Construction of a Square-Planar Molecular Box: Self-Assembly of Palladium(II) Complexes of 3,6,9,16,19,22-Hexaazatricyclo[22.2.2.2^{11,14}]triacon-11,13,24,26(1),27,29-hexaene through Hydrogen-Bonding Interactions

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Binuclear palladium(II) complexes of the macrocyclic polyamine 3,6,9,16,19,22-hexaazatricyclo[22.2.2.2^{11,14}]-triacon-11,13,24,26(1),2 7,29-hexaene (**L**) are used to construct molecules having special shapes. In this study two binuclear palladium(II) complexes $[Pd_2\mathbf{L}I_2]I_2$ and $[Pd_2\mathbf{L}Cl_2](NO_3)_2\cdot H_2O$ are synthesized and structurally characterized. X-ray crystallography shows that both complexes exist as one-dimensional chains formed via intermolecular hydrogen-bonding N(3)−H(3C)---X in which X is I and Cl. Moreover, the ligands in both complexes adopt a boatlike conformation that may facilitate the formation of the tetranuclear complex. The cationic aqua complex $[Pd_2\mathbf{L}(H_2O)_m(NO_3)_n]^{(4-n)+}$, obtained by the treatment of $[Pd_2\mathbf{L}I_2]I_2$ and $[Pd_2\mathbf{L}Cl_2]Cl_2$ with $AgNO_3$, is used as a building block for the construction of a tetranuclear palladium(II) complex $[Pd_4\mathbf{L}_2(C_2O_4)_2](NO_3)_4\cdot 6H_2O$. X-ray crystallography shows that the tetranuclear complex forms an open, hydrophobic box. These molecular boxes are connected via the hydrogen bond N(3)−H(3C)---O(4B) (symmetry code B: x, $1 + y$, z) into a one-dimensional chain. A two-dimensional structure is formed via $\pi-\pi$ stacking of the plane defined by C6 to C11 in the one chain and its symmetry-related plane (symmetry code C: $-x$, $-1 - y$, $2 - z$) in another chain. This study exemplifies a new method for the assembly of molecular boxes using a macrocyclic ligand.

Introduction

Synthetic polyhedral molecular assemblies are potentially important for the study of inclusion phenomena, molecular recognition, and catalysis. For these reasons, much attention is being paid to the synthesis of molecules with regular shapes.[1−5] Excellent recent studies in the field of molecular architecture have used metal ions to great advantage.[6−12] Fujita et al. synthesized nanometer-sized hexahedral coordination capsule using an exo-hexadentate ligand having coordination sites located at its three corners.[6] Lippert et al. obtained a molecular triangle using $[(en)Pd(2,2'\text{-bipyrazine-}N^1,N^{1''})]^{2+}$ (**1**) as an angular link, leaving the N4 and N4′ atoms for construction of the sides of the triangle.[7] When $[(en)M]^{2+}$ in which M is Pd(II) or Pt(II) are used as angular links while *cis*- and *trans*-$[Pt(2,2'\text{-bipyrazine-}N,{}^4N^{4''})]^{2+}$ are used as linear building blocks, different topologies such as loop, vase, and barrel are formed.[7] The combination of $[Pd(2,2'\text{-bipyrazine-}N^1,N^{1''})]^{2+}$ as angular blocks and 4,4′-bipyridine as a linear bridging block leads to a molecular square.[13]

Macrocyclic compounds may have extraordinary properties because of the stereochemistry of the donor atoms and the size and shape of the central cavity.[14,15] Their polynuclear complexes hold promise in the study of catalysis, metalloenzyme mechanisms,[16−22] and molecular recognition[23−28] because of the high

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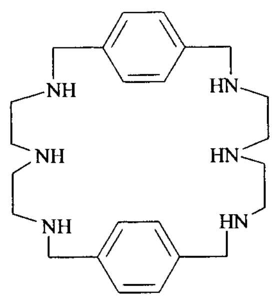
Table 1. Crystal Data Collection and Refinement Parameters for $[Pd_2\mathbf{L}I_2]I_2$

chem formula	fw 1131.00
$C_{24}H_{38}I_4N_6Pd_2$	space group $C2/c$ (No. 15)
$a = 16.881(3)$ Å	$T = 293(2)$ K
$b = 8.9716(12)$ Å	$\lambda = 0.710\ 73$ Å
$c = 23.055(5)$ Å	$\rho_{calcd} = 2.159$ g cm^{-3}
$\beta = 94.629(11)°$	$\mu = 46.04$ cm^{-1}
$V = 3480.3(11)$ Å^3	$R(F_o) = 0.0543^a$
$Z = 8$	$R_w(F_o) = 0.0783^a$

^{a} $R = \sum||F_o| - |F_c||/|F_o|$.

degree of preorganization brought about by metal binding. For example, the inclusion properties of macrocyclic compounds can be adjusted by controlling the ring size. In the macrocyclic polyamine 3,6,9,16,19,22-hexaazatricyclo[22.2.2.2^{11,14}]triacon-11,13,24,26(1),27,29-hexaene, designated **L**, two identical diethyl triamine moieties can be considered as the two arms of the large molecule. X-ray crystallography shows that the macrocycle **L** adopts a chairlike conformation, with one diethyl triamine moiety flipped up and the other flipped down.[29] The purpose of introducing the phenylene rings into the molecule is to import rigidity to the macrocycle. In this study the ligand **L** is used to synthesize binuclear palladium(II) complexes, which are then used as building blocks together with the bridging ligand oxalate, to construct novel tetranuclear complexes.



L

Results and Discussion

Structures of Two Bi-Pd(II) Complexes: $[Pd_2LI_2]I_2$ and $[Pd_2LCl_2](NO_3)_2 \cdot H_2O$. The conformation of the ligand in the two binuclear Pd(II) complexes was determined by X-ray crystallography.

$[Pd_2LI_2]I_2$. Crystallographic parameters are given in Table 1, and selected molecular dimensions, in Table 2. The molecular structure is shown in Figure 1. I(3), one of the two iodide counterions, was refined disordered with the sof (site occupancy factor) fixed at 0.5. Each Pd(II) atom is coordinated by three N atoms and one I^- ion in a somewhat distorted square-planar geometry. The three Pd−N bonds in length are equal (ca. 2.05 Å), and the Pd−I bond is somewhat longer (2.62 Å). The dihedral angle between the two N_3I coordination planes is 24.3°, and the mean deviation of these four ligand atoms in the coordination plane is 0.02 Å. The free macrocycle $\mathbf{L} \cdot 5H_2O$ adopts a chair conformation,[29] but $[Pd_2\mathbf{L}I_2]I_2$ adopts a boatlike conformation, with the two N_3I planes act as the stern. The two phenylene rings, with a dihedral angle of 73.6 °, act as the body of the boat. The distance between the two Pd(II) atoms is 6.85 Å. The dihedral angles between N_3I coordination plane and the two phenylene rings are 81.2 and 79.8°, respectively. The I(2) atom lies on the 2-fold axis and interacts with two N atoms [N(2) and N(2A)] to form two weak H---I bonds [H---I(2) is 2.66 Å; N−H---I(2) is 155°] inside the channel formed by the rings of the polyamine column. The coordinated I^- ions also engages in hydrogen bonding with the coordinated amino group (symmetry code B: $2 - x, -y, 1 - z$) in the symmetry-related molecule [I(1)---H(1CB), 2.70 Å; I(1)---H−N(1B), 168°], to form a one-dimensional chain along the c axis (Figure 2).

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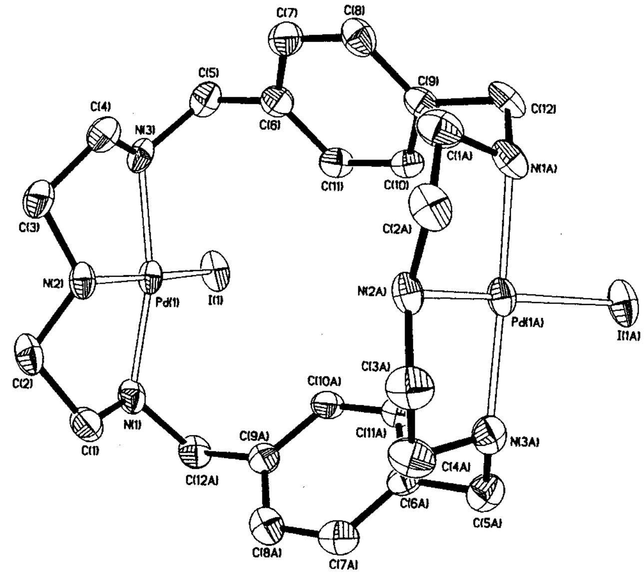

Figure 1. ORTEP drawing of $[Pd_2\mathbf{L}I_2]I_2$ molecule, top view. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $[Pd_2\mathbf{L}I_2]I_2$

Pd(1)−N(1)	2.052(11)	C(2)−N(2)	1.47(2)
Pd(1)−N(2)	2.040(10)	N(2)−C(3)	1.48(2)
Pd(1)−N(3)	2.061(11)	C(3)−C(4)	1.50(2)
Pd(1)−I(1)	2.6193(14)	C(4)−N(3)	1.48(2)
N(1)−C(1)	1.50(2)	N(3)−C(5)	1.50(2)
C(1)−C(2)	1.52(2)	C(5)−C(6)	1.50(2)
N(1)−Pd(1)−I(1)	95.8(3)	C(2)−N(2)−C(3)	116.4(11)
N(1)−Pd(1)−N(2)	84.2(4)	N(2)−C(3)−C(4)	106.3(11)
N(2)−Pd(1)−N(3)	83.5(4)	C(3)−C(4)−N(3)	109.3(12)
N(3)−Pd(1)−I(1)	95.6(3)	C(4)−N(3)−C(5)	110.6(11)
N(1)−C(1)−C(2)	108.8(12)	N(3)−C(5)−C(6)	113.3(11)
C(1)−C(2)−N(2)	106.3(11)	C(5)−C(6)−C(7)	119.0(13)

$[Pd_2LCl_2](NO_3)_2 \cdot H_2O$. For crystallographic details and salient molecular structure, see Tables 3 and 4, respectively. The structure of the title molecule resembles that of $[[Pd_2\mathbf{L}I_2]I_2$ (Figure S1). The dihedral angle between the two N_3Cl planes is 21.4°. Because the mean deviation of the two Pd atoms from their respective N_3Cl planes is only ca. 0.06 Å, the two coordination moieties are virtually planar. Evidently, the Pd(II) configuration in $[Pd_2\mathbf{L}Cl_2](NO_3)_2 \cdot H_2O$ is closer to square planar than that in $[Pd_2\mathbf{L}I_2]I_2$. The distance between the two Pd(II) atoms is 6.763 Å, slightly shorter than in $[Pd_2\mathbf{L}I_2]I_2$. The macrocyclic ligand in this complex also adopts a boatlike conformation, but the dihedral angle between the two phenylene rings is 57°, corresponding to a more flattened boat. The dihedral angles between the N_3Cl coordination plane and the two phenyl rings are 82 and 74°, respectively.

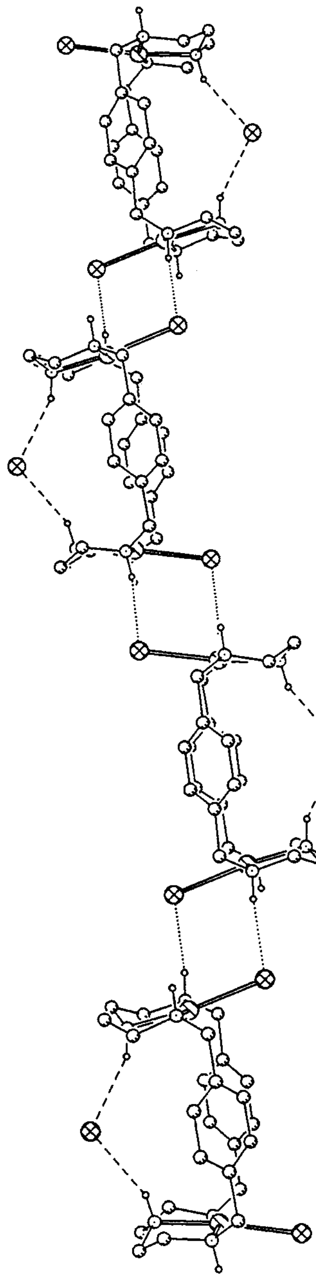

Figure 2. One-dimensional chain formed via hydrogen bonding, I(1)---H(1CB)−N(1B) (symmetry code B: $2 - x, -y, 1 - z$).

Table 3. Crystal Data Collection and Refinement Parameters for $[Pd_2\mathbf{L}Cl_2](NO_3)_2 \cdot H_2O$

chem formula $C_{24}H_{40}Cl_2N_8O_7Pd_2$	fw 836.34
	space group $P2/c$ (No. 13)
$a = 21.744(3)$ Å	$T = 293(2)$ K
$b = 9.2435(15)$ Å	$\lambda = 0.710\ 73$ Å
$c = 16.259(2)$ Å	$\rho_{calcd} = 1.703$ g cm^{-3}
$\beta = 93.580(9)°$	$\mu = 13.20$ cm^{-1}
$V = 3261.5(8)$ Å^3	$R(F_o) = 0.0722^a$
$Z = 4$	$R_w(F_o) = 0.1268^a$

^{a} $R = \sum||F_o| - |F_c||/|F_o|$.

In the structure, the O(82) atom of NO_3^- is inserted into the two N_3Cl planes and also interacts with N2 and N5 via hydrogen bonds [H(2N)---O(82A) (symmetry code A: $x, -y, -0.5 + z$), 2.15 Å; N(2)−H(2N)---O(82), 175 °; H(5N)---O(82A), 2.17 Å; N(5)−H(5N)---O(82A), 178°]. The two Cl^- ligands form hydrogen bonds with the amino groups of symmetry-related molecules [H(6N)---Cl(2B), 2.30 Å; N(6)−H(6N)---Cl(2B)- (symmetry code B: $1 - x, -1 - y, -1 - z$), 175 °; H(3N)---Cl(1C), 2.49 Å; N(3)−H(3N)---Cl(1C) (symmetry code C: $-x, -1 - y, -1 - z$), 163°]. This hydrogen bonding makes the complex molecules form one-dimensional chains along the *a* axis (Figure S2), as in $[[Pd_2\mathbf{L}I_2]I_2$. The multiple hydrogen bonds involving water, nitrate anions, and amino groups of the ligands (Table 5) act as the driving force for the self-assembly of the chain structure.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for $[Pd_2\mathbf{L}Cl_2](NO_3)\cdot H_2O$

Pd(1)−N(1)	2.052(10)	C(2)−N(2)	1.503(15)
Pd(1)−N(2)	2.007(8)	N(2)−C(3)	1.481(14)
Pd(1)−N(3)	2.046(9)	C(3)−C(4)	1.527(15)
Pd(1)−Cl(1)	2.313(3)	C(4)−N(3)	1.508(13)
N(1)−C(1)	1.493(14)	N(3)−C(5)	1.483(13)
C(1)−C(2)	1.552(16)	C(5)−C(6)	1.484(15)
N(1)−Pd(1)−Cl(1)	94.9(3)	C(2)−N(2)−C(3)	114.0(9)
N(1)−Pd(1)−N(2)	85.6(6)	N(2)−C(3)−C(4)	105.1(9)
N(2)−Pd(1)−N(3)	83.7(3)	C(3)−C(4)−N(3)	105.8(9)
N(3)−Pd(1)−Cl(1)	95.4(2)	C(4)−N(3)−C(5)	112.0(8)
N(1)−C(1)−C(2)	107.9(10)	N(3)−C(5)−C(6)	113.4(8)
C(1)−C(2)−N(2)	105.4(10)	C(5)−C(6)−C(7)	119.0(10)

Table 5. Hydrogen-Bonding Geometry (Å, deg) in Complex $[Pd_2\mathbf{L}Cl_2](NO_3)_2\cdot H_2O$

D−H---A	H---A	D---A	D−H---A
O1w−H1wA---O92^{i}	2.35	3.14(2)	155
O1w−H1wA---O91^{i}	2.16	2.860(14)	139
N3−H3N---Cl1^{iii}	2.49	3.369(9)	163
N4−H4N---O72^{ii}	2.27	3.078(14)	148
N5−H5N---O82^{ii}	2.17	3.080(15)	178
N6−H6N---Cl2^{iv}	2.30	3.210(9)	175
N2−H2N---O82^{ii}	2.15	3.062(14)	175

Factors Affecting the Conformation of $[Pd_2LI_2]I_2$ and $[Pd_2LCl_2](NO_3)_2\cdot H_2O$. The free macrocyclic ligand **L** adopts a chairlike conformation, and the flexible triamine moieties are flipped up and down with respect to the remainder of the ligand. The coordination to Pd(II) induces drastic conformation change of the ligand, which adopts a boatlike conformation in $[Pd_2\mathbf{L}I_2]I_2$ and $[Pd_2\mathbf{L}Cl_2](NO_3)_2\cdot H_2O$. The phenylene rings, which are parallel in $\mathbf{L}\cdot 5H_2O$, turn to form a dihedral angle, while the diethyl triamine moieties become flipped to the same side of the ligand. Moreover, the weak interaction between the anions inserted into the boat on one hand and N2 and N(2A) atoms on the other can stabilize this conformation. According to a conformation analysis by the simulation of EPR spectrum and molecular mechanics,[30] $[Cu_2\mathbf{L}](ClO_4)_4\cdot H_2O$ adopts a boatlike conformation in solution with the Cu−Cu distance of 6.9 Å. But in this copper complex the fold of the triamine plane from the rest of ligand molecule is much smaller than that in $[Pd_2\mathbf{L}I_2]I_2$ and $[Pd_2\mathbf{L}Cl_2](NO_3)_2\cdot H_2O$, and the molecule can be considered as roughly planar. In the structure of $[Cu_2\mathbf{L}(OAC)_2](ClO_4)_2\cdot 2H_2O$, which also takes a boatlike conformation,[31] each Cu is coordinated by three N atoms from **L** and one O atom from ACO^- in a square-planar geometry. The coordination planes are more perpendicular to the two phenylene rings than PdN_3X (X = I or Cl) planes to the phenylene rings in our case, and the intramolecular Cu−Cu distance 6.738 Å is a little bit smaller than those for Pd−Pd. While in the structure of $[Cu_2L(OAC)_2(H_2O)_2](ClO_4)_2$,[31] although Cu is coordinated in a distorted square-pyramidal geometry, it is still coordinated by three N

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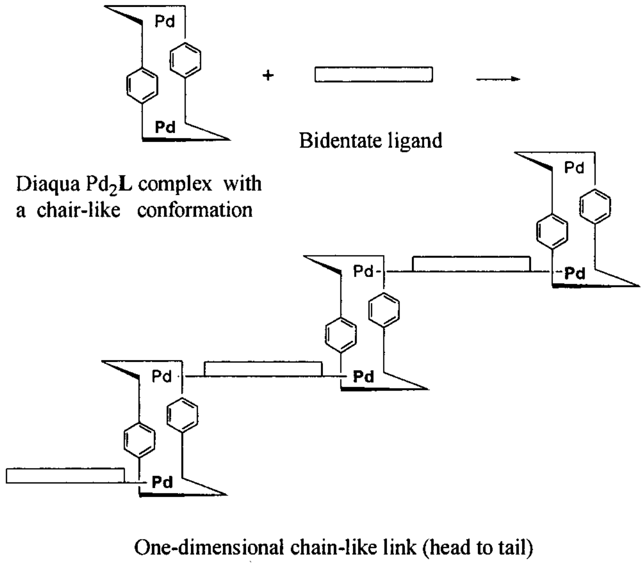
Scheme 1



Scheme 2

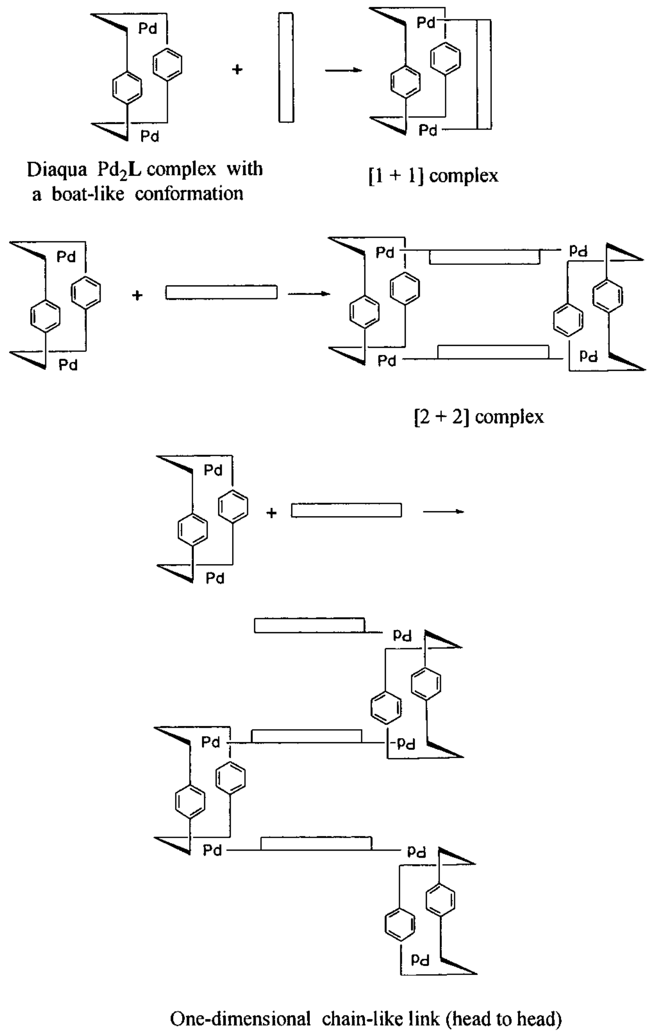
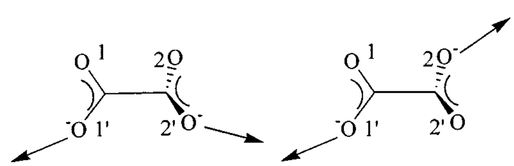


Chart 1



atoms from **L** and one O atom from ACO^- in a distorted square-planar geometry at basal plane, with one O atom from H_2O weakly coordinating to it at the axial site. It also takes a boatlike conformation. The binuclear Cu(II) complexes evidently has the similar conformation to the binuclear Pd(II) complexes.

It probably is the square-planar geometry of Pd(II) that is responsible for the boatlike conformation of our two palladium(II) complexes. In the chairlike conformation, the two phenylene rings are parallel. To meet the requirement of the square-planar coordination geometry, the adoption of a zigzag form of the diethyl triamine moieties will inevitably bring the two phenylene rings toward each other. This movement is unfavorable in view of the steric effect. But the macrocycle adopts a boatlike conformation just as in [[Pd_2**L**I_2]I_2 and [Pd_2**L**Cl_2]$(NO_3)_2 \cdot H_2O$, the two phenylene rings forming a dihedral angle to avoid the steric strain. As discussed below, the boatlike conformation may favor the formation of the [2 + 2] complex, especially when shorter bidentate ligands are used.

Construction of a Hydrophobic Open Molecular Box. Possible Structures: Introduction of Bidentate Oxalate Ligand. When the coordinating halide atoms in such binuclear Pd(II) complexes are replaced by bidentate ligands, various bridged complexes are possible. If the binuclear Pd(II) complex still adopts the chairlike conformation after binding of the bidentate ligands, the *head-to-tail* structure is possible because the rigid bidentate ligand cannot pass though the macrocyclic ring. If the binuclear Pd(II) complex adopts the boatlike conformation, besides the *head-to-head* form, the [1 + 1] and [2 + 2] complexes also become possible when a rigid bidentate ligand is introduced (Schemes 1 and 2).

To construct special molecular structures, especially the [2 + 2] form, we chose oxalate anion because it is a short bidentate ligand capable of two modes of coordination designated $O^{1'}$ $O^{2'}$ and $O^{1'}$ O^2 in Chart 1. If both oxygen atoms are coordinated to metal centers, many species may be expected in the experiment. When the coordination mode is $O^{1'}$ $O^{2'}$, the [1 + 1] or [2 +2] complexes may form, whereas $O^{1'}$ O^2 mode may yield a one-dimensional chainlike complex (Schemes 1 and 2).

To avoid rapid precipitation, the oxalate anions are supplied by the hydrolysis of diethyl oxalate in the aqueous solution of [Pd_2**L**$(H_2O)_m(NO_3)_n]^{(4-n)+}$ at pH ~ 2. This method for the crystal formation is similar to the diffusion method, because the oxalate anions are released slowly. Hydrolysis of diethyl oxalate, followed by ^1H NMR spectroscopy, obeys first-order kinetics with the observed rate constant of 1.72×10^{-3} min^{-1} at 40 °C, which is essentially similar to 1.75×10^{-3} min^{-1} for hydrolysis of diethyl oxalate in water at pH ~ 2.0. This agreement shows that the hydrolysis of diethyl oxalate in the presence of aqua Pd(II) complex is caused by H^+ ions.

Formation of the Aqua Complex Cations [$Pd_2L(H_2O)_m(NO_3)_n]^{(4-n)+}$ ($n = 0-4$). This aqua complex was formed from [Pd_2**L**I_2]I_2 and [Pd_2**L**Cl_2]Cl_2 by treatment with 4 mol equiv of $AgNO_3$ in aqueous solution. The acetic acid added to the reaction mixture product releases acetate anions, which react with [Pd_2**L**$(H_2O)_m(NO_3)_n]^{(4-n)+}$. The resulting acetate complexes are detected in the ESMS spectra (Figure S3). The ESMS spectra of the aqua complexes obtained from [Pd_2**L**I_2]I_2 and from [Pd_2**L**Cl_2]Cl_2 are identical. There are only two main clusters of peaks at $m/z \sim 371$ and $m/z \sim 806$. The zoom scan spectra for the main cluster of peaks and the corresponding calculated isotope patterns indicate that the observed peaks with m/z = 368.4−374.9 separated by 0.5 m/z fit quite well to those calculated for [Pd_2**L**$(CH_3COO)_2]^{2+}$. The peaks at $m/z \sim 806$

Table 6. Crystal Data Collection and Refinement Parameters for $[Pd_4\mathbf{L}_2(C_2O_4)_2](NO_3)_4{\cdot}6H_2O$

chem formula $C_{52}H_{88}I_4N_{16}O_{26}Pd_4$	fw 1778.98
$a = 9.6960(19)$ Å	space group $P\bar{1}$ (No. 2)
$b = 13.320(3)$ Å	$T = 293(2)$ K
$c = 14.605(3)$ Å	$\lambda = 0.710\,73$ Å
$\alpha = 93.30(3)°$, $\beta = 90.63(3)°$, $\gamma = 104.05(3)°$	$\rho_{calcd} = 1.618$ g cm^{-3}
	$\mu = 10.54$ cm^{-1}
$V = 1826.2(6)$ Å^3	$R(F_o) = 0.0496^a$
$Z = 1$	$R_w(F_o) = 0.0847^a$

^{a} $R = \sum||F_o| - |F_c||/|F_o|$.

Table 7. Selected Bond Lengths (Å) and Bond Angles (deg) for $[Pd_4\mathbf{L}_2(C_2O_4)_2](NO_3)_4{\cdot}6H_2O$

Pd(1)−N(1)	2.051(4)	C(1)−C(2)	1.490(7)
Pd(1)−N(2)	1.992(4)	C(2)−N(2)	1.481(7)
Pd(1)−N(3)	2.056(4)	N(2)−C(3)	1.497(7)
Pd(1)−O(3A)	2.040(3)	C(3)−C(4)	1.489(8)
Pd(2)−N(4)	2.061(4)	C(4)−N(3)	1.503(7)
Pd(2)−N(5)	1.993(4)	N(3)−C(5)	1.490(7)
Pd(2)−N(6)	2.045(4)	C(5)−C(6)	1.497(7)
Pd(2)−O(1)	2.027(3)	N(1)−C(24)	1.504(7)
N(1)−C(1)	1.494(7)		
N(1)−Pd(1)−O(3A)	177.35(15)	C(2)−N(2)−C(3)	116.9(4)
N(1)−Pd(1)−N(2)	84.52(17)	C(5)−C(6)−C(7)	120.0(5)
N(2)−Pd(1)−N(3)	84.68(17)	N(2)−C(3)−C(4)	106.6(4)
N(3)−Pd(1)−O(3A)	96.93(15)	C(3)−C(4)−N(3)	109.2(4)
N(4)−Pd(2)−N(5)	85.01(17)	C(4)−N(3)−C(5)	113.0(4)
N(5)−Pd(2)−N(6)	84.07(17)	N(3)−C(5)−C(6)	113.4(4)
N(6)−Pd(2)−O(1)	95.23(16)	N(6)−C(17)−C(18)	112.4(4)
O(1)−Pd(2)−N(4)	95.99(16)	C(1)−C(2)−N(2)	107.0(5)
N(1)−C(1)−C(2)	108.2(5)		

can be attributed to $\{[Pd_2\mathbf{L}(CH_3COO)_2](NO_3)\}^+$. In the absence of acetic acid, the ESMS spectrum of the reaction mixture product is complicated and difficult to assign, probably because of the weak ligands such as NO_3^-, H_2O, or CH_3OH coordinate to Pd(II) competitively, giving rise to many cationic species $[Pd_2\mathbf{L}(H_2O)_m(NO_3)_n]^{(4-n)+}$. The counteranions can be NO_3^-. Since the boatlike conformation is formed in the crystal structure of $[Pd_4\mathbf{L}_2(C_2O_4)_2](NO_3)_4{\cdot}6H_2O$ (see below), $[Pd_2\mathbf{L}(H_2O)_m(NO_3)_n]^{(4-n)+}$ may also adopt the boatlike conformation in solution.

Formation of the [2 + 2] Complex: Structure of $[Pd_4L_2(C_2O_4)_2](NO_3)_4{\cdot}6H_2O$. The complex $[Pd_2\mathbf{L}(H_2O)_m(NO_3)_n]^{(4-n)+}$ and diethyl oxalate are mixed in aqueous solution in a molar ratio of 1:1 for 2 days at 40 °C. The product is $[Pd_4\mathbf{L}_2(C_2O_4)_2](NO_3)_4{\cdot}6H_2O$, a tetranuclear complex that may be considered a product of a [2 + 2] condensation of two binuclear complexes.

Crystallographic parameters are given in Table 6, selected molecular dimensions are listed in Table 7, and the molecular structure is shown in Figure 3. In this molecule, there are two identical moieties, each containing one macrocyclic ligand and two Pd(II) atoms. Each Pd(II) atom is bonded to three N atoms from the same lateral arm of the ligand and an oxygen atom of the oxalate bridging ligand. The two moieties are connected by two oxalate anions, each spanning a pair of Pd(II) atoms. The mean deviations of Pd(II) from the N_3O coordination planes are ca. 0.07 Å on the average, evidence that the configuration geometry of Pd(II) in $[Pd_4\mathbf{L}_2(C_2O_4)_2](NO_3)_4{\cdot}6H_2O$ is closer to square planar than that in $[Pd_2\mathbf{L}I_2]I_2$. Both macrocyclic polyamine ligands adopt boatlike conformations. In both ligands the phenylene rings form dihedral angles of 66.6°. The dihedral angle between the two N_3O coordination planes is 10°. The Pd1−Pd2 and Pd1−Pd2A distances are 6.73 and 6.72 Å, respectively. Therefore, the whole molecule looks like a box.

In the crystal, there are many hydrogen bonds involving the disordered water molecule, disordered NO_3^- ions, the amino groups, and the bridging oxalate anions. Especially important one is N(3)−H(3C)---O(4B) (symmetry code B: x, $1 + y$, z) [H(3C)---O(4), 2.05 Å; N(3)−H(3C)---O(4), 156°]. These hydrogen bonds array the boxes into a one-dimensional chain (Figure 4). The chains may be connected via two kinds of $\pi-\pi$ stacking shown in Figure 5 to form two-dimensional structure. One such interaction involves the phenylene ring defined by C(6) to C(11) and symmetry-related ring. The vertical separation is 3.37 Å, and the shorter interplanar atom-to-atom separation is ca. 3.39 Å [C(8)---C(8C) (symmetry code C: $-x$, $-1 - y$, $2 - z$)].

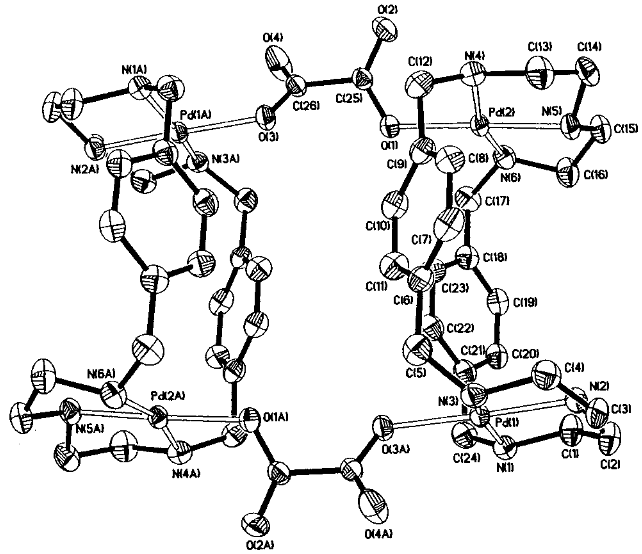


Figure 3. ORTEP drawing of $[Pd_4\mathbf{L}_2(C_2O_4)_2](NO_3)_4{\cdot}6H_2O$ molecule. Hydrogen atoms are omitted for clarity.

In the molecular box, the quadrilateral cavity is composed of the four phenylene rings (Figure S4a,b). Moreover, each $Pd_2\mathbf{L}$ unit is connected in the form of a wedge in it with the diagonal phenylene rings parallel and the dihedral angles between the neighbor phenylene rings being 66.6°. The four phenylene rings make the molecular box hydrophobic and potentially capable of forming inclusion compounds with suitable organic molecules as guests. These compounds and molecular recognition that they may provide will be the subject of our future study.

Experimental Section

All the common chemicals were of analytical grade. Melting points are uncorrected. ^{1}H NMR spectra were obtained with a Bruker AM 500 spectrometer. Elemental analyses were performed on Perkin-Elmer 240C instrument. Molecular masses were determined by electrospray mass spectrometer (LCQ, Finnigan) in positive mode.

Preparation of the Title Ligand L and Its Polynuclear Metal Complexes. The macrocyclic ligand $C_{24}H_{38}N_6$ was synthesized by an improved published procedure.[29,32] The product was recrystallized from CH_3CN before use, mp 146−147 °C. ^{1}H NMR (D_2O, DSS): 7.31 (m, 8H, *Ar H*), 3.66 (s, 8H, Ar−*CH₂*), 2.59 (m, 16H, NH−*CH₂*). Anal. Calcd for $C_{24}H_{38}N_6$: C, 70.20; H, 9.33; N, 20.47. Found: C, 70.11; H, 9.50; N, 20.30. ESMS data are as follows. Measured m/z values: $[M + H]^+$, 411.5, 412.5, 413.5; $[M + 2H]^{2+}$, 206.3, 206.8, 207.1. Calcd m/z values: 411.3, 412.3, 413.3; 206.2, 206.7, 207.2.

$[Pd_2LCl_2]Cl_2$. A 300 mg (0.73 mmol) amount of **L** was dissolved in 120 mL of CH_3OH, and 324.9 mg (1.83 mmol) of $PdCl_2$ powder was added. The mixture was refluxed for 8 h with stirring. A solid was filtered off after 12 h, and a yellow solution was obtained. After removal of solvent in vacuo, the solid residue was dissolved in methanol, and the solution was filtered again. Then the filtrate was

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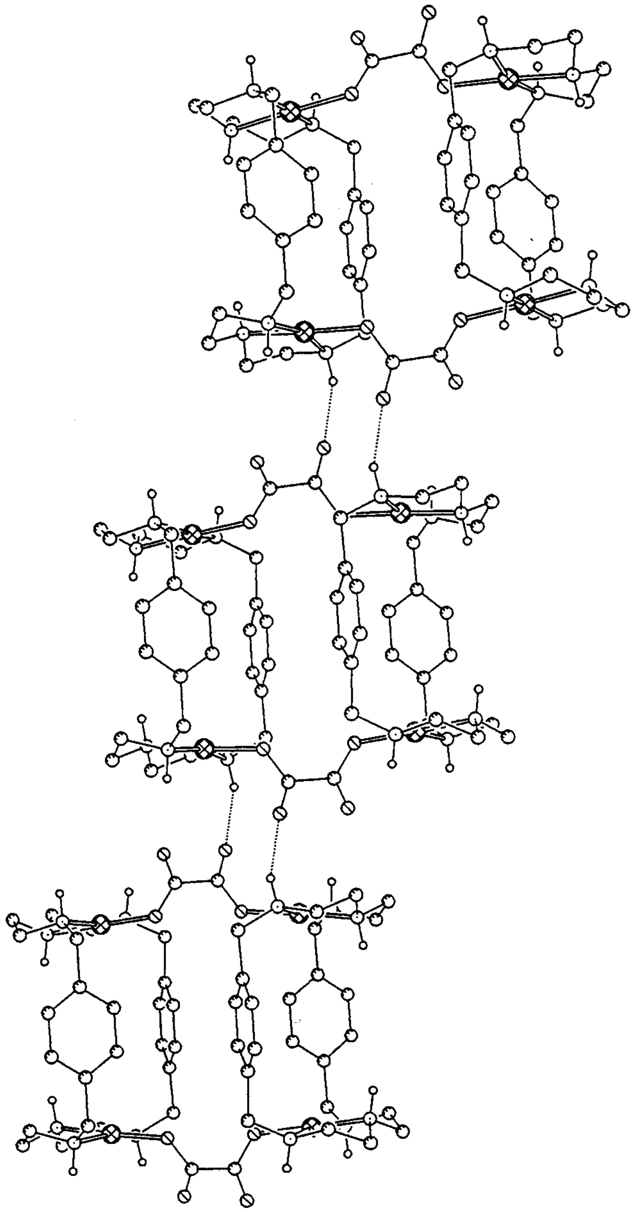

Figure 4. One-dimensional chain formed via hydrogen-bonding N(3)−H(3C)---O(4B) (symmetry code B: *x*, 1 + *y*, *z*).

evaporated in vacuo, and the concentrated solution was stored in a refrigerator overnight. The obtained yellow crystals quickly turned into yellow powder. Yield: 82%. Anal. Calcd for $C_{24}H_{38}N_6Cl_4Pd_2$: C, 37.67; H, 5.01; N, 10.98. Found: C, 37.52; H, 5.28; N, 11.15. ESMS data are as follows. Measured *m*/*z* values: $[Pd_2\mathbf{L}Cl_2]^{2+}$, 343.6, 344.2, 344.7, 345.1, 345.6, 346.1, 346.6, 347.1, 347.6, 348.1, 348.6, 349.1, 349.6, 350.1, 350.6; $[Pd_2\mathbf{L}Cl_3]^+$, 724.1, 725.1, 726.1, 727.1, 728.0, 729.1, 730.1, 731.1, 732.1, 733.1, 734.1, 735.1, 736.0, 736.9. Calcd *m*/*z* values: $[Pd_2\mathbf{L}Cl_2]^{2+}$, 343.5, 344.0, 344.5, 345.0, 345.5, 346.0, 346.5, 347.0, 347.5, 348.0, 348.5, 349.0, 349.5, 350.0, 350.5; $[Pd_2\mathbf{L}Cl_3]^+$, 724.0, 725.0, 726.0, 727.0, 728.0, 729.0, 730.1, 731.1, 732.1, 733.1, 734.1, 735.1, 736.1, 737.1.

$[Pd_2\mathbf{L}I_2]I_2$. The yellow solution of $[Pd_2\mathbf{L}Cl_2]Cl_2$ was cooled in an ice−water bath, and 1.3 g of KI was added slowly, with stirring. After standing for 24 h, the solution was filtered, and the filtrate was slowly evaporated. Orange yellow crystals suitable for crystallographic analysis were obtained. Yield: 71%. Anal. Calcd for $C_{24}H_{38}N_6I_4Pd_2$: C, 25.49; H, 3.39; N, 7.43. Found: C, 25.21; H, 3.58; N, 7.25, ESMS data are as follows. Measured *m*/*z* values: $[Pd_2\mathbf{L}I_3]^+$, 999.0, 1000.0, 1001.0, 1002.0, 1003.1, 1004.1, 1005.0, 1006.0, 1006.9, 1007.9,1008.9,1010.0. Calcd *m*/*z* values: $[Pd_2\mathbf{L}I_3]^+$, 998.8, 999.8, 1000.8, 1001.8, 1002.8, 1003.8, 1004.8, 1005.8, 1006.8, 1007.8,1008.8,1009.8.

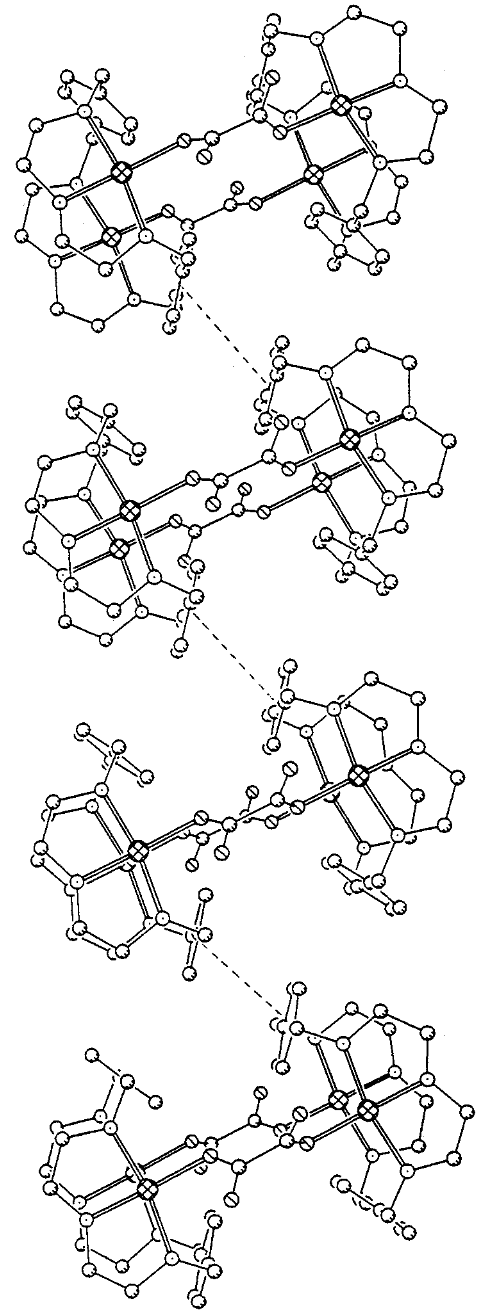

Figure 5. Simple stacking drawing in which the one-dimensional chains are connected via two kinds of $\pi-\pi$ stacking.

$[Pd_2\mathbf{L}Cl_2](NO_3)_2\cdot H_2O$. The complex was obtained by partial dehalogenation of $[Pd_2\mathbf{L}Cl_2]Cl_2$ by addition of 2 mol equiv of $AgNO_3$ in aqueous solution. The mixture was stirred in the dark for 5 h at 30 °C. After removal of AgCl by centrifugation, the resulting clear solution was slowly evaporated at room temperature, and pale-yellow crystals were collected.

$[Pd_4\mathbf{L}_2(C_2O_4)_2](NO_3)_4\cdot 6H_2O$. A 74 μL amount of 0.5 M $AgNO_3$ aqueous solution was added to 7.0 mg of $[Pd_2\mathbf{L}Cl_2]Cl_2$ in 840 μL of water. White precipitate of AgCl formed at once, and the mixture was stirred at 35 °C for 5 h in dark. After centrifugation, a clear yellow solution was obtained and stored at 4 °C. Such a solution can also be obtained from $[Pd_2\mathbf{L}I_2]I_2$ in a similar procedure (see below). A 400 μL amount of this solution was mixed with 150 μL of a 26.7 mM aqueous solution of diethyl oxalate. The mixture was kept at room temperature for 2 days, and needle crystals suitable for X-ray crystal analysis formed. Yield: 81.5%. Anal. Calcd for $C_{52}H_{88}N_{16}O_{26}Pd_4$: C, 35.11; H, 4.99; N, 12.60. Found: C, 35.28, H, 5.10, N, 12.88.

$Pd_2\mathbf{L}(NO_3)_4$ ($[Pd_2\mathbf{L}(H_2O)_m(NO_3)_n]^{(4-n)+}$). A mixture of $[Pd_2\mathbf{L}Cl_2]$-Cl_2 or $[Pd_2\mathbf{L}I_2]I_2$ and 4 equiv of $AgNO_3$ in aqueous solution was stirred at 35 °C for 5 h in dark. After centrifugation, a 40 mM solution of the aqua complex was obtained. A 10 μL amount of this solution was diluted by 200 μL of water, and 2 μL of acetic acid was then added. A 2 μL amount of this solution was taken out for ESMS analysis.

Crystallography. Intensities of $[Pd_2\mathbf{L}I_2]I_2$ and $[Pd_2\mathbf{L}Cl_2](NO_3)_2{\cdot}H_2O$ were collected on a Siemens P4 diffractometer with graphite-monochromatic Mo Kα radiation ($\lambda = 0.710\,73$ Å) using the $\omega-2\theta$ scan mode. Data were corrected for Lorentz-polarization effects during data reduction using XSCANS,[33] and a semiempirical absorption correction from Ψ-scans was applied. Intensities of $[Pd_4\mathbf{L}_2(C_2O_4)_2](NO_3)_4{\cdot}6H_2O$ were collected on an Enraf-Nouris CCD system with graphite-monochromatic Mo Kα radiation ($\lambda = 0.710\,73$ Å).[34] Data were reduced using HKL Denzo and maXus program,[35] and a semiempirical absorption correction from Ψ-scans was applied.[36] The structures were solved by direct methods and refined on F^2 using full-matrix least-squares methods using SHELXTL version 5.0.[37] Anisotropic thermal parameters were refined for non-hydrogen atoms. Hydrogen atoms of cations were located in the calculated position and refined using riding model. Hydrogen atoms of lattice water molecules were found from difference Fourier maps but were refined using riding model.

Electrospray Mass Spectrometry. An LCQ electrospray mass spectrometer (ESMS, Finnigan) was used to determine molecular masses of polynuclear Pd(II) complexes with macrocyclic polyamine and their aqua derivatives. Samples dissolved in methanol were diluted to 100 μmol L^{-1}. A 1.0 or 2.0 μL aliquot of this solution was loaded into the injection valve of the LCQ unit and then injected into the mobile phase (CH_3OH) and carried through the electrospray interface into the mass analyzer at a rate of 200 μL min^{-1}. The applied voltage at the electrospray needle was 5 kV, and the capilliary was heated to 200 °C. A maximum ion injection time of 200 ms along with 10 scans was used in these experiments. The predicted isotope distribution patterns for each complex cations were calculated using the IsoPro 3.0 program.

Kinetics of Hydrolysis of Diethyl Oxalate. The hydrolytic product, C_2H_5OH, was monitored by ^{1}H NMR spectroscopy. The total volume in the NMR tube was 500 μL. The sample contained 300 μL of 25 mM $[Pd_2\mathbf{L}(H_2O)_m(NO_3)_n]^{(4-n)+}$, 150 μL of 50 mM diethyl oxalate, and 5 μL of 100 mM DDS as internal reference. The acquisition of the spectra began as quickly as possible and continued every 1 h. The reaction was monitored for 3 half-lives. The hydrolysis of diethyl oxalate, promoted by $DClO_4$ instead of $[Pd_2\mathbf{L}(H_2O)_m(NO_3)_n]^{(4-n)+}$, was monitored in the same way. Total volume of the sample was 500 μL. It contained 150 μL of 50 mM diethyl oxalate, 25 μL of 100 mM $DClO_4$, and 5 μL of 100 mM DDS.

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Supporting Information Available: An ORTEP drawing of the $[Pd_2\mathbf{L}Cl_2](NO_3)_2{\cdot}H_2O$ molecule (Figure S1), the one-dimensional chain formed via hydrogen bonding in the crystal of $[Pd_2\mathbf{L}Cl_2](NO_3)_2{\cdot}H_2O$ (Figure S2), the ESMS spectra of $[Pd_2\mathbf{L}(H_2O)_m(NO_3)_n]^{(4-n)+}$ (Figure S3), the relationship among the four phenyl rings in the same box $[Pd_2\mathbf{L}Cl_2](NO_3)_2{\cdot}H_2O$ (Figure S4), and CIF files of $[Pd_2\mathbf{L}I_2]I_2$, $[Pd_2\mathbf{L}Cl_2](NO_3)_2{\cdot}H_2O$, and $[Pd_2\mathbf{L}(C_2O_4)](NO_3)_4{\cdot}6H_2O$ (Figures S5-S7). This material is available free of charge via the Internet at http://pubs.acs.org.

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