

对乙酰氨基苯甲酸和含氮配体构筑铜、锌配合物的合成、结构及性质研究

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摘要: 利用对乙酰氨基苯甲酸(HPABA)和邻菲咯啉(phen)、硝酸铜在 DMF/CH₃OH/H₂O 溶液中合成了单核铜配合物[Cu(PABA)(phen)(H₂O)₂](NO₃)·H₂O (**1**), 然后又和 4,4'-联吡啶(4,4'-bpy)、硝酸锌在 DMF/CH₃OH/H₂O 溶液中获得配位聚合物 {[Zn(PABA)₂(4,4'-bpy)]·4H₂O}_n (**2**)。根据 X 射线衍射分析结果, 配合物 **1** 中每个铜离子周围有 2 个氮原子和 3 个氧原子与之配位形成畸变的四方锥配位构型, 然而在配合物 **2** 中, 六配位八面体构型的锌离子通过配体 4,4'-联吡啶扩展为一维 Zigzag 型链。分别对这两个配合物的热稳定性和电化学性质进行了研究。

关键词: 铜(II)配合物; 锌(II)配合物; 对乙酰氨基苯甲酸; 晶体结构

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Synthesis, Crystal Structure and Properties of Copper and Zinc Complexes Constructed from 4-Acetylamino benzoic Acid and N-Donor Ligands

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Abstract: [Cu(PABA)(phen)(H₂O)₂](NO₃)·H₂O (**1**) was synthesized by mixing 4-acetylamino benzoic acid (HPABA), 1,10'-phenanthroline (phen) and Cu(NO₃)₂ in DMF/CH₃OH/H₂O solution, while {[Zn(PABA)₂(4,4'-bpy)]·4H₂O}_n (**2**) was produced by dissolving HPABA, 4,4'-bipyridine (4,4'-bpy) and Zn(NO₃)₂ in DMF/CH₃OH/H₂O solution. After that their crystal structures were determined by X-ray diffraction analysis, which revealed that each Cu ion is coordinated with two N atoms from phen and three O atoms from PABA ligand and water molecules by tetragonal pyramid, while, in complex **2**, the central Zn ion shows a one-dimensional zigzag chain bridged by 4,4'-bpy molecules. Thermal properties and the cyclic voltammetric behaviors of the two complexes were investigated. CCDC: 817613, **1**; 945696, **2**.

Keywords: Cu(II) complex; Zn(II) complex; 4-acetylamino benzoic acid; crystal structure

0 Introduction

In recent years, rational design and synthesis of metal-organic frameworks (MOFs) constructed from

metal salts and functional organic ligands have attracted great attention, not only because of their intriguing variety of architectures^[1-7], but also due to their potential applications in ion-exchange, nonlinear

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optics, molecular sieves, gas storage, catalysis, magnetism, and molecular sensing^[8-11]. However, it is still a great challenge to exactly predict structures and compositions of MOFs because even very small tuning factors can dramatically change the framework structure. Of all these factors, the choice of ligands is mostly important for constructing the aimed structures^[12-13]. Furthermore, mixed ligands with N-donor groups acting as ancillary connector are proved to be effective building units to construct novel coordination polymers, because they have strong coordination affinity and can satisfy the geometric need of the metal centers. The 4-acetamidobenzoic acid (HPABA)^[14], which may act as a polydentate ligand and present a variety of coordination modes because of the presence of two carboxyl functions and a acetyl group, has been limited studied so far. In order to further investigate the influence of organic ligands on the coordination architectures and related properties, reactions of metal ions with HPABA as well as N-donor ligands were carried out. Herein we report the syntheses, crystal structures, properties of two complexes, namely [Cu(PABA)(phen)(H₂O)₂]·(NO₃)·H₂O (**1**) and {[Zn(PABA)₂(4,4'-bpy)]·4H₂O}_n (**2**).

1 Experimental

1.1 Materials and instruments

All the reagents and solvents were used as commercially delivered without further purification. The IR spectra were recorded on an AVATAR 360 spectrophotometer using KBr discs. Thermal analysis was recorded on an STA409PC thermogravimetry. The crystal structure was determined on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromatized Mo K α radiation($\lambda=0.071\ 073\ \text{nm}$). Cyclic voltametric graph was recorded by a CHI660d electrochemical analysis system.

1.2 Preparation of the complexes [Cu(PABA)

(phen)(H₂O)₂]·(NO₃)·H₂O and {[Zn(PABA)₂(4,4'-bpy)]·4H₂O}_n

For the complex **1**, to a solution of 4-acetylaminobenzoic (HPABA) acid (1mmol) dissolved in DMF (7 mL), an aqueous solution (5 mL) of Cu(NO₃)₂

·3H₂O (1 mmol) and a solution of 1,10-phenanthroline (1 mmol) in ethanol (95%, 5 mL) was added. After refluxed for 12 h at 70 °C, the mixture was filtered off at room temperature. The blue blocky single crystals suited for X-ray analysis were obtained by slow evaporation of the filtrate at room temperature after 2 months. Following main IR bands (cm⁻¹) were detected: 3 427 (s), 1 668 (w), 1 599(s), 1 561 (w), 1 522 (s), 1 429 (m), 1 384 (vs), 1 313 (s), 1 272 (w), 1 181 (m), 1 150 (w), 1 109 (w), 1 038(w), 1 003(vw), 852 (s), 815 (w), 783 (m), 722 (s), 698 (m), 593 (w), and 469 (w).

For complex **2**, to a solution of 4-acetylaminobenzoic acid (HPABA) (1 mmol) in DMF (7 mL), an aqueous solution (5 ml) of ZnSO₄·7H₂O (1mmol) and a solution of 4,4'-bipyridine (1 mmol) in methanol (95%, 5ml) was added. After refluxed for 12 h at 70 °C, the mixture was also filtered off at room temperature. The colorless single crystal samples for X-ray analysis were gained by slow evaporation of the filtrate at room temperature after 4 weeks. In IR spectrum, about 20 main bands (cm⁻¹) were observed: 3 415 (s), 1 679 (w), 1 603 (s), 1 564 (w), 1 526 (s), 1 429 (m), 1 391 (vs), 1 320 (s), 1 265 (w), 1 177 (m), 1 141 (w), 1 071 (w), 1 013 (vw), 867 (s), 819 (m), 790 (s), 699 (s), 640 (m), 508 (vw), and 458 (w).

1.3 X-ray crystallography and structure determination

The two kinds of crystals were selected for the X-ray measurement. The diffraction data were collected at 296(2) K (**1**) and 293(2) K (**2**) on a Bruker Apex-II CCD diffractometer equipped with a graphite-monochromatized Mo K α radiation ($\lambda=0.071\ 073\ \text{nm}$) respectively. All structures were solved by direct methods by using the SHELXS program of the SHELXTL package and refined with SHELXL by the full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F^2 . All hydrogen atoms were generated geometrically (C-H bond lengths fixed at 0.093 ~0.096 nm), assigned appropriated isotropic thermal parameters and included in structure factor calculations. Table 1 shows crystallographic crystal data of the complexes.

CCDC: 817613, **1**; 945696, **2**.

Table 1 Crystal data and structure parameters for the title complexes

Complex	1	2
Empirical formula	C ₂₁ H ₂₂ N ₄ CuO ₉	C ₂₈ H ₃₂ N ₄ ZnO ₁₀
Formula weight	537.97	649.95
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> / nm	0.796 31(17)	1.142 19((15)
<i>b</i> / nm	1.202 4(3)	1.176 28(15)
<i>c</i> / nm	1.361 8(3)	1.237 56(16)
α / (°)	110.555(9)	88.559(2)
β / (°)	97.461(10)	86.842(2)
γ / (°)	107.795(10)	65.001(2)
<i>V</i> / nm ³	1.120 6(4)	1.504 6(3)
<i>Z</i>	2	2
Absorption coefficient / mm ⁻¹	1.036	0.878
<i>F</i> (000)	554	676
Reflections collected / unique	6 192 / 4 313 (<i>R</i> _{int} =0.016)	8 867 / 5 574 (<i>R</i> _{int} =0.034 4)
Data / restraints / parameters	4 313 / 0 / 317	5 574 / 0 / 390
Final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> ^a =0.031 9, <i>wR</i> ^b =0.085 0	<i>R</i> ^a =0.034 0, <i>wR</i> ^b =0.091 2
Largest diff. peak and hole / (e·nm ⁻³)	338 and -355	282 and -365

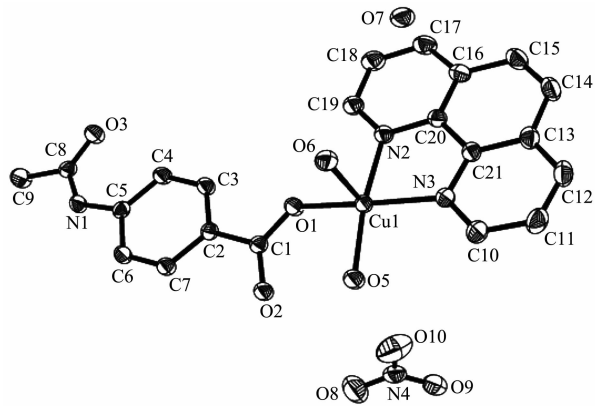
^a Conventional *R* on *F*_{obs}: $\sum ||F_o|-|F_c|| / \sum |F_o|$; ^b Weighted *R* on *|F_{obs}|*²: $\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$

2 Results and discussion

2.1 Crystal structure of the title complex

The molecular structure of the complex **1** is shown in Fig.1, and the 2D network structure is shown in Fig.2. The selected bond lengths and bond angles are given in Table 2. Parameters of hydrogen bonds are given in Table 3.

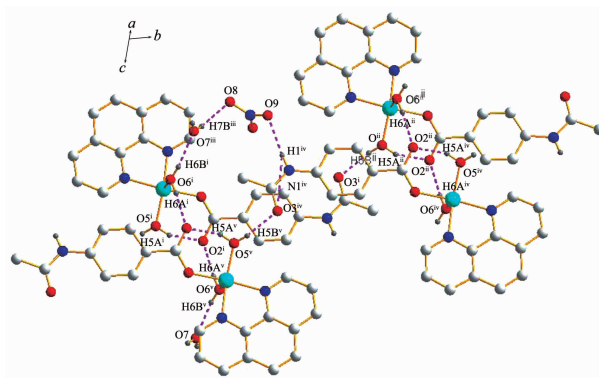
There are one Cu(II), one phen molecule, one unique PABA ligand, one nitrate ion, two coordinated water and one free water molecule in the asymmetric



All hydrogen atoms are omitted for clarity

Fig.1 Molecular structure of the complex **1** showing 30% probability displacement ellipsoids

unit of complex **1**. As shown in Fig.1, each Cu(II) is coordinated by three oxygen atoms and two nitrogen atoms with a distorted square-pyramidal coordination geometry. The Cu-O bond distances range from 0.192 83(17) to 0.226 33(19) nm, while the Cu-N bonds from 0.200 00(18) to 0.202 27(18) nm, respectively. It is interesting that the PABA acts as a single dentate ligand in the complex, which uses only one of the carboxyl oxygen atoms to bond with the Cu ion, while



Some hydrogen atoms are omitted for clarity; Symmetry codes:

ⁱ 1-x, 1-y, 1-z; ⁱⁱ 2-x, 2-y, 1-z; ⁱⁱⁱ -x, 1-y, 1-z; ^{iv} x, 1+y, z;

^v -1+x, y, z

Fig.2 2D layers structure for the complex **1** formed by hydrogen bonds

Table 2 Selected bond lengths (nm) and bond angles (°) for the complexes 1 and 2

1					
Cu1-O5	0.192 83(17)	Cu1-O1	0.196 66(15)	Cu1-N2	0.200 00(18)
Cu1-N3	0.202 27(18)	Cu1-O6	0.226 33(19)		
O5-Cu1-O1	92.58(7)	O5-Cu1-N2	169.94(9)	O5-Cu1-O6	92.98(9)
O1-Cu1-N2	90.82(7)	O5-Cu1-N3	93.15(8)	N2-Cu1-O6	96.15(7)
O1-Cu1-N3	169.65(7)	N2-Cu1-N3	82.15(7)	O1-Cu1-O6	95.03(7)
N3-Cu1-O6	93.28(7)				
2					
Zn1-O2	0.240 20(16)	Zn1-O3	0.204 04(15)	Zn1-O5	0.201 05(16)
Zn1-O6	0.239 16(17)	Zn1-N3	0.209 37(17)	Zn1-N4	0.206 80(17)
O5-Zn1-O3	155.16(7)	O5-Zn1-N4	95.24(7)	O3-Zn1-N4	102.54(7)
O5-Zn1-N3	103.00(7)	O3-Zn1-N3	91.47(6)	N4-Zn1-N3	98.53(7)
O5-Zn1-O6	58.64(6)	O3-Zn1-O6	101.08(6)	N4-Zn1-O6	153.38(6)
N3-Zn1-O6	92.96(6)	O5-Zn1-O2	104.86(6)	O3-Zn1-O2	58.19(5)
N4-Zn1-O2	90.86(6)	N3-Zn1-O2	149.59(6)	O6-Zn1-O2	91.22(6)

Table 3 Parameters of hydrogen bonds for the complexes 1 and 2

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠D-H...A / (°)
1				
N1 ^{iv} -H1...O9	0.085 99	0.211 85	0.296 2(4)	166.69
O5 ⁱ -H5A...O2 ⁱ	0.082 02	0.177 48	0.254 7(3)	156.13
O5 ⁱⁱ -H5B...O3 ⁱ	0.079(4)	0.195(4)	0.270 2(3)	160(4)
O6 ^v -H6A...O2 ⁱ	0.081 98	0.202 85	0.284 5(3)	173.60
O6 ⁱ -H6B...O7 ⁱⁱⁱ	0.078(3)	0.199(3)	0.276 7(3)	171(3)
O7 ⁱⁱⁱ -H7B...O8	0.068(4)	0.220(4)	0.285 7(5)	165(4)
2				
O1W-H1WA...O3	0.091 00	0.190 00	0.279 7(3)	167.00
N1 ^{iv} -H1D...O2W	0.084 00	0.211 00	0.293 4(3)	170.00
N2-H2...O1 ^v	0.092 00	0.202 00	0.293 5(2)	173.00
O1W-H1WB...O3W ⁱ	0.090 00	0.187 00	0.275 9(3)	170.00
O2W-H2WA...O1W ^v	0.095 00	0.194 00	0.285 9(3)	161.00
O2W-H2WB...O1W	0.091 00	0.194 00	0.283 5(3)	171.00
O3W-H3WA...O6 ⁱⁱ	0.095 00	0.183 00	0.278 0(3)	178.00
O3W-H3WB...O4W	0.098 00	0.190 00	0.285 8(3)	164.00
O4W-H4WA...O4 ^{viii}	0.099 00	0.202 00	0.295 3(3)	156.00
O4W-H4WB...O2 ^{iv}	0.099 00	0.186 00	0.281 0(3)	160.00

Symmetry codes: **1:** ⁱ 1-x, 1-y, 1-z; ⁱⁱ 2-x, 2-y, 1-z; ⁱⁱⁱ -x, 1-y, 1-z; ^{iv} x, 1+y, z; ^v -1+x, y, z. **2:** ⁱ 1-x, 1-y, 1-z; ⁱⁱ x, 1+y, z;

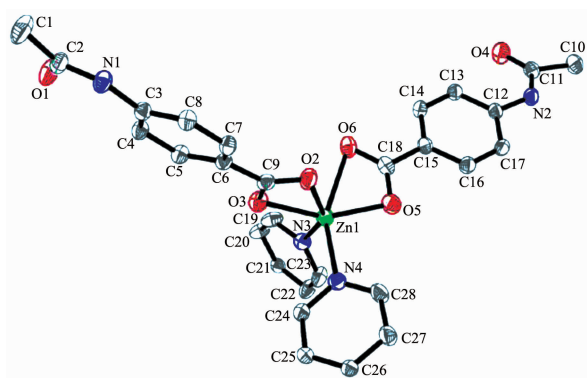
^v 2-x, -y, 1-z; ^{vi} -x, 1-y, 2-z; ^{viii} 1+x, y, z.

the other oxygen atoms do not take part in the coordination and deprotonation. The mononuclear Cu complex is further formed into a two dimensional (2D) layer structure (Fig.2) through hydrogen bonds interactions between uncoordinated nitrate, PABA

ligand, and coordination waters (Table 3). Furthermore, there are other hydrogen bonds such as C-H...O which extend the complex into a 3D network structure.

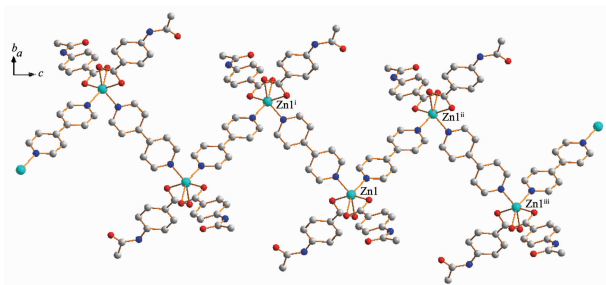
In addition to the chelating ligands of phen used

in the complex **1** as described above, the bridging auxiliary ligands 4,4'-bpy was employed in the reactions of PABA with Zn(II) salts. As illustrated in Fig.3, the Zn ion with a octahedral coordination geometry is coordinated by four O atoms from two PABA anions, two N atoms ions from the 4,4'-bpy molecules, which is entirely different from that of complex **1**. In complex **2**, the Zn-O distances range from 0.201 05(16) to 0.240 20(16) nm, and the Zn-N distances are 0.206 80 (17) and 0.209 37 (17) nm,



All hydrogen atoms are omitted for clarity

Fig.3 Molecular structure of the complex **2** showing 30% probability displacement ellipsoids



All hydrogen atoms and water molecules are omitted for clarity;
Symmetry codes: Symmetry codes: ⁱ 1-x, 1-y, 1-z; ⁱⁱ 2-x, -y, 2-z; ⁱⁱⁱ 1+x, -1+y, -1+z

Fig.4 1D chain structure linked by PABA, 4,4'-bpy ligands and Zn(II) centers of the complex **2**

respectively (Table 2). The carboxylate groups of the PABA ligands adopts the same bidentate chelating coordination mode to connect the Zn(II) ions, which is similar to the reported Cd complex [15]. Then the adjacent six-coordinated Zn ions are interlinked by the rigid 4,4'-bpy bridging ligands to form a 1D Zigzag chain structure as showed in Fig.4. There are a lot of hydrogen bonds like complex **1**. These hydrogen bonds play an important role in stabilizing the crystal structure.

2.2 IR and thermal gravimetric analyses

The IR spectra of the complexes have been recorded and some important assignments are shown above. The band at 3 427 cm⁻¹, due to the $\nu(\text{O-H})$ absorptions of water molecules. Two strong peaks at 1 599 and 1 522 cm⁻¹ for complex **1** and 1 603 and 1 526 cm⁻¹ for complex **2** could be assigned to the $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ stretching vibration of carboxyl in 4-acetamidobenzoic acid ligand. In complex **1**, compared to those of free phen (1 421, 858 and 725 cm⁻¹), the IR peaks shift to some extent, indicating that phen has participated in coordination. The peak at 1 384 cm⁻¹ could be assigned to characteristic peak of the NO₃⁻. And in complex **2**, 4,4'-bpy adsorption peaks are 790 and 640 cm⁻¹ respectively. These IR results are coincident with the crystallographic structural analyses.

In addition, thermal gravimetric analyses (TGA) were performed to verify the thermal stability of the complexes. For complex **1**, the first stage, occurring between 64 and 187 °C, is attributed to the loss of one free and two coordinated water molecules per formula (Observed weight loss, 10.03%; Calcd., 10.04%). The weight is almost unchanged in the temperature range

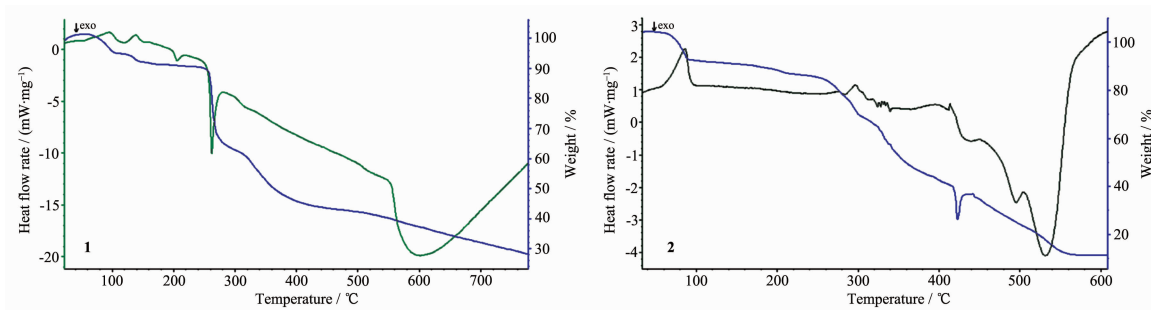


Fig.5 TG-DSC curves of complexes **1** and **2**

187~265 °C. Above 265 °C, the residue begins to decompose. Complex 2 lost a weight of 11.08% was observed in the temperature range of 50~90 °C, which corresponds to the release of all uncoordinated water molecules (Calcd. 11.07%), and then the residue decomposed upon further heating at about 310 °C, which the ligand PABA decompose with 27.24% (Calcd. 27.38%). Therefore, the results indicate that the complexes have high stability (Fig.5).

2.3 Electrochemical property

Fig.6 shows the cyclic voltammogram (CV) curves of complex 1 and 2. In the CV measurement of complex 1, we employed a conventional three-electrodes system where a platinum electrode was chosen as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a glass/C electrode as the counter electrode. In the electrochemical measurement, the crystal of complexes 1 and 2 was dissolved in DMF. HAc-NaAc solution (pH=4.0) was used as a buffer solution, and KCl is used as the supporting electrolyte. The scanning range is -1.0~0.6 V, as

revealed by Fig.6. In complex 1, there exists a pair of redox peak Cu(II)/Cu(I) in the CV curve, $E_{pa} = -0.036$ V and $E_{pc} = -0.103$ V. The average formal potential $(E_{pa} + E_{pc})/2$ is -0.0695 V. The peak to peak separation is 0.067 V and the i_{pc}/i_{pa} ratio is -0.17 , indicating that the electron transfer in the electrode reaction is quasi-reversible. On the other hand, in complex 2, the result shows that only one restore peak appears with $E_{pc} = -0.440$ V, so the electron transfer in the electrode reaction is irreversible.

2.4 Quantum chemistry research of the complex 1

According to the atomic coordinates of crystal structure of the compound, with the B3LYP/Lanl2dz basis set of Gaussian 03W program and the method reported, quantum chemistry research was conducted for the complex 1. The total energy of the molecule is $-1\,548.595\,290\,3$ a.u., the HOMO energy is $-0.309\,47$ a.u., and the LUMO energy is $-0.129\,28$ a.u.. Thus, the total energy and occupied orbital energy are fairly lower, and the energy gap between HOMO and LUMO

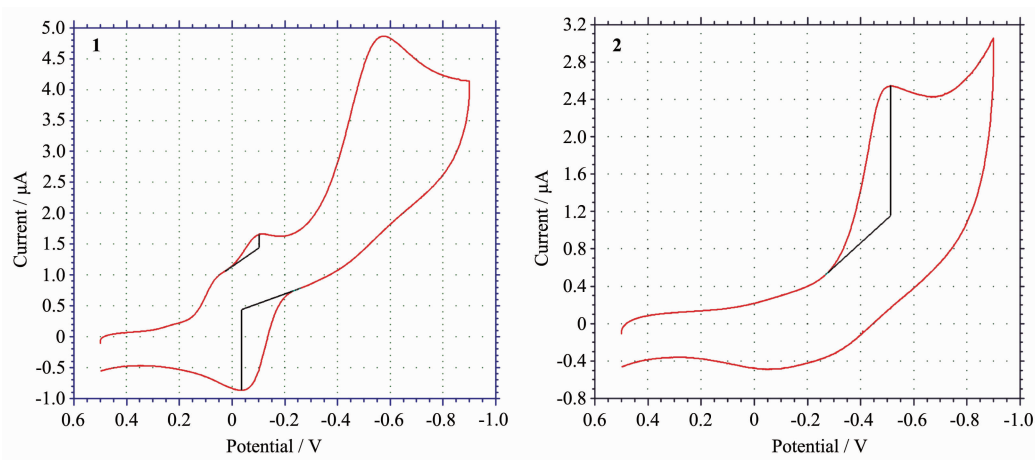


Fig.6 Cyclic voltammogram (CV) curves of complexes 1 and 2

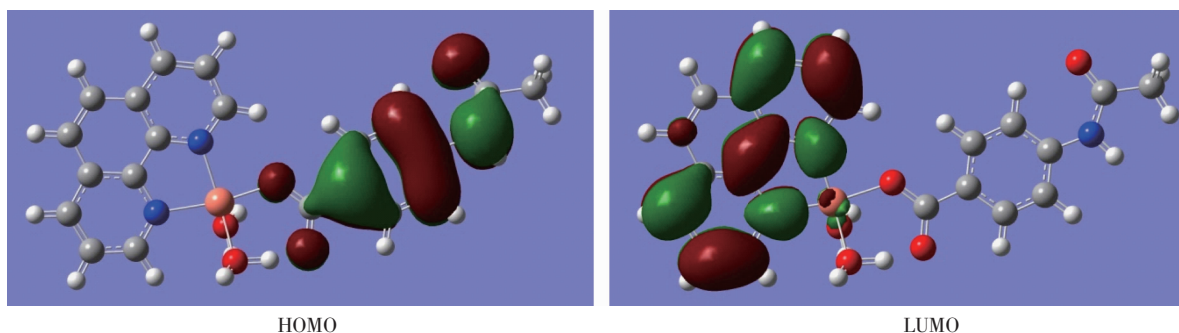


Fig.7 Schematic diagram of the frontier MO for the complex 1

Table 4 Atomic charge populations at B3LYP/Lanl2dz level for the complex 1

Cu(1)	0.654 751	C(1)	0.292 683	C(10)	-0.235 009	C(19)	-0.217 062	H(9C)	0.256 215	H(5A)	0.393 150
O(1)	-0.483 835	C(2)	0.296 878	C(11)	-0.152 235	C(20)	0.072 387	H(10)	0.270 206	H(5B)	0.414 134
O(2)	-0.451 759	C(3)	-0.319 454	C(12)	-0.300 485	C(21)	0.075 182	H(11)	0.257 027	H(1)	0.312 061
O(3)	-0.281 662	C(4)	-0.320 053	C(13)	0.469 695	H(3)	0.223 006	H(12)	0.270 861	H(6A)	0.449 167
O(5)	-0.779 716	C(5)	0.466 094	C(14)	-0.405 499	H(4)	0.315 088	H(14)	0.256 293	H(6B)	0.429 936
O(6)	-0.700 022	C(6)	-0.419 802	C(15)	-0.404 744	H(6)	0.226 961	H(15)	0.256 899		
N(1)	-0.454 604	C(7)	-0.319 210	C(16)	0.469 001	H(7)	0.274 978	H(17)	0.270 066		
N(2)	-0.280 714	C(8)	0.258 091	C(17)	-0.30 0648	H(9A)	0.252 830	H(18)	0.258 409		
N(3)	-0.246 121	C(9)	-0.722 966	C(18)	-0.151 002	H(9B)	0.205 770	H(19)	0.298 782		

is only 0.102 87 a.u., Based on the analysis of the system energy and frontier orbital energy, the complex 1 is fairly difficult to lose electron, and its base state is fairly stable.

Mulliken charge distributions of all atoms in the complex are calculated and the results were illustrated in Table 4. The results show that Cu, H and C (non-bonding with H atoms) are all positive. N, O and C (bonding with H atoms) are all negative. The net charge of Cu is +0.6547 51, deviating from +2. The net charges of N atoms (N(2) and N(3)) range from -0.280 714 to -0.246 121, O atoms (O (1), O (2), O (5W) and O (6W)) range from -0.483 835, -0.451 759, -0.779 716 to -0.700 022, showing part electrons of N and O atoms transfer to Cu and then covalent bonds come into being. The analysis of the Mulliken charge distributions is consistent with the crystal determination.

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