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ORIGINAL PAPER

Mononuclear Co(III) and Ni(II) Complexes with Polypyridyl Ligands, $[Co(phen)_2(taptp)]^{3+}$ and $[Ni(phen)_2(taptp)]^{2+}$: Synthesis, Photocleavage and DNA-binding

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Abstract Two novel, mixed ligand complexes of cobalt(III) and nickel(II), $[Co(phen)_2(taptp)]^{3+}$ (**1**) and $[Ni(phen)_2(taptp)]^{2+}$ (**2**) (phen = 1,10-phenanthroline and taptp = 4,5,9,18-tetraazaphenanthreno [9,10-b]triphenylene), were synthesized and characterized by elemental analyses, UV-visible and NMR spectroscopies. The binding interactions of the two complexes with DNA have been investigated using absorption and emission spectroscopy methods and electrophoresis measurement mode. The intrinsic binding constants for these complexes to DNA are in the order of 10^5. In Tris buffer, the Co(III) complex shows a moderate luminescence which was enhanced after binding to DNA. However for complex Ni(II), no emission was observed in Tris buffer. The $[Co(phen)_2(taptp)]^{3+}$ and $[Ni(phen)_2(taptp)]^{2+}$ can cause the photocleavage of DNA supercoiled pBR322 upon irradiation by 360 nm light. Based on the data, an intercalative mode of DNA binding is suggested for the two complexes.

Keyword Photocleavage · Intercalative mode · Polypyridyl ligands · Co (III) and Ni(II) complexes · Mixed-ligand · DNA binding

Introduction

Nucleic acid binding metal complexes are currently being investigated in many laboratories because of their utility as DNA structural probes, DNA dependent electron transfer probes, DNA foot printing and sequence-specific cleaving agents and potential anticancer drugs [1–4]. Metal complexes of 1,10-phenanthroline (phen) or modified phen ligands are particularly attractive species for developing new diagnostic and therapeutic agents that can recognize and cleave DNA [5]. Many transition metal polypyridyl complexes have been synthesized and widely employed in studies of DNA in view of their applications in several research areas, including bioinorganic and biomedicinal chemistry [6–12]. These complexes can bind to DNA in noncovalent modes such as electrostatic, intercalative and groove binding [13]. Many useful applications require that the complexes bind to DNA through an intercalative mode with the ligand intercalating into the adjacent base pairs of DNA. In such complexes, the ligand or metal may be varied in an easily controlled way to facilitate the individual application. Barton has reported that chiral phenanthroline-cobalt (III) complexes recognized different local structure of DNA [14]. Aromatic ring stacking between nucleobases is considered to be a major driving force that leads to binding and the extent of binding is expected to depend on the size and electron density of the interacting aromatic rings, as well as on the combined effect of hydrophobic and hydrophilic interactions. These complexes have been exploited as luminescent probes for DNA, tools to examine the local structural polymorphism of nucleic acids, photoreactive and electrochemically active probes of DNA structure and protein binding [15–20]. In order to design new complexes as probes and luminescent reporters for nucleic acids it is important to have a firm understanding of the factors governing the DNA-binding modes and affinities of the complexes. The most significant factor appears to be the molecular shape to the extent that those complexes fitting best against the DNA helical structure display the highest binding affinity [21].

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This article reports the synthesis, spectral characterization, DNA-binding and photo-cleavage properties of the cobalt(III) and nickel(II) complexes: $[Co(phen)_2(taptp)]^{3+}$ (**1**) and $[Ni(phen)_2(taptp)]^{2+}$(**2**) with taptp, a polypyridyl bidentate ligand having a fully planar and π-conjugated system. This ligand can be prepared by condensation reaction of a dimine with a dione in several organic solvents such as ethanol.

Experimental Section

Materials and Methods

Cis-$[Co(phen)_2Cl_2]^{3+}$[22], *cis*-$[Ni(phen)_2Cl_2]^{2+}$ [23] and 1,10-phenanthroline5,6-diamine[24] were prepared according to literature procedures. Other materials were of commercially available and used without further purification unless otherwise noted. Doubly distilled water was used to prepare the buffer (5 mM Tris–HCl, 50 mM NaCl, pH 7.2) and all the spectroscopic titration was carried out in this buffer at room temperature. DNA pRC/CMV2 (Invitrogen) was used as received. A solution of DNA in the buffer (5 mM Tris–HCl, 50 mM NaCl, pH 7.2) gave a ratio of UV absorbance at 260 and 280 nm of ca. 1.8:1, indicating that DNA was sufficiently free of proteins [25]. The DNA concentration per nucleotide was determined by absorption spectroscopy using the molar absorption coefficient (6,600 $M^{-1}cm^{-1}$) at 260 nm [26], The ligand taptp was prepared by the reaction of 1,10-phenanthroline5,6-dione with 1,10-phenanthroquinone as detailed earlier [27].

Synthesis of $[Co(phen)_2(taptp)](PF_6)_3$ (1)

taptp (0.38 g, 1 mmol) was dissolved in 100 ml acetonitrile and refluxed then $[Co(phen)_2Cl_2]Cl$ (0.58 g, 1 mmol) dissolved in 25 ml ethanol was added to the solution. The resulting mixture was refluxed for 4 h, allowed to cool to room temperature and then filtered. The desired complex was precipitated out upon the addition of NH_4PF_6 to the aqueous solution of the filtrate. The yellow solid was collected and washed with small portions of water, ethanol and diethyl ether respectively, then dried under vacuum and recrystallized from an acetonitrile-diethyl ether mixture. Yield 0.90 g (72 %) (Anal. Found: C, 48.67; H, 2.49; N, 9.09. Calc. for $C_{50}H_{30}N_8P_3F_{18}Co$: C, 48.54; H, 2.49; N, 9.06 %). ^{1}H NMR, δ ppm (DMSO-d_6, TMS): 9,992 (d, 2H), 9.64 (d, 2H), 8.99 (d, 2H), 8.80 (d, 4H), 8.40 (s, 4H), 8.30 (d, 2H), 8,23 (d,2H), 8.10(d, 2H) 8.00 (t, 2H), 7.96–7.99 (m, 4H), 7.78–7.81 (m, 4H).

Synthesis of $[Ni(phen)_2(taptp)](PF_6)_2$ (2)

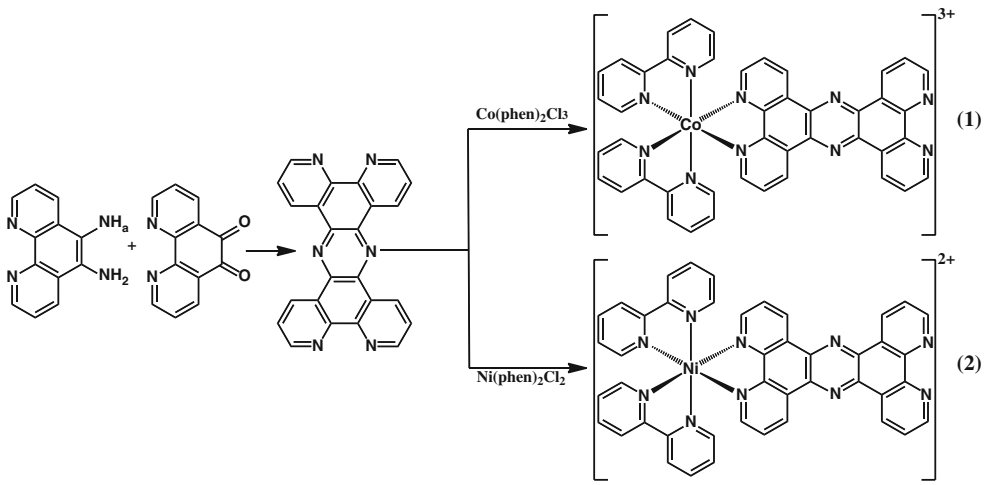
The same synthetic method as above using nickel complex instead of cobalt, afforded $[Ni(phen)_2(taptp)](PF_6)_2$. Yield 0.81 g (74 %) (Anal. Found: C, 54.93; H, 2.79; N, 10.21. Calc. for $C_{50}H_{30}N_8P_2F_{12}Ni$: C, 55.01; H, 2.75; N, 10.27 %). Synthetic routines of ligand and the complexes are showed in Scheme 1.

Instrumentation

Elemental analyses were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer Electronic spectra were recorded using a CARY 100 Bio VARIAN UV–vis spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker FT-NMR 500 (500 MHz) Ultra Shield spectrometer at ambient temperature DMSO-d6. Fluorescence measurements were made on a Cary Eclipse spectrophotometer equipped with quartz cuvettes of 1 cm path length.

DNA-Binding and Cleavage Experiments

The DNA-binding and cleavage experiments were performed at room temperature. The absorption titration of



Scheme 1 Synthetic routines of ligand and complexes (**1** & **2**)

the complexes in buffer (5 mM Tris–HCl, 50 mM NaCl, pH 7.2, Tris = Tris (hydroxymethyl)methylamine) was performed by using a fixed concentration of the complexes to which increments of the DNA stock solution were added. The solution concentration of the complexes was 15 μM and DNA stock solutions were added up to the ratio of 10:1 [*DNA*]/[*Complex*]. Complex-DNA solutions were allowed to incubate for 10 min before the absorption spectra were recorded. The intrinsic binding constant K_b of the complexes to DNA was calculated using the following [28]:

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

Where [*DNA*] is the concentration of DNA in base pairs, ε_a, ε_f and ε_b are the apparent, free, and bound metal complex extinction coefficients, respectively. In plots of $[DNA]/(\varepsilon_a - \varepsilon_f)$ versus [*DNA*], K_b is given by the ratio of slope to the intercept.

Luminescence titration experiments were performed at a fixed cobalt complex concentration (15 μM) to which increments of a stock DNA solution (0–300 μM) containing the same concentration of the metal complex were added.

Fluorescence quenching experiments were conducted by adding small aliquots of a 80 μM complex solution to the samples containing 4 μM ethidium bromide (EB) and 80 μM DNA in buffer. Sample was then excited at 360 nm and the emission was observed between 500 and 700 nm. According to the classical Stern-Volmer equation [29]:

$$\frac{I_0}{I} = 1 + K_{sv}r \quad (2)$$

Where I_0 and I are the fluorescence intensities in the absence and the presence of complex, respectively. K_{sv} is a linear Stern-Volmer quenching constant dependent on a ratio of r is the ratio of the total concentration of complex to that of DNA. In the plot of I_0/I versus [*Complex/DNA*], K_{sv} is given by the ratio of slope to intercept.

For gel electrophoresis experiment, supercoiled pBR 322 DNA (10 μg) was treated with the metal complex **1** in Tris buffer (50 mM Tris-acetate, 18 mM NaCl, pH 7.2), and the solutions were irradiated at room temperature with a UV lamp (360 nm 30 W) after incubation for 10 min. Irradiated and not irradiated samples were then run on a 1 % agarose gel containing 10 μg/ml ethidium bromide in a 5 V/cm field for 1 h and in Tris Boric acid buffer. The results were then visualized using a UV transilluminator with CCD camera (UVP gel doc system, UVP, Cambridge).

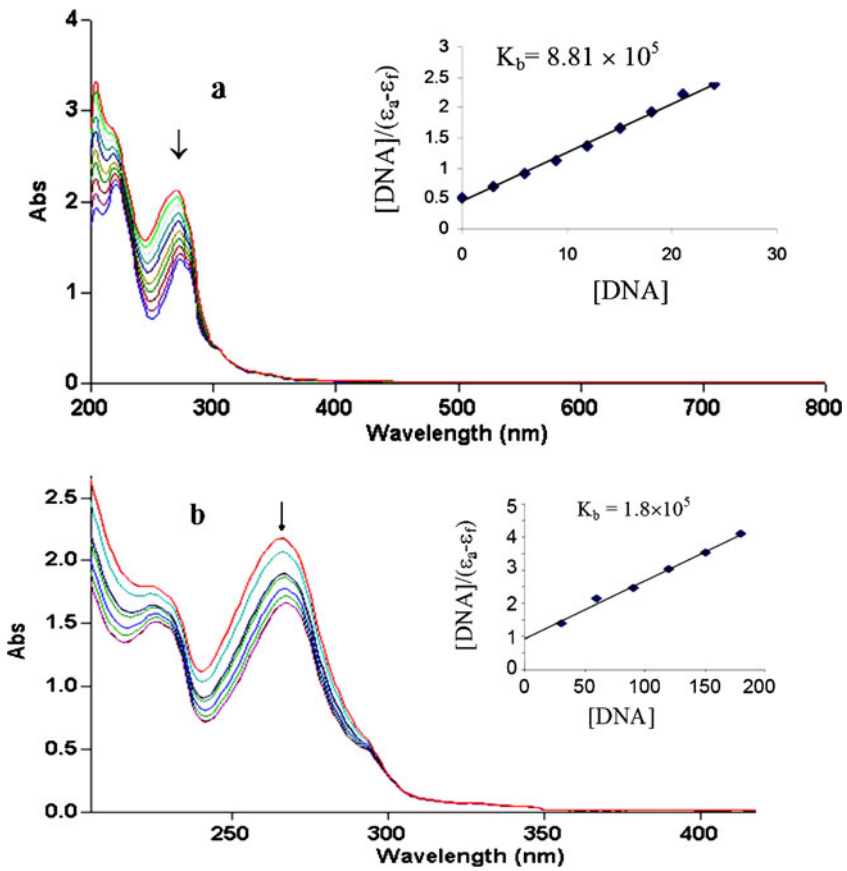


Fig. 1 Absorption spectra of Co(III) and Ni(II) complexes in acetonitrile:buffer mixture (1:10) on addition of DNA: **a** [Co]=15 μM; [*DNA*]/[*Co*]=0, 2, 4, 6, 8, 10 (**b**) [Ni]=15 μM; [*DNA*]/[*Ni*]=0, 2, 4, 6, 8, 10. The *arrows* show the absorption changes on increasing DNA concentration. *Inset*: results calculated from Eq. 1 producing intrinsic binding constant K_b

Results and Discussion

Absorption Spectroscopic Studies

The absorption spectra of the complexes in the absence and presence of DNA are shown in Fig. 1. With the increase of the DNA concentration, complex **1** showed a strong decrease in the absorption intensity; the hypochromism in the band at 286 nm reaches as high as 34.7 % with a red shift of 20 nm. UV/Vis absorption spectra of complex **2**, also shows a bathochromic shift (3 nm) and a hypochromism about 41.9 % under the same experimental conditions. These complexes interact with DNA through an intercalation mode; the above results reveal that the two complexes most likely interact with DNA through a mode that involves a stacking interaction between the aromatic chromophore and the base pairs of DNA, the π^* orbital of the intercalated ligand can couple with the π orbital of the base pairs, thus decreasing the π—π^* transition energy and resulting in the bathochromism. On the other hand, the coupled π orbital is partially filled by electrons, thus decreasing the transition probabilities and concomitantly resulting in hypochromism. The intrinsic binding constant K_b obtained from the decay of the absorbance for complexes **1** and **2** were 8.81×10^5 and1.8×10^5 respectively. Comparing the intrinsic binding constant of the two complexes with those of DNA-intercalative Co(III) and Ni(II) complexes such as $[Co(phen)_2(PIP)]^{3+}$ ($2.15\times10^5 M^{-1}$) [30], $[Co(phen)_2(HNOIP)]^{3+}$ ($2.88\times10^5 M^{-1}$) [31], $[Co(phen)_2(dppz)]^{3+}$ ($9\times10^5 M^{-1}$)[32] and $[Ni(phen)_2(dicnq)]^{2+}$ ($2.1\times10^4 M^{-1}$)[33], we can deduce that complexes **1** and **2** bind strongly to DNA by intercalation. This result is expected since taptp is a completely planer ligand which can bind strongly to DNA though π-stacking.

Luminescence Spectroscopic Study

Complex **1** emits a weak luminescence in Tris buffer at ambient temperature, with a maximum at about 370 nm. Interaction of the complex 1 with a double-strand DNA was

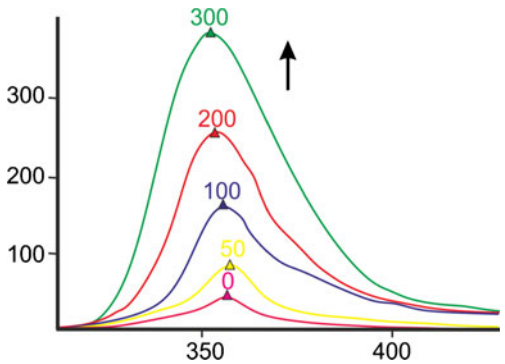


Fig. 2 Emission spectra of $[Co(phen)_2(taptp)]^{3+}$ in presence of increasing amount of DNA. [*Co*]=15 μM, [*DNA*]=0–300 μM

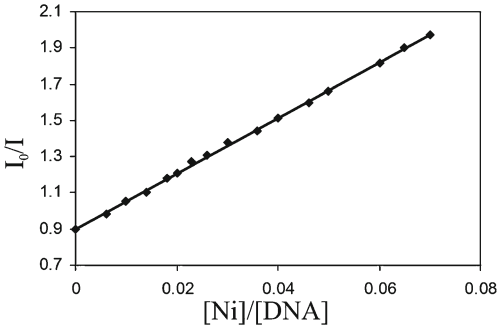


Fig. 3 Fluorescence quenching curves of ethidium bromide bound to DNA by nickel complex (**2**): [*DNA*]=80 μM, [*EB*]=4 μM and [*Complex*]=0 to 4 μM. Where I_0 and I are the fluorescence intensities in the absence and the presence of complex, respectively (Eq. 2)

also monitored via luminescence. The result of the emission titration for complex **1** with DNA is illustrated in Fig. 2. As it is known, the interaction of water molecules with metal complexes results in quenching of their luminesce emissions. It is well known that the intercalation with DNA can dull this water quenching and enhance the luminescence. The emission of the complex **1** exhibits a pronounced enhancement upon the addition of DNA. The emission intensity increases steadily to around 10 times larger than the original and saturates at a [*DNA*]/[*Complex **1***] ratio 20:1.

For the complex **2**, no emission was observed in Tris buffer due to the paramagnetic characteristic of the complex which leads to the quenching of the emission in metal complexes through other forms of relaxations. Hence, for this complex, competitive binding study using an ethidium bromide (EB) bound to DNA was carried out. The quenching extent to fluorescence of EB bound to DNA is used to determine the binding of the second molecule and DNA. Binding of the complex with DNA resulted in the displacement of DNA bound EB molecule with a reduction of emission intensity due to fluorescence quenching of free EB by water. The fluorescence quenching curve of EB bound to DNA by the Ni complex containing the planer taptp ligand is shown in Fig. 3. This curve illustrates that the quenching of EB bound to DNA by complex **2** is in good agreement with the linear fit plot of I_0/I versus [*Complex **2***]/[DNA]. K_{sr} is given by the ratio of slop to intercept (Eq. 2) which is calculated to be 17.03 (R=0.997). The quenching of EB bound to DNA emission in the presence of DNA is due to displacement of EB from the helix, which is a characteristic feature of intercalators.

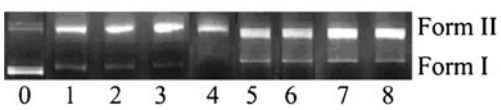


Fig. 4 Photoactivated cleavage of pBR322 DNA in the presence of complexes **1** and **2** after irradiation. Lane 0, DNA alone; Lane 1–4 in different concentration of $[Co(phen)_2(taptp)]^{3+}$: (*1*) 5; (*2*) 10; (*3*) 20; (*4*) 40 μM; Lane 5–8, in the different of $[Ni(phen)_2(taptp)]^{2+}$: (*5*) 20; (*6*) 40;(*7*) 80; (*8*) 100 μM

Photo-Cleavage of p*BR322* DNA by Co(III) and Ni(II) Complexes

Binding the two complexes to DNA was also investigated by DNA photo-cleavage assay. Upon UV irradiation, In Tris buffer, complexes **1** and **2** were found to promote the cleavage of plasmid p*BR322* DNA from supercoiled form (form I) to the nicked form (form II) (Fig. 4). No such a DNA cleavage was observed when the metal complex was absent (lane 0) or incubation of the plasmid DNA with different concentrations of either complex in the dark (data not presented). With increasing concentration of the cobalt (III) complex (lane 1–4), the amount of form I of p*BR322 DNA* diminished gradually, whereas the amount of Form II increased. On the other hand, the complexes exhibit different cleavage efficiency for the plasmid DNA. $[Co(phen)_2(taptp)]^{3+}$ can induced the obvious cleavage of the plasmid DNA at the concentration of 5 μM. At the concentration of 40 μM, the Co(III) complex can almost promote the complex conversion of DNA from Form I to Form II. However, the nickel (II) complex exhibited much lower cleavage efficiency for p*BR322* DNA. Even at the concentration of 100 μM, it cannot promote the complete conversion of DNA from Form I to Form II. In both cases a decrease in supercoiled DNA by increasing the concentration of the added complexes are obvious. The different DNA-cleavage efficiency of the two complexes may be due to the difference in binding affinity of the complexes to DNA [30, 31, 34–37].

Conclusions

Two novel cobalt (III) and nickel(II) complexes, $[Co(phen)_2(taptp)]^{3+}$ (**1**) and $[Ni(phen)_2(taptp)]^{2+}$ (**2**), were synthesized and characterized. Binding of these complexes to DNA was also investigated by absorption and emission measurements. Experimental results indicate that the complexes can intercalate into DNA base pairs and the DNA-binding constants (K_b) are in order of $10^5 M^{-1}$. Upon UV irradiation the Co (III) and Ni (II) complexes can efficiently cleave the plasmid pBR322 DNA. In both cases a decrease in supercoiled DNA by increasing the concentration of the added complexes were observed.

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