

二维网状 Pd(II)配合物的合成、晶体结构及电化学性质

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关键词: 钯(II)配合物; 2,2'-联吡啶-3,3'-二羧酸; 晶体结构; 电化学性质

中图分类号: O614.82·3 文献标识码: A 文章编号: 1001-4861(2010)11-2109-04

Synthesis, Crystal Structure and Electrochemical Properties of 2D Network Palladium(II) Complex

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Abstract: A novel palladium(II) complex $[\text{Pd}(\text{H}_2\text{bpdc})\text{Ala}]\text{Cl}\cdot 3\text{H}_2\text{O}$ (where H_2bpdc is 2,2'-bipyridine-3,3'-dicarboxylic acid and Ala is L-alanine) has been synthesized and characterized by IR spectra and elemental analysis. The crystal structure of the complex has been determined by single-crystal X-ray diffraction analysis. It crystallizes in triclinic system, space group $P\bar{1}$ with $a=0.685\ 5(2)$ nm, $b=0.988\ 4(4)$ nm, $c=1.349\ 6(4)$ nm, $\alpha=98.375(8)^\circ$, $\beta=97.900(15)^\circ$, $\gamma=90.118(15)^\circ$, $V=0.895\ 9(5)$ nm³, $Z=2$. In the molecule, Pd(II) atom is four-coordinated and located at the centre of a planar quadrangle. The complex is assembled via intramolecular π - π stacking interactions and hydrogen bonds, which forms 2D network. The cyclic voltammetric behavior of the complex was also investigated. CCDC: 792221.

Key words: palladium(II) complex; 2,2'-bipyridine-3,3'-dicarboxylic acid; crystal structure; electrochemical property

2,2'-bipyridine-3,3'-dicarboxylic acid (H_2bpdc) is a typical example of multidentate ligand. In it, nitrogen atom of bipyridyl moiety and oxygen atom of dicarboxyl functional group can act not only as hydrogen bond donors but as acceptors, which make it a wonderful candidate for the construction of supramolecular networks. 2,2'-bipyridine-3,3'-dicarboxylic acid has been proved to be a suitable ligand for the formation of 1D, 2D and 3D network structures^[1-4]. In addition, some studies have revealed that its complexes have potential applications as spectroscopic, electrochemical and

magnetic materials^[5-7]. But there are very few reports on ternary transition metal complexes coordinated with it. In this paper, a novel mixed ligand complex with 2,2'-bipyridine-3,3'-dicarboxylic acid and amino acid is synthesized, the crystal structure is determined by single-crystal X-ray diffraction, the electrochemical property of the complex is also further investigated.

1 Experimental

1.1 Reagents and apparatuses

All reagents are analytically pure. IR spectra were

收稿日期: 2010-05-10。收修改稿日期: 2010-08-09。

沈阳化工学院青年科研启动基金(No.200303)资助。

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performed on a NEXUS 470 spectrometer with KBr pellets. Crystal structure determination was carried out on a Rigaku Saturn CCD X-ray diffractometer. The electron transfer behavior of the complex was examined using cyclic voltammogram on a CHI-660c electrochemical analysis system. C, H and N analyses were recorded on a Finnigan EA1112 elemental analyzer.

1.2 Synthesis of the complex

2,2'-bipyridine-3,3'-dicarboxylic acid and Pd(H₂bpdC)Cl₂ were synthesized according to literature^[8-9]. 0.421 g (1 mmol) Pd(H₂bpdC)Cl₂, was suspended into 20 mL water, and 0.089 g (1 mmol) L-alanine was added. The mixture was stirred for 2 h, then the solution was concentrated in a rotary evaporator. Finally the buff crystals were obtained after four weeks. Anal. Calcd. for C₁₅H₂₀ClN₃O₉Pd(%): C 34.10, H 3.79, N 7.96; found(%): C 34.25, H 3.24, N 8.23. IR (KBr, cm⁻¹): 3 516 s, 3 195 w, 3 099 m, 1 670 vs, 1 570 m, 1 458 m, 1 421 m, 1 362 vs, 1 286 m, 1 243 w, 1 119 m, 859 w, 831 m, 772 m, 694 m, 517m.

1.3 Structure determination of the complex

All measurements were made on a Rigaku Saturn CCD detector with graphite monochromatized Mo K α radiation ($\lambda=0.071\ 073\ \text{nm}$). The data were collected using φ - ω scans at 113(2) K. A total of 8 144 reflections were collected in the range of $1.54^\circ \leq \theta \leq 27.87^\circ$, of which 4 179 ($R_{\text{int}}=0.028\ 1$) were independent and 830 were observed ($I>2\sigma(I)$). The structures were solved by direct methods and refined by full matrix least squares on F² with SHELXTL program. All-non hydrogen atoms were refined anisotropically.

CCDC: 792221.

2 Results and discussion

2.1 Crystal structure determination

The crystal parameters and details of data collection are summarized in Table 1. The selected bond lengths and bond angles are listed in Table 2. The molecular structure and 2D net structure of the complex are shown in the Fig.1 and 2.

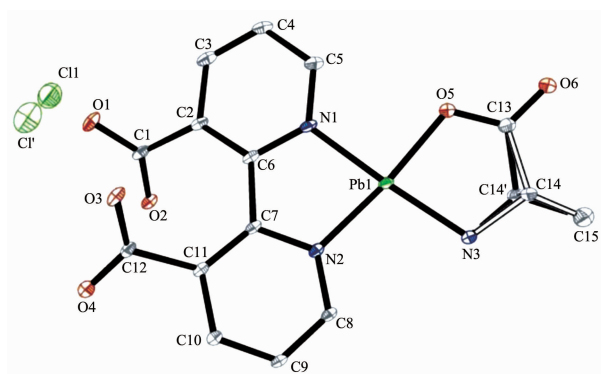
Single-crystal X-ray diffraction analysis indicates

Table 1 Crystallographic data and details of the structure refinement

Empirical formula	C ₁₅ H ₂₀ ClN ₃ O ₉ Pd	Z	2
Formula weight	528.21	$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.958
Temperature / K	113(2)	$F(000)$	532
Crystal system	Triclinic	Crystal size / mm	0.20×0.20×0.20
Space group	$P\bar{1}$	θ range for data collection / (°)	1.54~27.87
a / nm	0.685 5(2)	Limiting indices	$-9 \leq h \leq 6, -12 \leq k \leq 11, -17 \leq l \leq 17$
b / nm	0.988 4(4)	Reflections collected / unique (R_{int})	8 144 / 4 179 (0.028 1)
c / nm	1.349 6(4)	Data / restraints / parameters	4 179 / 830 / 286
$\alpha / (^\circ)$	98.375(8)	Refinement on F^2	1.074
$\beta / (^\circ)$	97.900(15)	Final R indices ($I>2\sigma(I)$)	$R_1=0.043\ 7, wR_2=0.125\ 3$
$\gamma / (^\circ)$	90.118(15)	R indices (all data)	$R_1=0.049\ 1, wR_2=0.129\ 0$
Volume / nm ³	0.895 9(5)	Largest difference peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	3 445, -1 682

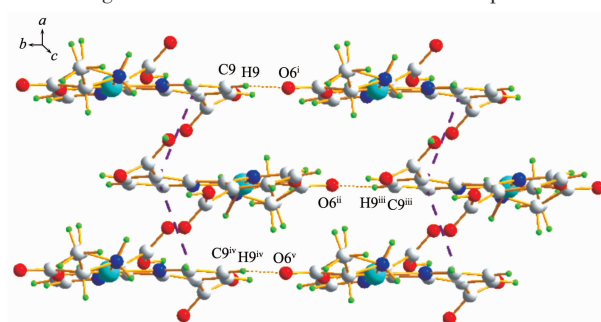
Table 2 Selected bond lengths (nm) and bond angles (°) for the title complex

N(1)-Pd(1)	0.199 9(3)	N(3)-Pd(1)	0.205 3(3)	O(5)-Pd(1)	0.198 9(3)
N(2)-Pd(1)	0.200 7(3)				
C(5)-N(1)-Pd(1)	121.2(3)	Pd(1)-N(3)-H(3C)	109.3	N(1)-Pd(1)-N(2)	80.19(13)
C(6)-N(1)-Pd(1)	115.8(3)	Pd(1)-N(3)-H(3B)	108.9	O(5)-Pd(1)-N(3)	82.61(12)
C(8)-N(2)-Pd(1)	123.0(3)	C(13)-O(5)-Pd(1)	116.7(3)	N(1)-Pd(1)-N(3)	175.61(13)
C(7)-N(2)-Pd(1)	116.0(2)	O(5)-Pd(1)-N(1)	94.04(13)	N(2)-Pd(1)-N(3)	103.23(13)
C(14)-N(3)-Pd(1)	109.7(2)	O(5)-Pd(1)-N(2)	174.02(11)		



Hydrogen atoms and crystal waters are omitted for clarity, 30% probability level

Fig.1 Molecular structure of the title complex



Symmetry codes: ⁱ $x, -1+y, z$; ⁱⁱ $2-x, 2-y, 1-z$; ⁱⁱⁱ $2-x, 1-y, 1-z$; ^{iv} $-1+x, y, z$; ^v $-1+x, -1+y, z$; π - π stacking interactions between the chains are indicated as “-----” and hydrogen bonding are indicated as “.....”

Fig.2 Extended 2D structure of the complex by π - π stacking and hydrogen bonding interactions

that the complex crystallizes in $P\bar{1}$ space group. The core structure of complex is composed of one $[\text{Pd}(\text{H}_2\text{bpdc})\text{Ala}]^-$, one chloride ion and three molecules of H_2O as lattice solvent. $\text{Pd}(\text{II})$ atom is four-coordinated via N1, N2 from H_2bpdc , and N3, O5 from L-alanine. From Table 2, bond lengths of N1-Pd1, N2-Pd1, N3-Pd1, O5-Pd1 are 0.199 9(3), 0.200 7(3), 0.205 3(3) and 0.198 9 (3) nm, respectively, which are close to those of some $\text{Pd}(\text{II})$ complexes^[10-12]. Bond angles of N1-Pd1-N3 and O5-Pd1-N2 are 175.61(13)° and 174.02(12)° respectively, which shows that the coordination geometry is slightly distorted planar square. The two pyridine rings are not planar since the dihedral angle between the pyridine rings of H_2bpdc is 18.81°. It is a usual feature for several complexes bridged by the ligands containing 2,2'-bipyridyl unit^[13-14].

The complex is involved in intramolecular π - π stacking and hydrogen bonding interactions, which plays an important role in the formation of the two-dimensional supramolecular networks. There are offset face-to-face π - π stacking interactions between the pyridine ring containing N2 and the same pyridine ring positioned in the nearest parallel molecule. Cg1, Cg2 and Cg3 are the centroid of three parallel pyridine ring. They interact via π - π stacking interactions with distance of Cg1-Cg2 0.370 5 nm and Cg2-Cg3 0.370 89 nm, perpendicular distance of the three plane are 0.324 8 nm and 0.352 8 nm. Due to these π - π stacking the complex has a 1D zigzag chain structure. The adjacent zigzag chains are linked each other by the hydrogen bond interactions between the uncoordinated carboxyl oxygen atom (O6) of L-alanine and the carbon atom (C9) of the pyridine rings of the adjacent zigzag chain, which lead to a 2D network (Fig.2).

2.2 Electrochemical property

The standard three-electrode system with Au disk working electrode, a Pt rod auxiliary electrode, and the SCE reference electrode was used for electrochemical detection. The cyclic voltammogram of the complex was obtained with 0.001 mol·L⁻¹ the complex in water. The scanning rate was 0.1 V·s⁻¹, at the range from 0 to 1.3 V. From the voltammogram curves (Fig.3), it shows only one pair of oxidation-reduction peaks corresponding to the oxidation-reduction couple of Pd^{2+}/Pd , $E_{\text{pa}}=0.470$ V, $E_{\text{pc}}=1.119$ V. The average formal potential ($E_{1/2}$) is 0.795 V. The peak-to-peak separation between the corresponding anodic and cathodic peak is 0.649 V, exhibiting a irreversible electrode process.

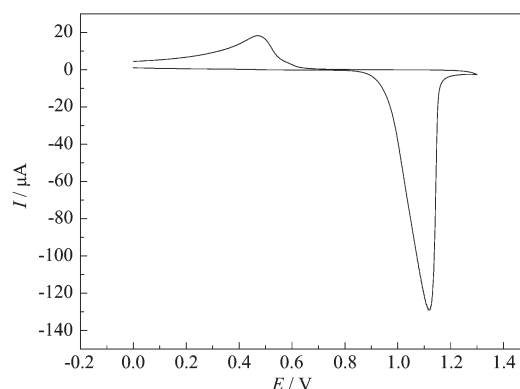


Fig.3 Cyclic voltammogram of the complex

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