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Synthesis, Spectral Characterization and Pharmacological Significance of Cr(III) and Mn(II) Complexes with Schiff Base and Thiocyanate Ion as Ligands

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ABSTRACT

Cr(III) and Mn(II) metal complexes of Schiff base ligand derived from phenylacetylurea condensed with salicylaldehyde (SBPS) and thiocyanate(SCN⁻) ion were synthesized by using microwave irradiation. Microwave assisted synthesis gives high yield of the complexes within a very short time. The molecular formulae and the geometry of the complexes have been deduced from elemental analysis, metal estimation, electrical conductance, magnetic moment, electronic spectra, FT- IR, Far IR spectra, cyclic voltammetry, thermal analysis and powder-XRD techniques. The molar conductance values indicate that the complexes are non-electrolyte (1:0) type. FT-IR spectra show that Schiff base and thiocyanate ion are coordinated to the metal ion in a monodentate manner. The electronic spectra and the magnetic moment indicate the geometry of the complexes is found to be octahedral. The antimicrobial activities of ligands and their Cr(III) and Mn(II) complexes were studied against the microorganisms, viz., *E. coli*, *Klebsiella Pneumonia*, *P. aeruginosa*, *S. aureus*, *Bacillus cereus*, *Aspergillus flavus*, *Aspergillus niger*, *Aspergillus oryzae*, *Aspergillus sojae* and *Candida albicans* by agar well diffusion method. The complexes show moderate activity against the bacteria and enhanced activity against the fungi as compared to free SBPS ligand. The free radical scavenging activity of the complexes and the ligands has been determined by measuring their interaction with the stable free radical, DPPH. The complexes have larger antioxidant activity as compared to the ligand. DNA-binding properties have been studied by fluorescence-emissions method. The results suggest that the complexes strongly bind to DNA because of metal complexes are well-known to speed up the drug action and the ability of a therapeutic agent which can frequently be enhanced upon coordination with a metal ion.

Keywords: SBPS, thiocyanate ion, antimicrobial, antioxidant, DNA-binding.

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INTRODUCTION

Schiff bases and their metal complexes have been investigated for their outstanding and imperative properties, such as their ability to reversibly bind oxygen [1], catalytic activity in the hydrogenation of olefins [2], photochromic properties [3-4] and complexing ability towards a number of toxic metals. [5] Schiff bases are a special group of ligands with a variety of donor atoms exhibiting interesting coordination modes towards various metals. [6-8] The azomethine linkage in Schiff bases is accountable for the biological activities such as antitumor, antibacterial, antifungal and herbicidal activities. [9] Designing a proper polydentate Schiff base ligand to combine with a metal ion along with pseudohalides anion has opened a new area of synthesizing metal complexes of particular choice. [10] Such complexes are readily assembled from diamines and various salicylaldehyde derivatives and are amenable to combinatorial syntheses. [11] Metal ions with schiff base complexes have been well known for their easy synthesis, stability and wide application. [12-14] Typically, metal complexes are well-known to speed up the drug action and the competence of a therapeutic agent which can frequently be enhanced upon coordination with a metal ion. [15-16] The biological action has also been found to be highly dependent on the nature of the metal ion and the donor sequence of the ligands as different ligands reveal different biological properties. [17]

In the present study aims at synthesis and spectral characterization of Cr(III) and Mn(II) complexes with the schiff base ligand (derived from phenylacetylurea and salicylaldehyde by condensation) and thiocyanate ion. The free ligands and their prepared complexes will be characterized by the physico-chemical, spectral, antibacterial, antifungal and antioxidant and DNA binding studies.

MATERIALS AND METHODS

Materials

Phenylacetylurea, salicylaldehyde, potassium thiocyanate and chromium nitrate and manganese nitrate were purchased from Alfa Aaser Company and used as such. The organic solvents used, were DMSO, DMF, methanol, ethanol which were of AnalaR grade, and used as such without further purification.

Preparation of Schiff base

The schiff base was prepared by refluxing an ethanolic solution of required mole ratios of phenylacetylurea condensed with salicylaldehyde in the presence of NaOH, for about an hour.

Synthesis of Metal Complexes

Synthesis of Cr(III) complex

2.06 g (7.49 mmol) of SBPS in ethanol and 0.95 g (7.49 mmol) of potassium thiocyanate in ethanol were added

to the chromium nitrate 1.00 g (2.50 mmol) in methanol followed by microwave irradiation for a few seconds after each addition by using IFB 25 BG-1S model microwave oven. The consequential precipitate was filtered off, washed with 1:1 ethanol: water mixture and desiccated under vacuum. A blue colored complex was obtained with 68.5% yield.

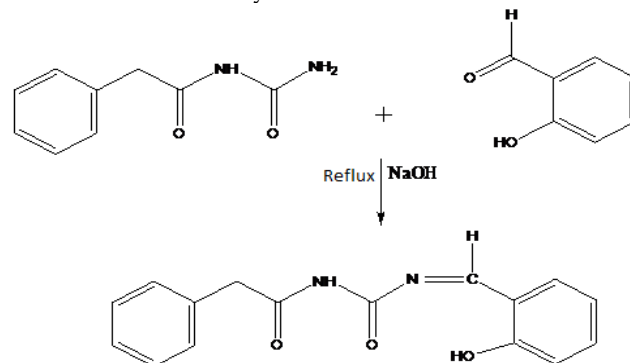


Fig. 1: Schiff Base of Phenylacetylurea condensed with Salicylaldehyde (SBPS)

Synthesis of Mn(II) complex

4.38 g (15.93 mmol) of SBPS in ethanol and 1.01 g (7.96 mmol) of potassium thiocyanate in ethanol were added to the manganese nitrate 1.00 g (3.98 mmol) in methanol followed by microwave irradiation for a few seconds after each addition by using IFB 25 BG-1S model microwave oven. The resulting impulsive was filtered off, washed with 1:1 ethanol: water mixture and dried under vacuum. A pale brown colored complex was obtained with the percentage yield of 71.8.

Instrumentations

CHN elemental analyses were performed using Thermo Finnegan make, Flash EA1112 Series CHNS(O) analyzer. The electrical conductivity measurements were conducted using 10^{-3} M solutions of the metal complex in acetonitrile with Systronic Conductivity Bridge (model number-304) at 30°C. The UV-Visible spectrum of the Cr(III) and Mn(II) complexes were recorded on Varian, Cary 5000 model UV Spectrophotometer. Infra red spectra for the complexes and the ligands were recorded on a Perkin Elmer, Spectrum RX-I, FT IR spectrometer in KBr discs at room temperature. The Far-IR Spectrum of the complex was recorded by Bruker 3000, FT IR Spectrometer. The cyclic voltammograms of the complexes were taken in acetonitrile medium using Princeton make (MC-Tech, Applied Research) equipment. Tetrabutylammonium tetrafluoroborate was used as the supporting electrolyte. The thermogravimetric analyses of the complexes were carried out using Perkin Elmer Diamond TGA/DTA Instrument. The powder X-ray diffraction analysis of a few complexes was recorded on a Rigaku model X-ray Diffractometer.

Biological activities

Antimicrobial activity

The Cr(III) and Mn(II) complexes and the free ligand were tested for *in vitro* antimicrobial activity by the well diffusion method [18] using agar nutrient as the medium. The antibacterial and antifungal activities of the ligands and the complexes were evaluated by well diffusion method against the strains, cultured on potato dextrose agar as medium. The stock solution (10^{-2} M) was prepared by dissolving the compounds in DMSO and the solutions were successively diluted to find Minimum Inhibitory Concentration values. According to the typical procedure [19] a well was made on the agar medium inoculated with the microorganisms. The well was filled with the test solution using a micropipette and the plate was incubated for 24 hours for bacteria and 72 hours for fungi at 35°C. At the end of the period, inhibition zones formed on the medium were evaluated in millimeters (mm) and diameter.

Antioxidant activity

Evaluation of antioxidant Activity Stock solution (1mg/ml) was diluted to final concentrations of 10-500µg/ml. Ethanolic DPPH solution (1 ml, 0.3 mmol) was added to sample solutions in DMSO (3 ml) at different concentrations (10-500µg/ml). [20] The mixture was shaken energetically and acceptable to stand at room temperature for 30 min. The absorbance was then measured at 517 nm in a UV-Vis Spectrophotometer. The lower absorbance of the reaction mixture indicates higher free radical scavenging activity. Ethanol was used as the solvent and ascorbic acid as the standard. The DPPH radical scavenging activity was designed by the following equation:

$$\text{Scavenging effect (\%)} = \frac{A_0 - A_1}{A_0} \times 100$$

Where A_0 is the absorbance of the control reaction and A_1 is the absorbance in the presence of the samples or standards.

DNA binding studies

The DNA binding experiments involving interaction of the complexes with calf thymus (CT)-DNA were conducted in Tris buffer containing HCl (0.01 M) adjusted to pH 7.2 with hydrochloric acid. The CT-DNA was dissolved in Tris-HCl buffer and was dialyzed against the same buffer overnight. Solutions of CT-DNA gave the ratios of UV absorbance at 260 and 280 nm above 1.8, demonstrating that the DNA was adequately free of protein. DNA concentration per nucleotide was determined by absorption spectroscopy using molar absorption coefficient $6600\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ at 260 nm. The stock solutions were stored at 4°C and used within 4 days. [21]

For fluorescence-quenching experiments, DNA was pre-treated with ethidium bromide (EtBr) for 30 minutes. The copper(II) complex samples were then added to this mixture and their effect on the emission intensity was measured. Samples were excited at 450 nm and emission was observed between 500 nm and 800 nm.

RESULTS AND DISCUSSION

Elemental analysis and metal estimation

From the elemental analytical data, the molecular formulae for the Cr(III) and Mn(II) complexes were determined. It is well consonance with the hypothetical values. The analytical data are given in the Table 1. The experimental values are in good agreement with the theoretical values (given in the parentheses).

Molar conductance

Molar conductance measurements of the complexes carried out using acetonitrile as the solvent at the concentration of 10^{-3} M, indicates non-electrolyte [22] nature of the complexes and the conductivity values were found to be $81.51\text{-}83.17\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Thus the prepared complexes are non-electrolytic nature and there is no ion present in the out of the coordination sphere.

Table 1: Elemental analysis and molar conductance

S. No.	Complex	Elements found (Calc) %				Δm ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
		C	H	N	M	
1	[Cr(SBPS) ₃ (SCN) ₃]	56.08 (57.03)	3.87 (3.90)	11.71 (11.73)	8.12 (8.18)	83.17
2	[Mn(SBPS) ₄ (SCN) ₂]	62.50 (62.53)	4.41 (4.43)	8.72 (8.73)	4.20 (4.23)	81.51

Magnetic moment and electronic spectra

In the electronic spectrum of Cr(III) complex exhibits three absorption bands at 18518 cm^{-1} , 26954 cm^{-1} and 29411 cm^{-1} , Which are assignable to the transitions ${}^4A_{2g} \rightarrow {}^4T_{2g}(v_1)$, ${}^4A_{2g} \rightarrow {}^4T_{2g}(F)(v_2)$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)(v_3)$ respectively indicates octahedral geometry. [23-24] The electronic spectrum of the chromium complex reported here is in reasonable agreement with those in literature. [25] The magnetic moment at room temperature is 3.39 B.M which corresponds to the expected value for octahedral geometry of chromium complexes, involving d^2sp^3 hybridisation in the Cr(III) ion.

The electronic spectrum of Mn(II) complex displays the weak absorption bands at 15384 , 17241 , 27397 and 38815 cm^{-1} which are characteristic of octahedral geometry corresponding to the transitions, ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)(v_1)$, ${}^6A_{1g} \rightarrow {}^4E_g(D)(v_2)$, ${}^6A_{1g} \rightarrow {}^4T_{1g}(P)(v_3)$ and ${}^6A_{1g} \rightarrow {}^4E_g(G)(v_4)$ respectively. [26] These bands are both Laporte and spin-forbidden. However, due to instantaneous distortion of the octahedral structures around the metal cations, weak bands sometimes appear. [27-28] The magnetic moment of the complex is 4.90 B.M. This indicates the presence of Mn(II) complex in an octahedral structure and d^2sp^3 hybridization. [29]

FT-IR spectra

The FT-IR spectra of free ligands and their complexes were recorded in the region of $4000\text{-}400\text{ cm}^{-1}$. The FT-IR spectrum of the pure ligand shows the characteristic frequencies as follows: the band at 3388 cm^{-1} indicates the $\nu(\text{N-H})$ stretching frequency of primary amine. The symmetric and asymmetric stretching frequency of $\nu(\text{N-H})$ in secondary amine noticed at 1668 cm^{-1} and 1622 cm^{-1} . The $\nu(\text{C=O})$ stretching frequency of the

ligand is observed at 1475 cm^{-1} . Upon comparison, the stretching frequency of $\nu(\text{N-H})$ is shifted to 1685 cm^{-1} and the symmetry stretching frequency at is shifted to 1605 cm^{-1} which confirms the entry of ligand into the coordination sphere. In addition to that, the value at 2068 cm^{-1} indicates the presence of SCN^- in the coordination sphere of the complexes. [30-31]

Far-IR Spectra

In the Far-IR spectrum of the complexes shows, the frequency at $440\text{--}450\text{ cm}^{-1}$ corresponds to HC=N (imine nitrogen) bond and at $342\text{--}360\text{ cm}^{-1}$ indicates the nitrogen (from thiocyanate) bond. [32]

Cyclic voltammetry

The Cr(III) complex exhibits one electron transfer quasi-reversible process with a reduction peak at $E_{pc} = 0.6\text{V}$ with the corresponding oxidation peak at $E_{pa} = 1.3\text{V}$ and the scan rate of 50mV/s . The peak separation (ΔE_p) of this couple is 0.7V . With increasing scan rates, the ΔE_p value also increases giving more evidence of quasi-reversible Cr(III)/Cr(II) couple. [33]

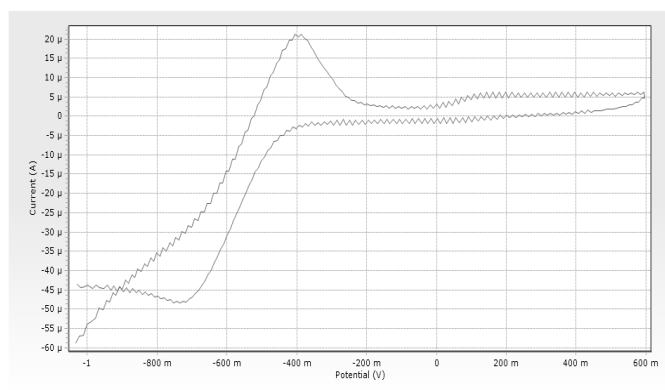


Fig. 2: Cyclic voltammogram of Cr(III) complex

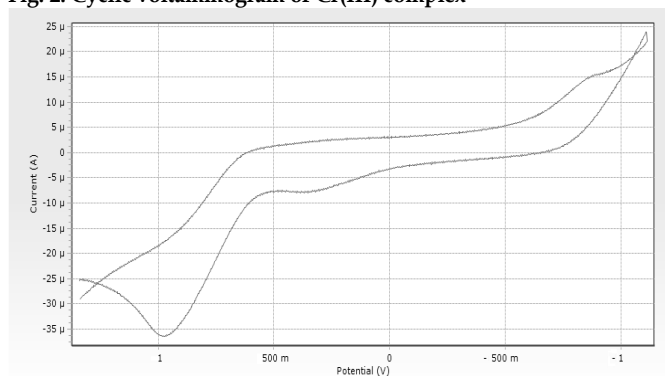


Fig. 3: Cyclic voltammogram of Mn(II) complex

The redox property of the Mn(II) complex has been studied in the potential range of $+1.3$ to -1.3V as shown in the Fig. 3. The Mn(II) complex is electroactive with respect to the metal center and exhibited two redox process, each reduction is associated with a single-electron transfer process at room temperature. [34-35] Two well defined quasi-reversible one-electron cyclic responses were observed, one at $E_{pc} = 0.6\text{V}$ with corresponding oxidation peak at $E_{pa} = 0.9\text{V}$ and the other at $E_{pc} = -0.9\text{V}$ with the corresponding oxidation peak at $E_{pa} = -0.5\text{V}$ respectively at the scan rate of 100mV/s .

Thermogravimetric analysis

Thermogravimetric analysis of Cr(III) and Mn(II) complexes of SBPS and thiocyanate ion show two significant temperature transitions of weight loss with common and specific stages, termed as two stages of thermal degradation. The TGA plateau of the complexes shows that these complexes exhibits no mass loss up to 190°C , indicating the absence of coordinated water [36] and a high thermal stability of the complexes. The weight loss at the range of $190\text{--}240^\circ\text{C}$ in TGA curves of complexes is termed the first stage of thermal degradation. In this case, the present weight loss is in the range of $(46.57\text{--}49.82\%)$, which may be attributed to the decomposition of less stable schiff's base. [37] The onset of second step decomposition occurs in the range of $220\text{--}280^\circ\text{C}$, which gives the loss of thiocyanate ion $(18.02\text{--}25.88\%)$ bonding with the metal complexes. The experimental values are in full agreement with the percent weight calculated on the basis of stoichiometry proposed for the complexes.

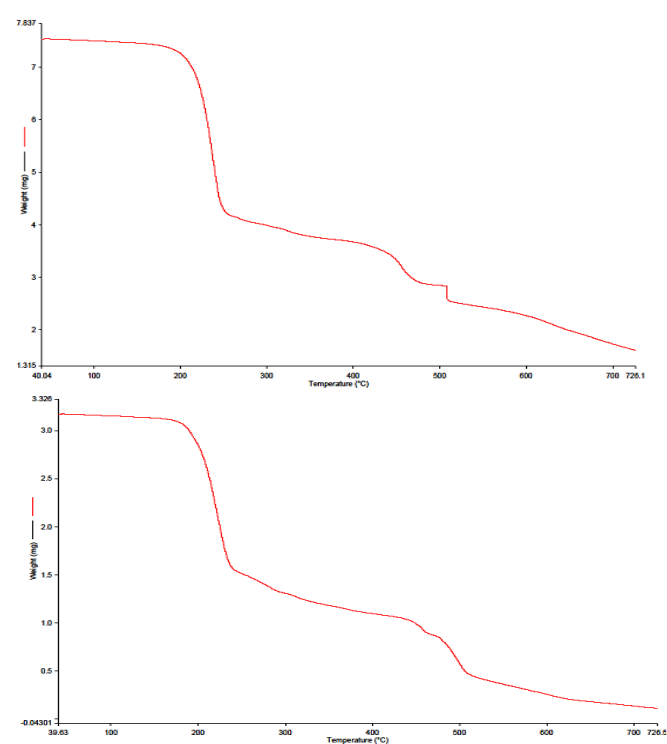


Fig. 4: Thermogram of a) Cr(III) and b) Mn(II) complexes

Powder X-ray diffraction technique

The Powder X-ray diffractogram of the Cr(III) and Mn(II) complexes were recorded in the range of 5° to $80^\circ 2\theta$ values. The XRD pattern indicates that the prepared complexes have well defined crystalline patterns, with various degrees of crystallinity. In these complexes, the trend of the curves decreases from maximum to minimum intensity indicating amorphous nature of the complexes. [38] The powder XRD patterns of the synthesized Cr(III) and Mn(II) complexes show the sharp crystalline peaks indicating their crystalline phase. The average crystallite size (d_{XRD}) of the complexes was calculated using Scherer's formula. [39-40]

The prepared complexes had an average crystallite size of 28-65 nm indicating its nanocrystalline in nature.

Biological activity

Antibacterial activity

The free ligands and their Cr(III) and Mn(II) complexes were evaluated against the bacteria *E. coli*, *Klebsiella Pneumonia*, *P. aeruginosa*, *S. aureus*, *Bacillus cereus* at MIC concentration using agar-well diffusion method. The complexes show enhanced activity against *P. aeruginosa*, *S. aureus*, *Bacillus cereus* and moderately active against the rest of the organisms. The increased activity of the metal complexes can be explained on the basis of chelation theory. [41] It is known that chelation tends to make the ligand act as powerful and potent bactericidal agents, killing more number of bacteria than the ligand.

Table 2: Antibacterial activity of ligands and complexes

S. No	Ligand/Complexes	Zone of Inhibition(mm)				
		<i>S. aureus</i>	<i>Bacillus cereus</i>	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>Klebsiella</i>
1	SBPS	06	10	10	06	05
2	[Cr(SBPS) ₃ (SCN) ₃]	11	15	08	18	09
3	[Mn(SBPS) ₄ (SCN) ₂]	14	16	12	07	21

05-10 Resistant; 11-16 Moderate; 16-21 Highly active

Antifungal activity

The synthesized Cr(III) and Mn(II) complexes and the free ligands were evaluated against the fungi, viz., *Aspergillus flavus*, *Aspergillus niger*, *Aspergillus oryzae*, *Aspergillus sojae* and *Candida albicans* at MIC concentration using agar-well diffusion method. The complexes show enhanced activity against the tested fungus. A comparative study of zone of inhibition diameter values of the ligands and their complexes indicate that, generally, the metal complexes have a better fungicidal activity than the free ligand. This is probably due to the greater lipophilic nature of the complexes. It is evident from the data that this activity significantly increases on coordination. [42]

Table 3: Antifungal activity of ligands and complexes

S. No	Ligand/Complexes	Zone of Inhibition(mm)				
		<i>Aspergillus Flavus</i>	<i>Aspergillus niger</i>	<i>Aspergillus oryzae</i>	<i>Aspergillus sojae</i>	<i>Candida albicans</i>
1	SBPS	09	05	08	07	06
2	[Cr(SBPS) ₃ (SCN) ₃]	14	16	12	07	21
3	[Mn(SBPS) ₄ (SCN) ₂]	18	21	27	19	20

05-10 Resistant; 11-16 Moderate; 16-21 Highly activity; 21-30 Enhanced activity

Antioxidant activity (Radical Scavenging Activity)

The 2,2'-diphenyl-1-picrylhydrazyl (DPPH) radical assay provides an easy and rapid way to evaluate the antiradical activities of antioxidants. Determination of the reaction kinetic types DPPH is a product of the reaction between DPPH• and an antioxidant.



The reversibility of the reaction is evaluated by adding DPPH at the end of the reaction. If there is an increase in the percentage of remaining DPPH• at the plateau, the reaction is reversible, otherwise it is a complete

reaction. DPPH was used as stable free radical electron accepts or hydrogen radical to become a stable diamagnetic molecule. [43] DPPH is a stable free radical containing an odd electron in its structure and usually used for detection of the radical scavenging activity in chemical analysis. [44] The reduction capability of DPPH radicals was determined by decrease in its absorbance at 517 nm induced by antioxidants. [45] The graph was plotted with percentage scavenging effects on the y-axis and concentration (µg/ml) on the x-axis. The scavenging ability of the metal complexes was compared with ascorbic acid as a standard. The metal complexes showed enhance activities as a radical scavenger compared with ascorbic acid, these results were in good agreement with previous metal complexes studies where the ligand has the antioxidant activity and it is expected that the metal moiety will increase its activity. [46]

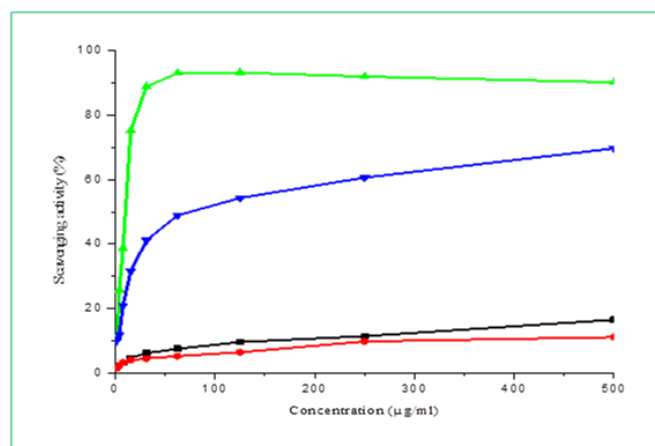


Fig. 5: Antioxidant activity of SBPS, Cr(III), Mn(II) and Vitamin C in vitro studies

DNA Binding - Emission study

As the present Cr(III) and Mn(II) complexes are non-emissive, ethidium bromide (EtBr) binding study was undertaken to gain support for the extent of binding of the complexes with DNA. Ethidium bromide (EtBr) was shown to emit intense fluorescence light in the presence of DNA, due to its strong intercalation between the adjacent DNA base pairs. It was previously reported that the fluorescent light could be quenched by the addition of a second molecule. [47] The quenching extent of the fluorescence of EtBr binding to DNA is used to determine the extent of binding between the second molecule and DNA. The addition of the complexes to DNA pretreated with EtBr causes appreciable change in the emission intensity. This behaviour can be analyzed through the Stern-Volmer equation [48], $I_0/I = 1 + K_{sv}r$, where I_0 and I are the fluorescence intensities in the absence and the presence of complex respectively. K_{sv} is a linear Stern-Volmer quenching constant, r is the ratio of the total concentration of complex to that of DNA. The quenching plot illustrates that the quenching of EtBr bound DNA by the Cr(III) and Mn(II) complexes is in good agreement with the linear Stern-Volmer equation,

which also indicates that the complex binds to DNA. In the plot of I_0/I versus $[\text{Complex}]/[\text{DNA}]$, K_{sv} is given by the ratio of the slope to intercept. The K_{sv} value for SBPS, Cr(III) and Mn(II) complexes thus obtained is 0.43, 1.05 and 1.43 respectively. This suggests that prepared complexes bind strongly with DNA, which is also consistent with our absorption spectral result. It is generally agreed that strong fluorescence decrement accompanies a strong interaction of the complexes with calf thymus DNA. Since, the studies have shown that macrocyclic complexes can interact with DNA in different binding fashions and exhibit effective nuclease activities. [49-50] In recent years, binding studies of transition metal complexes have become very important in the expansion of DNA molecule probes and chemotherapeutics. [51]

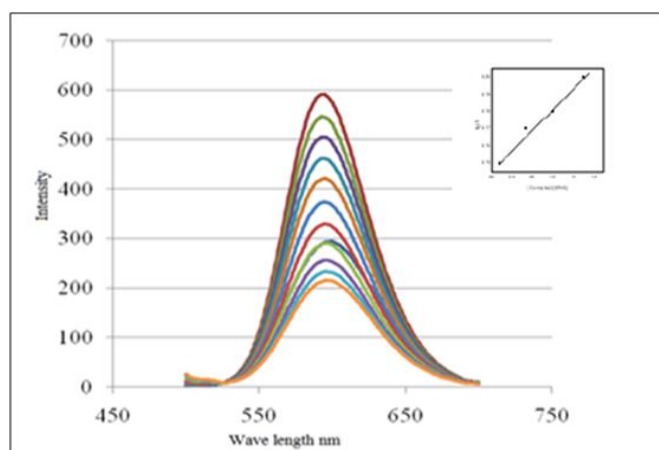


Fig. 6: Emission spectrum of EtBr bound to DNA in the absence and presence of Cr(III) complex

In the present study, our efforts were to synthesize and characterize the Cr(III) and Mn(II) metal complexes with the schiff base and thiocyanate ion as ligands. The new complexes were synthesized by using microwave irradiation. The synthesized metal complexes were characterized by various physico-chemical and spectral analyses. Based on the analytical, electrical conductance, spectral and magnetic moment, octahedral geometry has been suggested for the Cr(III) and Mn(II) complexes. The synthesized complexes were tested for antimicrobial activities. The metal complexes were significant antimicrobial and antioxidant activities as compared to the free ligands. The effectiveness of the DNA binding of the complexes is being confirmed by means of change in intensity of emission in the case of emission spectral studies.

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