The interaction of native DNA with iron(III)- N,N-bis(2,4-dihydroxybenzylidene) -1,2-diaminobenzene –chloride

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Introduction

The interaction of transition metal complexes, containing multidentate aromatic ligands, with DNA has recently gained much attention following the important biological and medical roles played by potential metallointercalators [1]. Schiff base metal complexes have been recognized as powerful catalysts in a great number of chemical reactions such as, electrochemical reduction of alkyl halides in aprotic solvents [2], oxygenation of indols, phenols, flavones, and others [3]. In addition, some of these complexes are able to bind in a reversible form to molecular oxygen and in consequence, have been investigated as model compounds in the study of the natural oxygen carriers such as, hemoglobin, myoglobin hemocyanin [4] or in the study of the catalytic properties of some cytochromes involved in the biological oxidative reactions. Finally, Schiff base tetradentate complexes of iron have been studied as mimetic models of peroxidases, catalases and superoxide dismutase [5]. In base to these applications, the synthesis and further structural and chemical characterization of new Schiff base tetradentate ligands is an interesting line of research in many chemical and biological fields. Three major binding modes have been proposed for the binding of Schiff bases to DNA intercalation, outside groove binding and outside binding with self-stacking in which the Schiff bases stacked along the DNA helix [6]. The central metal ion strongly influences both the binding characteristics of the Schiff base complex to DNA and the DNA cleavage properties [7]. The interaction of a number of iron(II) and iron(III) derivatives with nucleic acids has been widely investigated, while, to our knowledge, no work has been published on the interaction of iron(III)- N,N-bis(dihydroxybenzylidene)-1,2-diaminobenzene complexes with DNA. The interaction between native calf thymus deoxyribonucleic acid (DNA) and FeIII-N,N-bis(dihydroxybenzylidene) -1,2-diaminobenzene, Fe(2,4-DHSalophen)Cl, was investigated in aqueous solutions by UV-visible (UV–vis) absorption, fluoreescence thermal denaturation and viscosity measurements.
Experimental section:

Fe(2,4-DHSalophen)Cl have been synthesized by combination of ortho-phenylenediamine and the corresponding isomer of the dihydroxy benzaldehyde in a solvent free system. These ligands containing ortho- and para-quinone functional groups were characterized using UV–vis and IR spectroscopies, in non aqueous solvents, such as dimethylformamide.

Result and discussion:

This compound shows an absorption peak at 312 nm with a molar absorptivity of $(2.7\pm0.2)\times10^4$ M$^{-1}$cm$^{-1}$ in 10.0mM Tris/HCl buffer, pH 7.2. The results obtained from fluorescence, UV–vis and viscosity measurements exclude DNA intercalation and can be interpreted in terms of an electrostatic binding between the Fe(2,4-DHSalophen) cation and the phosphate groups of DNA. The trend of the UV–vis absorption band of the Fe(2,4-DHSalophen)Cl complex at different ratios [DNAtric-HCl]/[Fe(DHSalophen)Cl] and the large increase of the melting temperature of DNA in the presence of Fe(2,4- DHSalophen)Cl, support the hypothesis of an external electrostatic interaction between the negatively charged DNA double helix and the axially stacked positively charged Fe(2,4-DHSalophen) moieties, analogously to what reported for a number of porphyrazines and metal–porphyrazine complexes interacting with DNA.

References: