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Crystal structure of bis(N,N,N-ethyldimethylethamaninum) bis(heptaselenido-κ²Se¹,Se⁷) palladate(II), C₁₂H₃₂N₂PdSe₁₄

Abstract

C₁₂H₃₂N₂PdSe₁₄, monoclinic, P2₁/n (no. 14), a = 9.2236(9) Å, b = 15.1503(14) Å, c = 12.2198(12) Å, β = 109.683(2)°, V = 1607.8(3) Å³, Z = 2, Rgt(F) = 0.0397, wRgt(F²) = 0.0958, T = 173 K.

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Table 1: Data collection and handling.

| Crystal: | Black block |
| Size: | 0.26 x 0.19 x 0.14 mm |
| Wavelength: | Mo Kα radiation (0.71073 Å) |
| μ: | 16.43 mm⁻¹ |
| Diffractometer, scan mode: | Bruker APEX-II CCD, φ and ω |
| θmax: | 28.2° |
| N(hkl) measured, N(hkl) unique, Rint: | 15584, 3665, 0.054 |
| Criterion for Iobs, N(hkl)gt: | Iobs > 2 σ(Iobs), 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

Na₂PdCl₄ (0.035 g, 0.12 mmol), Na₂Se₄ (0.129 g, 0.36 mmol) and Et₂Me₂NI (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 [Et₂Me₂N]₂[Pd(Se₇)₂] were obtained in 15% yield, based on Pd.

Experimental details

H atoms were positioned geometrically and treated asriding, with C—H = 0.97 (CH₃) and 0.96 (CH) Å with Uiso(H) = 1.2 (1.5 for methyl) Ueq(C). H atoms of the CH₃ were positioned to be staggered with respect to the shortest other bond to the atom to which the CH₃ is attached.
The counterion effect had been documented, leading to a number of Pd polyselenides with novel structures. The title compound, \((\text{Et}_2\text{Me}_2\text{N})_2[\text{Pd(Se}_7\text{)}_2]\), which has been prepared by the solvothermal reaction of \(\text{Na}_2\text{PdCl}_4\), \(\text{Na}_2\text{Se}_4\) and \(\text{Et}_2\text{Me}_2\text{NI}\) with \(\text{MeOH}\) as a solvent, is composed of a 2D layered \([\text{Pd(Se}_7\text{)}_2]^{2-}\) anion and charge-balancing \(\text{Et}_2\text{Me}_2\text{N}^+\) cations. (\(\text{Et}_2\text{Me}_2\text{N})_2[\text{Pd(Se}_7\text{)}_2]\) features to possess the longest bridging polyselenide anion, the \(\text{Se}^{2-}\) ligand. So far \(\text{Se}^{2-}\) is the longest one as found in \({\{(\text{CH}_3)\text{N(CH}_2\text{CH}_2)\text{3N}}\}_2[\text{Pd(Se}_6\text{)}_2]\), \((\text{EtNH}_3)_2[\text{Pd(Se}_6\text{)}_2]\), \(\text{K}_2\text{PdSe}_{10}\). Coexistence of two large interpenetrating three-dimensional frameworks of \([\text{Pd(Se}_6\text{)}_2]^{2-}\) and \([\text{Pd(Se}_6\text{)}_2]^{3-}\).\(\text{J. Am. Chem. Soc. 114}(1992)4878–4883\).

For the structure of \([\text{Pd(Se}_7\text{)}_2]^{3-}\) in \((\text{Et}_2\text{Me}_2\text{N})_2[\text{Pd(Se}_7\text{)}_2]^{3-}\), 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 \([\text{Pd(Se}_6\text{)}_2]^{2-}\) complexes [1–3, 7–9]. In the layers of \([\text{Pd(Se}_7\text{)}_2]^{3-}\), heptaselenide \(\text{Se}^{2-}\) ligands 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 \({\{(\text{CH}_3)\text{N(CH}_2\text{CH}_2)\text{3N}}\}_2[\text{Pd(Se}_6\text{)}_2]\). Compared to the \((\text{CH}_3)\text{N(CH}_2\text{CH}_2)\text{3N}\)\(^+\) cation, the smaller \(\text{Et}_2\text{Me}_2\text{N}^+\) cation interestingly stabilized the \([\text{Pd(Se}_7\text{)}_2]^{2-}\) anion with longer polyselenides and larger rings. As we can see from the side view of the \([\text{Pd(Se}_6\text{)}_2]^{3-}\) 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 \(\text{Et}_2\text{Me}_2\text{N}^+\) cations (cf. the lower figure).

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