

# **Part I**

## **Synthesis and Characterization**

### **Chapter 6**

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 6**  
**STUDIES ON SCHIFF BASE, 4-(5-[(2-PHENYLHYDRAZONO)METHYL]**  
**THIOPHEN-2-YL)BENZOIC ACID AND ITS TRANSITION METAL**  
**COMPLEXES**

This chapter deals with the synthesis and characterization of a novel Schiff base, (E)-4-(5-[(2-phenylhydrazono)methyl]thiophen-2-yl)benzoic acid (PHMT2YBA). The chelating efficiency of this ligand was investigated by complexation with Cr(III), Co(II), Ni(II), Cu(II) and Zinc(II) ions. These complexes were also subjected to characterization studies like elemental analysis, magnetic moment measurements, conductance studies and spectroscopic analysis like IR, UV-Visible and NMR spectroscopy.

The Schiff base was prepared by a two step process, first step being Meervin arylation of the thiophene-2-carbaldehyde, followed by condensation reaction with phenylhydrazine. The arylation process was explained in detail in the previous chapter.

**Synthesis of ligand**

4-(5-formylthiophen-2-yl)benzoic acid solution was prepared by dissolving 2mM in hot ethanol and it was refluxed on a water bath. To this, hot solution of phenylhydrazine in ethanol-water mixture was added slowly. Continued the refluxing for 2 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 (E)-4-(5-[(2-phenylhydrazono)methyl]thiophen-2-yl)benzoic acid (PHMT2YBA) was found to be 292 °C.

## Characterization of ligand

The ligand 4-(5-[(2-phenylhydrazono)methyl]thiophen-2-yl)benzoic acid was subjected to characterization studies in order to determine the structure. Elemental analysis and spectral studies were carried out and the details are as follows.

### *Elemental analysis*

The elemental analysis data of the Schiff base PHMT2YBA is given in Table 1.11. The experimentally obtained percentages of elements like carbon, hydrogen, nitrogen and sulphur were in good agreement with the calculated values.

### *IR spectral studies*

In the IR spectrum, the characteristic vibrational frequencies of N-H bond were shown at  $3308\text{cm}^{-1}$ . The aromatic C-H bond was observed at  $3054\text{cm}^{-1}$ . The symmetric and asymmetric vibrations of the carboxylate group were assigned at  $1514\text{cm}^{-1}$  and  $1685\text{cm}^{-1}$  respectively. The azomethine group was identified by a peak at  $1618\text{cm}^{-1}$ . A strong band appeared at  $1257\text{cm}^{-1}$  can be attributed to C-O stretching vibrations. The in-plane deformation was shown at  $1109\text{cm}^{-1}$  and out of plane deformations were at  $750\text{cm}^{-1}$  and  $696\text{cm}^{-1}$ . The IR spectral data is given in Table 1.12.

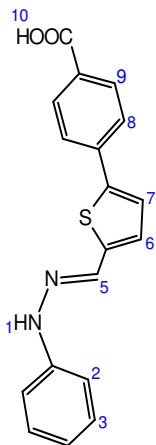
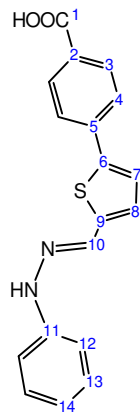
### *NMR spectral studies*

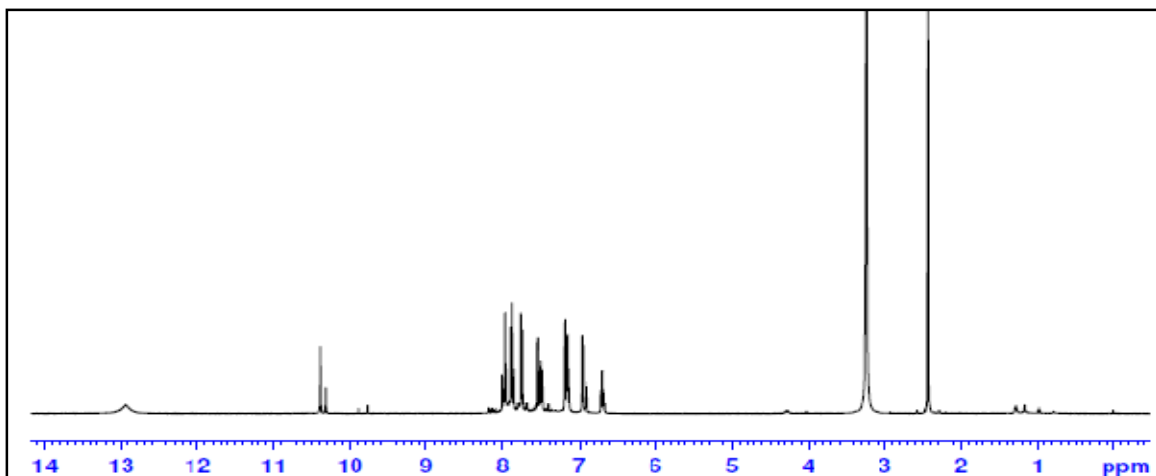
In the proton NMR spectra, ten nonequivalent protons were identified. A broad singlet at  $8.01\delta$  was assigned to the NH proton. A double doublet appeared at  $7.88\delta$  was due to the aromatic proton which is adjacent to nitrogen in the phenyl hydrazine ring. The protons on next carbon atoms of the ring gave a doublet signal at  $7.15\delta$  and a medium signal  $6.69\delta$  respectively. Proton on the azomethine carbon gave a singlet peak at  $10.4\delta$ . The aromatic protons of the thiophene ring were identified at  $6.95\delta$  and  $7.49\delta$ , whereas

protons on the benzene ring were at 7.53 $\delta$  and 7.98 $\delta$ . The carboxylic acid proton gave a broad singlet peak at 12.93 $\delta$ . The spectrum is shown in Figure 1.17.

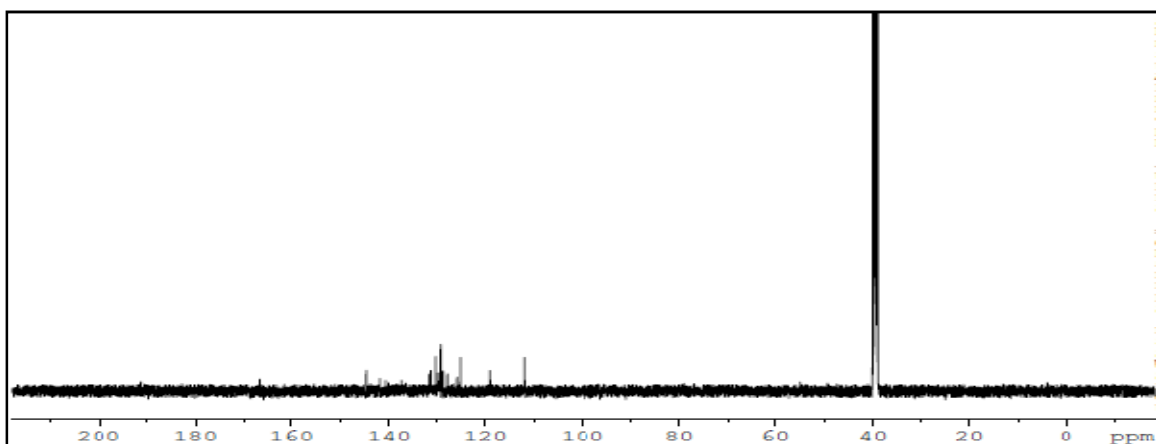
The proton decoupled  $^{13}\text{C}$ nmr spectrum of PHMT2YBA gave characteristic peaks for 14 chemically different carbon atoms. The carboxylic acid and azomethine carbons were assigned with signals at 166.28ppm and 131.42ppm respectively. All the carbon atoms of aromatic rings in the molecule gave characteristic peaks in the range 112ppm-145ppm. The assignments of signals are given in Table 1.10 and the spectrum is given in Figure 1.18.

**Table 1.10**  $^1\text{H}$ nmr and  $^{13}\text{C}$ nmr spectral data of PHMT2YBA

	$^1\text{H}$ nmr		$^{13}\text{C}$ nmr		
	$\delta$ value	Assignment/ Labelled No.	$\delta$ value	Assignment/ Labelled No.	
	8.01(br,s)	1(NH)	166.28	1	
	7.88(dd)	2	144.74	2	
	7.15(dd)	3	130.15	3	
	6.69(m)	4	125.75	4	
	10.40(s)	5(CH=N)	127.80	5	
	7.49(d)	6	131.12	6	
	6.95(d)	7	128.97	7	
	7.53(d)	8	129.15	8	
	7.98(d)	9	131.12	9	
	12.93(br,s)	10(COOH)	131.42	10	
			141.95	11	
			129.68	12	
			112.02	13	
			119.07	14	



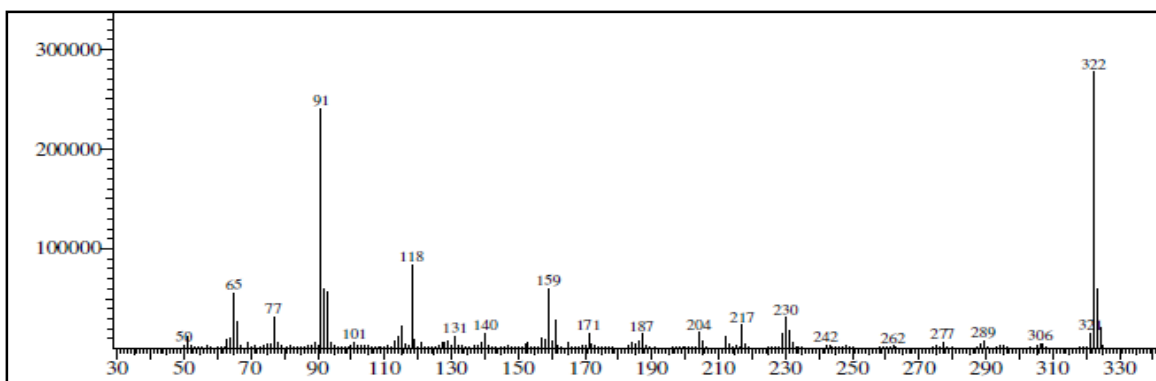
**Fig.1.17**  $^1\text{H}$ nmr spectrum of PHMT2YBA



**Fig.1.18**  $^{13}\text{C}$ nmr spectrum of PHMT2YBA

### *Mass spectral studies*

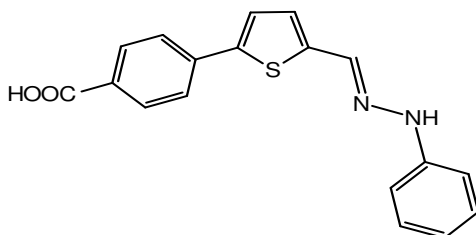
The molecular ion peak at  $m/z$  322 was the base peak itself for PHMT2YBA. Appearance of peak at  $m/z$  323 can be assigned to the  $[\text{M}+1]^+$  species. The  $[\text{M}]^+:[\text{M}+1]^+$  ratio (100:20.0) suggest that 18 carbon atoms were present in the molecule. Loss of an oxygen atom gave a peak at  $m/z$  306. The peaks at  $m/z$  159 and 187 were due to the fragments  $[\text{C}_{10}\text{H}_6\text{S}]^+$  and  $[\text{C}_{11}\text{H}_7\text{OS}]^+$  respectively.  $[\text{C}_7\text{H}_6\text{N}_2]^+$  and  $[\text{C}_6\text{H}_5\text{N}]^+$  fragments from phenyl hydrazone part gave peaks at  $m/z$  118 and 91 respectively. The mass spectrum is given in Figure 1.19.



**Fig.1.19** Mass spectrum of PHMT2YBA

### *Electronic spectral studies*

The Schiff base PHMT2YBA exhibited two important peaks in the UV-visible spectrum at  $33113\text{cm}^{-1}$  and  $38986\text{cm}^{-1}$ , which can be assigned to  $n\rightarrow\pi^*$  and  $\pi\rightarrow\pi^*$  electronic transitions. From the discussion, the structure of the Schiff base can be represented as in Figure 1.20.



**Fig.1.20** Structure of PHMT2YBA

### **Synthesis of complexes**

Transition metal complexes of the Schiff base PHMT2YBA were synthesized with Cr(III), Co(II), Ni(II), Cu(II) and Zn(II) ions. 2mM solution of the Schiff base PHMT2YBA 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. The precipitated complex was filtered, washed several times with ethanol-water mixture and dried. Melting points of all

the complexes were found to be greater than 300<sup>0</sup>C. All the complexes were coloured and obtained in good yield. The copper complex was obtained with maximum yield compared to other complexes. The yield and colours of the complexes are given in Table 1.11.

### **Characterization of complexes**

Different analytical techniques adopted for the characterization of complexes include magnetic moment measurements, elemental analysis, conductance measurements, electronic and infrared spectral studies. These analyses are described in detail here.

#### ***Elemental analysis***

Estimation of different elements in the complexes gave a definite idea about the exact molecular formula of the complexes. The CHNS analysis data is provided in Table 1.11. The experimentally obtained values were found to be very close to the theoretical 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***

The geometry of the complexes can be identified by the measurement of magnetic moments. Chromium(III) complex was assigned octahedral geometry whereas cobalt(II) and nickel(II) complexes were found to be in distorted octahedral geometry since they exhibited magnetic moment values 3.81BM, 4.01BM and 3.15BM respectively<sup>57-60</sup>. The copper(II) chelate exhibited 1.63BM and a square planar geometry was fixed for it. For the zinc(II) complex diamagnetic nature was observed since there was d<sup>10</sup> configuration and tetrahedral geometry was ascertained for this complex.

### ***Molar conductance studies***

The electrical conductivity of the complexes were analysed in the solvent dimethyl sulphoxide. The molar conductance values obtained were in the range  $5\text{-}16\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ , suggesting that all the complexes were non-electrolytic in nature and counter ions were not present in them. Table 1.11 includes the conductance data of the complexes.

### ***IR spectral studies***

The assignments of IR spectral peaks are given in the Table 1.12. The presence of new vibrational bands around  $3400\text{cm}^{-1}$  signified the presence of coordinated water molecule in each complex. The vibrational frequencies of C=N were found to be decreased suggesting the participation of this group in the complexation process. Appearance of new M-O and M-N bonds strongly support the coordination of the oxygen and nitrogen atom to the metal ion. Since there is not much shift in the symmetric and asymmetric stretching vibrations of the carboxylate group in the spectra of complexes, compared with that of the ligand, it can be concluded that the carboxylate group is not involved in coordination with the metal ions in all the complexes.

### ***<sup>1</sup>Hnmr spectral studies***

In the proton magnetic resonance spectra of the complexes, the characteristic peak of the carboxylate group was not found to be shifted, compared with that of the ligand. The appearance of peak at  $12.9\delta$  supported the fact that carboxylate group was not coordinated to the central metal ion in the complexes. The downward shift of the azomethine proton peak in the spectra of the complexes confirmed the involvement of azomethine group in the coordination.



### ***Electronic spectral studies***

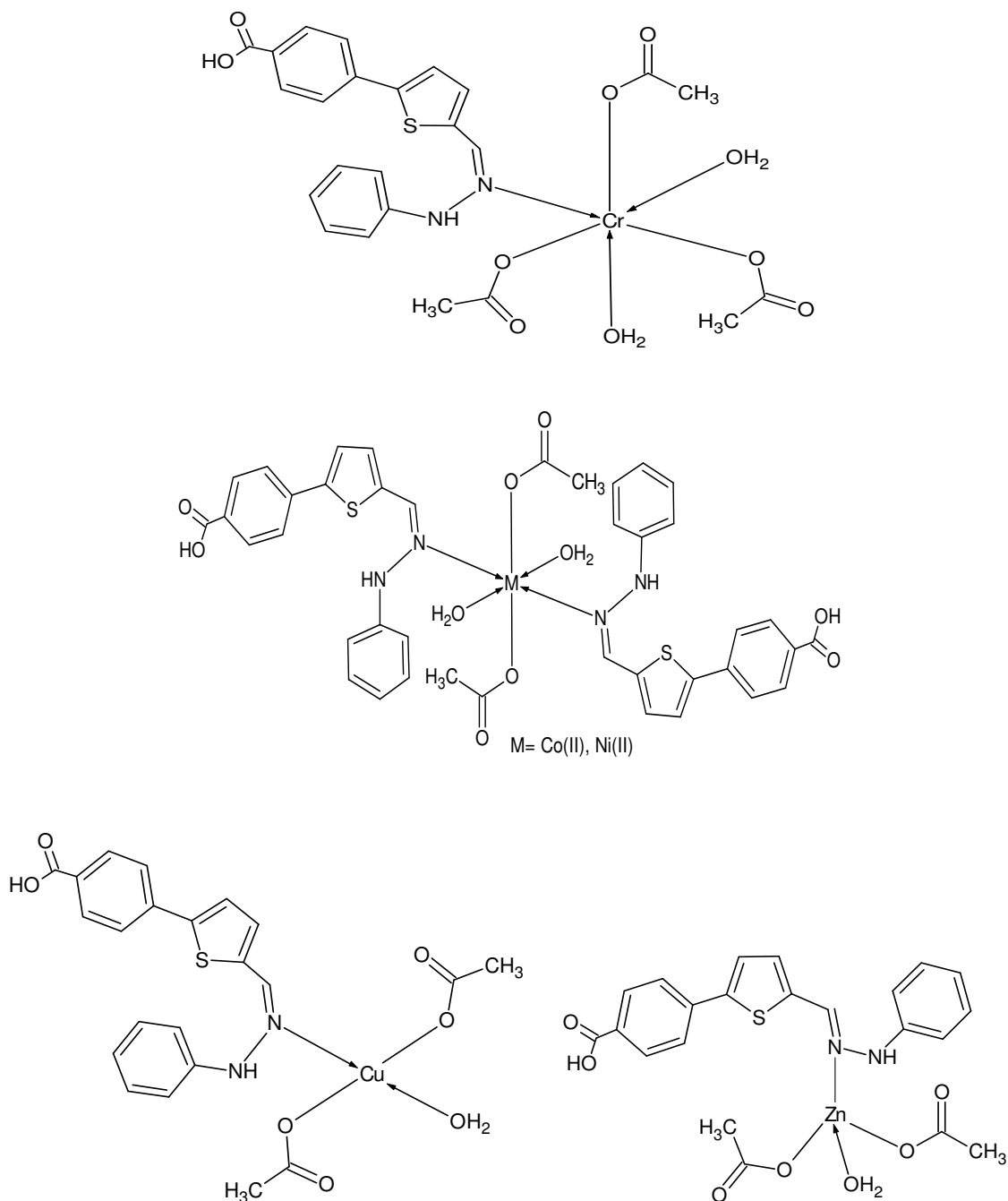
Both the K band and R band undergone bathochromic shift in the electronic spectra of the complexes, compared to that of the ligand, which established the coordination of the Schiff base with the metal ion.

The appearance of three bands in the electronic spectrum of Cr(III) complex at  $24213\text{cm}^{-1}$ ,  $33333\text{cm}^{-1}$  and  $38834\text{cm}^{-1}$  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. The 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  ${}^4\text{T}_1(\text{F})\rightarrow{}^4\text{T}_1(\text{P})$  for Co(II) which was a  $d^7$  system, were exhibited at  $24540\text{cm}^{-1}$ ,  $33956\text{cm}^{-1}$  and  $38911\text{cm}^{-1}$  respectively.  ${}^3\text{A}_2\rightarrow{}^3\text{T}_2$ ,  ${}^3\text{A}_2\rightarrow{}^3\text{T}_1(\text{F})$  and  ${}^3\text{A}_2\rightarrow{}^3\text{T}_1(\text{P})$  electronic transitions in Ni(II) complex gave three absorption bands at  $24301\text{cm}^{-1}$ ,  $32949\text{cm}^{-1}$  and  $38911\text{cm}^{-1}$  respectively and octahedral geometry was assigned for the complex. In the Cu(II) complex, for which 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  $33727\text{cm}^{-1}$  and  $39063\text{cm}^{-1}$  respectively. An intense peak at  $38986\text{cm}^{-1}$  in the electronic spectrum of Zn(II) chelate was assigned to ligand to metal charge transfer transition.

### ***Thermogravimetric studies***

The thermogram of the Cr(III) complex showed three stages of decomposition. Two coordinated water molecules and one acetate group were lost in the first and second stages respectively. In the third stage, the ligand and two acetate groups are removed from the complex molecule at  $700^\circ\text{C}$ . Ni(II) complex underwent a two stage decomposition pattern. Loss of two water molecules and two carboxyphenyl moieties were observed at  $70\text{-}342^\circ\text{C}$  in the initial stage. Two acetate groups and the rest of both the ligands were lost in the second stage.

Based on the above explanations, the structures of the complexes of the Schiff base PHMT2YBA can be represented as in Figure 1.21. Also it is confirmed that in all the complexes, the Schiff base behaves as a monodentate species.



**Fig.1.21** Structures of metal complexes of PHMT2YBA

**Table 1.11** Microanalytical, magnetic and conductance data of the ligand PHMT2YBA 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)	$\mu_{\text{eff}}$ (BM)	Molar Conductance ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ )	Geometry
PHMT2YBA (LH)	Pale brown	68	322	292	-	66.98 (67.08)	4.06 (4.35)	9.58 (8.70)	8.99 (9.94)	-	-	-
[CrLAc <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Pale brown	66	587	>300	7.35 (8.86)	48.51 (49.06)	5.12 (4.60)	5.38 (4.77)	6.73 (5.54)	3.81	8	Octahedral
[CoL <sub>2</sub> Ac <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Black	60	857	>300	6.02 (6.88)	55.5 (56.01)	3.62 (4.43)	5.74 (6.53)	6.98 (7.47)	4.01	12	Octahedral (distorted)
[NiL <sub>2</sub> Ac <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Pale Green	68	857	>300	6.01 (6.85)	55.86 (56.03)	4.98 (4.44)	5.99 (6.54)	8.02 (7.47)	3.15	6	Octahedral (distorted)
[CuLAc <sub>2</sub> (H <sub>2</sub> O)]	Brown	72	522	>300	12.86 (12.18)	49.59 (50.62)	4.13 (4.60)	6.04 (5.37)	7.01 (6.14)	1.63	7	Square planar
[ZnLAc <sub>2</sub> (H <sub>2</sub> O)]	Off white	64	523	>300	12.25 (12.49)	50.89 (50.44)	4.33 (4.56)	4.86 (5.35)	5.68 (6.11)	D	10	Tetrahedral

Ac: Acetate, D: Diamagnetic

**Table 1.12** Characteristic infrared absorption frequencies of PHMT2YBA 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	$\nu_{\text{M-N}}$
PHMT2YBA (LH)	3308	-	3054	1685	1618	1514	1257	1109	750, 696	-
[CrLAc <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3305	3373	3070	1687	1604	1544	1259	1120	775, 690	565
[CoL <sub>2</sub> Ac <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3305	3414	3064	1689	1598	1566	1257	1103	750, 692	547
[NiL <sub>2</sub> Ac <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3304	3381	3037	1691	1597	1498	1255	1109	752, 694	551
[CuLAc <sub>2</sub> (H <sub>2</sub> O)]	3315	3400	3066	1656	1593	1544	1259	1102	775	536
[ZnLAc <sub>2</sub> (H <sub>2</sub> O)]	3305	3404	3062	1687	1600	1517	1259	1111	781, 748, 694	508