Solid-State Architectures of Aggregates of the Cubic Cluster [Pd_6Cl_{12}] with Polynuclear Aromatic Hydrocarbons

Marilyn M. Olmstead,* Pin-pin Wei, and Alan L. Balch*[a]

Abstract: Deeply colored, air-stable molecular solids consisting of planar polynuclear aromatic hydrocarbon (PAH) molecules and cubic clusters of [Pd_6Cl_{12}] are readily formed from solutions of bis(benzonitrile)palladium(II) dichloride and the appropriate PAH in benzene. Three compounds, [Pd_6Cl_{12}] · 1.5 (naphthalene), [Pd_6Cl_{12}] · (1-methylanthracene), and [Pd_6Cl_{12}] · 0.5 (1,2:5,6-dibenzanthracene) · 0.5 (benzene), have been isolated in crystalline form, and the geometric structures of each of these three compounds have been determined by X-ray crystallography. The structure of the [Pd_6Cl_{12}] unit, which consists of an octahedral array of six palladium atoms that are surrounded by twelve equivalent chlorine atoms in edge-bridging sites, is invariant within this group of compounds. In each of the three new compounds described here, alternating molecules of [Pd_6Cl_{12}] and the PAH are organized into columnar structures so that flat surfaces of the cubic cluster and the PAH make contact. The separations of these organic and inorganic surfaces is about 3.3 Å, and no covalent bonding is present between the individual molecular components. In these columns each [Pd_6Cl_{12}] molecule is sandwiched between two PAH molecules and each PAH is sandwiched between two clusters. For [Pd_6Cl_{12}] · 0.5 (1,2:5,6-dibenzanthracene) · 0.5 (benzene), the PAH is sufficiently extended to span two columns. In each structure the columns are arranged in a side-by-side manner with small slip angles. Consequently, a common feature is the existence of extended layer of organic PAHs alternating with one of inorganic clusters.

Keywords: charge compounds · cluster compounds · crystal engineering · palladium · polynuclear aromatic hydrocarbons

Introduction

The study of formation and structures of complex solids through noncovalent interactions of two or more individual molecules is an aspect of supramolecular chemistry that is currently undergoing considerable development.[1–3] The identification of compatible molecular components that have specific proclivities to form ordered solids is a significant goal in this area. Situations in which components drawn from such disparate areas as inorganic and organic molecules, which are found to aggregate, are particularly interesting.[4] In that context, it is known that weak charge-transfer interactions can be observed when certain metal halides are exposed to aromatic hydrocarbons.[5–7] In some cases, these interactions lead to the formation of π complexes, in which covalent bonding occurs between the aromatic component and the metal as is the case, for example, in [(η^6-durene)$ZrCl_2$(μ-Cl)$_3$$ZrCl_3$][8] and [($\eta^6$-$C_6H_6$)$_2$Ga($GaCl_4$)].[9, 10] However, coordination of this sort is not required, and crystalline compounds such as $SbCl_3$ · 0.5 (naphthalene)[11] and Al_2Br_6 · (benzene)[12] lack any covalent bond between the constituent molecules.

Recently, this laboratory reported that a number of supramolecular aggregates [e.g., [Pd_6Cl_{12}] · (mesitylene) and [Pd_6Cl_{12}] · (durene)] of the cubic cluster [Pd_6Cl_{12}] with methylated benzenes can be isolated in crystalline form.[13] These compounds consist of individual molecules of [Pd_6Cl_{12}] with the aromatic molecule arranged in close, face-to-face proximity. The [Pd_6Cl_{12}] cluster itself is soluble in aromatic solvents. Spectroscopic studies on solutions of [Pd_6Cl_{12}] in various methylated benzenes (e.g., mesitylene, xylene, toluene) are consistent with a charge-transfer interaction between the aromatic donors and the palladium cluster. A ternary compound, which is comprised of molecules of [Pd_6Cl_{12}], benzene, and C_{60}, has also been isolated form solutions of the fullerene and bis(benzonitrile)palladium(II) dichloride.[13]

Here we describe the formation and structures of crystalline compounds that involve co-crystallization of [Pd_6Cl_{12}] with polynuclear aromatic hydrocarbons (PAHs). The ionization potentials (IP) of PAHs such as naphthalene (IP 8.12 eV) and anthracene (IP 7.43 eV) fall within or below the range of

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Table 1. Selected interatomic distances and angles in $[Pd_6Cl_{12}]$ clusters.

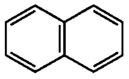
	$[Pd_6Cl_{12}]\cdot 1.5$ (naphthalene)	$[Pd_6Cl_{12}]\cdot$ (1-methylanthracene)	$[Pd_6Cl_{12}]\cdot 0.5$(1,2:5,6-dibenanthracene $\cdot$ 0.5(benzene)
Distance [Å]			
Pd–Cl (ave)	2.312 (5)	2.311(8)	2.303(5)
(range)	2.300(5) – 2.342(5)	2.327(7) – 2.302(7)	2.299(4) – 2.318(5)
Pd ··· Pd (ave)	4.698(14)	4.68(2)	4.68(2)
face-to-face (range)	4.687(2) – 4.714(2)	4.670(2) – 4.711(2)	4.664(1) – 4.701(1)
Angles [°]			
Cl–Pd–Cl (ave)	90.0(3)	90.0(5)	90.0(4)
cis (range)	89.2(2) – 90.5(2)	89.3(3) – 90.9(3)	89.4(2) – 90.5(2)
Cl–Pd–Cl (ave)	178.1(3)	178.4(4)	178.4(5)
trans (range)	177.2(2) – 178.5(2)	177.7(3) – 178.8(3)	177.7(2) – 179.4(2)
Pd–Cl–Pd (ave)	91.9(3)	91.6(6)	91.6(4)
(range)	91.4(2) – 92.3(2)	90.9(3) – 92.5(3)	91.1(2) – 92.3(2)

ionization potentials for the aromatic compounds such as *p*-xylene (IP 8.44 eV) and durene (IP 8.05 eV), which are known to form crystalline adducts with $[Pd_6Cl_{12}]$. Consequently, these PAHs should be suitable donors to interact effectively with $[Pd_6Cl_{12}]$.

In the context of this work, it is important to note that palladium(II) chloride is known to form several polymorphs. The α-form consists of infinite, linear chains in which each palladium is coordinated by four chlorine atoms in a square, while each chlorine atom bridges two palladium atoms.[14] The β-form consists of discrete molecules of $[Pd_6Cl_{12}]$ that have an octahedral array of metal atoms.[13, 15, 16] Each metal atom is again surrounded by four equivalent chlorine atoms that bridge edges of the octahedron. The β-form can be prepared in several ways. Treatment of $[Pd_3(acetate)_6]$ with carbon monoxide in glacial acetic acid that contains some perchloric acid yields polycrystalline $[Pd_6Cl_{12}]$.[17] Larger, single crystals of $[Pd_6Cl_{12}]$ have been prepared by gradual precipitation of $[Pd_6Cl_{12}]$ from a solution of bis(benzonitrile)palladium(II) dichloride in benzene/chloroform[13] or by treatment of $[Pd_2(\mu\text{-}Cl)_2Cl_2(CO)_2]$ with thionyl chloride.[15] Commercial $PdCl_2$ is not soluble in aromatic solvents and has been reported to consist of another polymorph of currently unknown structure.[18] The β-form of $[Pd_6Cl_{12}]$ crystallizes in the space group $R\bar{3}$, which is the space group that is predicted for the packing of cubic molecules with a simple octapole model.[19] Other cubic molecules including cubane, C_8H_8,[20] and octa-(methylsilsesquioxane), $(CH_3SiO)_8$,[21] crystallize in this same space group.

Results

Bis(benzonitrile)palladium(II) dichloride is a labile complex that readily loses benzonitrile to form complexes with coordinated $PdCl_2$ groups or $[Pd_6Cl_{12}]$, in the absence of strong ligating molecules.[22, 23] Upon standing, yellow solutions of bis(benzonitrile)palladium(II) dichloride and the appropriate polynuclear aromatic hydrocarbon (PAH), naphthalene (**1**), 1-methylanthracene (**2**), or 1,2:5,6-dibenzanthracene (**3**), in benzene gradually produce deep red crystals of the new compounds: $[Pd_6Cl_{12}]\cdot 1.5$(naphthalene), $[Pd_6Cl_{12}]\cdot$(1-methylanthracene), and $[Pd_6Cl_{12}]\cdot 0.5$(1,2:5,6-dibenzanthracene) $\cdot$ 0.5 (benzene), respectively. Molecules **1** and **2** were chosen for study as representative PAHs. Other arenes such as anthracene itself and triphenylene also produced crystalline adducts, but these suffered from severe disorder. The extended hydrocarbon **3** was chosen as the smallest PAH that could conceivably span a pair of $[Pd_6Cl_{12}]$ clusters. The structures of each of these compounds have been determined by single-crystal X-ray diffraction. Relevant data from these crystal structures are summarized in Table 1, which contains data on the $[Pd_6Cl_{12}]$ clusters, and Table 2, which contains crystallographic data. Views of the individual structures are presented in Figures 1 – 7.



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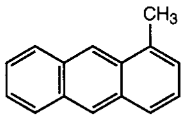

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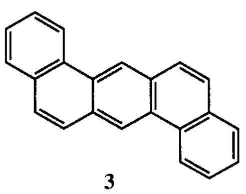

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$[Pd_6Cl_{12}]\cdot 1.5$(naphthalene): Figure 1 shows a view of the molecules present in the solid and the numbering scheme employed here. Figure 2 shows how these components are

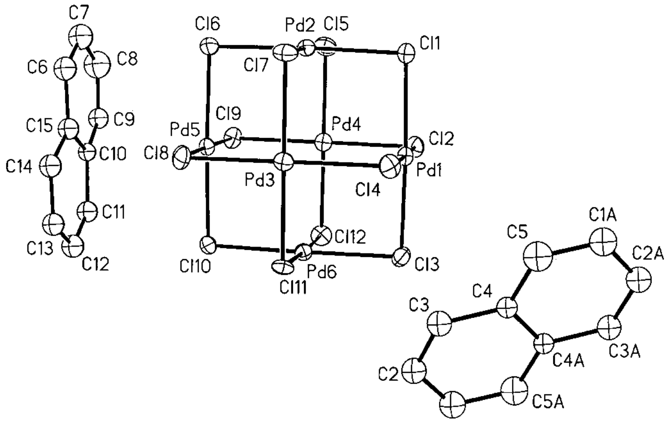

Figure 1. A view of the components in the structure of $[Pd_6Cl_{12}]\cdot 1.5$(naphthalene) showing the atom-numbering scheme and 50% probability thermal elipsoids.

Table 2. Crystallographic data for the [Pd_6Cl_{12}] clusters.

	[Pd_6Cl_{12}]·1.5 (naphthalene)	[Pd_6Cl_{12}]· (1-methylanthracene)	[Pd_6Cl_{12}]·0.5(1,2:5,6-dibenanthracene·0.5(benzene)
formula	$C_{15}H_{12}Cl_{12}Pd_6$	$C_{15}H_{12}Cl_{12}Pd_6$	$C_{14}H_{10}Cl_{12}Pd_6$
M_w	1256.04	1256.05	1242.02
a [Å]	8.006(3)	8.142(4)	8.122(3)
b [Å]	11.384(4)	8.163(4)	11.304(3)
c [Å]	16.031(4)	11.488(4)	15.270(4)
α [°]	97.80(3)	99.22(3)	82.21(2)
β [°]	102.65(3)	100.30(3)	79.58(3)
γ [°]	102.38(3)	110.15(3)	77.76(3)
V [$Å^3$]	1366.6(8)	684.6(5)	1340.6(7)
Z	2	1	2
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
T [K]	140(2)	140(2)	140(2)
λ [Å]	0.71073 ($Mo_{K\alpha}$)	0.71073 ($Mo_{K\alpha}$)	0.71073 ($Mo_{K\alpha}$)
ρcalcd [g cm^{-3}]	3.052	3.047	3.077
μ [mm^{-1}]	5.045	5.036	5.142
max/min transmission	0.85/0.77	0.60/0.38	0.99/0.50
$R1$ (observed data)[a]	0.059	0.130	0.066
$wR2$ (all data, F^2 refinement)[b]	0.116	0.60	0.188

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, observed data ($>4\sigma I_0$). [b] $wR2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$, all data

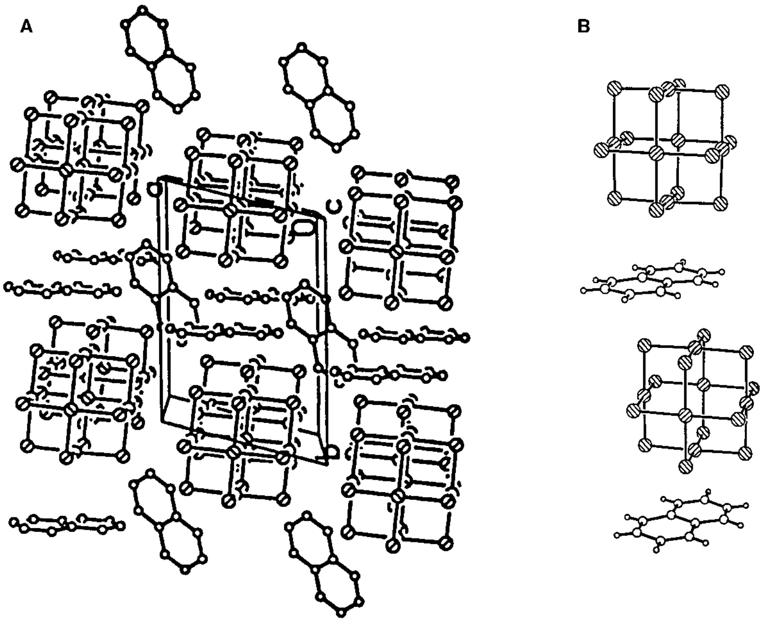

Figure 2. The molecular packing within [Pd_6Cl_{12}]·1.5(naphthalene). **A** shows the entire structure, while **B** emphasizes the chains of alternating [Pd_6Cl_{12}] and naphthalene molecules.

organized within the crystalline solid. The asymmetric unit consists of a [Pd_6Cl_{12}] cluster with no crystallographically imposed symmetry, a naphthalene molecule (naphthalene-1) with no crystallographically imposed symmetry, and one-half of a naphthalene molecule (naphthalene-2), which is positioned on a center of symmetry. There are no unusual features in the molecular geometry of any of the three components of this solid.

The molecular packing reveals columns of alternating [Pd_6Cl_{12}] clusters and naphthalene-1 molecules as seen in Figure 2. Within these columns there is close face-to-face contact between the cubic clusters and the planar aromatic molecules. These contacts result in an asymmetric sandwiching of each [Pd_6Cl_{12}] cluster between a pair of naphthalene-1 molecules and a corresponding sandwich arrangement of two [Pd_6Cl_{12}] clusters about each naphthalene-1 molecule. In both cases the $PdCl_4$ plane and the plane of the hydrocarbon are nearly parallel. The angle between the Pd1-Cl1-Cl2-Cl3-Cl4 plane and that of naphthalene-1 is 2.0°, while the angle between the Pd5-Cl6-Cl8-Cl9-Cl10 plane and that of naphthalene-1 is 2.2°. Pd5 is situated near the center of the naphthalene-1 molecule, while Pd1 is off on an edge. The closest Pd–C distances for Pd5 are: Pd5···C15, 3.397 Å; Pd5···C14, 3.641 Å. The shortest contacts between Pd1 and adjacent carbon atoms are: Pd1···C14, 3.273 Å; Pd1···C13, 3.313 Å; Pd1···C15, 3.623 Å. Within the group of chlorine atoms bonded to Pd5, the closest contacts between these and naphthalene carbon atoms is 3.354 Å between Cl10 and C12. The closest Cl···C distances involving the chlorine atoms bonded to Pd1 are 3.345 Å between Cl2 and C10 and 3.355 Å between Cl2 and C11.

The naphthalene-2 molecules do not participate in this columnar stacking. Indeed, they do not closely approach the [Pd_6Cl_{12}] cluster. The closest contact involves Cl4 and C3, which are 3.590 Å apart.

Individual [Pd_6Cl_{12}] clusters within the stacks are arranged so that they make face-to-face contact with other clusters. However, the distances involved in these contacts are all longer than those seen in related compounds and in pristine [Pd_6Cl_{12}] itself.[13] The closest intermolecular contact (3.404 Å) involves Pd3 ··· Pd3′, while the closest Pd ··· Cl contact is the 3.678 Å separation between Pd4 and Cl1′.

$[Pd_6Cl_{12}]$ · (1-methylanthracene): Figure 3 shows a view of the structure. The asymmetric unit consists of half of the $[Pd_6Cl_{12}]$ cluster and half of the 1-methylanthracene molecule. Both the $[Pd_6Cl_{12}]$ cluster and the 1-methylanthracene molecule are located on crystallographic centers of symmetry. Consequently, there is disorder in the position of the methyl group within the 1-methylanthracene molecule. The two symmetry related sites have fractional occupancies of 0.5. The bond lengths and angles within the $[Pd_6Cl_{12}]$ cluster show no unusual features. Because of apparent twinning (see Experimental Section) the geometry of the 1-methylanthracene was constrained during refinement. The plane of each 1-methylanthracene molecule is nearly parallel to the surface of the $[Pd_6Cl_{12}]$ cluster that is defined by Pd-Cl1-Cl2-Cl3-Cl4. The angle between these two planes is only 2.6°. The palladium atom closest to the 1-methylanthracene molecule is 3.342 Å from C2, 3.392 Å from C3, and 3.612 Å from C1A. The closest carbon – chlorine contact between the $[Pd_6Cl_{12}]$/1-methylanthracene pair is 3.479 Å and involves Cl3 and C2.

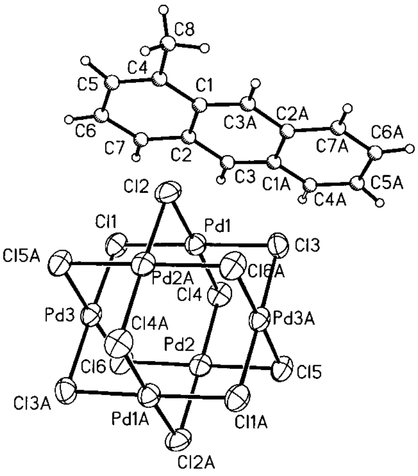

Figure 3. A view of the components in the structure of $[Pd_6Cl_{12}]$ · (1-methylanthracene). Only one postiton of the disordered methyl group is shown. The other resides on C4A. Thermal elipsoids are shown at the 50 % probability level.

The molecular organization of the solid, as shown in Figure 4, is dominated by columnar packing of alternating $[Pd_6Cl_{12}]$ and 1-methylanthracene molecules into an arrangement in which each $[Pd_6Cl_{12}]$ unit is sandwiched between a pair of 1-methylanthracene molecules. Similarly, each 1-methylanthracene unit is sandwiched between a pair of $[Pd_6Cl_{12}]$ clusters. The columns of alternating $[Pd_6Cl_{12}]$ clusters and 1-methylanthracene molecules interact with one another through parallel, face-to-face contacts between clusters. The closest nonbonded Pd ··· Cl contacts involve faces that contain Pd2 and occur in pairs that are similar to those seen in $[Pd_6Cl_{12}]$ itself. These contacts are seen in Figure 4. The Pd2 ··· Cl6′ separation is 3.211 Å. Similar pairwise, face-to-face contacts involve the faces that contain Pd3. In these cases the nonbonded Pd3 ··· Cl1″ contact is 3.287 Å. These pairwise Pd ··· Cl contacts produce layers of $[Pd_6Cl_{12}]$ clusters which run in a stepwise pattern throughout the structure. Similar stair-step patterns of clusters are seen in the structures of pristine $[Pd_6Cl_{12}]$, $[Pd_6Cl_{12}]$ · (mesitylene), and $[Pd_6Cl_{12}]$ · (durene).

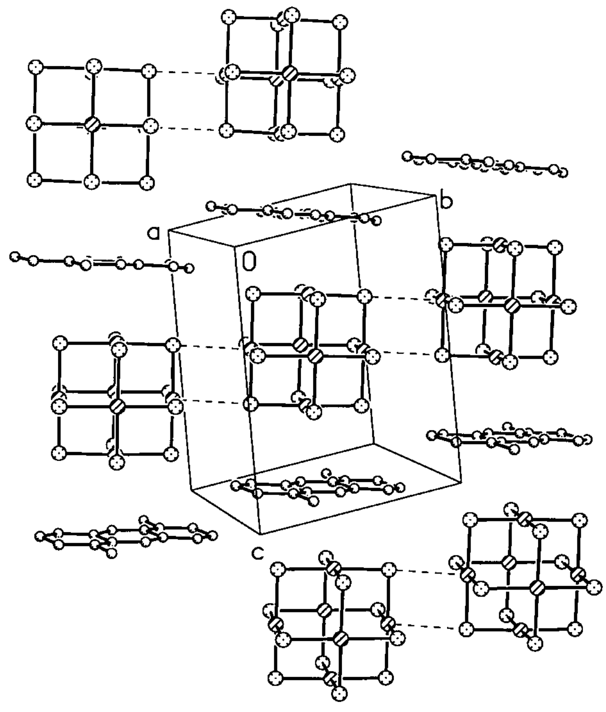

Figure 4. The molecular packing within $[Pd_6Cl_{12}]$ · (1-methylanthracene). Both positions for the disordered methyl carbon atoms are shown, while for any one molecule only one of these positions is occupied.

$[Pd_6Cl_{12}]$ · 0.5 (1,2:5,6-dibenzanthracene) · 0.5 (benzene): Figure 5 shows the relative orientations of the three molecular components and the numbering scheme employed here. The asymmetric unit consists of one molecule of $[Pd_6Cl_{12}]$ with no crystallographically imposed symmetry, one-half of a molecule of 1,2:5,6-dibenzanthracene, with the other half gener-

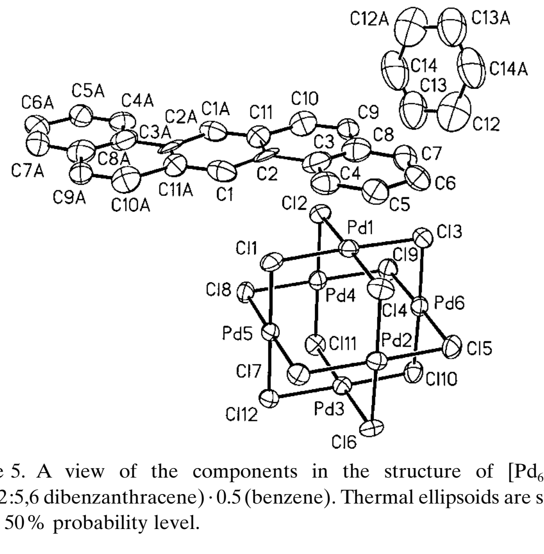

Figure 5. A view of the components in the structure of $[Pd_6Cl_{12}]$ · 0.5 (1,2:5,6 dibenzanthracene) · 0.5 (benzene). Thermal ellipsoids are shown at the 50 % probability level.

ated by an inversion center within the molecule, and one-half of a benzene molecule, with the other half generated by another center of symmetry.

Figure 6 shows the extended interactions that are present in the solid. As with the other two structures considered here, the [Pd_6Cl_{12}] clusters and the 1,2:5,6-dibenzanthracene molecules are organized into columns. However, in this case the 1,2:5,6-dibenzanthracene molecules span two cluster units, and there are four cluster molecules that make face-to-face contact with each 1,2:5,6-dibenzanthracene molecule.

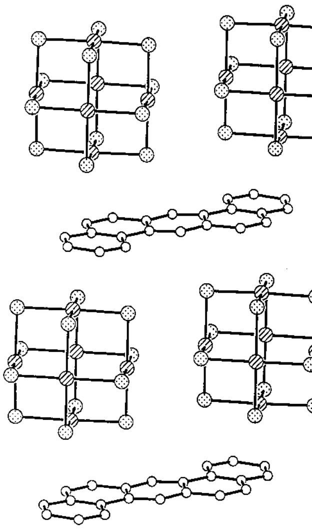

Figure 6. The molecular packing within [Pd_6Cl_{12}]·0.5(1,2:5,6 dibenzanthracene)·0.5(benzene) that shows the columns of alternating [Pd_6Cl_{12}] and (1,2:5,6 dibenzanthracene) molecules. The postions of the benzene molecules are not shown.

Figure 7 (Part **B**) shows a view of [Pd_6Cl_{12}]·0.5(1,2:5,6-dibenzanthracene)·0.5(benzene) perpendicular to the plane of the PAH. The two cluster/PAH interactions are slightly different. The closest Pd···C distances are: Pd1–C8 3.319 Å, Pd1–C9 3.411 Å, Pd1–C3 3.669 Å, Pd3C–C8A 3.361 Å, Pd3C–C7A 3.385 Å, and Pd3C–C9A, 3.641 Å. The shortest chlorine to carbon contacts for each cluster are 3.266 Å between Cl1 and C2 and 3.250 Å between Cl6C and C6A. Symmetry requires that the adjacent $PdCl_4$ faces of the cubic cluster and the plane of the 1,2:5,6-dibenzanthracene are parallel.

Within the 1,2:5,6-dibenzanthracene/2[Pd_6Cl_{12}] unit shown in Figure 7, the two clusters also make face-to-face contact and are held close to one another. The nonbonded Pd···Cl separation between Pd5 and Cl8C is 3.124 Å, and there are two such contacts between the two clusters in this array. This Pd···Cl distance is shorter than the corresponding distance (3.364 Å) in pristine [Pd_6Cl_{12}] and shorter than the shortest such contact [3.243 Å in [Pd_6Cl_{12}]·(mesitylene)] seen in any of the other adducts of this type.

There also are Pd···Cl contacts between clusters in different columns. The cluster face containing Pd2 makes contact with an adjacent face of another cluster that contains Pd4. The closest nonbonded contacts involve Pd2···Cl2′ at 3.295 Å and Pd4′···Cl6 at 3.301 Å. Likewise, the cluster face that contains Pd6 makes face-to-face contact with another cluster through a face containing Pd6′. However, the pairwise Pd6···Cl5′ distance (3.651 Å) between these faces is considerably longer than the other such contacts in this compound, and the Pd6···Pd6′ contact (3.472 Å) is somewhat shorter.

The benzene molecules in [Pd_6Cl_{12}]·0.5(1,2:5,6-dibenzanthracene)·0.5(benzene) do not interact strongly with the [Pd_6Cl_{12}] clusters. The closest contact between these entities is 3.932 Å, which involves Cl10 and C14.

Figure 7 also compares the inter-cluster separations of a single stair-stepped layer of cluster molecules in [Pd_6Cl_{12}] (**A**) and in the structure of [Pd_6Cl_{12}] with co-crystallized 1,2:5,6-dibenzanthracene and benzene (**B**). A regular separation of cluster faces is seen in all three directions in [Pd_6Cl_{12}] itself, but in the co-crystal the pattern is slipped to allow the PAH to span two cluster faces and to fit the inter-cluster, diagonally placed benzene molecule.

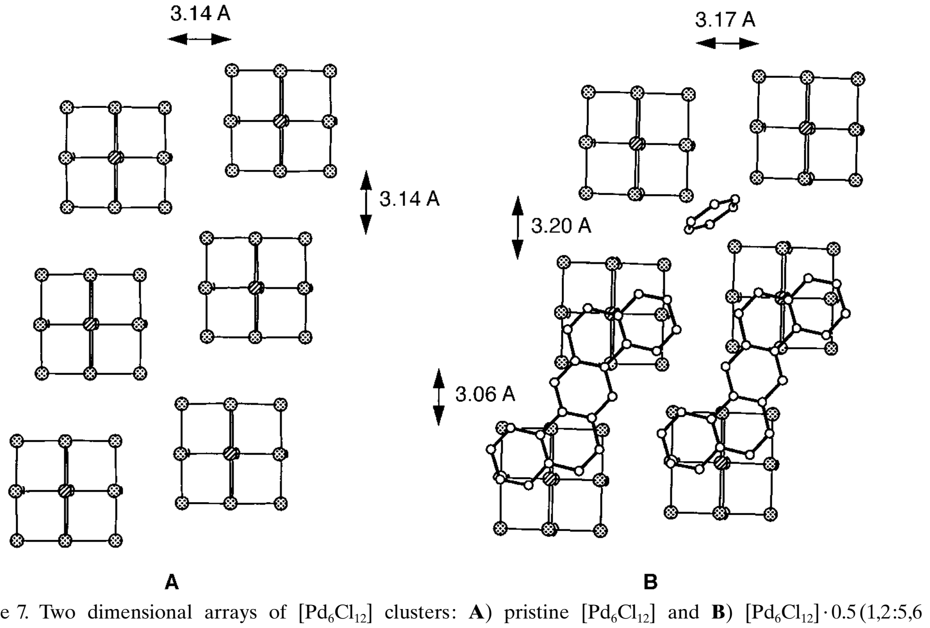

Figure 7. Two dimensional arrays of [Pd_6Cl_{12}] clusters: **A**) pristine [Pd_6Cl_{12}] and **B**) [Pd_6Cl_{12}]·0.5(1,2:5,6 dibenzanthracene)·0.5(benzene) which show the differences in cluster separations and the location of the aromatic molecules.

Discussion

The results described here demonstrate that [Pd_6Cl_{12}] clusters are formed from condensation of bis(benzonitrile)palladium(II) dichloride in the presence of PAHs and that co-crystalline solids result. Within these solids, the individual molecular components maintain their intrinsic geometric features without distortion. The data in Table 1 show that the geometry of the [Pd_6Cl_{12}] cluster is invariant in these three compounds.

As seen from the data in reference [13] and this article, the structures of the solids that result from co-crystallization of [Pd$_6$Cl$_{12}$] with molecules with conjugated π-systems conform to the following generalizations.

1) The planar π-conjugated molecules are sandwiched between [Pd$_6$Cl$_{12}$] clusters and make face-to-face contact with these clusters on both sides.
2) In cases where two different π-conjugated molecules are present within the solid, the molecule with the lower ionization potential preferentially makes face-to-face contact with the [Pd$_6$Cl$_{12}$] cluster.
3) Individual [Pd$_6$Cl$_{12}$] clusters interact with pairs of planar π-conjugated molecules in a face-to-face arrangement on two opposite faces of the cluster.
4) [Pd$_6$Cl$_{12}$] clusters interact with one another through nearly parallel, face-to-face contacts with the closest contacts generally, but not exclusively, between a palladium atom of one cluster and a chlorine atom of another.

All of the three compounds reported here follow this set of precepts, and all compounds that contain three components, [Pd$_6$Cl$_{12}$] · 0.5 (1,2:5,6-dibenzanthracene) · 0.5 (benzene), [Pd$_6$Cl$_{12}$] · (CH$_3$)$_3$C$_6$H$_3$ · 0.5 C$_6$H$_6$, [Pd$_6$Cl$_{12}$] · 0.5 C$_{60}$ · 1.5 C$_6$H$_6$, follow statement 2. However, [Pd$_6$Cl$_{12}$] · 1.5 (hexamethylbenzene) deviates from statement 3. In this compound there are three hexamethylbenzene molecules that make contact with any one [Pd$_6$Cl$_{12}$] cluster, and those contacts involve mutually adjacent but orthogonal faces of the cluster.[13]

Although palladium chloride exists in three polymorphic forms, only the [Pd$_6$Cl$_{12}$] clusters found in the β-form are produced in the reactions that occur when solutions of bis(benzonitrile)palladium(II) dichloride and aromatic hydrocarbons are allowed to stand. The α-form of palladium chloride also has neutral, planar PdCl$_4$ faces, and it would seem reasonable to expect that the linear chains of the α-form might also be found to interact with aromatic hydrocarbons. So far that has not been observed in these sorts of solids.

Extrapolation of the structural features present in [Pd$_6$Cl$_{12}$] · 0.5 (1,2:5,6-dibenzanthracene) · 0.5 (benzene) leads to consideration of larger PAHs and of graphite itself. Palladium(II) chloride is known to intercalate into graphite, and the available data indicate that it is the α-form that is involved in the intercalation.[24] The reported 9.87 Å spacing between the graphitic layers is too short to accommodate the [Pd$_6$Cl$_{12}$] clusters, which would require a separation of 11.2 Å based on the distance between aromatic hydrocarbons in the structure of [Pd$_6$Cl$_{12}$] · 0.5 (1,2:5,6-dibenzanthracene) · 0.5 (benzene). However, the chains of palladium(II) chloride in the intercalated materials are reported to be inclined at an angle of 59° with respect to the plane of the graphite layers. In view of the face-to-face orientations of [Pd$_6$Cl$_{12}$] clusters and hydrocarbons seen in the present work, the difference in orientation in the intercalated material is somewhat surprising. Additionally, the question arises of whether aromatic hydrocarbons can be intercalated into α-palladium(II) chloride.

Experimental Section

Preparation of compounds: Bis(benzonitrile)palladium(II) dichloride was prepared as described in the literature.[25]

[Pd$_6$Cl$_{12}$] · 1.5 (naphthalene): A solution of bis(benzonitrile)palladium(II) dichloride (11.2 mg, 0.029 mmol) and naphthalene (0.196 mg, 1.53 mmol) in benzene (1 mL) was filtered, and the filtrate placed in a glass tube. The color of the solution was dark red. The tube was capped and set aside. Dark red crystals formed within 24 h. After 32 days, the crystals were harvested by cracking the tube and collecting the solid by filtration followed by rapid washing with benzene: yield 2.2 mg, 39 %.

[Pd$_6$Cl$_{12}$] · (1-methylanthracene): A solution of bis(benzonitrile)palladium(II) dichloride (2.0 mg, 0.0052 mmol) and 1-methylanthracene (95 mg, 0.49 mmol) in benzene (1 mL) was filtered, and the filtrate was placed in a glass tube. The color of the solution was yellow-green. The tube was capped and set aside for one week. Dark red crystals formed. The crystals were harvested by cracking the tube and collecting the solid by filtration followed by rapid washing with benzene: yield 0.1 mg, 9 %.

[Pd$_6$Cl$_{12}$] · 0.5 (1,2:5,6-dibenzanthracene) · 0.5 (benzene): A solution of bis(benzonitrile)palladium(II) dichloride (2.0 mg, 0.0052 mmol) and of 1,2:5,6-dibenzanthracene (7.0 mg, 0.025 mmol) in benzene (1 mL) was filtered, and the filtrate placed in a glass tube. The color of the solution was orange. The tube was capped. After 24 h, tiny crystals had formed. Dark red crystals were harvested after 70 days by opening the tube and collecting the solid by filtration followed by rapid washing with benzene: yield 0.2 mg, 20 %.

X-ray crystallography: The crystals were removed from the glass tubes together with a small amount of mother liquor and immediately coated with a hydrocarbon oil on the microscope slide.[26] Suitable crystals were mounted on glass fibers with silicone grease and placed in the cold stream of a Siemens R3m/V diffractometer equipped with an Enraf-Nonius low-temperature apparatus. The diffractometer was equipped with a sealed Mo tube that operated at 2 kW and a graphite monochromator. All the data sets were collected at 140 K. Only random fluctuations of less than 2 % were observed in the check reflections for all data sets. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[27] The structures were solved by Patterson or direct methods, and refined against all data (based on F^2) by use of the SHELXTL software, version 5. An absorption correction was applied to the structures with the program XABS2 which calculates 24 coefficients from a least-squares fit of [$1/A$ vs. $\sin^2(q)$] to a cubic equation in $\sin^2(q)$ by minimization of F_o^2 and F_c^2 differences.[28] Hydrogen atoms were added geometrically and refined with a riding model. All non-hydrogen atoms were refined with anisotropic thermal parameters.

For [Pd$_6$Cl$_{12}$] · (1-methylanthracene) twinning was a problem in all crystals examined. A several percent reduction in R values was realized by application of the twin law (0 1 0 1 0 0 0 0 1). This twinning can be understood by the near equality of the a and b axes, and the crystal growth pattern which yielded plates. The twin parameter refined to 0.206(5). Carbon atoms were refined isotropically owing to the problem with twinning. In addition, the ring system of 1-methylanthracene was restrained to be flat and C–C bond lengths were restrained to be equal. Disorder was also present as a reuslt of the packing of the 1-methylanthracene on a center of symmetry; this required that the methyl group and a hydrogen share a common site with 50 % occupancy of each component.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-113634, CCDC-113635, and CCDC-113636. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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