

Microwave Synthesis, Characterization and DNA-binding Properties of a New Cobalt(II) Complex with 2,6-Bis(benzimidazol-2-yl)pyridine

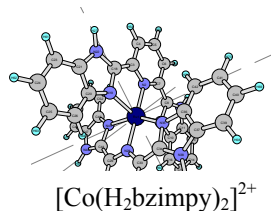
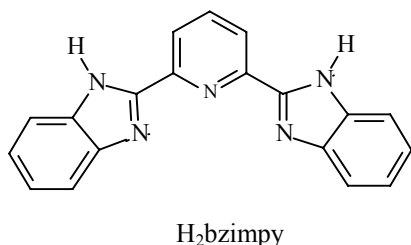
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Abstract: A new cobalt(II) complex with tridentate ligand 2,6-bis(benzimidazol-2-yl)pyridine has been synthesized by microwave irradiation method and characterized by elemental analysis, electrochemical and spectral methods. The binding of the complex with calf thymus DNA has also been investigated by absorption and fluorescence spectra.

Keywords: Microwave irradiation, Co(II) complex, DNA-binding.

The potential of substitution-inert metal complexes as photochemical structural and stereoselective probes of nucleic acids has been explored extensively over the past decades^{1,2}. However, most of those complexes only contain bidentate ligands, and investigations of the complexes with tridentate ligands as DNA-binding reagents are very few^{3,4}. In fact, among other factors, which contribute to stabilizing the metal complexes on the DNA helix, the molecule shape is the most significant factor⁵. In this work, a new Co(II) complex of $[\text{Co}(\text{H}_2\text{bzimpy})_2](\text{ClO}_4)_2$ (H_2bzimpy =2,6-bis(benzimidazol-2-yl)pyridine) was synthesized and characterized successfully. The DNA binding behaviors of the complex have also been observed by absorption spectra and fluorescence spectra. The results should be valuable in understanding the mode of the complexes binding to DNA, as well as laying the foundation for the design of new probes for study of helical conformations and searching antitumor drugs.



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Experimental

Electrochemical experiment was performed on a CHI660A electrochemical system with a saturated calomel electrode (SCE) as reference, a platinum wire as counter electrode and a glassy carbon electrode as working electrode. Electronic absorption spectra and fluorescence spectra of the complex were determined at room temperature. All the experiments involving the interaction of the complex with DNA were conducted using solutions of the complexes in Tris-HCl buffer (pH 7.2) containing 5 mmol/L Tris and 50 mmol/L NaCl.

The following procedures are recommended for synthesis of the complex $[\text{Co}(\text{H}_2\text{bzimpy})_2](\text{ClO}_4)_2$: The mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.119 g ; 0.5 mmol) and 2,6-bis-(benzimidazol-2-yl)pyridine⁶ (0.328 g; 1.05 mmol) in ethylene glycol (20 mL) was refluxed for 25 minutes under microwave irradiation. The solution was cooled to room temperature and filtrated. The filtrate was poured into saturated NaClO_4 solution to obtain a yellowish orange precipitate, $[\text{Co}(\text{H}_2\text{bzimpy})_2](\text{ClO}_4)_2$, which was recrystallized from Et_2O . Yield: *ca.* 57.4%. Element analysis: Calcd.: C, 51.84; H, 2.98; N, 15.91. Found: C, 51.45; H, 3.07; N, 15.68%.

Results and Discussion

The cobalt() complex of $[\text{Co}(\text{H}_2\text{bzimpy})_2](\text{ClO}_4)_2$ has successfully been synthesized by microwave irradiation. The method greatly reduces the reaction time with better yield comparing to the conventional method. The procedure is simple and may be used for synthesis of a variety of metal complexes⁷.

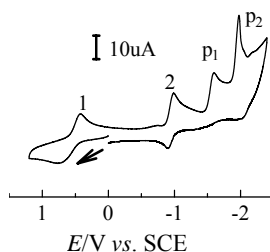
Table 1 The absorption spectral data of the ligand and the complex

Compound	$\lambda/\text{nm}(\times 10^3 \varepsilon/\text{mol}^{-1} \text{cm}^{-1} \text{L})$			
H_2bzimpy	240(sh)(18.2)	308(sh)(40.3)	328(48.4)	340(sh)(40.3)
$[\text{Co}(\text{H}_2\text{bzimpy})_2]^{2+}$		309(57.5)	340(52.3)	

In acetonitrile solution containing 0.1 mol/L NEt_4ClO_4 , the complex $[\text{Co}(\text{H}_2\text{bzimpy})_2]^{2+}$ has shown two pairs of redox peaks (1 and 2) and two cathodic peaks (P_1 and P_2) in the range from 1.2 V to -2.4 V vs. SCE (**Figure 1**). The E_{pa} and E_{pc} of the first pair of redox peak are 0.665 V and 0.43 V for the $\text{Co}^{3+}/\text{Co}^{2+}$ redox couple. Those of the second pair of redox peak are -0.872 V and -0.944 V for the $\text{Co}^{2+}/\text{Co}^+$ redox couple. The separations of the anodic and the cathodic peak potentials are 235 mV and 72 mV. It indicated that the redox reaction of the $\text{Co}^{3+}/\text{Co}^{2+}$ couple was quasi-reversible process. In the range of 50~300 mV/s, the peak potentials the $\text{Co}^{2+}/\text{Co}^+$ couple are independent of scan rates () and the i_{pa} and i_{pc} are proportional to $v^{1/2}$. The redox reaction of the couple was reversible process. The two cathodic peaks at -1.593 V and -1.978 V may be assigned to the reduction the H_2bzimpy ligand⁸.

The absorption spectral data of the free ligand and the complex in CH₃CN are recorded in **Table 1**. The complex [Co(H₂bzimpy)₂]²⁺ showed intense absorption bands at 309 and 340 nm. The bands become broader and the intensity increases in comparison with those of ligand H₂bzimpy, which can be attributed to the overlap of the ligand metal charge transfer transition with the π-π* transition in the same region⁹.

Figure 1 CV curve of the complex [Co(H₂bzimpy)₂]²⁺ (0.1 mmol/L) in CH₃CN (scan rate 100 mV/s).



The absorption spectra of the complex [Co(H₂bzimpy)₂]²⁺ in the absence and the presence of calf thymus DNA (with subtraction of the DNA absorbance) are illustrated in **Figure 2**. The hypochromism of the complex [Co(H₂bzimpy)₂]²⁺ is about 20.1% in the presence of DNA in comparison with that of the complex in the absence of DNA, and the band is red shifted from 325 to 327 nm. For the complex [Co(H₂bzimpy)₂]²⁺ the benzimidazolyl group in the potential intercalative ligand H₂bzimpy is basically planar. So it seems that the complex can intercalate its benzimidazole moiety into the DNA base pairs.

Figure 2 Electronic absorption spectra of [Co(H₂bzimpy)₂]²⁺ (1 μmol/L) with no DNA (a) and [DNA]/[Co]=3 (b) with subtraction of the DNA absorbance.

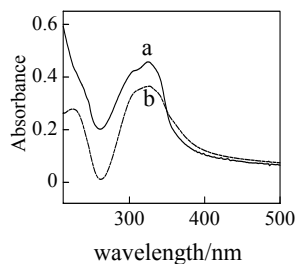
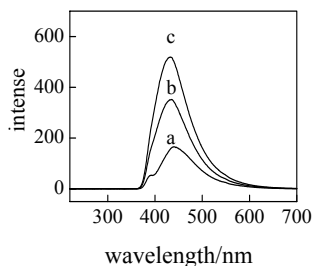


Figure 3 Fluorescence spectra of [Co(H₂bzimpy)₂]²⁺ (10 μmol/L) in the absence and presence of DNA. [DNA]/[Co]=0, 28, 56 for a-c, respectively.



When the complex $[\text{Co}(\text{H}_2\text{bzimpy})_2]^{2+}$ in CH_3CN is excited with 340 nm, there is an emission band at about 443 nm. **Figure 3** shows the steady-state of $[\text{Co}(\text{H}_2\text{bzimpy})_2]^{2+}$ in buffer solution both in the absence and presence of double-stranded DNA. Binding of the complex to DNA was found to increase the fluorescence intense. It suggests that the complex intercalate into the DNA base pairs, which is consistent with the absorption spectral result.

Acknowledgments

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