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# Crystal Structures and Pressure-Induced Redox Reaction of $Cs_2PdI_4{\cdot}I_2$ to $Cs_2PdI_6$

**B. Schüpp,[†] P. Heines,[†] A. Savin,[‡] and H.-L. Keller*[,†]**

Anorganische Chemie, Universität Dortmund, D-44221 Dortmund, Germany, and Laboratoire de
Chimique Théorique, Université Pierre et Marie Curie, F-75252 Paris Cedex 05, France

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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, $Cs_2PdI_4{\cdot}I_2$, 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 $Cs_2Au^IAu^{III}Cl_6$ 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. $Cs_2PdI_4{\cdot}I_2$ 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 = Cl, Br, I) contain palladium(II), which exhibits a square-planar coordination, whereas in compounds of the general type $M_2PdX_6$ (M = alkaline metal, X = Cl, Br, 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 $Tl_8Pd_7Br_{22}$,[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 CsCl−$PdCl_2$ utilizing hydrothermal synthesis. $Cs_{12}Pd_9Cl_{30}{\cdot}2H_2O$, $Cs_6Pd_5Cl_{16}{\cdot}2H_2O$, and $CsPdCl_3$ contain $[Pd_2Cl_6]^{2-}$ 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 $[(PdCl_2Cl_{2/2})_4]^{4-}$ group in thallium(I) chloropalladate(II) $Tl_4Pd_3Cl_{10}$.[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 $Cs_2PdI_4{\cdot}I_2$ (**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 und 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 $H_2O$ ($K_L = 3.73 \times 10^{-16}$ mol$^3$/L$^3$ at 25 °C, potentiometric measurement).[13] Thus, we made use of the complex $[PdI_4]^{2-}$, 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 (∅ 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: $Cs_2PdI_4{\cdot}I_2$ (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 $Cs_2PdI_4{\cdot}I_2$ (**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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* To whom correspondence should be addressed. E-mail: keller@pop.uni-dortmund.de. Phone: +49 231 755 3804. Fax: +49 231 755 5048.

[†] Universität Dortmund.

[‡] Université Pierre et Marie Curie.

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**Table 1.** Crystallographic Data for $Cs_2PdI_6$ and $Cs_2PdI_4 \cdot I_2$

| | $Cs_2PdI_6$ | $Cs_2PdI_4 \cdot I_2$ |
|---|---|---|
| space group | $Fm\bar{3}m$ (no. 225) | $I4/mmm$ (no. 139) |
| $a$, Å | 11.332(1) | 8.987(1) |
| $c$, Å | | 9.240(1) |
| $V$, Å$^3$ | 1455.2 | 746.3 |
| $\rho_{calcd/obsd}$, g·cm$^{-3}$ | 5.174/5.209(6) | 5.045/5.105(8) |
| $M$, g·mol$^{-1}$ | 1133.66 | 1133.66 |
| $Z$ | 4 | 2 |
| $T$, K | 293 | 293 |
| $\mu$, mm$^{-1}$ | 18.88 | 18.41 |
| $\lambda$(Mo K$\alpha$), Å | 0.71069 | 0.71069 |
| wR2[a] | 0.0858 | 0.0637 |
| R1 ($F_o > 4\sigma(F_o)$)[b] | 0.0327 (98 reflections) | 0.0248 (229 reflections) |
| R1 (all $F_o$) | 0.0377 (113 reflections) | 0.0351 (248 reflections) |

[a] $wR2 = \{\sum(w(F_o^2 - F_c^2)^2/\sum(w(F_o^2)^2)\}^{0.5}$. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.

**Table 2.** Fractional Atomic Coordinates and Displacement Parameters $U_{eq}$(Å$^2$) ($U_{eq} = 1/3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$) of $Cs_2PdI_6$ and $Cs_2PdI_4 \cdot I_2$

| atom | site | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|---|
| | | $Cs_2PdI_6$ | | | |
| 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) |
| | | $Cs_2PdI_4 \cdot I_2$ | | | |
| Cs | (4d) | 0 | $^1/_2$ | $^1/_4$ | 0.0525(4) |
| Pd | (2a) | 0 | 0 | 0 | 0.0312(4) |
| I(1) | (8h) | 0.79379(5) | $x$ | 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 $\kappa$-CCD single-crystal diffractometer (Nonius) showed that, apart from red crystals of $CsI_3$,[14] two other compounds were isolated. Two black lustrous crystals, needle-shaped $Cs_2PdI_4 \cdot I_2$ as well as cubic $Cs_2PdI_6$, were examined with monochromatic Mo K$\alpha$ radiation ($\lambda$ = 0.71069 Å). $\varphi$-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+Scalepack[15] program package. We regret the lack of the possibility of perfoming absorption correction for the measurements at that time. We suppose no serious inaccuracy is contained. For **1**, a total of 2884 reflections with $-12 \le h \le 12$, $-14 \le k \le 14$, and $-14 \le l \le 14$ were collected. The number of independent reflections was 113 ($R_{int}$ = 0.0687). For **2**, 2801 collected and 248 independent reflections were observed with $-11 \le h,k,l \le 11$ ($R_{int}$ = 0.0818). Starting models for structure refinement were found using direct methods (SHELXS 86[16]), and the structural data were refined versus $F^2$ by full-matrix least-squares methods (SHELXL 93[17]).

See Tables 1−3 for crystallographic data, atomic coordinates and displacement parameters, and bond distances and angles, respectively, for $Cs_2PdI_6$ and $Cs_2PdI_4 \cdot I_2$.

## Results and Discussion

**Crystal Structure of $Cs_2PdI_6$.** $Cs_2PdI_6$ (Figure 1) crystallizes isotypic to $K_2PtCl_6$ as well as the other dicesium hexahalogenopalladates(IV) $Cs_2PdX_6$.[1,18]

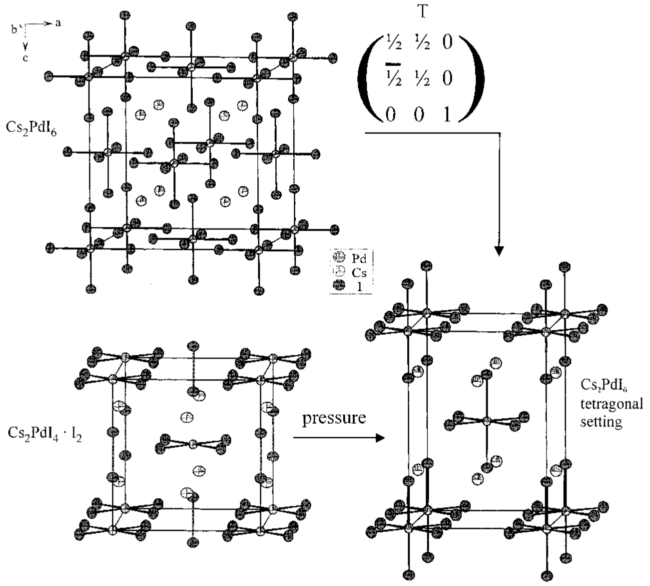

**Figure 1.** Crystal structure of $Cs_2PdI_6$ and $Cs_2PdI_4 \cdot I_2$, and transformation of $Cs_2PdI_6$ into a "tetragonal setting" (calculated parameters for a tetragonal setting of $Cs_2PdI_6$: $I4/mmm$, $a' = a/\sqrt{2}$ = 8.013(1) Å, $c' = a$ = 11.332(1) Å, $V$ = 727.6 Å$^3$). Thermal ellipsoids are at the 50% probability level.

**Table 3.** Selected Interatomic Distances (Å) and Angles (deg) for $Cs_2PdI_6$ and $Cs_2PdI_4 \cdot I_2$

| | | | | | |
|---|---|---|---|---|---|
| | | $Cs_2PdI_6$ | | | |
| Pd−I(1) | 2.697(1) | 6× | | | |
| Cs−I(1) | 4.009(1) | 12× | | | |
| | | $Cs_2PdI_4 \cdot I_2$ | | | |
| 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× | | | |

**Crystal Structure of $Cs_2PdI_4 \cdot I_2$.** The crystal structure of $Cs_2PdI_4 \cdot I_2$ (Figure 1) resembles the basic structure motif of $Cs_2Au^IAu^{III}Cl_6$[19,20] and $Cs_2HgPdCl_6$,[21] though $[AuCl_2]^-$- and $[HgCl_2]$-dumbbells, respectively, are substituted by $I_2$ 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 $I_2$ 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 $I_{12}^{2-}$, observed in $[K(Crypt\text{-}2.2.2)]_2I_{12}$,[24] which can be described as $(I_3^- \cdot I_2) \cdot I_2 \cdot (I_3^- \cdot I_2)$ with I−I distances for the $I_2$ units of 2.758(2) and 2.797(2) Å, and the compound $[Co(NH_3)_6]I_3I_4$[25] containing $I_4^{2-}$ units, which can be described by the species $(I^- \cdot I_2 \cdot I^-)$ showing a bond length of 2.791(2) Å for the $I_2$ group. In

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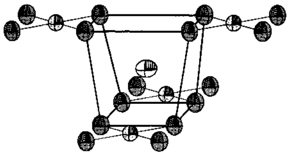

**Figure 2.** Section of the crystal structure of $Cs_2PdI_4{\cdot}I_2$ showing the coordination sphere of the Cs site. Thermal ellipsoids are at the 50% probability level.

compounds with a simple $I_2$ molecule (e.g., $C_6H_{12}N_4{\cdot}3I_2$) an iodine−iodine bond length of 2.746(1) Å has been reported.[26]

The centers of $[PdI_4]^{2-}$ 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 $\bar{4}m2$. 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 $[PdI_4]^{2-}$ 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 $[PdI_4]^{2-}$ unit, to 4.752(4) Å for iodine atoms from different $[PdI_4]^{2-}$ 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 $Cs_2HgPdCl_6$ 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 $[PdI_4]^{2-}$ 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 $A_2BX_4{\cdot}X_2$ and $A_2BX_4{\cdot}HgX_2$, respectively.

The first example of this structure type is $Cs_2Au^{I}Au^{III}Cl_6$ and has already been reported by Elliott and Pauling[19] in 1938. Unlike the examples discussed so far, $Cs_2PdI_4{\cdot}I_2$ reveals a smaller *c*/*a*-ratio of 1.03 ($Cs_2AuAuCl_6$ 1.45, $Cs_2AgAuCl_6$[19] 1.49, and $Cs_2HgPdCl_6$ 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 CN = 12 [$Cs_2AuAuCl_6$, $d$(Cs−Cl) = 3.768 Å (4×) and 3.802 Å (8×); $Cs_2AgAuCl_6$, $d$(Cs−Cl) = 3.710 Å (4×) and 3.806 Å (8×); $Cs_2HgPdCl_6$, $d$(Cs−Cl) = 3.739 Å (4×) and 3.796 Å (8×)] to CN = 8, or CN = 8 + 4 with $d$(Cs−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 $Cs_2HgPdCl_6$.[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 (tight-binding linear muffin-tin orbital in the atomic sphere approximation).[30] In Figure 3 the electron localization function is visualized by the program SciAn[31] 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 $I_2$ (compair 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.

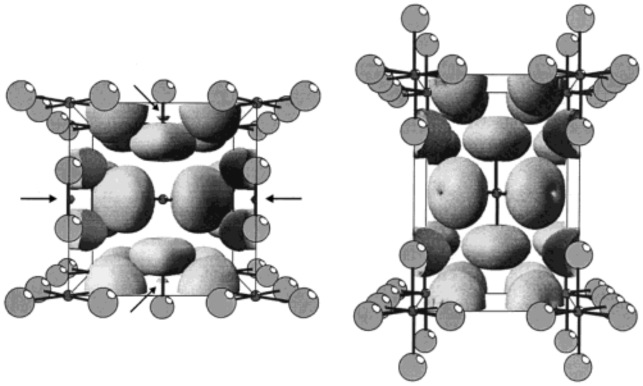

**Figure 3.** Illustration of the ELF for $Cs_2PdI_4{\cdot}I_2$ (a, left) and $Cs_2PdI_6$ (b, right) with an isovalue of 0.42.

**DTA Measurements.** The chemical relationship of the cesium iodopalladates **1** and **2** is obvious in the alternating sequence of $[PdI_4]^{2-}$ 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 $Cs_2PdI_4{\cdot}I_2$ 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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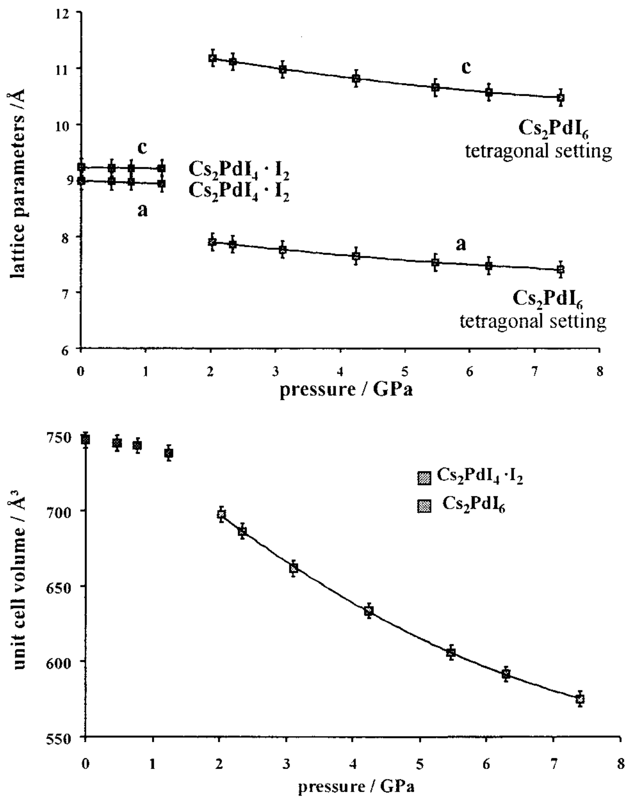

**Figure 4.** Results of the pressure measurements for $Cs_2PdI_4 \cdot I_2$.

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 change in the diffraction patterns as a result of the structural transition from $Cs_2PdI_4 \cdot I_2$ 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 $Cs_2PdI_4 \cdot I_2$ (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 CsI−$PdI_2$, we were able to isolate two compounds with the same empirical formula and related crystal structures. The proposed transition from $Cs_2PdI_4 \cdot I_2$ 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.

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**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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