Part I
Synthesis and Characterization

Chapter 3

CHAPTER 3

STUDIES ON SCHIFF BASE, 3-(1H-INDOL-3-YL)-2-[(E)-(THIOPHEN-2-YL METHYLIDENE)AMINO]PROPANOIC ACID AND ITS TRANSITION METAL COMPLEXES

The Schiff base, 3-(1H-indol-3-yl)-2-[(E)-(thiophen-2-ylmethylidene)amino] propanoic acid (I3YT2YMAPA) was synthesized and characterized by IR, UV-visible, NMR and mass spectroscopic techniques. Elemental analysis was also carried out. Transition metal complexes of this ligand were prepared with Cr(III), Ni(II), Cu(II) and Zn(II) ions. All the complexes were characterized by NMR, IR and UV-visible spectroscopic methods, magnetic moment measurements, elemental analysis and molar conductance measurements. The synthesis and characterization of the ligand and complexes are detailed in this chapter.

Synthesis of ligand

Equimolar mixture of thiophene-2-carbaldehyde and (s)-2-amino-3-(3-indolyl) propanoic acid were taken in ethanol medium and was refluxed for 3 hours on a water bath. The volume of the reaction mixture was reduced by evaporation and cooled. Then the mixture was poured into ice cold water to obtain pale yellow coloured solid. The heterocyclic Schiff base, 3-(1H-indol-3-yl)-2-[(E)-(thiophen-2-ylmethylidene)amino] propanoic acid was obtained with 78% yield and the melting point noted was 264^0C. The elemental analysis data of the ligand is given in Table 1.2.

Characterization of ligand

All the ligands were amorphous solids and stable to light and air. They were characterized by various techniques and the details are given below.

IR spectral studies

Characteristic stretching frequencies of various bonds in I3YT2YMAPA were obtained from the IR spectrum. The data is given in Table 1.3. A sharp peak observed at $3400cm^{-1}$, corresponds to stretching vibration of the N-H group in the indole ring. Another band of fairly strong intensity at $3039cm^{-1}$ was due to the aromatic C-H bond stretching vibration. The C-H bond involving sp^3 hybridized carbon gave characteristic bands at $2927cm^{-1}$ and $2854cm^{-1}$. The asymmetric stretching vibrations of the caboxylate group appeared as a band of medium intensity at $1664cm^{-1}$. A sharp peak was obtained at $1591cm^{-1}$ which was characteristic of the azomethine group. A band at $1014cm^{-1}$ corresponds to υ_{C-O}. In plane and out of plane deformations were shown at $1014cm^{-1}$ and $746cm^{-1}$ respectively.
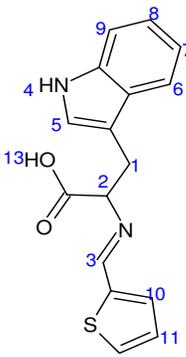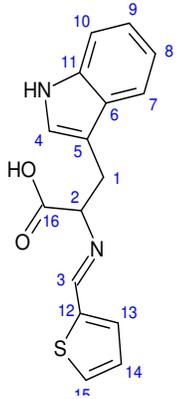
NMR spectral studies
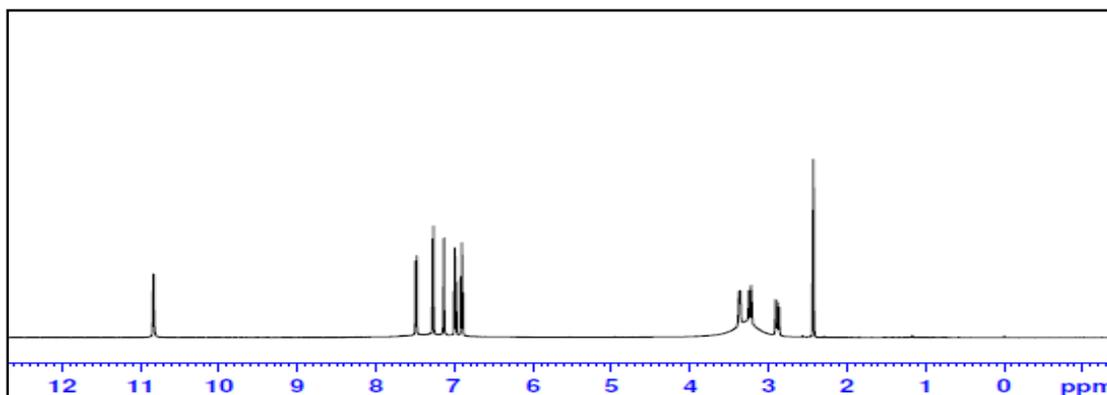
The ^1Hnmr spectrum of the Schiff base is given in Figure 1.1. Thirteen non equivalent hydrogen atoms which were in different electronic environments gave characteristic peaks in the nmr spectrum. The assignments of the signals are given in Table 1.1. The carboxylic proton in the molecule gave a distinct singlet at 10.83δ. A peak at 3.37δ can be assigned to the azomethine proton. The NH proton in the tryptophan part appeared as a broad signal at 3.24δ. The presence of a sharp singlet at 2.43δ can be assigned to the CH proton in the five membered ring of the tryptophan part. A peak obtained at 2.89δ can be assigned to CH_2 group adjacent to the indole ring. The aromatic protons gave characteristic peaks at 6.8-7.5δ.

The proton decoupled $^{13}Cnmr$ spectrum of the Schiff base is represented in Figure 1.2. Sixteen carbon atoms in different electronic environments gave their own
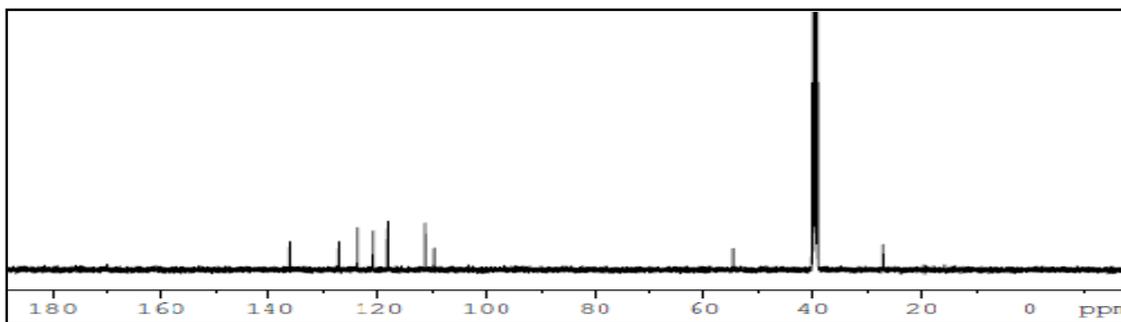
characteristic peaks in the spectrum. The signal of the carboxylic acid carbon appeared at 169.78ppm. The azomethine carbon showed a peak at 136.32ppm. The aromatic carbons in the thiophene and tryptophan rings appeared at 109.73-136.32ppm region. Methylene and azomethine carbon atoms exhibited their peaks at 27.19 and 54.78ppm respectively. The signal assignments are given in Table 1.1.

Table 1.1 ^{1}Hnmr and ^{13}Cnmr spectral data of I3YT2YMAPA

| ^{1}Hnmr			^{13}Cnmr		
	δ value	Assignment/ Labelled No.	δ value	Assignment/ Labelled No.	
	2.89	1(CH₂)	27.19	1(CH₂)	
	2.43	2	54.78	2	
	3.37	3(CH=N)	136.32	3(CH=N)	
	3.24	4(NH)	123.96	4	
	7.13	5	109.73	5	
	7.27	6	109.73	6	
	6.91	7	118.23	7	
	6.99	8	111.28	8	
	7.49	9	111.28	9	
	7.27	10	118.23	10	
	6.90	11	136.32	11	
	7.49	12	127.26	12	
	10.83	13(COOH)	118.34	13	
			120.86	14	
			118.34	15	
			169.78	16(COOH)	

Fig.1.1 ^{1}Hnmr spectrum of I3YT2YMAPA

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Fig.1.2 ^{13}Cnmr spectrum of I3YT2YMAPA

Mass spectral studies

The molecular ion peak appeared at m/z 298 as a very weak signal and isotopic peaks were found to be absent. The base peak was shown at m/z 130 due to $[C_9H_8N]^+$ ion. The loss of OH moiety gave a signal at m/z 281. A medium intensity peak at m/z 204 corresponds to the fragment $[C_{11}H_{12}N_2O_2]^+$. The $[C_8H_7N]^+$ fragment showed a signal at m/z 117. The appearance of peaks at m/z 103 and 77 were due to the fragments $[C_8H_7]^+$ and $[C_6H_5]^+$ respectively. The mass spectrum is represented in Figure 1.3.
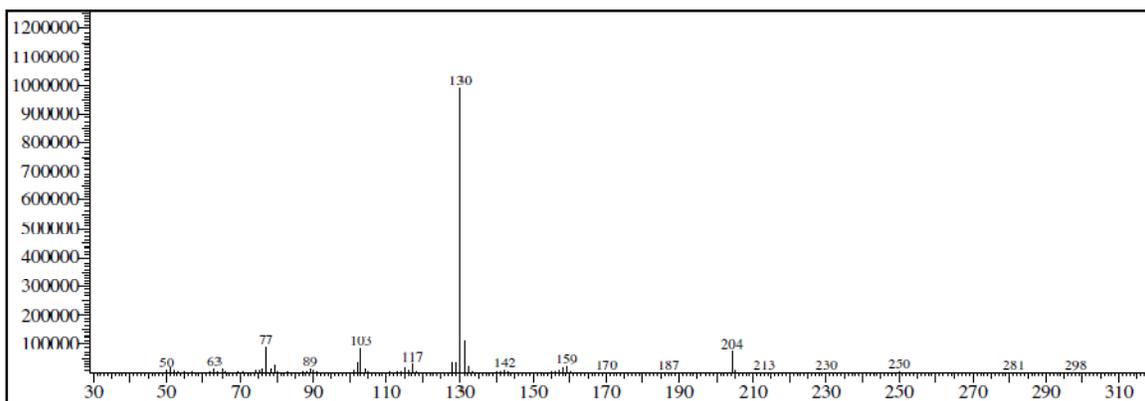

Fig.1.3 Mass spectrum of I3YT2YMAPA

Electronic spectral studies

Two peaks were obtained in the UV-visible spectrum of the Schiff base. They were exhibited at 35335cm^{-1} and 32679cm^{-1} which can be assigned to $\pi \rightarrow \pi^*$ and n$\rightarrow \pi^*$ transitions respectively.

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All the above characterization results lead to the assignment of structure of the Schiff base, 3-(1H-indol-3-yl)-2-[(E)-(thiophen-2-ylmethylidene)amino]propanoic acid (I3YT2YMAPA) as shown in Figure 1.4.
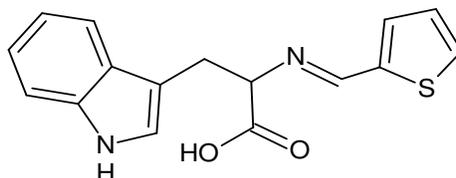
Fig.1.4 Structure of I3YT2YMAPA

Synthesis of complexes

Cr(III), Ni(II), Cu(II) and Zn(II) complexes of the Schiff base, 3-(1H-indol-3-yl)-2-[(E)-(thiophen-2-ylmethylidene)amino]propanoic acid (I3YT2YMAPA) were synthesized as follows.

Acetate salts of chromium, nickel, copper and zinc were used for the synthesis. 2mM solution of the Schiff base, I3YT2YMAPA in 15ml ethanol was refluxed on a water bath. When the solution was boiled, 2mM hot ethanolic solution of the metal salt was added and again refluxed for 2 hours. Then reduced the volume, cooled and poured the contents into ice cold water. The precipitated complex was filtered, washed and dried over an. $CaCl_2$. Melting points of the complexes were noted. The melting points of all the complexes were higher than that of the ligand.

Characterization of complexes

All the complexes were amorphous solids and stable to light and air. They are characterized by various techniques like elemental analysis, magnetic moment

measurements, molar conductance studies, spectral studies and thermogravimetric analysis. The details are given below.

Elemental analysis

Elemental analysis provides the key to structural determination of the complexes. The metal percentage of copper complex was determined by volumetric method iodometrically while that of chromium and nickel complexes were done by colorimetric and gravimetric methods respectively. The theoretical and calculated values were found to be in good agreement in the case of all complexes. 1:1 stoichiometry was found to exist between the metal and ligand in all the chelates. The CHNS data of the complexes are given in Table 1.2 which also establishes the 1:1 ratio between metal and ligand.

Magnetic moment studies

Magnetic moment measurements helped in ascertaining the geometries of the complexes. The Cr(III) and Ni(II) chelates were found to have magnetic moment 3.61BM and 2.99BM respectively and octahedral geometry was assigned for both complexes. In the case of copper complex μ_{eff} was 1.61BM and hence square planar geometry was fixed for it[46]. Diamagnetic character was found for Zn(II) complex, which is quite justifiable with its d^{10} configuration and hence tetrahedral geometry was assigned[47].

Molar conductance studies

The electrolytic behaviour of metal chelates was investigated by molar conductance studies. The measurements were done in DMSO medium and all chelates showed molar conductance in the range $5\text{-}7\Omega^{-1}cm^2mol^{-1}$. So non-electrolytic behaviour was assigned for all the chelates. It can also be confirmed that counter ions were absent outside the coordination sphere. The data is represented in Table 1.2.

IR spectral studies

The IR spectral data of the ligand and metal chelates are displayed in Table 1.3. The shifting in vibrational frequencies of the complexes on comparison with that of the ligand can be clearly understood from the data provided. The vibrational frequency of the azomethine group was found to be lowered in the case of all complexes which confirmed the coordination of the group towards the metal ion[48-50]. Appearance of new bands around $3330cm^{-1}$ for all the complexes ensured the presence of coordinated water molecules. Antisymmetric and symmetric stretching vibrations of the COO group gave characteristic peaks in the spectrum of all the chelates. The shift in frequency of these bands to lower region establishes the coordination through the carboxylate oxygen to the central metal ion. Moreover the appearance of new bands for M-O and M-N bonds, unequivocally confirm the ON donor sites of the Schiff base.

NMR spectral studies

The NMR spectra of the complexes were complicated when compared to that of the ligand. All the peaks showed downward shift in the spectra which ensured the binding of the ligand with the metal ion through coordination sites. The disappearance of COOH peak in the spectra of chelates confirms the metal-oxygen bond through carboxylate group, after deprotonation.

Electronic spectral studies

The complexes exhibited additional bands for d-d transitions and charge transfer processes, other than the intra ligand electronic transitions (ILT). Upon complex formation all the ILT bands were shifted to longer wavelength region. Cr(III) complex showed three d-d transitions at $26463cm^{-1}$, $31354cm^{-1}$ and $37325cm^{-1}$ which were due to

$^4A_2(F) \rightarrow {}^4T_2$, $^4A_2(F) \rightarrow {}^4T_2(F)$ and $^4A_2 \rightarrow {}^4T_1(P)$ transitions respectively in the octahedral field. The Ni(II) complex exhibited two bands at $31328cm^{-1}$ and $33671cm^{-1}$ which corresponds to $^3A_2 \rightarrow {}^3T_2$ and $^3A_2 \rightarrow {}^3T_1(F)$ electronic transitions. These transitions confirmed the octahedral geometry for the chelate[51]. For the Cu(II) complex, two bands at $29158cm^{-1}$ and $39217cm^{-1}$ can be assigned to the transitions $^2B_1 \rightarrow {}^2A_1$ and $^2B_1 \rightarrow {}^2B_2$ respectively and hence suggested square planar geometry. Appearance of an intense peak at $26732cm^{-1}$ in the electronic spectrum of Zn(II) complex was due to ligand to metal CT band.

Thermogravimetric studies

Thermogravimetric analysis of the Ni(II) complex of I3YT2YMAPA exhibited three stage decomposition pattern. The first stage comprised of two substages. In the first substage $(60-120^0C)$ the coordinated water molecule was lost from the chelate molecule. The remaining two water molecules and the acetate group were lost in the next substage $(120-305^0C)$. The second stage represented the loss of tryptophan moiety from the ligand. Finally rest of the ligand was undergone decomposition so as to yield the oxide (NiO) and represented the third stage. The overall mass loss according to the TG curve is 84.20%. The theoretical mass loss for the conversion of the complex into metal oxide is 84.08%. The results are well documented in part IV.

All the above discussions clearly established that the structures of metal chelates of I3YT2YMAPA are as represented in Figure 1.5.
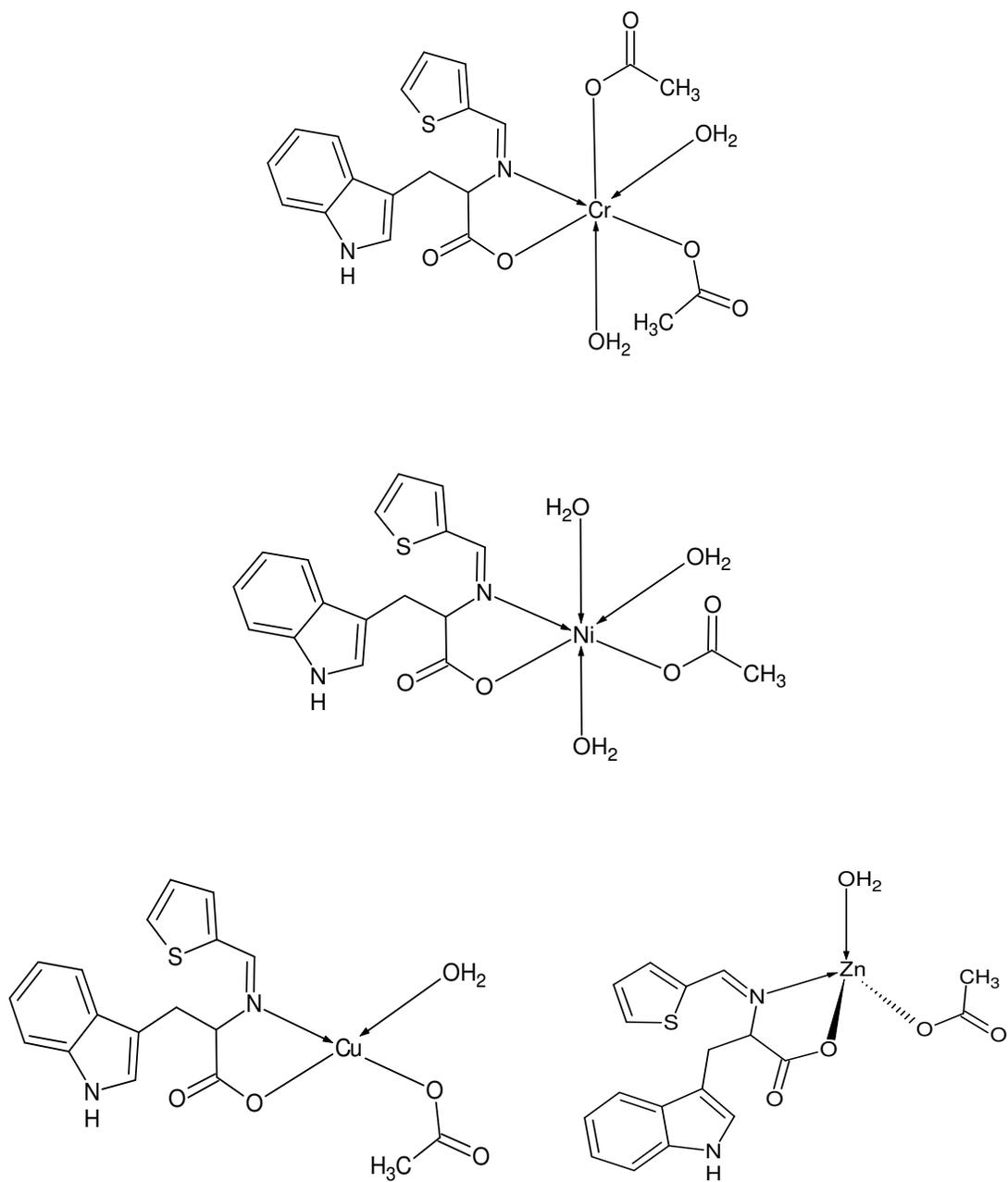
Fig.1.5 Structures of metal complexes of I3YT2YMAPA

Table 1.2 Microanalytical, magnetic and conductance data of the ligand I3YT2YMAPA and its transition metal complexes

Complex	Colour	Yield (%)	Mol. Wt.	M.P (^{0}C)	Metal % Found (Calculated)	C % Found (Calculated)	H % Found (Calculated)	N % Found (Calculated)	S % Found (Calculated)	μ_{eff} (BM)	Molar Conductance ($\Omega^{-1}cm^2mol^{-1}$)	Geometry
I3YT2YMAPA (LH)	Palle yellow	78	298	264	-	63.98 (64.43)	4.67 (4.70)	9.84 (9.40)	10.68 (10.74)	-	-	-
[CrLAc$_2$(H$_2$O)$_2$]	Pale brown	68	503	>300	10.26 (10.34)	46.88 (47.71)	4.31 (4.77)	6.21 (5.57)	5.86 (6.36)	3.61	6	Octahedral
[NiLAc(H$_2$O)$_3$]	Pale Green	73	469	>300	13.25 (12.52)	45.97 (46.08)	4.71 (5.33)	5.74 (5.97)	6.04 (6.83)	2.99	5	Octahedral
[CuLAc(H$_2$O)]	Blue	80	438	262	14.98 (14.52)	50.34 (49.37)	4.53 (4.11)	6.98 (6.39)	8.57 (7.31)	1.61	6	Square planar
[ZnLAc(H$_2$O)]	Off white	66	440	>300	14.80 (14.88)	48.46 (49.16)	5.11 (5.00)	6.27 (6.37)	7.10 (7.28)	D	7	Tetrahedral

Ac: Acetate, D: Diamagnetic

Table 1.3 Characteristic infrared absorption frequencies of I3YT2YMAPA and its transition metal complexes

Complex	υ_{N-H}	υ_{H2O}	υ_{C-H} (Ar)	υ_{C-H} (SP^{3}C)	υ_{COO} (asym)	$\upsilon_{C=N}$	υ_{COO} (sym)	υ_{C-O}	In plane bending	Out of plane bending	υ_{M-O}	υ_{M-N}
I3YT2YMAPA (LH)	3400	-	3039	2927, 2854	1664	1591	-	1129	1014	746	-	-
[CrLAc$_2$(H$_2$O)$_2$]	3402	3305	3138	2929	1631	1583	1541	1242	1004	758	640	510
[NiLAc(H$_2$O)$_3$]	3404	3332	3057	2922, 2852	1630	1583	1456	1233	1045	744	628	503
[CuLAc(H$_2$O)]	3388	3334	3095	2906	1625	1571	1473	1105	1006	738	601	508
[ZnLAc(H$_2$O)]	3402	3331	3120	2954, 2389	1618	1595	1454	1089	1043	740	598	491