$CsPd_2Cl_5$ − A New Structural Type Containing $^{1}_{\infty}[(PdCl_{3/2}Cl)_2{}^-]$ Chains

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$CsPd_2Cl_5$ has been obtained by hydrothermal reaction of cesium chloride and palladium chloride in a 1:2 ratio in quartz glass ampoules at 150 °C. Its crystal structure has been determined by single-crystal X-ray diffraction analysis [*Pnma*, $Z = 4$, $a = 15.725(3)$ Å, $b = 10.526(2)$ Å, $c = 5.275(1)$ Å]. $CsPd_2Cl_5$ represents the first example of a new structural type made up of infinite $^{1}_{\infty}[(PdCl_{3/2}Cl)_2{}^-]$ chains, in which $PdCl_4$ units are connected through their edges as well as their vertices.

Introduction

Halopalladates(II) invariably contain monomeric square-planar $[PdX_4]^{2-}$ groups, although fluoropalladates(II), MPd_2F_5 (M = K, Rb, Cs),[1−2] possess both square-planar and octahedrally coordinated Pd^{II}. Recent experiments have led to the structural characterization of halopalladates(II) with connected groups. Thus, $CsPdCl_3$[3] contains dinuclear $[(PdCl_{2/2}Cl_2)_2]^{2-}$ groups formed by edge connection, whereas $Tl_4Pd_3Cl_{10}$[4] contains corner-sharing tetrameric $[(PdCl_{2/2}Cl_2)_4]^{4-}$ units. The first compound shown to contain edge-to-edge and corner links in a pentameric $[Pd_5Br_{14}]^{4-}$ unit has been the ternary thallium(I) bromopalladate $Tl_8Pd_7Br_{22}$.[5]

The system $CsCl/PdCl_2$ seemed to be sufficiently interesting for further experiments. Safonov and Mireev[6] described the existence of two compounds − Cs_2PdCl_4 and $CsPd_3Cl_7$ − on the basis of phase equilibria studies, although no structural information was given for $CsPd_3Cl_7$. A compound of this formula would be of interest as one would expect it to contain condensed units of the monomeric $PdCl_4$ group. The characterization of the $CsCl/PdCl_2$ system by Safonov and Mireev[6] was incomplete, as was first shown by the detection of Cs_3PdCl_5[7] with a higher proportion of cesium. The first compound to be found with a lower CsCl content, $CsPdCl_3$, involves dinuclear Pd_2Cl_6 units. We expected to observe continuing linkage of these dinuclear units with increasing Pd content. Experiments aimed at preparing $CsPd_3Cl_7$ have not yet been successful, but single crystals of $CsPd_2Cl_5$ have been obtained, the structural characterization of which is reported herein. The compound does not crystallize isotypically to cesium pentafluoropalladate(II), $CsPd_2F_5$, but instead forms a hitherto unknown structural type.

Results and Discussion

Crystal Structure

$CsPd_2Cl_5$ was prepared under hydrothermal conditions. In contrast to the fluoropalladate of the same formula type, it shows exclusively planar coordination at Pd^{II}.

Pd−Cl distances in $CsPd_2Cl_5$ range from 2.260 to 2.326 Å. The average distance of 2.298 Å corresponds to that found in mononuclear $PdCl_4$ groups. The exclusive presence of planar coordinated Pd^{II} necessitates linkage of these units in order to achieve the formula $CsPd_2Cl_5$. In the crystal structures of $CsPdCl_3$ and $PdCl_2$, the linked units are assembled through their edges. In view of the formula type, we expected the formation of tetrameric linear or angular chains $[Pd_4Cl_{10}]^{2-}$, but this could not be confirmed. The $[Pd_2Cl_5]^-$ part stems from $[Pd_2Cl_6]^{2-}$ units, which are connected through opposite vertices forming one-dimensional infinite chains (see Figure 1, a).

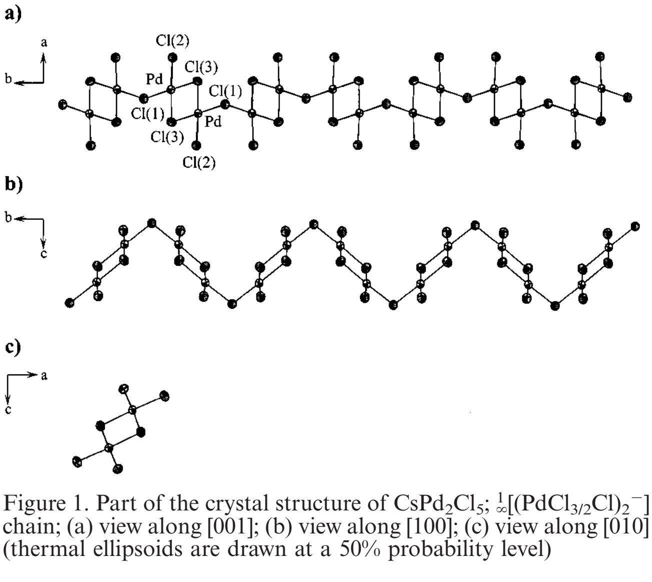

Figure 1. Part of the crystal structure of $CsPd_2Cl_5$; $^{1}_{\infty}[(PdCl_{3/2}Cl)_2{}^-]$ chain; (a) view along [001]; (b) view along [100]; (c) view along [010] (thermal ellipsoids are drawn at a 50% probability level)

The dinuclear Pd_2Cl_6 group is thus the basic unit, just as it is in $CsPdCl_3$. The angle Cl(3)−Pd−Cl(3) at the bridging edge is reduced [86.07(4)°] and is slightly smaller than the corresponding angle in $PdCl_2$.[8] Three crystallographic

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atom positions for chlorine were found by X-ray analysis: Cl(3) are edge-bridging, Cl(2) are terminal chlorine atoms, and the infinite chains are built by corner-sharing Cl(1). Due to the symmetry, the corner-sharing atoms lie *trans* to one another. The terminal Cl(2) atoms show the shortest Pd−Cl distance and the $^{1}_{\infty}[(\mathrm{PdCl}_{3/2}\mathrm{Cl})_2^{-}]$ chains are arranged in such a way that viewed along [100] (Figure 1, b) puckered infinite chains are observed. These are totally eclipsed in the view along [010] (Figure 1, c).

The Pd−Cl structural motif is reminiscent of the connection of Pd units in β-PdI_2,[9] where the dinuclear units build puckered layers. Figure 2 shows a section of the crystal structure of PdI_2. The substructure similar to the Pd−Cl unit in $\mathrm{CsPd}_2\mathrm{Cl}_5$ is marked. Comparison of these structural units indicates the different puckered sequence of the chains, even though they have almost the same Pd−X−Pd angle (see Figure 3).

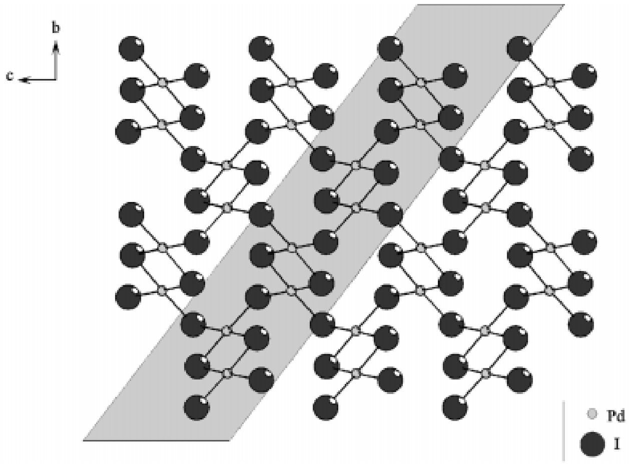

Figure 2. Part of the crystal structure of β-PdI_2

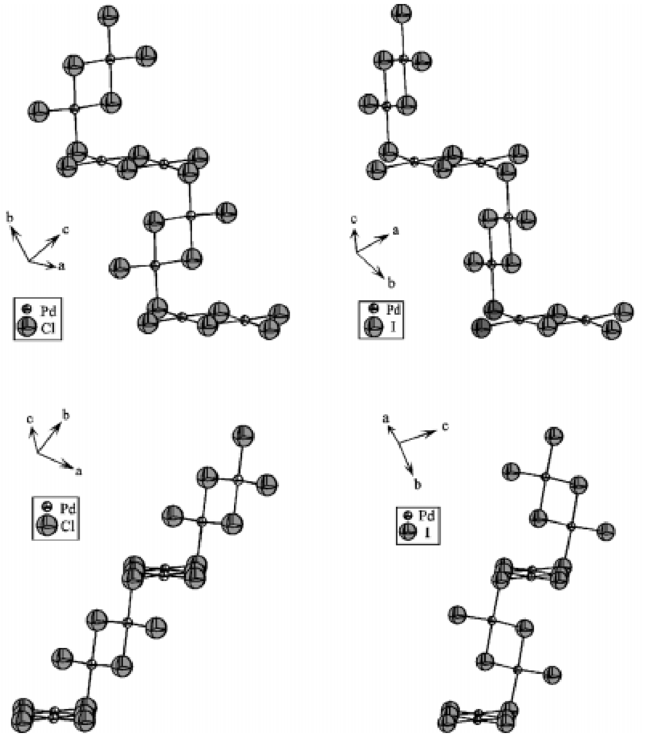

Figure 3. Comparison of a $^{1}_{\infty}[(\mathrm{PdCl}_{3/2}\mathrm{Cl})_2^{-}]$ chain to part of the β-PdI_2 layer

The Pd−Cl motif is also reminiscent of the infinite chains in PdCl_2.[8] Opening these chains after every second palladium atom and adding a Cl atom leads to the $^{1}_{\infty}[(\mathrm{PdCl}_{3/2}\mathrm{Cl})_2^{-}]$ chain found in $\mathrm{CsPd}_2\mathrm{Cl}_5$, as shown in Figure 1, a.

The arrangement in $\mathrm{CsPd}_2\mathrm{Cl}_5$ can be rationalized by considering the coordination spheres of the cesium cations. Each Cs is coordinated by nine chlorine atoms belonging to four different $^{1}_{\infty}[(\mathrm{PdCl}_{3/2}\mathrm{Cl})_2^{-}]$ chains. We chose a distance of up to 3.85 Å as a first sphere for analysis of the Cs coordination by Cl. Four Cl atoms belong to the first chain, two pairs each come from two further chains, while the ninth Cl comes from the fourth chain. The relevant distances are shown in Table 1.

Table 1. Coordination of Cs by Cl

chain	atom	distance [Å]
1	Cl(2)	3.495(1) (2×)
	Cl(3)	3.722(1) (2×)
2	Cl(2)	3.507(1) (2×)
3	Cl(2)	3.537(1) (2×)
4	Cl(1)	3.818(2) (1×)

The average Cs−Cl distance of 3.593 Å falls within the expected range for Cs−Cl distances with CN 9 (3.519−3.738 Å, from a statistical analysis of ICSD data[10]). The polyhedra around Cs are mainly built-up from terminal chlorine atoms.

The bridging Cl atoms have a coordination number of 3, which is rather unusual. Cl(2) shows a more typical fourfold coordination. Selected distances and angles are collected in Table 2.

Table 2. Selected distances [Å] and angles [°] in $\mathrm{CsPd}_2\mathrm{Cl}_5$ (ORFFE[19])

Pd−Cl(2)	2.260(1)
Pd−Cl(1)	2.302(1)
Pd−Cl(3)	2.304(1)
Pd−Cl(3)	2.326(1)
Pd−Pd	3.3840(7)
Pd−Pd	3.4961(9)
Pd−Pd	3.6826(8)
Cs−Cl(2)	3.495(1) (2×)
Cs−Cl(2)	3.507(1) (2×)
Cs−Cl(2)	3.537(1) (2×)
Cs−Cl(3)	3.722(1) (2×)
Cs−Cl(1)	3.818(2)
Cl(2)−Pd−Cl(1)	91.70(5)
Cl(1)−Pd−Cl(3)	92.56(5)
Cl(3)−Pd−Cl(3)	86.07(4)
Cl(3)−Pd−Cl(2)	89.68(4)
Pd−Cl(3)−Pd	93.93(4)
Pd−Cl(1)−Pd	98.79(6)
Cl(2)−Cl(3)−Cl(1)	177.83(5)
Cl(2)−Pd−Cl(3)	175.72(4)
Cl(1)−Pd−Cl(3)	178.73(5)
torsion angle Cl(1)−Cl(3)−Cl(3)−Cl(1)	180
torsion angle Cl(2)−Cl(3)−Cl(3)−Cl(2)	180

The $^1_\infty[(PdCl_{3/2}Cl)_2{}^-]$ chains are aligned along the crystallographic *b* axis. Their arrangement can be described as a distorted hexagonal packing of parallel rods separated only by cesium atoms (Figure 4).

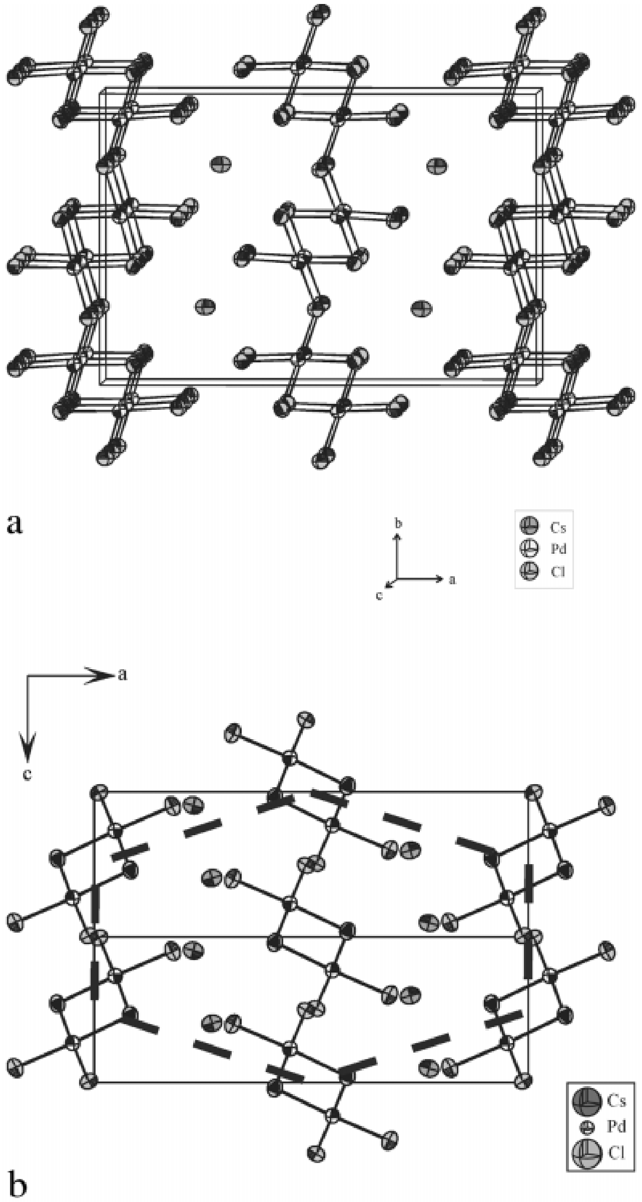

Figure 4. Part of the crystal structure of $CsPd_2Cl_5$; (a) unit cell; (b) hexagonal packing (thermal ellipsoids are drawn at a 50% probability level)

Comparison with Other Compounds of Formula Type AB_2X_5

Few compounds of the formula type AB_2X_5 have appeared in the literature, in which cations B^{2+} show planar coordination. $CsCu_2F_5$ [11] and fluoropalladates(II), MPd_2F_5 (M = K, Rb, Cs),[1,2] are known. $CsPd_2Cl_5$ is not isotypic with any of these.

MPd_2F_5 species, besides containing Pd(1) in square-planar coordination environment, also possess octahedrally coordinated Pd(2). The octahedra are connected through opposite corners forming infinite chains. The remaining fluorine atoms share corners with the planar PdF_4 units of Pd(2), thereby creating Pd−F layers. In contrast, $CsCu_2F_5$ has a complicated structure with CN = 4, 5, and 6 for Cu^{2+}. Consequently, $CsPd_2Cl_5$ represents the first example of a new structural type. Binary palladium halides are the only compounds to which the palladium−chlorine structural motif may be compared.

Calculation of Lattice Energy

The **MA**delung (coulombic) **P**art of **L**attice **E**nergy can be calculated using the program MAPLE.[12−14] Close correspondence between the calculated value and the sum $E_c(CsCl) + 2E_c(PdCl_2)$ lends support to the validity of our structure determination. The calculated Madelung Part of Lattice Energy of $CsPd_2Cl_5$ yields a value of 1358.55 kcal·mol^{-1}, as compared to the sum of 1347.11 kcal·mol^{-1}, a difference of just 0.85%. An analysis of the Madelung Part of Lattice Energy for the different chlorine positions proved interesting (Table 3). The highest MAPLE value was obtained for the corner-sharing Cl, whereas the lowest value was obtained for the terminal Cl. The obtained value was also lower than that for mononuclear $PdCl_4$ units, e.g. in Cs_2PdCl_4 (MAPLE ≈ 100−102 kcal·mol^{-1}). The edge-bridging Cl contributes 40% more to the overall lattice energy compared to the terminal ones. The value is also slightly increased compared to that in $PdCl_2$. The difference between the potentials of the corner-sharing and terminal Cl atoms is again increased (57%). The value for the corner-sharing atoms can only be compared with that for the tetrameric group $[(PdCl_{2/2}Cl_2)_4]^{4-}$ in $Tl_4Pd_3Cl_{10}$. The MAPLE value for the bridging atoms in $Tl_4Pd_3Cl_{10}$ amounts to 146 kcal·mol^{-1}, which is 10 kcal·mol^{-1} more than that for these atoms in $CsPd_2Cl_5$. A comparison of values for corner-sharing Cl atoms adjacent to edge-bridging ones is not

Table 3. Results of lattice energy calculations on $CsPd_2Cl_5$ with MAPLE[12−14]

Atom	^{1}MEFIR	^{1}ECoN	distance	potential	PMF	MAPLE[a]	*MAPLE	1MAPLE
Cs	178.48	9.8170	349.56	−0.61497	0.69492	102.0271	102.0271	230.5826
Pd	59.99	3.9841	226.00	−1.05817	2.39148	351.1120	87.7780	198.3795
Cl(1)[b]	173.38	2.6534	230.25	0.82335	0.93039	136.5977	136.5977	308.7127
Cl(2)[b]	173.67	3.8808	226.00	0.52460	0.59280	87.0330	87.0330	196.6957
Cl(3)[b]	175.62	3.1237	230.42	0.73426	0.82972	121.8177	121.8177	275.3098

[a] Madelung constant: 9.2533; Madelung Part of Lattice Energy: 1358.5502 (2) kcal/mol, 5686.8924 (7) kJ/mol. − [b] Cl(1) corner-sharing, Cl(2) terminal, Cl(3) edge-bridging.

possible, because no chloropalladates with such structural characteristics have hitherto been isolated. The importance of the bridging Cl atoms in the adoption of the observed structural type is clearly highlighted by their increased potentials compared to those of the Cl atoms in CsCl, $PdCl_2$, and monomeric $PdCl_4$ units.

Conclusion

$CsPd_2Cl_5$ represents a new compound with a hitherto unknown structural type. Palladium is not coordinated octahedrally as it is in fluoropalladates of the same formula type. Instead, the planar $PdCl_4$ units build polynuclear infinite chains by sharing corners and edges. The bridging motif corresponds to the results of our experiments concerning higher cesium chloropalladates(II). Besides $CsPdCl_3$, we have been able to prepare two further compounds based on dinuclear Pd_2Cl_6 units. We propose following nomenclature for chloropalladates:

Cs_3PdCl_5 [7] $= (Cs^+)_3[PdCl_4]^{2-}Cl^-$
Cs_2PdCl_4 [15] $= (Cs^+)_2[PdCl_4]^{2-}$
$Cs_{12}Pd_9Cl_{30}{\cdot}2H_2O$ [15] $=$
$(Cs^+)_{12}([PdCl_4]^{2-})_3\text{-}\{[(PdCl_{2/2}Cl_2)_2]^{2-}\}_3{\cdot}2H_2O$
$Cs_6Pd_5Cl_{16}{\cdot}2H_2O$ [15] $=$
$(Cs^+)_6([PdCl_4]^{2-})\text{-}\{[(PdCl_{2/2}Cl_2)_2]^{2-}\}_2{\cdot}2H_2O$
$CsPdCl_3$ [3] $= (Cs^+)_2\{[(PdCl_{2/2}Cl_2)_2]^{2-}\}$
$CsPd_2Cl_5 = (Cs^+)\ {}^1_\infty[(PdCl_{3/2}Cl)_2{}^-]$

Increasing Pd content leads to additional linkage of the square-planar groups.

Perspective

Further investigations of the system $CsCl/PdCl_2$ can be expected to yield new compounds with several additional connecting patterns, e.g. $CsPd_3Cl_7$, as proposed by Safonov and Mireev.[6]

Experimental Section

Cesium Pentachloropalladate(II), $CsPd_2Cl_5$: The first indication of the existence of a compound containing an increased Pd content in the $CsCl/PdCl_2$ system was obtained in the course of heating experiments. A mixture of CsCl (Merck) and $PdCl_2$ (prepared according to Brauer[20]) in a molar ratio of 1:3 was melted, quenched, and annealed in an evacuated quartz glass ampoule. After heating the ampoule for 6 weeks at 280 °C, the powder diffraction pattern (PW 1050/25, Philips) showed unknown peaks, which did not correspond to those reported for $CsPd_3Cl_7$ in ref.[6]

Preparation under hydrothermal conditions proved more successful. A quartz glass ampoule was charged with 0.5 g of a mixture of

Table 4. Crystal data and details of the data collection for $CsPd_2Cl_5$

Empirical formula	$CsPd_2Cl_5$
Molecular weight	523.01
Diffractometer	CAD4 (Enraf−Nonius)
Radiation, wavelength [Å]	Mo-K_α, 0.71069
Monochromator	graphite
Data collection mode	$\omega-2\theta$ scan
T [K]	298
Crystal system	orthorhombic
Space group	*Pnma* (no. 62)
a [Å]	15.725(3)
b [Å]	10.526(2)
c [Å]	5.275(1)
$V_{calcd.}/V_{BILTZ}$[18] [Å^3]	873.13/890.2
$\rho_{calcd.}$ [g·cm^{-3}]	3.978
θ range [°]	$4 \le 2\theta \le 70$
Range of indices	$-25 \le h \le 25$ $-16 \le k \le 16$ $-8 \le l \le 8$
Data collected	4470
Unique data	2002
$R_{int.}$	0.0376
Refinement method	full-matrix least-squares [SHELXL-93[17]]
Parameters	40
$R1$ [$F_o > 4\sigma(F_o)$]	0.0361 (1208 data)
$R1$ (all data)	0.0850 (2002 data)
$wR2$	0.0758
GooF	1.004
Largest diff. peak/hole [e Å^{-3}]	1.51 (d_{Cs} = 0.70 Å)/−1.26

Table 5. Atomic coordinates, equivalent displacement parameters U_{eq} [Å^2] ($U_{eq} = 1/3\ \Sigma_i\ \Sigma_j\ a_i^*\ a_j^*\ \mathbf{a}_i\ \mathbf{a}_j$), and anisotropic displacement parameters U_{ij} [Å^2] {exp [$-2\pi^2$ ($U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + ... + 2U_{12}hka^*b^*$)]} for $CsPd_2Cl_5$

Atom		x	y	z	U_{eq}
Cs	4c	0.22858(3)	1/4	0.09477(9)	0.0411(1)
Pd	8d	0.45086(2)	0.08393(3)	0.76896(6)	0.02635(8)
Cl(1)	4c	0.9882(1)	1/4	0.9924(3)	0.0335(3)
Cl(2)	8d	0.31915(8)	0.0743(1)	0.5986(2)	0.0372(2)
Cl(3)	8d	0.58392(7)	0.0802(1)	0.9613(2)	0.0362(2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs	0.0530(3)	0.0319(2)	0.0384(2)	0	0.0044(2)	0
Pd	0.0264(1)	0.0240(1)	0.0287(2)	−0.0015(1)	0.0001(1)	0.0008(1)
Cl(1)	0.0383(8)	0.0299(8)	0.0321(7)	0	−0.0061(7)	0
Cl(2)	0.0327(5)	0.0332(5)	0.0456(6)	0.0004(5)	−0.0089(5)	−0.0010(5)
Cl(3)	0.0298(5)	0.0372(6)	0.0417(6)	0.0079(5)	−0.0031(5)	−0.0051(5)

$CsCl$ and $PdCl_2$ (molar ratio 1:2). After the addition of H_2O (0.5 mL), the solvent was frozen and the ampoule (ϕ 6 mm, length 60 mm) was evacuated and sealed. The reaction was carried out at 150 °C. After cooling, the mixture was filtered and the crude product was washed with H_2O, ethanol, and diethyl ether. Dark red-brown single crystals were selected for X-ray investigations.

X-ray Crystallographic Study: The crystal structure was determined by single-crystal X-ray analysis at 298 K. Data were collected on a CAD4 diffractometer (Enraf−Nonius). An empirical absorption correction employing psi-scans was applied to the data set (absorption coefficient = 9.66 mm^{-1}). The crystal structure was determined by direct methods (SHELXS-86[16]) and refined by full-matrix least-squares calculations using the program SHELXL-93.[17] Details of the structural investigations and salient crystallographic data are summarized in Table 4, whereas the final atomic coordinates, equivalent displacement parameters U_{eq}, as well as anisotropic displacement parameters are presented in Table 5. Selected interatomic distances and angles are given in Table 2.

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-411722.

Acknowledgments

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