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The interaction of native DNA with iron(III)-N,N'-ethylene-bis(salicylideneiminato)-chloride

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Abstract

The interaction between native calf thymus deoxyribonucleic acid (DNA) and Fe^{III}-N,N'-ethylene-bis (salicylideneiminato)-chloride, Fe(Salen)Cl, was investigated in aqueous solutions by UV–visible (UV–vis) absorption, circular dichroism (CD), thermal denaturation and viscosity measurements.

The results obtained from CD, UV–vis and viscosity measurements exclude DNA intercalation and can be interpreted in terms of an electrostatic binding between the $Fe(Salen)^{+}$ cation and the phosphate groups of DNA.

The trend of the UV–vis absorption band of the Fe(Salen)Cl complex at different ratios $[DNA_{phosphate}]$/[Fe(Salen)Cl] and the large increase of the melting temperature of DNA in the presence of Fe(Salen)Cl, support the hypothesis of an external electrostatic interaction between the negatively charged DNA double helix and the axially stacked positively charged $Fe(Salen)^{+}$ moieties, analogously to what reported for a number of porphyrazines and metal–porphyrazine complexes interacting with DNA.
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Keywords: DNA; Iron(III); Schiff bases; Salen

1. 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 [1,2].

We have previously reported on the interaction of organotin(IV) [3–6], iron(II) [7] and iron(III) [8] derivatives with native calf thymus DNA and of iron(III) ions with the anticancer antibiotic adriamycin [9].

In this paper we focus our attention on the interaction of native DNA with Fe^{III}(Salen)Cl, where Salen is the anion of the Schiff base [N,N'-ethylene-bis (salicylideneimine)] (H_2Salen), whose ligand properties toward organotin^{IV} and tin^{IV} chlorides have been previously investigated by us [10].

The interaction of H_2Salen transition metal complexes, including Cu [11,12], Ni [11,13–15], Mn [11,16,17], Co [11,18] and Ru [19], with DNA was studied and great changes of spectroscopic properties were generally noticed, indicating binding interactions between DNA and such compounds. An intercalating interaction mode was proposed for Co(Salen) [11,18]; an external binding with the surface of the double helix was suggested for a functionalized Cu(Salen) complex [11,12], while Ni(Salen) presented a high affinity toward the N7 atom of guanosine residues [11,13–15]. Moreover, all the investigated transition metal–Salen complexes showed the ability to cleave DNA via redox processes [11–19]. The solubilities of these metal complexes in water solutions usually increase by functionalizing the ligand by means of polar groups [11–19].

The interaction of a number of iron(II) and iron(III) derivatives with nucleic acids has been widely investigated [20], while, to our knowledge, no work has been

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published on the interaction of iron–Salen complexes with DNA.

Some structural and chemical similarities between Fe^{III}(Salen)Cl and Fe^{III} porphyrins exist [21,22]. As in Fe^{III} porphyrins, the iron atom of Fe^{III}(Salen)Cl is pentacoordinated in a pyramidal geometry, with the tetradentate Salen ligand in a square planar coordination, the fifth chloride ligand in an apical position and an open sixth coordination site. Although the Salen tetradentate ligand consists of two nitrogen and two oxygen, rather than four nitrogen donor atoms [21], Salen ligands have been shown to form complexes that mimic porphyrin chemistry [23]. Fe^{III}(Salen), analogously to Fe^{III} porphyrins, shows a catalytic activity toward the bland oxidation of hydrocarbons [21] and undergoes electron transfer reactions [22], mimicking the catalytic functions of peroxidases [22].

Moreover, the affinity of Fe(Salen)Cl for the oxygen molecule and the capability to form oxo-complexes is similar to what observed for Fe^{III} porphyrin derivatives [21,22] and for all the transition metal–Salen complexes showing the property to cleave DNA [11–19].

The interaction of cationic porphyrin complexes with DNA has been thoroughly studied and related literature data have been considered for comparison, in order to analyze and rationalize the results presented in this paper.

Three major binding modes have been proposed for the binding of cationic porphyrins to DNA [24–26]: intercalation, outside groove binding and outside binding with self-stacking in which the porphyrins are stacked along the DNA helix. The central metal ion strongly influences both the binding characteristics of the porphyrin complex to DNA and the DNA cleavage properties [24–26].

In this paper the interaction of native DNA and Fe(Salen)Cl in solution was studied by circular dichroism, UV–vis absorption, thermal denaturation and viscosity measurements.

2. Materials and methods

All reagents and solvents were commercial products and used without further purification.

The H_2Salen ligand was synthesized by the classical reaction [27] of salicylaldehyde with ethylenediamine in ethanol at room temperature. Yellow crystals with m.p. 128 °C were obtained. The compound Fe(Salen)Cl was synthesized according to the literature [28], recrystallized from CH_2Cl_2 and characterized by elemental analysis, IR and ^{57}Fe Mössbauer spectroscopy. IR spectra were recorded on a Jasco FT/IR-420 spectrometer, in KBr disk sample holders. The Mössbauer spectrometer and the data reduction method have been described earlier [7]. The isomer shift was reported with respect to the centroid of an α-Fe absorber spectrum at room temperature.

Lyophilized calf thymus DNA (from Serva Fenbiochemica) was resuspended in 1.0×10^{-3} M tris-hydroxymethyl-aminomethane (Tris) (pH 7.5) and dialyzed [29], for at least 6 h, against a solution containing 5.0×10^{-3} M ethylenediamine-N,N,N',N'-tetra-acetate disodium salt (EDTA) and 1.0×10^{-3} M Tris–HCl, pH 7.5, and then washed five times with 1.0×10^{-3} M Tris–HCl, pH 7.5. Doubly distilled water was used to prepare the buffers.

The DNA concentration (monomer units) of the stock solution, 1.0×10^{-2} M per nucleotide, was determined by UV spectrophotometry, in properly diluted samples, using the molar absorption coefficient 7000 $M^{-1}\,cm^{-1}$ at 258 nm [30]. The Fe(Salen)Cl–DNA interaction studies were performed by adding Fe(Salen)Cl methanol solutions (2.5×10^{-3} M) to calf thymus DNA in 1.0×10^{-3} M Tris–HCl aqueous solutions, pH 7.5.

CD, variable temperature UV–vis and viscosity measurements were carried out on 1.0×10^{-4} M DNA solutions in the presence of Fe(Salen)Cl, at stoichiometric ratios, $r_1 =$ [Fe(Salen)Cl]/[$DNA_{phosphate}$] (i.e. mmol Fe(Salen)Cl/mmol DNA momomer), in the range 0.0–2.0. Room temperature UV–vis spectra were recorded on Fe(Salen)Cl 1.0×10^{-4} M in the presence of increasing amounts of CT DNA at stoichiometric ratios, $r_2 =$ [$DNA_{phosphate}$]/[Fe(Salen)Cl] (i.e. mmol DNA momomer/mmol Fe(Salen)Cl), in the range 0.0–3.0.

To allow their equilibration, samples of aqueous Fe(Salen)Cl solutions were let for one week at room temperature. After this equilibration, stable and reproducible UV–vis absorption spectra were obtained. All the solutions were extensively degassed under vacuum before measurements.

CD spectra (four scans per spectrum) were recorded at room temperature in the range 350–200 nm on a Jasco J-715 spectropolarimeter, using a 1 cm path-length cuvette, and subtracting the buffer baseline.

Variable temperature UV–vis spectra were recorded in the range 420–220 nm on a Varian Cary 1E spectrophotometer, equipped with a double cell Peltier thermostating system, using 1 cm path-length cuvettes. Melting temperatures (T_m) were numerically evaluated as the inflection point of the melting plot. Their experimental error, determined by replicate thermal denaturation experiments on different Fe(Salen)Cl–DNA samples, was estimated to be ±2 °C.

Viscosity measurements were performed on a Ubbelodhe viscosimeter maintained at 25.0 ± 0.1 °C. Flow time was measured with a digital stopwatch; mean values of replicated measurements were used to evaluate the viscosity η of the samples. The data are reported as $(\eta/\eta°)^{1/3}$ vs. the [Fe(Salen)Cl]/[$DNA_{phosphate}$] ratio [31], where $\eta°$ is the viscosity of the DNA solution alone.

3. Results

3.1. Structural characterization of Fe(Salen)Cl

The ^{57}Fe Mössbauer parameters, obtained at 77.3 K (IS = 0.50 mm s^{-1}; QS = 1.37 mm s^{-1}; Γ = 0.38 mm s^{-1}), and the IR frequencies (889 cm^{-1} (s), 865 cm^{-1} (m), 851 cm^{-1} (w)), reproduce literature data [32,33] relative to a dimeric structure of Fe(Salen)Cl.

Fe(Salen)Cl is slightly soluble in 1.0 × 10^{-3} M Tris–HCl solutions, showing in this solvent the same UV–vis absorption spectrum recorded in dimethyl sulfoxide–water (DMSO–H_2O) 4:1 solutions [22,34], with a strong peak at 260 nm, a weak peak at 320 and a weak and broad peak around 485 nm.

3.2. Circular dichroism spectra

The CD spectra of DNA 1.0 × 10^{-4} M, in the presence of increasing amounts of Fe(Salen)Cl, are shown in Fig. 1. The right band of the DNA spectrum was monotonously decreased by the increase of the Fe(Salen)Cl complex concentration up to $r_1 = 1.0$ (Fig. 1(a)). The shape of the CD spectrum recorded at $r_1 = 2.0$ was almost coincident with the one recorded at $r_1 = 1.0$ (Fig. 1(b)); the signal to noise ratio decreased at $r_1 = 2.0$, probably due to the onset of precipitation of reddish insoluble products within the solution, detectable at slightly higher Fe(salen)Cl concentrations.

3.3. UV–vis absorption spectra

The UV band of Fe(Salen)Cl 1.0 × 10^{-4} M, at about 320 nm, was monitored in the presence of increasing amounts of DNA (Fig. 2). At 1:1 molar ratio, the absorption band of the metal complex practically disappears, while it is present at both higher and lower r_2 values. Moreover, no bathochromic shift was observed.

3.4. Thermal denaturation experiments

The melting plot of DNA 10^{-4} M, monitored by plotting the UV maximum absorption of DNA at 258 nm vs. the temperature, in the absence and in the presence of Fe(Salen)Cl at molar ratios r_1 = [Fe(Salen)Cl]/[$DNA_{phosphate}$] = 0.0–2.0, is shown in Fig. 3. An increase in the DNA melting temperature of 12, 20, 23 and 22 °C was observed respectively for r_1 = 0.25, 0.5, 1.0 and 2.0 values (Fig. 3).

3.5. Viscosity measurements

Relative viscosity data are reported in Fig. 4. The linear regression analysis of the data plotted as $(\eta/\eta°)^{1/3}$ vs. r_1, square symbols, showed a high linear correlation

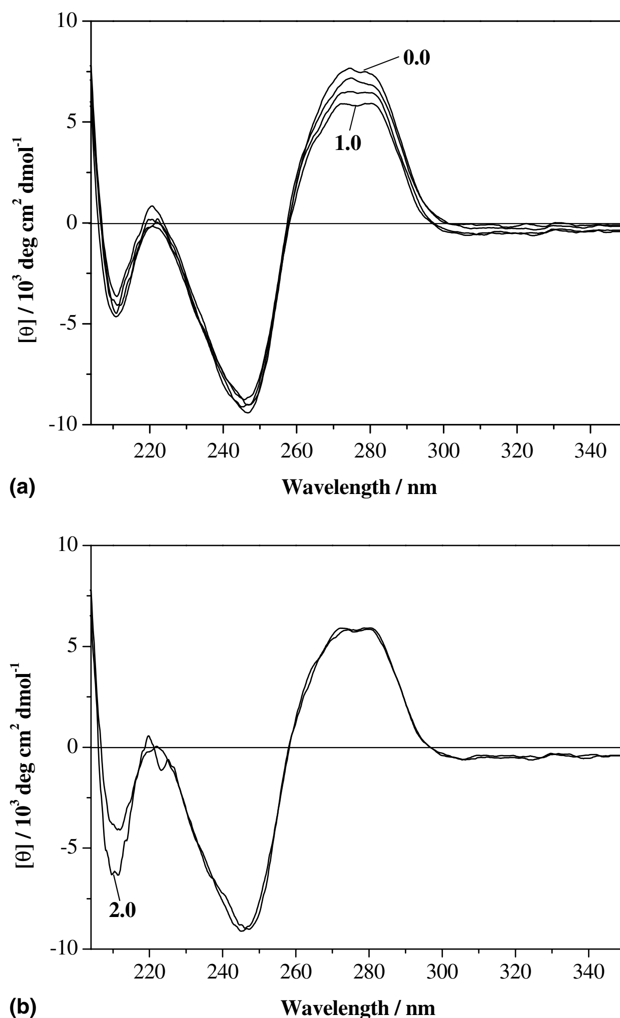

Fig. 1. Circular dichroism spectra of calf thymus DNA 1.0 × 10^{-4} M in Tris–HCl 1.0 × 10^{-3} M, in the presence of increasing amounts of Fe(Salen)Cl at the following stoichiometric ratios: (a) r_1 = [Fe(Salen)Cl]/[$DNA_{phosphate}$] = 0.0, 0.25, 0.5, 1.0 (indicated are the r_1 values 0.0 and 1.0); (b) r_1 = 1.0, 2.0.

with a slope of 0.028 (mm^2/s)$^{1/3}$. Also shown (circle) is the value of the relative viscosity of DNA in the presence of the same amount of methanol used to prepare the solution with molar ratio $r_1 = 2.0$.

4. Discussion

Fe(Salen)Cl has been structurally characterized in the solid state and in solution [34–37]. It is known that, depending on the solvent used to recrystallize it, Fe(Salen)Cl can be obtained as a monomer [21,35] or as a dimer [36]. In the dimeric structure, the iron atoms of two square pyramidal structures are connected by two oxygen bridges [36], filling the sixth coordination sites of the metal in a distorted octahedral coordination geometry.

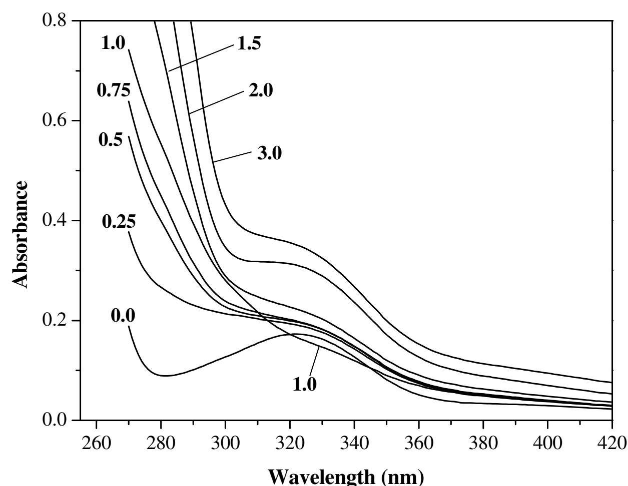

Fig. 2. UV–vis absorption spectra of Fe(Salen)Cl 1.0×10^{-4} M, in the presence of increasing amounts of calf thymus DNA, in Tris–HCl 1.0×10^{-3} M, at the stoichiometric ratios $r_2 = [DNA_{phosphate}]/[Fe(Salen)Cl] = 0.0, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 3.0$, as indicated.

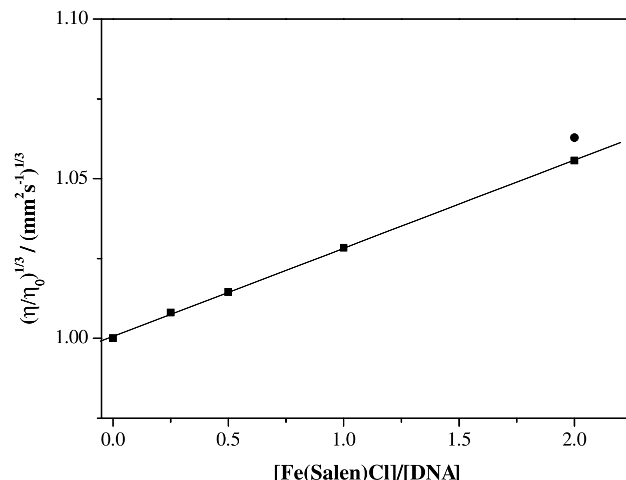

Fig. 4. Relative viscosity of calf thymus DNA 1.0×10^{-4} M in Tris–HCl 1.0×10^{-3} M in the presence of increasing amounts of Fe(Salen)Cl at stoichiometric ratios $r_1 = [Fe(Salen)Cl]/[DNA_{phosphate}] = 0.0–2.0$, plotted as $(\eta/\eta°)^{1/3}$ vs. r_1 (■). The symbol (●) represents the value of relative viscosity of DNA measured in the presence of 800 µl of methanol, i.e. the same amount used to prepare the solution with molar ratio $r_1 = 2.0$.

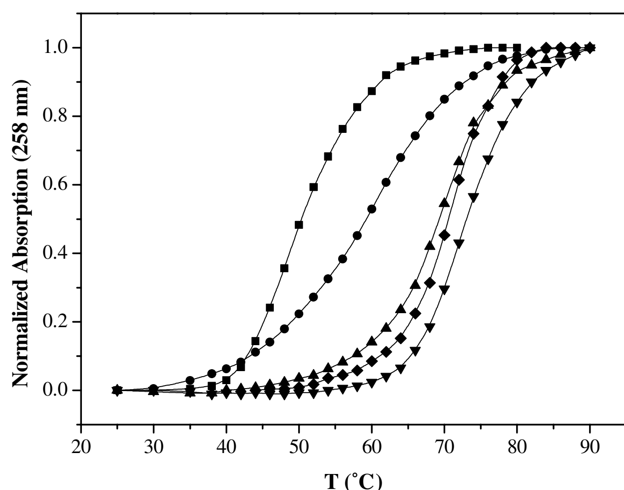

Fig. 3. Melting plots, by UV–vis spectrophotometry, of calf thymus DNA 1.0×10^{-4} M in Tris–HCl 1.0×10^{-3} M (■), $T_m = 49 \pm 2$ °C, and in the presence of Fe(Salen)Cl, at $r_1 = [Fe(Salen)Cl]/[DNA_{phosphate}] = 0.25$ (●), $T_m = 61 \pm 2$ °C, 0.5 (▲) $T_m = 69 \pm 2$ °C, 1.0 (▼), $T_m = 72 \pm 2$ °C, and 2.0 (◆), $T_m = 71 \pm 2$ °C.

The IR and ^{57}Fe Mössbauer spectroscopy results show that the solid Fe(Salen)Cl complex recrystallized by CH_2Cl_2 is a dimeric molecule [32,33].

The complex Fe(Salen)Cl is very soluble in DMSO–H_2O 4:1 mixture [22,34], while it is sparingly soluble in water and in methanol. Conductivity measurements, performed in DMSO–H_2O 4:1, pointed out the existence of the complex Fe(Salen)$^+$ cation in solution [22,34] where, presumably, a solvent molecule replaces the chloride ion in the apical position of the coordination sphere of the metal [34].

The aqueous buffered Fe(Salen)Cl solutions used in the present work showed the same UV–vis absorption spectrum recorded in DMSO–H_2O 4:1 [22,34]. This result suggests the existence of the same cationic Fe(Salen)$^+$ species in solution.

The small decrease in the intensity of the right band of the CD spectrum of DNA, upon addition of Fe(Salen)$^+$ up to 1:1 molar ratio (Fig. 1), indicates that the interaction between the metal complex and DNA induces only slight modifications to the native conformation of DNA. We can then exclude DNA intercalation as a major binding interaction, which usually produce [38] bigger changes in the intensity and position of the left and/or right band of the CD spectrum of native DNA.

The trend observed in the UV–vis spectra (Fig. 2) can also be explained by an external electrostatic binding interaction, between the cationic Fe(Salen)$^+$ complex and the negatively charged phosphate groups of DNA. The hypochromism observed in the absorption band at 320 nm of the Fe(Salen)$^+$ complex, up to $r_2 = 1.0$, can be attributable to "self stacking" interactions established among the planar Fe(Salen)$^+$ cations. Such electrostatic interaction mechanism has been proposed for cationic porphyrin derivatives interacting with DNA [24–26], in particular for one octa-plus copper–porphyrazine complex [24], and involves a self-stacking of the porphyrin planes, externally bound to DNA, giving rise to a super-helical structure with an electrostatic double layer. The appearance of the absorption band at 320 nm, at molar ratios r_2 greater than 1.0 can be explained considering that the electrostatic interaction

sites on the DNA molecule have been already occupied and the extra number of $Fe(Salen)^+$ cations are simply dissolved in the buffer solution, and detected by the UV–vis spectrum.

The DNA intercalating binding mode is definitely excluded after viscosity measurements of 1.0×10^{-4} M DNA solutions in the presence of increasing amounts of $Fe(Salen)^+$ up to $r_1 = 2.0$ (Fig. 4). There is in fact a small increase in the relative viscosity of DNA by increasing the concentration of the $Fe(Salen)^+$ complex. It has been reported [38–43] that a compound binding to DNA without intercalation, induces only small changes in the viscosity of DNA, while drastic increments of the viscosity were observed in cases of ascertained DNA intercalation by chemicals. Moreover, the results obtained show that the observed small linear increase of the relative viscosity of the solution, with the increase of the Fe(Salen)Cl concentration, is essentially attributable to the addition of the methanol solvent [44] in which Fe(Salen)Cl is dissolved.

The increase of 12–23 °C of the melting temperature of DNA, at r_1 values of 0.25–2.0, indicates that this electrostatic binding interaction between the stacked $Fe(Salen)^+$ cations and DNA strongly stabilizes the native conformation of DNA.

The 1:1 Fe(Salen)–$DNA_{phosphate}$ interaction stoichiometry is supported by both CD and thermal denaturation experiments. In fact, within the experimental error and taking into account that at slightly higher Fe(salen)Cl concentrations the solution becomes turbid due to the onset of precipitation of reddish products, the CD spectrum and the T_m value of DNA at $r_1 = 2.0$ and at $r_1 = 2$ are coincident. This means that the presence of additional amount of $Fe(Salen)^+$ species at higher ratios than $r_1 = 1.0$ do not change the melting temperature and the conformation of the Fe(Salen)–DNA system.

The cationic layered arrangement of $Fe(Salen)^+$ moieties should be favoured by the presence of the negative charges of the phosphate groups of DNA and by their mutual axial distance. Interestingly, it has been also reported [37] that the structure of the complex in the solid state, as determined by X-ray crystallography, can involve an ionic layered arrangement in which parallel, planar $Fe(Salen)^+$ moieties are stacked together and separated by 3.4 Å. In such structure, the chlorine anions are placed at a distance in the same plane of the cationic complexes [37]. This result, although questioned by a successive work [36], would very well support the interpretation of the results obtained for the Fe(Salen)–DNA solutions in terms of electrostatic interaction, between the stacked $Fe(Salen)^+$ cations and the negative DNA polyelectrolyte. We wish to remind that the axial spacing between monomer units of native B-DNA is just 3.4 Å [45], and this suggests that the two charged interacting moieties in our solution samples would be separated by about the same axial distance, by allowing the full DNA charge neutralization in a system of 1:1 Fe(Salen)–$DNA_{phosphate}$ molar ratio.

Such electrostatic interaction only slightly modifies the DNA conformation, as observed by CD measurements (Fig. 1) and strongly stabilizes the DNA structure, as confirmed by the increase in the melting temperature of the Fe(Salen)–DNA systems (Fig. 3).

Opposite to what observed for Mn^{III}(Salen) derivatives [16], there is no considerable base pair specificity in the DNA binding.

The absence of an isosbestic point in the UV–vis spectra could be interpreted by invoking the coexistence of more than two species (free and bound $Fe(Salen)^+$ complex) in the DNA solutions rather than the presence of more DNA binding modes [46]. We speculate that these species could be monomer, dimer and/or polymer species, either free or bound to DNA.

5. Conclusions

The small perturbations of the CD spectra and of the viscosity of DNA aqueous solutions, in the presence of increasing amounts of $Fe(Salen)^+$, and the absence of bathochromic shift in the UV absorption band at 320 nm, allow us (i) to conclude that the $Fe(Salen)^+$ complex induces small conformational distortions in the native conformation of DNA and (ii) to exclude the DNA intercalation by $Fe(Salen)^+$ moieties.

The strong stabilization of the DNA structure, as evidenced by the large increase in the T_m of DNA in the presence of $Fe(Salen)^+$, is explained by taking into account a 1:1 interaction stoichiometry between $Fe(Salen)^+$ and $DNA_{phosphate}$ units, involving an external electrostatic interaction between the negatively charged DNA chain and the positively charged polymer produced by the aggregation of axially stacked $FeSalen^+$ cations.

Such “self stacking” interaction among $Fe(Salen)^+$ moieties is supported by the hypochromism observed in the UV absorption at 320 nm, that shows a maximum at molar ratio $[DNA_{phosphate}]/[Fe(Salen)Cl] = 1$.

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