

DNA-Binding Properties of Iron(II) Mixed-Ligand Complexes Containing 1,10-Phenanthroline and Dipyrido[3,2-*a*:2',3'-*c*]phenazine

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An iron(II) mixed-ligand complex with 1,10-phenanthroline (phen) and dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppz), $[\text{Fe}(\text{phen})_2(\text{dppz})]^{2+}$, has been synthesized. The DNA-binding properties of the mixed-ligand complex have been studied in terms of equilibrium binding constant, thermodynamic parameter, thermal denaturation as well as Pfeiffer effect upon binding to DNA. The spectrophotometric titration of $[\text{Fe}(\text{phen})_2(\text{dppz})]^{2+}$ with calf thymus DNA (ct-DNA) has shown that the iron(II) mixed-ligand complex binds effectively to ct-DNA in an intercalation mode as indicated by remarkable hypochromicity (*ca.* 36%) and moderate bathochromic shift (8 nm) of the absorption spectra. This intercalative mode is supported by a significant increase ($\Delta T_m = 21^\circ\text{C}$) in the melting temperature (T_m) of ct-DNA at $R([\text{complex}]/[\text{ct-DNA}]) = 1.5$. The binding of $[\text{Fe}(\text{phen})_2(\text{dppz})]^{2+}$ to ct-DNA is entropically driven as characterized by a positive enthalpy change and a large negative $T\Delta S$ term. An intense CD signal in the UV and visible region develops upon addition of ct-DNA to the racemate solution of $[\text{Fe}(\text{phen})_2(\text{dppz})]^{2+}$. This has revealed that a shift in diastereomeric inversion equilibrium takes place in the solution to yield an excess of one enantiomer of the DNA-iron(II) complex (Pfeiffer effect). The striking resemblance of the CD spectral profiles to those of the corresponding Δ -enantiomer indicates that Δ - $[\text{Fe}(\text{phen})_2(\text{dppz})]^{2+}$ is preferentially bound to ct-DNA.

Key words: Iron(II), Mixed Ligand Complex, Phenanthroline, Dppz, DNA Binding