

以 N,N' -二异丁基-2,3-二胺基喹喔啉为配体的钴和 锌配合物的合成、晶体结构以及性质研究

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摘要: 以 2,3-二氯喹喔啉和异丁胺为原料, 合成了 N,N' -二异丁基-2,3-二胺基喹喔啉(L), 并合成了两个标题配合物([Co(DIDAQX)Cl₂]) (**1**, DIDAQX= N,N' -Diisobutyl-2,3-(1*H*,4*H*)-diaminoquinoxaline)和([Zn(DIDAQX)Cl₂]) (**2**)。并对其进行了红外、元素分析、单晶衍射、热重、荧光、电化学性质等性质研究。且对 **1** 做了密度泛函理论(DFT)计算。单晶结构分析表明 **1** 和 **2** 同构, 都属于正交晶系, *Pbca* 空间群, **1** 的晶胞参数: $a=1.408\ 2(3)\ \text{nm}$, $b=1.462\ 8(3)\ \text{nm}$, $c=1.797\ 0(4)\ \text{nm}$; $V=3.701\ 7(14)\ \text{nm}^3$, $Z=8$ 。**2** 的晶胞参数: $a=1.408\ 2(3)\ \text{nm}$, $b=1.464\ 8(3)\ \text{nm}$, $c=1.796\ 9(4)\ \text{nm}$; $V=3.706\ 5(14)\ \text{nm}^3$, $Z=8$ 。在配合物结构中每个金属原子以四配位的形式分别与 2 个 Cl 原子和来自配体的 2 个 N 原子配位, 形成了一个扭曲的四面体结构。

关键词: 钴(II)配合物; 锌(II)配合物; 晶体结构; 性质; 密度泛函理论

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Syntheses, Crystal Structure, Properties of Cobalt and Zinc Complexes Based on N,N' -Diisobutyl-2,3-diaminoquinoxaline

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Abstract: N,N' -Diisobutyl-2,3-diaminoquinoxaline was synthesized by 2,3-dichloroquinoxaline and isobutylamine. And the complexes ([Co(DIDAQX)Cl₂]) (**1**, DIDAQX= N,N' -Diisobutyl-2,3-(1*H*,4*H*)-diaminoquinoxaline) and ([Zn(DIDAQX)Cl₂]) (**2**) (Same revision as above) were prepared, which characterized by elemental analysis, IR spectra, single crystal X-ray diffraction, TG analysis, fluorescence and electrochemical properties. For **1**, DFT and TD-DFT calculations have been performed to obtain its UV-Vis absorption spectrum, and a satisfactory theoretical-experimental agreement was achieved. The crystal structures of complexes **1** and **2** show that they crystallize in orthorhombic space group *Pbca* with $a=1.408\ 2(3)\ \text{nm}$, $b=1.462\ 8(3)\ \text{nm}$, $c=1.797\ 0(4)\ \text{nm}$; $V=3.701\ 7(14)\ \text{nm}^3$, $Z=8$ of **1** and $a=1.408\ 2(3)\ \text{nm}$, $b=1.464\ 8(3)\ \text{nm}$, $c=1.796\ 9(4)\ \text{nm}$; $V=3.706\ 5(14)\ \text{nm}^3$, $Z=8$ of **2**. In the structure of complexes, each metal atom is four coordinated. Besides chelated by the DIDAQX with two nitrogen atoms, the atom is also coordinated by two Cl atoms, thus form a distorted tetrahedral geometry. CCDC: 993271, **1**; 993272, **2**.

Key words: Cobalt(II) complex; Zinc(II) complex; crystal structure; property; density functional theory

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0 Introduction

The quinoxaline core is one of the most important *N*-heterocycles that has been of considerable importance because of their interesting chemical as well as biological properties^[1-4]. Quinoxaline-type ligands could act as either neutral or anionic chelators, which also act as bridging ligands in defined circumstance, thus leading various coordination modes in metal complexes, it is even possible that they can function as controlling ligands in catalytic reactions^[5-9]. The present work describes studies on a new compound of *N,N'*-Diisobutyl-2,3-diaminoquinoxaline obtained by the reaction of commercially available 2,3-dichloroquinoxaline with isobutylamine, two transition metal zinc and cobalt complexes were prepared by the ligand. Herein, we report single crystal structure analysis for these two complexes and most of the cases luminescence, thermogravimetric analyses, electrochemical properties, the rationalization of UV-Vis absorption spectra through TD-DFT calculations have been investigated thoroughly for cobalt complex and properties have also been discussed for ligand and complexes. To the best of our knowledge, past research works on thermal, electrochemical property and TD-DFT calculations of quinoxaline derivative and their complexes are limited^[10-12] and has been carefully investigated in this paper.

1 Experimental

1.1 Materials and physical measurements

All of the commercially available chemicals and reagents in this work were analytical grade and used without further purification. Elemental analyses were determined with a Perkin-Elmer 240 instrument. The FT-IR spectra were recorded from KBr pellets in the range of 4 000~400 cm^{-1} on a Nicolet FT-170SX spectrometer. Thermogravimetric analyses (TGA) were performed on a NETZSCH STA 449C analyzer with a heating rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$. Fluorescence spectra were taken on a CaryEclipse fluorescence spectrophotometer at room temperature. Cyclic voltammetry was performed in a three-electrode cell using a Chi-730C electro-

chemistry station.

Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were performed to characterize the experimental absorption spectra by using the Gaussian 09 program^[13]. The model compound was selected from experimental X-ray single-crystal structure. The unrestricted doublet wave function of complex **1** in acetonitrile (dielectric constant, $\epsilon=35.69$) solution was test to be stable with the framework of the polarized continuum model (PCM) using unrestricted PBE functional^[14]. Here, the basis set LanL2DZ*+6-31G* (using 6-31G* basis set for C, N, Cl, and H atoms, adding the *f*-type polarization function to Co atom at the basis set LanL2DZ) was employed in view of the influence of *d* and *f* functions on the absorption spectra. The exponent (2.780) of *f* orbital for Co atom was selected as those in previous work^[15]. The vertical electronic excitation energies of complex in acetonitrile solution were then obtained through TD-DFT/PCM calculation at the same level.

1.2 Preparations of the compounds

1.2.1 Synthesis of the ligand

N,N'-Diisobutyl-2,3-diaminoquinoxaline was synthesized by modification with the previous method^[16]. An autoclave (80 mL), charged with 2,3-dichloroquinoxaline (4.0 g, 20.1 mmol) and isobutylamine (40 mL, reactant and solvent), was heated to 120 $^{\circ}\text{C}$ for 3 h. After cooling to room temperature, a small excess hexane was added and well-stirred, then filtered off and washed with hexane again. The solvent was evaporated in vacuum and pale yellow solid was obtained. Yield: 78%. Anal. Calcd. for $\text{C}_{16}\text{H}_{24}\text{N}_4$ (%): C, 70.59; H, 8.82; N, 20.59; Found (%): C, 70.48; H, 8.86; N, 20.66. FT-IR (KBr, pellet, cm^{-1}): 3 387(s), 3 349(s), 2 953(s), 1 589(w), 1 567(w), 1 551(s), 1 501(s), 1 458(w), 756(s), 605(w).

1.2.2 Synthesis of $\text{Co}(\text{DIDAQX})\text{Cl}_2$ (**1**)

A solution of Cobalt (II) chloride hexahydrate (0.023 7 g, 0.1 mmol) in acetonitrile (2 mL) was added dropwisely to a solution of L (0.027 2 g, 0.1 mmol) in acetonitrile (5 mL). The color of the mixing solution turned blue immediately, and then the

solution was stirred at 50 °C for 5 h. The result solution was filtered after cooling to room temperature and the filtrate was stored for a few days. Several deep blue single crystals appeared whose were suitable for X-ray crystallographic analysis. Yield: 65%. Anal. Calcd. for $C_{16}H_{24}N_4CoCl_2$ (%): C, 47.76; H, 5.97; N, 13.93; Found (%): C, 47.69; H, 5.93; N, 13.98. FT-IR (KBr, pellet, cm^{-1}): 3 222(s), 3 149(w), 2 958(s), 1 643(s), 1 466(w), 1 421(s), 1 034(s), 754(s).

1.2.3 Synthesis of $Zn(DIDAQX)Cl_2$ (**2**)

The preparation of complex **2** is similar to that of complex **1**, but with a solution of Zinc(II) chloride dihydrate (0.013 6 g, 0.1 mmol) in place of Cobalt(II) chloride hexahydrate. The color of the mixing solution turned muddy immediately, and then the solution was stirred at 50 °C for 2 h. The result solution was filtered after cooling to room temperature and the filtrate was stored for a few days. Several colourless single crystals appeared whose were suitable for X-ray crystallographic analysis. Yield: 64%. Anal. Calcd. for

$C_{16}H_{24}N_4ZnCl_2$ (%): C, 47.05; H, 5.88; N, 13.72; Found (%): C, 47.35; H, 5.98; N, 13.92. FT-IR (KBr, pellet, cm^{-1}): 3 250(s), 3 102(w), 2 958(s), 1 673(s), 1 476(s), 1 431(w), 1 012(w), 754(s).

1.3 Crystal structure determination

Suitable single crystals of complexes **1** and **2** were selected for data collection at 293(2) K, using a Bruker SMART APEX CCD area detector diffractometer equipped with a Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm). Empirical absorption corrections were applied using SADABS program. The crystal structures were solved by direct methods using SHELXS-97^[17], and refined by full-matrix least-squares method using the SHELXL-97 program^[18]. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added according to the theoretical method. Selected bond distances and bond angles are listed in Table 1 and 2. Crystal data and structural refinement parameters for the complexes **1** and **2** are summarized in Table 3.

CCDC: 993271, **1**; 993272, **2**.

Table 1 Selected bond lengths (nm) and bond angles (°) of the complex **1**

Co(1)-N(1)	0.198 7(7)	Co(1)-Cl(1)	0.224 2(2)	Co(1)-N(2)	0.200 2(6)
Co(1)-Cl(2)	0.223 7(2)				
N(1)-Co(1)-N(2)	82.5(3)	N(1)-Co(1)-Cl(1)	116.35(18)	N(2)-Co(1)-Cl(2)	119.27(19)
N(1)-Co(1)-Cl(2)	113.04(18)	N(2)-Co(1)-Cl(1)	111.79(18)	Cl(2)-Co(1)-Cl(1)	111.32(9)
C(2)-N(2)-Co(1)	112.7(5)	C(9)-N(2)-Co(1)	124.2(5)	C(1)-N(1)-Co(1)	113.6(5)
C(13)-N(1)-Co(1)	125.7(5)	N(1)-C(1)-C(2)	113.9(7)	C(2)-N(2)-C(9)	123.0(6)

Table 2 Selected bond lengths (nm) and bond angles (°) of the complex **2**

Zn(1)-N(1)	0.202 6(3)	Zn(1)-Cl(1)	0.223 8(10)	Zn(1)-N(2)	0.202 4(3)
Zn(1)-Cl(2)	0.222 7(10)				
N(1)-Zn(1)-N(2)	82.10(11)	N(1)-Zn(1)-Cl(1)	111.27 (9)	N(2)-Zn(1)-Cl(2)	113.26(9)
N(1)-Zn(1)-Cl(2)	118.47(9)	N(2)-Zn(1)-Cl(1)	115.08(9)	Cl(2)-Zn(1)-Cl(1)	113.26(4)
C(2)-N(2)-Zn(1)	112.4(2)	C(9)-N(2)-Zn(1)	124.5(2)	C(1)-N(1)-Zn(1)	112.2(2)
C(13)-N(1)-Zn(1)	123.7(3)	N(1)-C(1)-C(2)	117.3(3)	C(2)-N(2)-C(9)	123.0(3)

Table 3 Crystal data and structure refinement for the two complexes

Complex	1	2
Empirical formula	$C_{16}H_{24}N_4CoCl_2$	$C_{16}H_{24}N_4ZnCl_2$
Formula weight	402.22	408.49
Crystal system	Orthorhombic	Orthorhombic
Temperature	293(2)	293(2)
Space group	<i>Pbca</i>	<i>Pbca</i>

Continued Table 3

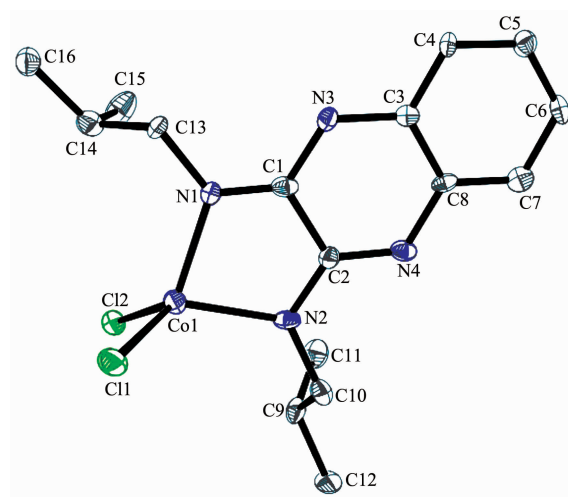
<i>a</i> / nm	1.408 2(3)	1.408 2(3)
<i>b</i> / nm	1.462 8(3)	1.464 8(3)
<i>c</i> / nm	1.797 0(4)	1.796 9(4)
<i>V</i> / nm ³	3.701 7(14)	3.706 5(14)
<i>Z</i>	8	8
<i>D_c</i> / (g·cm ⁻³)	1.443	1.464
<i>F</i> (000)	1672	1512
Theta range for data collection	3.01 to 25.00	3.00 to 26.03
Data / restraints / parameters	3 104 / 0 / 212	3 558 / 0 / 208
<i>S</i> on <i>F</i> ²	1.084	1.135
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ =0.097 9, <i>wR</i> ₂ =0.225 2	<i>R</i> ₁ =0.045 0, <i>wR</i> ₂ =0.108 6
<i>R</i> indices (all data)	<i>R</i> ₁ =0.130 8, <i>wR</i> ₂ =0.251 8	<i>R</i> ₁ =0.060 1, <i>wR</i> ₂ =0.124 7
Largest different peak and hole / (e·nm ⁻³)	426 and -549	494 and -529

2 Results and discussion

2.1 Crystal structure of complex 1 and 2

2.1.1 [Co(DIDAQX)Cl₂] (1)

The ORTRP diagram of complex **1** with the atomic numbering scheme is shown in Fig.1 and selected bond lengths and angles are listed in Table 1. The complex is monomeric, which consists of one Co(II) atom, one unit of DIDAQX and two atoms of chlorine. The cobalt atom is surrounded by two chlorine atoms and two nitrogen atoms, and exhibits tetrahedral coordination. The cobalt atom and the chelate ligand form a five membered ring. The coordination figure is tetrahedral and somewhat distorted, because two Co-N distances in complex are very similar. However, Co-Cl distances 0.224 2(2) nm and 0.223 7(2) nm are significantly different though both refer to terminal chlorine atoms. The N(1)-Co(1)-N(2) angle is 82.5(3)° and Co-N(1) bond distance is 0.198 7(7) nm whose are slightly smaller than similar complexes^[19-21]. But the bond angle Cl(2)-Co(1)-Cl(1) of 111.32(9)° is smaller than most similar Co complex^[22] and also larger than the normal tetrahedral values, the bond distances Co(1)-Cl(2) of 0.223 7(2) nm is somewhat higher than those reported for relevant complexes^[23]. There are π - π stacking interactions between the pyrazine rings (Cg2=N3, N4, C1, C2, C3, C8) and benzene rings (Cg3=C3~C8) of each parallel pair of ligands, with a centroid...centroid distance of 0.360 1 nm for Cg2...Cg3, which showed in Fig.2.



Thermal ellipsoids are shown at the 30% probability level

Fig.1 Molecular structure of complex **1**

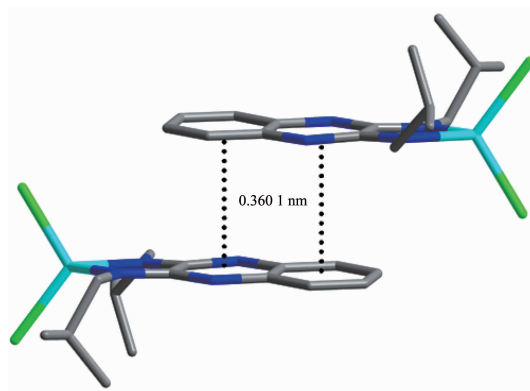
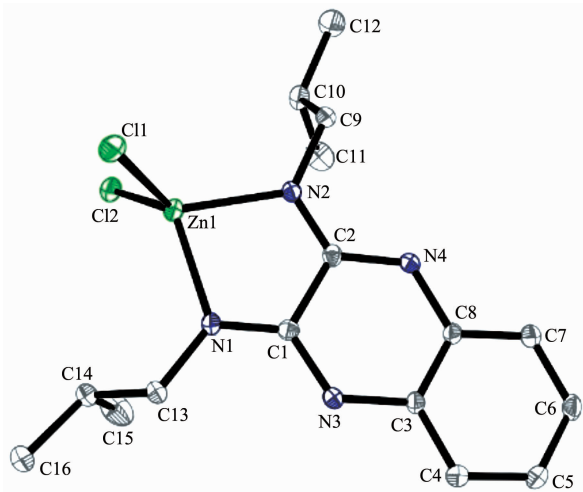


Fig.2 π - π stacking interactions of complex **1**

2.1.2 [Zn(DIDAQX)Cl₂] (2)

The atomic numbering scheme of crystal structure of Zn complex is shown in Fig.3 and selected bond lengths and angles are listed in Table 2.

The ORTRP diagram revealed that the crystal structure of Zn complex is shown good similarity in terms of bond lengths and bond angles with the molecular structure of Co complex. The central Zn ion was coordinated by two nitrogen atoms of DIDAQX and two chlorine atoms in a distorted tetrahedral arrangement. Most of cases same structure arrangements have been obtained for Zn complex which has been made an easier way to find the structure determination of Zn complex like Co. Noted that some bond lengths and also bond angles of Zn are exist very close to Co structure. Specially, Zn(1)-Cl(1) and Zn(1)-Cl(2) are shown same bond lengths and these values are surprisingly close with those synthesized related complexes^[24-25]. The bond angles of N-Zn-Cl are in the range of $111.27(9)^\circ \sim 118.47(9)^\circ$, which are distorted from ideal tetrahedral geometry as a consequence of the opening of the two chlorine ligands. The bond angle of N(2)-Zn(1)-Cl(2) of $113.26(9)^\circ$ is remained in the above range, and the other bond angle N(1)-Zn(1)-N(2) of $82.10(11)^\circ$ is smaller than those found in Zn(R,R-bmbcd)Cl₂ [bmbcd=*N,N'*-bis(4-methoxy-benzyl)-cyclohexane-1,2-dia-mine] ($85.66(9)^\circ$) and ZnCl₂(2,2'-bis(pyrazolyl-1-yl)propane) ($89.5(1)^\circ$)^[26]. So after closely observation with other bond lengths and bond angles of Zn complex it can be conveniently say that Zn complex has shown relevant characteristics for assigning a distorted tetrahedral structure complex. There are π - π stacking interactions between



Thermal ellipsoids are shown at the 30% probability level

Fig.3 Molecular structure of complex 2

the pyrazine rings (Cg2=N3, N4, C1, C2, C3, C8) and benzene rings (Cg3=C3~C8) of each parallel pair of ligands, with a centroid...centroid distance of 0.360 1 nm for Cg2...Cg3 showed in Fig.4, which is same to the Co complex.

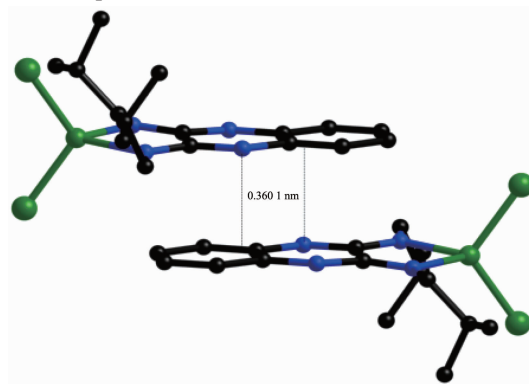


Fig.4 π - π stacking interactions of complex 2

2.2 Luminescent properties

The emission spectra of the free ligand and two complexes were all investigated in acetonitrile ($4 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) at room temperature. As shown in Fig.5, the ligand displays two broad emission bands around 385.3 nm and 404.5 nm, while the complex 1 exhibits two emission peaks at 384.9 nm and 404.2 nm. By comparing the emission spectra of the ligand and the complex, they may be tentatively assigned to the intraligand and intraligand π - π^* transitions^[27]. But with the same density, the fluorescence intensity of the title complex is enhanced by the ligand.

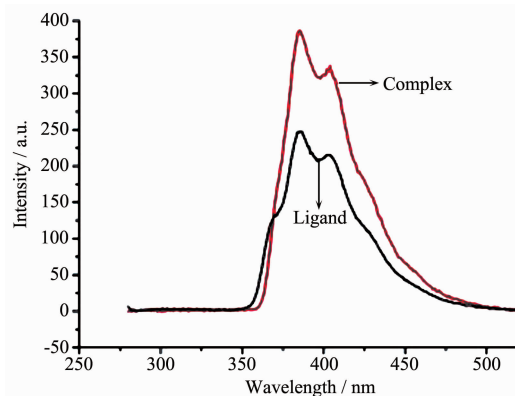


Fig.5 Emission spectra of the free ligand and the complex 1 in t acetonitrile ($4 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) at room temperature

The complex 2 exhibits two emission peaks at 389.5 nm and 418.5 nm, which is similar to complex 1.

2.3 Thermogravimetric analysis

To characterize the thermal stability of the two complexes, thermal gravimetric analyses (TGA) were carried out in the range of 20~1 000 °C. As show in Fig.6, the TGA curve of the complex **1** reveals that it is almost stable up to 300 °C. The initial weight loss of 68.56% (Calcd. 67.66%) occurred from 308~450 °C corresponding to the loss of the ligand. The second loss is 16.40% (Calcd. 17.66%) from 450~800 °C, corresponding to consecutive loss of two chloride ions. The resulting residue is CoO (Found 15.04%, Calcd. 14.68%).

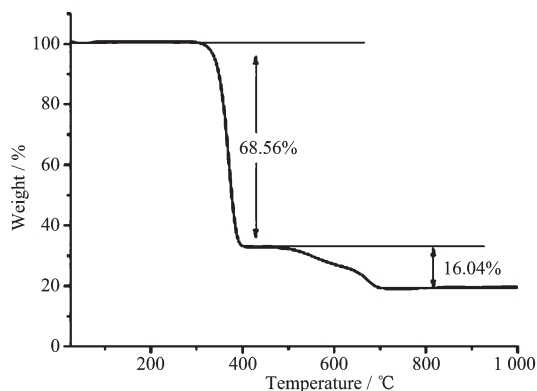


Fig.6 TG curve of complex **1**

Thermogravimetric analysis has also been measured for complex **2**. The complex is stable up to 305 °C, then the product begins to decompose and be oxidized. The weight loss of 65.50% from 305~550 °C corresponds to the loss of the ligand (Calcd. 66.67%). The weight loss of 18.50% from 550~950 °C due to the removal of two chloride ions (Calcd. 17.40%). The resulting residue is ZnO (Found 16.00%, Calcd. 15.93%).

2.4 Electrochemical properties

The electrochemical behavior of the complex was investigated by cyclic voltammetry (CV) in DMF containing 0.1 mol·L⁻¹ TBAP^[28]. Fig.7 displays the cyclic voltammogram for the complex **1** during scanning from -2.0 to 1.5 V at a scan rate of 0.1 V·s⁻¹. It exhibits only one reductive response at $E_{\text{pa}} = -1.36$ V and no oxidative responses, which should be due to the reduction of Co(II).

Fig.8 displays the cyclic voltammogram for the complex **2** during scanning from -2.5 to 2.0 V at a

scan rate of 0.1 V·s⁻¹. It exhibits only one irreversible reductive response at $E_{\text{pa}} = -1.48$ V and one irreversible oxidative responses at $E_{\text{pi}} = 1.03$ V. The part of reductive response should be due to the reduction of Zn(II).

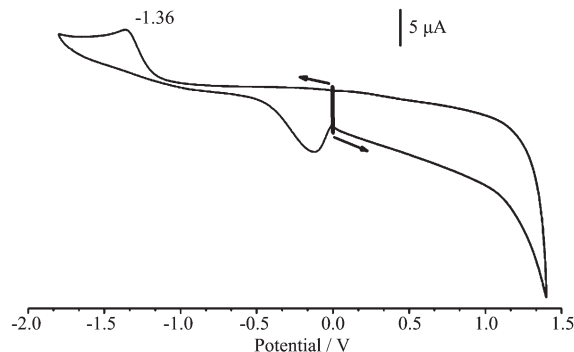


Fig.7 Cyclic voltammogram of **1** in DMF containing 0.1 mol·L⁻¹ TBAP at a scan rate of 0.1 V·s⁻¹

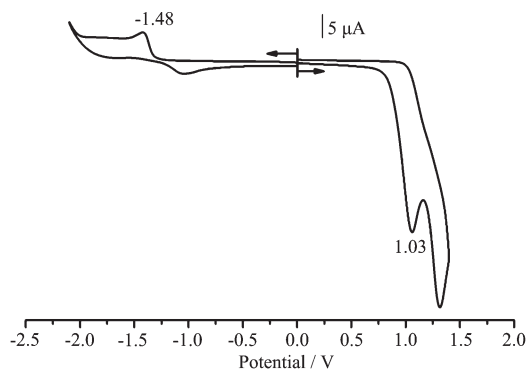


Fig.8 Cyclic voltammogram of complex **2** in DMF containing 0.1 mol·L⁻¹ TBAP at a scan rate of 0.1 V·s⁻¹

2.5 DFT calculations

The theoretical absorption spectrum of complex **1** obtained from TD-DFT/PCM calculation at the UPBE/6-31G*+LanL2DZ* level is in good agreement with the experimental observation, which displayed in Fig. 9. Herein, the Lorentzian function is adopted with the spectral line width set to be 50 nm. The theoretical spectrum is systematically right-shifted by 20 nm from TD-DFT excitation energies. The vertical dipole-allowed absorption bands (Peak 1 and Peak 2) are mainly assigned to be $\pi \rightarrow \pi^*$ transitions, as schematically illustrated in Fig.10. The π orbital of Peak 1 is contributed from the *p* orbitals of Cl atoms and *d* orbital of Co atom. For the relatively stronger absorption bands (Peak 2), the π orbital of the complex **1** is dominated by the *p* orbital of C, N, and

Cl atoms. And the contribution of π^* orbital are mainly from the p orbitals of C and N atoms in ligand. More importantly, the $\pi \rightarrow \pi^*$ transitions result in the intramolecular charge transfer from Cl atoms to the ligand, which indicates the potential fluorescence properties for the compound.

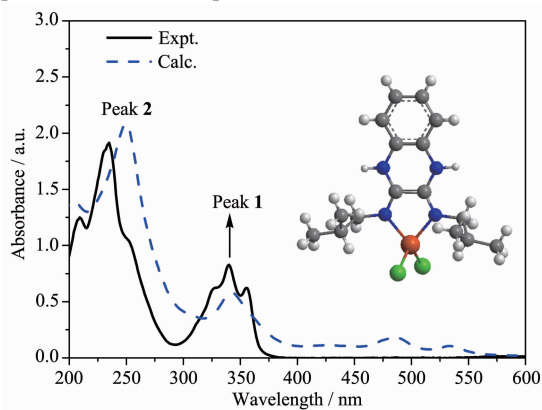


Fig.9 Absorption spectra of **1** in acetonitrile solution obtained from experimental observation and TD-DFT/PCM calculation at the UPB-E/LanL2DZ*+6-31G* level

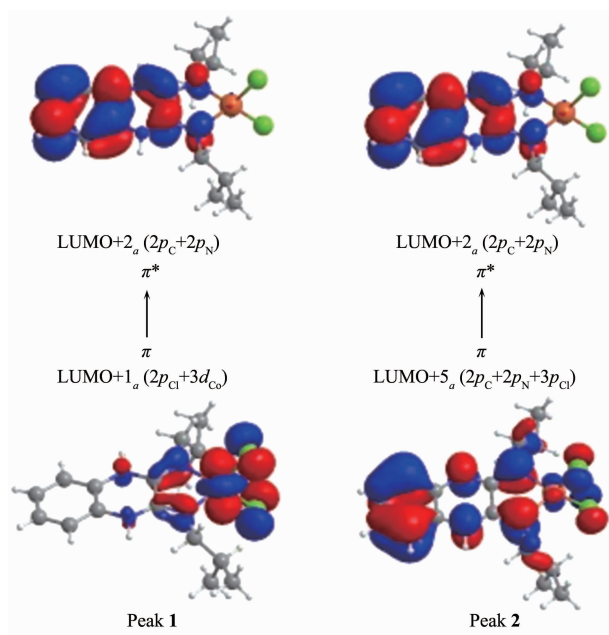


Fig.10 Assignment to absorption peaks of **1**

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