

基于 1-(1',3'-苯并噁唑-2'-甲基)苯并咪唑的钴(II)配合物: 晶体结构、弱相互作用和荧光发射光谱

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摘要: 配体 1-(1',3'-苯并噁唑-2'-甲基)苯并咪唑(L)是通过苯并咪唑与 2-(氯甲基)-1,3-苯并噁唑烷基化制备而来。配体 L 与 $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ 反应得到了配合物 $[\text{CoCl}_2\text{L}_2]$ (**1**)。配合物 **1** 通过 π - π 堆积作用和 C-H...Cl 氢键形成了三维超分子框架结构。测定了 L 和 **1** 的荧光发射光谱。

关键词: 1-(1',3'-苯并噁唑-2'-甲基)苯并咪唑; 钴配合物; π - π 堆积作用; 氢键

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Cobalt(II) Complex Based on 1-(1',3'-Benzoxazole-2'-methyl)benzimidazole: Crystal Structure, Weak Interactions and Fluorescent Emission Spectra

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Abstract: The ligand 1-(1',3'-benzoxazole-2'-methyl)benzimidazole (L) was prepared from benzimidazole by alkylation with 2-(chloromethyl)-1,3-benzoxazole. Reaction of ligand L with $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ afforded a complex $[\text{CoCl}_2\text{L}_2]$ (**1**). In complex **1**, 3D supramolecular frameworks were formed through π - π interactions and C-H...Cl hydrogen bonds. The fluorescence emission spectra of L and **1** are described. CCDC: 843658.

Key words: 1-(1',3'-benzoxazole-2'-methyl)benzimidazole; cobalt complex; π - π interactions; hydrogen bonds

0 Introduction

Metallo supramolecular species assembled from transition metals and organic ligands with novel structures and properties have been extensively studied due to their intriguing structural diversity and potential applications as functional materials^[1-2]. Thus, structural design or modification of the coordination polymers have become a very active field in crystal engineering^[3-8]. Some weak interactions, such as hydrogen bonds^[9] and π - π interactions^[10], often affect the struc-

tures of complexes, and they can further link discrete subunits or low-dimensional entities into high-dimensional supramolecular networks^[11-12]. Ligands containing benzimidazole ring play important roles in coordination chemistry, and they can coordinate with a variety of transition metals to form one-, two- and three-dimensional coordination polymers through the use of nitrogen atom of benzimidazole. In this paper, we report the preparation, crystal structures, weak interactions and fluorescence emission spectra of complex $[\text{CoCl}_2\text{L}_2]$ (**1**).

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1 Experimental

1.1 General procedures

Melting points were determined with a Boetius Block apparatus. ^1H NMR spectra was recorded on a Varian Mercury Vx 400 spectrometer at 400 MHz. Chemical shifts, δ , are reported in ppm relative to the internal standard TMS for ^1H NMR. Elemental analyses were measured using a Perkin-Elmer 2400C Elemental Analyzer. IR spectra (KBr) were taken on an Bruker Equinox 55 spectrometer. The luminescent spectra were conducted on Cary eclipse fluorescence spectrophotometer.

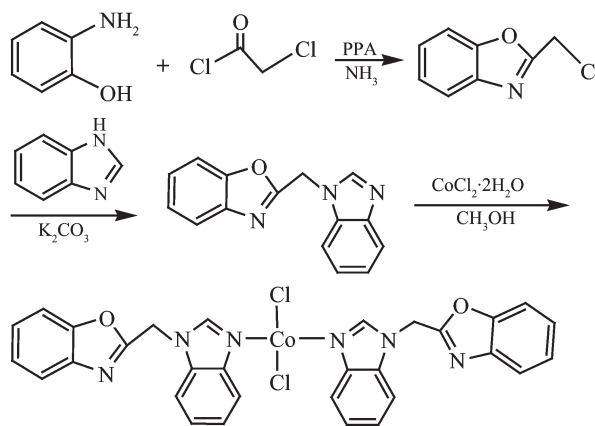
1.2 Preparation of 1-(1',3'-benzoxazole-2'-methyl)benzimidazole (L)

The 2-aminophenol (4.000 g, 36.6 mmol) was dissolved in 2-chloroacetyl chloride (15 mL) with stirring in ice water bath for 0.5 h, and a pink solid was formed. Then the pyrophosphoric acid (PPA) (15 mL) was dropwise added to above solution, and the mixture was stirred for 4 h at 150 $^{\circ}\text{C}$. A green sticky liquid was obtained. The sticky liquid was added to ammonia water of 25% (100 mL) under stirring and a brown solution was obtained. Then adjust pH value of the mixed solution to 7~8 using ammonia water. The solution was extracted with CH_2Cl_2 (3 \times 20 mL), and the extracting solution was dried over anhydrous MgSO_4 . After removing CH_2Cl_2 , a red brown liquid 2-(chloromethyl)-1,3-benzoxazole was obtained. Yield: 6.13 g (56.6%). An acetone solution (50 mL) of benzimidazole (4.568 g, 38.7 mmol) and K_2CO_3 (6.413 g, 46.4 mmol) was stirred for 0.5 h under refluxing, and an acetone solution (25 mL) of 2-(chloromethyl)-1,3-benzoxazole (5.400 g, 32.2 mmol) was dropwise added to above solution. The mixture was stirred for 4 h at 60 $^{\circ}\text{C}$, and a yellow solution was obtained. The solvent was removed with a rotary evaporator and H_2O (30 mL) was added to the residue. The mixture was extracted with CH_2Cl_2 (3 \times 20 mL), and the extracting solution was dried over anhydrous MgSO_4 . After removing CH_2Cl_2 , the solid was washed with diethyl ether and a pale yellow solid of 1-(1',3'-benzoxazole-2'-methyl)benzimidazole (L) was obtained. The ligand L is soluble

in polar organic solvents such as dichloromethane, acetonitrile and methanol, and insoluble in diethyl ether, petroleum ether and water. Yield: 3.810 g (48%), m.p. 98~100 $^{\circ}\text{C}$. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 5.98 (s, 2H, CH_2), 7.26 (m, 2H, PhH), 7.38 (m, 2H, PhH), 7.62 (m, 1H, PhH), 7.72 (m, 3H, PhH), 8.44 (s, 1H, 2-benzimidazoleH).

1.3 Preparation of $[\text{CoCl}_2\text{L}_2]$ (1)

A methanol solution (10 mL) of ligand L (0.050 g, 0.2 mmol) was added to a methanol solution (10 mL) of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (0.057 g, 0.4 mmol). After ca. 30 min of vigorous mixing, the filtrate was allowed stand at room temperature. The red single crystals suitable for X-ray analysis were obtained within one week. This complex is partly soluble in DMSO, and insoluble in diethyl ether, hydrocarbon solvents and water. Yield: 0.067 g (53%), m.p. 257~259 $^{\circ}\text{C}$. Anal. Calcd. for $\text{C}_{30}\text{H}_{22}\text{Cl}_2\text{CoN}_6\text{O}_2$ (%): C, 57.34; H, 3.52; N, 13.37. Found(%): C, 57.41; H, 3.33; N, 13.64%. IR (KBr, cm^{-1}): 3386(m), 3076(s), 2990(m), 1610(m), 1561(m), 1517(s), 1449(m), 1392(m), 1260(m), 1205(m), 1156(m), 1103(m), 980(m), 917(m), 835(s), 743(vs).



Scheme 1 Preparation of ligand L and complex 1

1.4 X-ray data collection and structure determinations

Single-crystal X-ray diffraction measurement of **1** (0.32 mm \times 0.28 mm \times 0.20 mm) was collected on a Bruker APEX II CCD diffractometer at 293(2) K with Mo $K\alpha$ radiation ($\lambda=0.071073$ nm) by φ - ω scan mode. There was no evidence of crystal decay during data collection in all cases. Semiempirical absorption corrections were applied by using SADABS and the

program SAINT was used for integration of the diffraction profiles^[13]. All structures were solved by direct methods by using the SHELXS program of the SHELXTL package and refined with SHELXL^[14] 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 ~0.097 nm), assigned appropriated isotropic thermal parameters and included in structure factor calculations. Selected bond lengths (nm) and angles ($^\circ$) and crystal data and structure refinement for **1** are presented in Table 1 and Table 2. Figures were generated by using Crystal-Maker^[15].

CCDC: 843658.

Table 1 Selected bond lengths (nm) angles ($^\circ$) for **1**

N1-C1	0.131(2)	O1-C9	0.134(2)	Co1-N1	0.203(1)
N2-C1	0.134(2)	N3-C9	0.128(2)	Co1-Cl1	0.224(6)
N1-Co1-Cl1	109.2(4)	N1-Co1-Cl1 ⁱ	106.5(4)	N1-Co1-N1 ⁱ	109.8(8)
Cl1 ⁱ -Co1-Cl1	115.6(4)	N1 ⁱ -Co1-Cl1	106.5(4)	N1 ⁱ -Co1-Cl1 ⁱ	109.2(4)
C1-N2-C8	125.1(1)	O1-C9-N3	115.6(1)		

Table 2 Summary of crystallographic data for **1**

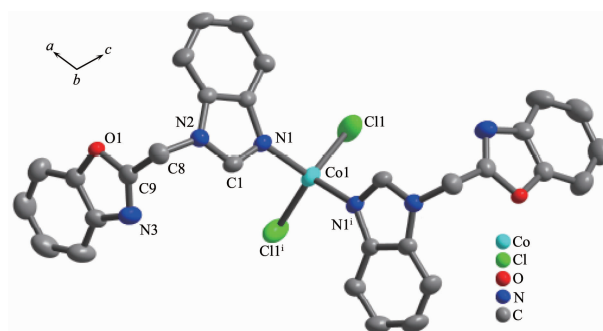
Empirical formula	$C_{30}H_{22}Cl_2CoN_6O_2$	$F(000)$	1284
Formula weight	628.37	Cryst size / mm	0.32×0.28×0.20
Crystal system	Monoclinic	θ range / ($^\circ$)	2.24~25.03
Space group	$C2/c$	T / K	296(2)
a / nm	1.406(2)	No. of data collected	6 862
b / nm	1.272(2)	No. of unique data	2 424
c / nm	1.652(3)	R_{int}	0.016
$\beta / (^\circ)$	112.144(2)	No. of refined params	186
V / nm^3	2.737(8)	Goodness-of-fit on F^2	1.062
Z	4	Final R indices ($I > 2\sigma(I)$)	$R_1=0.027\ 5$, $wR_2=0.071\ 8$
$D_c / (g \cdot cm^{-3})$	1.525	R indices (all data)	$R_1=0.030\ 8$, $wR_2=0.074\ 3$
Abs coeff / mm^{-1}	0.863		

2 Results and discussion

2.1 Structure of complex $[CoCl_2L_2]$ (**1**)

The preparation of complex **1** is shown in Scheme 1. In crystal structure of the complex **1**, Co(II) center is tetracoordinated with two nitrogen atoms from two benzimidazoles and two chlorine atoms to form a slightly distorted tetrahedral geometry. The Co-Cl and Co-N distances are 0.224(6) and 0.203(1) nm, respectively. The bond angles of N1-Co1-Cl1, N1-Co1-Cl1A, N1-Co1-N1A, Cl1A-Co1-Cl1, N1A-Co1-Cl1 and N1A-Co1-Cl1A are 109.2(4) $^\circ$, 106.5(4) $^\circ$, 109.8(8) $^\circ$, 115.6(4) $^\circ$, 106.5(4) $^\circ$ and 109.2(4) $^\circ$, respectively (Fig.1). The dihedral angle between two benzimidazole rings is 73.1 $^\circ$. The dihedral angles between benzoxazole ring and benzimidazole ring in the same ligand is 76.7 $^\circ$. The

dihedral angle between two benzoxazole rings is 86.2 $^\circ$.

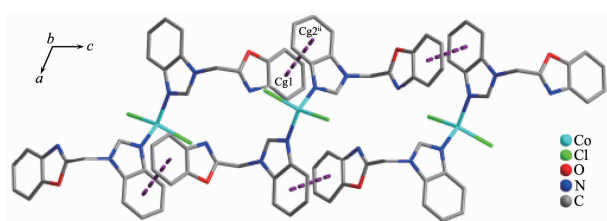


All hydrogen atoms were omitted for clarity; Symmetry code: $i -x, y, 0.5-z$

Fig.1 Perspective view of **1** and anisotropic displacement parameters depicting 30% probability

An interesting feature in the crystal packing of **1** is that 1D polymeric chain is formed by the π - π stacking interactions^[10] from intermolecular benzene rings of

benzimidazole rings and benzene rings of benzoxazole rings with the inter-planar separation of 0.319(1) nm (center-to-center separation 0.369(1) nm) as shown in Fig.2. Additionally, 1D polymeric chains are further extended into 3D supramolecular frameworks via C–H \cdots Cl hydrogen bonds^[16] (H \cdots Cl distance 0.288(1) nm, C–H \cdots Cl angle 163.7(1)°).



Hydrogen atoms have been omitted for clarity; Symmetry code for center of mass of benzene: $\bar{x}, y, -0.5-z$

Fig.2 1D polymeric chain formed through π - π interactions in **1**

2.2 Fluorescent emission spectra of ligand L and complex **1**

As shown in Fig.3, the fluorescent emission spectra of ligand L and complex **1** are obtained upon excitation at 305 nm in acetonitrile at room temperature in CH_3CN ($5.0 \mu\text{mol} \cdot \text{L}^{-1}$) solution. ligand L and complex **1** show similar emission bands in the range of at 300~350 nm, however, the fluorescence emission of complex **1** is weaker than that of ligand L, which probably results from the incorporation of metal-organic ligand coordination interactions^[17-18]. In ligand L and complex **1**, the emission peak in 310 nm results from the transitions of benzene ring in benzoxazole, and the

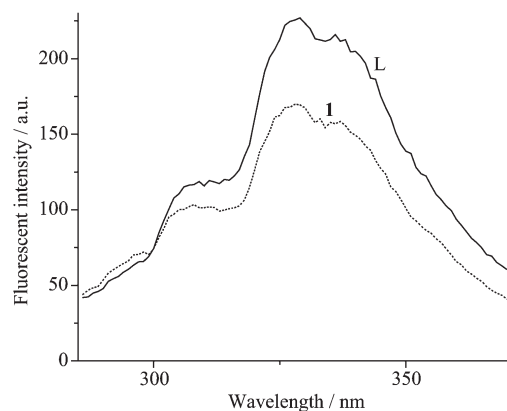


Fig.3 Emission spectra of L and **1** at room temperature

double peaks in 330 ~340 nm correspond to the transitions of benzimidazole rings.

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