

Part I

Synthesis and Characterization

Chapter 7

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 7

STUDIES ON SCHIFF BASE, 4-(5-[(2-CARBAMOTHIOYLHYDRAZONO) METHYL]FURAN-2-YL)BENZOIC ACID AND ITS TRANSITION METAL COMPLEXES

A novel heterocyclic Schiff base, (E)-4-(5-[(2-carbamothioylhydrazono)methyl]furan-2-yl)benzoic acid (CTHMF2YBA) was synthesized and characterized. The chelating efficiency of this ligand was investigated with metal ions Cr(III), Co(II), Ni(II), Cu(II) and Zn(II). The synthetic methods and characterization techniques like elemental analysis, magnetic moment measurements and spectroscopic studies like IR, ^1H nmr and ^{13}C nmr electronic spectroscopy are detailed in this chapter.

Synthesis of ligand

The Schiff base was synthesized by a two step process. In first step furan-2-carbaldehyde was arylated by Meervin arylation process, followed by condensation reaction with the amino compound, thiocarbamoyl hydrazide.

4-(5-formylfuran-2-yl)benzoic acid solution was prepared by dissolving 2mM in hot ethanol and it was heated to boiling on a water bath. To this, hot solution of thiocarbamoyl hydrazide in ethanol-water mixture was added slowly. This mixture was refluxed continuously for 3 hours. The reaction mixture was reduced in volume by evaporation and then cooled. Then the contents were added to ice cold water and stirred well. The precipitated ligand was filtered, washed with ethanol-water mixture and dried. The melting point of the Schiff base CTHMF2YBA was found to be 278°C .

Characterization of ligand

Elemental analysis

The elemental analysis data of the Schiff base CTHMF2YBA is given in Table 1.14.

The experimentally obtained percentages of elements like carbon, hydrogen, nitrogen and sulphur were in good agreement with the calculated values.

IR spectral studies

The IR spectral assignments are given in Table 1.15. The NH₂ group gave its characteristic vibrational frequencies at 3377cm⁻¹ and 3259cm⁻¹. The aromatic C-H bond vibration was observed at 3165cm⁻¹. The S-H bond of the ligand gave one peak at 2540cm⁻¹. The symmetric and asymmetric vibrations of carboxylate group were found at 1553cm⁻¹ and 1689cm⁻¹ respectively. The azomethine group was identified by a peak at 1614cm⁻¹. $\nu_{C=O}$ was observed at 1286cm⁻¹. The in-plane deformation was shown at 1103cm⁻¹ and out of plane deformations were observed at 921cm⁻¹, 798cm⁻¹ and 771cm⁻¹.

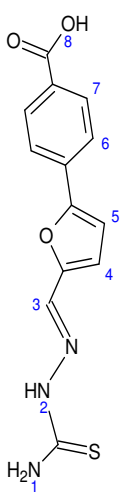
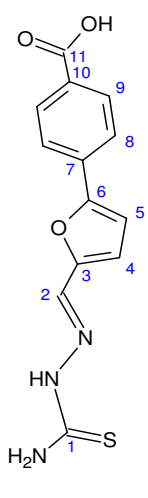
NMR spectral studies

According to the proton NMR spectrum of CTHMF2YBA nine distinct protons were there in the Schiff base molecule. The assignments of peaks are given in Table 1.13. A broad singlet observed at 3.25 δ was due to the NH₂ protons. Another broad singlet at 8.23 δ was assigned to NH proton of the thiosemicarbazide part. The azomethine proton gave a peak at 7.74 δ which was a broad singlet. Aromatic protons in the thiophene ring appeared as doublets at 7.21 δ and 7.05 δ and those in the benzene ring appeared as two proton doublets at 7.88 δ and 7.92 δ . The carboxylic proton exhibited its signal at 11.47 δ . Possibility of tautomerism in the molecule was confirmed by the appearance of a broad singlet peak at 12.9 δ due to the SH proton.

¹³Cnmr spectrum is shown in Figure 1.23. Eventhough the molecule contains 13 carbon atoms, the presence of eleven chemically different carbon atoms was confirmed by this spectrum. The thiosemicrbazone carbon exhibited its signal at 166.84ppm. The

azomethine carbon was identified at 123.82ppm. Carbon atoms of the thiophene ring appeared at 149.98ppm, 131.62ppm and 110.45ppm. The aromatic carbons of the benzene ring exhibited four signals in the range 129ppm-153ppm. The peak at 177.81ppm was due to carboxylate carbon. The assignment of signals to different carbon is expressed in Table 1.13.

Table 1.13 $^1\text{Hnmr}$ and $^{13}\text{Cnmr}$ spectral data of CTHMF2YBA

	$^1\text{Hnmr}$		$^{13}\text{Cnmr}$		
	δ value	Assignment/ Labelled No.	δ value	Assignment/ Labelled No.	
	3.25(br,s,2H)	1(NH ₂)	166.84	1	
	8.23(br,s,1H)	2(NH)	123.82	2	
	7.74(br,s,1H)	3(CH=N)	149.98	3	
	7.21(d,1H)	4	131.62	4	
	7.05(d,1H)	5	110.45	5	
	7.88(d,2H)	6	133.20	6	
	7.92(d,2H)	7	115.26	7	
	11.47(s,1H)	8(COOH)	129.77	8	
	12.9(br,s,1H)	9(SH)	129.94	9	
			153.37	10	
			177.81	11	

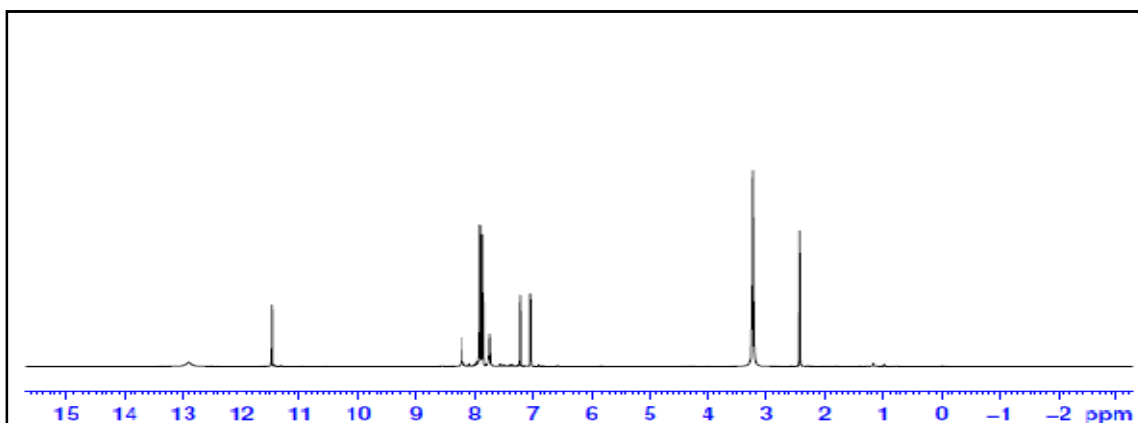


Fig.1.22 $^1\text{Hnmr}$ spectrum of CTHMF2YBA

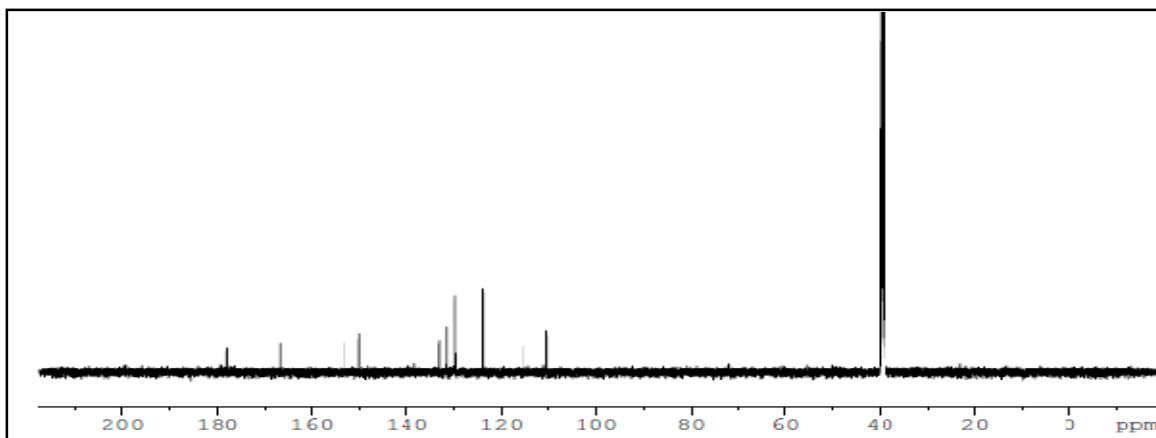


Fig.1.23 ^{13}C nmr spectrum of CTHMF2YBA

Mass spectral studies

The appearance of only one peak in the gas chromatogram indicated the purity of the synthesized compound. In the mass spectrum of CTHMF2YBA, the molecular ion peak was observed at m/z 289. Appearance of peak at m/z 290 can be assigned to the $[\text{M}+1]^+$ species. The $[\text{M}]^+:[\text{M}+1]^+$ ratio (100:16.5) suggested that 13 carbon atoms were present in the molecule. $[\text{M}+2]^+$ peak at m/z 292 was also present with $[\text{M}]^+:[\text{M}+2]^+$ ratio 100:5. The loss of OH moiety resulted in a peak at m/z 272 which was the base peak. The formation of fragments at m/z 230 and m/z 213 were due to the fragments $[\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_3]^+$ and $[\text{C}_{12}\text{H}_7\text{NO}_3]^+$ respectively. Further fragmentation resulted in species $[\text{C}_{12}\text{H}_8\text{O}_3]^+$, $[\text{C}_{12}\text{H}_6\text{NO}_2]^+$, $[\text{C}_{11}\text{H}_8\text{O}_3]^+$ and $[\text{C}_{10}\text{H}_7\text{O}_2]^+$ which gave their peaks at m/z values at 200, 196, 188 and 159 respectively. The fragment $[\text{C}_3\text{H}_7\text{N}_3\text{O}_2\text{S}]^+$ was shown at m/z 149 and $[\text{C}_3\text{H}_5\text{N}_3\text{OS}]^+$ at m/z 131. Two important peaks at m/z 76 and m/z 59 were due to $[\text{CH}_4\text{N}_2\text{S}]^+$ and $[\text{HS-C}\equiv\text{N}]^+$ species respectively. Figure 1.24 gives the mass spectrum of the CTHMF2YBA molecule.

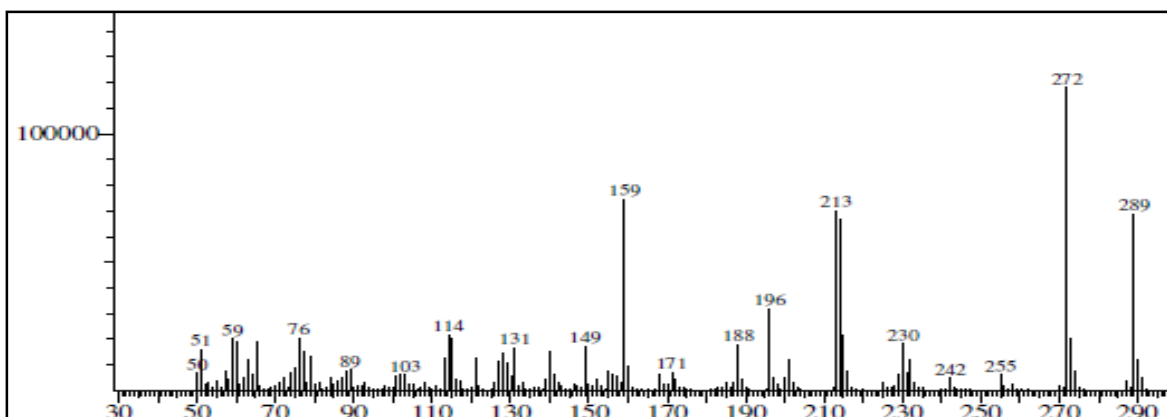


Fig.1.24 Mass spectrum of CTHMF2YBA

Electronic spectral studies

The Schiff base CTHMF2YBA exhibited two peaks in the UV-visible spectrum at 26595cm^{-1} and 33557cm^{-1} , which can be assigned to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ electronic transitions. Based on the analytical data observed, the following structure is assigned for the Schiff base (Figure 1.25), which can exist in thioketo-thioenol tautomeric forms.

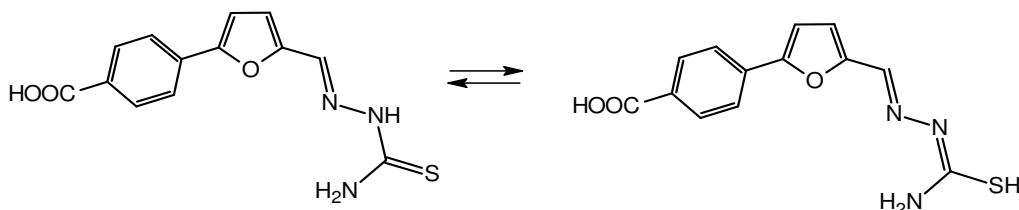


Fig.1.25 Tautomeric forms of CTHMF2YBA

Synthesis of complexes

Transition metal complexes of the Schiff base CTHMF2YBA were synthesized with Cr(III), Co(II), Ni(II), Cu(II) and Zn(II) ions. 2mM solution of the Schiff base CTHMF2YBA was heated to boiling on a waterbath. To that added hot ethanolic solution of the metal salt (2mM) slowly. The mixture was refluxed continuously for 3 hours. Finally the volume was reduced by boiling and cooled. Then the contents were poured into crushed ice and shaken well. The precipitated complex was filtered, washed with

ethanol-water mixture and dried. Melting points of the complexes were noted. All the complexes were found to have higher melting points than the ligand. The yield and colours of the complexes are given in Table 1.14.

Characterization of complexes

All the complexes were found to be light and air stable. Generally they were soluble in aprotic polar solvents like DMSO and DMF. But solubility was very poor in common organic solvents like ethanol, diethyl ether, benzene, chloroform etc. All the complexes were subjected to different characterization techniques like magnetic moment measurements, elemental analysis, conductance measurements and spectral studies like IR and electronic spectra. The descriptions of these analyses are followed.

Elemental analysis

Estimation of elements in the complexes gave a definite idea about the exact molecular formula of the complexes. The CHNS analysis data is provided in Table 1.14. A good correlation was found between the observed values and calculated values. It was found that Cr(III), Cu(II) and Zn(II) complexes were of 1:1 stoichiometry whereas in Co(II) and Ni(II) complexes 1:2 stoichiometry was followed between the metal ion and the ligand.

Magnetic moment studies

Measurement of magnetic moment values gave an idea about the geometry of the complexes. Chromium and cobalt complexes were found to have octahedral geometry since they exhibited magnetic moment values 3.01BM and 3.31BM respectively. The nickel complex had a magnetic moment value of 2.56BM which indicated that it is of high spin octahedral geometry. The copper complex showed 1.97BM and a square planar

geometry was assigned for it. For the zinc complex diamagnetic nature was observed and tetrahedral geometry was fixed for it.

Molar conductance studies

For all the CTHMF2YBA complexes, the molar conductance data was measured in DMSO medium. Solutions of 10^{-3} M concentration were used for the measurements. The values obtained were in the range $6-14\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ suggesting that in all the complexes counter ions were not present outside the coordination sphere and thus all were non-electrolytic in nature.

IR spectral studies

Table 1.15 shows the assignments of IR spectral peaks of the complexes. The presence of new vibrational bands around 3250cm^{-1} showed the presence of coordinated water molecule in each complex. The $\nu_{\text{S-H}}$ was absent in the spectra of all the complexes which was observable in the ligand spectrum. The involvement of the sulphur atom of the thiocarbamoyl hydrazide part in coordination was thus confirmed. The decrease in vibrational frequency of C=N group gave a clear indication of participation of azomethine nitrogen in the complexation process. Further confirmation regarding the coordination sites in the ligand was established from the appearance of additional bands in the lower frequency regions such as $\sim 670-680\text{cm}^{-1}$ (M-N) and $\sim 500-550\text{cm}^{-1}$ (M-S). The absence of shifts in the symmetric and asymmetric stretching vibrations of the carboxylate group in the spectra of complexes suggested that COOH group is not coordinated to the metal ion in all the complexes.

Electronic spectral studies

In all metal chelates the intra ligand electronic transitions were shifted to longer

wavelength region suggesting the occurrence of complexation. In the electronic spectra of Cr(III) chelate absorption peaks at 26595cm^{-1} , 33898cm^{-1} and 39215cm^{-1} were due to ${}^4\text{A}_2(\text{F})\rightarrow{}^4\text{T}_2$, ${}^4\text{A}_2(\text{F})\rightarrow{}^4\text{T}_2(\text{F})$ and ${}^4\text{A}_2\rightarrow{}^4\text{T}_1(\text{P})$ electronic transitions in an octahedral field. For the Co(II) complex three electronic transitions ${}^4\text{T}_1(\text{F})\rightarrow{}^4\text{T}_2$, ${}^4\text{T}_1(\text{F})\rightarrow{}^4\text{A}_2$ and ${}^4\text{T}_1(\text{F})\rightarrow{}^4\text{T}_1(\text{P})$ were exhibited at 26560cm^{-1} , 33670cm^{-1} and 39062cm^{-1} respectively. ${}^3\text{A}_2\rightarrow{}^3\text{T}_2$ and ${}^3\text{A}_2\rightarrow{}^3\text{T}_1(\text{F})$ electronic transitions in Ni(II) complex gave peaks at 26490cm^{-1} and 39062cm^{-1} respectively and octahedral geometry was assigned for the complex. In the Cu(II) complex, for which a square planar geometry was assigned, ${}^2\text{B}_1\rightarrow{}^2\text{A}_1$ and ${}^2\text{B}_1\rightarrow{}^2\text{B}_2$ transitions were expressed at 26525cm^{-1} and 39138cm^{-1} respectively. An intense peak at 39138cm^{-1} in the electronic spectrum of Zn(II) chelate was assigned to ligand to metal charge transfer transition.

Thermogravimetric studies

Cr(III) complex of the ligand CTHMF2YBA had a four stage decomposition pattern in the TGA analysis. Loss of two water molecules was observed in the temperature interval $62\text{-}137^\circ\text{C}$. Then in the second stage two amino groups, two CO_2 molecules and two acetate groups were lost. Two bridged acetate groups were removed and in the third stage of decomposition. Lastly, rest of both the ligands were lost with the peak temperature 451°C . But for the Ni(II) complex a three stage decomposition pattern was observed. Loss of two water molecules was assigned in the first stage. Two COOH groups, two NH_2 molecules and two phenyl rings were lost at around 235°C , 259°C and 319°C respectively in second stage. In the third stage the rest of both the ligands were lost. The mass loss according to the thermogravimetric curves and the theoretical values were found to be in good agreement for both the complexes.

Based on the above explanations, the structures of the complexes of the Schiff base CTHMF2YBA can be represented as in Figure 1.26.

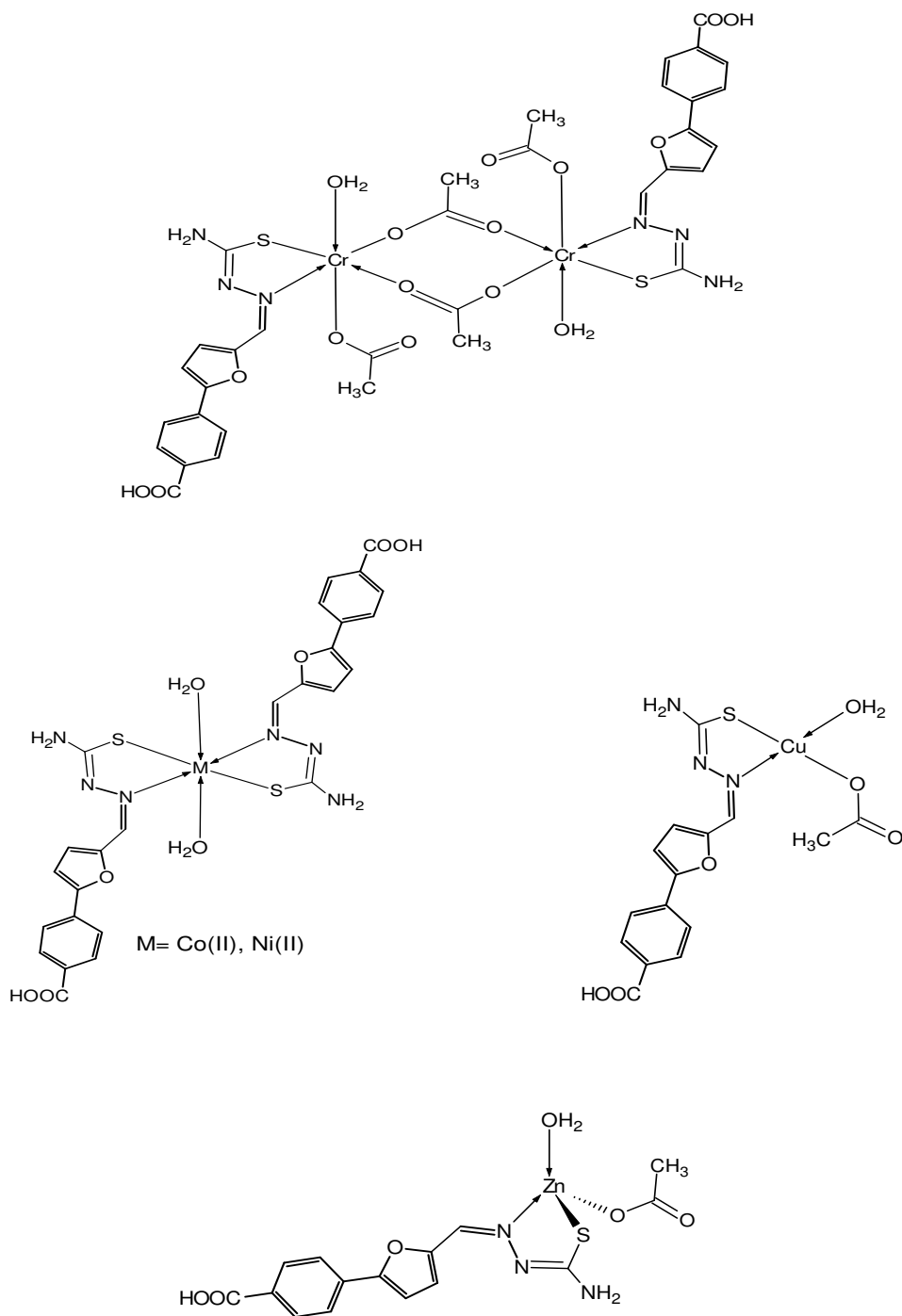


Fig.1.26 Structures of metal complexes of CTHMF2YBA

Table 1.14 Microanalytical, magnetic and conductance data of the ligand CTHMF2YBA and its transition metal complexes

Complex	Colour	Yield (%)	Mol. Wt.	M.P (°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
CTHMF2YBA(LH)	Pale brown	66	289	278	-	53.02 (53.98)	4.02 (3.81)	13.94 (14.53)	10.87 (11.07)	-	-	-
[CrLAc ₂ (H ₂ O) ₂]	Pale brown	74	476	>300	11.22 (10.92)	41.69 (42.86)	4.12 (3.58)	12.00 (12.52)	8.66 (9.54)	3.01	6	Octahedral
[CoL ₂ (H ₂ O) ₂]	Gray	62	671	>300	8.04 (8.79)	45.65 (46.50)	3.64 (3.58)	11.88 (12.52)	9.96 (9.54)	3.31	10	Octahedral
[NiL ₂ (H ₂ O) ₂]	Pale Green	68	671	>300	9.69 (8.76)	47.35 (46.52)	4.34 (3.58)	12.14 (12.52)	8.62 (9.54)	2.56	14	Octahedral
[CuLAc(H ₂ O)]	Brown	76	429	>300	14.36 (14.83)	42.68 (42.00)	4.23 (3.50)	8.65 (9.80)	7.91 (7.47)	1.97	7	Square planar
[ZnLAc(H ₂ O)]	Off white	70	430	>300	14.38 (15.19)	40.88 (41.82)	4.43 (3.49)	9.14 (9.76)	6.84 (7.44)	D	12	Tetrahedral

Ac: Acetate, D: Diamagnetic

Table 1.15 Characteristic infrared absorption frequencies of CTHMF2YBA and its transition metal complexes

Complex	$\nu_{\text{N-H}}$	$\nu_{\text{H}_2\text{O}}$	$\nu_{\text{C-H(Ar)}}$	$\nu_{\text{COO(asym)}}$	$\nu_{\text{C=N}}$	$\nu_{\text{COO(sym)}}$	$\nu_{\text{C-O}}$	In plane bending	Out of plane bending	$\nu_{\text{M-N}}$	$\nu_{\text{M-S}}$
CTHMF2YBA (LH)	3377, 3259	-	3165	1689	1614	1553	1286	1103	921, 798, 771	-	-
[CrLAc ₂ (H ₂ O) ₂]	3419, 3398	3263	3157	1680	1604	1544	1282	1105	795,760	670	515
[CoL ₂ (H ₂ O) ₂]	3419, 3403	3277	3157	1685	1606	1546	1282	1101	792,769	671	520
[NiL ₂ (H ₂ O) ₂]	3408, 3383	3319	3155	1678	1604	1510	1278	1058	799,771	677	503
[CuLAc(H ₂ O)]	3421, 3408	3292	3163	1687	1606	1546	1276	1111	790,773	672	549
[ZnLAc(H ₂ O)]	3392, 3403	3263	3155	1680	1602	1544	1282	1122	930, 802,783	671	533

SUMMARY

Five novel heterocyclic Schiff bases namely 3-(1H-indol-3-yl)-2-[(E)-(thiophen-2-ylmethylidene)amino]propanoic acid (I3YT2YMAPA), (E)-3-[thiophen-2-ylmethylene amino]benzoic acid (T2YMABA), (E)-4-(5-[(2-carbamothioylhydrazono)methyl]thiophen-2-yl)benzoic acid (CTHMT2YBA), (E)-4-(5-[(2-phenylhydrazono)methyl]thiophen-2-yl)benzoic acid (PHMT2YBA) and (E)-4-(5-[(2-carbamothioylhydrazono)methyl]furan-2-yl)benzoic acid (CTHMF2YBA) were synthesized and characterized by different techniques like CHNS analysis and spectral studies such as FTIR, NMR, mass and UV-visible. The chelating abilities of these Schiff bases were investigated by synthesizing a number of transition metal complexes. Then these complexes were also subjected to characterization studies by elemental analysis, magnetic moment measurements, conductance measurements, IR, UV-visible and $^1\text{Hnmr}$ spectral analysis. All the results are detailed in this part. The thermogravimetric studies of Cr(III) and Ni(II) complexes of all the ligands were also conducted.

The Schiff base 3-(1H-indol-3-yl)-2-[(E)-(thiophen-2-ylmethylidene)amino]propanoic acid (I3YT2YMAPA) was synthesized from thiophene-2-carbaldehyde and the amino acid (s)-2-amino-3-(3-indolyl)propanoic acid. Transition metal complexes of this ligand were prepared with Cr(III), Ni(II), Cu(II) and Zn(II) ions. 1:1 stoichiometry was found to exist between the metal and ligand in all the complexes. The Cr(III) and Ni(II) chelates were found to have octahedral geometry. In the case of copper complex a square planar geometry was fixed. Diamagnetic character was found for Zn(II) complex in the magnetic studies and tetrahedral geometry was assigned for it. The ligand acted as a monovalent bidentate ligand in all the complexes. The azomethine group and the

carboxylate group were coordinated to the metal ion, which was verified by FTIR spectral analysis. The TGA and DTA analysis of the Ni(II) complex exhibited a three stage decomposition pattern.

The chelating efficacy of the ligand T2YMABA was explored by synthesizing transition metal complexes with metal ions of chromium, nickel, copper, zinc and cadmium. All the complexes were found to have 1:1 stoichiometry between the metal and ligand T2YMABA. The ligand was monovalent and bidentate in nature coordinating through azomethine group nitrogen and carboxylate group oxygen atoms. The Cr(III) complex was found to exist in dimeric form. For chromium(III) and nickel(II) complexes octahedral geometry were assigned according to their magnetic behavior. Copper(II) chelate was exhibiting square planar geometry. Tetrahedral geometry was assigned for both the zinc(II) and cadmium(II) complexes. Molar conductance data suggested that all the compounds were non-electrolytic in nature. The Cr(II) complex and Ni(II) complex exhibited four stage and two stage decomposition pattern respectively in TGA and DTA studies.

The Schiff base CTHMT2YBA was prepared by a two step process, first step being Meervin arylation of the thiophene-2-carbaldehyde, followed by condensation reaction with thiocarbamoyl hydrazide. Transition metal complexes of CTHMT2YBA were synthesized with Cr(III), Co(II), Ni(II), Cu(II) and Zn(II) ions and characterized by different techniques. It was concluded that Cr(III), Cu(II) and Zn(II) complexes were of 1:1 stoichiometry whereas in Co(II) and Ni(II) complexes 1:2 stoichiometry was followed. The Cr(III) complex was found to exist in a dimeric form. The Schiff base CTHMT2YBA exhibited tautomerism which was verified by NMR and IR spectral

studies. This Schiff base acted as a monovalent bidentate ligand during complexation. The thermogravimetric analysis of Cr(II) and Ni(II) complexes exhibited well defined three stage decomposition patterns .

Transition metal complexes of the Schiff base PHMT2YBA were synthesized with Cr(III), Co(II), Ni(II), Cu(II) and Zn(II) ions and characterized. It was found that Cr(III), Cu(II) and Zn(II) complexes were of 1:1 stoichiometry whereas Co(II) and Ni(II) complexes followed 1:2 stoichiometry. The denticity of the ligand was found to be one. Chromium(III) complex was assigned octahedral geometry whereas cobalt(II) and nickel(II) complexes were given distorted octahedral geometry. For copper(II) and zinc(II) complexes square planar and tetrahedral geometries were assigned respectively. The Cr(III) and Ni(II) complexes showed three and two decomposition stages respectively in their TGA/ DTA analysis.

Cr(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes of the Schiff base CTHMF2YBA were synthesized and characterized. It was found that Cr(III), Cu(II) and Zn(II) complexes were of 1:1 stoichiometry whereas in Co(II) and Ni(II) complexes 1:2 stoichiometry was followed. The ligand exhibited thioketo-thioenol tautomerism as revealed by the NMR and IR studies. Chromium, cobalt and nickel complexes were found to have octahedral geometry and copper complex showed square planar geometry. For the zinc complex diamagnetic nature was observed and tetrahedral geometry was assigned for it. The thermogravimetric curves of Cr(III) and Ni(II) complexes were recorded and it was found that chromium complex had four and nickel complex had three decomposition stages.

In short, five potential novel heterocyclic Schiff base ligands derived from thiophene-2-carbaldehyde and furan-2-carbaldehyde with different amino compounds and their twenty four transition metal chelates were synthesized and characterized using most modern analytical tools and explained in detail in this part.

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