

共平面的 μ -S 桥联(1,10-菲咯啉)钯(II)双核配合物的晶体结构与 π - π 堆积

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Crystal Structure and π - π Stacking of a Coplanar μ -S Bridged 1,10-Phenanthroline Palladium(II) Dinuclear Complex

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Abstract: A novel μ -S-bridged di-palladium(II) complex, $\{[(\text{phen})\text{Pd}(\mu\text{-SPR})_2\text{Pd}(\text{phen})](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}\}$ (**1**) was synthesized and characterized by the ¹H NMR, element analysis and single crystal X-ray diffraction. It crystallizes in the monoclinic space group *C2/c* with unit cell parameters: $a=2.165\ 1(3)$ nm, $b=1.291\ 4(2)$ nm, $c=2.716\ 2(3)$ nm, $\beta=111.987(3)^\circ$, and $V=7.041\ 8(16)$ nm³, $Z=8$, $R=0.054\ 4$, $wR=0.127\ 4$. The X-ray crystal structure analysis revealed that two 1,10-phenanthroline palladium(II) moieties were bridged by two *n*-propylmercaptan molecules in coplanar fashion with the dimensions of $1.55\ \text{nm} \times 0.88\ \text{nm}$. The plane-to-plane distance of the complex **1** is $0.33\ \text{nm}$, which reveals strong aromatic-aromatic π - π interaction. CCDC: 292998.

Key words: μ -S-Bridged; dipalladium(II) complex; 1,10-phenanthroline; π - π stacking; crystal structure

0 Introduction

Aromatic-aromatic or π - π interactions are important noncovalent intermolecular forces, which play an important role in the binding and conformations

from large biological systems to synthetic molecules^[1,2]. There are two different patterns of the stacked arrangements in general aromatic systems with the range of $0.33 \sim 0.38\ \text{nm}$ for aromatic-aromatic π - π interaction: offset face-to-face and edge-to-face packing. Re-

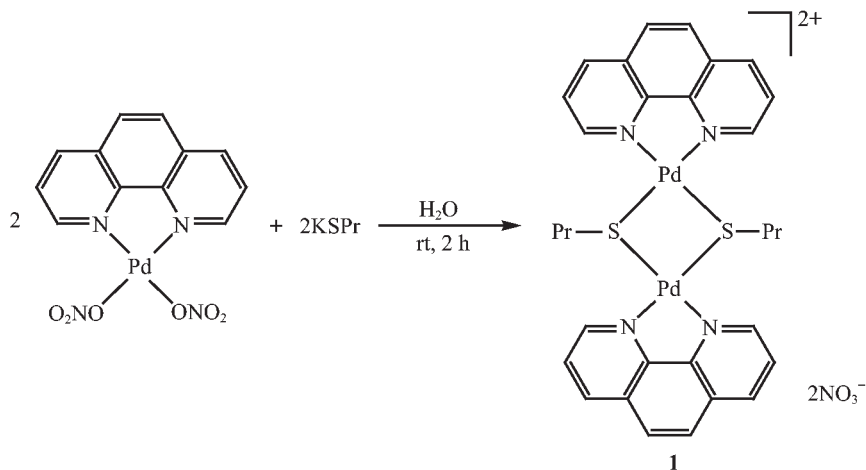
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cently an increased reference of π - π interactions can be noted. Polypyridyl ligands such as phenanthroline and bipyridine can act as a bridge to assemble multi-dimensional supramolecular architecture through polydentate ligands or aromatic ring stacking and hydrogen bonds^[3-10].



Scheme 1

1 Experimental

1.1 Materials and instrumentation

All reagents are received commercially and used without further purification. ^1H NMR experiment was performed on a Bruker Avance DMX400 spectrometer using TMS as internal standard. Elemental analyse (C, H, N) was carried on a Thermoquest Flash EA 1112 analytical instrument.

1.2 Preparation of $\{[(\text{phen})\text{Pd}(\mu\text{-SPr})_2\text{Pd}(\text{phen})](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}\}$ (**1**)

A mixture of fine powdered K_2CO_3 (83.0 mg, 0.6 mmol) and *n*-propylmercaptan (46 mg, 0.6 mmol) in dry DMF (10 mL) was reacted for 2 h at room temperature under stirring condition. The resulting solution was filtered, and then DMF was removed in vacuo. The residue was dissolved in deionized water (20 mL), and $(\text{phen})\text{Pd}(\text{NO}_3)_2$ (246.0 mg, 0.6 mmol) was added under stirring at room temperature. After 2 h, a yellow clear solution was obtained, and water was removed in vacuo. The resulting yellow solid was dissolved in methanol (10 mL). Yellow block single crystals were obtained by the vapor diffusion of diethyl ether at room temperature. Yield: 227.4 mg (89%). ^1H NMR

Herein we report a novel coplanar μ -S doubly-bridged 1,10-phenanthroline palladium (II) dinuclear complex $\{[(\text{phen})\text{Pd}(\mu\text{-SPr})_2\text{Pd}(\text{phen})](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}\}$ (**1**) (Scheme 1), that shows much stronger π - π stacking interactions, compared to that of the common aromatic systems.

(CD_4O , 400 MHz) δ : 1.00 (t, 6H, CH_3), 2.03 (m, 4H, CH_2), 2.96 (t, 4H, CH_2), 7.94 (s, 4H, phen- $\text{H}_{5,6}$), 8.05 (dd, $J_1=7.5$, $J_2=3.6$ Hz, 4H, phen- $\text{H}_{3,8}$), 8.68 (dd, $J_1=7.5$ Hz, 4H, phen- $\text{H}_{4,7}$), 9.05 (d, $J_1=3.6$ Hz, 4H, phen- $\text{H}_{2,9}$). Anal. Calcd. (%) for $\text{C}_{30}\text{H}_{30}\text{N}_6\text{O}_6\text{Pd}_2\text{S}_2$ (847.52): C, 42.52; H, 3.57; N, 9.92. Found(%): C, 42.41; H, 3.69; N, 9.85.

1.3 X-ray structure determination

The crystal sample of **1** selected for investigation has dimensions of 0.32 mm \times 0.28 mm \times 0.26 mm. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer equipped with a graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm) at 293 K. A total 17 985 reflections were measured to give 6 920 independent reflections ($R_{\text{int}}=0.036$ 0). Semiempirical absorption correction was applied using the SADABS program. The structure was solved by direct method and expanded using Fourier techniques (SHELXS-97). All non-hydrogen atoms were refined anisotropically employing full-matrix least-square techniques on F^2 by using SHELXTL (Bruker 2000) program. The hydrogen atoms bonded to carbon atoms were added geometrically and refined using riding model, whereas hydrogen atoms of disordered water

molecules were located from difference Fourier maps and refined isotropically. The weighting scheme is $w=1/[\sigma^2(F_o^2)+(0.07P)^2+1.99P]$ where $P=(F_o^2+2F_c^2)/3$. Crystal data for **1**: $C_{30}H_{34}N_6O_8Pd_2S_2$, monoclinic, $C2/c$ (No. 15), $a=2.165\ 1(3)$ nm, $b=1.291\ 4(2)$ nm, $c=2.716\ 2(3)$ nm, $\beta=111.987(3)^\circ$. $V=7.041\ 8(16)$ nm³, $Z=8$, $M_r=883.55$, $D_c=1.667$ g·cm⁻³, $\mu=1.196$ mm⁻¹, $F(000)=3\ 552$, $R=0.054\ 4$, $wR=0.127\ 4$, $GOF=1.114$, $(\Delta/\sigma)=0.000$, $\Delta\rho_{\max}=-857$ e·nm⁻³, $\Delta\rho_{\min}=-412$ e·nm⁻³.

CCDC: 292998.

2 Results and discussion

The ORTEP view of **1** with atom labeling is shown in Fig.1, and the crystal-packing diagrams are given in Fig.2 and Fig.3. The selected bond distances and angles are listed in Table 1. Table 2 gives the distances and angles related with hydrogen bonding.

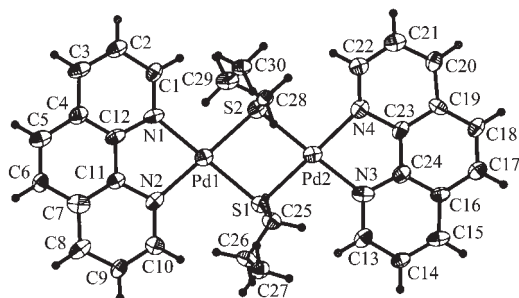


Fig.1 ORTEP diagram (30% probability ellipsoids, anion ions and solvent molecules of crystallization omitted for clarity) showing the solid-state structure and atom numbering scheme for **1**

As shown in Fig.1, two (phen)Pd moieties are bridged by two propylmercaptan molecules in an coplanar fashion with the dimensions of $1.55\text{ nm} \times 0.88\text{ nm}$. The separation of $Pd1 \cdots Pd2$ ($0.344\ 7(1)$ nm)

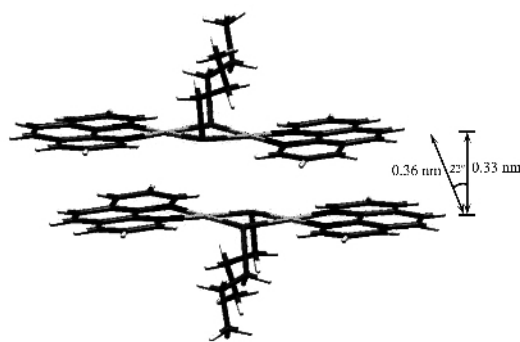


Fig.2 Offset face-to-face π - π stacking interaction of **1**

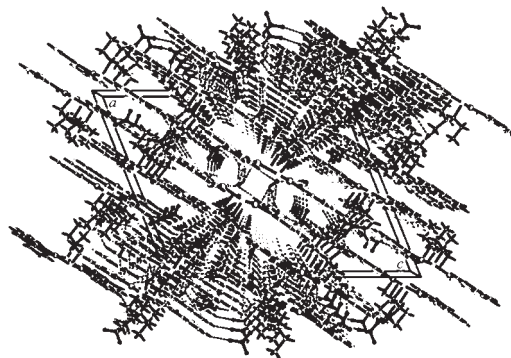


Fig.3 Crystal packing diagram of **1** along b axis

is longer the sum of the van der Waals radii of palladium (the typical value is 0.16 nm), which reveals quite weak $Pd \cdots Pd$ interaction. The coordination around the Pd atoms is square-planar. The deviations from the least-squares plane defined by the Pd, N and S atoms are less than 0.002 nm . The central four-membered ring consisting of the two Pd atoms and the two S atoms has a planar conformation with Pd-S distances between $0.227\ 2(2)$ and $0.231\ 9(1)$ nm and S-Pd-S angles of *ca.* 82° . The deviations from the least-squares plane defined by the Pd and S atoms are less than 0.004 nm .

In the crystal, molecules of complex **1** pack by

Table 1 Selected bond distances (nm) and angles ($^\circ$) of **1**

Pd1-N1	0.205 6(5)	Pd2-N3	0.204 3(5)	S1-C25	0.190 2(6)
Pd1-N2	0.207 3(5)	Pd2-N4	0.207 2(5)	S2-C28	0.184 1(5)
Pd1-S1	0.231 9(1)	Pd2-S1	0.228 9(1)	S1 \cdots S2	0.301 7(2)
Pd1-S2	0.227 2(2)	Pd2-S2	0.228 7(2)	Pd1 \cdots Pd2	0.344 7(1)
N1-Pd1-N2	81.3(2)	C25-S1-Pd1	104.3(2)	Pd1-S1-Pd2	96.8(1)
S1-Pd1-S2	82.2(1)	C25-S1-Pd2	94.6(2)	Pd1-S2-Pd2	98.2(1)
N3-Pd2-N4	81.7(2)	C28-S2-Pd1	105.0(2)		
S1-Pd2-S2	82.5(1)	C28-S2-Pd2	99.5(2)		

Table 2 Hydrogen bond lengths (nm) and angles (°) for **1**

D-H...A	<i>d</i> (D-H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)
O9-H9C...O4 ^a	0.085 00	0.199	0.275 9(6)	150
O9-H9A...O8	0.085 00	0.241	0.287 5(8)	115
O8-H8B...O7 ^b	0.085 00	0.227	0.273 1(10)	114
O7-H7C...O5 ^c	0.085 00	0.254	0.277 1(10)	96
O7-H7C...O8 ^b	0.085 00	0.214	0.273 1(10)	126
C1-H1...O8	0.093 00	0.245	0.328 9(9)	151
C3-H3...O5 ^d	0.093 00	0.247	0.331 7(7)	151
C3-H3...O6 ^d	0.093 00	0.237	0.324 2(7)	156
C6-H6...O1 ^e	0.093 00	0.257	0.337 8(7)	145
C8-H8...O1 ^e	0.093 00	0.259	0.338 7(7)	144
C10-H10...O7	0.093 00	0.241	0.327 3(10)	154
C20-H20...O3 ^f	0.093 00	0.258	0.335 0(8)	141
C22-H22...O9	0.093 00	0.236	0.313 3(7)	140
C30-H30...O3	0.093 00	0.254	0.343 9(7)	155

Symmetry codes: ^a $x-1/2, y-1/2, z$; ^b $1-x, 1-y, -z$; ^c $3/2-x, 3/2-y, -z$; ^d $3/2-x, 1/2-y, -z$; ^e $x, 1-y, -1/2+z$; ^f $1-x, y, 1/2-z$.

strong intermolecular offset face-to-face π - π stacking interactions, hydrogen bonding and ion-pairing (Fig.2 and 3). The interplanar distance is reported to be 0.33 nm for **1**. The centroid-centroid contact between two phenanthroline molecules is 0.36 nm, and the angle between the ring-centroid vector and the ring normal to one of the phenanthroline planes is about 22°.

The extensive hydrogen bonding between the 1,10-phenanthroline units, NO₃⁻ anions and water molecules throughout the lattice plays important roles in stabilizing the crystal (Table 2). The water molecules are disordered in the crystal. The occupancies of O7 and O8 atoms are 50%. Only the O9 atom is fully occupied. Interestingly, the water molecules and the bridging nitrate anion afford a ten-membered hydrogen-bonded ring. The O4 and O5 atoms of the bridging nitrate anion bond to O7 and O9 acting as hydrogen donor: O7-H7C...O5=0.277 1(10) nm (symmetry operation is $3/2-x, 3/2-y, -z$) and O9-H9C...O4=0.275 9(6) nm (symmetry operation is $x-1/2, y-1/2$). The O7, O8 and O9 atoms act as hydrogen donor and acceptor each other.

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