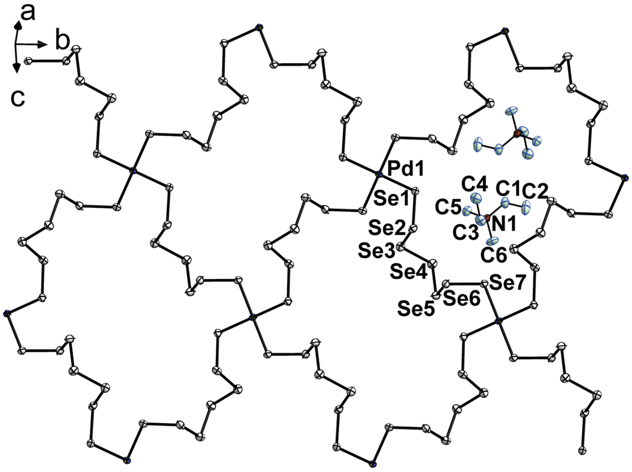
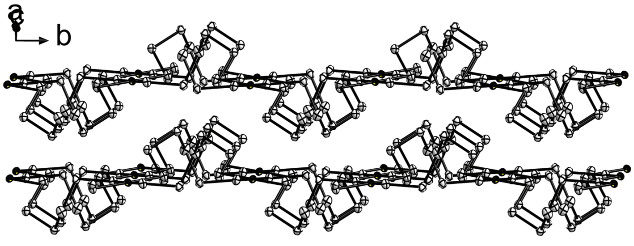
DE GRUYTER Z. Kristallogr. NCS 2017; 232(6): 965–967

Kang-Woo Kim* and Di Wang

Crystal structure of bis(*N*,*N*,*N*-ethyldimethylethanaminium) bis(heptaselenido-$\kappa^2 Se^1,Se^7$) palladate(II), $C_{12}H_{32}N_2PdSe_{14}$





DOI 10.1515/ncrs-2017-0101
Received April 7, 2017; accepted August 9, 2017; available online September 16, 2017

Abstract

$C_{12}H_{32}N_2PdSe_{14}$, monoclinic, $P2_1/n$ (no. 14), $a = 9.2236(9)$ Å, $b = 15.1503(14)$ Å, $c = 12.2198(12)$ Å, $\beta = 109.683(2)°$, $V = 1607.8(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0397$, $wR_{ref}(F^2) = 0.0958$, $T = 173$ K.

CCDC no.: 1567742

Table 1: Data collection and handling.

Crystal:	Black block
Size:	0.26 × 0.19 × 0.14 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	16.43 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, ϕ and ω
θ_{max}:	28.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	15584, 3665, 0.054
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2915
$N(param)_{refined}$:	133
Programs:	SHELX [10], WinGX [11], Diamond [12], Bruker programs [13]

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.

Source of material

Na_2PdCl_4 (0.035 g, 0.12 mmol), Na_2Se_4 (0.129 g, 0.36 mmol) and Et_2Me_2NI (0.109 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 as 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. Reddish black block crystals were isolated by filtration and washed with MeOH and diethyl ether several times. Crystals of $[Et_2Me_2N]_2[Pd(Se_7)_2]$ were obtained in 15% yield, based on Pd.

Experimenal 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.

***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

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Pd1	0.5000	0.0000	0.0000	0.01933(15)
Se1	0.48036(7)	0.14493(4)	0.07921(6)	0.02584(15)
Se2	0.31769(7)	0.14255(4)	0.18877(5)	0.02622(15)
Se3	0.44708(8)	0.07441(4)	0.36965(6)	0.02924(16)
Se4	0.50652(8)	0.19350(4)	0.49904(6)	0.03013(16)
Se5	0.27843(9)	0.22367(5)	0.53511(6)	0.03686(19)
Se6	0.10631(8)	0.28396(4)	0.36411(6)	0.03090(17)
Se7	0.12727(7)	0.43654(4)	0.37272(5)	0.02603(16)
N1	0.5595(6)	0.4203(3)	0.2744(4)	0.0230(11)
C1	0.6563(8)	0.4905(4)	0.2444(6)	0.0320(15)
H1A	0.7552	0.4933	0.3063	0.038*
H1B	0.6751	0.4730	0.1740	0.038*
C2	0.5860(11)	0.5808(5)	0.2267(7)	0.054(2)
H2A	0.4907	0.5796	0.1628	0.081*
H2B	0.6554	0.6217	0.2102	0.081*
H2C	0.5670	0.5989	0.2959	0.081*
C3	0.3999(7)	0.4121(4)	0.1863(6)	0.0333(16)
H3A	0.3422	0.4650	0.1895	0.040*
H3B	0.3484	0.3626	0.2075	0.040*
C4	0.3967(8)	0.3992(5)	0.0623(6)	0.0379(17)
H4A	0.4544	0.3474	0.0582	0.057*
H4B	0.4415	0.4497	0.0386	0.057*
H4C	0.2921	0.3924	0.0118	0.057*
C5	0.6426(8)	0.3346(4)	0.2855(6)	0.0325(15)
H5A	0.7468	0.3416	0.3367	0.049*
H5B	0.6426	0.3160	0.2104	0.049*
H5C	0.5919	0.2908	0.3166	0.049*
C6	0.5413(8)	0.4404(5)	0.3892(6)	0.0393(17)
H6A	0.6108	0.4043	0.4485	0.059*
H6B	0.4373	0.4282	0.3848	0.059*
H6C	0.5640	0.5015	0.4078	0.059*

Comment

The title compound, $(Et_2Me_2N)_2[Pd(Se_7)_2]$, which has been prepared by the solvothermal reaction of Na_2PdCl_4, Na_2Se_4 and Et_2Me_2NI with MeOH as a solvent, is composed of a 2D layered $[Pd(Se_7)_2]^{2-}$ anion and charge-balancing $Et_2Me_2N^+$ cations. $(Et_2Me_2N)_2[Pd(Se_7)_2]$ features to possess the longest bridging polyselenide anion, the $Se_7{}^{2-}$ ligand. So far $Se_6{}^{2-}$ is the longest one as found in $\{(CH_3)N(CH_2CH_2)_3N\}_2[Pd(Se_6)_2]$, $(EtNH_3)_2[Pd(Se_6)_2]$, K_2PdSe_{10} and so on [1–4]. In the case of polysulfide anions, the $S_7{}^{2-}$ ligand already exists as the longest bridging polysulfide ligand, as found in $(Ph_4P)_4[In_2S_{27}]$ [5]. Instead of symmetric tetraalkylammonium cations such as Me_4N^+, Et_4N^+, and $(n\text{-}Pr)_4N^+$, an unsymmetric mixed alkyl ammonium cation, $Et_2Me_2N^+$ was adopted to construct a new Pd polyselenide complex by virture of the counterion effect. The counterion effect had been documented, leading to a number of Pd polyselenides with novel structures [1–4, 6].

For the structure of $[Pd(Se_7)_2]^{2-}$ in $(Et_2Me_2N)_2[Pd(Se_7)_2]$, the square planar geometry around Pd(II), coordinated by four bridging heptaselenide ligands, is quite ideal as Se-Pd-Se angles are in the range of 89.18(2)–90.82(2)° (*cf.* the upper figure). The Pd—Se and Se—Se distances are also typical, ranging from 2.4308(6) to 2.4396(6) Å, and from 2.3192(9) to 2.3661(9) Å, respectively, similar to those found in other $[Pd(Se_x)_2]^{2-}$ complexes [1–3, 7–9]. In the layers of $[Pd(Se_7)_2]^{2-}$, heptaselenide $Se_7{}^{2-}$ ligand chains are connecting Pd metal centers, resulting in 32-membered rings composed of four Pd and twenty eight Se atoms (*cf.* the upper figure). The distances between two couples of Pd centers faced diagonally in the 32-membered ring are 15.1503(14) and 17.6160(13) Å. These distances are 10.807(4) and 15.050(5) Å for the 28-membered rings of $\{(CH_3)N(CH_2CH_2)_3N\}_2[Pd(Se_6)_2]$. Compared to the $(CH_3)N(CH_2CH_2)_3N^+$ cation, the smaller $Et_2Me_2N^+$ cation interestingly stabilized the $[Pd(Se_7)_2]^{2-}$ anion with longer polyselenides and larger rings. As we can see from the side view of the $[Pd(Se_7)_2]^{2-}$ layers, the highly folded heptaselenide chains are considered to fill the possible empty space inside and between the layers, to leave smaller empty space enough for being filled with $Et_2Me_2N^+$ cations (*cf.* the lower figure).

Acknowledgements: This work was supported by the Incheon National University Research Grant in 2015. The authors thank Dr. Ji-Eun Lee at Central Instrument Facility, Gyeongsang National University for the X-ray measurements.

References

1. Kim, K.-W.; Wang, D.: Crystal structure of bis(ethanaminium) poly[bis(hexaselenido-κ^2*Se*^{1},*Se*^{6})palladate(II)], $C_4H_{16}N_2PdSe_{12}$. Z. Kristallogr. NCS **231** (2016) 933–934.
2. 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.
3. 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.
4. Ruck, M.; Locherer, F.: Coordination chemistry of homoatomic ligands of bismuth, selenium and tellurium. Coord. Chem. Rev. **285** (2015) 1–10.
5. Dhingra, S. S.; Kanatzidis, M. G.: Syntheses and characterization of the new homoleptic indium-polysulfide complexes $[In_2S_{27}]^{4-}$, $[In_2S_{14}]^{2-}$, and $[In_2S_{16}]^{2-}$. Inorg. Chem. **32** (1993) 3300–3305.
6. Sheldrick, W. S.: Polychalcogenide anions: structural diversity and ligand versatility. Z. Anorg. Allg. Chem. **638** (2012) 2401–2424.
7. 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.

8. 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.
9. Kim, K.-W.; Kim, J.: Crystal structure of bis(*N*,*N*,*N*-triethylammonium) bis(tetraselenido-$\kappa^2 Se^1,Se^4$)palladate(II), $C_{12}H_{32}N_2PdSe_8$. Z. Kristallogr. NCS **230** (2015) 269–270.
10. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. A **64** (2008) 112–122.
11. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Cryst. **45** (2012) 849–854.
12. Putz, H.; Brandenburg, K.: DIAMOND – crystal and molecular structure visualization. Crystal Impact, Bonn, Germany (2015).
13. Bruker, SAINT, APEX2 Buker inc., Madison, USA (2008).