

Cs₂Pd₃(P₂O₇)₂ and Cs₂Pd₃(As₂O₇)₂: A 3D Palladium Phosphate with a Tunnel Structure and a 2D Palladium Arsenate Containing Strings of Palladium Atoms

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Cs₂Pd₃(P₂O₇)₂ (**1**) and Cs₂Pd₃(As₂O₇)₂ (**2**) have been synthesized by molten flux reactions and characterized by single-crystal X-ray diffraction. The structure of **1** consists of discrete Pd^{II}O₄ squares which are linked by P₂O₇ groups via corner-sharing to generate a 3D framework containing 12-ring channels in which Cs⁺ cations are located. Compound **2** adopts a 2D layer structure with the interlayer space filled with Cs⁺ cations. Within a layer there are PdO₄ squares and As₂O₇ groups fused together via corner-sharing. Adjacent layers are stacked such that strings of Pd atoms are formed. The PdO₄ squares show eclipsed and staggered stacks with alternate short and long Pd···Pd distances. The two compounds adopt considerably different structures although they have the same general formula: Cs₂Pd₃(X₂O₇)₂. Compound **2** is the first palladium arsenate reported. Crystal data for **1**: orthorhombic, space group *Cmc*2₁ (No. 36), *a* = 7.6061(4) Å, *b* = 14.2820(7) Å, *c* = 14.1840(7) Å, and *Z* = 4. Crystal data for **2**: tetragonal, space group *P4/n* (No. 85), *a* = 16.251(1) Å, *c* = 5.9681(5) Å, and *Z* = 4.

Introduction

A large number of transition metal phosphates have been prepared or found as minerals. Their great structural diversity results from the variations of the phosphate species, a large number of transition metals with variable oxidation states to which the phosphate species may be coordinated, and a large selection of inorganic or organic cation templates.^{1,2} Two synthetic approaches, namely high-temperature solid state reaction and hydrothermal methods, are commonly used to obtain these solid phosphates. All elements in the first transition series and most elements in the second and third series form crystalline phosphates. However, a few phosphates of the platinum-group metals, namely Ru, Os, Rh, Ir, Pd, and Pt, have been reported. Solid phosphates of osmium

and iridium are actually not known. The structural chemistry of the corresponding arsenates is even more limited. We believe that use of proper starting materials and a choice of suitable preparative methods may be the key to the crystallization of these phosphates that have never been crystallized. For example, crystals of RhPO₄ and RhP₃O₉ were obtained from chemical vapor transport reactions.³ PtP₂O₇ was synthesized by reaction between Pt metal and P₄O₁₀ vapor in a dried oxygen stream at high temperatures.⁴ An amorphous precursor “H₂RuP₃O₁₀” prepared by the reaction of ruthenium chloride hydrate with phosphoric acid was used to prepare metaphosphate Ru(PO₃)₃ and mixed-valence diphosphates ARu₂(P₂O₇)₂ (A = Li, Na, Ag, and Cu).^{5,6} We have therefore undertaken an investigation of the phosphates and arsenates of the platinum-group metals. This paper reports the results of our exploratory synthesis and single-crystal X-ray structural characterization of a cesium palladium phosphate and a cesium palladium arsenate. Much to our surprise the phosphate and arsenate adopt two

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considerably different structures although they have the same general formula: $\text{Cs}_2\text{Pd}_3(\text{X}_2\text{O}_7)_2$.

Experimental Section

Synthesis. A mixture of 0.690 g of CsH_2PO_4 , 0.198 g of $(\text{NH}_4)_2\text{HPO}_4$, and 0.177 g of PdCl_2 (Cs/P/Pd mole ratio = 3:4.5:1) was placed in a 5-mL platinum crucible and thermally treated as follows: heated from r.t. to 850 °C over 8 h; cooled to 450 °C at 5 °C/h; and quenched to r.t. by turning off the power of the furnace. The flux was still a liquid at 450 °C. The flux was dissolved with hot water, and the solid product was obtained by suction filtration. The product contained olive crystals of $\text{Cs}_2\text{Pd}_3(\text{P}_2\text{O}_7)_2$ (denoted as **1**) and olive polycrystalline solid. The X-ray powder pattern of the bulk product indicated that a single phase of $\text{Cs}_2\text{Pd}_3(\text{P}_2\text{O}_7)_2$ had been obtained (see Figure S1 in the Supporting Information). The yield was 43% based on Pd. CsH_2AsO_4 was prepared from a solution of As_2O_3 dissolved in H_2O_2 with cesium hydroxide. $\text{NH}_4\text{H}_2\text{AsO}_4$ was prepared in a similar way with ammonium hydroxide. For the crystal growth of $\text{Cs}_2\text{Pd}_3(\text{As}_2\text{O}_7)_2$ (denoted as **2**), a mixture containing CsH_2AsO_4 , $\text{NH}_4\text{H}_2\text{AsO}_4$, and PdCl_2 (Cs/As/Pd mole ratio = 3:4.5:1) was slowly heated to 800 °C, cooled to 450 °C at 5 °C/h, and then quenched to r.t. The flux was a solid at 450 °C. Besides the maroon crystals of **2**, the product also contained much unidentified orange crystalline solid, as indicated by powder X-ray diffraction. Subsequently, reaction mixtures containing stoichiometric CsH_2AsO_4 , $\text{NH}_4\text{H}_2\text{AsO}_4$, and PdO (or PdCl_2) (Cs/As/Pd mole ratio = 2:4:3) were heated at 600 °C (or 650 °C) for 36 h with several intermittent grindings. The reactions yielded $\text{Cs}_2\text{Pd}_3(\text{As}_2\text{O}_7)_2$ as the major product along with a small amount of unidentified impurities (see Figure S2 in the Supporting Information).

Single-Crystal X-ray Diffraction. An olive crystal of dimensions $0.05 \times 0.05 \times 0.10 \text{ mm}^3$ for **1** and a maroon crystal of dimensions $0.05 \times 0.05 \times 0.01 \text{ mm}^3$ for **2** were selected for indexing and intensity data collection on a Bruker APEX CCD diffractometer equipped with a fine-focus, 2-kW, sealed-tube X-ray source. The data were collected at room temperature in 1270 frames with ω scans (width 0.30° per frame). Empirical absorption corrections based on symmetry equivalents were applied ($T_{\text{min,max}} = 0.582, 0.947$ for **1**; $0.461, 0.990$ for **2**). On the basis of systematic absences, statistics of intensity distribution, and successful solution and refinement of the structures, the space groups were determined to be $Cmc2_1$ (No. 36) for **1** and $P4/n$ (No. 85) for **2**. The structures were solved by direct methods and difference Fourier syntheses. The site occupancy factors of Cs atoms were allowed to refine. The Cs(1) and Cs(2) positions in **1** and Cs(1) position in **2**, respectively, refined to values of 0.498(1), 0.497(1), and 0.998(3), indicating that all Cs positions are fully occupied. The final cycles of least-squares refinement including atomic coordinates and anisotropic thermal parameters for all atoms converged at $R_1 = 0.0228$ and $wR_2 = 0.0544$ for **1** and $R_1 = 0.0271$ and $wR_2 = 0.0814$ for **2**. The Flack x parameter for **1** was 0.02(2), indicative of a correct absolute structure. All calculations were performed using the SHELXTL Version 5.1 software package.⁷ Crystallographic data for **1** and **2** are summarized in Table 1. Selected bond lengths for **1** and **2** are provided in Table 2.

Results and Discussion

As revealed by single-crystal X-ray crystallography, the 3D framework structure of $\text{Cs}_2\text{Pd}_3(\text{P}_2\text{O}_7)_2$ consists of discrete

Table 1. Crystallographic Data for $\text{Cs}_2\text{Pd}_3(\text{P}_2\text{O}_7)_2$ (**1**) and $\text{Cs}_2\text{Pd}_3(\text{As}_2\text{O}_7)_2$ (**2**)

	1	2
chemical formula	$\text{Cs}_2\text{O}_{14}\text{P}_4\text{Pd}_3$	$\text{As}_4\text{Cs}_2\text{O}_{14}\text{Pd}_3$
$a/\text{Å}$	7.6061(4)	16.251(1)
$b/\text{Å}$	14.2820(7)	16.251(1)
$c/\text{Å}$	14.1840(7)	5.9681(5)
$V/\text{Å}^3$	1540.8(1)	1576.2(4)
Z	4	4
formula weight	932.9	1108.7
space group	$Cmc2_1$ (No. 36)	$P4/n$ (No. 85)
$T, \text{°C}$	23	23
$\lambda(\text{Mo K}\alpha), \text{Å}$	0.71073	0.71073
$D_{\text{calc}}, \text{g}\cdot\text{cm}^{-3}$	4.022	4.672
$\mu(\text{Mo K}\alpha), \text{cm}^{-1}$	86.0	163.4
R_1^a	0.0228	0.0271
wR_2^b	0.0544	0.0814

^a $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\text{Max}(F_o, 0) + 2(F_c)^2]/3$, where $a = 0.0288$ and $b = 1.64$ for **1** and $a = 0.0416$ and $b = 0.00$ for **2**.

Table 2. Selected Bond Lengths (Å) for $\text{Cs}_2\text{Pd}_3(\text{P}_2\text{O}_7)_2$ (**1**) and $\text{Cs}_2\text{Pd}_3(\text{As}_2\text{O}_7)_2$ (**2**)

Compound 1			
Cs(1)—O(3)	3.142(4) (2×)	Cs(1)—O(4)	3.270(4) (2×)
Cs(1)—O(6)	3.407(4) (2×)	Cs(1)—O(7)	3.192(4) (2×)
Cs(1)—O(8)	3.418(4) (2×)	Cs(2)—O(1)	3.091(4)
Cs(2)—O(2)	3.342(4) (2×)	Cs(2)—O(4)	3.671(4) (2×)
Cs(2)—O(5)	3.102(5)	Cs(2)—O(6)	3.691(4) (2×)
Cs(2)—O(7)	3.358(4) (2×)	Pd(1)—O(4)	1.999(4) (2×)
Pd(1)—O(8)	2.008(4) (2×)	Pd(2)—O(3)	2.002(4) (2×)
Pd(2)—O(6)	1.996(4) (2×)	Pd(3)—O(2)	2.011(4) (2×)
Pd(3)—O(7)	2.004(4) (2×)	P(1)—O(1)	1.610(2)
P(1)—O(2)	1.523(4)	P(1)—O(3)	1.524(4)
P(1)—O(4)	1.504(3)	P(2)—O(5)	1.613(3)
P(2)—O(6)	1.504(4)	P(2)—O(7)	1.518(4)
P(2)—O(8)	1.517(4)		
Compound 2			
Cs(1)—O(1)	3.006(4)	Cs(1)—O(2)	3.142(4)
Cs(1)—O(3)	3.465(4)	Cs(1)—O(4)	3.297(5)
Cs(1)—O(5)	3.259(6)	Cs(1)—O(5)	3.478(5)
Cs(1)—O(6)	3.023(4)	Cs(1)—O(6)	3.023(4)
Cs(1)—O(7)	3.183(4)	Pd(1)—O(1)	2.000(4) (2×)
Pd(1)—O(5)	1.988(5) (2×)	Pd(2)—O(6)	2.000(4) (2×)
Pd(2)—O(7)	2.032(4) (2×)	Pd(3)—O(3)	2.030(4) (4×)
Pd(4)—O(2)	2.024(4) (4×)	As(1)—O(1)	1.676(4)
As(1)—O(2)	1.678(4)	As(1)—O(3)	1.671(4)
As(1)—O(4)	1.757(4)	As(2)—O(4)	1.753(4)
As(2)—O(5)	1.667(4)	As(2)—O(6)	1.673(5)
As(2)—O(7)	1.675(5)		

$\text{Pd}^{\text{II}}\text{O}_4$ squares which are linked by P_2O_7 groups via corner-sharing to generate narrow channels along the a -axis containing 12-ring windows in which Cs^+ cations are located (Figure 1a). The 12-membered rings, which are formed by alternating PdO_4 squares and PO_4 tetrahedra, adopt a herringbone array. The two distinct Cs atoms, three Pd atoms, and the bridging oxygen atoms, O(1) and O(5), in two distinct P_2O_7 groups sit on mirror planes and all other oxygen atoms are at general positions. Thus, the diphosphate groups are in eclipsed conformation. As shown in Figure 1b, Pd(1) and Pd(2) are linked to three P_2O_7 groups, while Pd(3) is linked to two P_2O_7 groups. There is only one type of channel in which are found two columns of Cs(1) and Cs(2) atoms. The window of the channel, which approximates to $3.7 \text{ Å} \times 9.5 \text{ Å}$ by measuring the $\text{O}\cdots\text{O}$ distances, is so narrow that the movement of Cs^+ cations is unlikely. A limit of 3.7 Å was set for the Cs—O interactions, which gives the following

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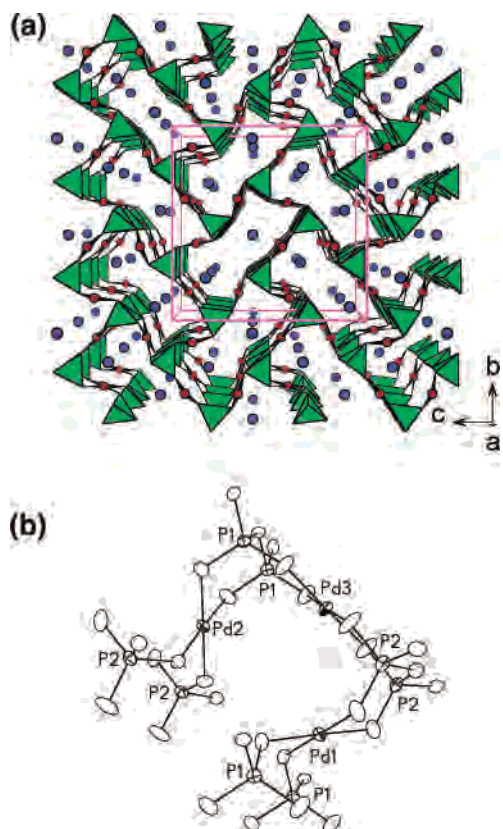


Figure 1. (a) Structure of **1** viewed along the *a* axis. The phosphate tetrahedra are shown in green. Red and blue circles are Pd and Cs atoms, respectively. (b) ORTEP plot of **1** showing the coordination environments of the Pd atoms viewed in a direction approximately parallel to the *a* axis. Thermal ellipsoids are shown at 50% probability.

coordinations: Cs(1), four-capped trigonal prism; Cs(2), two-capped square prism.

To the best of our knowledge, $\text{Cs}_2\text{Pd}_3(\text{As}_2\text{O}_7)_2$ is the first palladium arsenate reported. Its structure consists of palladium arsenate layers in the *ab*-plane with the interlayer space filled with Cs^+ cations, as illustrated in the perspective view parallel to the [100] direction (Figure 2a). There is only one crystallographically distinct layer within the repeat distance *c*. Adjacent layers are aligned such that 7-ring channels along the *c*-axis are formed. The nine-coordinate Cs^+ cations are located within the channels (Figure 2b). Within a layer there are PdO_4 squares and As_2O_7 groups fused together via corner-sharing. Each asymmetric unit contains one Cs atom at general position, four Pd atoms at special positions, and one As_2O_7 group at general position. The diarsenate group is in a staggered conformation. Pd(1) is linked to two As_2O_7 groups, whereas Pd(2), Pd(3), and Pd(4) are linked to four As_2O_7 groups. Adjacent layers are stacked such that strings of Pd atoms along *c*-axis are formed. As shown in Figure 3, Pd(1) O_4 squares show such stacking, at an uninteresting Pd \cdots Pd separation of 5.968 Å. More interesting are the other two Pd strings. The Pd(2) O_4 squares show an eclipsed stack with alternate short (2.871 Å) and long (3.097 Å) Pd \cdots Pd distances. Pd(3) O_4 and Pd(4) O_4 squares are also arranged in a stack, but staggered, with alternate short and long Pd \cdots Pd distances of 2.791 Å and 3.177 Å. The longer distances are the Pd \cdots Pd separations

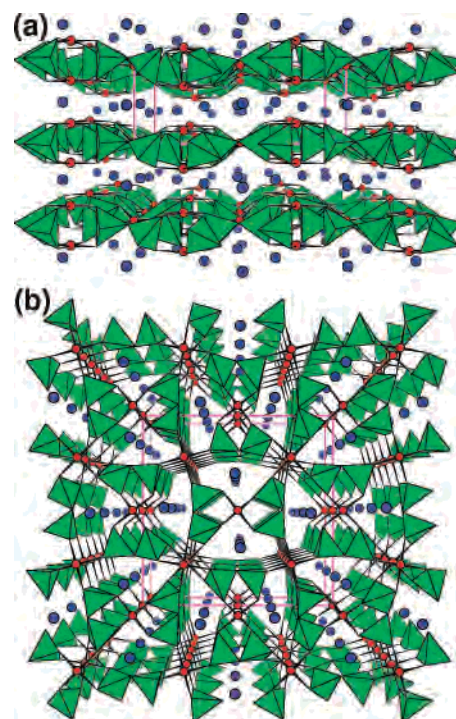


Figure 2. Structure of **2** viewed (a) along the *a* axis and (b) along the *c* axis. The arsenate tetrahedra are shown in green. Red and blue circles are Pd and Cs atoms, respectively.

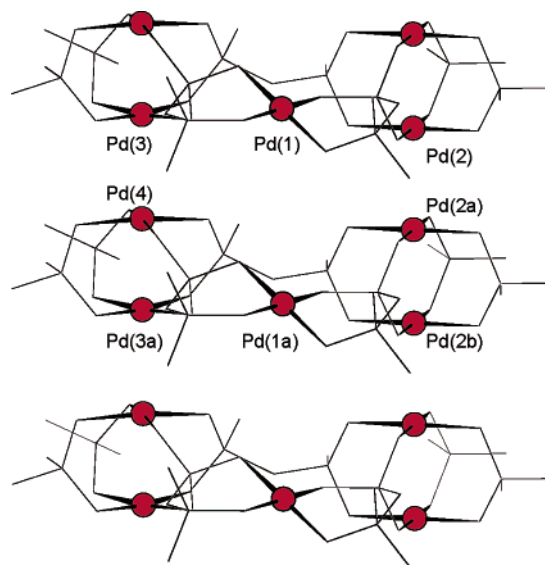


Figure 3. Strings of Pd atoms in **2**. For clarity the radii for As and O are set zero. Selected interatomic distances: Pd(2) \cdots Pd(2a) = 2.871(1) Å, Pd(2a) \cdots Pd(2b) = 3.097(1) Å, Pd(3) \cdots Pd(4) = 2.791(1) Å, Pd(4) \cdots Pd(3a) = 3.177(1) Å.

within a layer, while the shorter distances are between adjacent layers. The shortest Pd \cdots Pd distance is comparable to that (2.75 Å) in Pd metal. The Pd strings in **2** are reminiscent of the stacked columnar complexes typified by $\text{K}_2\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$.⁸ These square planar $[\text{Pt}(\text{CN})_4]^{2-}$ ions adopt a closely spaced parallel arrangement, allowing for considerable interaction among the d_z^2 orbitals of the Pt atoms. These orbitals are normally filled with electrons, so

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the compound is white and a nonconductor of electricity. Partial oxidation of $[\text{Pt}(\text{CN})_4]^{2-}$ by nitric acid, Cl_2 , H_2O_2 , or other reagents yields electrical conducting bronze-colored forms of the compound. However, partially oxidized palladium analogues have not been reported. The attempted preparations of partially oxidized compound **2** by Br_2 in methanol were not successful. The synthesis of a platinum analogue of **2** is therefore of great interest with respect to one-dimensional conductivity properties.

Phosphates of palladium are rare in the literature and only five compounds have been structurally characterized by X-ray diffraction methods. Most of them are either maroon or olive, except $\text{Na}_2\text{PdP}_2\text{O}_7$ which is yellow.^{9–12} The 3D framework of $\text{Pd}(\text{PO}_3)_2$ consists of tunnels which are formed by $(\text{PO}_3)_x$ chains cross-linked by PdO_4 squares.⁹ The structures of $\text{Li}_2\text{PdP}_2\text{O}_7$ and $\text{Na}_2\text{PdP}_2\text{O}_7$,^{10,11} which were determined by the Rietveld technique from X-ray powder diffraction data, can be described by alternate stacking of layers containing alkali metal cations and zigzag ribbons formed by PdO_4 squares and P_2O_7 groups. $\text{K}_2\text{PdP}_2\text{O}_7$ consists

of 2D layers formed of linked PdO_4 squares and P_2O_7 groups, between which are found the K^+ cations.¹² The structure of $\text{K}_2\text{PdP}_2\text{O}_7$ is considerably different from those of $\text{Li}_2\text{PdP}_2\text{O}_7$ and $\text{Na}_2\text{PdP}_2\text{O}_7$ despite the three having the same general formula. $\text{K}_{3.5}\text{Pd}_{2.25}(\text{P}_2\text{O}_7)_2$ crystallizes with tunnels of various sizes in which are found the K^+ cations.¹² We have synthesized a new palladium diphosphate with Cs^+ cation, $\text{Cs}_2\text{Pd}_3(\text{P}_2\text{O}_7)_2$. It adopts a 3D framework structure with one type of narrow channel where Cs^+ cations are located. Much to our surprise, the arsenate analogue with the same general formula has a 2D layer structure containing strings of Pd atoms. During the synthesis of **2** we noted that there are additional new compounds in the phase space. Compound **2** is the first member of this family. The diverse chemical compositions may provide rich opportunities in exploring new palladium arsenates with novel structures.

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Supporting Information Available: Crystallographic data in CIF format and X-ray powder patterns for both compounds (pdf). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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