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Novel Bimetallic Macrocyclic Complexes Assembled from Pd^{II} and Flexible Pyridyl Dithioether Bridging Spacers

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Two novel dimeric palladium(II) complexes with flexible pyridyl dithioether bridging ligands, $[Pd(L^1)Cl_2]_2$ (1) and $[Pd(L^2)Cl_2]$ (2), where L^1 = 1,3-bis(2-pyridylthio)propane and L^2 = 1,3-bis(4-pyridylthio)propane, have been synthesized and structurally characterized by X-ray diffraction analyses. In both complexes, each Pd^{II} center is four-coordinated in the *trans*-form by two chloride anions and two nitrogen donors from two distinct ligands. Complex 1 exhibits a unique 20-membered metallomacrocyclic structure with twisted conformation, while 2 shows a dinuclear 28-membered metallomacrocycle with planar conformation. In addition, there are weak C—H···Cl or C—H···S hydrogen bonding interactions in both complexes, resulting in different 3-D supramolecular architectures.

Keywords: Self-assemble; Pyridyl dithioether; Crystal structure; Palladium(II) complexes

INTRODUCTION

Coordination-driven self-assemblies of discrete inorganic or organometallic supramolecular architectures, such as metallacyclophanes, molecular square and coordination cages, have witnessed tremendous growth over the past decade [1,2]. The Pd^{II} center is widely used in constructing these discrete multinuclear molecules due to its inherent well-defined coordination orientation, and there have been numerous recent publications based mainly on N-donor bridging ligands in the construction of coordination supramolecules with Pd^{II} or Pt^{II} ions, which exhibit a variety of novel structural features [3–10]. However, most of those ligands containing N-donors are characterized by a rigid skeleton. Because of the high flexibility of pyridyl dithioether ligands, wide structural diversities are anticipated upon complexation. In addition, although flexible dithioethers are well-established ligands in the coordination chemistry of palladium(II) and platinum(II) [11–15], to the best of our knowledge, Pd^{II} complexes with pyridyl dithioethers characterized by X-ray diffraction analysis have not yet been reported. We recently synthesized two new pyridyl dithioether ligands and their palladium(II) complexes. Herein, we report the syntheses and crystal structures of two novel palladium(II) metallacyclophane complexes with pyridyl dithioether ligands.

EXPERIMENTAL

Materials and General Methods

All reagents for syntheses and analyses were of analytical grade. FT-IR spectra (KBr pellet) were obtained on an FT-IR 170 SX (Nicolet) spectrometer. Elemental analyses were carried out using a Perkin-Elmer 240C analyser.

Synthesis of the Ligands L^1 and L^2

The two ligands, 1,3-bis(2-pyridylthio)propane ($\mathbf{L^1}$) and 1,3-bis(4-pyridylthio)propane ($\mathbf{L^2}$), were prepared by a procedure similar to that reported for the synthesis of 1,4-bis(phenylthio)butane [16], as follows.

The reaction of 1,3-dibromopropane with the appropriate pyridine-2-thiol or pyridine-4-thiol,

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TABLE I Crystal data and structure refinement summary for **1** and **2**

	1	**2**
Empirical formula	$C_{26}H_{28}Cl_4N_4Pd_2S_4$	$C_{13}H_{14}Cl_2N_2PdS_2$
Formula weight	879.36	439.68
Crystal system	Orthorhombic	Monoclinic
Space group	*Pccn*	*C2/c*
Unit cell dimensions (Å,°)	$a = 9.010(3)$ $b = 15.067(4)$ $c = 25.080(8)$	$a = 15.080(5)$ $b = 14.398(5)$ $c = 15.696(5)$ $\beta = 107.495(6)$
Volume (Å^3)	3404.9(18)	3250.5(18)
Z	4	8
D_{calcd} (g cm^{-3})	1.715	1.797
μ (mm^{-1})	1.639	1.717
F (000)	1744	1744
Range of h, k, l	$-11/11$, $-18/9$, $-29/31$	$-18/17$, $-18/17$, $-19/14$
Reflections collected/unique	18268/3493	8334/3321
Max. and min. transmission	1.0000 and 0.8017	1.0000 and 0.6813
Data/restraints/parameters	3493/0/182	3321/0/181
Goodness-of-fit on F^2	1.072	0.989
R^* and $R_w{}^{\dagger}$	0.0610 and 0.1386	0.0387 and 0.0789
Largest diff. peak and hole (e Å^{-3})	0.754 and -0.488	0.486 and -0.332

$^*R = \Sigma(||F_0| - |F_C||)/\Sigma|F_0|$; $^{\dagger}wR = [\Sigma w(|F_0|^2 - |F_C|^2)^2/\Sigma w(F_0^2)]^{1/2}$.

respectively, in the presence of potassium hydroxide, gave $\mathbf{L^1}$ and $\mathbf{L^2}$ in good yield, and the products were fully characterized by ^{1}H NMR, FT-IR (KBr pellet) and elemental analysis. For $\mathbf{L^1}$, Yield: 88%. Found: C, 59.30; H, 5.36; N, 10.73. Calcd for $C_{13}H_{14}N_2S_2$: C, 59.51; H, 5.38; N, 10.68. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.14 (m, 2H, —CCH_2C—), 3.32 (t, 4H, —SCH_2—), 6.95, 7.18, 7.45, 8.41 (8H, C_6H_4N—). IR (KBr pellet, cm^{-1}): 3044*w*, 2923*w*, 1662*m*, 1578*s*, 1556*s*, 1454*s*, 1414*s*, 1282*m*, 1124*s*, 1088*w*, 1043*m*, 985*m*, 757*s*, 724*m*. For $\mathbf{L^2}$, Yield: 85%. Found: C, 59.69; H, 5.34; N, 10.61. Calcd for $C_{13}H_{14}N_2S_2$: C, 59.51; H, 5.38; N, 10.68. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.12 (m, 2H, —CCH_2C—), 3.15 (t, 4H, —SCH_2—), 7.12, 8.41 (8H, C_6H_4N—). IR (KBr pellet, cm^{-1}): 3026*w*, 1575*vs*, 1538*m*, 1407*s*, 1220*w*, 1108*w*, 981*w*, 780*s*, 710*s*, 495*s*.

Preparation of $[Pd(L^1)Cl_2]_2$ (1) and $[Pd(L^2)Cl_2]$ (2)

Complex **1** was synthesized by carefully layering a solution of $PdCl_2$ (0.2 mmol) in acetonitrile on top of a solution of $\mathbf{L^1}$ (0.2 mmol) in chloroform in a test-tube. After 3 days at room temperature, red single crystals suitable for X-ray investigation appeared at the boundary between the acetonitrile and chloroform. FT-IR (KBr, cm^{-1}): 3018*w*, 1589*s*, 1560*s*, 1456*s*, 1420*s*, 1158*w*, 1146*m*, 1094*m*, 1033*w*, 967*w*, 837*w*, 777*s*, 753*s*, 729*m*. Anal. Calcd for $C_{26}H_{28}Cl_4N_4Pd_2S_4$: C, 35.51; H, 3.21; N, 6.37; found: C, 35.75; H, 3.10; N, 6.21. Complex **2** was prepared by the same method as **1** except using $\mathbf{L^2}$ instead of $\mathbf{L^1}$. FT-IR (cm^{-1}): 3031*w*, 2922*w*, 1599*vs*, 1482*m*, 1423*s*, 1118*s*, 1063*s*, 813*s*, 738*s*, 718*w*, 509*m*. Anal. Calcd for $C_{13}H_{14}Cl_2N_2PdS_2$: C, 35.51; H, 3.21; N, 6.37; found: C, 35.71; H, 3.13; N, 6.48.

X-ray Crystallographic Studies of Complexes 1 and 2

Single-crystal X-ray diffraction measurements were carried out on a Bruker Smart 1000 CCD area detector. Intensities of reflections were measured using graphite-monochromatized MoKα radiation ($\lambda = 0.71073$ Å) with ω scan mode at 293(2) K in the range $1.62 < \theta < 26.4°$ for **1** and $2.00 < \theta < 26.43°$ for **2**. Unit cell dimensions were obtained with least-squares refinements and semi-empirical absorption corrections were applied using the SADABS program [17]. All the structures were solved by the direct method [18] and non-hydrogen atoms were obtained in successive difference Fourier syntheses. The final refinements were performed by full-matrix least-squares methods on F^2 by the SHELXL-97 program package [19]. Hydrogen atoms were included in the calculated positions and refined with fixed thermal parameters riding on their parent atoms. Further crystallographic data and experimental details for structural analyses are summarized in Table I.

RESULTS AND DISCUSSION

The crystal structure of **1** consists of a neutral dinuclear molecule with C_2 crystallographic symmetry. Figure 1 shows a perspective view of the structure with atom labeling, and the selected bond lengths and angles are listed in Table II. Each Pd^{II} atom is four-coordinated by two pyridine nitrogen atoms from different ligands and two terminal chloride anions in the *trans*-form, exhibiting a square planar coordination environment. Two ligands adopt an *N*,*N*-bidentate *cis*-bridging mode to bridge two

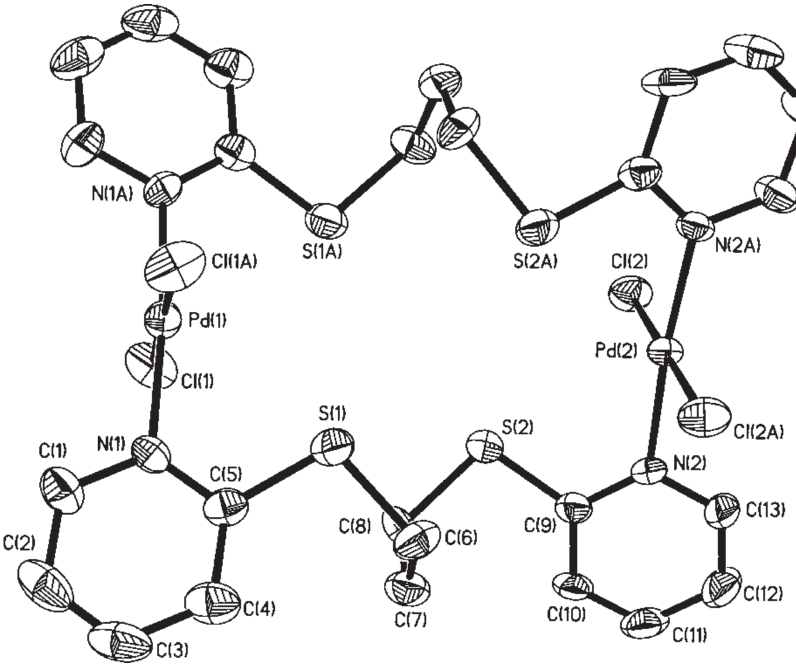

FIGURE 1 ORTEP view with atom labeling (displacement ellipsoids drawn at 30% probability) of the structure of complex **1**.

Pd^{II} ions forming a highly twisted 20-membered metallomacrocycle with the intramolecular Pd···Pd separation of 7.630 Å. In this dinuclear structure, it should be noted that the coordination geometries of the two Pd^{II} centers are slightly different. For Pd(1), the two Pd—N bond lengths are equivalent with the value of 2.031(6) Å within the range expected for such coordination [20–22], and the two Pd(1)—Cl(1) [2.294(2) Å] distances are also equivalent, being in the normal range of the terminal Pd—Cl distances [15,22]. Pd(1) deviates from the coordination plane by 0.0450 Å and the bond angles around Pd(1) are divided into two groups [N(1)—Pd(1)—Cl(1) = N(1A)—Pd(1)—Cl(1A) = 90.16(18)° and N(1)—Pd(1)—Cl(1A) = N(1A)—Pd(1)—Cl(1) = 89.83(18)°]. In the case of Pd(2), the bond length of Pd(2)—Cl(2) [2.295(2) Å] is almost the same as that of Pd(1)—Cl(1), while the Pd(2)—N(2) distance of 2.041(6) Å is slightly longer than the distance of Pd(1)—N(1). The two terminal pyridine rings in the same ligand are inclined to each other at an angle of 42.5°, while the two dihedral angles formed by the two pyridine rings around Pd(1) and Pd(2) are similar with the value of 20.4°.

TABLE II Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

1			
Bond lengths			
Pd(1)—N(1)	2.031(6)	Pd(2)—N(2)	2.041(6)
Pd(1)—Cl(1)	2.294(2)	Pd(2)—Cl(2)	2.295(2)
Bond angles			
N(1)^{i}—Pd(1)—N(1)	175.2(4)	N(2)—Pd(2)—N(2)^{i}	174.3(4)
N(1)—Pd(1)—Cl(1)	90.2(2)	N(2)—Pd(2)—Cl(2)	90.1(2)
N(1)—Pd(1)—Cl(1)^{i}	89.8(2)	N(2)—Pd(2)—Cl(2)^{i}	89.9(2)
Cl(1)—Pd(1)—Cl(1)^{i}	179.7(1)	Cl(2)—Pd(2)—Cl(2)^{i}	179.8(1)
2			
Bond lengths			
Pd(1)—N(1)	2.008(3)	Pd(1)—Cl(1)	2.295(1)
Pd(1)—N(2)^{ii}	2.022(3)	Pd(1)—Cl(2)	2.313(1)
Bond angles			
N(1)—Pd(1)—N(2)^{ii}	178.3(1)	N(1)—Pd(1)—Cl(2)	90.8(1)
N(1)—Pd(1)—Cl(1)	88.5(1)	N(2)^{ii}—Pd(1)—Cl(2)	89.1(1)
N(2)^{ii}—Pd(1)—Cl(1)	91.7(1)	Cl(1)—Pd(1)—Cl(2)	179.01(4)

Symmetry transformations used to generate equivalent atoms:
i: $-x+1/2,\ -y+3/2,\ z$; ii: $-x,\ -y+2,\ -z+1$.

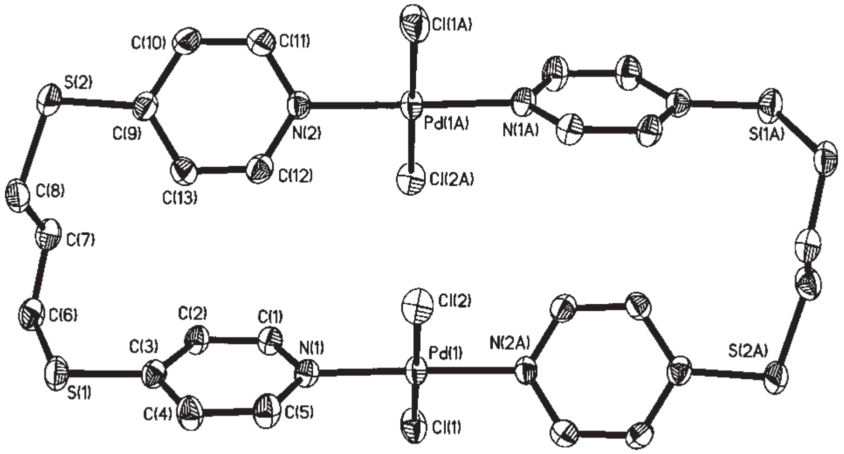

FIGURE 2 ORTEP view with atom labeling (displacement ellipsoids drawn at 30% probability) of the structure of complex **2**.

The crystal structure of **2** also consists of a neutral dinuclear molecule having a crystallographic center of symmetry, rather than the twofold axis as in **1**. The perspective view of the binuclear entity in **2** with atomic labeling is given in Fig. 2 and the selected bond lengths and angles are listed in Table II. Each Pd^{II} atom is also four-coordinated by two N-donors from two ligands and two chloride anions, forming a square planar geometry. Unlike **1**, the two Pd^{II} centers in this dinuclear entity have similar coordination environments, which are equivalently bridged by two $\mathbf{L^2}$ ligands to form a 28-membered rectangle metallomacrocycle with the sulfur atoms occupying the four corners [the S(1)···S(2) distance is 4.913 Å and the S(1)···S(2A) distance is 13.05 Å]. The Pd^{II} center is almost in the basal plane formed by N—Cl—N—Cl. The Pd···Pd distance within the metallomacrocycle is 4.855 Å, which is shorter than that of complex **1**. Possibly due to smaller steric hindrance, the average Pd—N bond length of 2.015(3) Å is slightly shorter than that of **1**, while the two Pd—Cl distances [Pd(1)—Cl(1) and Pd(1)—Cl(2)] are not equivalent, with values of 2.2945(13) and 2.3134(12) Å, respectively. The least-square planes of the pyridine rings are inclined at the angles of 62.0 and 65.2° to that of the coordination basal plane, while the two terminal pyridine rings of the ligand are inclined to each other with an angle of 53.1°.

Because of their relative flexibility, the ligands in both complexes can bend and rotate to coordinate to the Pd^{II} center to fit the steric requirements. To sustain the square planar geometry of the Pd^{II} atom, $\mathbf{L^1}$ in **1** is highly twisted to coordinate to the Pd^{II} atoms, forming a twisted 20-membered metallomacrocycle. This conformation is preferred because it allows all the Cl—Pd—N bond angles to be 90°. The average Pd—N length in **1** (2.036 Å) is slightly longer than that in **2** (2.015 Å), which can be attributed to the presence of greater steric hindrance in **1**. In addition, although the sulfur atom can form a strong coordinate bond with the Pd^{II} atom [14,15], only the nitrogen atoms of the two ligands coordinate to the Pd^{II} atoms in complexes **1** and **2**. The same situation has also been observed in other mixed N/S-donor ligands [23].

Since the pioneering investigations by Fujita *et al.* [24] and Saalfrank *et al.* [25] on metallomacrocycles, considerable efforts have been focused on the design and synthesis of macrocyclic structures composed of metal centers connected by organic fragments [1,26]. Most of these examples reported so far are based on bis-pyridine ligands interconnected by rigid spacers and metal centers such as Pd^{II}, Pt^{II} and Ag^{I}. Complexes **1** and **2** described here are two interesting neutral metallomacrocycles directly self-assembled by Pd^{II} and flexible organic ligands. Another very interesting point is the stacking pattern of the two assembly species in the solid state. For complex **1**, four hydrogen atoms from the pyridine rings at the corners of the metallomacrocycle have been activated by the positive charge due to the coordination of the nitrogen atoms to the Pd^{II} centers, and three coordinated chloride donors and one uncoordinated sulfur atom in the ligand form the acceptors of C(1)—H(1)···$Cl(2)^i$ ($i = x, -y + 1.5, z + 0.5$), C(2)—H(2)···$Cl(2)^i$ ($i = -x, y - 0.5, 0.5 - z$), C(3)—H(3)···$S(2)^i$ ($i = -x, y - 0.5, 0.5 - z$) and C(13)—H(13)···$Cl(1)^i$ ($i = x, -y + 1.5, z - 0.5$) intermolecular hydrogen bonds as shown in Fig. 3, which link the complex molecules to form a 3-D supramolecular structure. The C···Cl and C···S separations are 3.638, 3.716, 3.793 and 3.594 Å with H···Cl and H···S distances of 2.909, 2.854, 2.932 and 2.903 Å, respectively, falling into the normal range of weak hydrogen bond interactions. The bond angles are 136.2, 154.8, 154.6 and 132.1°. For

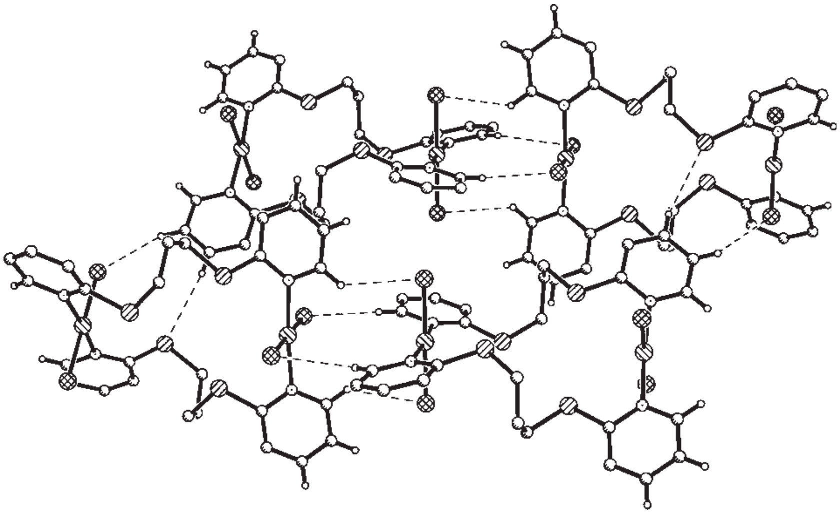

FIGURE 3 View of the hydrogen bonds in the structure of **1**.

complex **2**, from investigation of the packing diagram we can observe two crystallographically independent intermolecular hydrogen bonds: C(2)—H(2)$\cdots$Cl(2)^i ($i = x, \ -y+2, \ -0.5+z$) and C(6)—H(6B)$\cdots$Cl(1)^i ($i = 0.5-x, \ y-0.5, \ 0.5-z$). Thus, each neutral molecule links four neighboring metallomacrocyclic motifs (Fig. 4) through C—H$\cdots$Cl interactions, resulting in the final 3-D structure. The C$\cdots$Cl separations are 3.556 and 3.621 Å with H$\cdots$Cl distances of 2.675 and 2.763 Å, respectively, falling into the normal range of weak hydrogen bond interactions. The bond angles are 158.2 and 147.9°, respectively.

In summary, we have synthesized and characterized two palladium(II) dinuclear metallomacrocycle complexes with flexible pyridyl dithioether ligands, in which each Pd^{II} atom is four-coordinated by two pyridine nitrogens and two chloride anions forming the square planar geometry. The difference in conformation between compounds **1** and **2** is mainly attributable to the difference in the position of the pyridine nitrogen in the two ligands. The weak C—H$\cdots$Cl or C—H$\cdots$S hydrogen bonds further result in different 3-D frameworks in the unit cell of complexes **1** and **2**. Further work is being directed to a systematic investigation on the use of these flexible ligands in the synthesis of other metal-organic supramolecular architectures and their properties.

Supplementary Material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos 205368 and 205369). This material can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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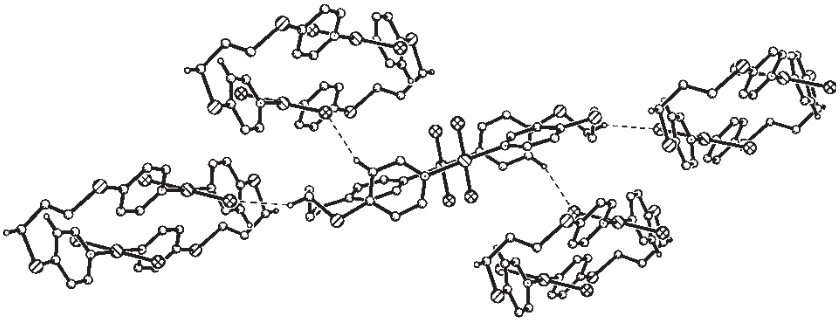

FIGURE 4 View of the hydrogen bonds in the structure of **2**.

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