

Crystal Structures and Pressure-Induced Redox Reaction of $\text{Cs}_2\text{PdI}_4 \cdot \text{I}_2$ to Cs_2PdI_6

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Received June 10, 1999

Two iodopalladates of the same empirical formula with palladium in different oxidation states were synthesized from aqueous HI solution. Their crystal structures were characterized by single-crystal X-ray analysis, and the effect of hydrostatic pressure on the structural properties has been investigated. Dicesium hexaiodopalladate(IV), Cs_2PdI_6 , crystallizes in a cubic system, space group $Fm\bar{3}m$, with $a = 11.332(1)$ Å and $Z = 4$, and is isotypic to K_2PtCl_6 . The second compound, dicesium tetraiodopalladate(II) diiodine, $\text{Cs}_2\text{PdI}_4 \cdot \text{I}_2$, shows tetragonal symmetry with space group $I4/mmm$, $a = 8.987(1)$ Å, $c = 9.240(1)$ Å, and $Z = 2$. The crystal structure can be described in resemblance to the $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6$ type. Structural relationships and chemical and structural transformation between both compounds will be discussed. DTA measurements at ambient pressure showed liberation of I_2 and decomposition of the compounds. $\text{Cs}_2\text{PdI}_4 \cdot \text{I}_2$ represents an excellent example for studying a solid-state electron-transfer reaction. The redox reaction to Cs_2PdI_6 can be demonstrated by performing pressure-dependent X-ray studies.

Introduction

Ternary and quaternary halides with palladium in the oxidation states +2 and +4 are known. Most of these halogenopalladates ($X = \text{Cl}, \text{Br}, \text{I}$) contain palladium(II), which exhibits a square-planar coordination, whereas in compounds of the general type M_2PdX_6 ($M = \text{alkaline metal}, X = \text{Cl}, \text{Br}, \text{I}$)^{1,2} palladium(IV) shows an octahedral coordination geometry. Compounds containing large organic cations^{3–6} form Pd_2X_6 units with edge-linked PdX_4 groups. In pure inorganic structures condensation of PdX_4 groups was found in $\text{Tl}_8\text{Pd}_7\text{Br}_{22}$,⁷ where a pentameric motif is created by connecting simple PdX_4 units via edges and vertexes.

Recently, we succeeded in preparing several ternary halogenopalladates in the system $\text{CsCl}-\text{PdCl}_2$ utilizing hydrothermal synthesis. $\text{Cs}_{12}\text{Pd}_9\text{Cl}_{30} \cdot 2\text{H}_2\text{O}$, $\text{Cs}_6\text{Pd}_5\text{Cl}_{16} \cdot 2\text{H}_2\text{O}$, and CsPdCl_3 contain $[\text{Pd}_2\text{Cl}_6]^{2-}$ units. In CsPd_2Cl_5 these units are trans-connected by vertexes to form one-dimensional endless chains.⁸ In addition we were able to isolate a new tetrameric $[(\text{PdCl}_2\text{Cl}_{1/2})_4]^{4-}$ group in thallium(I) chloropalladate(II) $\text{Tl}_4\text{Pd}_3\text{Cl}_{10}$.⁹

It is surprising to note the small number of well-characterized iodopalladates. Apart from K_2PdI_4 ¹⁰ only Cs_2PdI_6 and its decomposition product Cs_2PdI_4 are reported.² Cs_2PdI_6 was

characterized by Krebs et al.,² who studied hexaiodometalates by X-ray powder diffraction ($a = 11.311$ Å, isotypic to K_2PtCl_6 ¹¹).

Here we report our efforts in preparation, single-crystal X-ray structure determination, DTA analysis, and pressure-dependent X-ray studies of the two compounds Cs_2PdI_6 (**1**) and $\text{Cs}_2\text{PdI}_4 \cdot \text{I}_2$ (**2**). Both are of identical chemical composition but occur in different oxidation states of Pd. These compounds, which were prepared in aqueous HI solution, serve as a very convenient model for electron-transfer reactions in the solid state. Upon application of pressure to **2** in a direct solid-state reaction, compound **1** can be afforded with oxidation from Pd(II) to Pd(IV) and cleavage of the inserted iodine dumbbell to iodide.

Experimental Section

Synthesis and Characterization. Since PdI_2 decomposes between 365 and 651 °C,¹² the iodopalladates were not prepared by melting, quenching, and annealing mixtures of CsI and PdI_2 . Preparation under hydrothermal conditions was not successful, due to the limited solubility product of PdI_2 in H_2O ($K_L = 3.73 \times 10^{-16}$ mol³/L³ at 25 °C, potentiometric measurement).¹³ Thus, we made use of the complex $[\text{PdI}_4]^{2-}$, which is formed from PdI_2 in aqueous HI (57%): 0.3 g of a mixture of CsI and PdI_2 (CsI , Fluka; PdI_2 , own preparation) with the molar ratio 10:1 was added to a quartz glass ampule. After addition of 1 mL of hydroiodic acid (57%, Chempur) the solvent was frozen, the ampule (\varnothing 6 mm, length 6 cm) was evacuated, sealed, then heated for 48 h at 150 °C, and slowly cooled to room temperature. The product contains three compounds: $\text{Cs}_2\text{PdI}_4 \cdot \text{I}_2$ (black needle-shaped crystals), Cs_2PdI_6 (black cubes), and CsI_3 (red plates) were found, which were isolated after filtration and washing with water and diethyl ether.

Having refined the experimental conditions, it was possible to yield the pure compounds Cs_2PdI_6 (**1**) and $\text{Cs}_2\text{PdI}_4 \cdot \text{I}_2$ (**2**). **1** is obtained by rapidly cooling the hydrothermal HI solution. Addition of I_2 (sublimed two times, Merck) on the other hand and slow cooling gives a mixture of **2** and CsI_3 , the latter of which is removed with ethanol.

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Table 1. Crystallographic Data for Cs₂PdI₆ and Cs₂PdI₄·I₂

	Cs ₂ PdI ₆	Cs ₂ PdI ₄ ·I ₂
space group	<i>Fm</i> $\bar{3}$ <i>m</i> (no. 225)	<i>I4/mmm</i> (no. 139)
<i>a</i> , Å	11.332(1)	8.987(1)
<i>c</i> , Å		9.240(1)
<i>V</i> , Å ³	1455.2	746.3
$\rho_{\text{calcd/obsd}}$, g·cm ⁻³	5.174/5.209(6)	5.045/5.105(8)
<i>M</i> , g·mol ⁻¹	1133.66	1133.66
<i>Z</i>	4	2
<i>T</i> , K	293	293
μ , mm ⁻¹	18.88	18.41
$\lambda(\text{Mo K}\alpha)$, Å	0.71069	0.71069
wR2 ^a	0.0858	0.0637
R1 (<i>F</i> _o > 4σ(<i>F</i> _o)) ^b	0.0327 (98 reflections)	0.0248 (229 reflections)
R1 (all <i>F</i> _o)	0.0377 (113 reflections)	0.0351 (248 reflections)

$$^a \text{wR2} = \{ \sum (w(F_o^2 - F_c^2)^2 / \sum (w(F_o^2)^2)) \}^{0.5}, \quad ^b \text{R1} = \sum | |F_o| - |F_c| | / \sum |F_o|$$

Table 2. Fractional Atomic Coordinates and Displacement Parameters *U*_{eq}(Å²) (*U*_{eq} = 1/3∑_i∑_jU_{ij}a_i^{*}a_j^{*}**a**_i) of Cs₂PdI₆ and Cs₂PdI₄·I₂

atom	site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Cs ₂ PdI ₆					
Cs	(8c)	1/4	1/4	1/4	0.0440(6)
Pd	(4a)	0	0	0	0.0282(7)
I	(24e)	0.23799(8)	0	0	0.0405(5)
Cs ₂ PdI ₄ ·I ₂					
Cs	(4d)	0	1/2	1/4	0.0525(4)
Pd	(2a)	0	0	0	0.0312(4)
I(1)	(8h)	0.79379(5)	<i>x</i>	0	0.0413(4)
I(2)	(4e)	0	0	0.6501(1)	0.0453(4)

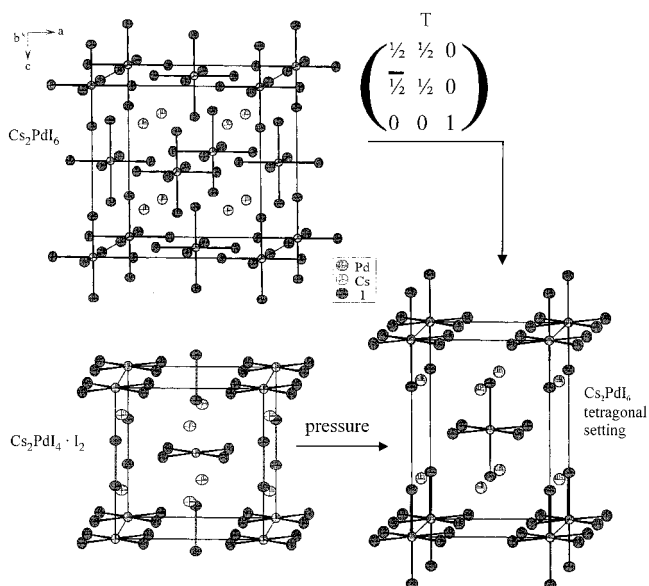
X-ray Studies. X-ray diffraction experiments with different crystals on a κ-CCD single-crystal diffractometer (Nonius) showed that, apart from red crystals of CsI₃,¹⁴ two other compounds were isolated. Two black lustrous crystals, needle-shaped Cs₂PdI₄·I₂ as well as cubic Cs₂PdI₆, were examined with monochromatic Mo Kα radiation (λ = 0.71069 Å). φ -Scans were performed with a rotation angle of 1°, and 360 frames have been taken, allowing a measuring time of 15 s/frame. Detector distances of 25 mm (1) and 26 mm (2) were chosen. Lattice parameters were determined and refined using the Denzo+Scalepack¹⁵ program package. We regret the lack of the possibility of performing absorption correction for the measurements at that time. We suppose no serious inaccuracy is contained. For **1**, a total of 2884 reflections with $-12 \leq h \leq 12$, $-14 \leq k \leq 14$, and $-14 \leq l \leq 14$ were collected. The number of independent reflections was 113 (*R*_{int} = 0.0687). For **2**, 2801 collected and 248 independent reflections were observed with $-11 \leq h, k, l \leq 11$ (*R*_{int} = 0.0818). Starting models for structure refinement were found using direct methods (SHELXS 86¹⁶), and the structural data were refined versus *F*² by full-matrix least-squares methods (SHELXL 93¹⁷).

See Tables 1–3 for crystallographic data, atomic coordinates and displacement parameters, and bond distances and angles, respectively, for Cs₂PdI₆ and Cs₂PdI₄·I₂.

Results and Discussion

Crystal Structure of Cs₂PdI₆. Cs₂PdI₆ (Figure 1) crystallizes isotopic to K₂PtCl₆ as well as the other dicesium hexahaloopalladates(IV) Cs₂PdX₆.^{1,18}

Crystal Structure of Cs₂PdI₄·I₂. The crystal structure of Cs₂PdI₄·I₂ (Figure 1) resembles the basic structure motif of Cs₂

**Figure 1.** Crystal structure of Cs₂PdI₆ and Cs₂PdI₄·I₂, and transformation of Cs₂PdI₆ into a “tetragonal setting” (calculated parameters for a tetragonal setting of Cs₂PdI₆: *I4/mmm*, *a*' = *a*/√2 = 8.013(1) Å, *c*' = *a* = 11.332(1) Å, *V* = 727.6 Å³). Thermal ellipsoids are at the 50% probability level.**Table 3.** Selected Interatomic Distances (Å) and Angles (deg) for Cs₂PdI₆ and Cs₂PdI₄·I₂

		Cs ₂ PdI ₆	
Pd–I(1)		2.697(1)	6×
Cs–I(1)		4.009(1)	12×
		Cs ₂ PdI ₄ ·I ₂	
Pd–I(1)	2.6208(5)	4×	I(1)–Pd–I(1) 90 4×
Pd–I(2)	3.233(1)	2×	I(2)–Pd–I(2) 180
Cs–I(1)	3.9676(5)	8×	I(1)–Pd–I(2) 90
I(1)–I(1)	3.7064(8)	2×	
I(1)–Cs	3.9676(5)	4×	
I(1)–I(2)	3.9832(6)	2×	
I(2)–I(2)	2.774(2)	1×	
I(2)–I(1)	3.9832(6)	4×	

Au^IAu^{III}Cl₆^{19,20} and Cs₂HgPdCl₆,²¹ though [AuCl₂]⁻ and [HgCl₂]-dumbbells, respectively, are substituted by I₂ molecules here. Palladium(II) shows a square-planar stereochemistry with palladium–iodine bond distances of 2.621(1) Å. The coordination sphere is supplemented by two more distant iodine atoms belonging to embedded I₂ molecules to form a strongly elongated octahedron around palladium. The iodine–iodine distance in the embedded iodine molecule is 2.774(2) Å, hereby slightly stretched compared to the value found in elementary iodine (*d*_{I–I} = 2.715(2) Å).^{22,23} In polyiodides similar distances had been found. As examples we will consider the anion I₁₂²⁻, observed in [K(Crypt-2.2.2)]₂I₁₂,²⁴ which can be described as (I₃⁻·I₂)·I₂·(I₃⁻·I₂) with I–I distances for the I₂ units of 2.758(2) and 2.797(2) Å, and the compound [Co(NH₃)₆]I₄²⁵ containing I₄²⁻ units, which can be described by the species (I⁻·I₂·I⁻) showing a bond length of 2.791(2) Å for the I₂ group. In

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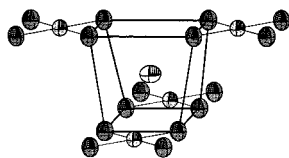


Figure 2. Section of the crystal structure of $\text{Cs}_2\text{PdI}_4 \cdot \text{I}_2$ showing the coordination sphere of the Cs site. Thermal ellipsoids are at the 50% probability level.

compounds with a simple I_2 molecule (e.g., $\text{C}_6\text{H}_{12}\text{N}_4 \cdot 3\text{I}_2$) an iodine–iodine bond length of 2.746(1) Å has been reported.²⁶

The centers of $[\text{PdI}_4]^{2-}$ units and of I_2 molecules are located alternately on a 4-fold rotation axis, $0\ 0\ z$ and $1/2\ 1/2\ z$, respectively, with $z = 0$ and $z = 1/2$ belonging to the point symmetry of $4m2$. Cesium is coordinated by four pairs of iodine atoms; each atom has a distance of 3.9676(5) Å to the central cesium atom. Each pair of these iodine atoms belongs to a $[\text{PdI}_4]^{2-}$ unit, so that there are different iodine–iodine distances within the resulting CsI_8 polyhedron. They range from 3.7064(8) Å for iodine atoms from the same $[\text{PdI}_4]^{2-}$ unit, to 4.752(4) Å for iodine atoms from different $[\text{PdI}_4]^{2-}$ units in the direction of the crystallographic c -axis, to 5.2806(9) Å in the directions [100] and [010]. This results in a strong distortion of the iodine polyhedron around cesium (Figure 2).

Iodine of site I(1) is 5-fold coordinated by one neighboring palladium atom and four cesium atoms, extending to a tetragonal pyramidal structure. Each I(2) is coordinated linearly by another I(2) atom, forming the I_2 molecule. At a distance of 3.233(1) Å Pd extends the coordination sphere of I(2).

The crystal structure of **2** can be described analogously to $\text{Cs}_2\text{HgPdCl}_6$ as the “filled-up” K_2PdCl_4 type.²¹ The empty channels in the K_2PdCl_4 -type structure are filled by I_2 and $[\text{PdI}_4]^{2-}$ along $1/2\ 1/2\ z$ in an alternating sequence. This special motif causes a change of the empirical formula A_2BX_4 in K_2PdCl_4 to $\text{A}_2\text{BX}_4 \cdot \text{X}_2$ and $\text{A}_2\text{BX}_4 \cdot \text{HgX}_2$, respectively.

The first example of this structure type is $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6$ and has already been reported by Elliott and Pauling¹⁹ in 1938. Unlike the examples discussed so far, $\text{Cs}_2\text{PdI}_4 \cdot \text{I}_2$ reveals a smaller c/a -ratio of 1.03 ($\text{Cs}_2\text{AuAuCl}_6$ 1.45, $\text{Cs}_2\text{AgAuCl}_6$ ¹⁹ 1.49, and $\text{Cs}_2\text{HgPdCl}_6$ 1.46). The reason for this lies in the shorter length of the dumbbell I_2 in relation to AuCl_2^- , AgCl_2^- , and HgCl_2 .

Substitution of triatomic dumbbells by I_2 molecules implies a change of the coordination number of Cs from $\text{CN} = 12$ [$\text{Cs}_2\text{-AuAuCl}_6$, $d(\text{Cs}-\text{Cl}) = 3.768$ Å (4×) and 3.802 Å (8×); $\text{Cs}_2\text{-AgAuCl}_6$, $d(\text{Cs}-\text{Cl}) = 3.710$ Å (4×) and 3.806 Å (8×); $\text{Cs}_2\text{HgPdCl}_6$, $d(\text{Cs}-\text{Cl}) = 3.739$ Å (4×) and 3.796 Å (8×)] to $\text{CN} = 8$, or $\text{CN} = 8 + 4$ with $d(\text{Cs}-\text{Cl}) = 3.9676(5)$ Å (8×) and 4.5873(5) Å (4×), respectively.

The relation to chloroperovskites can be rationalized by the group–subgroup relationship of space groups as described for the compound $\text{Cs}_2\text{HgPdCl}_6$.²¹

Relationship between 1 and 2. The structural relationship between **1** and **2** can be more clearly understood by transformation of the original setting for Cs_2PdI_6 into a tetragonal setting, which is illustrated in Figure 1 including the corresponding transformation matrix.

The contrasting kind of chemical bonding in both compounds can be indicated by ELF calculations (ELF = electron localization function).^{27–29} ELF describes chemical bonding by localized pairs of electrons. On the basis of density functional theory, calculations were performed with the program TB-LMTO-ASA

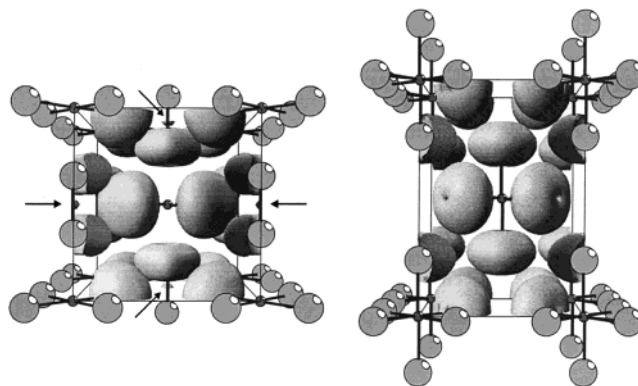


Figure 3. Illustration of the ELF for $\text{Cs}_2\text{PdI}_4 \cdot \text{I}_2$ (a, left) and Cs_2PdI_6 (b, right) with an isovalue of 0.42.

(tight-binding linear muffin-tin orbital in the atomic sphere approximation).³⁰ In Figure 3 the electron localization function is visualized by the program SciAn³¹ and displayed for an isovalue of 0.42. In the case of **2** (Figure 3a) we can see that this isosurface encloses a maximum of ELF (“localized electrons”) between the iodine atoms of the embedded I_2 dumbbell which does *not* appear in the case of **1** (Figure 3b) for the same isovalue. The relatively low ELF value between the I atoms is related to the weakness of the bond in I_2 (compare the long I–I distance). Pd–I bonds can be made visible (not displayed) for an isovalue of 0.57 in both compounds. This higher level shows the stronger attraction for localized electrons within the Pd–I bond.

DTA Measurements. The chemical relationship of the cesium iodopalladates **1** and **2** is obvious in the alternating sequence of $[\text{PdI}_4]^{2-}$ and I_2 units in the direction [001]. It should be possible to cause a transition between the compounds in direct solid-state redox reaction by application of pressure or temperature. To verify our assumption, we first performed TG/DTA experiments. We expected to gain additional information about the decomposition reaction of Cs_2PdI_6 as reported by Krebs.² Thermogravimetry showed for **1** a loss of mass in two steps, which corresponds to liberation of iodine (I_2). The products, which were isolated from step 1 and step 2, show different X-ray powder patterns. Several peaks in the powder pattern of the decomposition product of step 1 can be assigned to CsI. The product of the second decomposition step shows a melting point at 430 ± 5 °C. Following our observations, we assume the formation of at least one other compound; due to the lowered CsI content it will contain linked PdI_4 units. This would correspond to the results of our experiments in cesium chloropalladates(II) which show this kind of linkage.⁸ Recently we were able to isolate a pure sample of the first decomposition step, and detailed structure investigations are to be published. DTA and TG lines of Cs_2PdI_6 and $\text{Cs}_2\text{PdI}_4 \cdot \text{I}_2$ are the same.

Pressure-Dependent X-ray Diffraction Experiments. Furthermore, application of pressure to **2** should induce a solid-state reaction to dicesium hexaiodopalladate(IV) involving cleavage of the I_2 dumbbell and oxidation of Pd(II) to Pd(IV).

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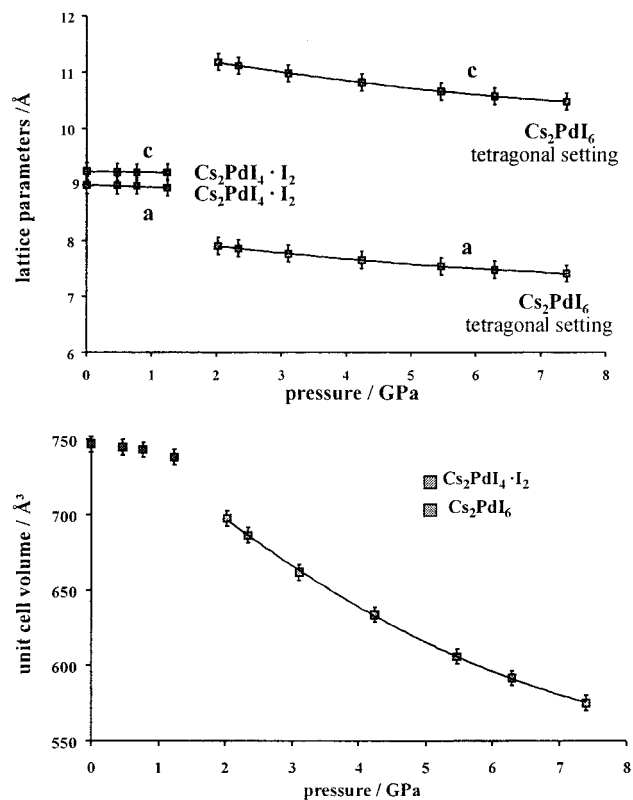


Figure 4. Results of the pressure measurements for $\text{Cs}_2\text{PdI}_4 \cdot \text{I}_2$.

For this purpose energy-dispersive X-ray experiments with synchrotron radiation (Hasylab, DESY, Hamburg) were performed at different pressures. Pressures were generated by diamond anvil cells (DAC); details concerning this method are given by Huber, Syassen, and Holzapfel.³² The ruby luminescence method was performed for pressure determination, as pressure-transmitting media mineral oil and N_2 were used. The

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change in the diffraction patterns as a result of the structural transition from $\text{Cs}_2\text{PdI}_4 \cdot \text{I}_2$ to Cs_2PdI_6 was quite obvious. At pressures $p \leq 1.24$ GPa we obtain a tetragonal indexing in agreement with the crystal structure of $\text{Cs}_2\text{PdI}_4 \cdot \text{I}_2$ (Figure 4). The length of the crystallographic a -axis decreases with increasing pressures ($p \leq 1.24$ GPa), while the c -axis remains virtually constant. At pressures $p \geq 2.03$ GPa the powder patterns can be indexed face-centered cubic. Presumably, at higher pressures another transition takes place. Further experiments are in progress to obtain more detailed information.

Conclusions

Investigating the system $\text{CsI}-\text{PdI}_2$, we were able to isolate two compounds with the same empirical formula and related crystal structures. The proposed transition from $\text{Cs}_2\text{PdI}_4 \cdot \text{I}_2$ to Cs_2PdI_6 can be demonstrated by pressure-dependent X-ray diffraction. The high-pressure experiments gave rise to the existence of another unknown modification ($p > 8$ GPa). The reverse reaction of **1** to **2** has not been observed yet, because performing temperature-dependent measurements has only been possible at ambient pressure so far.

DTA analysis demonstrated the liberation of iodine and simultaneous partial decomposition of **1** and **2** to CsI and another compound with a presumably higher palladium iodide content.

Acknowledgment. We are grateful to Dr. Hans-Josef Hesse (group of Prof. Dr. Wortmann) and Dipl.-Phys. Ing. Werner Sievers (group of Prof. Dr. Holzapfel), Universität-Gesamthochschule Paderborn, for their essential support concerning the pressure measurements. For their kind support in translating this manuscript, we thank Dipl.-Chem. Frank Hipler and Heather N. Heines. We also thank Degussa for donating chemicals and the Fonds der Chemischen Industrie for financial support.

Supporting Information Available: X-ray crystallographic files, in CIF format, and a table giving a comparison of relevant structure types. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Table 8. Comparison of relevant structure types. Transformation of the Unit Cell of Cs₂PdI₆ and Comparison of the resulting Lattice Parameters and Fractional Atomic Coordinates with Cs₂PdI₄ · I₂

Compound	Cs ₂ PdI ₆ cubic			Cs ₂ PdI ₆ transformed tetragonal setting			Cs ₂ PdI ₄ · I ₂ tetragonal		
Space group type	F m $\bar{3}$ m			I 4/mmm			I 4/mmm		
Lattice parameters	a = 11.332(1) Å			$a' = \frac{a}{\sqrt{2}} = 8.013(1) \text{ Å}$			a = 8.987(1) Å		
				c' = a = 11.332(1) Å			c = 9.240(1) Å		
Volume of unit cell	1455.2 Å ³			727.6 Å ³			746.3 Å ³		
Z	4			2			2		
Fractional atomic coordinates	x	y	z	x	y	z	x	y	z
	Cs 1/4	1/4	1/4	Cs 0	1/2	1/4	Cs 0	1/2	1/4
	Pd 0	0	0	Pd 0	0	0	Pd 0	0	0
	I 0.23799	0	0	I 0.23799	x	0	I 0.20621	x	0
				I 0	0	0.23799	I 0	0	0.3499