ligands, is quite ideal as Se—Pd—Se angles are in the range of 89.29(4)–90.71(4)°. The Pd—Se and Se—Se distances are also typical, ranging from 2.4456(11) to 2.4468(11) Å, and from 2.3230(18) to 2.3704(18) Å, respectively, similar to those found in the other $[Pd(Se_x)_2]^{2-}$ complexes [5, 6, 9–13]. In the layers of polymeric $[Pd(Se_7)_2]^{2-}$, heptaselenide Se_7^{2-} ligand chains are connecting Pd metal centers, resulting in 32-membered rings composed of four Pd and 28 Se atoms. The distances between two couples of Pd centers faced diagonally in the 32-membered ring are 14.3446(11) and 17.9874(12) Å, respectively. These distances are 15.1503(14) and 17.6160(13) Å for $(Et_2Me_2N)_2[Pd(Se_7)_2]$. A little smaller cation, $EtMe_3N^+$ is considered to be responsible for the shrinkage of the 32-membered ring into a little narrower shape and smaller size, compared to the ring with the cation, $Et_2Me_2N^+$.

Acknowledgements: This work was supported by the Incheon National University Research Grant in 2016.

References

1. Rigaku/MSC: CrystalClear. Rigaku/MSC Inc., The Woodlands, TX, USA (2006).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Cryst. **45** (2012) 849–854.
4. Putz, H.; Brandenburg, K.: DIAMOND – Crystal and Molecular Structure Visualization. Crystal Impact, Bonn, Germany (2015).
5. Kim, K.-W.; Wang, D.: Crystal structure of bis(*N,N,N*-ethyldimethylethanaminium) bis(heptaselenido-κ^2Se^1, Se^7)palladate(II)], $C_{12}H_{32}N_2PdSe_{14}$. Z. Kristallogr. NCS **232** (2017) 965–967.
6. Kim, K.-W.; Kanatzidis, M. G.: Counterion effects in Pd polyselenides: evolution from molecular to three-dimensional framework structures. J. Am. Chem. Soc. **120** (1998) 8124–8135.
7. Sheldrick, W. S.: Polychalcogenide anions: structural diversity and ligand versatility. Z. Anorg. Allg. Chem. **638** (2012) 2401–2424.
8. Ruck, M.; Locherer, F.: Coordination chemistry of homoatomic ligands of bismuth, selenium and tellurium. Coord. Chem. Rev. **285** (2015) 1–10.
9. Kim, K.-W.; Kanatzidis, M. G.: Hydrothermal synthesis of K_2PdSe_{10}. Coexistence of two large interpenetrating three-dimensional frameworks of $[Pd(Se_4)_2]^{2-}$ and $[Pd(Se_6)_2]^{2-}$. J. Am. Chem. Soc. **114** (1992) 4878–4883.
10. Wachhold, M.; Kanatzidis, M. G.: Powerful templating effect in Rb/Pd/Se_x promoted by crown ether-like $[Rb(Se_8)]^+$

coordination. Formation of $Rb_2[Pd(Se_4)_2]\cdot Se_8$: a layered Pd polyselenide with "encapsulated" eight-membered selenium Rings. J. Am. Chem. Soc. **121** (1999) 4189–4195.
11. Chen, Z.; Wang, R.-J.; Li, J.: Solvothermal synthesis of alkaline metal selenides Cs_2PdSe_{16} and studies of thermal stabilities. Chem. J. Chinese Univ. **22** (2001) 1091–1094.
12. Kim, K.-W.; Kim, J.: Crystal structure of bis(*N*,*N*,*N*-triethylammonium) bis(tetraselenido-κ^2Se^1,Se^4)palladate(II), $C_{12}H_{32}N_2PdSe_8$. Z. Kristallogr. NCS **230** (2015) 269–270.
13. Kim, K.-W.; Wang, D.: Crystal structure of bis(ethanaminium) poly[bis(hexaselenido-κ^2Se^1,Se^6)palladate(II)], $C_4H_{16}N_2PdSe_{12}$. Z. Kristallogr. NCS **231** (2016) 933–934.