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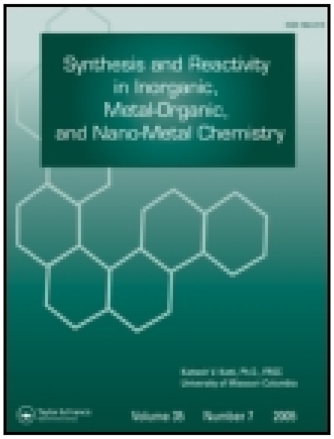

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
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Synthesis, Crystal Structure, and DNA-Binding Studies of Transition Metal Complexes with 2′-(4-Dimethylaminobenzylidene)-2-hydroxybenzoylhydrazide

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Synthesis, Crystal Structure, and DNA-Binding Studies of Transition Metal Complexes with 2′-(4-Dimethylaminobenzylidene)-2-hydroxybenzoylhydrazide

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A series of transition metal complexes of the general formula $M(HL)_2$ (where H_2L=2′-(4-dimethylaminobenzylidene)-2-hydroxybenzoylhydrazide, M=Ni, Cu, Zn, Cd) were prepared and characterized by elemental analysis, spectroscopic (IR, UV–vis) and the $Ni(HL)_2$ was structurally characterized by X-ray crystallography. Single-crystal X-ray diffraction results suggest that Ni(II) central atom situated in a distorted square planar geometry is four-coordinated. The DNA-binding properties of these complexes with calf thymus DNA were also investigated by electronic absorption titration (UV spectroscopy) and fluorescence emission titration. The results showed that these complexes bind to DNA mainly via intercalative mode.

Keywords 2′-(4-dimethylaminobenzylidene)-2-hydroxybenzoylhydrazide, crystal structure, DNA-binding, transition metal complex

INTRODUCTION

For years, hydrazones have been intensively investigated because of biological activity and pharmacological activity,[1] such as antimicrobial, anticonvulsant, analgesic, anti-inflammatory, antiplatelet, antitubercular, and antitumoral activities. Because hydrazones have the structure of $R_1R_2C{=}NNH_2$, these compounds display a versatile behavior in metal coordination, and their biological activity is often increased by bonding to transition metals. Moreover, metal complexes of hydrazones proved to have potential applications as nonlinear optical materials,[2] catalysts,[3] luminescent probes,[4] molecular sensors,[5] and so on. In addition, the interaction of transition metal complexes containing multidentate aromatic ligands with DNA has gained much attention. This is due to their possible application as new therapeutic agents and their photochemical properties which make them potential probes of DNA structure and conformation.[6–10] The studies of interaction between hydrazones and their metal complexes with DNA are important to further understand pharmacology of hydrazones.[11–15] The modes of the DNA interaction with metal complex show intercalative behavior, the electrostatic binding mode, and DNA cleavage ability.[16,17] In our previous studies, a series of metal complexes with N-(2-propionic acid)-salicyloyl hydrazone as ligand have been investigated.[18–21] In order to continue to study DNA-binding model of the benzoyl hydrazone transition metal complexes, in this article a series of transition metal complexes of the general formula $M(HL)_2$ were synthesized; the DNA-binding properties of these complexes with calf thymus DNA (CT-DNA) were investigated by electronic absorption titration (UV spectroscopy) and fluorescence emission titration.

EXPERIMENTAL

General Information

Calf thymus DNA (CT-DNA) was purchased from Sigma (USA) All chemicals used were of analytical grade. The C, H and N analyses were taken with a Perkin Elmer model 2400 CHN analyzer. The metal ion was determined by titration. The UV–vis absorption spectra were obtained with an UV-1700 spectrophotometer (Pharmaspec, SHIMADZU Limited, Japan) at room temperature. Fluorescence measurements were made on an F-4500 spectrophotometer (Hitachi Ltd., Tokyo, Japan). The interaction of the complex with CT-DNA was studied in a doubly distilled water buffer containing of Tris (hydroxymethyl) amino methane (Tris) (5 mmol), 0.4% DMSO, and NaCl (5 mmol). The system was adjusted to pH 7.1 with hydrochloric acid.

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TABLE 1
Crystal data and structure refinement for $Ni(HL)_2$

Crystal data	$Ni(HL)_2$
Formula	$C_{32}H_{32}N_6NiO_4$
Formula weight	623.36
Temp. (K)	293(2) K
Crystal system	Monoclinic
space group	P2(1)/c
a (Å)	13.580(6)
b (Å)	5.848(2)
c (Å)	18.550(7)
α (°)	90
β (°)	101.772(8)
γ (°)	90
V (Å^3)	1442.2(10)
Z	2
Dc(mg m^{-3})	1440
Abs coeff. (mm^{-1})	0.722
F(000)	656
Reflns collected	6774
Unique reflns	2543
Params	202
GOF on F^2	0.821
$R1$, wR [$I > 2\sigma(I)$]	0.0459, 0.0533
$R1$, wR (all data)	0.1451, 0.0600
Largest diff. peak and hole(Å^{-3})	0.250 and –0.432

Synthesis of $M(HL)_2$ (M = Ni, Cu, Zn, Cd)

The synthesis route and physical-chemical property of ligand 2′-(4-dimethylaminobenzylidene)-2-hydroxybenzoylhydrazide (H_2L) was reported in the literature.[22] A mount of ligand H_2L (0.1483 g, 0.5 mmol) was added to a DMF-ethanol mixture (v/v = 5:1, 40 mL). Then a solution of these metal nitrates (0.25 mmol) in water (20 mL) was added dropwise to the system. After being stirred at 75°C for 5 h, there is some precipitate that was isolated by filtration. Resulting solution was allowed to evaporate slowly at the room temperature, and the red single crystals suitable for X-ray analysis of $Ni(HL)_2$ were obtained.

Interaction with Calf Thymus DNA

In order to eliminate the absorbance of nucleic acid itself, an equal amount of CT-DNA was added to the sample and reference cells. Spectrometric titrations were performed according to Wang et al.[23] $K_4[Fe(CN)_6]$ emission quenching was performed according to the Liu et al.[19]

X-Ray Crystallography

Single-crystal X-ray diffraction was carried out with Bruker Smart 1000 CCD X-ray diffractometer (Siemens). Intensities of reflections were measured at 298 K using graphite monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å) with ω scan mode. Empirical absorption correction was applied using SABADS program (University of Göttingen, Göttingen, Germany). The crystal structures were solved by direct methods and Fourier-difference syntheses. All the non-hydrogen atoms were refined anisotropically. Full-matrix least-squares refinement on F^2 was performed by the SHELXL-97 program package (Bruker AXS Inc., Madison, WI, USA). Crystal data, data collection, and refinement details are given in Table 1. The final R_1, wR_2, and other refinement parameters are also presented in Table 1.

RESULTS AND DISCUSSION

Composition of the Complexes

Element Analysis

The results of element analysis for all the complexes are listed in Table 2 along with their formulae. From the table, it can be seen that the found values are in agreement with the calculated ones. These complexes are quite stable at room temperature and do not show any decomposition after a long period of standing.

IR Spectra

The main IR frequencies of the ligand and its complexes along with their relative assignments are recorded in Table 3. IR spectra of the complexes and the (H_2L) are identified according to the literature.[24] The bands appearing in the infrared spectra of the free ligand (H_2L) at 3435, 1635, and 1605 cm^{-1} are assigned to $\nu_{N\text{-}H}$, $\nu_{C=O}$, and $\nu_{C=N}$, respectively. Compared with the ligand, the C=O vibration bands at 1624–1631 cm^{-1} show a little shift to short wavenumbers, which can explain that the C=O (O atom) was coordinated; all complexes show a strong band in 1590–1602 cm^{-1} assigned to ν(C=N) vibration, which indicates

TABLE 2
Element analysis data for the complexes

Complexes	C%	H%	N%	RE%
$Ni(HL)_2$	61.38 (61.65)	4.78 (5.17)	13.26 (13.48)	9.32 (9.41)
$Zn(HL)_2$	60.87 (61.00)	5.12 (5.11)	12.91 (13.33)	10.30 (10.38)
$Cu(HL)_2$	60.98 (61.18)	4.82 (5.13)	13.16 (13.37)	9.89 (10.11)
$Cd(HL)_2$	56.55 (56.76)	4.48 (4.76)	12.35 (12.41)	16.50 (16.60)

TABLE 3
The main spectral data for the ligand and complexes (cm^{-1})

Samples	$\nu_{\text{N-H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$
H_2L	3435(s)	1635(s)	1605(s)
Ni(HL)$_2$	3435(s)	1626(s)	1591(s)
Zn(HL)$_{2:}$	3435(s),	1627(s)	1601(s)
Cu(HL)$_2$	3437(s)	1624(s)	1602(s)
Cd(HL)$_2$	3431(s)	1631(s)	1602(s)

TABLE 4
Selected bond length (Å) and angle (°) of Ni(HL)$_2$

Bond	d, Å	Angle	ω, °
Ni(II)-O(1A)	1.831 (3)	O(1A)-Ni(II)-N(2)	95.50 (14)
Ni(II)-N(2)	1.869 (3)	O(1A)-Ni(II)-N(2A)	84.50 (15)
Ni(II)-O(1)	1.831 (3)	N(2)-Ni(II)-N(2A)	180.0 (3)
Ni(II)-N(2A)	1.869 (3)	O(1A)-Ni(II)-O(1)	179.997 (1)
		O(1)-Ni(II)-N(2)	84.50 (15)
		O(1)-Ni(II)-N(2A)	95.50 (14)

that the C=N (N atom) was coordinated. The intensities of the adsorption bands at 3431–3437 cm^{-1} in all complexes are without evident changes. This indicates that proton is not put off from the N-H bond.

Description of crystal structure of Ni(HL)$_2$

The molecular structure of the Ni(HL)$_2$ along with the atomic numbering scheme is shown in Figure 1. Selected bond lengths and angles are given in Table 4.

In Ni(HL)$_2$, the Ni(II) ion is four-coordinated by two deprotonated 2′-(4-dimethylaminobenzylidene)-2-hydroxybenzoylhydrazide ligands in a bidentate fashion through the acyl oxygen and imido nitrogen (Figure 1). Thus, two five-member rings sharing Ni(II) ion are formed by the two ligands. At the same time, the atoms O1, N2, O1A, and N2A are coplanar approximately [angles N(2)-Ni(II)-N(2A) = 180.0(3)°, and O(1A)-Ni(II)-O(1) = 179.997(1)°], and form a parallelogram. The angle of the clamp O1-Ni-N2 is 84.50° and the angle of the clamp O1-Ni-N2A is 95.50°, so the coordination polyhedron around Ni(II) was described as a square planar geometry. The bond lengths of O(1)-C(1) and O(1A)-C(1A) are 1.255 Å, so they show double-bond character between the C(1) atom and O(1) atom in (HL-) (bond lengths of C–O and C = O are about 1.44 and 1.20 Å, respectively, which suggests that (HL$^-$) coordinates with central Ni in keto-form. The dihedral angle of parallelogram and hydroxybenzoyl plane is 4.67°, the other dihedral angle of parallelogram and dimethylaminobenzylidene plane is 10.67°. These indicate that the molecular structure of the Ni(HL)$_2$ is nearly coplanar.

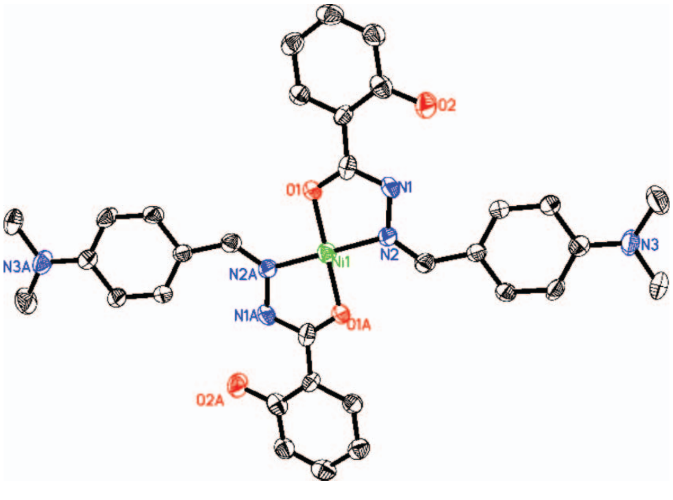

FIG. 1. ORTEP drawing of Ni(HL)$_2$ with hydrogen atoms omitted for clarity (30% thermal ellipsoids probability) (color figure available online).

The Studies of Complex Interaction with CT-DNA

Electronic absorption spectra

Electronic absorption spectroscopy is one of the most useful techniques for DNA-binding studies of metal complex. The absorption spectra of these complexes M(HL)$_2$ (M = Ni, Cu, Zn, Cd) in the absence or presence of CT-DNA are given in Figure 2. In the presence of CT-DNA, the absorption bands of Ni complex at 373 nm exhibited hypochromism of about 33% and bathochromism of about 3 nm, and the absorption bands of Cd complex at 369 nm exhibited hypochromism of about 37% and bathochromism of about 4 nm. These results suggest an intimate interaction of the Ni(HL)$_2$ and Cd(HL)$_2$ with CT-DNA and the interaction is also likely that complexes bind to the helix via intercalation.[25] After the compounds intercalate to the base pairs of DNA, the π^* orbit of the intercalated ligands on the compounds could couple with orbits of the base pairs, thus decreasing the π-π^* transition energies. On the other hand, the coupling π^* orbits are partially filled by electrons, thus, decreasing the transition probabilities. Therefore, these interactions resulted in the observed hypochromism and bathochromism.[26] So, the previous phenomena imply that these Ni(II) and Cd(II) complexes interact with CT-DNA quite probably by intercalating the ligand into the base pairs, but the kind of Cu(II) and Zn(II) complexes interact with CT-DNA need more experiment to determine.

Fluorescence spectra

The enhancements in the emission intensity of these complexes M(HL)$_2$ (M = Ni, Cu, Zn, Cd) with increasing CT-DNA concentrations are shown in Figure 3. In the absence of DNA, these complexes emit weak luminescence in Tris buffer at ambient temperature, with a maximum appearing at 475–477 nm. When DNA is present, the intensity of the emission for these complexes all increase along with increasing DNA concentration. The results of the emission titrations suggest that these complexes are protected from solvent water molecules by the

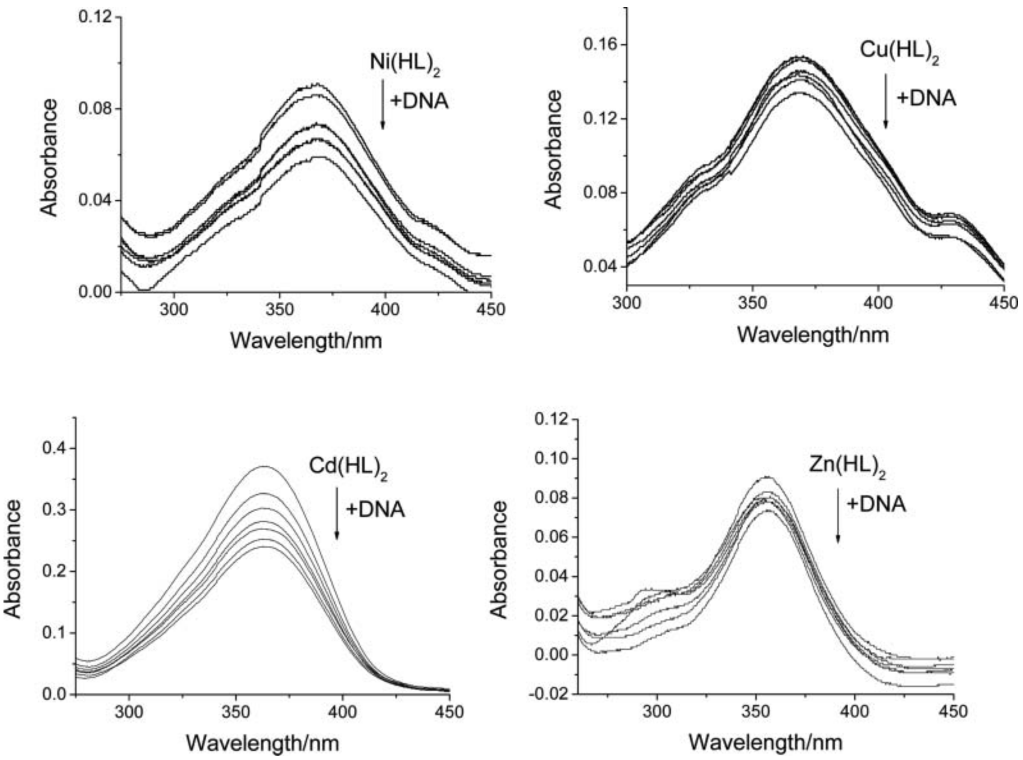

FIG. 2. Electronic spectra of these complexes (10 μM) in the presence of increasing amounts of CT-DNA, $c_{\text{DNA}} = 0, 5, 10, 15, 20, 25$, and 30 μM. The arrow indicates the absorbance changes upon increasing DNA concentration.

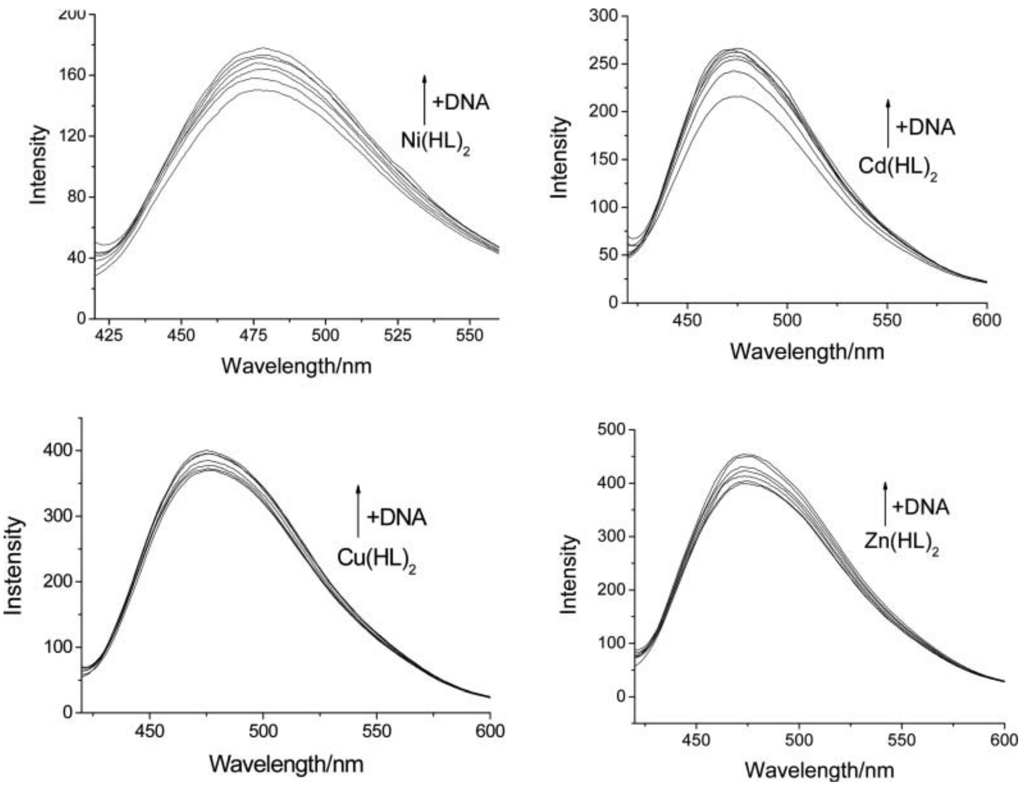

FIG. 3. The emission enhancement spectra of these complexes (10 μM) in the presence of 0, 5, 10, 15, 20, 25, and 30 μM CT-DNA. The arrow indicates the emission intensity changes upon increasing DNA concentration.

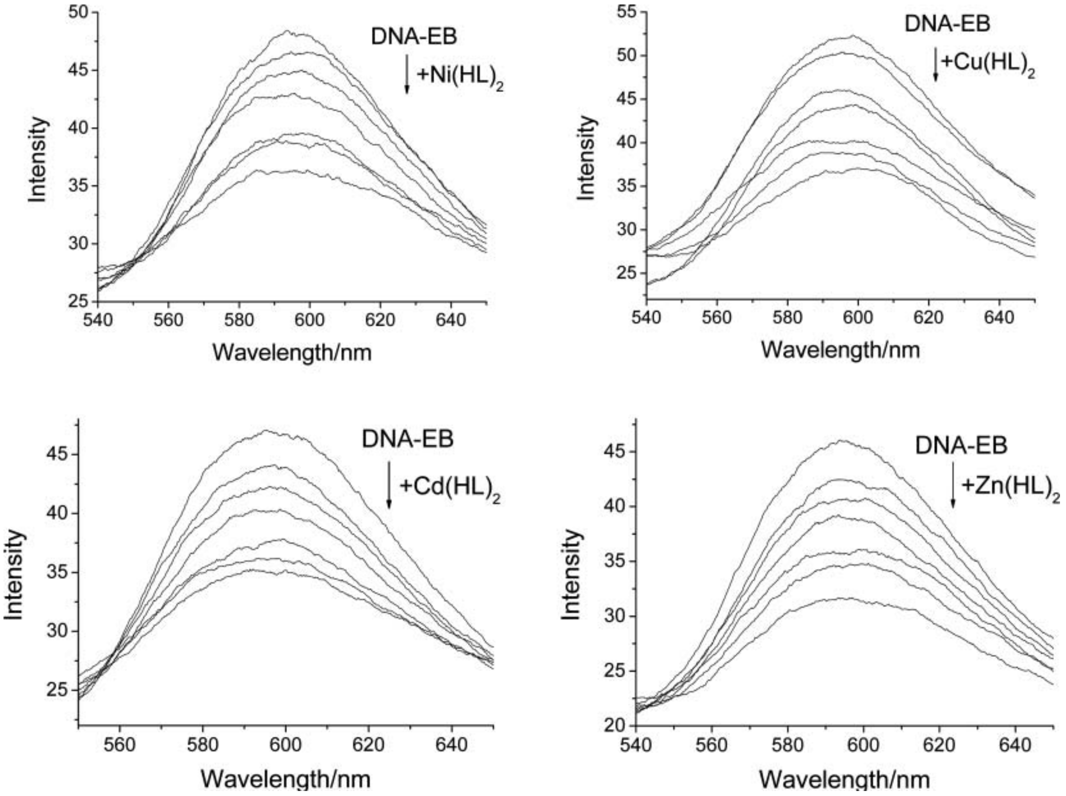

FIG. 4. The emission spectra of DNA- EB system (10 μM DNA and 0.32 μM EB) in the presence of 0, 5, 10, 15, 20, 25, and 30 μM these complexes. The arrow indicates the emission intensity changes upon increasing complex concentration.

hydrophobic environment inside the DNA helix. This suggests that these complexes penetrate into the hydrophobic environment inside the DNA, thereby avoiding the quenching effect of solvent water molecules. Since the hydrophobic environment inside the DNA helix reduces the accessibility of the solvent water molecules into these complexes, these complexes are restricted at the binding site, decreasing the vibrational mode. The binding of these complexes to DNA leads to a marked increase in the emission intensity, this phenomenon for Ni(II) and Cd(II) complexes agree with those observed for the UV spectra, while the phenomenon for Cu(II) and Zn(II) complexes suggest that the two complexes have an interaction with the CT-DNA. The binding of these complexes to DNA leads to a marked increase in the emission intensity, which also agrees with those observed for other intercalations.[27]

In order to test if the complexes could bind to DNA by intercalation, ethidium bromide (EB) was employed, as EB interacts with DNA as a typical indicator of intercalation. As shown in Figure 4, the emission intensity of the DNA-EB system (λem = 592 nm) decreased along with the concentration of these complexes increased. An isobathic point appeared at 550 nm, which indicated the formation of a complex-DNA system. These changes show that complex replaced EB from the DNA-EB system, leading to the decreased emission of the DNA-EB system. The results were caused by EB being expelled from the hydrophobic environment into the water solution.[28] Since these changes indicate only one kind of quenching process, it may be concluded that these complexes bind to CT-DNA via the same mode (intercalation mode) and this result agrees with those observed for the UV spectra and emission spectra.

The emission quenching spectra of these complexes in the absence and presence of DNA are shown in Figure 5. With the increase of the $K_4[Fe(CN)_6]$ quencher concentrations, the emission intensity of these complexes and complex-DNA is obviously reduced. The only difference is that the emission intensity of these complexes in the absence of DNA are less than that in the presence of DNA under the same concentration of the $K_4[Fe(CN)_6]$ quencher. This result represents that these complexes can interact with DNA and be protected by DNA efficiently, since the hydrophobic environment inside the DNA helix reduces the accessibility of the quenching of the $K_4[Fe(CN)_6]$ quench to the complexes. The spectral characteristic suggests these complexes possibly are bound to CT-DNA mainly by intercalation and agree with those observed for the UV spectra, fluorescence emission spectra, and DNA-EB system fluorescence spectra.

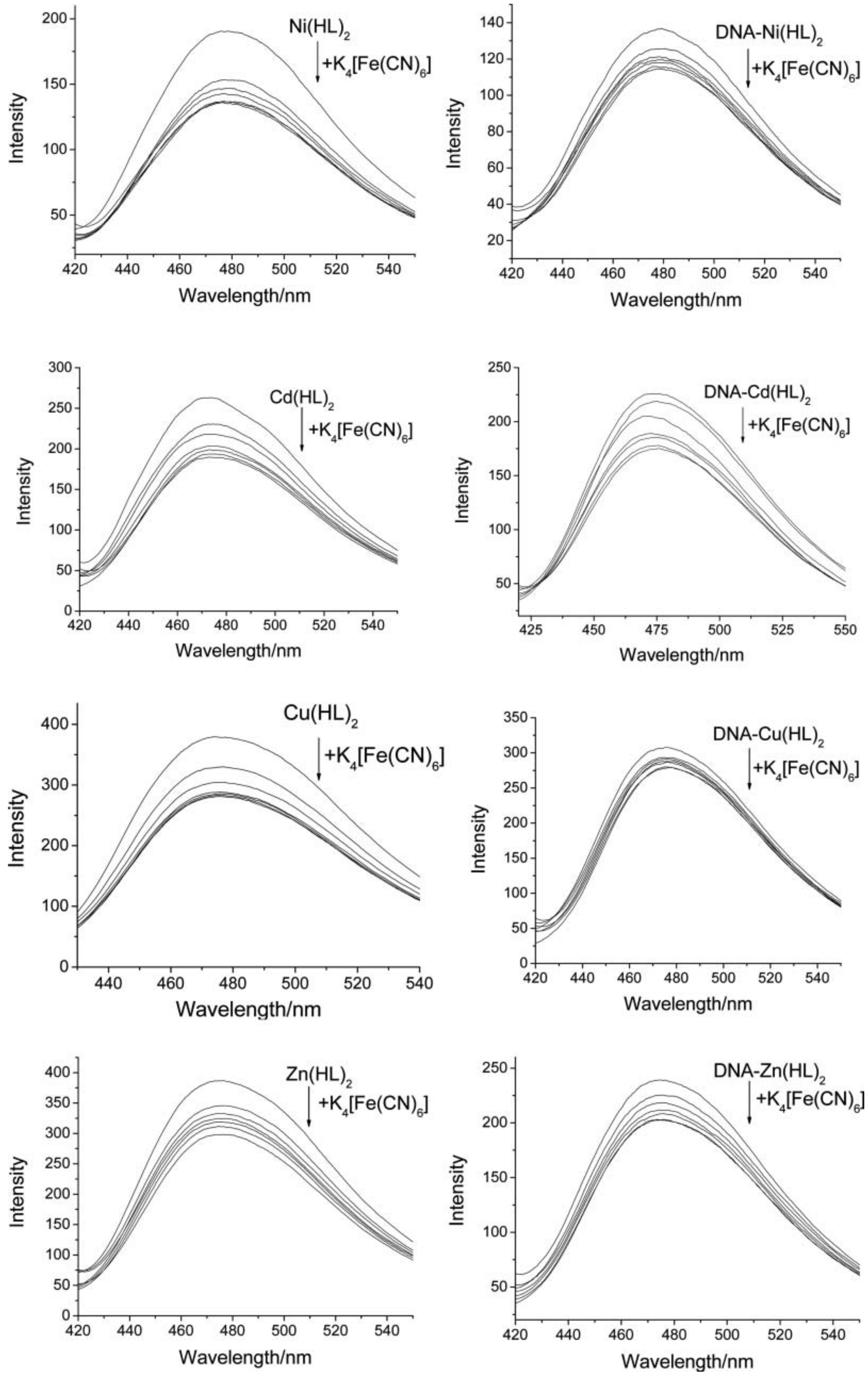

FIG. 5. Emission quenching spectra of these complexes and complex-DNA, with increasing of the concentration of the $K_4[Fe(CN)_6]$ quencher. $c_{\,M(HL)2} = 1.0 \times 10^{-4}$ mol/L; $c_{\,K4[Fe(CN)6]} = 0, 0.5, 1, 1.5, 2, 2.5,$ and 3×10^{-3} mol/L, and $c_{\,DNA} = 40 \times 10^{-6}$ mol/L.

CONCLUSIONS

A series of single-ligand transition metal complexes of the general formula M(HL)$_2$ (H$_2$L=2′-(4-dimethylaminobenzylidene)-2-hydroxybenzoylhydrazide, M = Ni, Cu, Zn, Cd) have been prepared and characterized. The Ni(HL)$_2$ crystal structure indicates the ligand functions as a keto-form and the molecular structure of the complex is nearly coplanar. The DNA-binding properties of these complexes were investigated. The results support the fact that these complexes bind to CT-DNA via intercalation.

SUPPLEMENTARY MATERIALS

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 800679 for Ni(HL)$_2$. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

REFERENCES

1. Rollas, S.; Guniz Kucukguzel, S. Biological activities of hydrazone derivatives. *Molecules* **2007**, *12*, 1910.
2. Mohammed, B.; Kamaluddin, A.R. Electro-optical properties of the first rhenium-hydrazone complex, fac-Re(CO)$_3$(dpknph)Cl. *Transit. Met. Chem.* **1999**, *24*, 384.
3. Pouralimardan, O.; Chamayou, A.C.; Janiak, C.; Hosseini-Monfared, H. Hydrazone Schiff base-manganese(II) complexes: synthesis, crystal structure and catalytic reactivity. *Inorg. Chim. Acta* **2007**, *360*, 1599.
4. Basu, C.; Chowdhury, S.; Banerjee, R.; Evans, H.S.; Mukherjee, S. A novel blue luminescent high-spin iron(III) complex with interlayer O–H. . .Cl bridging: synthesis, structure and spectroscopic studies. *Polyhedron* **2007**, *26*, 3617.
5. Bakir, M.; Green, O.; Mulder, W.H. Synthesis, characterization and molecular sensing behavior of [ZnCl$_2$(η^3-N,N,O-dpkbh)] (dpkbh = di-2-pyridyl ketone benzoyl hydrazone). *J. Mol. Struct.* **2008**, *873*, 17.
6. Erkkila, K.E.; Odom, D.T.; Barton, J.K. Recognition and reaction of metallointercalators with DNA. *Chem. Rev.* **1999**, *99*, 2777.
7. Metcalfe, C.; Thomas, J.A. Kinetically inert transition metal complexes that reversibly bind to DNA. *Chem. Soc. Rev.* **2003**, *32*, 215.
8. Haq, I.; Lincoln, P.; Suh, D.; Norden, B.; Choedhry, B.Z.; Chaires, J.B. Interaction of Δ- and σ-[Ru(phen)$_2$DPPZ]$^{2+}$ with DNA: a calorimetric and equilibrium binding study. *J. Am. Chem. Soc.* **1995**, *117*, 4788.
9. Arturo, S.; Giampaolo, B.; Giuseppe, R.; Maria, L.G.; Salvatore, T. The interaction of native DNA with Iron (III)-N, N′-ethylene-bis (salicylideneiminato)-chloride. *J. Inorg. Biochem.* **2004**, *98*, 589.
10. Maribel, N.; Efren, J.C. F.; Anibal, S.; Mercedes, F.M.; Pedro, S.; Dwight, A.; Edgar, M. Design of copper DNA intercalators with leishmanicidal activity. *J. Biol. Inorg. Chem.* **2003**, *8*, 401.
11. Catherine, H.; Marguerite, P.; Michael, R.; Heinz, G.; Stephanie, S.; Bernard, M. Preparation, characterization and crystal structures of manganese (II), iron (III) and copper (II) complexes of the bis[di-1,1-(2-pyridyl) ethyl] amine (BDPEA) ligand; evaluation of their DNA cleavage activities. *J. Biol. Inorg. Chem.* **2001**, *6*, 14.
12. Wang, Y.; Wang, Y.; Yang, Z.Y. Synthesis, characterization and DNA-binding studies of 2-carboxybenzaldehydeisonicotinoylhydrazone and its La(III), Sm(III) and Eu(III) complexes. *Spectrochim. Acta, Part A* **2007**, *66*, 329.
13. Wang, B.D.; Yang, Z.Y.; Li, T.R. Synthesis, characterization, and DNA-binding properties of the Ln(III) complexes with 6-hydroxy chromone-3-carbaldehyde-(2′-hydroxy) benzoyl hydrazone. *Bioorg. Med. Chem.* **2006**, *14*, 6012.
14. Wang, B.D.; Yang, Z.Y.; Wang, Q.; Cai, T.K.; Crewdson, P. Synthesis, characterization, cytotoxic activities, and DNA-binding properties of the La(III) complex with Naringenin Schiff-base. *Bioorg. Med. Chem.* **2006**, *14*, 1880.
15. Srinivasan, S.; Annaraj, J.; Athappan, P. Spectral and redox studies on mixed ligand complexes of cobalt(III) phenanthroline/bipyridyl and benzoylhydrazones, their DNA binding and antimicrobial activity. *J. Inorg. Biochem.* **2005**, *99*, 876.
16. Cox, P.J.; Psomas, G.; Bolos, C.A. Characterization and DNA-interaction studies of 1,1-dicyano-2,2-ethylene dithiolate Ni(II) mixed-ligand complexes with 2-amino-5-methyl thiazole, 2-amino-2-thiazoline and imidazole. Crystal structure of [Ni(i-MNT)(2a-5mt)2]. *Bioorg. Med. Chem.* **2009**, *17*, 6054.
17. Barone, G.; Cambino, N.; Ruggirello, A.; Silvestri, A.; Terenzi, A.; Liveri, V. T. Spectroscopic study of the interaction of Ni(II)-5-triethyl ammonium methyl salicylidene ortho-phenylendiiminate with native DNA. *J. Inorg. Biochem.* **2009**, *103*, 731.
18. Wu, W.T.; He, S.-Y.; Liu, F.; Chen, F.Y.; Wang, Y.Y.; Shi, Q.Z. Synthesis, characterization and crystal structures of Ni(II), Cd(II) complexes with N-(2-propionic acid)-salicyloyl hydrazone and bipy/phen. *J. Coord. Chem.* **2008**, *61*, 2703.
19. Liu, F.; Zhang, W.P.; He, Sh.Y.; Wang, L.J.; Liu, X.R. Synthesis, crystal structure and properties of the binuclear complex [Sm$_2$(C$_{10}$H$_9$N$_2$O$_4$)$_2$(C$_{10}$H$_8$N$_2$O$_4$)$_2$(H$_2$O)$_4$]. *J. Chem. Cryst.* **2008**, *38*, 755.
20. Liu, F.; Zhang, W.P.; He, S.Y.; Wang, L.J. Synthesis, Crystal Structure and DNA-Binding Studies of the Complex [Co(C$_{10}$H$_9$N$_2$O$_4$)$_2$] · 3H$_2$O. *Russ. J. Coord. Chem.* **2009**, *35*, 454.
21. Wang, L.J.; Guo, H.L.; Wu, W.T.; He, S.Y. Crystal structures of some lanthanide(III) complexes with acylhydrazone and their coordination chemistry. *Russ. J. Coord. Chem.* **2009**, *35*, 925.
22. Yang, J.G.; Pan, F.Y. Crystal structure of 2’-(4-dimethylaminobenzylidene) -2-hydroxy benzoylhydrazide, (CH$_3$)$_2$N(C$_6$H$_4$)(CH)N(NH)(CO)(C$_6$H$_4$OH). *Z. Kristallogr. - New Cryst. Struct.* **2005**, *220*, 515.
23. Wang, B.D.; Yang, Z.Y.; Crewdson, P.; Wang, D.Q. Synthesis, crystal structure and DNA-binding studies of the Ln(III) complex with 6-hydroxychromone-3-carbaldehyde benzoyl hydrazone. *J. Inorg. Biochem.* **2007**, *101*, 1492.
24. Kazuo, N. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Beijing: Chemical Industry Press, **1986**.
25. Hecht, S.M. Bleomycin: new perspectives on the mechanism of action. *J. Nat. Prod.* **2000**, *63*, 158.
26. Eriksson, M.; Leijon, M.; Hiort, C.; Norden, B.; Graeslund, A. Binding of DELTA- and LAMBDA-[Ru(phen)$_3$]$^{2+}$ to [*d* (CGCGATCGCG)]$_2$ studied by NMR. *Biochemistry* **1994**, *33*, 5031.
27. Satyanarayana, S.; Dabrowiak, J.C.; Chaires, J.B. Neither DELTA- nor LAMBDA -tris(phenanthroline)ruthenium(II) binds to DNA by classical intercalation. *Biochemistry* **1992**, *31*, 9319.
28. Zeng, Y.B.; Yang, N.; Liu, W.S.; Tang, N. Synthesis, characterization and DNA-binding properties of La(III) complex of chrysin. *J. Inorg. Biochem.* **2003**, *97*, 258.