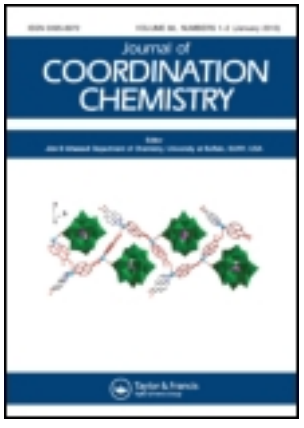

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# Crystal structure, interaction with DNA, and bovine serum albumin of the cobalt(II) complex of demethylcantharate and 2,2′-bipyridine

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A new cobalt(II) complex [Co(DCA)(bipy)($H_2O$)] (DCA = demethylcantharate, 7-oxabicyclo[2.2.1] heptane-2,3-dicarboxylate, $C_8H_8O_5$; bipy = 2,2′-bipyridine, $C_{10}H_8N_2$) was synthesized from cobalt acetate, demethylcantharidin, and bipy. This complex was characterized by elemental analysis, molar conductance, infrared spectra, and X-ray single-crystal diffraction. It crystallized in orthorhombic crystal system and *Pbca* space group. The DNA binding of the complex was investigated by electronic absorption spectra and viscosity measurements. The complex binds to DNA via partial intercalation with binding constant $K_b$ of $4.02 \times 10^4\,L\,M^{-1}$. The complex could quench the intrinsic fluorescence of bovine serum albumin through static quenching. The binding constant $K_A$ was $7.28 \times 10^6\,L\,M^{-1}$ and binding site was one.

*Keywords*: Crystal structure; Demethylcantharate; Cobalt(II) complex; DNA binding; Interaction with BSA

## 1. Introduction

Research on DNA and protein interaction with transition metal complexes has achieved progress. This research contributes to new drug development [1]. Demethylcantharidin (NCTD, 7-oxabicyclo[2,2,1]heptane-2,3-dicarboxylc acid anhydride) and disodium demethylcantharate ($Na_2$(DCA)), as derivatives of cantharidin, have been used in clinical trials [2]. Previous research showed that the antiproliferative activities of ligand were significantly improved [3, 4]. Demethylcantharate (DCA) could inhibit the bioactivities of PP1 and PP2A [5, 6]. Transition metal complexes of DCA have been reported to possess strong DNA-binding ability [7, 8]. Some preliminary findings of the interactions between these complexes with bovine serum albumin (BSA) have been previously reported [9, 10].

Cobalt is an essential micronutrient in the human body, and it plays a critical physiological role. Thus, studying the synthesis and physiological activity of cobalt(II) complexes is important. Satyanarayan *et al*. [11] and Balachandran *et al*. [12] reported DNA binding

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and photocleavage studies of several polypyridine complexes of cobalt(III) in 2009 and 2007. Cobalt complexes of DCA and imidazole have also been reported [13, 14].

Since DCA complexes could interact with various biomacromolecules (such as DNA and protein), designing and synthesizing DCA complexes is meaningful. In this research, a new Co(II) complex of DCA and 2,2′-bipyridine was synthesized. The interactions between the complex and DNA and BSA were investigated.

## 2. Experimental

### 2.1. *Materials and instruments*

All chemicals were obtained from commercial sources. Demethylcantharidin (NCTD, $C_8H_8O_4$) was obtained from Nanjing Zelang Medical Technology Co. Ltd; 2,2′-bipyridine (bipy, $C_{10}H_8N_2$) and ct-DNA were obtained from Sinopharm Chemical Reagent Co. Ltd; ct-DNA ($\rho = 200\,\mu g\,mL^{-1}$, $c = 3.72 \times 10^{-4}\,M\,L^{-1}$), which $A_{260}/A_{280} = 1.8$–$2.0$, was prepared by $50\,mM\,L^{-1}$ NaCl; BSA was purchased from Beijing BioDee BioTech Co. Ltd. and stored at 4 °C; BSA ($\rho = 500\,\mu g\,mL^{-1}$, $c = 7.47 \times 10^{-6}\,M\,L^{-1}$) was prepared by $5\,mM\,L^{-1}$ NaCl. Other chemical reagents in analytical reagent grade were used without purification.

C, H, and N elemental analyses were carried out in a Vario EL III elemental analyzer. The molar conductance value was obtained from Orion 150 Aplus conductometer. Infrared spectra were obtained using KBr disks with a NEXUS-670 FTIR spectrometer from 4000 to $400\,cm^{-1}$. Diffraction intensities for the complex were collected at 293 K on a Bruker SMART APEX II CCD diffractometer. Electronic absorption spectra were obtained using a UV-2501 PC spectrophotometer. Viscosity experiments were measured with an Ubbelodhe viscometer. Fluorescence emission spectra were obtained by a Perkin-Elmer LS-55 spectrofluorometer.

### 2.2. *Synthesis of the complex*

Methanol solution of $Co(Ac)_2{\cdot}4H_2O$ (0.5 mM) and 2,2′-bipyridine (0.5 mM) was stirred at room temperature for 1 h. Aqueous solution of NCTD (0.5 mM) was added dropwise into the solution. The pH of the solution was adjusted to 6.5 using dilute NaOH solution and the solution was filtered after 2 h. One week later, crystals with suitable size for single-crystal X-ray diffraction were obtained.

Anal. Calcd for $C_{18}H_{18}N_2O_6Co$ (%): C, 51.81; H, 4.35; N, 6.71. Found: C, 51.82; H, 4.45; N, 6.65. IR spectra (KBr, $cm^{-1}$): 1599 ($\upsilon_{as}(COO^-)$); 1408 ($\upsilon_s(COO^-)$); 1269, 1022, 980 ($\upsilon$(C–O–C)); 1437 ($\upsilon$(C=N)). The value of molar conductance for the complex is $26\,s\,cm^2\,M^{-1}$ in $10^{-3}\,M\,L^{-1}$ DMF at 20 °C, which suggests that the complexes are non-electrolytes [15]. These results indicate the molecular formula is [Co(DCA)(bipy)($H_2O$)].

### 2.3. *DNA binding*

**2.3.1. Electronic absorption spectra.** Electronic absorption spectra were carried out at 25 °C by fixing the concentration of the complex or bipy ($2.00 \times 10^{-5}\,M\,L^{-1}$), with DNA concentration ranging from 0 to $2.98 \times 10^{-5}\,M\,L^{-1}$. The stock solution of complex

($1.00 \times 10^{-3}$ M L$^{-1}$) was used in the experiment with water as solvent. Absorption spectra were measured at 200–400 nm and DNA in Tris–HCl buffer solution (pH = 7.4) was used as reference.

**2.3.2. Viscosity measurement.** Viscosity measurement was performed by adding compounds to DNA solution ($3.72 \times 10^{-4}$ M L$^{-1}$) with microsyringe. The concentrations of the compounds were controlled within the range 0–$3.33 \times 10^{-6}$ M L$^{-1}$. The relative viscosities $\eta$ were calculated using $\eta = (t - t_0)/t_0$ [16], where $t_0$ and $t$ represent the flow time of DNA solution through the capillary in the absence and presence of complex. Average values of three replicated measurements were used to evaluate the viscosity of the samples. Data were presented as $(\eta/\eta_0)^{1/3}$ *versus* the ratio of the concentration of compounds to DNA, where $\eta$ was the viscosity of DNA in the presence of compound and $\eta_0$ was the viscosity of DNA alone.

### 2.4. *Interaction with BSA*

**2.4.1. Fluorescence spectra.** The complex (0–$4.00 \times 10^{-8}$ M L$^{-1}$) was added to solution containing $4.98 \times 10^{-7}$ M L$^{-1}$ BSA and Tris–HCl buffer (pH = 7.4). Fluorescence spectra were obtained by recording the emission spectra (260–500 nm) corresponding to excitation at 260 nm.

**2.4.2. Synchronous fluorescence spectra.** Synchronous fluorescence spectra were scanned under the same conditions as in Section 2.4.1. The spectra were measured at two different $\Delta\lambda$ ($\Delta\lambda = \lambda_{em} - \lambda_{ex}$) values, which were 15 nm and 60 nm.

### 2.5. *Crystal structure determination*

Single crystal, 0.292 mm × 0.082 mm × 0.062 mm, was used for X-ray diffraction analysis. The structure was solved by direct methods and refined by full-matrix least-squares using SHELXTL-97 [17, 18]. All non-hydrogen atoms were refined anisotropically; hydrogens on oxygen were located from the difference Fourier maps; other hydrogens were generated geometrically. Crystal data and experimental detail for structural analyses are listed in table 1.

## 3. Results and discussion

### 3.1. *Structural description of the complex*

Molecular structure of [Co(DCA)(bipy)($H_2O$)] is shown in figure 1 and the packing diagram in figure 2. Selected bond lengths and angles are presented in table 2 and the hydrogen bond lengths and angles are given in table 3.

Each Co(II) was six-coordinate by O1W from water, one bridging oxygen O(5) and two carboxylate oxygens O(1), O(3) from one DCA, and two nitrogens N(1), N(2) from bipy.

Table 1. Crystal data of the complex.

| | |
|---|---|
| Chemical formula | $C_{18}H_{18}N_2O_6Co$ |
| Formula weight | 417.27 |
| Crystal system | Orthorhombic |
| Space group | *Pbca* |
| *a* (Å) | 12.677(4) |
| *b* (Å) | 22.555(8) |
| *c* (Å) | 11.926(3) |
| *α* (°) | 90 |
| *β* (°) | 90 |
| *γ* (°) | 90 |
| Volume (Å$^3$) | 3410.0(18) |
| *Z* | 8 |
| Shape | Block |
| Color | Pink |
| $D_c$ (g/cm$^{-3}$) | 1.626 |
| *θ* Range for data collection (°) | 1.81–25.00 |
| Reflections collected/unique | 43,174/3008 |
| *R* (int) | 0.2490 |
| Absorption coefficient (mm$^{-1}$) | 1.047 |
| *F* (000) | 1720 |
| *R*/*wR* [$I > 2\sigma(I)$] | 0.0330/0.0797 |
| Restraints/parameters | 1/246 |
| Goodness-of-fit on $F^2$ | 0.810 |
| Largest diff. peak and hole ($e$·Å$^{-3}$) | 0.256, −0.240 |



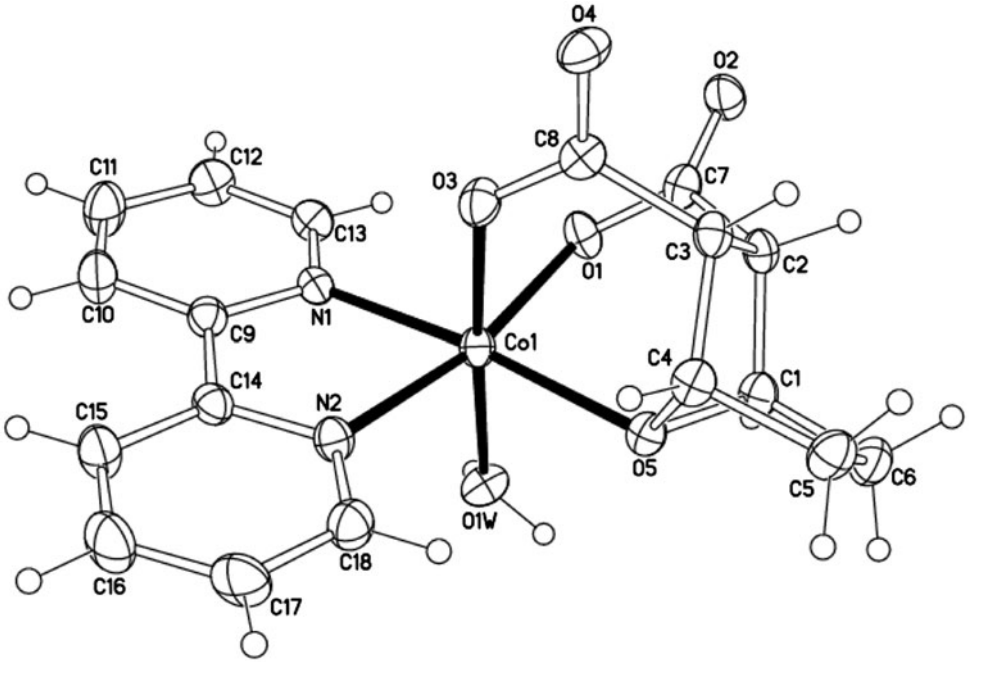


Figure 1. Labeled ORTEP diagram of the complex with 30% thermal probability ellipsoids.

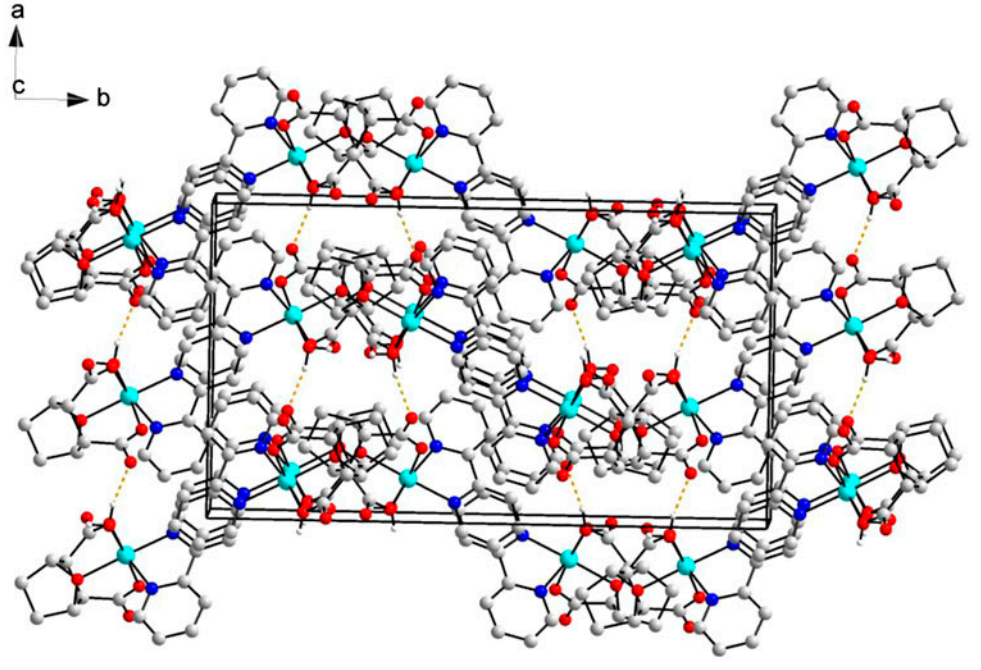


Figure 2. Packing diagram of the complex showing hydrogen bonding interactions (dashed lines).

Table 2. Selected bond lengths (Å) and angles (°).

| Bond | (Å) | Bond | (Å) |
|---|---|---|---|
| Co(1)–O(1) | 2.045(2) | Co(1)–O(3) | 2.048(2) |
| Co(1)–O(5) | 2.1811(19) | Co(1)–O(1W) | 2.070(2) |
| Co(1)–N(1) | 2.104(2) | Co(1)–N(2) | 2.128(2) |
| Angle | (°) | Angle | (°) |
| O(1)–Co(1)–O(5) | 91.11(7) | O(1)–Co(1)–O(1W) | 94.63(8) |
| O(1)–Co(1)–N(1) | 93.93(8) | O(1)–Co(1)–N(2) | 168.20(9) |
| O(1W)–Co(1)–O(5) | 86.48(8) | O(1W)–Co(1)–N(1) | 90.24(8) |
| O(1W)–Co(1)–N(2) | 93.85(8) | O(3)–Co(1)–O(1) | 85.68(9) |
| O(3)–Co(1)–O(5) | 89.52(8) | O(3)–Co(1)–O(1W) | 175.99(8) |
| O(3)–Co(1)–N(1) | 93.73(8) | O(3)–Co(1)–N(2) | 86.44(9) |
| N(1)–Co(1)–O(5) | 174.20(8) | N(1)–Co(1)–N(2) | 77.83(9) |
| N(2)–Co(1)–O(5) | 86.48(8) | | |

Table 3. Hydrogen bonds [(Å) and (°)] for the complex.

| D-H···A | d(D-H) | d(H···A) | d(D···A) | ∠(DHA) |
|---|---|---|---|---|
| O(1W)–H(1WA)···O(4)#1 | 0.86 | 1.85 | 2.696(3) | 167.5 |
| O(1W)–H(1WB)···O(2)#2 | 0.87 | 1.80 | 2.665(3) | 178.0 |

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $y-1/2$, $-z+1/2$; #2 $-x+1$, $y+1/2$, $-z+1/2$; #3 $x+1$, $-y+1/2$, $z+1/2$.

O(1), O(5), N(2), and N(1) are in the equatorial plane with torsion angle of 8.250(82)°. O(3) and O1W are axial with a bond angle ((O)3–Co(1)–O1W) of 175.99(8)°.

Hydrogen-bonding interactions of O(1W)–H(1WA)···O(4)#1 and O(1W)–H(1WB)···O(2)#2 formed between coordinated hydrogen from water and carboxyl oxygen from DCA of neighboring molecules; $\pi$–$\pi$ stacking interactions were also observed from stacking interaction of bipy. The hydrogen-bonding and packing interactions stabilized this crystal structure. It is possible that synergistic effect, containing $\pi$–$\pi$ stacking and hydrogen-bonding interactions, exists between the complex and biomacromolecules [19].

### 3.2. *DNA binding studies*

**3.2.1. Electronic absorption spectra.** To investigate the binding and to calculate the binding constant ($K_b$) of the complex to DNA, we studied the UV absorption spectra by DNA titration to the complex at 298 K. Spectral results are shown in figure 3. Absorptions of this complex were mainly from 2,2′-bipyridine; $Na_2$(DCA) cannot be characterized using UV absorption spectra. By increasing DNA concentration, hypochromic effect was observed, which indicated interaction existed between the complex and DNA [20].

The intrinsic binding constant ($K_b$) was determined by $[DNA]/(\varepsilon_A - \varepsilon_F) = [DNA]/(\varepsilon_B - \varepsilon_F) + 1/[K_b(\varepsilon_B - \varepsilon_F)]$, where [DNA] was the concentration of DNA, $\varepsilon_A$, $\varepsilon_F$, and $\varepsilon_B$ corresponded to the apparent extinction coefficient, the extinction coefficient for the free compound and its fully DNA-bound combination, respectively [21]. In plots of $[DNA]/(\varepsilon_A - \varepsilon_F)$ *versus* [DNA] (insert in figure 3), $K_b$ is the ratio of the slope to intercept. $K_b$ values of the complex were $4.02 \times 10^4$ (complex) and $7.21 \times 10^3\,L\,M^{-1}$ (bipy). The values suggest that the complex has moderate binding with DNA. The binding constant of the complex with DNA was one or two orders of magnitude less than classical intercalator,

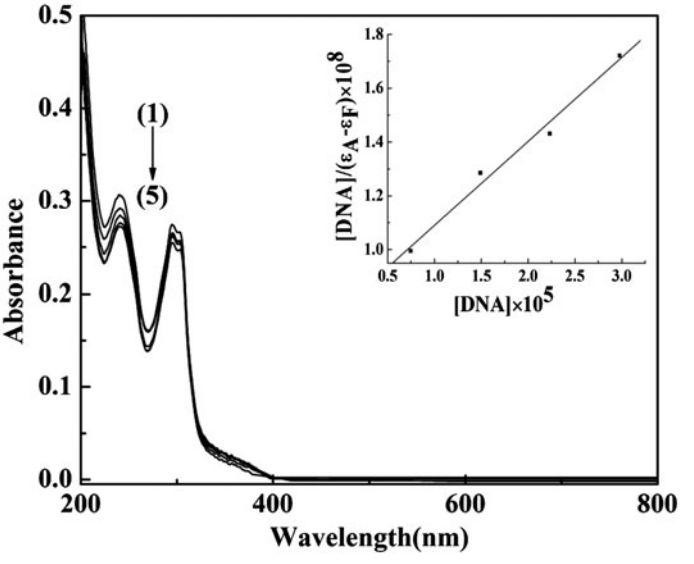


Figure 3. Absorption spectra of the complex in the presence of increasing amounts of DNA. [Complex] = $2.00 \times 10^{-5}\,M\,L^{-1}$, from (1) to (5): $[DNA] \times 10^5 = 0$, 0.74, 1.48, 2.24 and 2.98 $M\,L^{-1}$, respectively.

which indicated that the binding mode between the complexes and DNA was nonclassical intercalation [22].

Compared to several other cobalt(II) complexes, $K_b$ of the title complex is lower than that of cobalt(II) mixed-polypyridyl complexes $[Co(phen)_2(dpta)]^{3+}$ ($4.53 \times 10^5\,L\,M^{-1}$) and $Co(phen)_2(amtp)]^{3+}$ ($3.23 \times 10^5\,L\,M^{-1}$) [23] and slightly higher than that of cobalt(II) Schiff base complex $[CoL_2Cl_2]$ ($2.54 \times 10^4\,L\,M^{-1}$) [24]. The comparison above shows that larger planar ring size of aromatic heterocyclic ligands and more heteroatoms give stronger interactions.

**3.2.2. Viscosity measurements.** To further investigate the binding of the complex with DNA, the DNA viscosity at 25 °C was studied (figure 4). The relative viscosity of DNA steadily decreased after adding complex and increased after adding 2,2′-bipyridine, but there was no significant viscosity change after adding $Na_2$(DCA). The steric hindrance of the complex from non-planar structure of DCA and the complex may partially intercalate into DNA. These results indicate a partial intercalative binding to DNA [25].

### 3.3. *Interaction with BSA*

**3.3.1. Fluorescence spectra and quenching mechanism.** The fluorescence spectra of BSA quenched by the complex and $Na_2$(DCA) were studied. The results are shown in figure 5. BSA has a strong fluorescence emission peak at 345 nm. The peak intensity decreased gradually and the decrease of wavelength emission maximum $\lambda_{max}$ (a blue shift) was observed with increasing concentration of complex (3.0 nm), implying that strong interactions and energy transfer exist between complex and BSA [26].

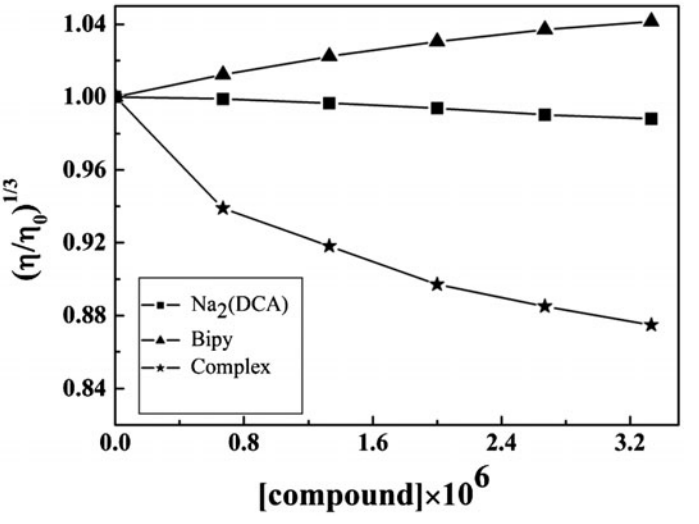


Figure 4. Effect of increasing amounts of the compounds on the relative viscosity of DNA at 25 °C. [DNA] = $3.72 \times 10^{-4}\,M\,L^{-1}$; [compound] $\times 10^6 = 0$, 0.67, 1.33, 2.00, 2.67 and $3.33\,M\,L^{-1}$, respectively.

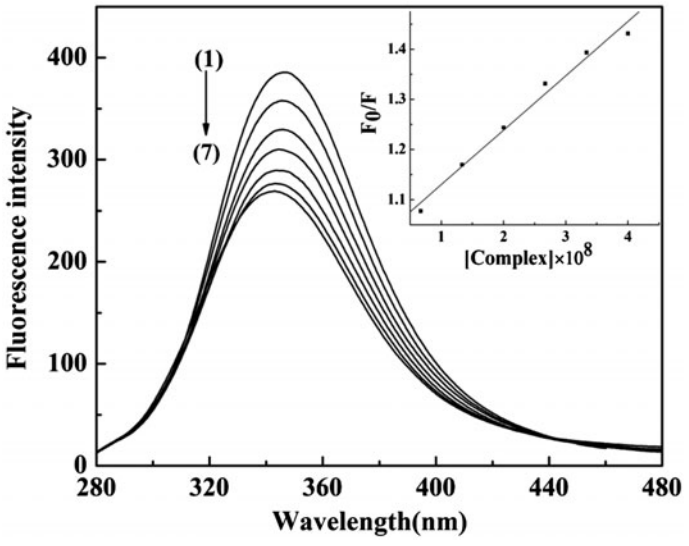


Figure 5. Fluorescence spectra of BSA in the absence and presence of complex. Inset: Stern-Volmer plots of the fluorescence titration data of the complex. [BSA] = $4.98 \times 10^{-7}$ M L$^{-1}$; [complex] × $10^8$ = 0, 0.67, 1.33, 2.00, 2.67, 3.33 and 4.00 M L$^{-1}$, from (1) to (7), respectively.

Fluorescence quenching can occur by static quenching and dynamic quenching. For dynamic quenching, the mechanism can be described by the Stern-Volmer equation [27]: $F_0/F = 1 + K_q\,\tau_0\,[Q]$, where $F_0$ and $F$ are the fluorescence intensities of BSA in the absence and presence of the complex, respectively. $[Q]$ is the concentration of the complex. For many proteins, $\tau_0$ is approximately $10^{-8}$ s [28]. The calculated quenching rate constant $K_q$ was $1.08 \times 10^{15}$ L M$^{-1}$ s$^{-1}$, much greater than the maximum possible value for diffusion-limited quenching in water. The result suggested that the quenching mechanism of complex to BSA was static quenching, generated via intense interaction [29].

Assuming there were $n$ identical and independent binding sites in protein, the binding constant $K_A$ can be calculated using $\lg (F_0 - F)/F = \lg K_A + n \lg [Q]$ [30]. The values of $K_A$ were $7.28 \times 10^6$ (complex) and $2.37 \times 10^4$ L M$^{-1}$ ($Na_2$(DCA)). The values of $n$ were 0.97 (complex) and 0.65 ($Na_2$(DCA)). The results indicated that strong interaction existed between the complex and BSA, which were mainly contributed by DCA. The binding intensity of complex was stronger than DCA and the binding site of complex was one.

**3.3.2. Effect of the complex on BSA conformation.** The conformational changes of BSA in the presence of the complex were evaluated by the synchronous fluorescence intensities of tyrosine (Tyr) residues and tryptophan (Trp) residues in protein. In the experiment, synchronous fluorescence spectra were obtained at different scanning intervals $\Delta\lambda$ ($\Delta\lambda = \lambda_{em} - \lambda_{ex}$). At $\Delta\lambda = 15$ nm, the characteristic peak of Tyr residues was observed and the characteristic peak of Trp residues was observed at $\Delta\lambda = 60$ nm [31]. The results are shown in figure 6.

The fluorescence of Tyr residue was hyperchromic and the Trp residue was hypochromic. Fluorescence intensities of Trp residues varied greatly with increasing concentration of complex. The results indicated that complex mainly interacted with Trp residues of

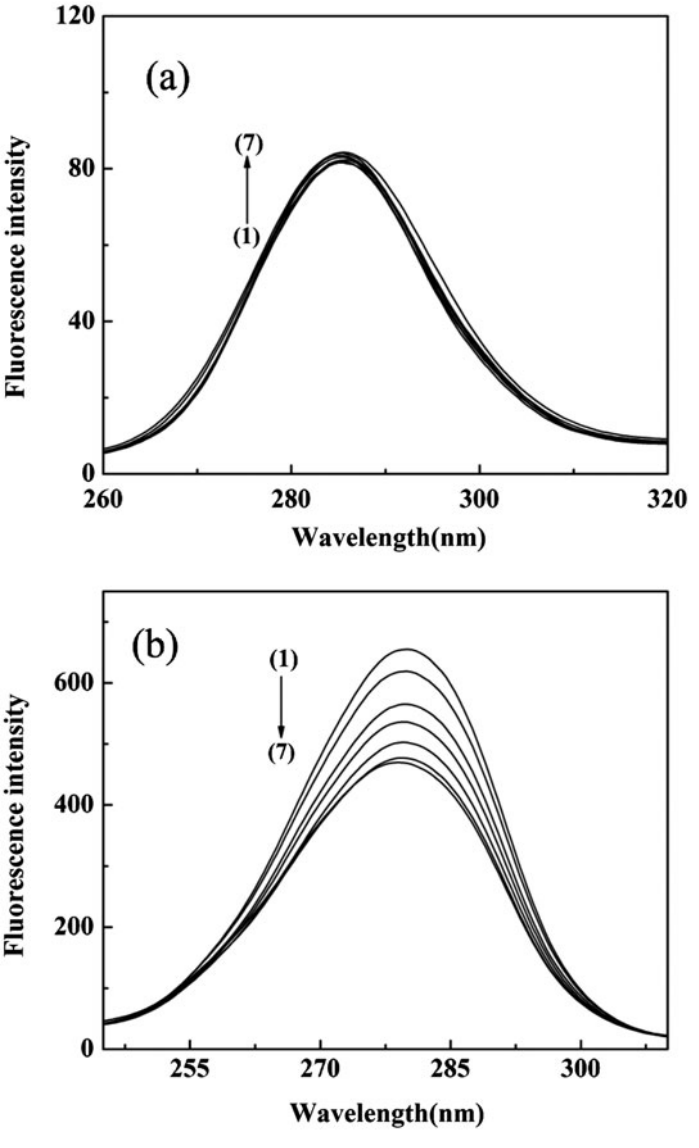


Figure 6. Synchronous fluorescence spectra of BSA in the absence and presence of the complex. [BSA] $= 4.98 \times 10^{-7}\,\mathrm{M\,L^{-1}}$; [complex] $\times 10^{8} = 0$, 0.67, 1.33, 2.00, 2.67, 3.33 and $4.00\,\mathrm{M\,L^{-1}}$, from (1) to (7), respectively. (a): $\Delta\lambda = 15$ nm; (b): $\Delta\lambda = 60$ nm.

BSA. The maximum emission peak of Tyr fluorescence shows a slightly red-shift and the maximum emission peak in Trp fluorescence shows a significant blue-shift. This suggests that the hydrophobicity of microenvironment around Tyr residues decreases in the presence of the complex. On the contrary, the hydrophobicity around Trp residues increases due to the intense interaction between complex and BSA [32]. Changes in microenvironment implied that the complexes combined with BSA mainly around Trp residues, causing conformational changes of protein.

Comparing figure 5 and figure 6, hypochromism ratios of complex to Trp residues (28.29%) were close to those for BSA (30.14%), further suggesting that the complex mainly interacted with Trp residues.

## 4. Conclusions

A new cobalt(II) complex [Co(DCA)(bipy)($H_2O$)] was synthesized and the structure determined by X-ray diffraction. The complex crystallized in the orthorhombic crystal system and *Pbca* space group. Hydrogen-bonding and packing interactions exist among the molecules. Electronic absorption spectra and viscosity measurements show that the complex binds to DNA via partial intercalation, which may be due to the synergistic effect of $\pi$–$\pi$ stacking and hydrogen-bonding interactions between the complex and DNA. The complex interacted strongly with BSA.



## Supplementary material

Crystallographic data for the structure reported in this article has been deposited with the Cambridge Crystallographic Data Center CCDC 849311. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (deposit@ccdc.cam.ac.uk).

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