

Part I

Synthesis and Characterization

Chapter 4

Nimmy Kuriakose “Physicochemical, thermoanalytical, electrochemical and antitumour studies of transition metal complexes of schiff bases derived from heterocyclic carbonyl compounds” Thesis. Department of Chemistry, St. Thomas College, University of Calicut, 2015

CHAPTER 4
STUDIES ON SCHIFF BASE, 3-[THIOPHEN-2-YLMETHYLENEAMINO]
BENZOIC ACID AND ITS TRANSITION METAL COMPLEXES

A novel Schiff base (E)-3-[thiophen-2-ylmethyleneamino]benzoic acid was synthesized and characterized by elemental analysis and various spectroscopic techniques. The chelating efficacy of the ligand was explored by synthesizing transition metal complexes with metal ions of chromium, nickel, copper, zinc and cadmium. The details of synthesis and characterization of both the ligand and complexes are detailed in this chapter.

Synthesis of ligand

The Schiff base (E)-3-[thiophen-2-ylmethyleneamino]benzoic acid (T2YMABA) was synthesized by mixing equimolar mixture of ethanolic solutions of thiophene-2-carbaldehyde and 3-aminobenzoic acid. The mixture was refluxed for 3 hours on a boiling water bath. Then volume of the reaction mixture was reduced by evaporation and allowed to cool. Finally the mixture was poured into ice cold water to get pale yellow coloured ligand. It was filtered and dried. The yield of the product was 82% and the melting point recorded was 136⁰C. The elemental analysis data of the ligand is given in Table 1.5.

Characterization of ligand

The ligand was characterized by different spectroscopic tools like infrared, NMR, mass and electronic spectroscopy.

IR spectral studies

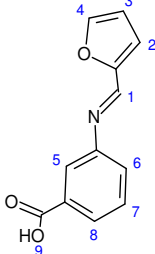
The IR spectrum of the compound showed a scalloped band at 3000cm^{-1} corresponding to vibration of the OH group, which was overlapped with aromatic C-H stretching vibration. The vibrational frequency band of sp^2 hybridized C-H bond showed the corresponding band at 3062cm^{-1} . The asymmetric stretching vibrations of carboxylic group gave a characteristic band at 1689cm^{-1} . The azomethine moiety (C=N) was identified by the peak at 1579cm^{-1} . $\nu_{\text{C-O}}$ was observed at 1292cm^{-1} . The in-plane deformation was shown at 1197cm^{-1} and out of plane deformations were at 914cm^{-1} and 717cm^{-1} . The data is given in Table 1.6.

NMR spectral studies

The proton NMR spectrum of the Schiff base T2YMABA is given in Figure 1.6. A singlet at 12.93δ can be assigned to the proton of the COOH group. The proton attached to the azomethine carbon gave a singlet at 3.25δ which was broadened due to presence of nearby nitrogen. The aromatic protons of both thiophene ring and benzene ring appeared in 7.17δ – 7.77δ region. These seven peaks showed multiplicity according to ortho, meta and para coupling. The assignments of signals are given in table 1.4.

In the ^{13}C nmr spectrum twelve peaks were obtained corresponding to twelve chemically different carbons. The carboxylic carbon gave a sharp peak at 167ppm . The azomethine carbon appeared at 154ppm . There were ten aromatic carbons present in thiophene ring and benzene ring together. Correspondingly ten different peaks were obtained in the region 121 – 150ppm region. The spectrum is given in Figure 1.7.

Table 1.4 $^1\text{Hnmr}$ and $^{13}\text{Cnmr}$ spectral data of T2YMABA

$^1\text{Hnmr}$			$^{13}\text{Cnmr}$	
	δ value	Assignment/ Labelled No.	δ value	Assignment/ Labelled No.
	3.25(br,s)	1(CH=N)	154.99	1(CH=N)
	7.67	2	128.29	2
	7.44	3	126.70	3
	7.17	4	121.34	4
	8.79	5	125.77	5
	7.73	6	142.19	6
	7.70	7	132.01	7
	7.77	8	129.54	8
	12.93(s)	9	131.57	9
			150.94	10
			134.19	11
			167.03	12(COOH)

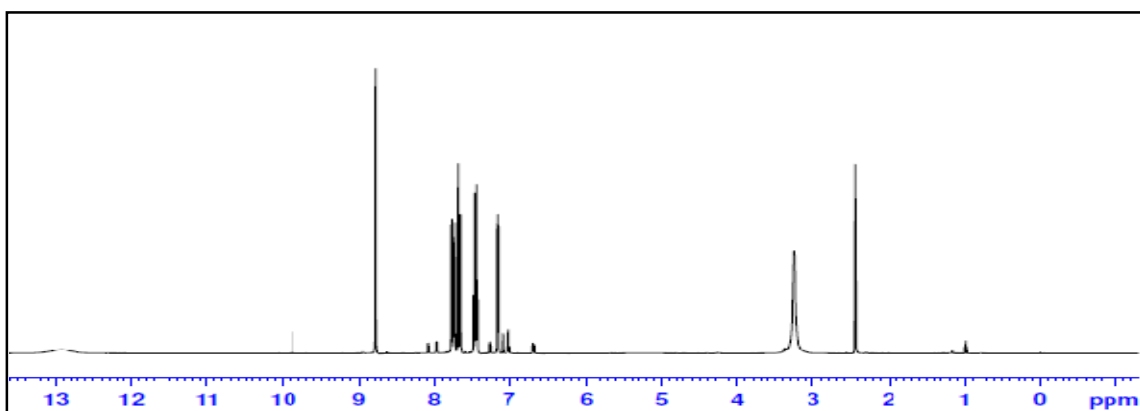


Fig.1.6 $^1\text{Hnmr}$ spectrum of T2YMABA

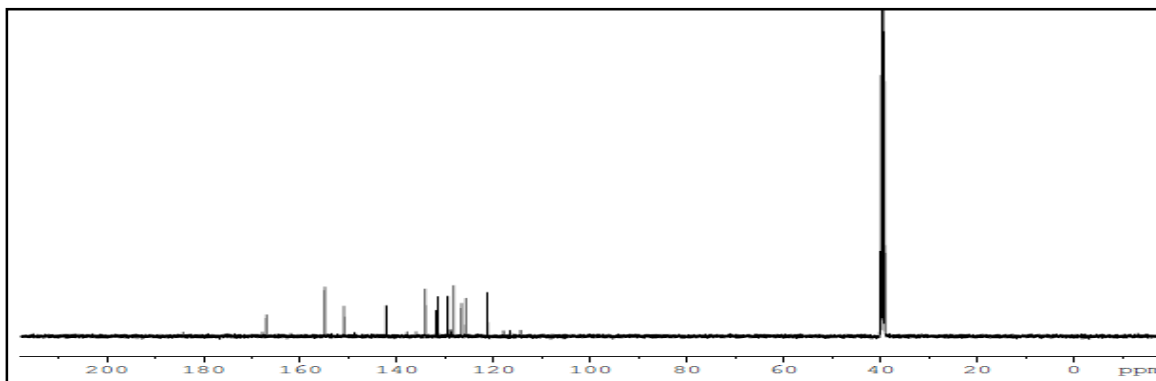


Fig.1.7 $^{13}\text{Cnmr}$ spectrum of T2YMABA

Mass spectral studies

The mass spectrum is represented in Figure 1.8. The presence of only one peak in the gas chromatogram showed the purity of the compound. The molecular ion peak was obtained at m/z 231 which was the base peak. This indicated the stability of the compound. A peak obtained at m/z 232 represents $[M+1]$ peak. The $[M]:[M+1]$ ratio observed in the EIMS was 100:13.5 which establishes the presence of twelve carbon atoms in the molecule. The $[M+2]$ peak at m/z 233 was due to presence of sulphur. The fragment $[C_{12}H_8NO_2S]^+$ was indicated by peak at m/z 230. Loss of a COOH from the molecule resulted with a peak at m/z 186 which corresponds to $[C_{11}H_8NS]^+$. Peaks at m/z 121 and 84 were due to the fragments $[C_7H_5O_2]^+$ and $[C_4H_4S]^+$ respectively.

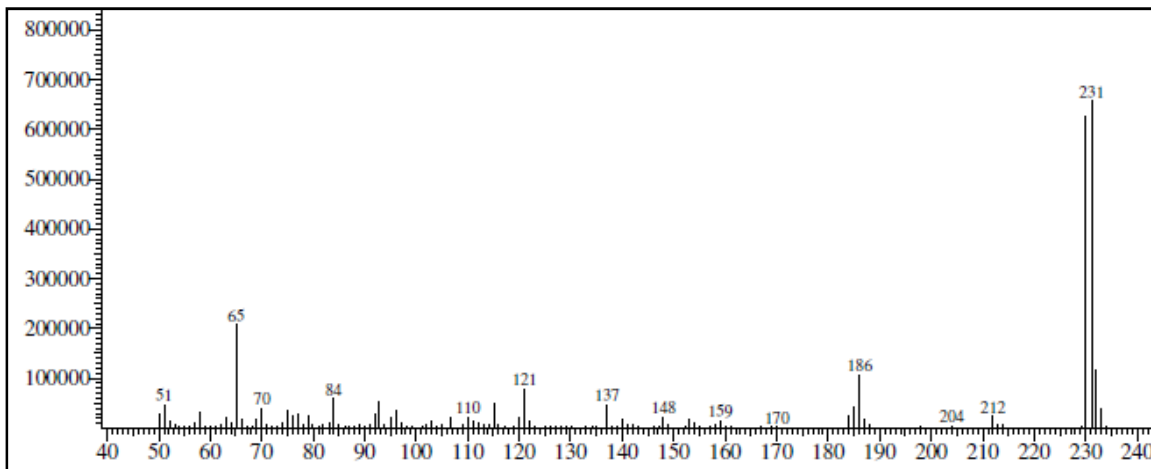


Fig.1.8 Mass spectrum of T2YMABA

Electronic spectral studies

The appearance of two peaks at 39062cm^{-1} and 32154cm^{-1} in the electronic spectrum of the Schiff base T2YMABA can be attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions in the molecule.

On the basis of all the above discussions the structure of the Schiff base T2YMABA can be represented as in Figure 1.9.

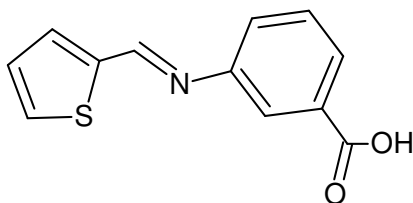


Fig.1.9 Structure of T2YMABA

Synthesis of complexes

Cr(III), Ni(II), Cu(II), Zn(II) and Cd(II) complexes of the Schiff base 3-[thiophen-2-ylmethyleneamino]benzoic acid were synthesized as per the procedure detailed hereafter. The Schiff base (E)-3-[thiophen-2-ylmethyleneamino]benzoic acid and the metal salt were taken in 1:1 ratio in ethanolic medium. The mixture was refluxed for two hours on a water bath. Finally the volume of the solution was reduced by evaporation and then cooled. The precipitated complexes were filtered and washed with ethanol-water mixture. The complexes were first dried on a water bath and then kept over an. CaCl_2 . Melting points of all the complexes were noted. All the chelates were obtained in good yield.

Characterization of complexes

The metallic chelates of T2YMABA were characterized by elemental and spectral studies. IR and $^1\text{Hnmr}$ spectral studies were helpful in determining the denticity of the ligand. All the complexes were found to be stable to air and light. The following explanations give the structural evaluation of the metal complexes.

Elemental analysis

Analysis of the elements in the complexes gave identification regarding the stoichiometry of the complexes. The elemental analysis data are given in Table 1.5. There is good correlation between the observed and calculated values. The percentages of

elements obtained indicated the correct molecular formula of the complexes. All the complexes were found to have 1:1 stoichiometry between the metal and ligand T2YMABA.

Magnetic moment measurements

The effective magnetic moment values of the chelates are given in the Table 1.5. Measurements of magnetic susceptibility values provided a strong support for the determination of exact geometry of the complexes. The chromium(III) complex with a d^3 system, had magnetic moment 3.41BM which is slightly less than the expected value. This may be due to the antiferromagnetic interaction between the metal ions and hence an octahedral dimeric structure with two bridged acetate groups was assigned for this complex⁵²⁻⁵⁴. In the case of nickel(II) complex also octahedral geometry was assigned since the magnetic behavior was shown with 2.69BM value. The existence of cupric ion state in the copper complex of T2YMABA was ascertained by the appearance of μ_{eff} value 1.72BM, which is quite expected for d^9 configuration. Therefore square planar geometry was fixed for Cu(II) chelate. Tetrahedral geometry was assigned for both the zinc(II) and cadmium(II) complexes. These chelates were found to be diamagnetic in their magnetic moment measurement studies and this result was very much expected since Zn(II) and Cd(II) ions were having no unpaired electrons⁵⁵⁻⁵⁷.

Molar conductance studies

Molar conductance measurements were conducted in DMSO solvent. All the transition metal complexes of T2YMABA exhibited molar conductance values in the range $3-10\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ suggesting that all the compounds were non-electrolytic in nature. The data is represented in Table 1.5.

IR spectral studies

The IR spectral data of all the complexes are given in Table 1.6. The coordination of the ligand through the azomethine group was confirmed by the downward shift of the peak in the spectra of all the complexes. The appearance of new bands around 3400cm^{-1} which was absent in the spectrum of the ligand, confirmed the presence of coordinated water molecules in all the chelates. The asymmetric stretching vibrations of the carboxylate group showed considerable shift in frequencies for all the complexes which clearly indicated the coordination of the group to the metal ion. The difference between the asymmetric and symmetric stretching vibrations ($\Delta\nu$) was found to be greater than 150cm^{-1} which confirmed the monodentate nature of the carboxylate group⁵⁸. The appearance of new bands corresponding to $\nu_{\text{M-N}}$ and $\nu_{\text{M-O}}$ transitions strongly confirmed the complexations in all chelates.

¹Hnmr spectral studies

The ¹Hnmr spectra of complexes provided supporting evidences in assigning the binding sites of the ligand. The down field shift of the peaks, compared with the spectra of the ligand, indicated the complexation. The disappearance of carboxylic proton peak in the ¹Hnmr spectra of the complexes confirmed the coordination of the deprotonated carboxylic group of the ligand to the central metal atom. The shift in the azomethine proton peak to low field region indicated the involvement of C=N group in coordination.

Electronic spectral studies

Intra ligand electronic transitions and d-d transitions were shown as peaks in the optical absorption spectrum of all the complexes. In the case of Cr(III) complex two additional bands at 38910cm^{-1} and 30441cm^{-1} were obtained which corresponds to and

${}^4A_2 \rightarrow {}^4T_1(P)$ and ${}^4A_2(F) \rightarrow {}^4T_2(F)$ transitions. ${}^3A_2 \rightarrow {}^3T_2$ and ${}^3A_2 \rightarrow {}^3T_1(F)$ electronic transitions in the nickel(II) complex in an octahedral environment gave characteristic peaks at 31104cm^{-1} and 38462cm^{-1} respectively. In copper(II) complex ${}^2B_1 \rightarrow {}^2A_1$ and ${}^2B_1 \rightarrow {}^2B_2$ transitions were shown as peaks at 30581cm^{-1} and 37665cm^{-1} respectively and complex was assigned square planar geometry. Only two intra ligand transition bands were exhibited in Zn(II) complex at 30912cm^{-1} and 38536cm^{-1} and charge transfer transitions were found to be absent in the electronic spectrum. Cd(II) complex exhibited a LMCT band at 38911cm^{-1} .

Thermogravimetric studies

TGA and DTA studies of Cr(III) complex of T2YMABA gave a four stage decomposition pattern. The loss of two coordinated water molecules from the sample moiety was observed in the temperature range of $60\text{-}140^\circ\text{C}$. The loss of two acetate groups and two CO_2 molecules occurred in two substages of the second stage, i.e., IIa and IIb respectively. Rest of both the ligands and two bridged acetate groups were removed in the third and fourth stages respectively. The overall mass loss according to the TG curve was 81.53% and the theoretical mass loss was 81.82% .

The decomposition pattern of Ni(II) complex of T2YMABA comprised of two stages. In the first stage all the three coordinated water molecules from the complex were lost in the temperature range $117\text{-}243^\circ\text{C}$. The loss of ligand and acetate group was observed in the second stage at 429°C . The overall mass loss according to the TG curve and the theoretical mass loss for the conversion of the complex into corresponding oxide were 81.15% and 81.34% respectively. These data were to be in agreement with the result obtained during pyrolytic studies.

All the characterization methods detailed above led to assignment of structures of the complexes of T2YMABA as given in Figure 1.10.

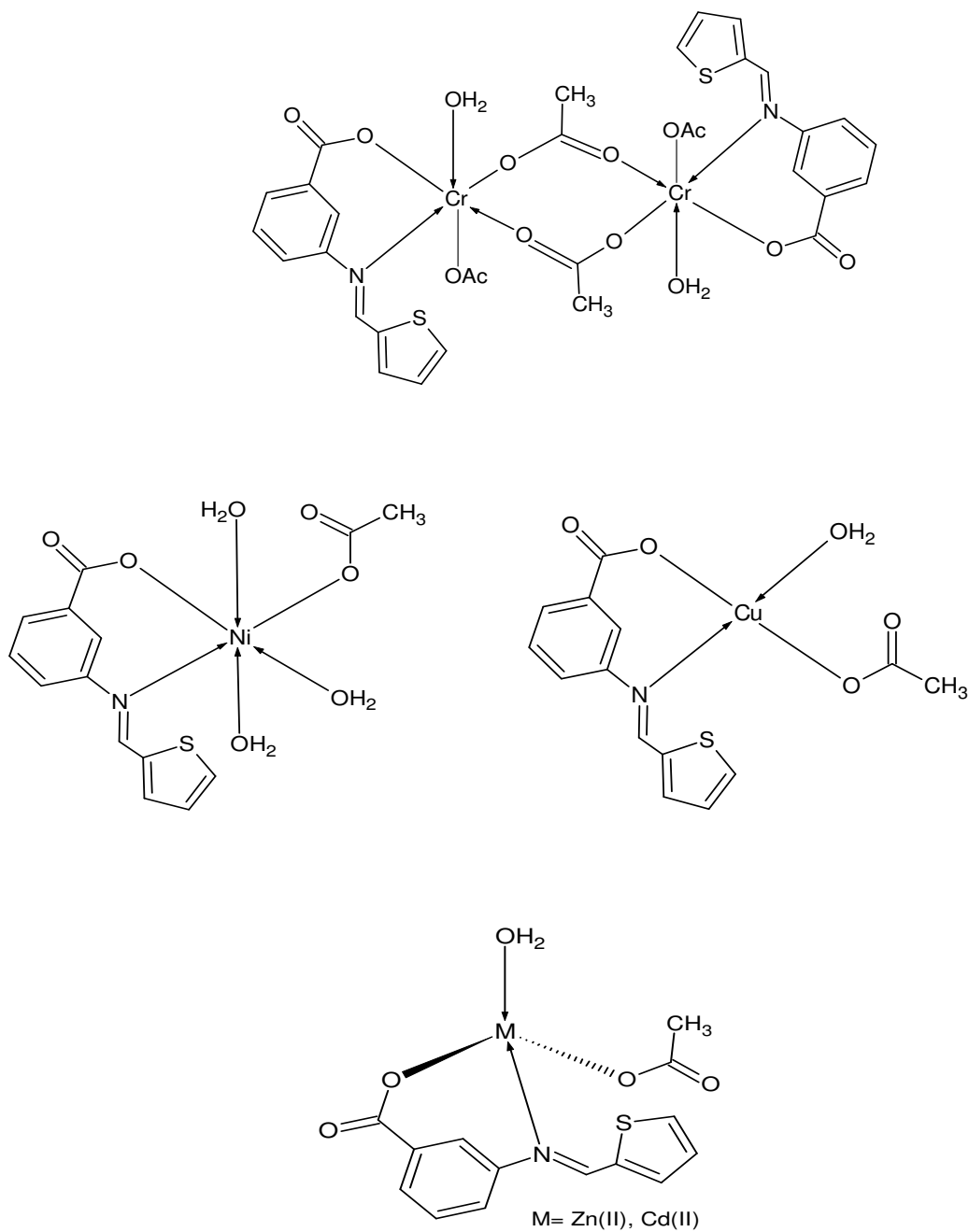


Fig.1.10 Structures of metal complexes of T2YMABA

Table 1.5 Microanalytical, magnetic and conductance data of the ligand T2YMABA and its transition metal complexes

Complex	Colour	Yield (%)	Mol. Wt.	M.P (^o C)	Metal % Found (Calculated)	C % Found (Calculated)	H % Found (Calculated)	N % Found (Calculated)	S % Found (Calculated)	μ_{eff} (BM)	Molar Conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	Geometry
T2YMABA(LH)	Pale yellow	70	231	136	-	63.84 (62.34)	3.81 (3.90)	7.04 (6.06)	14.11 (13.85)	-	-	-
[CrLAc ₂ (H ₂ O)] ₂	Pale green	76	418	>300	13.86 (12.44)	46.75 (45.93)	3.76 (3.83)	2.48 (3.55)	6.48 (7.66)	3.41	5	Octahedral
[NiLAc(H ₂ O)] ₃	Pale Green	81	402	>300	15.28 (14.61)	42.60 (41.82)	4.30 (4.23)	4.20 (3.49)	8.65 (7.97)	2.69	8	Octahedral
[CuLAc(H ₂ O)]	Blue	81	371	>300	17.13 (17.16)	45.16 (45.33)	3.01 (3.51)	4.34 (3.78)	8.75 (8.63)	1.72	7	Square planar
[ZnLAc(H ₂ O)]	Grey	64	372	>300	18.50 (17.56)	46.45 (45.11)	3.92 (3.49)	4.04 (3.76)	8.68 (8.59)	D	10	Tetrahedral
[CdLAc(H ₂ O)]	Pale brown	70	419	>300	25.89 (26.73)	41.17 (40.10)	3.09 (3.10)	4.28 (3.34)	8.18 (7.64)	D	3	Tetrahedral

Ac: Acetate, D: Diamagnetic

Table 1.6 Characteristic infrared absorption frequencies of T2YMABA and its transition metal complexes

Complex	$\nu_{\text{O-H}}$	$\nu_{\text{H}_2\text{O}}$	$\nu_{\text{C-H}(\text{SP}^2)}$	$\nu_{\text{COO}(\text{asym})}$	$\nu_{\text{C=N}}$	$\nu_{\text{COO}(\text{sym})}$	$\nu_{\text{C-Hbend}}$	$\nu_{\text{C-O}}$	In plane bending.	Out of plane bending	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$
T2YMABA(LH)	~3000 (Scalloped band)	-	3062	1689	1579	-	1415	1292	1197	914, 717	-	-
[CrLAc ₂ (H ₂ O)] ₂	-	3373	3103	1616	1560	1541	1456, 1406	1202	1042	903, 767	576	518
[NiLAc(H ₂ O)] ₃	-	3387	3064	1606	1552	1527	1452, 1398	1244	1014	925, 771	582	504
[CuLAc(H ₂ O)]	-	3423	3136	1629	1568	1525	1456, 1404	1151	1074	896, 759,677	564	459
[ZnLAc(H ₂ O)]	-	3452	3099	1627	1571	1498	1404, 1390	1165	1078	925, 759,680	538	439
[CdLAc(H ₂ O)]	-	3354	3057	1681	1579	1543	1448, 1388	1240	988	916, 777,678	557	513