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Synthesis, Characterization and their biological studies of Mixed ligand Metal (II) complexes of Diketimines

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Abstract

Copper, Nickel, Manganese, Cobalt and Iron complexes of Mixed ligands (L: Diketimines & 1,10-Phenanthraline) have been prepared and characterized by IR, UV-Vis and Cyclic voltammetry. Planar compound have numerous application in biological system such as antioxidant, antiviral and antimutagenic activities. Current research works have been published on Diketimines moiety with metal to explain the factors that are key in their biological character. It is also expected that the ability of Diimines and planar compound to chelate with metals is very important factor for their biological activities. Therefore, we here tried to explore the interaction of these mixed metal complexes with herring sperm DNA using spectral and electrochemical methods. Complexes **1-3** exhibits hypochromism with red shift and octahedral complexes shows hyperchromism with blue shift. All these metal complexes observed binding constants fall in the range of 0.85 x 10^5 M^{-1}- 2.1 x 10^3 M^{-1} and electronic spectra conclude that, complexes **1-3** and **4-5** bind with DNA through intercalation and groove binding respectively. Electrochemical studies expose that the metal complexes (**1-3**) prefer to bind with DNA in M(II) form. The stong positive potential shift in complexes, **1-3** may be attributed to the intercalation binding and the slight positive potential shift in the complexes, **4 & 5** may be due to groove binding. CD spectral studies also suggest that the complexes, **1-3** and **4-5** bind with DNA through intercalation and groove binding respectively.

Introduction

The area of inorganic chemistry, which most widely developed in the last few decades, is mainly due to that of coordination chemistry and applies very particularly to the coordination compounds of transition metals. However, the chemistry of coordination compounds has always been a challenge to the inorganic chemists as it has more branches now. They are the most widespread and diverse class of inorganic substances. The achievements of theoretical and applied chemistry in recent years are in many respects associated with the coordination compounds. This is manifested in the recent journals in this field and in a number of publications ranging from purely synthetic to highly theoretical work. The rapidly developing field of bioinorganic chemistry is centered on the presence of coordination compounds in living system.

The modern study of coordination compounds begins with Alfred Werner and Jorgenson. While most of the pre-Werner theories were mutually exclusive and competitive with each other, Werner's idea soon encompassed almost the whole of systematic inorganic chemistry and even found application in organic, analytical, medicinal and biochemistry. The later developments were amplifications and expansion of this theory rather than ideas incompatible with or conflicting to it. The essential idea in the coordination theory of Werner is that a metal ion surrounds itself with ligands and the nature of the ligands, the character of the metal ligand bonds and the geometry of the ligands around the metal atom determine the physical and chemical properties of the compounds.

At present transition metal coordination chemistry is undergoing an unprecedented growth because of the development of sensitive physico-chemical techniques for investigation. Instrumental methods such as, IR, UV-VIS & EPR spectroscopy and magnetic moment measurement are useful to ascertain the configuration and stereochemistry of complexes formed by these metals.

Recent developments in coordination chemistry has received not only a large amount of experimental study but also a moderately extensive theoretical treatment. The unique aspects of metal centers have stimulated many physical and biological chemists to investigate metallo-macromolecules. The many new and exhilarating developments in the biochemistry field create interest out of inorganic chemists to work in the bioinorganic chemistry. Bioinorganic chemistry, according to Williams, is the biochemistry of the coordination compounds of living system [1]. Most of the transition metals are

essential in a trace amount are complexes with proteins in metalloproteins, which are needed to various body functions [2].

Many metal ions are known to play very important roles in biological processes in the human body [2,3], for example, zinc(II) and copper(II) ions are the second and third most abundant transition metals present in human body systems. They are found either at the active sites or as structural components of a good number of enzymes [4,5].

Among multi-site donors, 1,10-phenanthroline (phen) and 2,2'-bipyridyl (bpy) with metal ions can be considered as the models for bioinorganic molecules, and as precursor in the synthesis of macrocyclic metal complexes of technical interest. Several investigations dealing with these molecules, their derivatives and metal complexes have been performed. Studies on the metal-nitrogen bonding from amino acids and their characterization are of paramount importance in biochemistry, are however scarce [6-8].

These metal ions and some of their complexes have been found to exhibit antimicrobial activities. The ligands, phen and bpy are strong field bidentate ligands that form very stable chelates with many first row transition metals [9-12]. These ligands, as well as some of their derived complexes, do exhibit antimicrobial properties [13,14]. A number of transition metal mixed-ligand complexes containing phen/bpy and other ligands such as Schiff bases derived from amino acids [15-18], oxydiacetate, diethylenetetramine, oxalate and halides, X (X = Cl, Br, I) have been reported[19-23].

After the pioneering investigation by Sigman *et al*. [24] with *bis*(1,10-phenanthroline) copper(I) as a useful reagent in foot-printing applications and for sequence specific binding to DNA, the chemistry of copper-phenanthroline complexes has been studied extensively [25-27]. Among copper complexes explored so far, the metal (II) complexes of 1,10-phenanthroline and its derivatives attract great attentions due to their high nucleolytic efficiency, which are able to break the DNA chain in the presence of H_2O_2 and other reducing agents. These complexes have also been broadly used as foot printing agents of both proteins and DNA, probes of the dimensions of the minor groove of duplex structures and identifiers of transcription starting sites [28-30]. However, in most cases the ability of metal(II) complexes in breaking the DNA chain rely in the presence of H_2O_2. Owing to the fact that these complexes show their own selectivity for a cleavage mechanism or for DNA interaction, the design of new DNA cleavage agents is of great interest.

Palaniandavar and coworkers have investigated the effect of methyl substitution on the nature of DNA binding of *bis*(phen)copper(II) complexes [31]. They have discovered the novel conversion of right-handed B-DNA to left-handed Z conformation on interaction of calf thymus (CT) DNA with $[Cu(5,6\text{-dmp})_2]^{2+}$, [5,6-dmp = 5,6-dimethyl-1,10-phenanthroline], though the Z form of a natural DNA would normally escape detection. Also it has been reported that some ternary metal (II) complexes of phen have antitumor activity [32-34]. Barton demonstrated that *tris*(phenanthroline) complexes of ruthenium(II) display enantiomeric selectivity in binding to DNA and can serve as spectroscopic probes in solution to distinguish right and left handed DNA helices [35,36].

Therefore, extensive studies using different structural polypyridyl ligands to evaluate and understand the factors that determine the mode of binding interactions with DNA and the cleavage mechanisms are necessary.

Scope of the present work

Transition metal complexes of Schiff bases are the most adaptable and thoroughly studied systems. These complexes also have applications in clinical, analytical and industrial areas in addition to their important roles in catalysis and organic synthesis [37]. Some of Schiff base complexes are used as model molecules for biological oxygen carrier systems, as metal indicators in complexometric titrations and colorimetric reagents, in addition to biochemical research. Schiff base complexes, derived from heterocyclic compounds, have increased the interest in the field of bioinorganic chemistry. Heterocyclic compounds such as pyridine, 1,10-phenanthroline and related molecules are good ligands due to the presence of at least one ring nitrogen atom with a localized pair of electrons. The successful application has led to the formation of a series of novel compounds with a wide range of physical, chemical and biological properties, spanning a broad spectrum of reactivity and stability.

Keeping in view of the noticeable biological activity of the metal complexes of mixed ligand such as phenanthroline and Schiff bases derived from heterocyclic compounds, it was thought of worthwhile to synthesize, characterize and explore DNA binding properties of some new Cu(II), Ni(II), Mn(II), Co(II) and Fe(II) complexes of new Schiff base (Diketimine-Cl) derived from 2-bromo-4-fluoro benzaldehyde actylacetone (bfacac) and p-chloroaniline. In addition, their possible interactions with DNA also have been studied in this chapter.

Experimental methods

In chapter II, details of the instruments used for various physical measurements (IR, UV-Vis, NMR, EPR, CV, CD and gel electrophoresis studies) have been discussed.

Synthesis of 2-bromo-4-fluoro benzaldehyde actylacetone (bfacac)

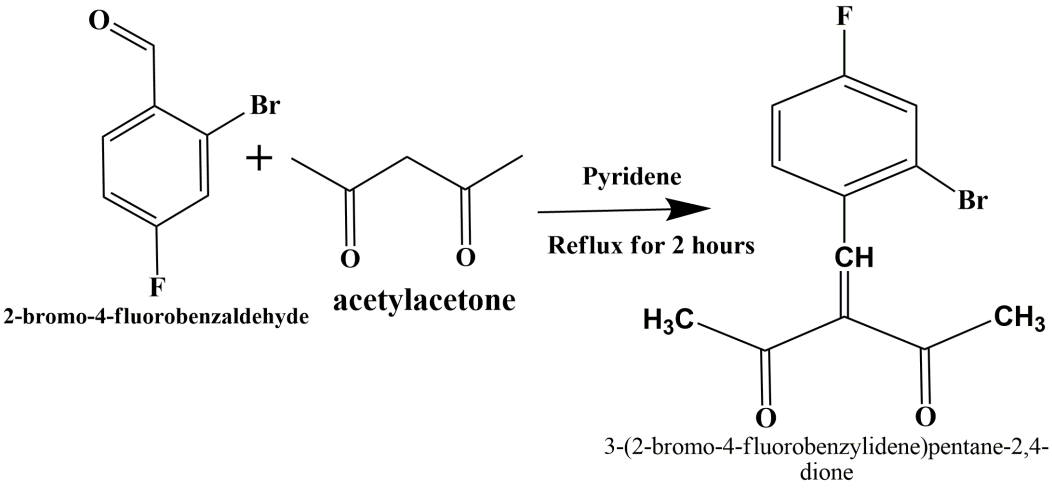
Synthesis of bfacac ligand is discussed in the previous chapter.

Synthesis of complexes

A solution of the corresponding metal(II) chloride (1 mmol) in methanol (10 ml) was added slowly to mixture of bfacac (1 mmol) and p-chloro aniline (20 mmol) and it was kept stirred for 8 h in acetonitrile (60 ml). The resulting solution was stirred under reflux for 2 hour with $AgNO_3$, the deposited AgCl was removed by filtration and to the filtrate was added the appropriate 1,10-phenanthroline (phen) (1 mmol). The resulting solution was refluxed for 2 hr, allowed to cool at room temperature. A coloured solid complex, instantly separated was stirred for further 30 min and then

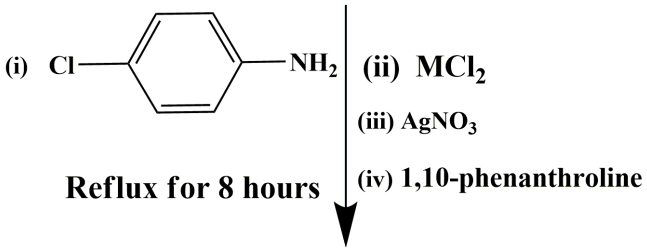
filtered, washed with mixture of methanol & Water and air-dried. The complex was recrystallized from acetonitrile. The structure of the complexes is $[M_1(L)(phen)]$ $[M_2(L)(phen)(H_2O)_2]$ Yield: 60% (L= Diketimines-Cl ; $M_1 = Cu^{2+}$,Mn^{2+} & Ni^{2+}) ($M_2 = Co^{2+}$ & Fe^{2+}). In this chapter, coordination number 4 & 6 complexes are successfully prepared by the above technique. All the five Schiff based Metal (II) complexes ([Cu(L)(phen)] (**1**), [Mn(L)(phen)] (**2**), [Ni(L)(phen)] (**3**), $[Co(L)(phen)(H_2O)_2]$ (**4**), $[Fe(L)(phen)(H_2O)_2]$ (**5**), synthesized using the above procedure, are shown in the **Scheme 5.1.**

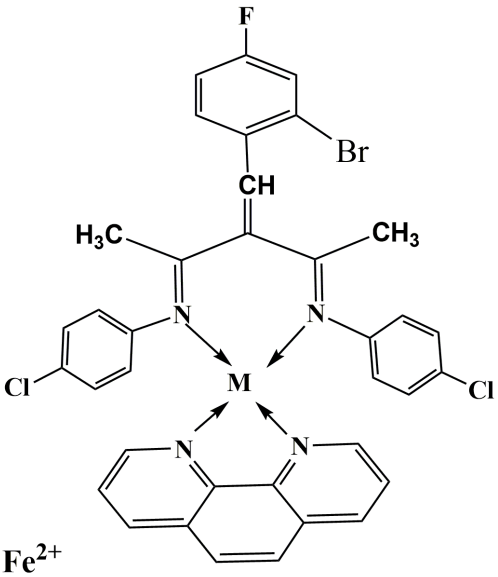
Coordination Number	**Metal (II) Complexes**	**Color**	**Yield (%)**
4	([Cu(L)(phen)] (**1**)	Greenish brown	68
	[Mn(L)(phen)] (**2**)	Deep brown	65
	[Ni(L)(phen)] (**3**)	Brown	65
6	$[Co(L)(phen)(H_2O)_2]$ (**4**)	Dark brown	66
	$[Fe(L)(phen)(H_2O)_2]$ (**5**)	Reddish brown	68
L= Diketimine-Cl; phen = 1,10 -phenanthroline			



3-(2-bromo-4-fluorobenzylidene)pentane-2,4-dione

Knoevenegal condensate





[M(diimine)(bpy)]NO_3

M = Cu^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+} & Fe^{2+}

Results and discussion

Infrared spectra

The IR spectra of the complexes, **1-5** were recorded using KBr disc and their characteristic bands are summarized in **Table 5.1**. The important absorption band at 470-495cm^{-1} region is assigned to the ν (M-N) vibration [38]. All the complexes show strong bands in the region, 1590-1610 cm^{-1} that may be assigned to ν (C=N) vibrations and these bands indicate the presence of coordinated azomethine group.

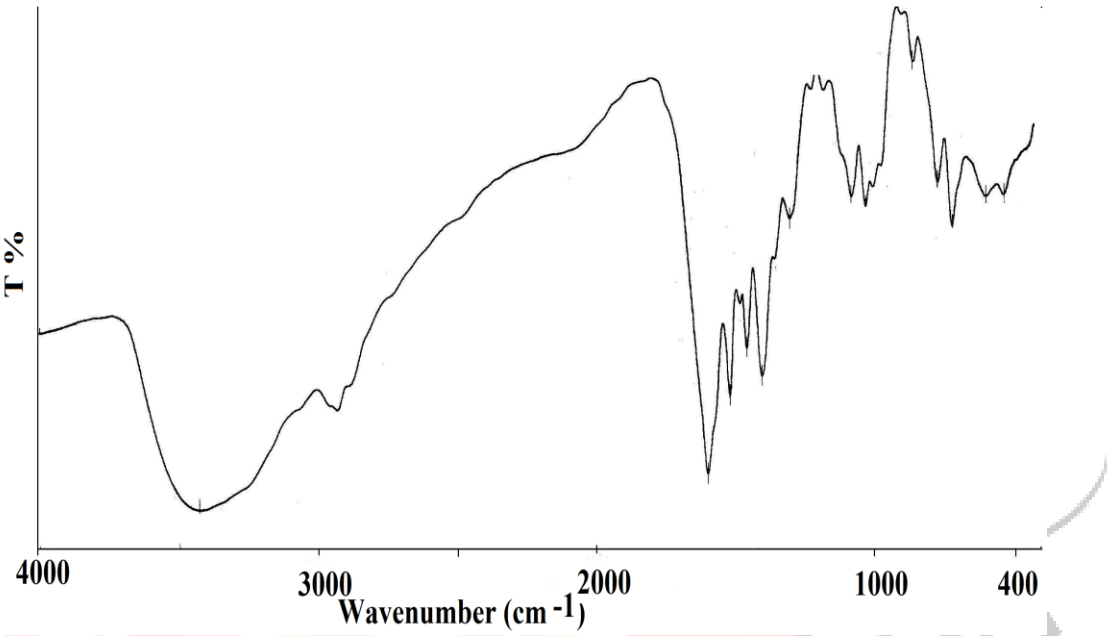


Fig. 5.1. IR spectrum of $[Co(L)(phen)(H_2O)_2]$ (**4**) in KBr disc

The phenyl moiety vibrations of all complexes are seemed in the region 1410-1460 cm^{-1} and 720-740 cm^{-1}. The above stretching frequencies are relevant to the characterization of the complexes. The representative spectrum of the complex is shown in the **Fig. 5.1**. The high frequency in the 3400–3600 cm-1 region for the hydrated complexes **4** & **5** is probably due to stretching vibrations of the water molecules[39]. Iron and cobalt complex are clearly shows a strong and board frequency above 3300 cm-1due to coordination of water [40]. Strong absorption bands at 2976 cm-1 to 2826 cm-1 can be related with the stretching vibration of the heterocyclic ring of C-H bonds for the all complexes.

Electronic absorption spectra

The energy required for promotion of an electron from its electronic ground state to an excited state corresponds to absorption of light in the near infrared, visible or ultraviolet regions of the electromagnetic spectrum. Transition metal complexes generally give low intensity d-d absorption bands and are associated with

transitions localized on the metal atom. Ligand field bands are due to the excitations of the electrons from the ground to the various excited states arising out of the crystal field splitting. These are 'Laporte forbidden' transitions with lower intensity. The observed intensities may be slightly higher due to distortions from regular geometries. The electronic spectral data of complexes (**1-5**) and their associated structural assignments are given in **Table 5.2**. The UV- Vis spectra of these complexes in methanol exhibit a sharp absorption at 264-278 nm and a broad absorption at 320-405 nm owing to intra-ligand and ligand to metal charge transfer transitions (LMCT) respectively.

For these copper complexes, the electronic spectra in DMSO were measured using shimadzu-160, UV-Visible spectrophotometer. For paramagnetic cobalt (II) complex a broad band appeared at 496 nm region, consistent with the square planar geometry [41]. Diamagnetic nickel (II) complexes (**2**) appeared a peak at 420 nm could be assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$ transition for a square planar environment.

The spectra copper complex (**1**) displays an intense band in the region, 570-680 nm **(Fig. 5.2)** and a very intense LMCT band around 325-420 nm. The band around 604 nm is assigned to the d-d band in a distorted square planar geometry. The intense LMCT band may be due to N→Cu **(Table 5.2)**.

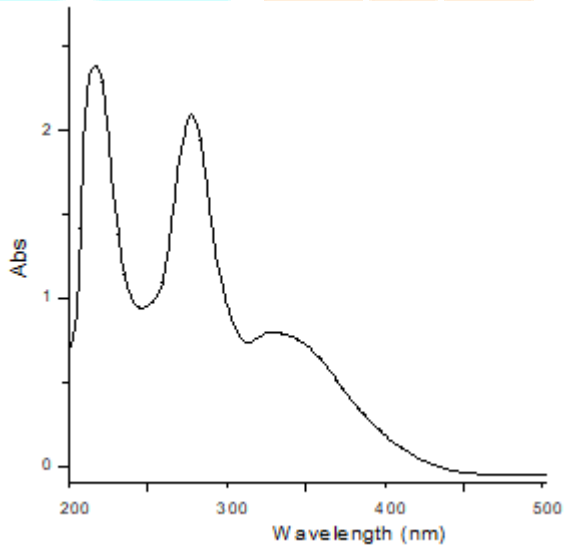


Fig. 5.2. Electronic spectrum of [Cu(L)(phen)] (**1**) in DMSO.

Electrochemical behaviour

Cyclic voltammogram of all metal (II) complexes (**1-5**) are recorded in DMSO and data are revealed in **Table. 5.3.** The cathodic peak in the 221 mV region and the associated anodic peak in the 269 mV region correspond to the redox couple $M^{II/I}$, while the peak-to-peak separation (△Ep) of 110 mV, indicates that this redox couple is quasi-reversible. The i_{pa}/i_{pc} value is close to unity, clearly confirms one electron transfer process. The cyclic voltammogram of the cobalt(II) complex (**Fig. 5.3**) in acetonitrile in the 900 to – 200 mV potential range shows a well-defined redox process corresponding to the formation of the redox couple $Co^{II/I}$ with a formal potential of 106 mV. The couple is found to be

quasi-reversible with ΔEp of 218 mV and the ratio of anodic to cathodic peak currents (i_{pa}/i_{pc} = 1) corresponding to the simple one-electron process.

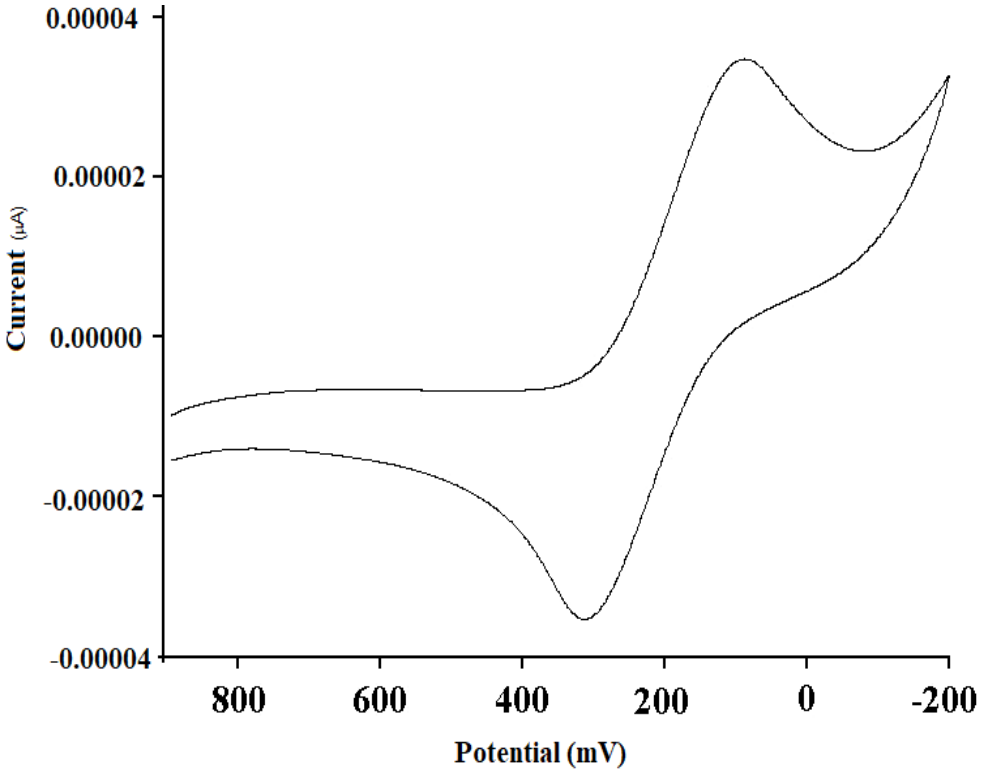


Fig. 5.3 Cyclic voltammogram of $[Co(L)(phen)(H_2O)_2]$ (**4**) (0.5 x 10^{-3} M) in CH_3CN *vs* Ag/AgCl with TBAP as supporting electrolyte at 100 mVs^{-1}

The cyclic voltammogram of nickel(II) complex in DMSO, exhibits one well defined redox couple at -528 mV and a diffused peak centered at 10 mV with i_{pa}/i_{pc} ratio close to unity. These results suggest diffusion controlled quasi-reversible Ni^{II}-Ni^{I} processes [42,43].

The cyclic voltammogram of the Mn(II) complex (Fig. 6) shows a clear redox wave in the cathodic scan at 138 mV and the corresponding anodic scan at 315 mV corresponds to the formation of the redox process $Mn^{III/II}$. It is a quasi-reversible one with ΔEp of 177 mV and the ratio of anodic to cathodic peak currents (i_{pa}/i_{pc} = 1) corresponds to a simple one-electron transfer process. The peak appearing at more positive potential (967 mV) may correspond to the slow oxidation of ligand molecules.

DNA binding and cleavage studies

Absorption spectroscopic studies

The binding of intercalative complexes to DNA helix has been characterized classically through absorption spectral titration, by following the changes in absorbance [44]. In the present investigation it has been used to monitor the interaction of mixed ligand Diketimito and phen metal (II) complexes in buffer (acetonitrile and buffer mixture) solutions with herring sperm DNA.

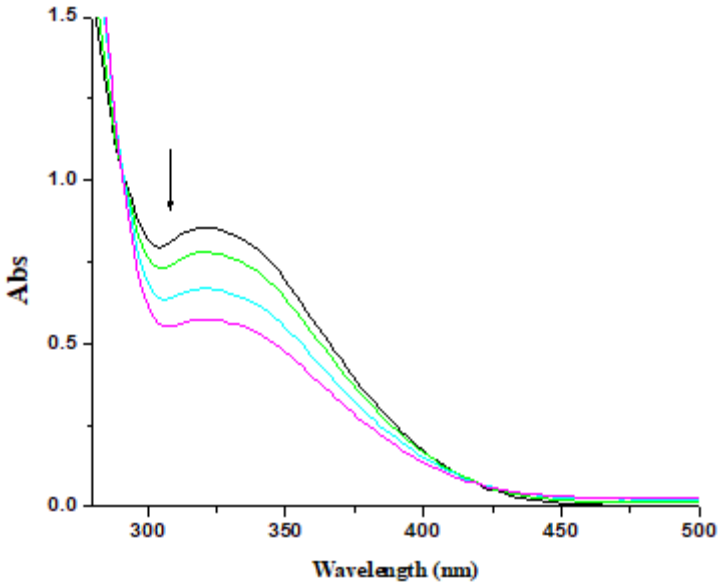


Fig. 5.4 Absorption spectrum of [Cu(L)(phen)] (**1**) (20 µM) in 5 mM Tris-HCl buffer at pH 7.1 in the absence (*R* = 0) and presence (*R* = 1.0, 2.0 and 3) of increasing amounts of DNA. (Arrow mark indicates the absorbance change upon increasing DNA concentration)

The intense ligand to metal charge transfer (LMCT) band of copper complex, observed in the range 322 nm region, was monitored as a function of added DNA (**Fig. 5.4**). There is a well-resolved hypochromism for Cu-N4 macrocycles up to R value of 3. (R = [DNA]/[complex]). On the addition of increasing concentrations of DNA to the complex, this complex shows a decrease in molar absorptivity along with a slight blue shift (1-2 nm). Hypochromism initiates a strong interaction of complex molecules with DNA [45]. For complexes **4 & 5** , LMCT bands observed in the 410 and 348 nm range were monitored as a function of added DNA. There is a considerable decrease in the absorbance without any significant shift in the LMCT band up to R value of 3(**Table 5.4.**). It reveals that complexes **1-3** and **4-5** bind with DNA through intercalation and groove binding respectively.

Electrochemical studies

The application of electrochemical methods to the study of metallo-intercalation and coordination of metal ions and chelates to DNA provides a useful complement to the previously used methods of investigation such as UV-Vis spectroscopy. In the present study these methods have been

used to understand the nature of DNA binding with metal complexes. On the addition of DNA to copper complexes (**Fig. 5.5.**), the current intensity decreases and shifts the redox couple slightly towards the positive side along with improving its reversibility on the increasing concentration of DNA. The ratio of cathodic and anodic peak currents, i_{pa}/i_{pc} (≈1) decreases with increasing [DNA], suggest that the slow diffusion of the Cu(II) complexes on the addition of herring sperm DNA.

In the case of cobalt(II) complex (**4**), the redox couple is a quasi-reversible one with △Ep of 188 mV. On the addition of increasing amounts of DNA the current intensity decreases along with a slight improvement of reversibility (△Ep = 178 mV). The decrease in the △Ep value may be due to the poor stability of Co^{II}-DNA complex and slow diffusion of complex with DNA molecules. The decrease in current could be viewed on the basis of poor mobility of the DNA bound cobalt(II) complexes.

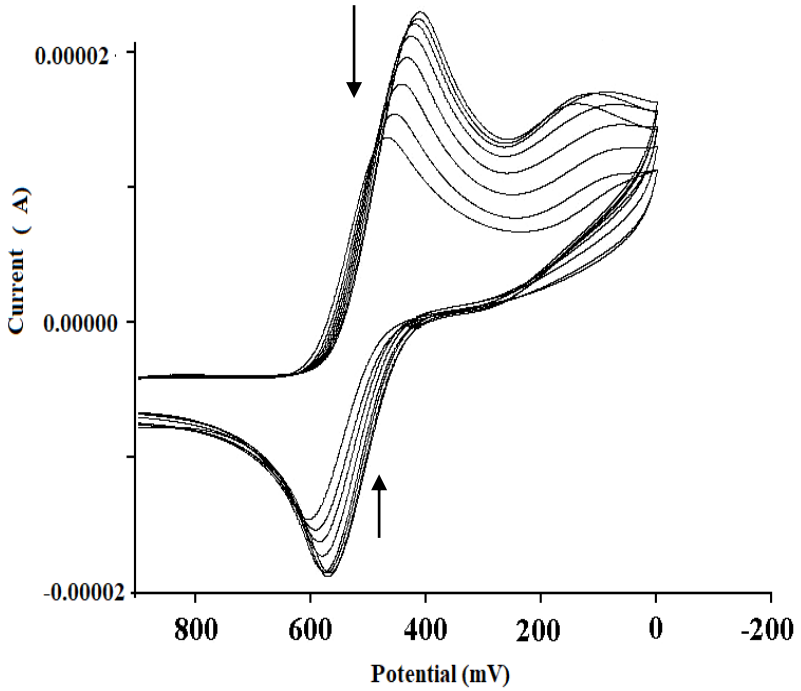


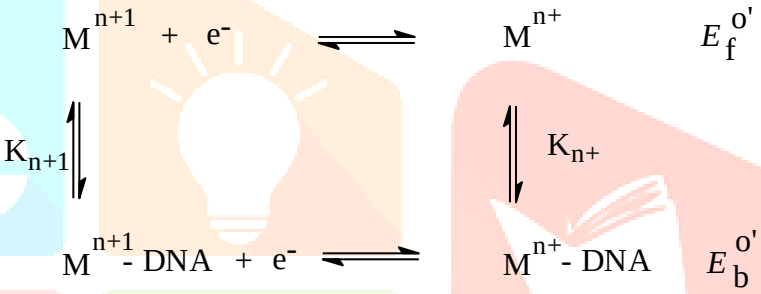
Fig. 5.5. Cyclic voltammogram of [Cu(L)(phen)] (**1**) in the absence (R = 0) and presence of DNA, R = 0.5, 1, 1.5, 2, 2.5 and 3 at a scan rate of 100 mVs^{-1} in Tris-HCl buffer, pH 7.1.

For Ni(II) complex (**3**), the current intensity decreases and shifts the redox couple (both cathodic and anodic peaks) slightly towards the positive side and the limiting peak potential separation △Ep of the voltammogram increases with increasing DNA (**Table 5.5**). The Ni^{II}/Ni^{I} redox potential increases its irreversibility with increasing amounts of DNA (R = [DNA]/[Ni] = 5). The ratio of cathodic and anodic peak currents, i_{pa}/i_{pc} (≈1) decreases with increasing [DNA], suggests slow diffusion of the Ni(II) complexes on the addition of DNA. The manganese(II) complex (**2**), it behaves like Ni(II) in their CV-DNA titration, the reversibility and slight decreasing current intensity were observed [46].

The ratio of equilibrium constants, K_{n+1}/K_n for the binding of metal complexes to DNA can be estimated from the net shift in $E_{1/2}$, assuming reversible electron transfer. For a Nernstian electron transfer in system in which both the oxidized and reduced forms associated with a third species such as DNA in solution, **Scheme 2** can be applied for a more detailed account. Here, ML^{n+}-DNA represents the metal complexes bound to DNA having n+ oxidation state of the corresponding metal. Thus for one electron transfer process,

$$E_b^{o'} - E_f^{o'} = 0.059 \log (K_+/K_{2+})$$

where, $E_f^{o'}$ and $E_b^{o'}$ are the formal potentials of the M^{n+}/M^{n+1} couple in the free and DNA bound forms, respectively. The average of the cathodic and anodic peak potentials for the redox couples shift to more positive values as the concentration of herring sperm DNA increases. From the net shift in $E_{1/2}$ values, K_{n+1}/K_{n+} ratios could be calculated.



Scheme 2

For all complexes K_{n+} is higher than K_{n+1} suggests that the DNA on complex formation tends to stabilize the M^{n+} over the M^{n+1}, obviously due to the electron flow from the sugar and phosphate groups in the back bone of the DNA double strands.

All these observed spectral and electrochemical results suggest that the four-coordinate metal complexes intercalate in a better way than the metal derivatives containing axial groups (six-coordinate) as they are blocked from intercalation and hence binds with herring sperm DNA through the grooves. For the present case, the octahedral complex (**4-5**) interacts with DNA through grooves while, the square planar complexes (**1-3**) binds between the DNA base pairs through intercalation.

Circular Dichroism study

The Sensitive mode of DNA binding interaction with molecules is studied using a wonderful Circular Dichroism in diagnosing changes in DNA morphology during drug–DNA interactions. The CD Spectrum of

DNA explains the positive band due to base stacking (275 nm) and the negative one due to right-handed helicity (248 nm). The experiential changes in CD signals of DNA on addition of drugs may often be assigned to the corresponding changes in DNA structure [47-48].

The binding studies were carried out by keeping a constant concentration of DNA solution and varying the concentration of metal complexes [1/R = 0, 1 & 2]. The observed CD spectral changes for herring sperm DNA during interaction with copper complex (**1**) was shown in **Fig. 5.6**. Upon the addition of incremental amounts of the metal complexes (**1**-**3**), both bands experience decrease in their intensities to a large extent. The high decrease in intensity of both positive and negative bands, are of typical for strong intercalation. Intensity of both the positive and negative elipticity bands of DNA decreased along with a slight red shift in the on positive band upon addition of complexes **4 & 5** and these observations clearly indicate that the complexes interact **4 & 5** with DNA through the grooves [49-50].

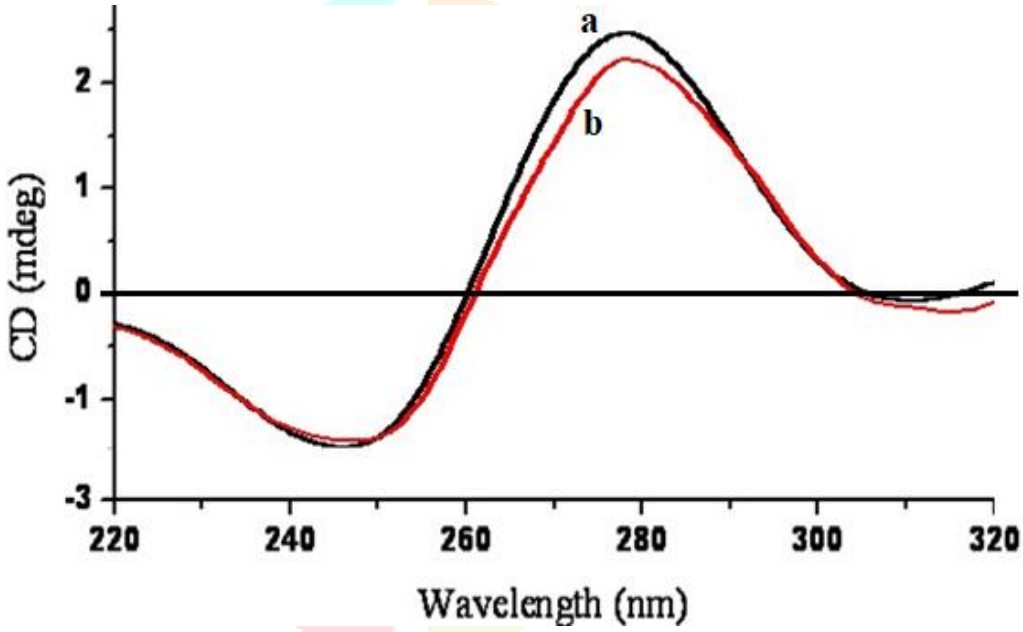


Fig. 5.6. CD spectrum of herring sperm DNA in the absence (a) and presence (b) of [Cu(L)(phen)] (**1**) [DNA] =200 µM, [complex] = 100 µM, (1/R=0.5).

Furthermore, with increasing concentration of complex, it proved difficult to detect any obvious perturbation in the CD spectrum; illustrating the inability of complexes to affect the conformational heterogeneity of DNA anymore by the interaction of complexes. These conclusions are also in unity with those from electronic spectral and cyclic voltammetric studies.

Table 5.1. IR spectral data (cm^{-1}) of metal complexes (**1-5**) in KBr disc

Complexes	υ(C=N)	υ(M-N)	υ(H_2O)
1	1620	495	---
2	1610	480	---
3	1612	472	---
4	1625	470	3300
5	1617	490	3395

Table 5.2. Elemental analysis and electronic spectral data of complexes, **1-5**

Complex	λmax (nm)		
	IL	LMCT	d-d
1	244	322	604
2	278	360	420
3	272	370	614
4	270	326	496
5	265	350	680

Table 5.3. Voltammetric behaviour* of complexes, **1-5** in Acetonitrile

Complex	E_{pc}/mV	E_{pa}/mV	ΔE_p mV	i_{pa}/ i_{pc}
1	221	369	148	0.92
2	-528	-282	246	0.84
3	138	315	177	0.87
4	108	296	188	0.92
5	290	152	138	0.86

* Measured vs Ag/AgCl with TBAP as supporting electrolyte at 100 mVs^{-1}

Table 5.4. Absorption spectral properties of the complexes, **1-5** with DNA in Tris-HCl buffer pH 7.1

Complex	LMCT band λ_{max}/nm Free	Bound	Change in absorptivity	Red shift $\Delta\lambda$(nm)	Binding constant K_b/M^{-1}
1	322	325	Hypochromism	3	0.85×10^5
2	360	362	Hypochromism	2	4.1×10^4
3	370	373	Hypochromism	2	2.9×10^4
4	326	326	Hypochromism	0	2.6×10^3
5	350	350	Hypochromism	0	2.1×10^3

Table 5.5. Voltammetric behaviour[a] of complexes, **1- 5** in the absence and in presence of DNA in Tris-HCl buffer pH 7.1

Complex	R	E_{pc}/V	E_{pa}/V	ΔE_p(mV)	K_{1+}/K_{2+}

1	0 3	0.221 0.226	0.369 0.372	148 146	1.62
2	0 3	-0.528 -0.526	-0.282 -0.278	246 244	2.35
3	0 3	0. 138 0.140	0. 315 0.318	177 178	1.18
4	0 3	0. 108 0.140	0. 296 0.318	188 178	1.18
5	0 3	0. 290 0.140	0. 152 0.318	138 178	1.18

[a]Measured vs. Ag/AgCl electrode: scan rate: 50 mVs^{-1}: supporting electrolyte 5 mM Tris- HCl/ 50 mM NaCl: complex concentration 100 µM

R = [DNA]/[Complex],

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