Supramolecular Aggregation of Pd_6Cl_{12}, a Cluster of Comparable Size to a Fullerene, with Aromatic Donors and with C_{60}

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Abstract: Molecular solids comprised of octahedra, hexagonal plates, and truncated icosahedra result from the cocrystallization of Pd_6Cl_{12}, benzene and its methylated derivatives, and C_{60}. Solutions of bis(benzonitrile)palladium(II) dichloride in benzene deposit deep red crystals of solvate-free Pd_6Cl_{12}, **1**, while solutions of bis(benzonitrile)palladium(II) dichloride in the following solvents or solutions produce binary or ternary compounds as follows: from mesitylene, $Pd_6Cl_{12}\cdot(CH_3)_3C_6H_3$ (**2**); from mesitylene/benzene, $Pd_6Cl_{12}\cdot(CH_3)_3C_6H_3\cdot0.5C_6H_6$ (**3**); from durene/benzene, $Pd_6Cl_{12}\cdot(CH_3)_4C_6H_2$ (**4**); from benzene/hexamethylbenzene, $Pd_6Cl_{12}\cdot1.5(CH_3)_6C_6$ (**5**); from benzene/biphenyl, $Pd_6Cl_{12}\cdot(C_6H_5)_2$ (**6**); and from benzene/fullerene C_{60}, $Pd_6Cl_{12}\cdot0.5C_{60}\cdot1.5C_6H_6$ (**7**). The geometric structures of each of these seven compounds have been determined by X-ray crystallography, and the electronic structure of Pd_6Cl_{12} has been probed with SCF−Xα−SW calculations. In each crystalline compound the structure of the Pd_6Cl_{12} unit is virtually invariant. It consists of an octahedral array of six palladium atoms that are surrounded by twelve equivalent chlorine atoms in edge-bridging sites. The long face-to-face Pd···Pd separations (4.675 Å in **1**) indicate that there is no direct Pd−Pd bonding in the cluster. In **1** these octahedra interact with one another through pairwise Pd···Cl contacts. In **2**, **3**, **4**, and **6**, layer-like structures are found in which each Pd_6Cl_{12} cluster makes face-to-face contact with an arene moiety on opposite $PdCl_4$ faces and each arene makes contact with two Pd_6Cl_{12} clusters. In these four compounds, the clusters also make contact with each other through pairwise Pd···Cl contacts that are like those found in **1**. The structure of $Pd_6Cl_{12}\cdot1.5(CH_3)_6C_6$ (**5**) is unique in that three hexamethylbenzene molecules make face-to-face contact with orthogonal faces of the Pd_6Cl_{12} cluster and the cluster−cluster separations are larger than those in **1**−**4** and **6**. The structure of $Pd_6Cl_{12}\cdot0.5C_{60}\cdot1.5C_6H_6$ (**7**) consists of a complex array of molecular components with face-to-face contacts between the benzene molecules and both C_{60} and Pd_6Cl_{12}. Pd_6Cl_{12} itself dissolves in aromatic solvents. The electronic spectra of the resulting solutions show variations that are indicative of a degree of charge transfer between the Pd_6Cl_{12} cluster as an electron acceptor and the arene as an electron donor.

Introduction

Considerable recent attention has been given to aspects of supramolecular chemistry[1] that lead to the formation of organized arrays of numbers of different molecules within a single crystal. Identification of the specific factors that can orient one molecule with respect to another may eventually lead to the preparation of crystals by design—i.e. crystal engineering.[2] However, for the present it is necessary to uncover the range of specific intermolecular interactions that can be expected to contribute to crystal organization. For crystals comprised of wholly organic molecules, considerable progress has been made toward identifying specific interactions that now range from an array of different types of hydrogen bonds[3] through the iodo−nitro interaction and halogen···halogen interactions. Examples of the use of many of these interactions to obtain new organic phases in which two or more molecular components are combined are now known. In inorganic chemistry labile coordination to metal ions has facilitated the preparation of an array of complex networked and layered systems.[4] Inorganic solids with network structures that are able to encapsulate small molecules have been designed.[5] Less attention has been given to the formation of crystalline compounds that consist of components drawn from both the inorganic and organic realms without the formation of classical coordination bonding between the components. However, in this area charge transfer interactions are a likely source of energetic stabilization. A number of examples of charge transfer complexes of aromatic hydrocarbons with simple inorganic compounds such as osmium(VIII) tetroxide,[6] titanium(IV) tetrachloride,[7] and tin(IV) tetrachloride[8] have been characterized spectroscopically, but these complexes have resisted attempts to crystallize them. This article is concerned with crystal organization in a range of new solids that consist of combinations of an inorganic halide cluster, Pd_6Cl_{12}, with an array of aromatic hydrocarbons.

Several polymorphic forms of $PdCl_2$ are known. The α-form consists of infinite, linear chains of $PdCl_2$ units in which each palladium atom is coordinated by four chlorine atoms and each chlorine atom is doubly bridging.[9] The β-form,[10] which is isomorphic with the crystallographically characterized β-$PtCl_2$,[11]

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Table 1. Comparative Distances (Å) for Compounds **1-7**

	Pd_6Cl_{12} (**1**)	$Pd_6Cl_{12}\cdot(CH_3)_3C_6H_3$ (**2**)	$Pd_6Cl_{12}\cdot(CH_3)_3C_6H_3\cdot0.5C_6H_6$ (**3**)	$Pd_6Cl_{12}\cdot(CH_3)_4C_6H_2$ (**4**)	$Pd_6Cl_{12}\cdot1.5(CH_3)_6C_6$ (**5**)	$Pd_6Cl_{12}\cdot C_{12}H_{10}$ (**6**)	$Pd_6Cl_{12}\cdot0.5C_{60}\cdot1.5C_6H_6$ (**7**)
Pd−Cl (ave)[a]	2.307(3)	2.308(4)	2.308(5)	2.310(5)	2.307(2)	2.305(3)	2.312(6)
Pd···Pd (bridged)[a]	3.306(23)	3.310(12)	3.313(7)	3.315(17)	3.313(8)	2.309(6)	3.311(18)
Pd···Pd (face to face)[b]	4.675(2)	4.682(26)	4.685(21)	4.688(27)	4.685(2)	4.679(13)	4.683(13)
Pd···Pd (intermolecular)	3.714(2)	3.598(2) 3.836(2)	3.701(2)	3.519(2)	5.534(2)	3.308(2) 3.520(2)	3.404(5)
Pd···Cl (intermolecular)	3.364(3)	3.290(2) 3.243(3) 3.249(3)	3.278(2) 3.298(2) 3.342(3) 3.343(3)	3.260(2) 3.362(2)	4.053(2)	3.488(2) 3.245(2)	3.465(7) 3.651(7) 3.647(7)
Pd···C−C (centroid)		3.240 3.334	3.219 3.407	3.264	3.346	3.330	3.254 3.376
$PdCl_4$(plane)···C_6(plane)		3.251 3.365	3.248 3.385	3.252	3.319	3.398	3.338 3.341

[a] Average values; average deviations in parentheses. [b] Values for **2**, **3**, **4**, **6**, and **7** are averages; average deviations in parentheses.

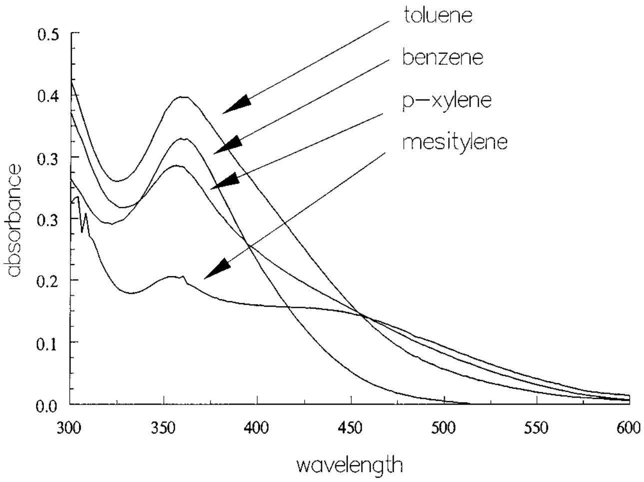

Figure 1. Electronic absorption spectra for solutions of Pd_6Cl_{12} in aromatic solvents.

consists of discrete molecules of Pd_6Cl_{12}. These molecules have an octahedral array of metal atoms. Each metal atom is surrounded by four equivalent chlorine atoms that bridge edges of the octahedron. The β-form has been prepared in polycrystalline form by treatment of $Pd_3(\text{acetate})_6$ with carbon monoxide in glacial acetic acid that contains some perchloric acid.[12] This phase is soluble in aromatic solvents, and it has been speculated that the donor properties of the solvent are responsible for altering the electronic spectrum of the cluster. Commercial $PdCl_2$, which is not soluble in aromatic solvents, is reported to consist of another polymorph whose structure is currently unknown.[13]

Results

Synthetic Studies. Dark red **1**, which consists of discrete molecules of Pd_6Cl_{12}, is readily obtained as X-ray quality single crystals by allowing solutions of bis(benzonitrile)palladium(II) dichloride in a benzene/chloroform mixture to stand. The dark red prisms of the product redissolve in aromatic solvents (benzene, toluene) but do not dissolve in dichloromethane or chloroform. Electronic absorption spectra of Pd_6Cl_{12} in benzene, toluene, *p*-xylene, and mesitylene are shown in Figure 1. The spectra show a prominent feature at 350−365 nm with a tail at lower energy. This tail becomes a distinct peak at 450 nm in the spectrum obtained from the mesitylene solution. The absorption spectrum obtained from a mull of Pd_6Cl_{12} dispersed in mineral oil also shows a prominent band at ca. 370 nm.

The aromatic molecules benzene, mesitylene, durene, and hexamethylbenzene as well as Buckminsterfullerene (C_{60}) form crystalline compounds with Pd_6Cl_{12}. These solids are readily prepared from the appropriate aromatic molecule and bis(benzonitrile)palladium(II) dichloride, a labile complex which is a good source of $PdCl_2$ units.[14a] The products all crystallize as dark red solids. Thus an orange solution of bis(benzonitrile)palladium(II) dichloride in mesitylene produces **2**, $Pd_6Cl_{12}\cdot(CH_3)_3C_6H_3$, upon standing for 48 h. Benzene solutions of bis(benzonitrile)palladium(II) dichloride in the presence of mesitylene, durene, hexamethylbenzene, and biphenyl produce **3**, ($Pd_6Cl_{12}\cdot(CH_3)_3C_6H_3\cdot0.5C_6H_6$), **4** ($Pd_6Cl_{12}\cdot$1,2,4,5-$(CH_3)_4C_6H_2$), **5** ($Pd_6Cl_{12}\cdot(CH_3)_6C_6$), and **6** ($Pd_6Cl_{12}\cdot C_{12}H_{10}$), respectively. Treatment of C_{60} with bis(benzonitrile)palladium(II) dichloride in benzene, which was expected to yield a palladium adduct of the fullerene, produced the crystalline compound **7** ($Pd_6Cl_{12}\cdot0.5C_{60}\cdot1.5C_6H_6$). Treatment of benzene solutions of Pd_6Cl_{12} with stronger donors, triphenylphosphine or pyridine, results in disruption of the cluster and the formation of the conventional compounds bis(triphenylphosphine)palladium(II) dichloride and bis(pyridine)palladium(II) dichloride, respectively.

Structural Studies. The structures of each of the compounds **1**−**7** have been determined by single-crystal X-ray diffraction. Relevant data from these crystal structures are summarized in Tables 1 and 2. Views of the individual structures are presented in Figures 2−10.

The Structure of 1, Pd_6Cl_{12}.[14b] Solvate-free **1** crystallizes with the Pd_6Cl_{12} cluster at a site of $\bar{3}$ point symmetry with the three-fold axis passing through the center of a Cl_3 triangle. Part A of Figure 2 shows a drawing of the highly regular cluster. The four independent Pd−Cl bonds have an average length of 2.307 Å with an average deviation of 0.003 Å. Similarly, all bond angles are very close to 90 or 180°. Within the cluster the closest Pd···Pd contact, which involves two palladium centers that are bridged by chloride ligands, is 3.306(23) Å. This distance is longer than those found where Pd−Pd bonds are present. The palladium atom is displaced 0.031 Å to the outside of the least-squares plane of the four adjacent chlorine

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Table 2. Crystallographic Data for Compounds **1-7**

	Pd_6Cl_{12} (**1**)	$Pd_6Cl_{12}\cdot(CH_3)_3C_6H_3$ (**2**)	$Pd_6Cl_{12}\cdot(CH_3)_3C_6H_3\cdot 0.5C_6H_6$ (**3**)	$Pd_6Cl_{12}\cdot(CH_3)_4C_6H_2$ (**4**)	$Pd_6Cl_{12}\cdot 1.5(CH_3)_6C$ (**5**)	$Pd_6Cl_{12}\cdot C_{12}H_{10}$ (**6**)	$Pd_6Cl_{12}\cdot 0.5C_{60}\cdot 1.5C_6H_6$ (**7**)
formula	$Cl_{12}Pd_6$	$C_9H_{12}Cl_{12}Pd_6$	$C_{12}H_{15}Cl_{12}Pd_6$	$C_{10}H_{14}C_{12}Pd_6$	$C_{18}H_{27}Cl_{12}Pd_6$	$C_{12}H_{10}Cl_{12}Pd_6$	$C_{39}H_9Cl_{12}Pd_6$
fw	1063.80	1184.0	1223.0	1198.01	1307.20	1218.00	1541.26
a, Å	12.971(3)	8.118(2)	8.169(3)	7.954(2)	15.326(5)	31.505(6)	12.544(3)
b, Å	12.971(3)	11.437(2)	11.378(4)	8.804(2)	15.326(5)	7.953(2)	50.655(10)
c, Å	8.552(2)	14.314(3)	15.160(4)	11.199(2)	23.465(7)	15.806(3)	24.669(5)
α, deg	90	71.85(2)	84.06(2)	99.23(2)	90	90	90
β, deg	90	87.48(2)	78.40(2)	106.90(2)	90	111.17(2)	90
γ, deg	120	79.42(2)	80.71(3)	109.17(2)	120	90	90
V, $Å^3$	1246.1(5)	1241.3(4)	1358.5(7)	624.2(2)	4773(3)	2520.9(11)	15675(8)
Z	3	2	2	1	6	4	16
crystal system	trigonal	triclinic	triclinic	triclinic	trigonal	monoclinic	orthorhombic
space group	$R\bar{3}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$R\bar{3}$	$C2/c$	Cmcm
T, °C	−143	−143	−75	−143	−143	−143	−143
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
ρ, g/cm^3	4.253	3.168	2.990	3.187	2.729	3.209	2.612
μ, cm^{-1}	8.26	5.54	5.07	5.51	4.34	5.46	3.55
R_1 (obsd data)[a]	0.057	0.059	0.073	0.034	0.033	0.056	0.093
$wR2$ (all data F^2 refinement)[b]	0.120	0.164	0.223	0.085	0.083	0.140	0.286

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR2 = \sqrt{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]}$.

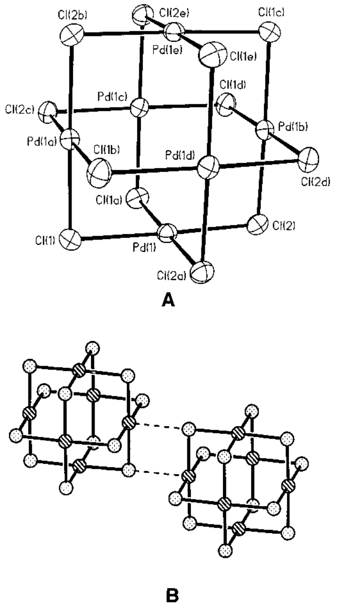

Figure 2. (A) Structure of solvate-free Pd_6Cl_{12}, **1**, showing anisotropic thermal ellipsoids at the 50% probability level. (B) A perspective drawing showing the pairwise Cl···Pd intermolecular contacts between two Pd_6Cl_{12} units in **1**.

atoms. The two parallel planes of four chlorine atoms in a single cluster are separated by 4.613 Å. The corresponding Pd···Pd separation is slightly longer, 4.675 Å.

As shown in part B of Figure 2, the intermolecular interactions are dominated by pairwise Pd···Cl contacts at 3.364 Å that are 21.8° from the normal to the $PdCl_4$ plane. The clusters are offset to allow these two complementary interactions on each face of the cluster. This produces stepped chains of the clusters. Figure 3 shows a stereoscopic view of the packing of individual Pd_6Cl_{12} molecules within the solid.

The Structures of 2, 3, 4, and 6. The structures of the binary compounds formed from Pd_6Cl_{12} and mesitylene, durene, and biphenyl (**2**, **4**, and **6**) and the ternary compound **3**, $Pd_6Cl_{12}\cdot(CH_3)_3C_6H_3\cdot 0.5C_6H_6$, have a number of features in common. Stereoviews of these structures are shown in Figures 4−6 and 8. As can be seen from Table 1, the Pd_6Cl_{12} clusters in these four compounds have similar geometries and dimensions to those of the parent cluster in solvate-free Pd_6Cl_{12}, **1**. Each of the compounds, **2**, **3**, **4**, and **6**, forms a layered-like solid in which the octahedral clusters and the flat aromatic molecules are interleaved. In each case the clusters make face-to-face contact with arene molecules on two opposite sides of the cluster. A view of a typical example of the arene−cluster−arene sandwich is shown in part A of Figure 11. Additionally, the two faces of the aromatic molecules make contact with different Pd_6Cl_{12} clusters. Relatively close, pairwise Pd···Cl contacts between clusters result in the formation of stepped chains in **2**, **4**, and **6**. In each of the Figures 4−6 and 8, the chains produced by these pairwise Pd···Cl contacts run parallel to the figure plane. These chains are generally similar to those found in solvate-free **1**. In **3**, however, these same pairwise contacts result in the formation of slightly different, zigzag chains as seen in Figure 5.

The Structure of 5, $Pd_6Cl_{12}\cdot 1.5(CH_3)_6C_6$. The binary compound, **5**, has a nonlayered structure that differs in important respects from those of **2**, **3**, **4**, and **6**. The cluster has crystallographic 3-fold symmetry while the aromatic molecule has inversion symmetry. In **5**, as in **2**, **3**, **4**, and **6**, the hexamethylbenzene molecules are sandwiched between two Pd_6Cl_{12} clusters. As shown in Figure 7 and in part B of Figure 11, three adjacent, orthogonal sides of the cluster make face-to-face contacts with hexamethylbenzene molecules. The other three sides of the cluster lack the close pairwise Pd···Cl contacts that are a significant characteristic of compounds **1**−**4** and **6**. In **5** the shortest Pd···Cl separation is 4.053 Å.

The Structure of 7, $Pd_6Cl_{12}\cdot 0.5C_{60}\cdot 1.5C_6H_6$ (6). A view of this complex structure is shown in Figure 9. The formula and asymmetric unit for this compound belies its overall complexity. There are eight individual components, and each possesses some degree of crystallographic symmetry. These components include the following: (1) a Pd_6Cl_{12} cluster with *mm* symmetry that involves atoms Pd(1)−Pd(3) and Cl(1)−Cl(5); (2) a Pd_6Cl_{12} cluster with 2/*m* symmetry that involves atoms Pd(4) and Pd(5) and Cl(6)−Cl(9); (3) a Pd_6Cl_{12} cluster with *m* symmetry that is comprised of atoms Pd(6)−Pd(9) and Cl(10)−Cl(16); (4) a benzene molecule with *m* symmetry that utilizes atoms C(1)−C(4) with these atoms lying within the mirror plane; (5) a benzene molecule with *m* symmetry that consists of atoms C(5)−C(7) with the mirror plane bisecting an edge of the six-membered ring; (6) a benzene molecule with *m* symmetry that consists of atoms C(8)−C(10); (7) one quarter

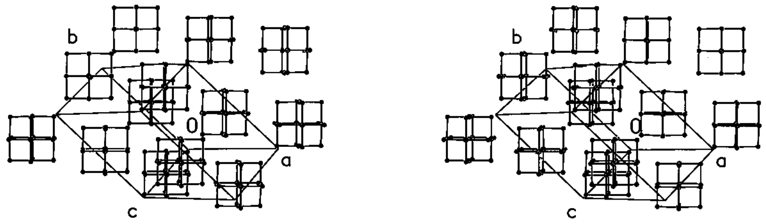

Figure 3. A stereoscopic view of the structure of solvate-free Pd_6Cl_{12}, **1**.

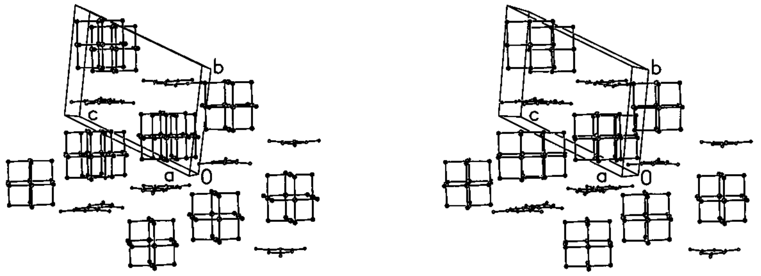

Figure 4. A stereoscopic view of the structure of $Pd_6Cl_{12}\cdot(CH_3)_3C_6H_3$, **2**.

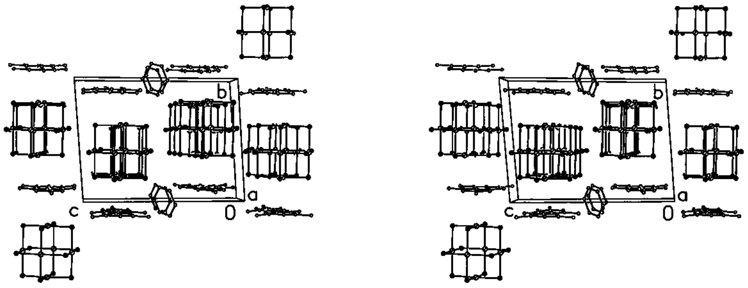

Figure 5. A stereoscopic view of the structure of $Pd_6Cl_{12}\cdot(CH_3)_3C_6H_3\cdot0.5C_6H_6$, **3**.

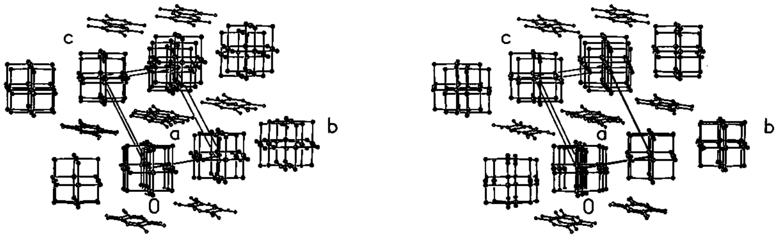

Figure 6. A stereoscopic view of the structure of $Pd_6Cl_{12}\cdot(CH_3)_4C_6H_2$, **4**.

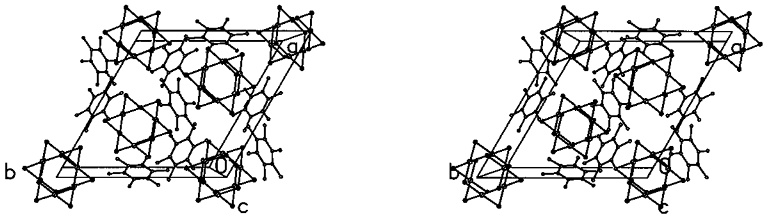

Figure 7. A stereoscopic view of the structure of $Pd_6Cl_{12}\cdot1.5(CH_3)_6C_6$, **5**.

of a disordered molecule of C_{60} with 2/*m* symmetry that involves atoms C(11)−C(31); and (8) a second, disordered quarter of a molecule of C_{60} with 2/*m* symmetry that involves atoms C(32)−C(50).

Few molecular solids can boast the collection of geometric shapes, truncated icosahedra, octahedra, and hexagons, that are found in this one. These figures have considerable similarity in their sizes. The C_{60} diameter of 7.1 Å is only slightly larger than the Pd_6Cl_{12} body diagonal of 6.6 Å, and in terms of van der Waals radii they are roughly the same size. Since the H···H span of benzene is ca. 4.8 Å, it is easily sandwiched between palladium clusters or C_{60}. In an examination of the packing in this unusual structure it is therefore not entirely clear what intermolecular forces come into play, whether the proximity of molecules is dictated by donor−acceptor interactions or simply by the efficient packing of similar-sized molecules. For example (see Figure 9), two of the benzene molecules are the middle layer in a stack of C_{60}/benzene/Pd_6Cl_{12}. The contacts are typical for π-stacking of these molecules, suggesting that benzene is acting as a bi-directional donor. However, the structure has other instances of C_{60} and Pd_6Cl_{12} in close proximity with no interleaving benzene molecules. In fact, the nearest neighbors for one of the C_{60} molecules consist of two face-on and four edge-on benzene molecules, two molecules of C_{60} and six Pd_6Cl_{12} clusters; the other C_{60} is surrounded by four face-on and two edge-on benzene molecules in addition to two C_{60} molecules and six Pd_6Cl_{12} clusters. The C_{60} molecules stack along the **a** direction in side-by-side columns. The separation between their

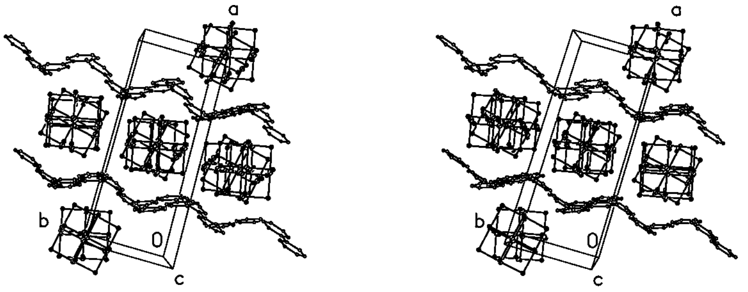

Figure 8. A stereoscopic view of the structure of $Pd_6Cl_{12}\cdot(C_6H_5)_2$, **6**.

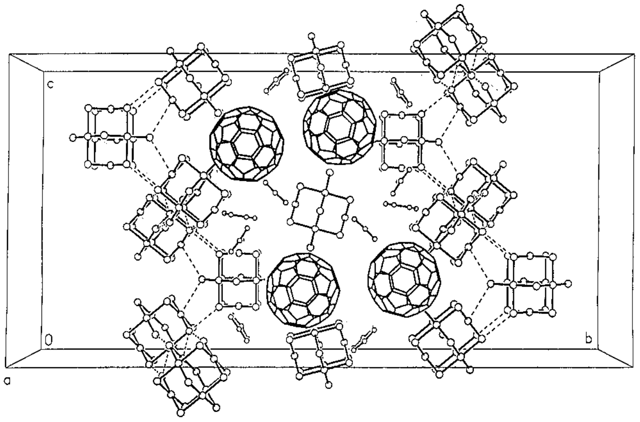

Figure 9. A view of the structure of $Pd_6Cl_{12}\cdot 0.5C_{60}\cdot 1.5C_6H_6$, **7**. The C_{60} molecules are disordered at sites of $2/m$ symmetry. In this view, ideal C_{60} molecules have been drawn at the appropriate locations.

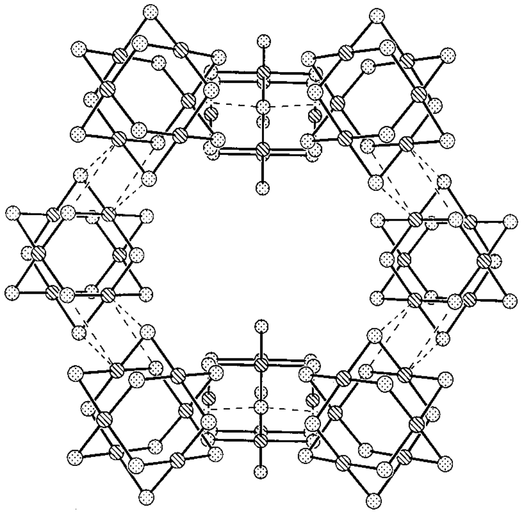

Figure 10. A portion of the structure of $Pd_6Cl_{12}\cdot 0.5C_{60}\cdot 1.5C_6H_6$, **7**. This view emphasizes the group of eight clusters that surround C_{60} molecules.

centers is 12.54 and 12.49 Å between like molecules and 9.99 Å between the two different molecules of C_{60}. Furthermore, the Pd_6Cl_{12} clusters have adopted an interesting arrangement to accommodate the spherical shape of the C_{60}. Figure 10 shows how a group of eight Pd_6Cl_{12} clusters form a pocket into which a C_{60} molecule can fit. Several intermolecular contacts between Pd_6Cl_{12} clusters allow this to form: a pairwise interaction between Pd7 and Cl11 of 3.465 Å and a longer one between Pd7 and Cl12 of 3.615 Å. There is also a triangular arrangement of Pd_6Cl_{12} clusters that form equal bifurcated contacts between Cl4 and Pd8 and Pd8′ of 3.647 Å.

The Electronic Structure of Pd_6Cl_{12}. In order to probe the binding within the cluster, a series of SCF−Xα−SW calculations were performed on $PdCl_2$ (C_{2v} symmetry), $PdCl_4^{2-}$ (D_{4h} symmetry), and Pd_6Cl_{12} (O_h symmetry). The first two systems

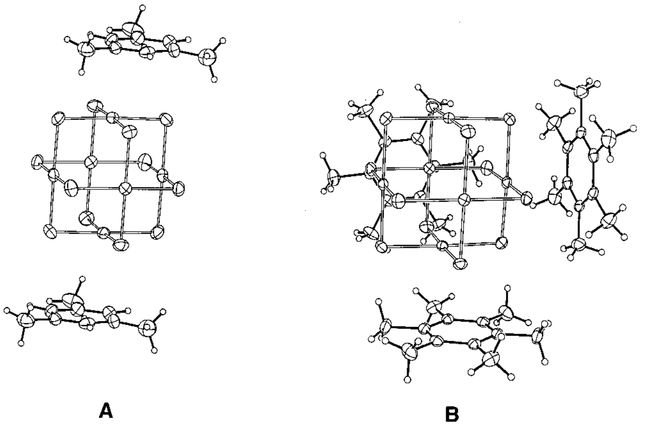

Figure 11. (A) A view of the contact between two mesitylene molecules and the Pd_6Cl_{12} cluster in $Pd_6Cl_{12}\cdot(CH_3)_3C_6H_3$, **2**. This is a common motif in the structures of **2**, **3**, **4**, and **6**. (B) A view of the contact between three hexamethylbenzene molecules and the Pd_6Cl_{12} cluster in $Pd_6Cl_{12}\cdot 1.5(CH_3)_6C_6$, **5**.

can be viewed as components of the third system. For example, the Pd_6Cl_{12} cluster is formally a collection of six interacting $PdCl_2$ units, each with a 90° bond angle and C_{2v} symmetry. Each $PdCl_2$ unit interacts directly with four other units: the two Cl atoms bond on the same side of the $PdCl_2$ plane to the Pd atoms of two other units and the Pd atom bonds within the $PdCl_2$ plane to a Cl atom of two additional units. The result is a cubic arrangement of six, square-planar $PdCl_4$ faces wherein each of the Cl atoms is shared between two faces. The bonding within a face should resemble the well-known $PdCl_4^{2-}$ complex.[15] The highest order rotation axis is chosen as the z axis in all cases. The other axes are chosen such that the molecule is in the yz plane for $PdCl_2$ and in the xy plane for $PdCl_4^{2-}$. The x and y axes are parallel to the Pd−Cl bond axes in both $PdCl_4^{2-}$ and Pd_6Cl_{12}. Accordingly, the correlations for $PdCl_2$ involve a change of axes; for example, d_{yz} in $PdCl_2$ correlates to $d_{x^2-y^2}$ in Pd_6Cl_{12} and $PdCl_4^{2-}$. The Pd-d orbitals in Pd_6Cl_{12} are labeled in terms of the $PdCl_4$ faces, so that $d_{x^2-y^2}$ in Pd_6Cl_{12} refers to orbitals that are predominantly in the $PdCl_4$ planes and directed along the Pd−Cl axes of all of the $PdCl_4$ faces.

Figure 11 shows the energy ordering of the higher valence orbitals. These are numbered with neglect of the core levels and labeled in terms of their symmetry and major Pd-d or Cl-p character. The predominantly Cl-p orbitals are identified further as to σ or π type, with the π type differentiated by the symmetry with respect to the molecular plane (h = horizontal or in-plane, v = vertical or out-of-plane) in $PdCl_2$ and $PdCl_4^{2-}$. The differentiation of π type is not made for Pd_6Cl_{12}, since π_v becomes σ and only π_h (parallel to an edge of the cube) remains π-type. The π_h and σ types also both include the t_{1u} representation. The orbitals of Pd_6Cl_{12} in Figure 12 not explicitly noted as Cl-p by the σ or π label are predominantly Pd-d. The orbitals

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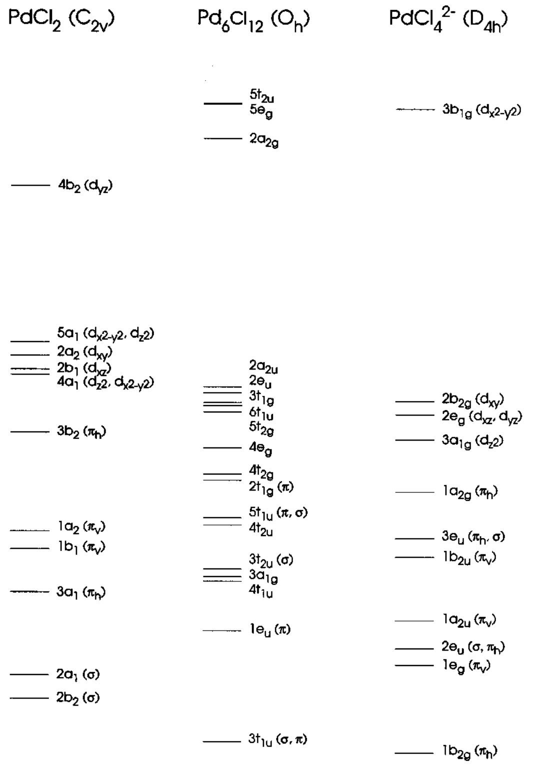

Figure 12. A molecular orbital energy diagram for the higher valence orbitals in the Pd_6Cl_{12} cluster.

have their correct relative energies within each system, but the systems have been displaced in energy to place the gap between the filled and virtual orbitals at similar energies.

The energy order of the Pd-d orbitals in $PdCl_2$ is d_{yz} ($4b_2$, LUMO) > $d_{x^2-y^2,\ z^2}$ ($5a_1$, HOMO) > d_{xy} ($2a_2$) > d_{xz} ($2b_1$) > $d_{z^2,\ x^2-y^2}$ ($4a_1$), but the $1a_2$ and $2a_2$ orbitals have nearly equal Pd-d_{xy} and Cl-pπ_v character. The highest energy, filled ligand orbital in $PdCl_2$ is $3b_2$ (Cl-pπ_h). Each of the orbitals in $PdCl_2$ correlates to six orbitals in Pd_6Cl_{12}. For example, the $3b_2$ Cl-pπ_h orbital in $PdCl_2$ correlates to the $2t_{1g}$ and $5t_{1u}$ Cl-pπ orbitals in Pd_6Cl_{12}. The Cl-pπ_v orbitals in $PdCl_2$ become Cl-pσ orbitals in Pd_6Cl_{12}. Similarly, the d_{yz} ($4b_2$) LUMO in $PdCl_2$ correlates to the six $d_{x^2-y^2}$ ($5t_{2u}$, $5e_g$, and $2a_{2g}$) lowest lying virtual orbitals in Pd_6Cl_{12}. The correlations for the filled Pd-d orbitals are more complicated, since the resulting groups of orbitals in Pd_6Cl_{12} overlap in energy and mixing occurs among orbitals of the same symmetry. However, the HOMO in Pd_6Cl_{12} ($2a_{2u}$, d_{xy}) derives from the HOMO in $PdCl_2$ ($5a_1$, $d_{x^2-y^2,\ z^2}$). In $PdCl_4^{2-}$, the Pd-d orbitals have the expected order $d_{x^2-y^2}$ ($3b_{1g}$, LUMO) > d_{xy} ($2b_{2g}$, HOMO) > d_{xz}, d_{yz} ($2e_g$) > d_{z^2} ($3a_{1g}$). The correlations between Pd_6Cl_{12} and $PdCl_4^{2-}$ are also as expected. The HOMO in $PdCl_4^{2-}$ ($2b_{2g}$, d_{xy}) correlates to the HOMO ($2a_{2u}$) and other high-energy filled Pd-d orbitals ($2e_u$ and $5t_{2g}$) in Pd_6Cl_{12}, although the $1e_u$ and $2e_u$ orbitals in Pd_6Cl_{12} have roughly equal Pd and Cl character. The ligand orbitals $1a_{2g}$ and $3e_u$ (Cl-pπ_h) in $PdCl_4^{2-}$ correlate to the ligand orbitals $2t_{1g}$ and $5t_{1u}$ (Cl-pπ) in Pd_6Cl_{12}.

Excitation energies, obtained simply from the ground state orbital energies, are given in Table 3 for the lower-lying palladium d−d and some of the chlorine-to-palladium charge transfer excitations. The d−d excitations are predicted to be lowest lying in all of the systems. The states that result from the d−d excitations are formally symmetry forbidden in absorption from the ground state only in $PdCl_4^{2-}$, but the transitions are expected to remain weak in Pd_6Cl_{12} based on the local site symmetry of the Pd. Similar arguments, based on the effect of the local symmetry, have been used in explaining the spectra of $Pd_2X_6^{2-}$, where X = Br and I.[16] The intense absorptions are expected to involve the allowed chlorine-to-palladium charge transfer (LMCT) excited states. These LMCT excitation energies are given in Table 3.

The calculations can be compared with experiment most readily for $PdCl_4^{2-}$, wherein the assignments and energies are well-known. The singlet states associated with the d−d transitions are observed at 2.73, 2.98, and 3.72 eV for $^1A_{2g}$, ^1E_g, and $^1B_{1g}$, respectively.[16] The order agrees with the calculations, but the calculated energies are too small by 0.2−0.8 eV. The lowest energy LMCT absorption is seen at 4.46 eV and assigned to the $^1A_{2u}$ state.[16] The lowest energy singlet LMCT state from the calculations is ^1E_u at 3.79 eV, with the $^1A_{2u}$ state at 3.96 eV. The calculated energies are again too small. Such errors are not unexpected, in part because the calculations at best refer to the mean of the singlet and triplet states resulting from a given excitation.

The low-energy onset of the d−d transitions in Pd_6Cl_{12} is calculated to occur at 2.19 eV (570 nm), while the lowest energy allowed LMCT transitions are calculated at 3.33, 3.66, and 3.79 eV. Hence, we predict that the absorption spectrum will be dominated by LMCT transitions somewhat above 3.3 eV (375 nm). This is in surprising agreement with the observed intense absorption band seen at ≈3.3 eV in mulls of neat Pd_6Cl_{12} and at 3.4 eV in solutions of Pd_6Cl_{12} in aromatic solvents. The enhanced agreement relative to the $PdCl_4^{2-}$ case may be fortuitous, but it also could reflect the better results anticipated for more spherical systems from SCF−Xα−SW calculations. The onset of absorption in benzene solution (≈2.3 eV) also agrees with the calculated energy for the onset of d−d transitions.

Discussion

As Table 1 shows, the Pd_6Cl_{12} cluster retains an invariant structure throughout the series of compounds, **1**−**7**. Since the palladium atoms protrude slightly to the outside of the plane of the four adjacent chlorine atoms, there is no evidence of direct Pd−Pd bonding. The face-to-face Pd•••Pd separation of 4.675 Å in **1** is considerably longer than the distance (2.5310(9) Å) found for the unsupported Pd−Pd single bond in $[Pd_2(CNCH_3)_6]^{2+}$.[17] The Pd_6Cl_{12} cluster is geometrically related to Pt_6Cl_{12} and to a number of early transition metal clusters which all have an octahedral array of metal atoms and twelve edge-bridging halogen atoms. However, in the early transition metal clusters with $[M_6X_{12}]^{n+}$ cores (where M = Nb or Ta, X = halogen, and n = 2, 3, or 4) there is significant metal−metal bonding, and the metal centers are drawn inward toward one another.[18,19]

The formation of the array of adducts **2**−**7**, in which an aromatic component is crystallized along with the Pd_6Cl_{12} cluster, is a direct consequence of the donor/acceptor interaction between these components. It is clear that the aromatic component is not merely occupying what would otherwise be a void in the structure, since the cluster is able to crystallize in the solvate-free form, **1**. The solubility of Pd_6Cl_{12} in aromatic solvents is also a consequence of these interactions. The empty $2a_{2g}$ $d_{x^2-y^2}$ orbital of Pd_6Cl_{12} should not be important in this

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Table 3. Calculated Energies of Some Palladium d−d and Chlorine-to-Palladium Charge Transfer (LMCT) Excitations in $PdCl_2$, Pd_6Cl_{12}. and $PdCl_4^{2-}$

	$PdCl_2$		Pd_6Cl_{12}		$PdCl_4^{2-}$	
	excitation (states)	Δ*E*/eV	excitation (states)	Δ*E*/eV	excitation (states)	Δ*E*/eV
d−d	$5a_1-4b_2$ ($^{1,3}B_2$)	1.37	$2a_{2u}-2a_{2g}$ ($^{1,3}A_{1u}$)	2.19	$2b_{2g}-3b_{1g}$ ($^{1,3}A_{2g}$)	2.58
	$2a_2-4b_2$ ($^{1,3}B_1$)	1.49			$2e_g-3b_{1g}$ ($^{1,3}E_g$)	2.70
	$2b_1-4b_2$ ($^{1,3}A_2$)	1.61			$3a_{1g}-3b_{1g}$ ($^{1,3}B_{1g}$)	2.92
	$4a_1-4b_2$ ($^{1,3}B_2$)	1.66				
LMCT	$3b_2-4b_2$ ($^{1,3}A_1$)	2.17	$2t_{1g}-5t_{2u}$ ($^{1,3}T_{1u}$)	3.33	$3e_u-3b_{1g}$ ($^{1,3}E_u$)	3.79
	$1a_2-4b_2$ ($^{1,3}B_1$)	3.04	$5t_{1u}-5e_g$ ($^{1,3}T_{1u}$)	3.66	$1b_{2u}-3b_{1g}$ ($^{1,3}A_{2u}$)	3.96
			$3t_{2u}-2a_{2g}$ ($^{1,3}T_{1u}$)	3.79		

regard since the orbital is concentrated in the $PdCl_4$ planes and very poor overlap will occur with any aromatic π-orbital. However, the empty $5e_g$ and $5t_{2u}$ $d_{x^2-y^2}$ orbitals of Pd_6Cl_{12} are contaminated with d_{z^2} and d_{xz}, d_{yz} character, respectively, which have large amplitudes normal to the $PdCl_4$ planes. Presumably, these orbitals are involved in the face-to-face interaction with an arene whose plane is parallel to the $PdCl_4$ face.

The absorption spectrum of Pd_6Cl_{12} in solutions of methylated benzenes shows an additional absorption band at ≈2.75 eV (450 nm). Based on the shift of this band that occurs with variation in the number of methyl substituents, the band must involve the arene moiety. One possibility is that the band represents the nominally spin-forbidden transition between the ground and lowest excited $^3\pi\pi^*$ states of the aromatic solvent, since this transition is expected to gain intensity from the external heavy-atom effect caused by the Pd_6Cl_{12} cluster. However, this assignment can be discounted on energy grounds since the band maxima in absorption would occur much further to the blue (electronic origins at ≤360 nm).[20] The assignment which we propose for the excited state of the band involves a charge-transfer transition from a π-orbital of the aromatic to a $d_{x^2-y^2}$ virtual orbital of Pd_6Cl_{12}. This assignment is prompted by the apparent red shift of the band that occurs with increasing number of methyl substituents among toluene, *p*-xylene, and mesitylene, which parallels the expected direction of their decreasing ionization energies. In order to check the viability of this assignment, the ionization energy and electron affinity of Pd_6Cl_{12} were estimated from transition state and total energy calculations. The calculated ionization energy is ≈12 eV, significantly greater than the ionization energies of methylated benzenes (8.8 eV in toluene and 8.4 eV in mesitylene),[21] so that the aromatic is expected to function as the donor in any charge-transfer state. The calculated electron affinity is ≈6.0 eV. Hence, a very crude estimate of the energy of the charge-transfer excited state is ≈2.6 eV (≈500 nm).

The face-to-face contacts between the square $PdCl_4$ portions of the clusters and the aromatic molecules are a major feature of the series of compounds **2**−**7**. Figure 13 shows views of these contacts which emphasize the relative positioning of the aromatic hexagon above the $PdCl_4$ square. In each drawing the view is made perpendicular to the $PdCl_4$ plane. Generally the aromatic groups are arranged so the palladium atom lies within the aromatic hexagon and generally near one of the carbon atoms. The exception is found in one of the benzene/Pd_6Cl_{12} contacts in **7**, where the palladium atoms lie beneath the center of the benzene ring (see H in Figure 13). The Pd···C distances in these compounds range from 3.171 to 3.410 Å. The $PdCl_4$ plane and the plane of the aromatic molecule that are involved in the face-to-face contact are nearly parallel. The separations between these (see Table 1) fall in a relatively narrow range, 3.247−3.385 Å. However, the interplanar separations and Pd···C contacts are well beyond the conventional bonding range. In typical palladium olefin complexes such as (norbornadiene)palladium(II) dichloride the Pd−C distances are 2.159(4) and 2.166(4) Å,[22] in η^3-alkyl complexes like (η^3-2-methallyl)palladium(II) chloride dimer the Pd−Cl distances are 2.082(19), 2.102(16), and 2.062(18) Å,[23] and in cases where two palladium atoms are sandwiched between two arene rings, as in $(C_6H_6)_2Pd_2(Al_2Cl_7)_2$, the shortest Pd−C distances range from 2.26 to 2.63 Å.[24] The Pd···C contacts are also longer than the metal−carbon contact observed in the weak hexamethylbenzene/mercury(II) bis(trifluoroacetate) dimer, where the Hg−C distances are 2.56 and 2.58 Å.[25] Perhaps the closest analogs to the interactions between the cluster and the aromatic molecules seen here are found in the adducts of aromatic molecules and tetrakis(triphenylacetato)dichromium(II).[26] In these crystalline materials, chains of alternating molecules of tetrakis(triphenylacetato)dichromium(II) and the aromatic molecule are formed with the aromatic component situated perpendicular to the Cr−Cr axis and centered between the two adjacent chromium atoms. The resulting Cr···ring centroid distances are in the range 3.310−3.388 Å. Although the individual Pd−C contacts are long in solids **2**−**7**, there is sufficient attraction between the clusters and the arenes to produce this remarkable array of binary and ternary solids.

The nature of the arene/cluster interactions in binary complex **2**, $Pd_6Cl_{12}\cdot(CH_3)_3C_6H_3$, and ternary compound **3**, $Pd_6Cl_{12}\cdot(CH_3)_3C_6H_3\cdot0.5C_6H_6$, is similar as can be seen by comparison of drawings A and B with C and D in Figure 13. In ternary compound **3**, $Pd_6Cl_{12}\cdot(CH_3)_3C_6H_3\cdot0.5C_6H_6$, it is the mesitylene molecules, which are the better π donors, rather than the benzene molecules that make the face-to-face contact with the Pd_6Cl_{12} cluster. In **3**, the benzene molecules are positioned within the layers of mesitylene molecules and are oriented with their planes roughly perpendicular to the direction of the mesitylene molecules as seen in Figure 5.

It is interesting to note that hexamethylbenzene, which is the best donor, forms a greater number of face-to-face contacts with the cluster than do the other aromatic donors utilized in this study. Hexamethylbenzene is also the largest of the donors, but as depicted in Figure 8 the dimensions of the aromatic molecule are large enough to allow the methyl groups to extend beyond the edges of the cluster face. Therefore, somewhat surprisingly, favorable donor−acceptor interactions between faces of the aromatic molecules and the Pd_6Cl_{12} cluster occur even in the presence of six methyl groups.

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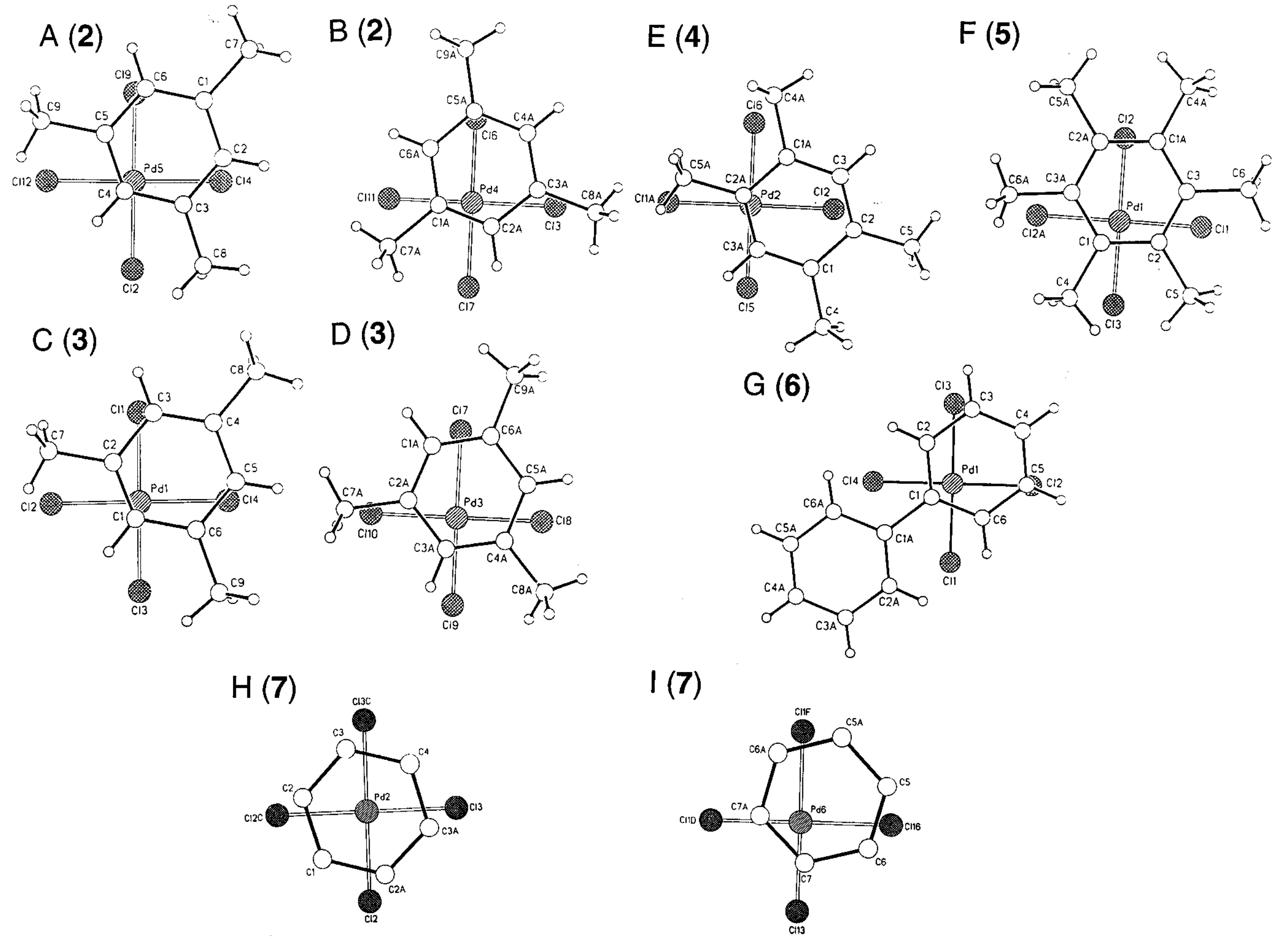

Figure 13. Views of the projection of the aromatic components of **2**−**7** onto the plane of the adjacent $PdCl_4$ face of the Pd_6Cl_{12} cluster: (A and B) $Pd_6Cl_{12}{\cdot}(CH_3)_3C_6H_3$, **2**; (C and D) $Pd_6Cl_{12}{\cdot}(CH_3)_3C_6H_3{\cdot}0.5C_6H_6$, **3**; (E) $Pd_6Cl_{12}{\cdot}(CH_3)_4C_6H_2$, **4**; (F) $Pd_6Cl_{12}{\cdot}1.5(CH_3)_6C_6$, **5**; (G) $Pd_6Cl_{12}{\cdot}(C_6H_5)_2$, **6**; (H and I) $Pd_6Cl_{12}{\cdot}0.5C_{60}{\cdot}1.5C_6H_6$, **7**. The closest Pd···C contacts are as follows: (A) 3.171 Å; (B) 3.410 Å; (C) 3.231 Å; (D) 3.395 Å; (E) 3.311 Å; (F) 3.389 Å; (G) 3.334 Å; (H) 3.328 Å; and (I) 3.474 Å.

The fullerene, C_{60}, shows a marked propensity to form both intercalation compounds with considerable electron transfer[27] and solids in which a range of other molecules are simply co-crystallized. The latter include examples such as $C_{60}{\cdot}(S_8)_2$,[28] $C_{60}{\cdot}(P_4)_2$,[29] $C_{60}{\cdot}I_2{\cdot}C_6H_5CH_3$,[30] $C_{60}{\cdot}\{(\eta^5C_5H_5)_2Fe\}_2$,[31] $C_{60}{\cdot}\{(\eta^5C_5H_5)_4Fe_4(CO)_4\}{\cdot}3C_6H_6$,[32] $C_{60}{\cdot}4\,C_6H_6$,[33] $C_{60}{\cdot}CH_2I_2{\cdot}C_6H_6$,[34] and $C_{60}{\cdot}$\{bis(dimethylthieno)tetratellurafulvalene\}${\cdot}CS_2$[35] where the other component is drawn from the inorganic, organometallic, or organic classes. The ter-molecular solid, **7**, belongs to this latter classification.

Experimental Section

Preparation of Compounds. Bis(benzonitrile)palladium(II) dichloride was prepared as described in the literature.[36]

Pd_6Cl_{12} (1). A solution of 5.5 mg (1.43×10^{-5} mol) of bis(benzonitrile)palladium(II) dichloride in 0.5 mL of benzene was transferred to a 20 cm × 6 mm inside diameter glass tube that was sealed at one end. The solution was red-orange in color. Chloroform (0.5 mL) was added drop by drop to the solution in the glass tube. The chloroform settled to the bottom of the tube and the color of the solution immediately turned to orange-yellow. The tube was sealed with a rubber septum and set aside for 24 h. Dark red rhombohedral prisms of Pd_6Cl_{12} formed: yield 1 mg, 39.5%.

$Pd_6Cl_{12}{\cdot}(CH_3)_3C_6H_3$ (2). A solution of 10 mg (2.61×10^{-5} mol) of bis(benzonitrile)palladium(II) dichloride in 1.5 mL (1.07×10^{-2} mol) of mesitylene was transferred to a glass tube. The color of the solution was orange. The tube was capped and set aside for 48 h. Dark red crystals formed. The crystals were harvested by cracking the tube: yield 1 mg, 19.5%.

$Pd_6Cl_{12}{\cdot}(CH_3)_3C_6H_3{\cdot}0.5C_6H_6$ (3). A solution of 10 mg (2.61×10^{-5} mol) of bis(benzonitrile)palladium(II) dichloride in 0.5 mL of benzene was added to 0.5 mL (3.58×10^{-3} mol) of mesitylene. The color of the solution turned from red-orange to orange upon the addition of mesitylene, and after stirring, the solution was transferred to a glass tube. The tube was capped and set aside for 24 h. Dark red plates formed: yield 1 mg, 20%.

$Pd_6Cl_{12}{\cdot}(CH_3)_4C_6H_2$ (4). A solution of 10 mg (2.61×10^{-5} mol) of bis(benzonitrile)palladium(II) dichloride in 0.5 mL of benzene was

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transferred to a glass tube. A solution of 100 mg (7.5×10^{-4} mol) of 1,2,4,5-tetramethylbenzene in 1 mL of benzene was added drop by drop to this solution. The color of the solution at the interface of the red-orange bis(benzonitrile)palladium(II) dichloride solution and the colorless tetramethylbenzene solution was light yellow. The tube was capped and set aside for 48 h. Dark red prismatic crystals formed: yield 1.3 mg, 25%.

$Pd_6Cl_{12}\cdot1.5(CH_3)_6C_6$ (5). A solution of 10 mg (2.61×10^{-5} mol) of bis(benzonitrile)palladium(II) dichloride in 0.5 mL of benzene was transferred to a glass tube. A solution of 50 mg (2.06×10^{-4} mol) of hexamethylbenzene in 1 mL of benzene was added drop by drop to this solution. The color of the solution at the interface of the red-orange bis(benzonitrile)palladium(II) dichloride solution and the colorless hexamethylbenzene solution turned brown. The tube was capped and set aside for 48 h. Dark red, hexagonal needles formed: yield 3.3 mg, 59%.

$Pd_6Cl_{12}\cdot(C_6H_5)_2$ (6). A solution of 10 mg (2.61×10^{-5} mol) of bis(benzonitrile)palladium(II) dichloride in 0.5 mL of benzene was transferred to a glass tube. A solution of 50 mg (3.24×10^{-4} mol) of biphenyl in 1 mL of benzene was added drop by drop to this solution. The color of the solution at the interface of the red-orange bis(benzonitrile)palladium(II) dichloride solution and the colorless biphenyl solution was light yellow. The tube was capped and set aside for 48 h. Dark red crystals formed. The crystals were harvested by cracking the tube: yield 1.7 mg, 32%.

$Pd_6Cl_{12}\cdot0.5C_{60}\cdot1.5\ C_6H_6$ (7). A solution of 0.25 mg (3.47×10^{-7} mol) of C_{60} in 0.75 mL of benzene was added to 5 mg (1.31×10^{-5} mol) of bis(benzonitrile)palladium(II) dichloride. The color changed from magenta to red brown upon dissolution of the bis(benzonitrile)palladium(II) dichloride in the C_{60} benzene solution. This solution was transferred to a glass tube. A 1-mL portion of *n*-hexane was added drop by drop to the tube. The tube was set capped and set aside for 14 h. Dark needles formed; yield 1.7 mg, 65.4%.

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.[37] Suitable crystals were mounted on glass fibers with silicone grease and placed in the cold stream of either a Siemens R3m/V diffractometer equipped with an Enraf-Nonius low temperature apparatus (**1**−**3**, **5**) or a Siemens P4 diffractometer equipped with an LT-2 low temperature device (**4**, **7**). The former diffractometer utilized a sealed Mo tube that operated at 2 kW and a graphite monochromator, while the latter employed a rotating Mo anode that operated at 15 kW and a Zr filter. All the data sets were collected at 130 K except for that of **3** which was collected at 198 K in order to avoid the cracking that occurred upon further cooling. 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.[38] The structures were solved by Patterson or direct methods using the software of SHELXTL Plus, VMS version, and refined by use of the program SHELXTL-93 (based on F^2). 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.[39] Hydrogen atoms were added geometrically and refined with a riding model. All non-hydrogen atoms were refined with anisotropic thermal parameters. No disorder was present in any of the structures except for that of **7**. For **7** there is severe disorder in the fullerene portions. There are two sites with $2/m$ symmetry that are occupied by disordered fullerene molecules. Similar disorder has been observed in $(C_{60})_{1.5}$-(cyclotriveratrylene)(toluene)$_{0.5}$.[40] Crystal data and some details of the refinements are given in Table 2.

Electronic Structure Calculations. Standard SCF−Xα−SW calculations were performed on $PdCl_2$ (C_{2v} symmetry), $PdCl_4^{2-}$ (D_{4h} symmetry), and Pd_6Cl_{12} (O_h symmetry).[41] In all cases, the Cl−Pd−Cl angles were taken as 90° (and 180°) and the Pd−Cl bond lengths as 2.3065 Å, which correspond to the average values found in crystals of Pd_6Cl_{12}. Atomic exchange parameters were taken from Schwarz,[42] with the valence electron weighted average used in the interatomic and outer regions. The Norman criterion was used to determine atomic sphere radii.[43] The outer sphere was reduced from tangency with the most distant atomic sphere by 0.1 bohr. A Watson sphere of charge +2 was used for $PdCl_4^{2-}$. The partial wave bases used l_{max} equal to 6 on the outer sphere, 3 on Pd, and 2 on Cl. The SCF calculations were spin restricted, used the quasirelativistic option for Pd, and treated the core levels ([Kr] for Pd and [Ne] for Cl) as single atom functions.

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Supporting Information Available: Tables including a full listing of data collection and structure refinement details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for compounds **1**−**7** (56 pages). See any current masthead page for ordering and Internet access instructions.

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