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RESEARCH ARTICLE

Electron Spin Resonance Spectral Characterization and DNA Binding Studies of Metal Complexes with Heterocyclic Ligands Derived from 4 -Aminoantipyrine and 5-Chlorosalicylaldehyde / 3-Ethoxysalicylaldehyde

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Abstract: Transition metal complexes of Cu(II), Ni(II)and Co(II) have been synthesized involving the heterocyclic Schiff bases, 2,3–dimethyl-1-phenyl-4-(5-chloro-2-hydroxybenzylideneamino)-pyrazol-5-one (5-ClSALAAP), L_1 and 2,3–dimethyl-1-phenyl-4-(3-ethoxy-2-hydroxy benzylideneamino)-pyrazol-5-one (3-OEtSALAAP), L_2 derived from 4–aminoantipyrine and 5-chlorosalicylaldehyde/ 3-ethoxysalicylaldehyde respectively. These Schiff bases act as tridentate ligands which coordinate through the azomethine nitrogen, phenolic oxygen and carbonyl of antipyrine ring. The ESR Spectra of Cu(II) complexes were recorded at room temperature in the polycrystalline state. These complexes exhibited well resolved anisotropic signals in the parallel and perpendicular regions. The trend, $g_{\Pi} > g_{\perp} > 2.0023$ observed for the complexes indicate that unpaired electron is localised in $d_{x^2-y^2}$orbital of the Cu(II) ion. Hence a distorted octahedral geometry is proposed for the complexes. The value of exchange interaction was estimated from the equation, $G = (g_{\Pi}-2) / (g_{\perp}-2)$. The complexes showed G values < 4 indicating the exchange interaction in complexes. Binding of these complexes with calf thymus DNA(CT DNA) was studied by spectroscopic methods and their binding constants were evaluated.

Keywords: Heterocyclic Schiff bases, DNA Binding Studies, Synthesis, 4 -Aminoantipyrine

Introduction

The heterocyclic Schiff base ligands and their transition metal complexes are known to possess numerous biological and other applications[1-3]. The synthesis, characterization and antibacterial studies of transition metal complexes involving 2,3–dimethyl-1-phenyl-4-(5-chloro-2-hydroxy-benzylideneamino)-pyrazol-5-one (5-ClSALAAP), L_1 and 2,3–dimethyl-1-phenyl-4-(3-ethoxy-2-hydroxy benzylideneamino)-pyrazol-5-one (3-OEtSALAAP), L_2 were reported in our earlier paper[4]. The present paper reports the ESR spectra and DNA binding study of these complexes.

Experimental

The synthesis and characterization of the ligands L_1 and L_2 and their Cu(II),Ni(II) and Co(II) metal complexes were same as those reported[4] in our earlier study.

ESR spectra

The ESR spectra of the Cu(II) complexes were recorded on Jeol, JES –FA 200 ESR spectrometer at room temperature.

DNA Binding studies

Concentrated CT –DNA stock solution was prepared in 5 mM Tris –HCl/ 50 mM NaCl in water at pH -7.5 and the concentration of DNA solution was determined by UV absorbance at 260 nm. The molar absorption coefficient[5] was taken as 6600 $M^{-1}cm^{-1}$. Solution of CT-DNA in 5 mM Tris –HCl/50 mM NaCl (pH=7.5) gave a ratio of UV absorption at 260 nm and 280 nm A_{260}/A_{280} of ca 1.8-1.9, indicating that the DNA was sufficiently free of protein[6].

All stock solutions were stored at 4 ^{0}C and were used within one week. Absorption spectra were recorded on Elico SL 159 UV-Visible spectrophotometer using 1 cm quartz microcuvettes. Absorption titrations were performed by keeping the concentration of the complex constant (16 µM) and by varying the concentration of CT–DNA from 0- 140 µM. For the complexes, the binding constants (K_b), have been determined from the spectroscopic titration data using the following equation[7,8].

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

The apparent extinction coefficient ε_a, was obtained by calculating A_{obs} / [complex], ε_f and ε_b correspond to the extinction coefficient for the free (unbound) and fully bound complex respectively. A plot of [DNA] / (ε_a -ε_f) *vs.* [DNA] will have a slope equal to 1/(ε_b -ε_f) and an intercept equal to 1/ K_b(ε_b -ε_f), K_b is then given by the ratio of the slope and the intercept.

Results and Discussion

ESR spectral studies of paramagnetic transition metal(II) complexes yield information about the distribution of the unpaired electrons and hence about the nature of the bonding between the metal ion and its ligands. There have been many reports concerning the applications of ESR to square -planar or distorted octahedral complexes of Cu(II) and of the interpretations of the ESR parameters in terms of covalency of the metal- ligand bonding[9]. The Cu(II) complexes exhibited well resolved anisotropic signals in the parallel and perpendicular regions as shown in Figures 1 and 2. The observed data (Table 1) showed that g_{Π} = 2.0 –2.49 and $g_{\perp}$ = 2.09 –2.24.

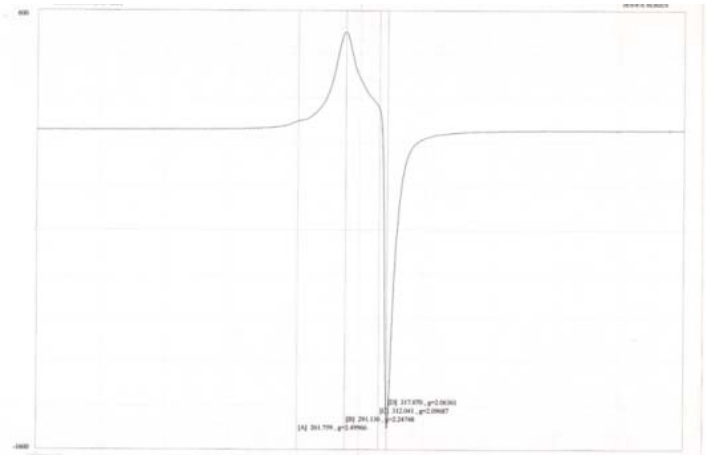

Figure 1. ESR spectrum of Cu(II)-5-Cl SALAAP

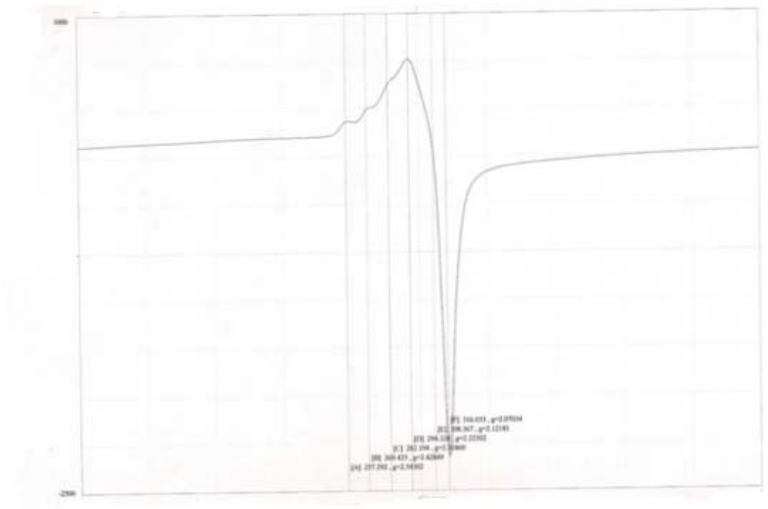

Figure 2. ESR spectrum of Cu(II)-3-OEt SALAAP

Table 1. ESR parameters of Cu(II) complexes

Complex	g_{Π}	$g_{\perp}$	g_{av}	G
Cu(II)- L_1	2.28	2.24	2.20	1.13
Cu(II)- L_2	2.34	2.22	2.12	1.52

The g_{Π} values are greater than $g_{\perp}$ suggesting major distortion from octahedral symmetry in the Cu(II) complexes[10]. The g_{II} is a moderately sensitive function for indicating covalency. The $g_{\Pi} > 2.3$ is characteristic of anionic environment and $g_{\Pi} < 2.3$ is of covalent environment in M –L bonding[11]. The observed g_{Π} values for the Cu(II)-5-Cl SALAAP complex is less than 2.3, in agreement with the covalent character of the M-L bond. While Cu(II) -3-OEt SALAAP complex showed $g_{\Pi} > 2.3$, which is characteristic of anion environment. The trend $g_{\Pi} > g_{\perp} > 2.0023$ observed for the complexes indicates that unpaired electron is localised in $d_{x^2-y^2}$ orbital of the Cu(II) ion. Thus a tetragonal geometry is proposed for the complexes[12]. Axial symmetry parameter $G=(g_{\Pi}-2)/(g_{\perp}-2)$, which measure the exchange interaction between the metal centres in a polycrystalline solid has been calculated, if G>4 the exchange interaction is negligible and if G< 4 indicates considerable exchange interaction in the solid complexes[13].

The above reported complexes showed G values < 4 indicating the exchange interaction in complexes. Earlier works reported[14] that g_{Π} is 2.4 for copper-oxygen bonds and 2.3 for copper -nitrogen bonds. For these complexes, g_{Π} values between 2.3–2.4 which further confirms the presence of copper- nitrogen and copper –oxygen bonds in these chelate complexes.

In general, complexes with aromatic moieties which bind to DNA through intercalation usually results in hypochromism and bathochromism due to the stacking interaction between aromatic chromophore of the complexes and the base pairs of DNA. The absorption spectra of the complexes, Ni(II)-5-Cl SALAAP (**1**), Co(II)-5-Cl SALAAP (**2**), Cu(II)-3-OEt SALAAP (**3**), in the absence and presence of calf thymus DNA are illustrated in Figures 3-5. In the presence of DNA, decrease of peak intensities were observed in the absorption spectra of complexes.

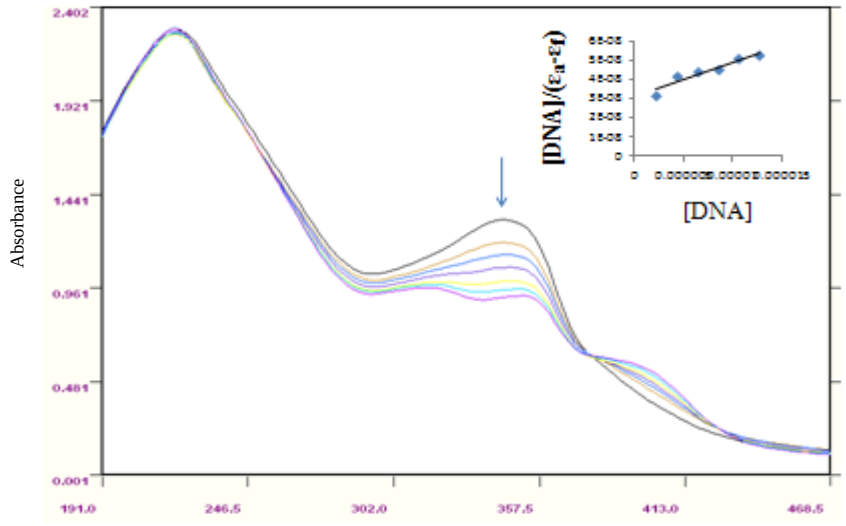

Figure 3. Absorption spectrum of complex [Ni(II)(5-Cl-SALAAP)$_2$] in Tris HCl buffer at 25 ^{0}C in the presence of increasing amounts of DNA. Conditions: [Ni] =16 µM. [DNA] =0-140 µM. The arrow indicates the change in absorbance upon increasing the DNA concentration. Insert: Plot of [DNA]/(ε_a - ε_f) *vs.* [DNA]

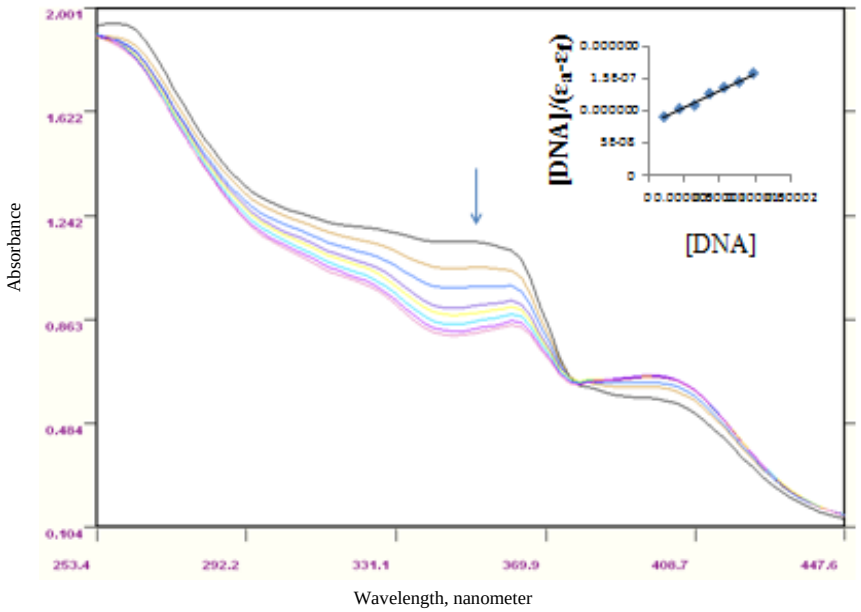

Figure 4. Absorption spectrum of complex [Co(II)(5-Cl-SALAAP)$_2$] in Tris HCl buffer at 25 ^{0}C in the presence of increasing amounts of DNA. Conditions: [Co] =16 µM, [DNA] =0-140 µM. The arrow indicates the change in absorbance upon increasing the DNA concentration. Insert: Plot of [DNA]/(ε_a - ε_f) *vs.* [DNA]

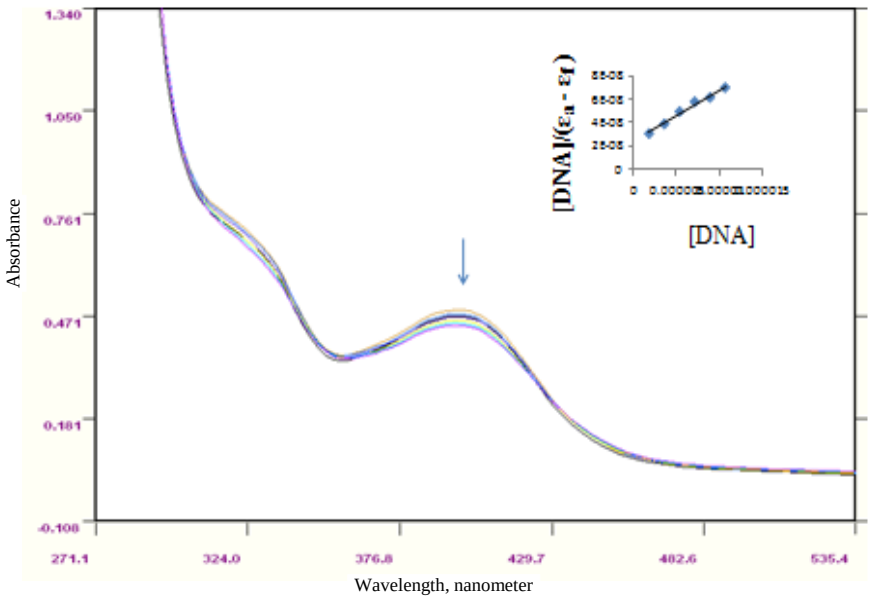

Figure 5. Absorption spectrum of complex [Cu(II)(3-OEt-SALAAP)$_2$] in Tris HCl buffer at 25 ^{0}C in the presence of increasing amounts of DNA. Conditions: [Cu] =16 µM, [DNA] = 0-140 µM. The arrow indicates the change in absorbance upon increasing the DNA concentration. Insert: Plot of [DNA]/(ε_a - ε_f) *vs.* [DNA]

Hypochromism was suggested to be due to the interaction between the electronic state of the intercalating chromophore and that of the DNA bases[15-19]. In addition to the decrease in intensity, a small red shift (bathochromism) was also observed in the spectra. These spectral changes are consistent with the intercalation of complexes into the DNA base stack. The plot of the absorption titration data according to equation **1** gave a linear plot and resulted in an intrinsic binding constant (K_b) of 3.3x10^4 M^{-1} for complex **1**, 6.25x10^4 M^{-1} for complex **2** and 2x10^5 M^{-1} for complex **3.** The binding constants (K_b) of different complexes are given in Table 2.

Table 2. DNA binding constants (K_b) of metal complexes

S.No.	Compound	K_b, M^{-1}
1	Ni(II)-5-Cl SALAAP	3.3x10^4
2	Co(II)-5- Cl SALAAP	6.25x10^4
3	Cu(II)-3-OEt SALAAP	2x10^5

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