

Article

Synthesis and Crystal Structures of Rhomb-Shaped Dimeric Pd(II) Complexes with Arylethynyl-Substituted 2,2'-Bipyridine through $\text{CH} \cdots \pi$ Interactions in the Crystalline States

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Abstract: Two molecular structures of a complex $\text{C}_{26}\text{H}_{16}\text{Cl}_2\text{N}_2\text{Pd}$ (**1**) with a benzene hemisolvate ($1 \bullet 0.5\text{C}_6\text{H}_6$) and a complex $\text{C}_{34}\text{H}_{20}\text{Cl}_2\text{N}_2\text{Pd}$ (**2**) revealed similar conformations: one side of the arylethynyl group is flat to the bipyridine plane while the other side of the arylethynyl group is highly twisted to the plane because rhomb-like dimer fragments are formed between respective two complexes through $\text{CH} \cdots \pi$ interactions. The Hirshfeld surface analysis indicates that the most important contributions for the crystal packing of **1** are from $\text{H} \cdots \text{H}$ (33.6%), $\text{C} \cdots \text{H}/\text{H} \cdots \text{C}$ (28.3%), $\text{Cl} \cdots \text{H}/\text{H} \cdots \text{Cl}$ (17.8%), and $\text{C} \cdots \text{C}$ (10.6%) interactions and those of **2** are from $\text{H} \cdots \text{H}$ (36.5%), $\text{C} \cdots \text{H}/\text{H} \cdots \text{C}$ (26.0%), $\text{Cl} \cdots \text{H}/\text{H} \cdots \text{Cl}$ (15.7%), and $\text{C} \cdots \text{C}$ (12.3%) interactions, indicating the remarkable $\text{CH} \cdots \pi$ and electron distribution of molecules by Cl ions. The benzene solvate molecule of $1 \bullet 0.5\text{C}_6\text{H}_6$ performs to fill the internal space instead of the naphthyl group. Detailed crystallographic and DFT studies were performed to understand the molecular structures and the corresponding supramolecular associations.

Keywords: bipyridine derivative; $\text{CH} \cdots \pi$ interaction; crystal engineering; DFT calculations; palladium



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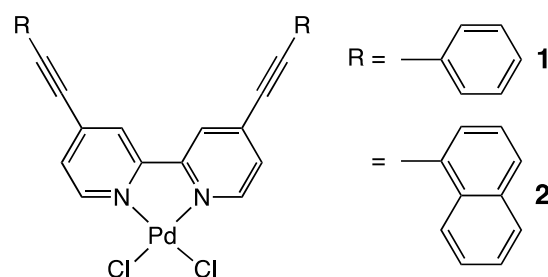
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1. Introduction

Bipyridine (bpy) derivatives have been an attractive target for their unique photo activities and for the applications of the related coordination materials [1–5]. Especially, metal arrays of bipyridine derivatives in the solid states are intriguing due to color exchanges by external conditions [6–9]. The metal characteristic with electron surface potentials (ESP) is also an important driving force for molecular arrangements in solids toward crystal engineering. The Pt^{2+} [10] and Pd^{2+} [11] centers of square-planar metal complexes can act as halogen-bond acceptors upon their interaction with σ -donating organohalides, and the complexes are co-crystallized with π -donating perfluoroaromatic species giving the sandwich structures based on π -hole $\cdots \pi$ interactions [12,13] when the nucleophile metal center and electron-poor molecule are opposite charge distributions [14]. We reported that the supramolecular association of square-planar Pt^{2+} , Pd^{2+} , and Cu^{2+} β -diketonate complexes [15,16], which nucleophile characteristics of Pt^{2+} and Pd^{2+} are clearly shown in the results of their crystal packings in the solid state and DFT calculations. The axial surface on the Pt^{2+} center in complexes shows high negative ESP and nucleophile that on Pd^{2+} center remarkably changed the surrounding substitutions, e.g., the negative value for $[\text{Pd}(\text{dbm})_2]$ and neutral~positive for the corresponding perfluorinated complex, $[\text{Pd}(\text{L})_2]$ (L = bis(pentafluorobenzoyl)methanido[−]), indicating the possibility of strict adjustment of the metal characteristics [15]. Such fields prompted us to develop the investigation of 4,4'-di(phenylethynyl)-2,2'-bipyridine (L^1), which forms a 1:1 cocrystal with 4,4'-bis(pentafluorophenylethynyl)-2,2'-bipyridine to give alternately stacking materials [17] through π -hole $\cdots \pi$ interactions [18,19].

The complexation and molecular recognition events of such bipyridine derivatives fascinate us while also promoting the understanding of the driving forces of aggregation and the corresponding weak interactions by crystallographic studies. In such molecular recognition strategies, it is necessary to have a flexible molecular design that allows the molecule itself to undergo thermodynamic stabilization due to intermolecular interactions. One effective method to achieve this goal is the incorporation of ethynyl linkers between aromatic rings, which generally permits rotation without steric hindrance, making it challenging to control the intramolecular stereo-conformation between the phenyl groups and the bipyridine moiety of L^1 . Such free rotation within the molecule has the potential to hinder photo activities and host functions in both solution and solid states but can also lead to interesting packing structures influenced by intermolecular interactions and external stimuli from a crystallographic perspective [17,20,21].

In this subject, we synthesized and found the molecular structure of $[\text{PdCl}_2(L^n)]$ (**1**), as shown in Scheme 1, in which one phenyl group is flat with respect to a plane of the bipyridine moiety and the other phenyl group is highly twisted, and each phenyl group forms a rhomb-like arrangement by two compounds through intermolecular $\text{CH} \cdots \pi$ interactions [22,23] in the single crystal of **1**•0.5C₆H₆. Thus, we synthesized a naphthalene derivative, 4,4'-di(naphthalen-1-ylethynyl)-2,2'-bipyridine (L^2), and the crystal of the corresponding Pd complex, $[\text{PdCl}_2(L^2)]$ (**2**), to confirm that the similar arrangement is a common stabilized structure of the motifs in crystal. In this report, we describe the syntheses and the detailed crystal structures of **1**•0.5C₆H₆ and **2** (Scheme 1), which were crystallized in a benzene-acetone solution to give pale yellow crystals and orange crystals, respectively. In a benzene-dimethylsulfoxide (dmsO) solution, the same crystals were obtained.



Scheme 1. Molecular structures of **1** and **2**.

2. Materials and Methods

2.1. General

All the chemicals were of reagent grade and used without further purification. The compounds of L^1 and $[\text{PdCl}_2(\text{dmsO})_2]$ were prepared by the previously reported protocol [17]. The ^1H NMR spectral data were recorded by a Bruker DRX600 (Bruker Japan, Yokohama, Japan) or JEOL ECS400 (JEOL Ltd., Tokyo, Japan) spectrometer. The melting points were determined by a Yanako MP-500D melting point apparatus (Yanako, Kyoto, Japan). IR spectra were measured by Shimadzu FTIR-8400S with a KBr disk spectrophotometer (Shimadzu Co., Kyoto, Japan). The results of the elemental analysis (EA) of C and H were determined by a Perkin-Elmer PE2400 analyzer (PerkinElmer Japan G.K., Yokohama, Japan). The DFT calculations were performed by the Spartan'18 package (V1.3.0, Wavefunction Inc., Tokyo, Japan) with B3LYP/6-31G* [24,25].

2.2. Synthesis and Crystallization

Preparation of L^2 . This was prepared by the general procedure of the Sonogashira coupling reaction [17,26,27]. Excess amounts of triethylamine (10 mL) were added into the mixture of 4,4'-dibromo-2,2'-bipyridine (0.640 mmol), CuI (0.016 mmol), and $[\text{PdCl}_2(\text{PPh}_3)_2]$ (0.016 mmol) in N₂ atmosphere. A triethylamine solution (3 mL) of 1-ethynynaphthalene (1.920 mmol, 3 eq.) was added to the mixture, and the solution was refluxed for 8 h. The residue was purified by column chromatography (silica, 20:1 CHCl₃-CH₃OH) and GPC to

give a pale yellow powder (yield 83%); m.p. 221–222 °C; E.A.: Calcd for C, 89.45; H, 4.42%; N, 6.14%; Found C, 89.17%; H, 4.29%; N, 6.20%; ^1H NMR (600 MHz, CDCl_3 , TMS): δ 8.76 (d, J = 5.1 Hz, Py, 2H), 8.68 (s, Py, 2H), 8.46 (d, J = 8.1 Hz, Ar, 2H), 7.92 (d, J = 8.1 Hz, Ar, 2H), 7.90 (d, J = 8.1 Hz, Ar, 2H), 7.83 (d, J = 8.1 Hz, Ar, 2H), 7.66 (t, J = 8.1 Hz, Ar, 2H), 7.58 (t, J = 8.1 Hz, Ar, 2H), 7.56 (d, J = 5.1 Hz, Py, 2H), 7.51 (t, J = 8.1 Hz, Ar, 2H); DI-MS: 456 m/z (M^+).

Compounds **1** and **2** were synthesized in one step using the corresponding ligands, L^1 [17] and L^2 (described below), respectively, with $[\text{PdCl}_2(\text{dmsO})_2]$. Typically, the ligand (0.02 mmol) was dissolved in benzene (5 mL), and the solution was added into an acetone solution of $[\text{PdCl}_2(\text{dmsO})_2]$ (0.02 mmol) for **1** [or into a dmsO solution of $[\text{PdCl}_2(\text{dmsO})_2]$ (0.02 mmol) for **2**]. The yellow single crystals of **1** and orange single crystals of **2** were quickly grown in the solution.

Complex **1**: yield 71%; m.p. > 335 °C (dec.); ^1H NMR (400 MHz, DMSO, TMS): δ 9.12 (d, J = 6.1 Hz, Py, 2H), 8.89 (s, Py, 2H), 7.91 (d, J = 6.1 Hz, Py, 2H), 7.67 (d, J = 7.4 Hz, Ar, 4H), 7.52 (m, Ar, 6H); IR (KBr disk, cm^{-1}): 2216, 2200, 2189, 1612, 1531, 1494, 1473, 1417, 1029, 837, 761, 688.

Complex **2**: yield 78%; m.p. > 375 °C (dec.); ^1H NMR (400 MHz, DMSO, TMS): δ 9.19 (d, J = 6.0 Hz, Py, 2H), 9.09 (s, Py, 2H), 8.51 (d, J = 7.9 Hz, Ar, 2H), 8.17 (d, J = 7.9 Hz, Ar, 2H), 8.11 (d, J = 6.0 Hz, Py, 2H), 8.10 (d, J = 7.9 Hz, Ar, 2H), 8.02 (d, J = 7.9 Hz, Ar, 2H), 7.79 (t, J = 7.9 Hz, Ar, 2H), 7.70 (t, J = 7.9 Hz, Ar, 2H), 7.67 (t, J = 7.9 Hz, Ar, 2H); IR (KBr disk, cm^{-1}): 2204, 1608, 1533, 1508, 1483, 1423, 1411, 1396, 802, 771.

2.3. Crystal Structure Determination

The single crystal X-ray structures were determined by a Bruker SMART APEX CCD diffractometer (Bruker Japan, Yokohama, Japan) with a graphite monochromator and $\text{MoK}\alpha$ radiation (λ = 0.71073 Å) generated at 50 kV and 30 mA. Crystals **1**•0.5 C_6H_6 and **2** were coated by paratone-N oil and measured at 100 and 120 K, respectively. SHELXT program was used for solving the structures [28]. Refinement and further calculations were carried out using SHELXL 2016 [29]. The crystal data and structure refinement of **1**•0.5 C_6H_6 and **2** are summarized in Table 1. All H atoms were placed in geometrically idealized positions and refined as riding, with aromatic C–H = 0.95 Å and $U_{\text{iso}}(\text{H})$ = 1.2 $U_{\text{eq}}(\text{C})$. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (accessed on 19 February 2024).

Table 1. Crystal data and structure refinement for **1**•0.5 C_6H_6 and **2**.

	1 •0.5 C_6H_6	2
Chemical formula	$\text{C}_{29}\text{H}_{19}\text{Cl}_2\text{N}_2\text{Pd}$	$\text{C}_{34}\text{H}_{20}\text{Cl}_2\text{N}_2\text{Pd}$
Formula weight	572.76	633.82
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P-1$
a [Å]	11.950(4)	8.019(3)
b [Å]	11.726(4)	8.623(4)
c [Å]	17.388(6)	19.261(8)
α [°]	90	102.519(5)
β [°]	104.727(3)	92.193(5)
γ [°]	90	93.798(5)
V [Å ³]	2356.4(13)	1295.5(9)
Z	4	2
D_c [Mg m^{-3}]	1.614	1.625
μ [mm^{-1}]	1.04	0.95
$F(000)$	1148	636
R_{int}	0.0264	0.0341
GOF	1.038	1.039
R [$(I) > 2\sigma(I)$]	0.0212	0.0321
wR (F_o^2)	0.0541	0.0730
CCDC No.	2031735	2031736

3. Results and Discussion

3.1. Preparations of **1** and **2**

4,4'-Di(naphthalen-1-ylethynyl)-2,2'-bipyridine (L^2) was prepared by Sonogashira coupling reaction [17] to yield a pale yellow powder in 83%. Complexations of **1** and **2** were examined in a one-step reaction with the corresponding ligand and $[\text{PdCl}_2(\text{dmsO})_2]$ in several solvents. The yellow and orange precipitates of **1** and **2**, respectively, of low solubility products quickly grew in the solution as a single product. The single crystals of $\mathbf{1} \cdot 0.5\text{C}_6\text{H}_6$ and **2** were obtained from a benzene-acetone solution suitable for single-crystal X-ray crystallographic studies.

3.2. Crystal Structure and Intermolecular Interactions of $\mathbf{1} \cdot 0.5\text{C}_6\text{H}_6$

The ORTEP views of $\mathbf{1} \cdot 0.5\text{C}_6\text{H}_6$ and **2** are shown in Figure 1a and Figure 3a, respectively, with the numbering schemes. In the crystal of $\mathbf{1} \cdot 0.5\text{C}_6\text{H}_6$, the asymmetric unit contains a whole complex and one half of benzene (Figure 1). The complex comprises one Pd^{2+} ion, two Cl ions, and one ligand (L^1) to give a mononuclear complex. The solvate benzene comprises $\text{C}27\text{--C}28\text{--C}29\text{--C}27^i\text{--C}28^i\text{--C}29^i$ [symmetry code: (i) $-x, -y + 1, -z + 1$]. The geometry around the metal center in **1** is pseudo-square planar. The bond distances of Pd1--N1 , Pd1--N2 , Pd1--Cl1 , and Pd1--Cl2 are 2.0180(16), 2.0287(16), 2.2884(7), and 2.2844(7) Å, respectively. Two pyridine planes (*rings-A* and *C*) are highly flat [the torsion angle of N1--C5--C14--N2 is $-3.1(2)^\circ$] by Pd coordination. The phenyl groups ($\text{C8--C9--C10--C11--C12--C13}$, *ring-B*) are also situated on the same plane as the Pd coordination center with the dihedral angle between *rings-A* and *B* of 0.84° . However, the phenyl group ($\text{C21--C22--C23--C24--C25--C26}$, *ring-D*) is highly twisted with respect to the coordination plane with the dihedral angle between *rings-C* and *D* of 60.66° .

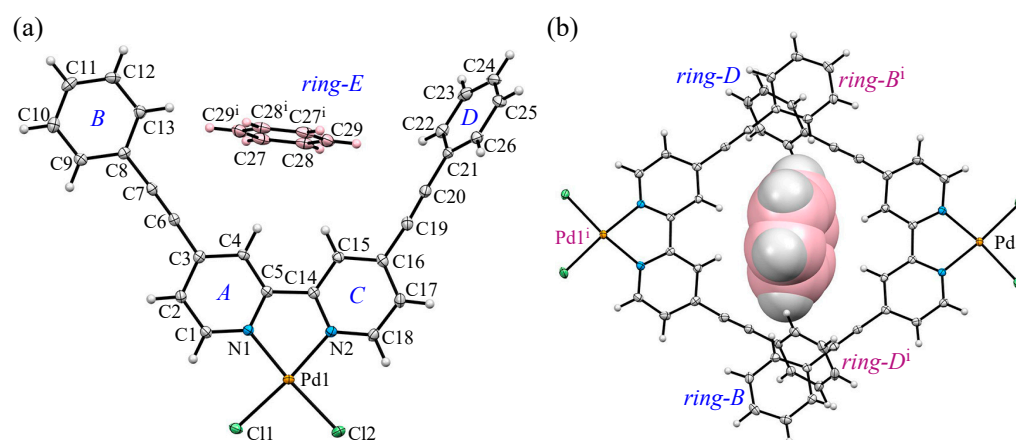


Figure 1. (a) The molecular structure and (b) a rhomb-like dimer of $\mathbf{1} \cdot 0.5\text{C}_6\text{H}_6$ at 100 K, showing the atom-labeling schemes. Displacement ellipsoids are drawn at the 50% probability level, symmetry code: (i) $-x, -y + 1, -z + 1$.

A benzene molecule, *ring-E*, is located in a rhomb-like dimer framework, which is formed by the surrounded four phenylethynyl groups of the complex and complexⁱ, as shown in Figure 1b. Two complexes are stabilized by $\text{CH} \cdots \pi$ interactions and the intermolecular distance of $\text{C}26\text{--H}26 \cdots \text{C}_g\langle\text{ring-B}^i\rangle$ is short (2.75 Å for $\text{H}26 \cdots \text{C}_g\langle\text{ring-B}^i\rangle$ and 3.591(3) Å for $\text{C}26 \cdots \text{C}_g\langle\text{ring-B}^i\rangle$). No remarkable $\pi \cdots \pi$ and $\text{CH} \cdots \pi$ interactions were observed between the benzene molecule and the frameworks.

The packing structures of $\mathbf{1} \cdot 0.5\text{C}_6\text{H}_6$ are shown in Figures 1b and 2. The two complexes form a dimer with the inversion center between the two complexes; e.g., the complex [symmetry code: x, y, z] closely interacts with the adjacent complexⁱⁱ [symmetry code: (ii) $-x + 1, -y + 1, -z + 1$] with the $\pi \cdots \pi$ stacking between the two bipyridine moieties (Figure 2a). The *ring-A* ($\text{N1--C1--C2--C3--C4--C5}$) of the bipyridine closely interacts with the *ring-C*ⁱⁱ ($\text{N}2^{\text{ii}}\text{--C}14^{\text{ii}}\text{--C}15^{\text{ii}}\text{--C}16^{\text{ii}}\text{--C}17^{\text{ii}}\text{--C}18^{\text{ii}}$) of the adjacent complexⁱⁱ; the distance of

$C_g<\text{ring-A}>\cdots C_g<\text{ring-C}^{\text{ii}}>$ is 3.4638 (16) Å, where $C_g<\text{ring-A}>$ and $C_g<\text{ring-C}^{\text{ii}}>$ are the centroids of the *rings-A* and C^{ii} , respectively, of the bipyridine moieties. The corresponding shortest perpendicular distance from the ring centroid to the adjacent plane is 3.2614(8) Å. According to the $\pi\cdots\pi$ stacking, the intermolecular distance between Pd1 and Pd1ⁱⁱ is 6.609(2) Å. A twisted phenyl *ring-D*ⁱⁱⁱ [symmetry code: (iii) $x, -y + 0.5, z - 0.5$] further interacts with the bipyridine moieties of the dimer and the shortest distance of $C_g<\text{Pd1-N1-C5-C14-N2}>\cdots C_g<\text{ring-D}^{\text{iii}}>$ is 3.4684(17) Å (Figure 2b), giving the twisted conformation of the *ring-D*. The phenyl *ring-D*ⁱⁱⁱ further interacted with the adjusted phenyl *ring-B*^{iv} [symmetry code: (iv) $x, y - 1, z$] through π - π interaction, and the $C_g<\text{ring-D}^{\text{iii}}>\cdots C_g<\text{ring-B}^{\text{iv}}>$ is 3.6678(18) Å. For the opposite side of *ring-B*^{iv}, $\text{CH}\cdots\pi$ interaction is observed with H22 of the *ring-D*^v [symmetry code: (v) $-x, -y, -z + 1$].

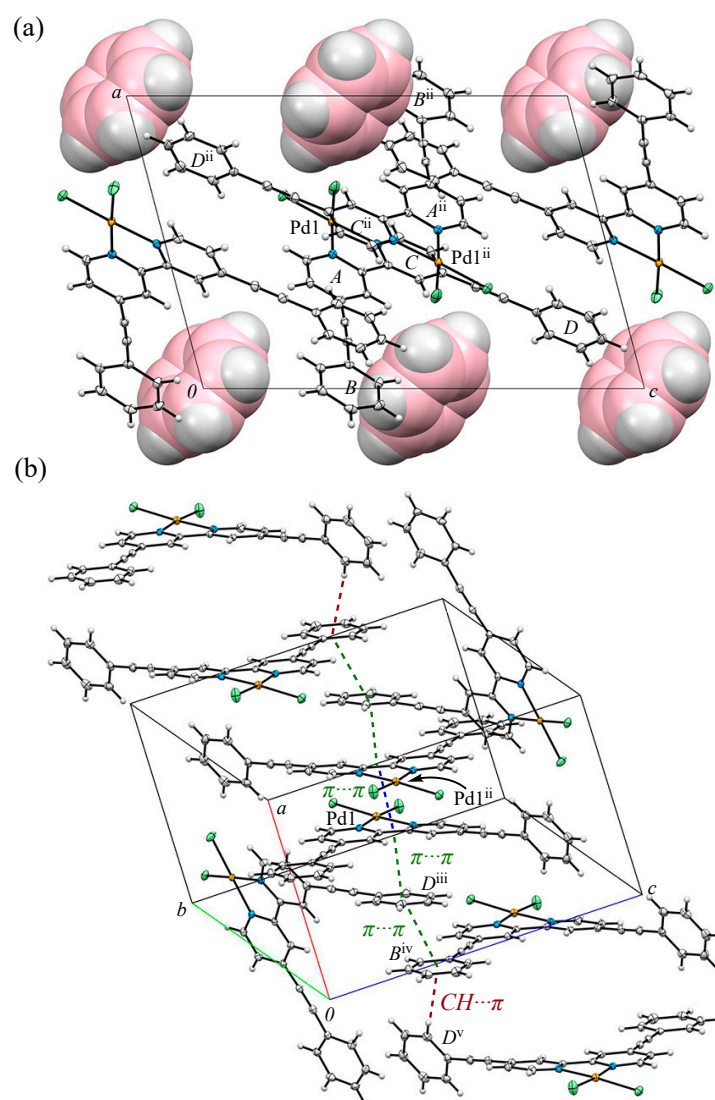


Figure 2. (a) Top and (b) side views of part of the crystal structure of **1**•0.5C₆H₆; Color scheme: C, gray; Cl, green; N, blue; Pd, orange; solvated benzene, pink, symmetry code: (ii) $-x + 1, -y + 1, -z + 1$, (iii) $x, -y + 0.5, z - 0.5$, (iv) $x, y - 1, z$, (v) $-x, -y, -z + 1$.

3.3. Crystal Structure and Intermolecular Interactions of **2**

Crystal **2** has a whole complex in the asymmetric unit, as shown in Figure 3. The geometry around the metal center in **2** is also square planar. The bond distances of Pd1–N1, Pd1–N2, Pd1–Cl1, and Pd1–Cl2 are 2.033(2), 2.029(2), 2.2799(9), and 2.2885(9) Å, respectively. The molecular structures of the two complexes in crystals **1**•0.5C₆H₆ and **2** are almost the

same. Two pyridine planes (*rings-A* and *C*) are highly flat by Pd coordination, and the torsion angle of N1-C5-C18-N2 is $3.7(3)^\circ$. The naphthalene group (C8-C9-C10-C11-C12-C13-C14-C15-C16-C17, *ring-B*) is situated on the same plane as Pd coordination with the dihedral angle between *rings-A* and *B* of 1.96° . The other naphthalene group (C25-C26-C27-C28-C29-C30-C31-C32-C33-C34, *ring-D*) is almost perpendicular to the coordination plane with the dihedral angle between *rings-C* and *D* of 85.76° , which is larger than that of **1** (60.66°).

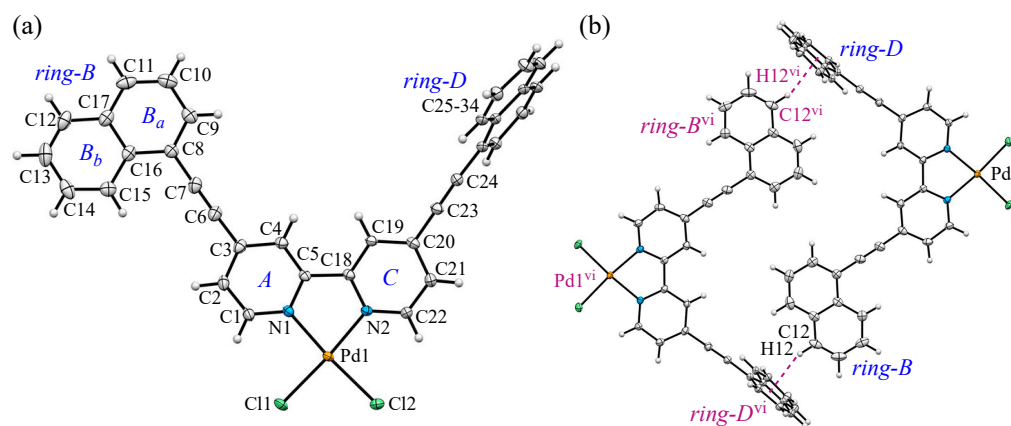


Figure 3. (a) The molecular structure and (b) a rhomb-like dimer of **2** at 120 K, showing the atom-labeling schemes. Displacement ellipsoids are drawn at the 50% probability level, symmetry code: (vi) $-x + 2, -y + 1, -z + 1$.

The packing structure of **2** is shown in Figures 3b and 4. The naphthalene groups (*rings-B* and *D*) of the complex $[x, y, z]$ closely interact with *rings-D*^{vi} and *B*^{vi}, respectively, of the complex^{vi} [symmetry code: (vi) $-x + 2, -y + 1, -z + 1$], forming a rhomb-like dimer fragment through intermolecular CH $\cdots\pi$ interactions (Figure 3b). Between the naphthalene groups, one six-membered ring, C25^{vi}-C26^{vi}-C27^{vi}-C28^{vi}-C34^{vi}-C33^{vi} (*ring-D*_a^{vi}), is only involved in the interaction, and the intermolecular distance of C12-H12 $\cdots$ C_g<*ring-D*_a^{vi}> is also short (2.80 Å for H12 $\cdots$ C_g<*ring-D*_a^{vi}> and 3.656(4) Å for C12 $\cdots$ C_g<*ring-D*_a^{vi}>). The intermolecular distance of H12 and the whole naphthalene *ring-D*^{vi} is 3.34 Å. The naphthalene *ring-B* further interacts with the bipyridine moiety of the adjacent complex^{vii} [symmetry code: (vii) $-x + 1, -y, -z + 1$] with the π - π stacking (Figure 4a). The *ring-B*_b (C12-C13-C14-C15-C16-C17) of the naphthalene closely interacts with the five-membered coordination *ring-E*^{vii} (Pd1^{vii}-N1^{vii}-C5^{vii}-C18^{vii}-N2^{vii}), and the distance of C_g<*ring-B*_b> $\cdots$ C_g<*ring-E*^{vii}> is 3.517(2) Å. The corresponding shortest perpendicular distance from the ring centroid to the adjacent plane is 3.342(1) Å. The distance of *rings-B*_b and *A*^{vii} is also short (C_g<*ring-B*_b> $\cdots$ C_g<*ring-A*^{vii}> is 3.631(2) Å). This $\pi\cdots\pi$ stacking is observed between the *ring-A* of bipyridine and *ring-B*_b^{vii} of the naphthalene group. It is pointed out that the weak CH $\cdots$ Cl interaction is shown between C26^{viii}-H26^{viii} in the naphthalene *ring-D*^{viii} [symmetry code: (viii) $x - 1, y - 1, z$] and the Cl⁻ ion in the complex (2.88 Å for H26^{viii} $\cdots$ Cl1). In Figure 4b, the remarkable $\pi\cdots\pi$ stacking was observed between the *rings-D* along the *c* axis and the shortest distance of C_g<*ring-D*> $\cdots$ C_g<*ring-D*^{ix}> [symmetry code: (ix) $-x + 3, -y + 1, -z + 2$] is 3.884(2) Å and the corresponding shortest perpendicular distance from the ring centroid to the adjacent plane is 3.4320(8) Å.

The intermolecular distances between two Pd ions are 7.971(3) Å along the *c* axis for Pd1 $\cdots$ Pd1^{ix} [symmetry code: (ix) $-x + 2, -y - 1, -z + 1$] and 8.019(3) Å along the *a* axis for Pd1 $\cdots$ Pd1^{iv} and Pd1 $\cdots$ Pd1^x [symmetry code: (x) $x + 1, y, z$], showing the no interaction between the metal ions. Thus, the orange color of crystal **2** is estimated due to the expanded π -conjugated system of the naphthalene rings and not metal $\cdots$ metal interactions. The twist differences between the two arylethynyl groups are induced by the rhomb-like structure for both **1** and **2**, which will give the common prospects for the stabilizing structure in similar compounds. While compound **1** encapsulated the benzene molecule, no solvated crystal was obtained for **2**. The results indicate that the large naphthalene groups behave

like guests instead of solvate benzenes in the space. Typically, from void space calculations using CCDC Mercury, the space calculated for the crystal $1 \cdot 0.5\text{C}_6\text{H}_6$, excluding benzene, was 12.5%, with a volume per unit lattice of about $294 \text{ \AA}^3$ (Van der Waals radius set to a minimum value of $1.2 \text{ \AA}$). The volume of benzene per molecule was about $150 \text{ \AA}^3$, with two molecules closely packed in the unit lattice. The volume of naphthalene is about $200 \text{ \AA}^3$, and changing from a phenyl group to a naphthyl group occupies about $50 \text{ \AA}^3$ of new space, which corresponds to $4/3$ of a benzene molecule when the two complexes forming the rhombic structure are changed to four naphthyl substituents.

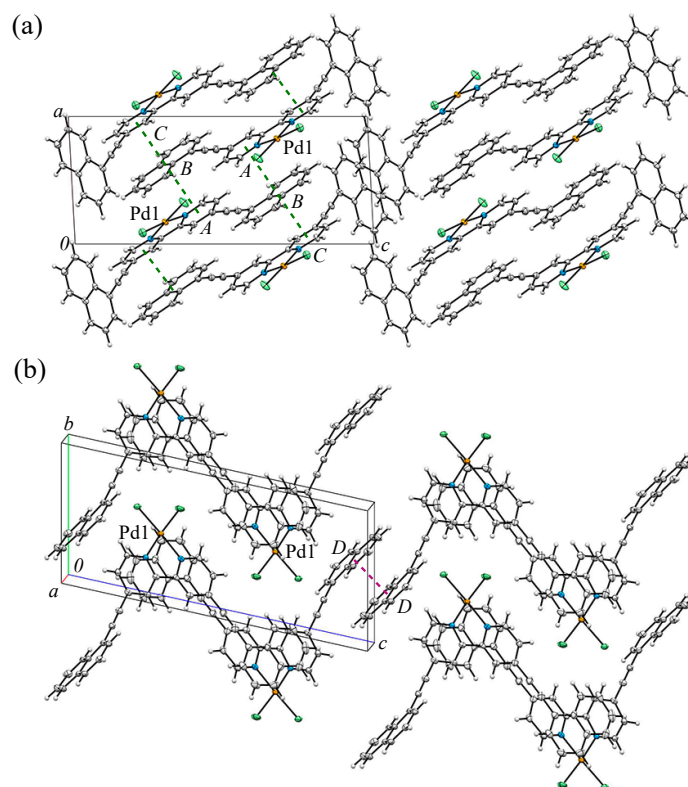


Figure 4. The crystal packing of **2**, viewed along the (a) *b* and (b) *a* axes.

3.4. Hirshfeld Surface Analysis of the Structures

To understand the detailed intermolecular interactions, the HS analysis [30,31] of each complex was carried out using Crystal Explorer 17.5 [32]. The results of **1** mapped with d_{norm} (the distance between the surface and external atoms) are shown in Figure 5. The red spots are short intermolecular distances of the molecules, indicating two important results: (1) the remarkable interactions, e.g., $\text{CH} \cdots \pi$, $\pi \cdots \pi$ and $\text{Cl} \cdots \text{H}$, are observed between the complexes and (2) no remarkable interactions are observed between the benzene molecule. The most important contributions for the crystal packing are from $\text{H} \cdots \text{H}$ (33.6%), $\text{C} \cdots \text{H}/\text{H} \cdots \text{C}$ (28.3%), $\text{Cl} \cdots \text{H}/\text{H} \cdots \text{Cl}$ (17.8%), and $\text{C} \cdots \text{C}$ (10.6%) interactions, and the values with the corresponding fingerprint plots are summarized in Figure 6. The C atoms of the phenyl ring-B contact with the H atom adjacent to the complex, but that of ring-A shows $\text{C} \cdots \text{C}$ interaction with the benzene molecule. The close contact from the C atom of benzene molecule (21.6%) shows only the $\text{CH} \cdots \pi$ interaction [$\text{C}(\text{inside}) \cdots \text{H}(\text{outside})$ 21.5%] without any $\pi \cdots \pi$ stacking [$\text{C}(\text{inside}) \cdots \text{C}(\text{outside})$ 0.1%] and that from the H atom shows weak $\text{H} \cdots \text{H}$ (58.0%), $\text{H} \cdots \text{C}$ (10.0%), $\text{H} \cdots \text{Cl}$ (10.0%). Very similar contributions are observed for **2** (Figures 7 and 8), and the most important contributions for the crystal packing of **2** are from $\text{H} \cdots \text{H}$ (36.5%), $\text{C} \cdots \text{H}/\text{H} \cdots \text{C}$ (26.0%), $\text{Cl} \cdots \text{H}/\text{H} \cdots \text{Cl}$ (15.7%), and $\text{C} \cdots \text{C}$ (12.3%) interactions. These slightly different contributions are estimated that the phenyl group has expanded to the naphthyl group. Thus, the crystallographic studies of $1 \cdot 0.5\text{C}_6\text{H}_6$ and **2** prove common structures and the corresponding intermolecular interactions.

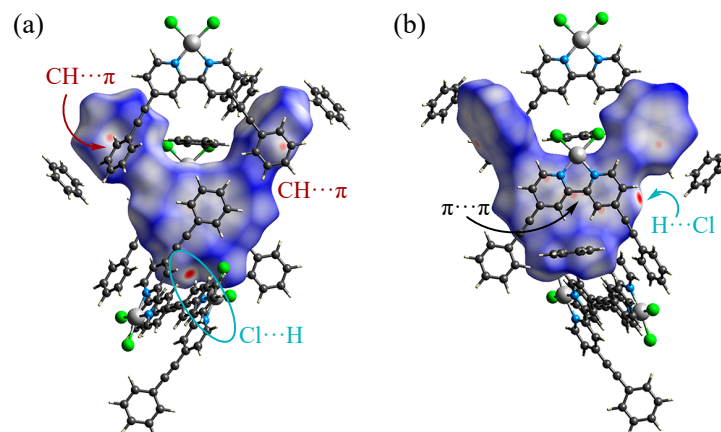


Figure 5. HS of the complex **1**•0.5C₆H₆ mapped with d_{norm} and the intermolecular interactions of the surrounding molecules: (a) and (b) show the front and back structures, respectively.

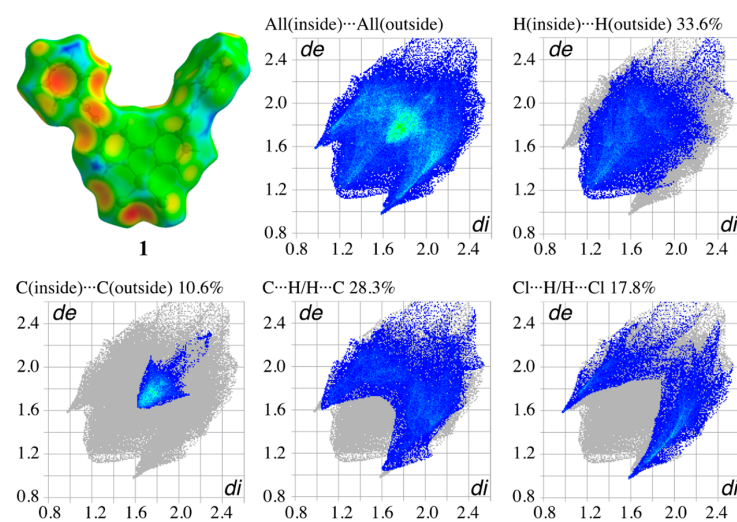


Figure 6. HS of **1** mapped with d_e and the fingerprint plots for the contributions of the remarkable intermolecular interactions of **1** in the crystal of **1**•0.5C₆H₆.

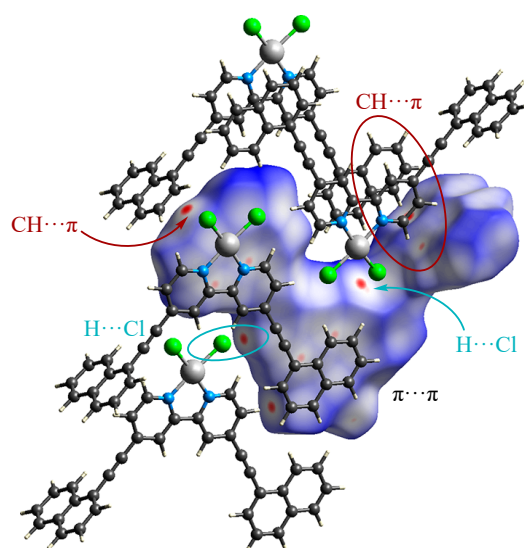


Figure 7. HS of the complex **2** mapped with d_e and the intermolecular interactions of the surrounding molecules.

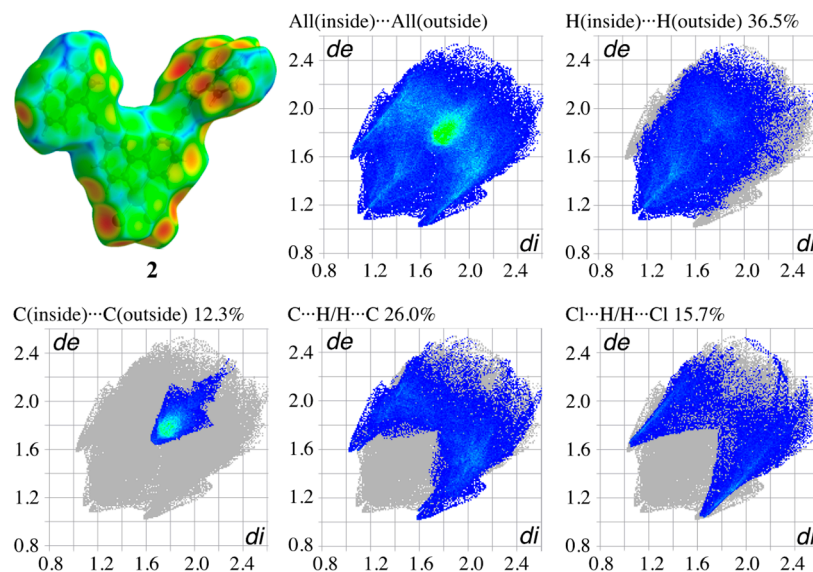


Figure 8. HS of **2** mapped with d_e and the fingerprint plots for the contributions of the remarkable intermolecular interactions of **2**.

3.5. Density Functional Theory Calculations of the Structures

DFT calculations were performed using the crystal structures of **1** and **2** to understand the quantitative value of the surface potential and the corresponding intermolecular interactions. The electrostatic potentials of each metal complex ranged from -303.75 to $+206.48$ kJ mol^{-1} for **1** and -302.92 to $+204.25$ kJ mol^{-1} for **2**, as shown in Figure 9a,b, respectively, showing almost the same values. The highest electrostatic potential, of which the electron-poor region is shown as blue, is on the top edge of the bipyridine protons, H4 and H15 for **1** (H4 and H19 for **2**), and the other protons of bipyridine and phenyl moieties. The electron-poor protons have a good possibility of forming the Intermolecular interaction with the guest, and the benzene molecule is inserted for **1** but self-association for **2**. The lowest electrostatic potential, as shown in red, is Cl1 and Cl2 of the coordinated anions. The lowest electrostatic potentials of the aromatic center of each complex were approximately -26 and -41 kJ mol^{-1} for phenyl and naphthyl groups, respectively, which interact with the next complex to form the rhombic structure. The potential energies of the Pd center in each complex are approximately -74 and -87 kJ mol^{-1} , which was in good agreement with similar complexes with nucleophilic characteristics. Since there is no extreme value around the Pd atom, it is assumed that the electrostatic potential near the palladium atom is largely contributed by the coordinated bipyridine and chlorine moieties.

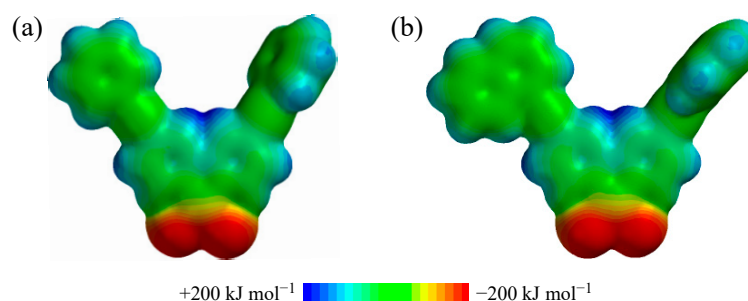


Figure 9. The energy potential maps of (a) **1** and (b) **2** from the crystal structures: the color of the potential is shown between -200 kJ mol^{-1} (red) and $+200$ kJ mol^{-1} (blue).

4. Conclusions

In conclusion, we prepared palladium complexes with a new naphthalene derivative, 4,4'-di(naphthalen-1-ylethynyl)-2,2'-bipyridine (L^2), to compare with the corresponding

phenyl derivative (L^1). We prepared the Pd complexes **1** and **2**, and the single crystals of **1**•0.5C₆H₆ and **2** were obtained from a benzene-acetone and/or benzene-dmso solution, which was investigated by single crystallographic and DFT studies. For complex **1**, the benzene solvent was useful for crystal growth, and sufficiently large crystals for crystallographic studies were obtained. Both structures show the rhomb-shaped dimer through the CH $\cdots\pi$ interactions between the complexes, indicating that the central cavity prefers to recognize the aromatic moieties by surrounding the organic wall of the complex. It was found that the rhomb shape within this crystal was prioritized in the crystal states, while palladium preferred the charge repulsion of each other over the metallophilic interaction. Crystals containing solvated aromatic compounds have the potential to be developed into molecular recognition materials that dynamically and selectively incorporate further aromatic compounds.

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Data Availability Statement: Crystallographic data have been deposited at CCDC. Additional data are available in Appendix A.

Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and the deposition CCDC numbers are 2031735 for **1**•0.5C₆H₆ and 2031736 for **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/structures/> (accessed on 19 February 2024).

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