Available online at www.sciencedirect.com
ScienceDirect
Journal of Photochemistry and Photobiology A: Chemistry 196 (2008) 77–83
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Synthesis, characterization, and DNA-binding properties of the cobalt(II) and nickel(II) complexes with salicylaldehyde 2-phenylquinoline-4-carboylhydrazone

Zhi-Hong Xu, Feng-Juan Chen, Pin-Xian Xi, Xiao-Hui Liu, Zheng-Zhi Zeng *

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China

Received 26 August 2007; received in revised form 19 November 2007; accepted 20 November 2007
Available online 23 November 2007

Abstract

Salicylaldehyde 2-phenylquinoline-4-carboylhydrazone (H_2L), and its novel cobalt(II), nickel(II) complexes $(M{\cdot}HL{\cdot}3H_2O){\cdot}NO_3$ (M=Co (**1**), M=Ni (**2**)), have been synthesized and characterized by elemental analysis, molar conductivity, mass spectra and IR spectra. The interaction of these complexes with calf-thymus DNA was investigated by UV absorption spectroscopy, fluorescence spectroscopy, circular dichroism (CD) spectroscopy, cyclic voltammetry, and viscosity measurements. The two complexes showed absorption hyperchromism in the range of 190–280 nm. The binding constant have been determined using absorption measurement and found to be $0.89 \times 10^5\ M^{-1}$ and $2.2 \times 10^5\ M^{-1}$, respectively. Results suggest that the two complexes bind to DNA via a groove binding mode.

Keywords: DNA; Salicylaldehyde 2-Phenylquinoline-4-carboylhydrazone; Complex; Groove binding

1. Introduction

The DNA-binding metal complexes have been extensively studied as DNA structural probes, DNA-dependent electron transfer probes and so on during the past decade [1–3]. In these complexes, metal or ligands can be varied in an easily controlled way to facilitate the individual applications. There are several types of sites in the DNA molecule where binding of metal complexes can occur: (i) between two base pairs (intercalation), (ii) in the minor groove, (iii) in the major groove, and (iv) on the outside of the helix [4]. Numerous biological experiments have also demonstrated that DNA is the primary intracellular target of anticancer drugs due to the interaction between small molecules and DNA, which can cause DNA damage in cancer cells, blocking the division of cancer cells and resulting in cell death [5–7]. In addition, the apoptosis can also cause the cell death [8].

Schiff bases play an important role in bioinorganic chemistry as they exhibit remarkable biological activity. Such as the Cr(III) complexes of Schiff bases like salen bring about apoptosis which can lead to DNA damage, plasmid cleavage, and protein cleavage [9–12]. The acid hydrazides R–CO–NH–NH_2, a class of Schiff base, their corresponding aroylhydrazones, R–CO–NH–N=CHR′, and the dependence of their mode of chelation with transition metal ions present in the living system have been of significant interest [13–17]. The coordination compounds of aroylhydrazones have been reported to act as enzyme inhibitors [18] and are useful due to their pharmacological applications [19–21]. Previously some work demonstrated that 4-quinolinecarboxylic acid amides and hydrazides, substituted at position 2, exhibit pronounced antiinflammatory and analgesic activity at a quite low toxicity [22–26], but no metal complexes of such drug have been reported in the past which can have better pharmaceutical effect possibly. Therefore, studies of the metal complexes are important to explore the possible new drug compare with the present drug.

In the present work, we synthesized and characterized the Salicylaldehyde 2-phenylquinoline-4-carboylhydrazone (H_2L) and its cobalt(II) and nickel(II) complexes. In addition, the DNA-binding properties with them have been studied with a view to evaluating their pharmaceutical activities.

* Corresponding author. Fax: +86 931 8912582.
E-mail addresses: zengzhzh@yahoo.com.cn, zengzhzh@lzu.edu.cn (Z.-Z. Zeng).

1010-6030/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2007.11.017

2. Experimental

All reagents and solvents were purchased commercially and used without further purification unless otherwise noted. Calf-thymus DNA (CT-DNA) was obtained from Sigma Chemicals Co. (USA) and used as received. Solutions of CT-DNA in 50 mM NaCl, 5 mM Tris–HCl (tris(hydroxymethyl)aminomethane hydrochloride) (pH 7.2) gave a ratio of UV–vis absorbance of 1.8–1.9:1 at 260 and 280 nm, indicating that the DNA was sufficiently free of protein [27]. The concentration of DNA was determined spectrophotometrically using a molar absorptivity of 6600 M^{-1} cm^{-1} (260 nm) [28]. Double-distilled water was used to prepare buffers.

2.1. Physical measurement

The melting points of the compounds were determined on a Beijing XT4-100× microscopic melting point apparatus (the thermometer was not corrected). Carbon, hydrogen, and nitrogen were analyzed on an Elemental Vario EL analyzer. Infrared spectra (4000–400 cm^{-1}) were determined with KBr disks on a Therrno Mattson FTIR spectrometer. The UV–vis spectra were recorded on a Varian Cary 100 UV–vis spectrophotometer. The fluorescence spectra were recorded on a Hitachi RF-4500 spectrofluorophotometer. ^{1}H NMR spectra were measured on a Varian VR 300-MHz spectrometer, using TMS as a reference in $CDCl_3$ or DMSO-d6. Mass spectra were performed on a VG ZAB-HS (FAB) instrument and electrospray mass spectra (ESI-MS) were recorded on a LQC system (Finngan MAT, USA) using CH_3OH as mobile phase.

2.2. DNA binding experiments

Absorption titration experiments were performed by maintaining the metal complex concentration as constant at 10 μM while varying the concentration of the CT-DNA within 0.5–10 μM. While measuring the absorption spectra, equal quantity of CT-DNA was added to both the complex and the reference solution to eliminate the absorbance of DNA itself.

For fluorescence measurements, fixed amounts (10 μM) of the complex **1** and **2** were titrated with increasing amounts (0–50 μM) of CT-DNA. The excitation and emission wavelength were 358 and 414 nm, respectively. Excitation and emission slit were set at 10 nm.

The CD spectra were recorded on an Olos RSM 1000 at increasing complex/DNA ratio ($r = 0.0, 0.5$). Each sample solution was scanned in the range of 220–320 nm. A CD spectrum was generated which represented the average of three scans from which the buffer background had been subtracted. The concentration of DNA was 1.0×10^{-4} M.

Viscosity experiments were conducted on an Ubbelodhe viscometer, immersed in a thermostated water-bath maintained at 25 ± 0.1 °C. Titrations were performed for the complexes (1–10 μM), and each compound was introduced into the CT-DNA solution (10 μM) present in the viscometer. Data were presented as $(\eta/\eta_0)^{1/3}$ versus the ratio of the concentration of the compound to CT-DNA, where η is the viscosity of CT-DNA in the presence of the compound and η_0 is the viscosity of CT-DNA alone. Viscosity values were calculated from the observed flow time of CT-DNA containing solutions corrected from the flow time of buffer alone (t_0), $\eta = t - t_0$ [29].

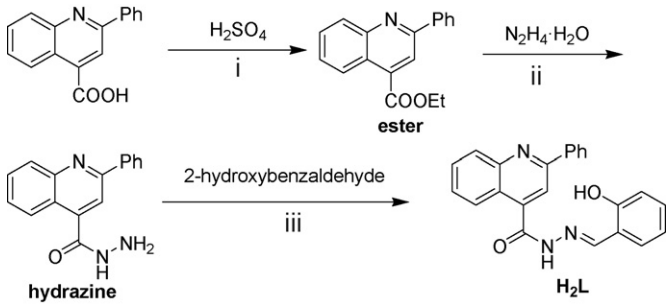

Fig. 1. The synthetic route of the ligand: (i) C_2H_5OH, reflux, 20 h; (ii) C_2H_5OH, reflux, 4 h; (iii) CH_3OH, reflux, 3 h.

Cyclic voltammetry experiments were performed at room temperature under an inert atmosphere (N_2) with a conventional three-electrode electrochemical cell, and using a CHI-420 electrochemical workstation (made in Shanghai, China). The three-electrode system used in this work consists of a glassy carbon electrode as working electrode, a saturated calomel electrode (SCE) as reference electrode and a Pt foil auxiliary electrode. Solution was prepared by dissolving the complexes in DMF and 0.1 M $NaClO_4$ was used as supporting electrode.

2.3. Synthesis of the ligand

The ligand (Fig. 1) was prepared according to a method of the literature [30]. 2-phenylquinoline-4-carboxylic acid (12.49 g; 50 mmol) was esterified to 2-phenylquinoline-4-carboxylate (yield: 12.86 g (93%)), treatments of the esters with N_2H_4 gave the corresponding hydrazine (10.98 g; (90%)), which was refluxed 3 h mixed with 2-hydroxybenzalhedyde, the H_2L was obtained in 86% yield.

Ester: yellowish solid, m.p. 51 °C. ^{1}H NMR (300 MHz, $CDCl_3$, s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet) δ (ppm): 1.49–1.53 (t, 3H, –CH_3), 4.52–4.59 (q, 4H, –CH_2–), 7.49–7.81 (m, 5H, –Ph), 8.20–8.27 (m, 3H, –quinoline), 8.40 (s, 1H, –quinoline), 8.73–8.76 (d, 1H, –quinoline).

Hydrazine: white solid, m.p. 222 °C. ^{1}H NMR (300 MHz, DMSO-d6) δ (ppm): 4.73 (s, 2H, –NH_2), 7.58–8.31 (m, 10H, –Ar), 10.04 (s, 1H, –NH–).

H_2L: white solid, ^{1}H NMR (300 MHz, DMSO-d6) δ (ppm): 6.93–8.41 (m, 14H, –Ar), 8.62 (s, 1H, –CH–), 11.08 (s, 1H, –NH–), 12.47 (s, 1H, –OH). IR (KBr) (cm^{-1}): ν_{O-H} 3436, ν_{N-N} 3144, $\nu_{C=O}$ 1676, $\nu_{C=N}$ 1564, δ_{N-H} 1492, ν_{C-N} 1357. UV: λ_{max} (nm): 220, 261, 329. FAB-MS: 368.4.

2.4. Synthesis of the complexes

2.4.1. Synthesis of $(Co{\cdot}HL{\cdot}3H_2O){\cdot}NO_3$ (*1*)

H_2L (0.919 g, 0.25 mmol) and NaOH (0.01 g, 0.25 mmol) was mixed in 10 ml C_2H_5OH and stirred for 0.5 h, $Co(NO_3)_2{\cdot}6H_2O$ (0.0873 g, 0.3 mmol) was added to the yellowish solution. The solution turned to deep red immediately

and further stirred 3 h at room temperature, the orange precipitate **1** was isolated by filtration and washed by C_2H_5OH and then dried under vacuum. Yield: 51%. (Found: C, 51.14; H, 4.16; N, 10.52. Calc. for $CoC_{23}H_{22}N_4O_8$: C, 51.03; H, 4.10; N, 10.35%). IR (KBr) (cm^{-1}): ν_{O-H} 3409, $\nu_{C=O}$ 1599, $\nu_{C=N}$ 1518, ν_{NO_3} 1386, ν_{Co-O} 617, ν_{Co-N} 470. ES–MS [CH_3OH, *m/z*]: $(Co{\cdot}HL{\cdot}NO_3 + H)^+$ 488.3, $(Co{\cdot}HL{\cdot}NO_3{-}NO_3)^+$ 425.3.

2.4.2. Synthesis of (Ni·HL·3H2O)·NO3 (2)

Compound **2** was prepared in a similar way to that of complex **1** except for $Ni(NO3)_2{\cdot}6H_2O$ instead of $Co(NO_3)_2{\cdot}6H_2O$, and the yellow precipitate was formed after the solution was stirred 3 h. Yield: 56%. (Found: C, 51.16; H, 4.20; N, 10.28. Calc. for $Co_4C_{92}H_{74}N_{12}O_{15}$: C, 51.05; H, 4.10; N, 10.35%). IR (KBr) (cm^{-1}): ν_{O-H} 3393, $\nu_{C=O}$ 1604, $\nu_{C=N}$ 1544, ν_{NO_3} 1384, ν_{Ni-O} 599, ν_{Ni-N} 465. ES–MS [CH_3OH, *m/z*]: $(Ni{\cdot}HL{\cdot}NO_3 + H)^+$ 488.1, $(Co{\cdot}HL{\cdot}NO_3{-}NO_3)^+$ 425.1.

3. Results and discussion

The complexes are stable in atmospheric conditions and soluble in ethanol, methanol, DMF and DMSO. The Λ_M values of the complexes in methanol are 94 and 98 S cm^2 mol^{-1}, respectively and in accord with them being formulated as 1:1 electrolytes [31].

3.1. IR spectra

The IR spectra of the two complexes are very similar. The $\nu_{C=O}$ of the free ligand are at 1676 cm^{-1}, for complex **1** and **2** this peak shifted to 1599 and 1604 cm^{-1}, $\nu_{(ligand-complexes)}$ is equal to 77 and 72 cm^{-1}, respectively. The band at 617 and 599 cm^{-1} for **1** and **2** is assigned to ν_{M-O} [32]. This data strongly indicates that the oxygen of the carbonyl has formed a coordinative bond with the metal ions. The band at 1564 cm^{-1} for the free ligand is assigned to the $\nu_{C=N}$ stretch, which shifts to 1518 and 1544 cm^{-1} for the complexes **1** and **2**. Weak bands at 470 and 465 cm^{-1} for complexes **1** and **2** are assigned to ν_{M-N} [33]. These further confirm that the nitrogen of the imino group bonds to the metal ions. The absorption band near 1384 cm^{-1} indicates that free nitrate is also present [34].

3.2. UV spectra

The study of the electronic spectra in the ultraviolet and visible ranges for the metal complexes and ligand was carried out in a buffer solution. The electronic spectra of ligand had a strong band at λ_{max} = 220 nm, a medium band at λ_{max} = 261 nm, and a weak band at λ_{max} = 329 nm. The complexes yield two bands, and the bands at 220 nm are shifted to 206 nm. These indicate that complexes are formed.

3.3. Structure of the complexes

Since the crystal structure of the metal complexes has not been obtained yet, we characterized the complexes and determined its possible structure by elemental analyses, molar conductivity, mass spectra, IR data and UV–vis measurements. The likely structure of the complexes is shown in Fig. 2.

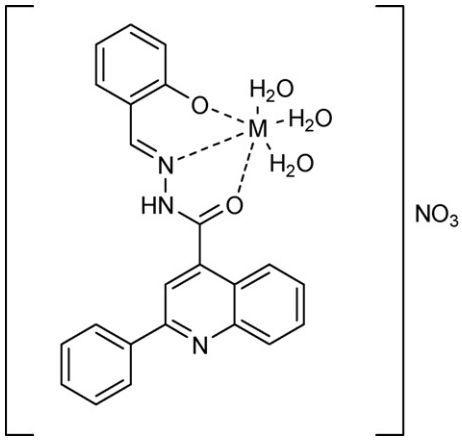

Fig. 2. The suggested structure of the complex. M=Co, Ni.

3.4. DNA-binding studies

3.4.1. Electronic absorption titration

Absorption titration can monitor the interaction of a metal complex and DNA. In general, hypochromism and red-shift are associated with the intercalative binding of the complex to the helix, due to strong stacking interactions between the aromatic chromophore of the complex and the base pairs of DNA [35]. The complexes show absorbance, which is due to metal-to-ligand charge transfer interactions. The complexes have three replaceable H_2O molecules and hence can coordinate with nucleotide bases. The intensity of the metal-to-ligand charge transfer (MLCT) band of the complexes, observed at the range of 190–280 nm (Fig. 3(a) and (b)), were monitored as a function of added DNA. Under the identical experimental conditions, the complexes didn't show bands in the visible area, so we just discuss here the UV bands show apparent changes when interact with CT-DNA. Upon addition of CT DNA, the absorption bands of **1** and **2** at about 206 nm show hyperchromism, and is accompanied by a small shift of 2 nm in λ_{max}, from 206 to 208 nm of **1**, and no shift for **2**, that is consistent with groove binding, leading to small perturbations. This hyperchromism can be attributed to external contact (surface binding) with the duplex. Some similar hyperchromism have been observed [36–38].

The absorption data were analyzed to evaluate the intrinsic binding constant K_b, which can be determined from Eq. (1) [39],

$$\frac{[DNA]}{(\varepsilon_a - \varepsilon_f)} = \frac{[DNA]}{(\varepsilon_o - \varepsilon_f)} + \frac{1}{K_b(\varepsilon_b - \varepsilon_f)} \quad (1)$$

where [DNA] is the concentration of DNA in base pairs, the apparent absorption coefficient ε_a, ε_f and ε_b correspond to A_{obsd}/[M], the extinction coefficient of the free compound and the extinction coefficient of the compound when fully bound to DNA, respectively. In plots of $[DNA]/(\varepsilon_a - \varepsilon_f)$ versus [DNA], K_b is given by the ratio of slope to the intercept. The intrinsic binding constants K_b of complexes **1** and **2** were 0.89×10^5 M^{-1} and 2.2×10^5 M^{-1}, respectively. The results indicate that the bind-

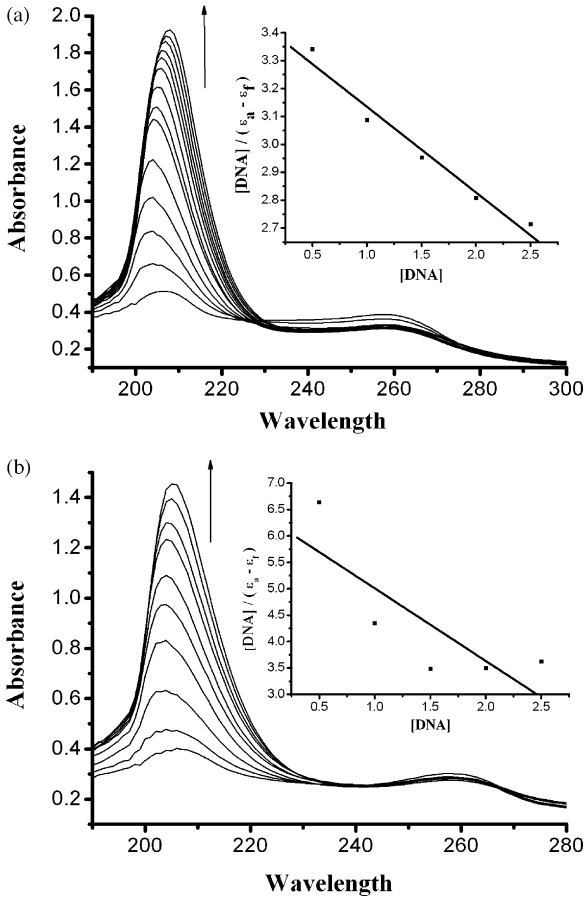

Fig. 3. Absorption spectra of the complex **1** (a) and **2** (b) inTris–HCl buffer upon addition of calf-thymus DNA. [complex] = 1×10^{-5} M, [DNA] = (0–1) $\times 10^{-5}$ M. Arrow shows the absorbance changing upon increasing DNA concentrations. Inset: plots of [DNA]/(ε_a–ε_f) versus [DNA] for the titration of DNA with the complex.

ing strength of complex **2** is stronger than that of **1**. The K_b value obtained here is lower than that reported for classical intercalator (for ethidium bromide and [Ru(phen)DPPZ] whose binding constants have been found to be in the order of 10^6–10^7 M) [40,41]. The observed binding constant is more in keeping with the groove binding with DNA, as observed in the literature [42].

3.4.2. CD spectral studies

Circular dichroic spectral techniques give us useful information on how the conformation of DNA is influenced by the binding of the metal complex to DNA. The observed CD spectrum of calf-thymus DNA consists of a positive band at 277 nm due to base stacking and a negative band at 245 nm due to helicity, which is characteristic of DNA in the right-handed B form. While groove binding and electrostatic interaction of small molecules with DNA show little or no perturbations on the base stacking and helicity bands, intercalation enhances the intensities of both the bands, stabilizing the right-handed B conformation of CT-DNA. The CD spectra of DNA taken after incubation of the complexes with CT DNA are shown in Fig. 4. In all two cases, the intensities of both the negative and positive bands decrease significantly (shifting to zero levels). This suggests that the DNA binding of the complexes induces certain

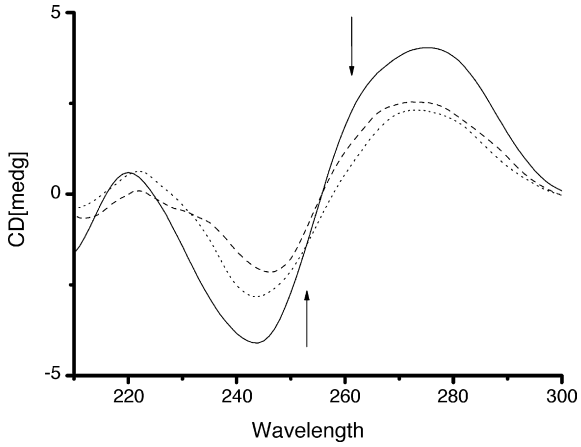

Fig. 4. CD spectra of CT-DNA (100 mM) in the absence (Solid line) and presence of compound **1** (Dash line) and **2** (Dot line) (50 mM).

conformational changes, such as the conversion from a more B-like to a more C-like structure within the DNA molecule [37]. These changes are indicative of a non-intercalative mode of binding of these complexes and offer support to their groove binding nature [43]. The changing intensity follow the order of **2** > **1**.

3.4.3. Fluorescence studies

It is noted that both complexes are in a DNA concentration-dependent manner and exhibit two emission bands (Fig. 5(a) and (b)), which is similar to the literature observed previously [44,45]. The intensity of emission at 412 nm increases steadily with the increasing concentration of the CT-DNA. On the other hand the intensity of the 446 nm exhibit small increase when bind to DNA. The emission maximum at about 412 nm shift by 2 nm to longer wavelength (414 nm) for compound **1**, and no shift for **2**. This effect arises because, in the presence of DNA, the metal complex is bound in a relatively non-polar environment compared to water. The increase in the fluorescence intensity is less than that for the intercalators. The binding site size was determined from the binding stoichiometry of the complex-DNA isotherm as shown in Fig. 6(a) and (b). The intersection point of the binding isotherm, gives a binding site size of ten base pairs per bound complex molecule. The binding site size allows one to distinguish between intercalating and non-intercalating binding agents [46]. Molecules showing large binding site sizes are indicative of non-intercalation as a probable mode of binding and they require correspondingly lower concentrations to saturate the sites. The binding isotherm of complex **1** and **2** is again indicative of non-intercalative binding of the complexes to DNA.

3.4.4. Viscometric titration

Hydrodynamic methods that are sensitive to length are regarded as one of the least ambiguous and most critical tests of a binding mode in solution in the absence of crystallographic structural data. Intercalating agents are expected to elongate the double helix to accommodate the ligands in between the base leading to an increase in the viscosity of DNA. In contrast, complex that bind exclusively in the DNA grooves by partial and/or

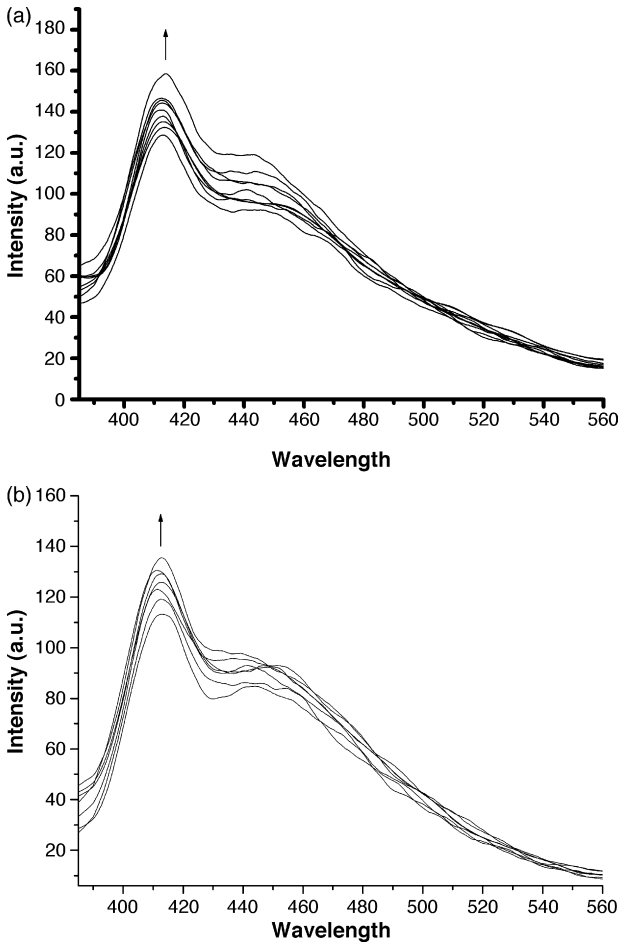

Fig. 5. Emission spectra of the complex **1** (a) and **2** (b) inTris–HCl buffer upon addition of calf-thymus DNA. [complex] = 1×10^{-5} M, [DNA] = (0–5) $\times 10^{-5}$ M. Arrow shows the intensity changing upon increasing DNA concentrations.

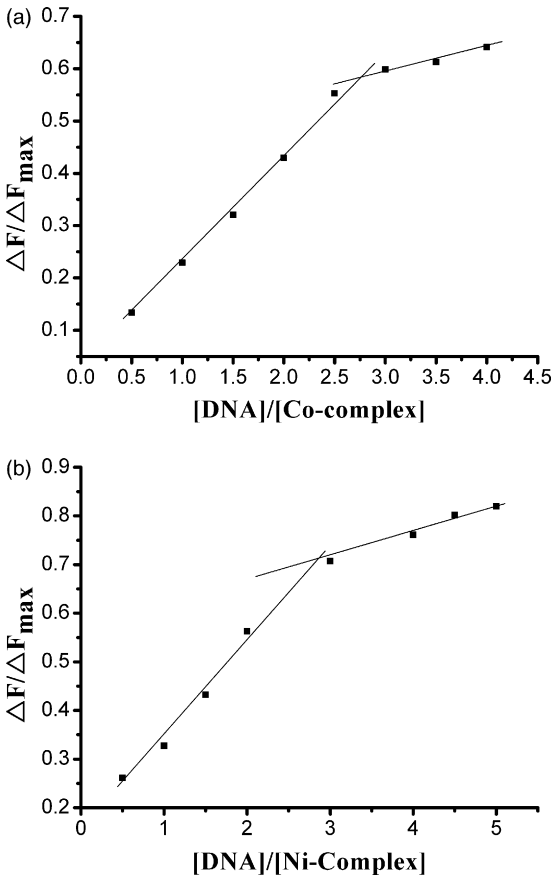

Fig. 6. Fluorescence binding isotherms for the association of complex **1** and **2** with DNA in Tris–HCl buffer (pH 7.2), containing 50 mM NaCl. The binding stoichiometry in terms of number of nucleotide bases/drug molecule is the value at the intersection of the two straight lines.

non-classical intercalation, under the same conditions, typically cause less pronounced (positive or negative) or no change in DNA solution viscosity [47]. The values of $(\eta/\eta_0)^{1/3}$ were plotted against [complex]/[DNA] (see Fig. 7). The results reveal that the complexes **1** and **2** effect relatively inapparent increase in DNA viscosity, which is consistent with DNA groove binding suggested above, which is also known to enhance DNA viscosity [48]. The increased degree of viscosity, which may depend on its affinity to DNA follows the order of **2** > **1**, which is consistent with our foregoing hypothesis.

3.4.5. Voltametric studies

The application of electrochemical methods to the study of metallointercalation and coordination of transitional metal complexes to DNA provides a useful complement to the previously used methods of investigation, such as UV–vis spectroscopy [49,50]. Fig. 8 shows the cyclic voltammograms of the complexes at the absence and presence of DNA. It can be seen that the cathode and anode peak currents decreased gradually with the addition of DNA. The decrease in current may be attributed to the diffusion of the complexes bound to the large, slowly diffusing DNA molecule. The decreases in the peak currents are ascribed to the stronger binding between the complexes and DNA. In addition, the peak potentials, E_{pc} and E_{pa}, as well as $E_{1/2}$ had a shift to more positive potential. The shift of the redox potential of the complexes in the presence of DNA to more positive values indicates a binding interaction between the complex and DNA that makes the complexes readily reducible. The decreased extents of the peak currents observed for the complexes upon addition of CT DNA may indicate that complex **2** possesses

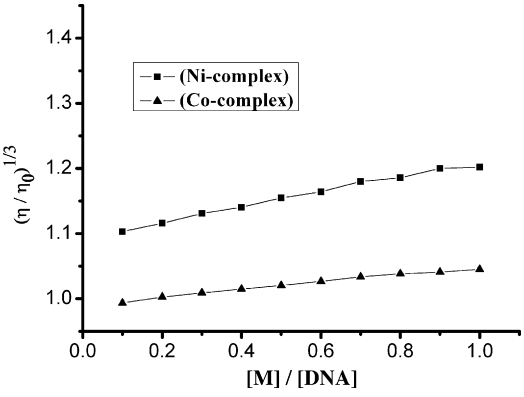

Fig. 7. Effect of increasing amounts of the Co and Ni complex on the relative viscosity of calf-thymus DNA at 25.0 °C.

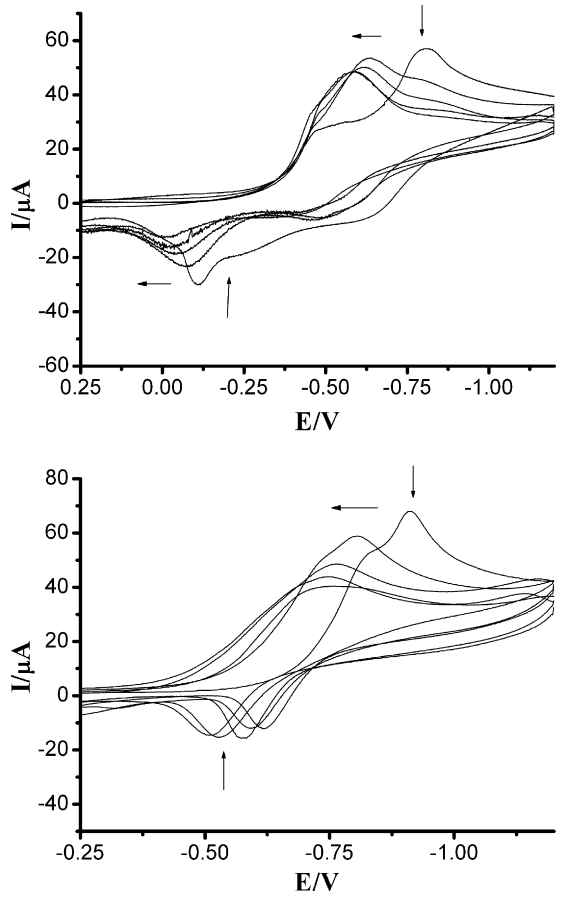

Fig. 8. Cyclic voltammogram of 0.50 mM complex **1** (upon) and **2** (below). Supporting electrolyte, 100 mM $NaClO_4$ in DMF, Sweep rate, 50 mV/s. Arrow shows the current and potential changing upon increasing DNA concentrations. (**1**: 0, 0.02, 0.03,0.04, 0.05 mM DNA) (**2**: 0, 0.01, 0.02, 0.03, 0.04 mM DNA).

higher DNA-binding affinity than complex **1** does. The results parallel the above spectroscopic and viscosity data of Co and Ni complexes in the presence of DNA.

4. Conclusion

Two new Co(II) and Ni(II) complexes have been synthesized and characterized. The DNA-binding properties of these complexes were examined by absorption and fluorescence and CD spectra, CV and viscosity measurements. Experimental results indicate that the complexes can bond to CT-DNA take the mode of groove binding, and complex **2** have stronger binding affinity than **1**.

Acknowledgement

The authors thank the National Natural Science Foundation of China (20171019) for financial support.

References

[1] K.E. Erkkila, D.T. Odom, J.K. Barton, Chem. Rev. 99 (1999) 2777–2795.
[2] C. Metcalfe, J.A. Thomas, Chem. Soc. Rev. 32 (2003) 215–224.
[3] I. Haq, P. Lincoln, D. Suh, B. Norden, B.Z. Choedhry, J.B. Chaires, J. Am. Chem. Soc. 117 (1995) 4788–4796.
[4] A.M. Pyle, J.P. Rehmann, R. Meshoyrer, C.V. Kumar, N.J. Turro, J.K. Barton, J. Am. Chem. Soc. 111 (1989) 3051–3058.
[5] H. Catherine, P. Marguerite, R.G. Michael, S. Stéphanie Heinz, M. Bernard, J. Biol. Inorg. Chem. 6 (2001) 14–22.
[6] V.S. Li, D. Choi, Z. Wang, L.S. Jimenez, M.S. Tang, H. Kohn, J. Am. Chem. Soc. 118 (1996) 2326–2331.
[7] G. Zuber, J.C. Quada Jr., S.M. Hecht, J. Am. Chem. Soc. 120 (1998) 9368–9369.
[8] H.Y. Shrivastava, T. Ravikumar, N. Shanmugasundaram, M. Babu, B.U. Nair, Free Radic. Bio. Med. 38 (2005) 58–69.
[9] R. Rajaram, B.U. Nair, T. Ramasami, Biochem. Biophys. Res. Commun. 210 (1995) 434–440.
[10] R. Vijavalakshmi, M. Kanthimathi, V. Subramanian, B.U. Nair, Biochim. Biophys. Acta 1475 (2000) 157–162.
[11] H.Y. Shrivastava, B.U. Nair, Biochem. Biophys. Res. Commun. 285 (2001) 915–920.
[12] H.Y. shrivastava, B.U. Nair, Biochem. Biophys. Res. Commun. 270 (2000) 749–754.
[13] L. Savanini, L. Chiasserini, A. Gaeta, C. Pellerano, Bioorg. Med. Chem. 10 (2002) 2193–2198.
[14] E. Ochiai, Bioinorganic Chemistry, Allyn and Bacon, Boston, 1977.
[15] J.A. Anten, D. Nicholis, J.M. Markpoulos, O. Markopoulou, Polyhedron 6 (1987) 1075–1080.
[16] I.A. Tossadis, C.A. Bolos, P.N. Aslanidis, G.A. Katsoulos, Inorg. Chim. Acta 133 (1987) 275–280.
[17] J.C. Craliz, J.C. Rub, D. Willis, J. Edger, Nature 34 (1955) 176.
[18] J.R. Dilworth, Coord. Chem. Rev. 21 (1976) 29–62.
[19] J.R. Merchant, D.S. Clothia, J. Med. Chem. 13 (1970), 335-335.
[20] N.S. Biradar, B.R. Havinale, Inorg. Chim. Acta 17 (1976) 157–160.
[21] H.N. Fox, Science 116 (1952) 129.
[22] A.V. Milyutin, L.R. Amirova, V.E. Kolla, F.Ya. Nazmetdinov, L.P. Drovosekova, Yu.S. Andreichikov, Pharm. Chem. J. 32 (1998) 422–424.
[23] O.Ya. Yanborisova, M.E. Kon'shin, V.E. Kolla, S.A. Vikhareva, Abstracts of Papers. The Sci.-Pract. Conf. "Resources for Development of Drug Production in Russia. Meet. All-Russia Soc. Pharmacists, Vladimir 1991, p. 106 [in Russian].
[24] A.V. Milyutin, T.M. Kon'shina, T.V. Nikiforova, et al., Abstracts of Papers., in: Proceedings of the 50th Sci.-Pract. Conf. of Teaching Staff of the Penn Pharm, Inst., Perm, 1994, pp. 15–18 [in Russian].
[25] S.A. Vikhareva, Abstracts of Papers, in: Proceedings of the 50th Sci.-Pract. Conf. of Teaching Staff of the Perm Pharm, Inst., Perm, 1994, p. 29 [in Russian].
[26] A.I. Mikhalev, M.E. Kon'shin, T.M. Kon'shina, A.S. Zaks, Interinstitution collection of papers, in: Proceedings of the 51st Sci.-Pract. Conf. "Current Problems of Pharmacy", Perm. Pharm. Inst., Perm, 1995, p. 12 [in Russian].
[27] J. Marmur, J. Mol. Biol. 3 (1961) 208–211.
[28] M.E. Reichmann, S.A. Rice, C.A. Thomas, P. Doty, J. Am. Chem. Soc. 76 (1954) 3047–3053.
[29] T.C. Michael, R. Marisol, J.B. Allen, J. Am. Chem. Soc. 111 (1989) 8901–8911.
[30] Z.H. Xu, P.X. Xi, F.J. Chen, X.H. Liu, Z.Z. Zeng, Transition. Met. Chem. 33 (2008) 267–273.
[31] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81–122.
[32] F.D. Lewis, S.V. Barancyk, J. Am. Chem. Soc. 111 (1989) 8653–8661.
[33] N. Raman, A. Kulandaisamy, K. Jeyasubramanian, J. Ind. Chem. 41A (2002) 942–949.
[34] K. Nakamato, Infrared and Raman Spectra of Inorganic and Coordination Compound, 3rd ed., Wiley-Interscience, New York, 1978.
[35] J.K. Barton, A.T. Danishefsky, J.M. Goldberg, J. Am. Chem. Soc. 106 (1984) 2172–2176.
[36] R.F. Pasternack, E.J. Gibbs, J.J. Villafranca, Biochemistry 22 (1983) 2406–2414.
[37] S. Mahadevan, M. Palaniandavar, Inorg. Chem. 37 (1998) 693–700.
[38] S. Kashanian, M.B. Gholivand, F. Ahmadi, A. Taravati, A. Hosseinzadeh Colagar, Spectrochim. Acta A 67 (2007) 472–478.
[39] A. Wolf, G.H. Shimer Jr., T. Meehan, Biochemistry 26 (1987) 6392–6396.

[40] M. Cory, D.D. McKee, J. Kagan, D.W. Henry, J.A. Miller, J. Am. Chem. Soc. 107 (1985) 2528–2536.
[41] M.J. Waring, J. Mol. Biol. 13 (1965) 269–282.
[42] V.G. Vaidyanathan, B.U. Nair, J. Inorg. Biochem. 94 (2003) 121–126.
[43] P.U. Maheswari, M. Palaniandavar, J. Inorg. Biochem. 98 (2004) 219–230.
[44] D. Lawrence, V.G. Vaidyanathan, B.U. Nair, J. Inorg. Biochem. 100 (2006) 1244–1251.
[45] C.V. Kumar, J.K. Barton, T. Nicolas, J. Am. Chem. Soc. 107 (1985) 5518–5523.
[46] A. Gopala Krishna, D. Vijay Kumar, B.M. Khan, S.K. Rawel, K.N. Ganesh, Biochim. Biophys. Acta 1381 (1998) 104–112.
[47] T.M. Kelly, A.B. Tossi, D.J. McConnell, T.C. Strekas, Nucleic Acids Res. 13 (1985) 6017–6034.
[48] P.T. Selvi, M. Palaniandavar, Inorg. Chim. Acta 337 (2002) 420–428.
[49] D.H. Johnston, H.H. Thorp, J. Am. Chem. Soc. 117 (1995) 8933–8938.
[50] R. Indumathy, S. Radhika, M. Kanthimathi, T. Weyhermuller, B.U. Nair, J. Inorg. Biochem. 101 (2007) 434–443.