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Synthesis, Characterization of Bis(Diketimines) Metal (II) complexes and its biological activities

S. Hilda Mabel1 [1], M. Malarvizhi[2]*,

[1]Department of Chemistry, St.John's College, Palayamkottai-627002, India

[2]Research Department of Chemistry, The Madura College, Madurai- 625011, India

Abstract

The Diketimines ligand is prepared from 2-bromo-4-fluoro benzaldehyde actylacetone (bfacac) and p-nitro aniline. These bidentate ligands are coordinated with metal (II) ions and characterized by UV-Vis, IR and CV studies. All the spectral data are confirmed the formation of giant metal (II) complexes. The DNA binding constants of these metal (II) complexes are investigated by UV-vis spectral technique indicate that they bind with an affinity less than the classical intercalators and exhibits relatively binding constant (5.5×10^3 - $5.1 \times 10^4 M^{-1}$). The decrease in current intensity and the small shift observed in formal oxidation potential without any significant shift in their cyclic voltammogram may be attributed to the slow diffusion of metal (II) complexes bound to the large DNA molecules. Complexes **4** and **5** exhibits negative shift and did not show any significant changes in Current intensity. The observed CD spectral studies along with UV-vis spectra reveal that the complexes **1-3** significantly bound to the grooves of the DNA duplex. The spectral and electrochemical studies of the coordination number 4 (complexes **1-3**) reveal that its deep penetration into the core of the DNA through the minor grooves where it forms H-bonding with floor nitrogen/oxygen atoms of the bases of DNA. Coordination number 6 (complexes **4-5**) interacts with DNA through surface mode of binding due to van der Waals force.

Introduction

Inorganic chemistry, most widely developed field in the last few decades is mainly due to that of coordination chemistry and applies very particularly to the coordination of transition metals; however the chemistry of coordination compounds has always been a challenge to the inorganic chemist as it has more branches recently.

In the early days, coordination chemistry seemed to be unusual due to the violation of the usual rules of valence. The modern study of coordination compounds came out after the ideas of Alfred Werner and Jorgensen. Since the formulation of Werner theory many advances have been made in understanding the structure and bonding in the field of coordination compounds. His essential thoughts in the coordination theory is that a metal ion surrounds itself with the ligands and the nature of the ligands, the character of metal ligand bonds and the geometry of the ligands around the metal ion determine the physical and chemical properties of the compounds.

The coordination chemistry has received not only a large amount of experimental study but also a rather extensive theoretical treatment, subsequent to the valence bond theory of metal-ligand bonding several, theoretical chemist used crystal field theory which is purely electrostatic to interpret the spectra of transition metal complexes since this approach was most successful then followed an immediate avalanche of research activity in this area.

Instrumental methods such as IR, UV-Vis and EPR spectroscopy have increased the ability to ascertain the configuration and stereochemistry of complexes formed by the metals. The more stable and wider formations of coordination number four and six are being extensively studied. A new very important developing field is the study of inorganic compounds of biological interest. Proteins, vitamins and enzymes contain metal ion in their structure having macromolecular ligands. Here interest centers on the synthesis of model compounds, which mimic the functional properties of these biomolecules.

The chemistry of metal complexes with multidentate ligands having delocalised orbital such as Schiff bases or porphyrins has recently gained much interest because of their use as models in biological systems especially those respiratory pigments or the coenzymes of vitamin B12.

Metal chelates constitute major and interesting group of coordination compounds. Many properties of chelates are determined by the nature of organic chelating agents, which combines with metal ion. The important consequence of chelating ligand is to force the coordination of donor atoms with the metals. Extensive studies have been conducted with metal complexes of bis-chelates having coordination number four and six. Bis-chelate complexes are formed by almost all the transition metals particularly first transition series. However only those of copper, cobalt, manganese, iron and nickel have been extensively studied from the point of view of their stereochemistry.

A number of metal chelate complexes reported are known to possess medicinal characteristics [1-4]. The first row transition metals are well known for their ability to form a wide range of coordination complexes in which octahedral, tetrahedral and square planar stereochemistries predominate. Copper(II) is a typical transition metal ion in forming coordination complexes but less typical in its reluctance to take up a regular octahedral or tetrahedral geometry. The coordination numbers four, five and six predominate, but variation occurs through bond length or bond angle distortions. Complexation of copper(II) with bidentate ligands depends on spatial arrangements of donor atoms and steric requirement of the ligand molecule.

Nickel is known for its ability to form six coordinate octahedral configuration, four coordinate square planar or tetrahedral configurations due to small free energy difference between each stereochemical form. Four coordinate nickel complexes may have either a square planar structure with A_{1g} or tetrahedral structure with T_{1g} ground term. The stereochemistry also depends on the bulkiness of the ligand structure. Thus in bis-N-alkylsalicylaldimine complexes, the branched alkyl groups stabilize tetrahedral form, while the N-alkyl derivatives stabilize planar structure.

Crystal field stabilization energies are good guide to the stereochemical preference of a metal ion for a particular coordination number. Therefore all six coordinate complexes are identified as octahedral or distorted tetrahedral. Only few such as tris(dithiocarbamate) complex of iron(III) is found to possess trigonal prismatic structure as an exception [5].

Square planar complexes are formed most readily with d^8 (Ni, Pd and Pt) and d9 Cu ions and to a lesser extent with d7 ions. Square pyramidal structures (C.N-5) have CFSE intermediate between octahedral and square planar structures. The Co(II) ion with d^7 configuration favors octahedral over tetrahedral coordination to a smaller extent than any other d^n configuration [6].

The electronic structure of planar complexes formed by divalent ions in the series of manganese and copper are considerably less clear and attempts are being continued towards their establishment. Maki and McGarvey studied the single crystal e.p.r spectra of bis(acetylacetonato)copper(II) [7] and bis(salicylaldiminato)copper(II) [8] have assigned planar structure for those complexes.

Transition metal complexes are of interest for many applications. Uses range from common ones such as catalyst in polymerization [9] and to more specialized one such as application in biological system also. To illustrate an example, one can think of Ziegler-Natta catalyst (Ti-Se) [10] for propylene polymerization. A variety of nickel and cobalt carbonyl may also be utilized [11].

Transition metal complexes derivative from Schiff base ligands have been among the most widely studied coordination compounds [12], since they are becoming increasingly important as biochemical, analytical and antimicrobial reagents. These complexes having certain metal ions are active in many biological processes. The fact that copper, magnesium, cobalt, iron, zinc, chromium and vanadium are essential metallic elements and exhibit great biological activity when allied with certain metal-protein complexes, participating in oxygen transport, electron transfer reactions or the storage of ions [13]. These biological activities have twisted massive attention in the study of systems containing these metals [14]. In some Schiff base metal chelates, it has been exposed that slight deviations in the structure of the ligands markedly affected the activity of the compounds [15-17].

Scope

In the present work, which has begun from our continued interest in the chemistry of metal (II) in different coordination environments, our objective is to explore the chemistry of metal (II) in the coordination environment of bidentated ligand contains Diketimines. These Diketimines are analogous to salicylaldehydimines and acetylacetonimines and hence suggestions a well-known knowledge in a modified system. The newly modified diketimine complexes has synthesized in this chapter (**Scheme -6.1**) and discuss their characterization using various technique.

Experimental methods

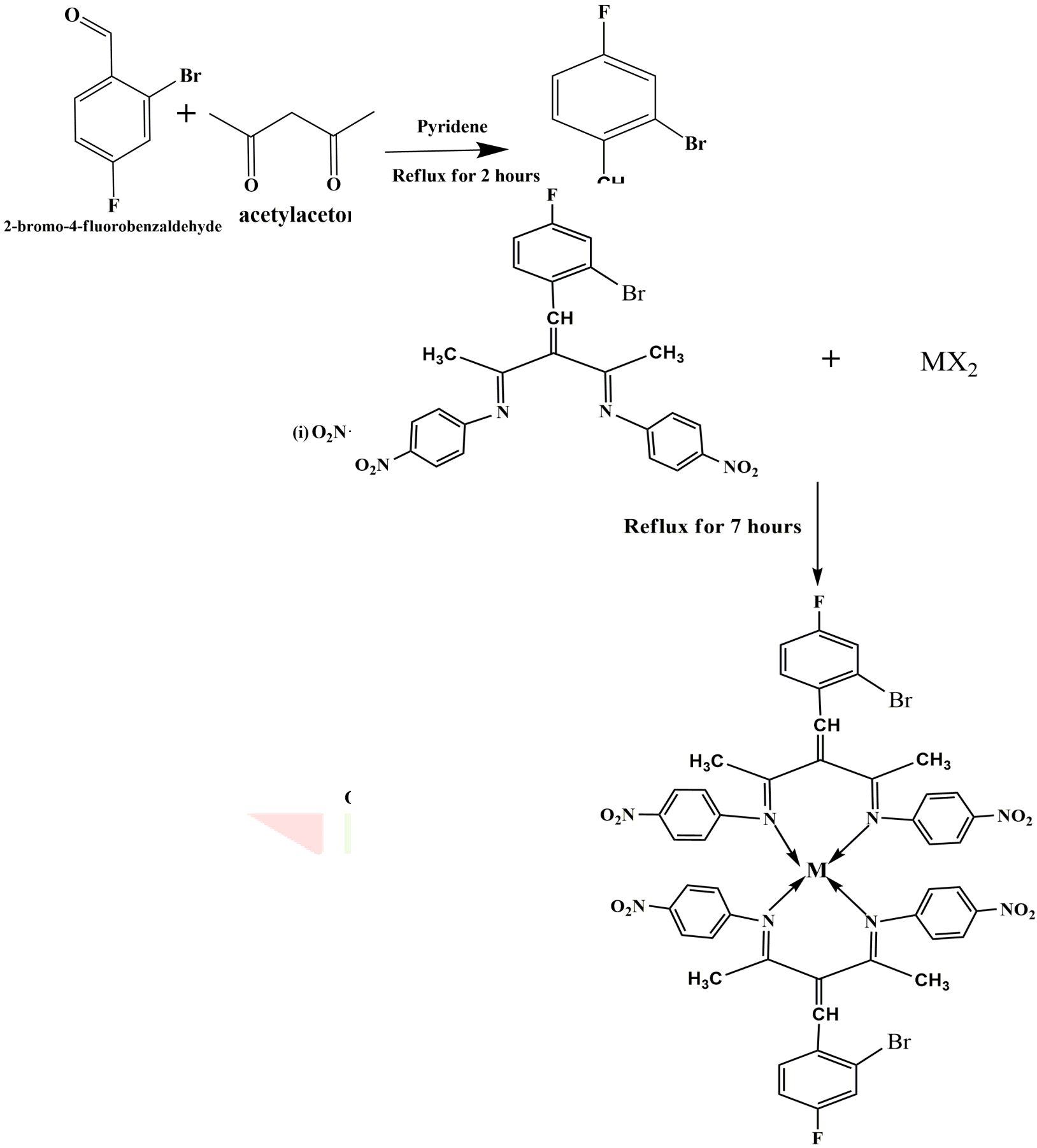
In chapter II, details of the instruments used for various physical measurements (IR, UV-Vis, NMR, EPR, CV, CD and gel electrophoresis studies) have been discussed.

Synthesis of Metal (II) complexes

IV and V chapters have discussed the preparation of metal (II) complexes in an *in-situ* manner as reported [18]. In this chapter, p-nitro aniline is used instead of p-chloro aniline. The metal (II) chloride ratio is reduced twice compare to the ligands (Metal (II) chloride and ligands ratio are 1: 2). The two bidentate ligands are coordinated with metal ions. It is characterized using various techniques in the result and discussion part.

The coloured solid metal (II) complexes were recrystallized from acetonitrile. The structure of the complexes and yield are listed below. In this chapter, coordination number 4 & 6 complexes are successfully prepared by the above technique. All the five Schiff based Metal (II) complexes ($[Cu(L)_2]$ (**1**), $[Mn(L)_2]$ (**2**), $[Ni(L)_2]$ (**3**), $[Co(L)_2 (H_2O)_2]$ (**4**), $[Fe(L)_2(H_2O)_2]$ (**5**), synthesized using the above procedure, are shown in the **Scheme 6.1.**

Coordination Number	Metal (II) Complexes	Color	Yield (%)
4	$[Cu(L)_2]$ (**1**)	Greenish brown	60
	$[Mn(L)_2]$ (**2**)	Deep brown	65
	$[Ni(L)_2]$ (**3**)	Brown	60
6	$[Co(L)_2(H_2O)_2]$ (**4**)	Dark brown	64
	$[Fe(L)_2(H_2O)_2]$ (**5**)	Reddish brown	65
L= Diketimines-NO_2			


Pyridene
Reflux for 2 hours
Reflux for 7 hours
+ MX2
2-bromo-4-fluorobenzaldehyde
acetylaceto
(i) O2N·

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 6.1**.

The IR spectra of the metal complexes show bands in the region 1616-1658 cm^{-1} which are assigned to υ(C=N) stretching vibration, which indicate the presence of azomethine group. The bands within 450 - 489 cm^{-1} are assigned to υ(M—N) stretching vibrations, respectively [19]. These bands confirmed the coordination of the schiff base to the metal ions. The band in the region 1396 - 1452 cm^{-1} corresponds to υ(C=C) stretching vibration due to phenyl group, indicating the coordination of schiff base to the metal ions. The above stretching frequencies are relevant to the characterization of the complexes. The representative spectrum of the complex is shown in the **Fig. 6.1. & 6.2**.

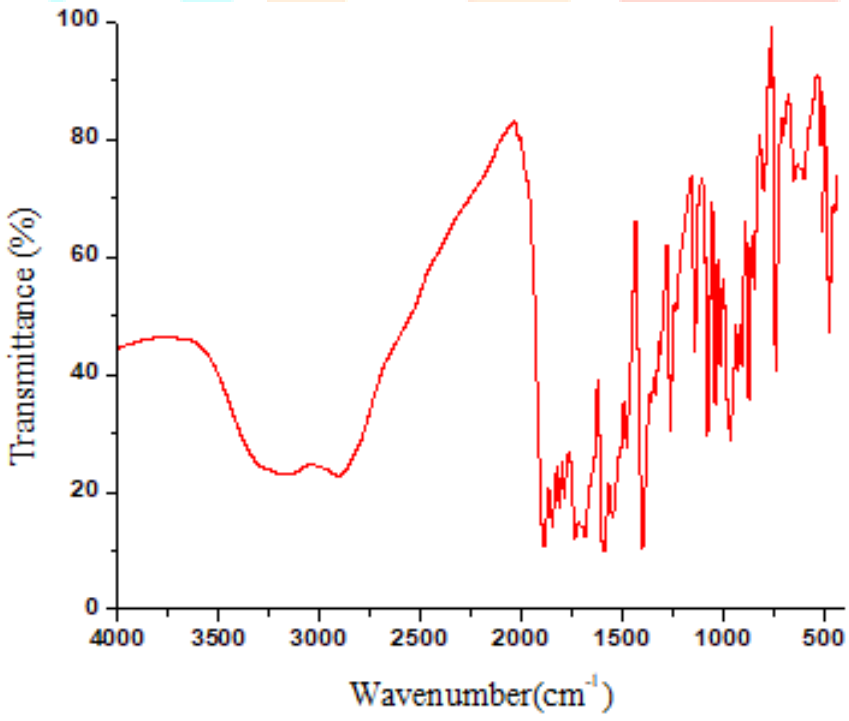


Fig. 6.1. IR spectrum of $[Co(L)_2(H_2O)_2]$ **(4)** in KBr disc

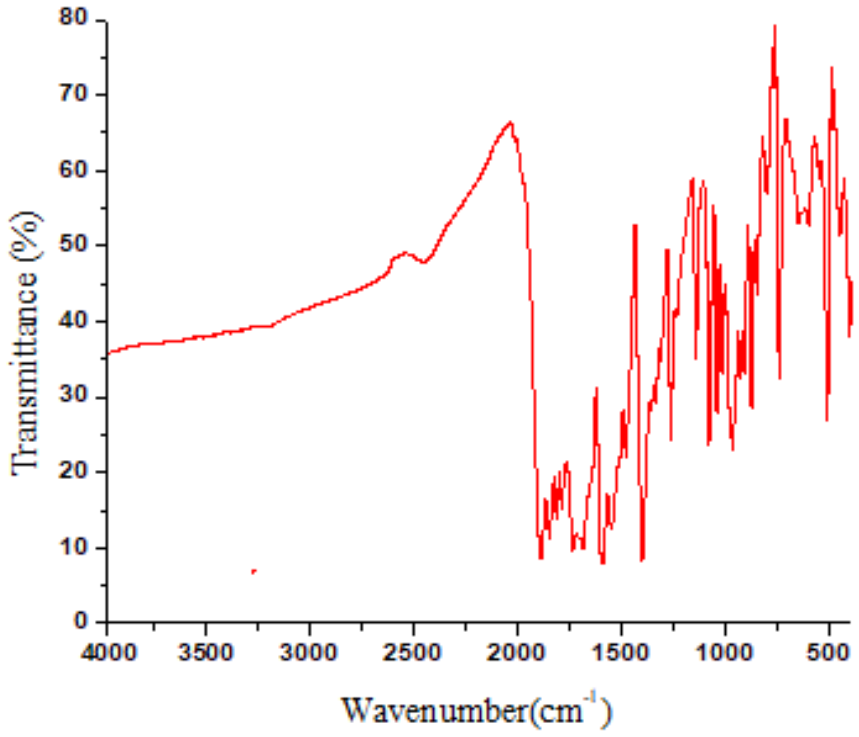


Fig. 6.2. IR spectrum of $[Cu(L)_2]$ (**1**) in KBr disc

The complex 4 shows a strong band in the 1390 cm^{-1} region correspond to ν (C-N) vibration. The phenyl ring vibrations of all complexes are appeared in the region 1410-1460 cm^{-1} and 720-740 cm^{-1}. The octahedral complexes (**4-5**) formation are confirmed by appearance of a broad stretching frequency around 3200-3400 cm^{-1} due to presence of water molecules. The stretching frequency of H_2O molecules did not appear in coordination number 4 (complexes **1-3**) due to metal chelated with bidentated ligand only.

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 charge transfer bands usually appear in the UV region may sometime tails into the visible region. Such charge transfer transitions are not forbidden by selection rules and hence they are more intense.

In the UV region, all the metal complexes (**1-5**), exhibited their corresponding d-d band in the 590-670 nm region [20]. The two strong bands are acquired in the range 370-440 nm and 260-310 nm due to the LMCT

band and inter-ligand band respectively (**Table 6.2**). The intense broad band in the region 550-650 nm for the copper(II) complex (**1**) may be assigned to the square planar copper (II) by analogy with the spectra of other square planar copper(II) species (**Fig. 6.3**.) [21].

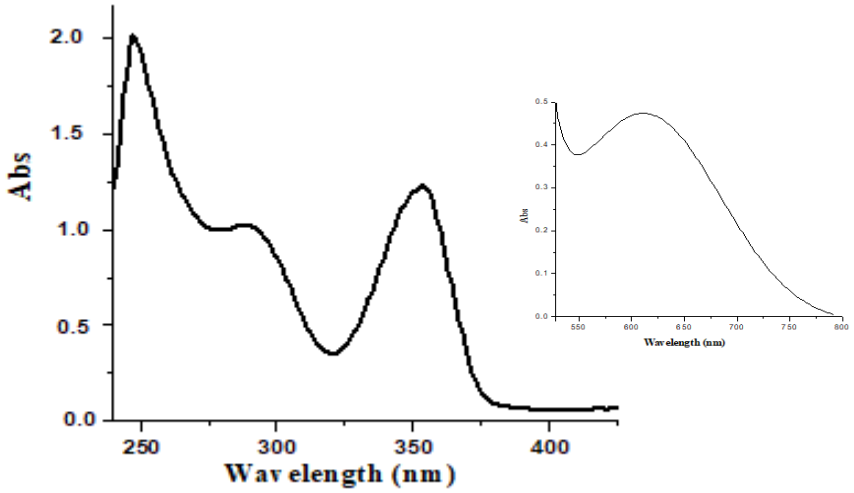


Fig. **6.3**. UV-vis absorption spectrum 1 x10^{-4} M solution of [Cu(L_2] (**1**) (insert : d-d transition) in acetonitrile.

Redox chemistry

Cyclic Voltammetry (CV) is perhaps the most versatile electro analytical technique for the study of electro active species. Its versatility combined with ease of measurement has resulted in extensive use of cyclic voltammetry in the field of electrochemistry. Cyclic voltammetry is often the best experiment performed in the electrochemical study of compounds, biological material or an electrode surface. The effectiveness of CV results from its capability of rapidly observing redox behavior over a wide potential range makes it one of the best for the study of electroactive species. The resulting voltammogram conveys information as a function of energy scan.

Cyclic voltammetry determines the electrode reversibility indirectly by measuring the apparent standard rate constant for electrons transfer from cathodic (or anodic) polarization. CV studies are great help in understanding the general theory of redox reactions providing useful insight into M-L bonding, intramolecular transfer and concept of oxidation state in coordination chemistry. They are also useful for tailoring of redox reagents, elucidation of mechanisms of redox catalyst and biological electron transfer process. Moreover as redox orbitals are involved in a redox series, they can be utilized to probe the extent to which different substituents effects the various redox orbitals involved. Copper(II), nickel(II), cobalt(II), manganese(II) and Iron (II) complexes in DMSO undergo one electron reduction and one electron oxidation to form monovalent and trivalent metal species. The representative CV's are shown in **Table 6.3.**

The bis(Diketimines) metal (II) complexes are exhibited a quasi-reversible redox couple with ΔEp around 110 – 250 mV [22,23]. In this chapter, the cathodic and anodic peaks of all the complexes are slight shifted towards positive potential compare to V chapter. It indicates a strong coordination between the two bidenate ligand and metal (II) ion. This bidentate ligands system exhibits a quasi-reversible redox couple with △Ep = 242 mV characteristic of $Mn^{II/III}$ redox couple with Epa at -275 mV and Epc at -517 mV.

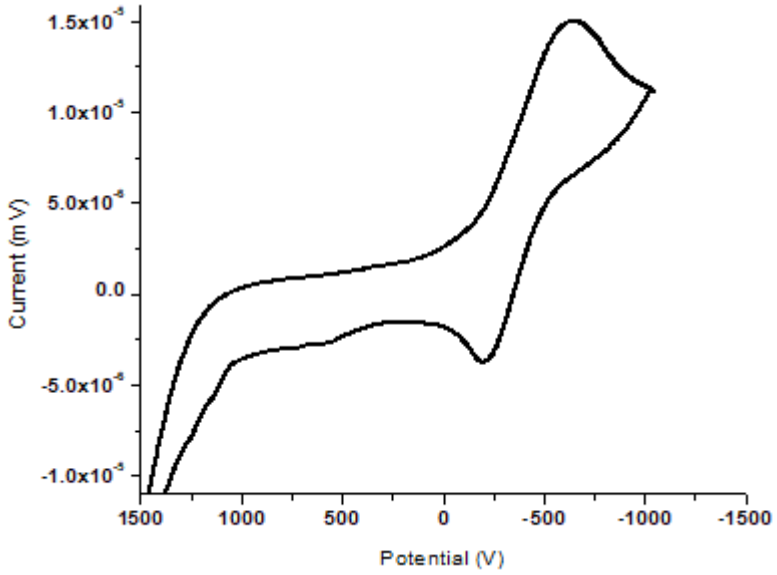


Fig. 6.4. Cyclic voltammogram of $[Mn(L)_2]$ (**2**) in DMSO with TBAP as supporting electrolyte at a scan rate of 100 mVs-1

DNA binding studies

Absorption spectral studies

The absorption spectral titration of the metal (II) complexes with herring sperm DNA was followed by monitoring the changes in their $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. Hypochromism along with a slight red shift was observed for complexes (**1-3**) in their UV-vis absorption studies indicate that they are weakly bound through the major grooves of the DNA, where the nitrogen and oxygen are projecting inside the floor of the DNA. The observed hyperchromism with slight blue shift for complexes (**4-5**) clearly indicates that there is an interaction on the surface of DNA through van der Waals interaction or H-bonding with the surface phosphate groups. The spectral titration data of all complexes (**1-5**) were given in **Table 6.4**., and the values of equilibrium DNA binding constants, K_b, were determined using the following Eq. (1) [24-25]:

$$[DNA]/(\varepsilon_A-\varepsilon_F) = [DNA]/(\varepsilon_B-\varepsilon_F) + 1/K_b(\varepsilon_B-\varepsilon_F) \quad \text{---------- (1)}$$

Where ε_A, ε_F, and ε_B correspond to A_{obsd}/[drug], the extinction coefficient for the free organic nanocrystalline drug and the extinction coefficient of fully bound form, respectively. From the slope and y-intercept of the linear

fit of [DNA]/(ε_A-ε_F) *versus* [DNA] plot, K_b which is equal to the ratio of slope to the intercept can be calculated.

The intrinsic binding constants (K_b) determined from the decay of the absorbance for the complexes **1-5** are 0.8 x 10^5 M^{-1}, 3.24 x 10^4 M^{-1}, 5.8 x 10^4 M^{-1} 2.5 x 10^3 M^{-1} and 1.5 x 10^3 M^{-1} respectively.

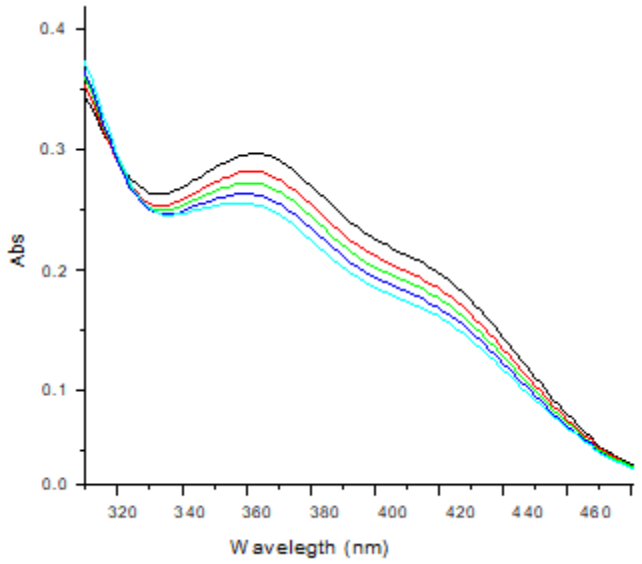


Fig. 6.5. UV-vis absorption spectra of Iron (II) complex (**5**): in the absence (R = 0) and in the presence (R = 0.5, 1, 1.5 and 2) of DNA in Tris-HCl buffer (pH = 7.1). R = [DNA]/[drug]

These characteristics changes observed in the UV-vis, suggest the contribution of these complexes in self-assembling with the DNA through the minor grooves. Due to differences in the molecular size, substituents and shape the mode of binding also changes.

Electrochemical studies

The electrochemical investigations of DNA interactions with meatl (II) complexes can offer a valuable supplement to spectroscopic methods. Electrochemical methods contrast from spectroscopic methods by their sensitivity, simplicity and versatility and yield more information about the mechanism of binding mode.

The peak potential and current intensity for these complexes in CV were monitored to study their mode of interactions during the increasing concentration of DNA [26].

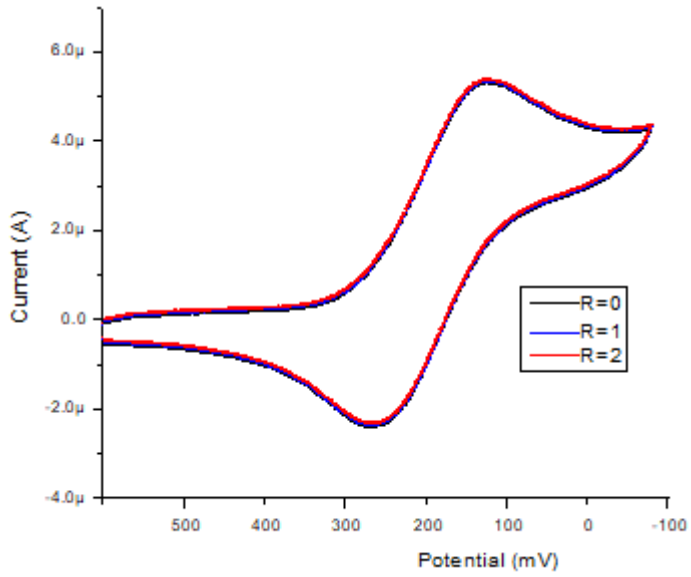


Fig. 6.6. Cyclic voltammograms of $[Co(L)_2(H_2O)_2]$ (**4**)in the absence and in the presence of DNA (R = 0, 1 & 2) in Tris-HCl buffer (pH = 7.1).

In the previous chapter (III-V), all metal complexes are exhibited decrease the current intensity with slight positive shift due to mode of binding relevant with partial intercalation. But here the complexes (**1-3**) did not show any significant shift in its formal potential while complexes (**4-5**) experiences a negative potential shift accompanied by a considerable decrease in voltammetric current.

In the light of Bard's report [25], the negative shift obtained in the peak potential for complexes (**4-5**) indicates a remarkable association of the drug with DNA through surface binding.

CD spectra

Circular dichroic spectral technique is useful in diagnosing the changes in the DNA structure during the small drugs-DNA interactions, as the bands at 275 and 248 nm due to base stacking and right-handed helicity respectively are quite sensitive to the mode of DNA interactions with small molecules [27]. The changes in CD signals of DNA observed on interaction with drugs may often be assigned to the corresponding changes in the DNA structure too [28].

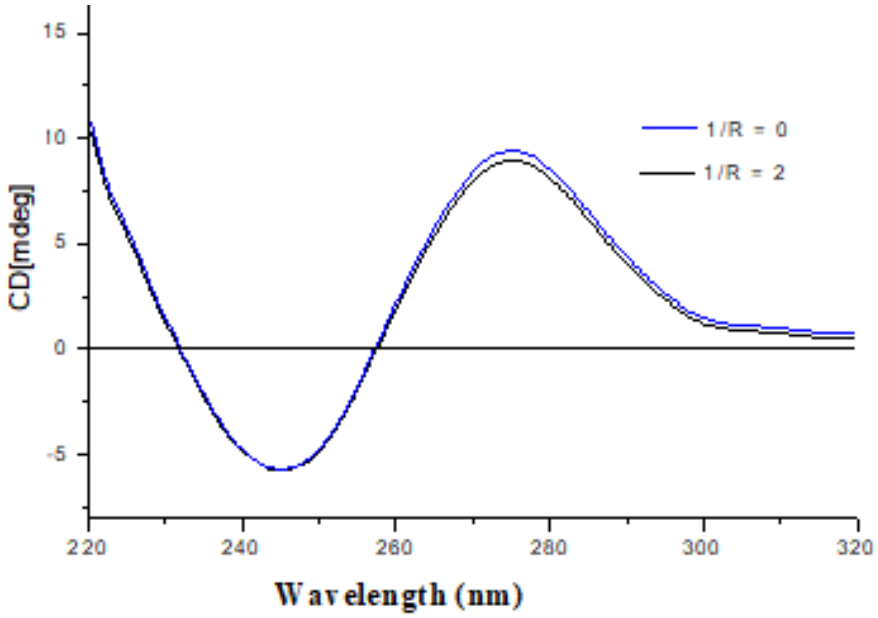


Fig. 6.7. CD spectra of herring sperm DNA in the absence and in the presence of [Cu(L_2] (**1**) (for 1/R = 0 & 2) in Tris-HCl buffer (pH = 7.1), (1/R = [complex]/[DNA]) .

Simple groove binding and electrostatic interaction of metal complexes will show less or no perturbation on the base-stacking and helicity bands. However, intercalation enhances the intensities of both positive and negative bands and stabilizes the right-handed B conformation of DNA as observed for the Ruthenium metal complexes [29].

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 (**1-3**) and these observations clearly indicate that the complexes (**1-3**) interact with DNA through the grooves [29]. But the presence of giant molecule of bidentated ligand contains the phenyl ring is not expected to allow it to stack in between the base pairs, instead it is expected that the complexes may sit on the minor grooves. The complexes (**4-5**) did not show any significant change during the addition of DNA in both bands due to its surface interaction.

The spectral and electrochemical studies for these complexes reveal that, different modes of binding are observed depending on the molecular structure, substituents, size and solubility. The complexes (**1-3**) sits on the minor grooves and the substituents penetrate deep into the core of the DNA to form H-bonding with the floor nitrogen and oxygen atoms of the bases. Interaction between complexes (**4-5**) and DNA might be through van der Waals force, on the surface of DNA duplex.

Table 6.1. IR spectral data (cm^{-1}) of metal complexes (**1-5**) in KBr disc

Complexes	υ(C=N)	υ(M-N)	υ(H_2O)
1	1638	489	---
2	1616	460	---
3	1620	450	---
4	1658	465	3250
5	1617	470	3305

Table 6.2. Elemental analysis and electronic spectral data of complexes, **1-5**

Complex	λmax (nm)		
	IL	LMCT	d-d
1	246	340	620
2	270	370	490
3	275	390	620
4	277	358	510
5	264	368	685

Table 6.3. Voltammetric behaviour* of complexes, **1-5** in Acetonitrile

Complex	E_{pc}/mV	E_{pa}/mV	ΔE_p mV	i_{pa}/ i_{pc}
1	225	372	147	0.90
2	-517	-275	242	0.81
3	142	326	184	0.77
4	112	280	168	0.83
5	298	157	141	0.86

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

Table 6.4. Absorption spectral properties of the complexes, **1-5** with DNA in Tris-HCl buffer pH 7.1

Complex	LMCT band λ_{max}/nm		Change in absorptivity	Red shift $\Delta\lambda$(nm)	Blue shift $\Delta\lambda$(nm)	Binding constant K_b/M^{-1}
	Free	Bound				
1	340	341	Hypochromism	1	---	0.8×10^5
2	370	371	Hypochromism	2	----	3.2×10^4
3	390	392	Hypochromism	2	----	5.8×10^4
4	358	356	Hypochromism	--	2	2.5×10^3
5	368	365	Hypochromism	--	3	1.5×10^3

Table 6.5. 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	0.225 0.226	0.372 0.372	147 148	1.60
2	0 3	-0.517 -0.517	-0.275 -0.276	242 243	2.15
3	0 3	0. 142 0.142	0. 326 0.326	184 184	1.10
4	0 3	0. 112 0.112	0. 280 0.278	168 166	1.18
5	0 3	0. 298 0.295	0. 157 0.155	141 140	1.16

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

R = [DNA]/[Complex],

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