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Fluorescence and DNA-binding properties of neodymium(III) and praseodymium(III) complexes containing 1,10-phenanthroline

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ABSTRACT

The binding of neodymium(III) and praseodymium(III) complexes containing 1,10-phenanthroline, $[M(phen)_2Cl_3{\cdot}OH_2]$ (M = Nd (**1**), Pr (**2**)), to DNA has been investigated by absorption, emission, and viscosity measurements. The complexes show absorption decreasing in charge transfer band, fluorescence decrement when bound to DNA. The binding constant K_b has been determined by absorption measurement for both complexes and found to be $(6.76 \pm 0.12) \times 10^4$ for **1** and $(1.83 \pm 0.15) \times 10^4$ M^{-1}, for **2**. The fluorescence of $[M(phen)_2Cl_3{\cdot}OH_2]$ (M = Nd (**1**), Pr (**2**)) has been studied in detail. The results of fluorescence titration reveal that DNA has the strong ability to quenching the intrinsic fluorescence of Nd(III) and Pr(III) complexes through the static quenching procedure. The binding site number n, apparent binding constant K_b and the Stern–Volmer constant k_{SV} are determined. Thermodynamic parameters, enthalpy change (ΔH°) and entropy change (ΔS°), are calculated according to relevant fluorescent data and Van't Hoff equation. The experimental data suggest that the complexes bind to DNA by non-intercalative mode. Major groove binding is the preferred mode of interaction for $[M(phen)_2Cl_3{\cdot}OH_2]$ (M = Nd (**1**), Pr (**2**)) with DNA.

1. Introduction

Lanthanide ions are known for their luminescence properties, which make them interesting candidates for luminescent applications such as bioactive probes for magnetic resonance and luminescence [1]. It is well known that the 4f–4f transitions in lanthanide ions are partly forbidden (Laporte rule), consequently the absorption and emission spectra of the Ln^{3+} ions show weak intensity. However, the population of the excited states of the Ln^{3+} ions can be increased by coordination to organic ligands that have lonepair and/or π-electrons, which act as the light absorbing chromophores [2]. Based on the different ligands and the central Ln^{3+}, many fluorescent complexes have been synthesized. The main ligands include aromatic carboxylic acid, 1,10-phenanthroline (phen),2,2′-bipyridine (bipy), pyridine and β-diketon, etc. [2,3].

The interactions of metal complexes with DNA have been the subject of interest for the development of anticancer drugs and effective chemotherapeutic agents for numerous diseases. The fluorescent method has been widely used in the DNA determination for its high sensitivity, good repeatability and accuracy [4]. The luminescent characteristics of lanthanide complexes and their binding affinity with DNA have led to their general application as spectroscopic probes for nucleic acids. And compared with lanthanide metal ions, their complexes may have different binding models and stronger binding affinity [5].

Previously, we reported the fluorescence and DNA-binding properties of $[M(bipy)_2Cl_3{\cdot}OH_2]$ (M = Nd, Pr) [6,7]. In the present study, fluorescence of Nd(III) and Pr(III) complexes containing phen, $[M(phen)_2Cl_3{\cdot}OH_2]$ (M = Nd (**1**), Pr (**2**)), have been studied. Also, the DNA-binding of the complexes has been examined by absorption and fluorescence spectroscopic methods as well as viscosity measurement. The binding site number n, apparent binding constant K_b, the Stern–Volmer constant k_{SV}, and thermodynamic parameters of the DNA binding were determined. Characterization of bonding mode has been studied in detail.

2. Experimental

2.1. Material and instrumentation

All reagents and solvents used in this study were obtained from Merck & Aldrich Chem. Co. Doubly distilled water was used throughout. $[M(phen)_2Cl_3{\cdot}OH_2]$ (M = Nd (**1**), Pr (**2**)) was synthesized by literature method [8,9]. Fish salmon DNA purchased from Sigma was stored at 4 °C and used as received. Solutions of DNA in Tris–HCl/NaCl buffer, gave the ratio of UV absorbance at 260 and 280 nm, A_{260}/A_{280}, of 1.9, indicating that the DNA was sufficiently free of protein [10]. The concentration of DNA was determined by

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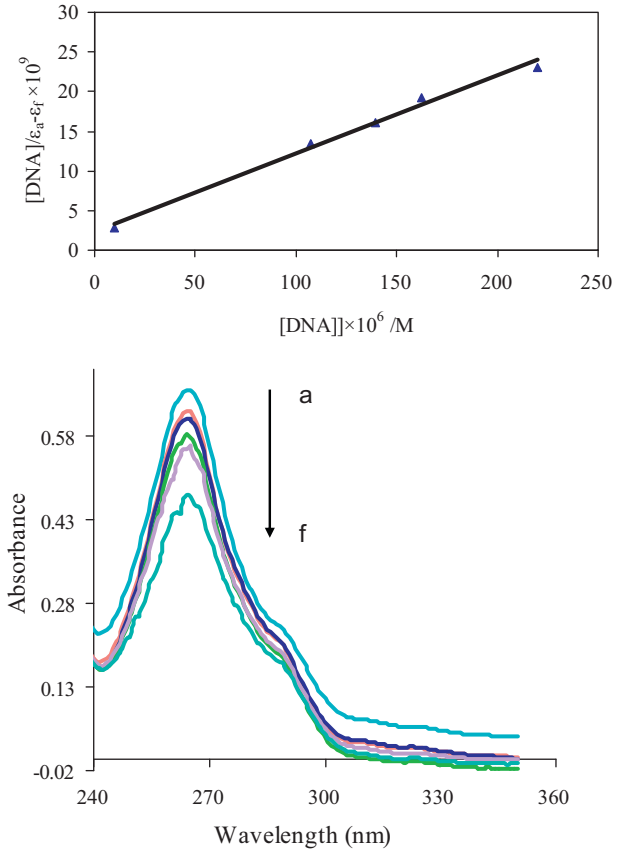

Fig. 1. Absorption spectra of $[Nd(phen)_2Cl_3{\cdot}OH_2]$ in absence (a) and in the presence of increasing amounts of DNA (b–f), [complex] = 1.0×10^{-5} M, [DNA] × 10^6 = 9.7–243 M. Arrow shows the absorbance changes upon increasing DNA concentration. Inset, plot of $[DNA]/(\varepsilon_a - \varepsilon_f)$ vs. [DNA].

UV absorbance at 260 nm after 1:100 dilutions by taking the extinction coefficient as 6600 M^{-1} cm^{-1}. Stock solutions were stored at 4 °C and used after no more than 4 days [11].

Absorption studies were performed using an analytikjena SPECORD S100 spectrometer with photodiode array detector with thermostat cell compartment, that control the temperature around the cell within ±0.1 °C. Fluorescence spectra were recorded on a PERKIN ELMER, LS-3. Viscosity experiments were conducted on a viscometer (SCHOT AVS 450), immersed in a thermostated water-bath maintained at 25.0 ± 0.5 °C.

2.2. DNA binding

2.2.1. Absorption spectral studies

The DNA binding experiments were performed in Tris–HCl/NaCl buffer (50 mM Tris HCl/1 mM NaCl buffer, pH 7.2) using aqueous solution of $[M(phen)_2Cl_3{\cdot}OH_2]$ (M = Nd (**1**), Pr (**2**)).

The electronic spectra of $[M(phen)_2Cl_3{\cdot}OH_2]$ (M = Nd (**1**), Pr (**2**)) were monitored in both the presence and absence of DNA (Fig. 1 for (**1**)). The binding constant for the interaction of Nd(III) and Pr(III) complexes with DNA was obtained from absorption titration data. A fixed concentration of the complexes (1×10^{-5} M) was titrated with increasing amounts of DNA over a range of 9.7×10^{-6}–2.43×10^{-4} M (9.7–243 μM). The solutions were allowed to incubate for 3 h before the absorption spectra were recorded. The titration processes were repeated until there was no change in the spectra for at least four titrations indicating binding saturation had been achieved.

The intrinsic binding constants, K_b, for the binding of the complexes to DNA were calculated by Eq. (1):

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

where ε_a, ε_f, and ε_b correspond to A/[Complex], the extinction coefficient for the free Nd(III) or Pr(III) complex, and the extinction coefficient for the complexes in the fully bound form, respectively. In plot of $[DNA]/(\varepsilon_a - \varepsilon_f)$ versus [DNA], K_b is given by the ratio of the slope to the intercept [10,12–15]. The non-linear least-squares analysis was done using Microsoft Office Excel. This approach, which adopted the neighbor-exclusion model, was originally reported by Benesi and Hildebrand [16], adapted by Schmechel and Crothers [17] and finally modified by Wolfe et al. [18]. Many reports [19–21] have also demonstrated that this half-reciprocal absorption titration method provides a useful route to obtain binding constants for the broad range of metal complexes containing phen and its derivatives.

2.2.2. Fluorescence spectral studies

The complexes at a fixed concentration (1×10^{-6} M) were titrated with increasing amounts of DNA. Excitation wavelength of the samples were 264 nm with scan speed = 60 nm/min, emission wavelength of $[Nd(phen)_2Cl_3{\cdot}OH_2]$ is 364 nm and emission wavelengths of $[Pr(phen)_2Cl_3{\cdot}OH_2]$ is 417 nm. All experiments were conducted at 25 °C in a buffer containing 50 mM Tris–HCl (pH 7.2) and 1 mM NaCl concentration.

2.2.3. Viscosity measurements

The DNA concentration was fixed at 4×10^{-5} M. Flow time was measured with a digital stop watch, the mean values of three replicated measurement were used to evaluate viscosity of each sample. The relative specific viscosity $(\eta/\eta_0)^{1/3}$ where η_0 and η are the specific viscosity contributions of DNA in the absence (η_0) and in the presence of the complex (η), were plotted against 1/R (R = [DNA]/[complex]) [22].

3. Results and discussions

The basic rationale for carrying out thermodynamic studies of drug–DNA interactions is to determine what factors are responsible for the overall binding affinity and specificity of the drug. The first step in most investigations is to experimentally determine the equilibrium binding constant (association constant, K_b) and hence the observed Gibbs free energy change. The value of K_b may be determined in a number of ways; most of these methods rely upon measuring the concentrations of free and bound ligand. For drug–DNA interactions spectroscopic methods are convenient and sensitive routes to obtaining K_b. In these experiments binding-induced changes in the spectral properties of the drug (or DNA) are monitored using an appropriate spectroscopic technique (e.g., UV–Vis, circular dichroism, NMR, or fluorescence). Here, the complex-DNA interactions were studied by UV–Vis and fluorescence spectroscopic methods.

3.1. Absorption spectral studies of DNA binding

Electronic absorption spectroscopy was widely employed to determine the DNA binding affinity of metal complexes. Uv-vis of both complexes were similar and show two bands, at 265 and 228 nm for $[Nd(phen)_2Cl_3{\cdot}OH_2]$ and at 264 and 227 nm for $[Pr(phen)_2Cl_3{\cdot}OH_2]$ due to ML/LMCT and π-π* transitions. Generally, it has been shown that the interactors with DNA will show bathochromic shift and hypochromism in their absorption spectra [12,23]. Here, with addition of DNA, there is no shift in absorption bands of Nd(III) and Pr(III) complexes, but the absorptivity of