

Part I

Synthesis and Characterization

Chapter 5

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

Synthesis and characterization of the Schiff base (E)-4-(5-[(2-carbamothioyl hydrazono)methyl]thiophen-2-yl)benzoic acid is explained in detail in this chapter. The chelating efficiency of this ligand was tested with metal ions Cr(III), Co(II), Ni(II), Cu(II) and Zn(II). These complexes were also subjected to characterization studies like elemental analysis, magnetic moment measurements and spectroscopic techniques 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 the amino compound.

Thiophene-2-carbaldehyde was arylated by the standard method for Meerwin arylation⁵⁶. A solution of p-aminobenzoic acid (75mM) in 100ml of water was prepared along with the addition of 40ml conc. HCl. This solution was cooled in an ice bath to lower the temperature of 0-5⁰C range. To this, a solution of 91mM solution of sodium nitrite in 35ml of water was added slowly and stirred well. In order to complete the diazotization reaction, the mixture was kept for 20 minutes. Then added 75mM solution of thiophene-2-carbaldehyde in 50ml acetone to the above solution followed by CuCl₂.2H₂O solution (23mM in 25ml water) with stirring. Kept this reaction mixture for two days with occasional shaking. A yellow coloured precipitate formed was filtered, washed with plenty of warm water and dried. The melting point of this arylated

derivative, 4-(5-formylthiophen-2-yl)benzoic acid (FT2YBA) was 281⁰C. The scheme of Meerwin arylation is given in Figure 1.11.

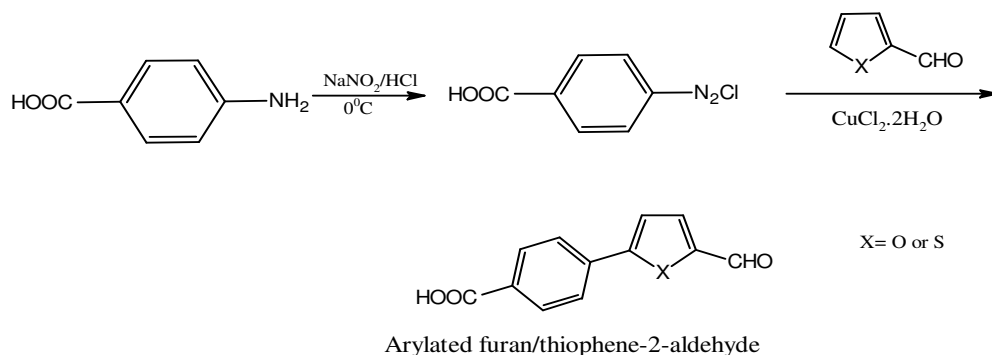


Fig.1.11 Synthetic strategy of arylated derivative (Meerwin arylation)

Synthesis of ligand

3mM of 4-(5-formylthiophen-2-yl)benzoic acid was dissolved in hot ethanol and refluxed on a water bath. To this, hot thiocarbamoyl hydrazide solution (3mM) prepared in ethanol-water mixture was added slowly. Continued the refluxing for further 3 hours. The volume of the reaction mixture was reduced by evaporation and cooled. Then the contents were added to ice cold water with constant stirring. The precipitated ligand, (E)-4-(5-[(2-carbamothioyl hydrazono)methyl]thiophen-2-yl)benzoic acid (CTHMT2YBA) was filtered, washed with ethanol-water mixture and dried. The melting point of CTHMT2YBA was 288⁰C.

Characterization of ligand

The Schiff base CTHMT2YBA was characterized as per the following methods.

Elemental analysis

The elemental analysis data of the Schiff base is given in Table 1.8. The experimentally obtained values were in good agreement with the calculated values. The

measured percentage of nitrogen content in the Schiff base prepared was 13.84% while the theoretically expected value was 13.70%.

IR spectral studies

The infrared spectral data of CTHMT2YBA is represented in Table 1.9. The characteristic vibrational frequencies of primary amino group were shown as distinct peaks at 3490cm^{-1} and 3369cm^{-1} . The carboxylate symmetric and asymmetric vibrations were assigned at 1577cm^{-1} and 1695cm^{-1} respectively. Medium intense band found at 1608cm^{-1} can be attributed to the stretching vibrations of azomethine group (CH=N). The in-plane deformation was shown at 1006cm^{-1} and out of plane deformations were at 814cm^{-1} and 777cm^{-1} .

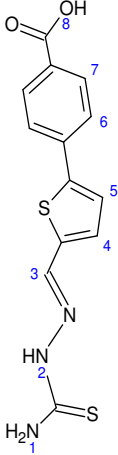
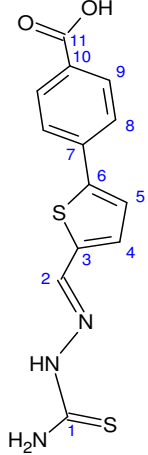
NMR spectral studies

The proton NMR spectrum of Schiff base CTHMT2YBA exhibited nine distinct proton signals. The assignments of peaks are given in Table 1.7. A broad singlet observed at 3.25δ was due to the NH_2 protons. Another broad singlet at 8.16δ was assigned to NH proton of the thiosemicarbazide part. The azomethine proton gave a peak at 8.27δ . Four aromatic protons both in the thiophene ring and benzene ring appeared as doublets in the region 7.50δ - 7.96δ . The appearance of a weak signal at 12.92δ due to the SH proton confirmed the existence of tautomerism. The carboxylic proton exhibited its signal at 11.47δ .

^{13}C nmr spectrum is shown in Figure 1.13. The presence of eleven chemically different carbon atoms was confirmed by this spectrum. The thionyl carbon exhibited its signal at 166.80ppm . The azomethine carbon was identified at 125.35ppm . Carbon atoms of the thiophene ring appeared at 139.41ppm , 134.21ppm and 131.11ppm . The aromatic carbons of the benzene ring exhibited four signals in the range 128ppm - 143ppm . The

presence of carbonyl group in the compound arising from the carboxylate group was established by a characteristic signal at 177.66ppm. The assignments of signals to different carbon are expressed in Table 1.7.

Table 1.7 $^1\text{Hnmr}$ and $^{13}\text{Cnmr}$ spectral data of CTHMT2YBA

$^1\text{Hnmr}$			$^{13}\text{Cnmr}$		
	δ value	Assignment/ Labelled No.	δ value	Assignment/ Labelled	
	3.25(br,s,2H)	1(NH ₂)	166.80	1	
	8.16(br,s,1H)	2(NH)	125.35	2	
	8.27(1H)	3(CH=N)	139.41	3	
	7.91(d,1H)	4	134.21	4	
	7.50(d,1H)	5	131.11	5	
	7.74(d,2H)	6	125.95	6	
	7.96(d,2H)	7	128.72	7	
	11.47(s,1H)	8(COOH)	137.33	8	
	12.92(br,s,1H)	9(SH)	139.41	9	
			143.80	10	
			177.66	11	

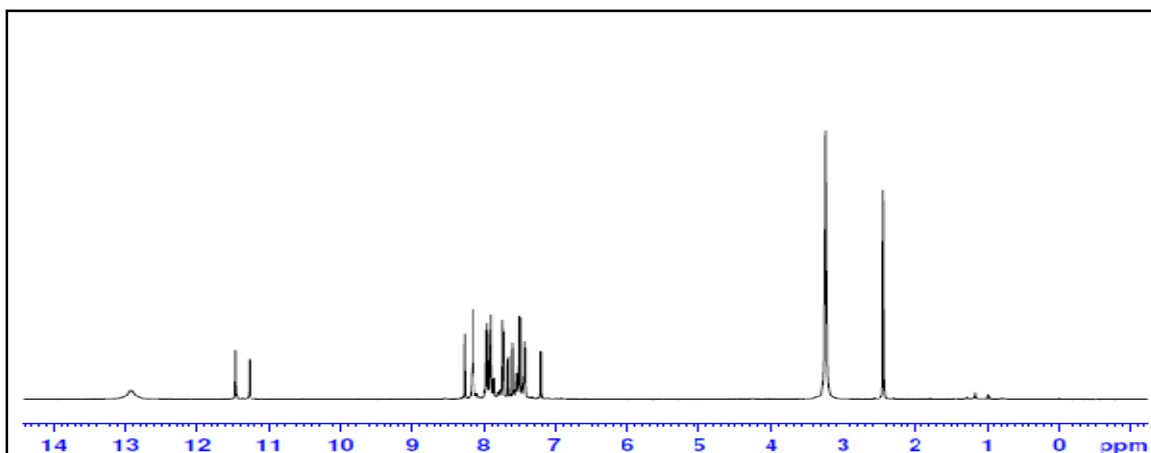


Fig.1.12 $^1\text{Hnmr}$ spectrum of CTHMT2YBA

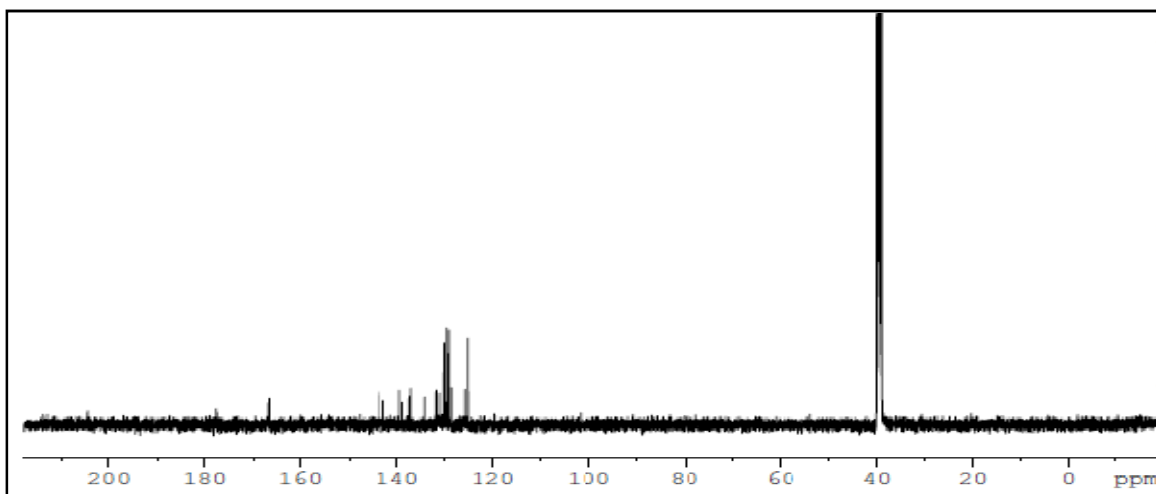


Fig.1.13 ^{13}C nmr spectrum of CTHMT2YBA

Mass spectral studies

In the mass spectrum of CTHMT2YBA, the molecular ion peak at m/z 305 was very much weak with relative abundance less than 5. The loss of OH moiety from the Schiff base resulted in a peak at m/z 288. The formation of fragments at m/z 256 and m/z 242 were due to the fragments $[\text{C}_{13}\text{H}_8\text{N}_2\text{O}_2\text{S}]^+$ and $[\text{C}_{13}\text{H}_{10}\text{N}_2\text{OS}]^+$ respectively. Further fragmentation resulted in the daughter ion $[\text{C}_{12}\text{H}_8\text{N}_2\text{S}]^+$ which had m/z value 212. A peak observed at m/z 204 can be attributed to the fragment $[\text{C}_{11}\text{H}_8\text{O}_2\text{S}]^+$. The base peak was obtained at m/z 139 by $[\text{C}_6\text{H}_7\text{N}_2\text{S}]^+$ fragment. Two peaks at m/z 96 and m/z 75 were due to $[\text{C}_5\text{H}_4\text{S}]^+$ and $[\text{NH}_2\text{-CS-NH}]^+$ species respectively. The spectrum is given in Figure 1.14.

Electronic spectral studies

The two important peaks were exhibited by the Schiff base CTHMT2YBA in the UV-visible spectrum at 26281cm^{-1} and 39063cm^{-1} , which were assignable 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 1.15.

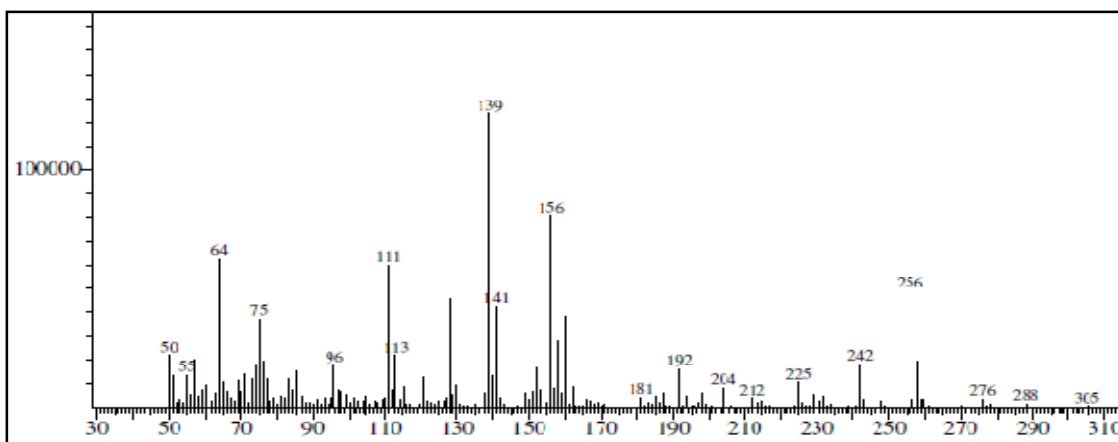


Fig.1.14 Mass spectrum of CTHMT2YBA

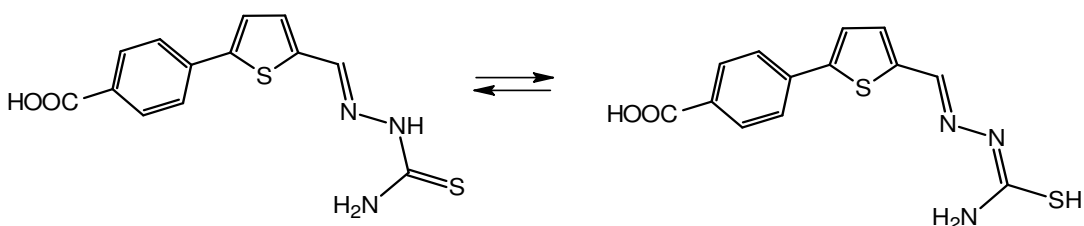


Fig.1.15 Tautomeric forms of CTHMT2YBA

Synthesis of complexes

Transition metal complexes of the Schiff base CTHMT2YBA were synthesized with Cr(III), Co(II), Ni(II), Cu(II) and Zn(II) ions. 2mM solution of the Schiff base CTHMT2YBA was heated to boiling on a waterbath and added hot ethanolic solution of the metal salt (2mM) slowly. The pH was adjusted by adding sodium acetate to the mixture. Then it was refluxed continuously for 4 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 all the complexes were noted. The yield, colour and other characteristics of the complexes are given in Table 1.8.

Characterization of complexes

Analytical tools adopted for the characterization of complexes include magnetic moment measurements, elemental analysis, conductance measurements and spectral studies like electronic and infrared spectroscopy. These analyses are described in detail here.

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 1.8. The observed values were very close to the theoretical values. It was found that Cr(III), Cu(II) and Zn(II) complexes were of 1:1 stoichiometry whereas Co(II) and Ni(II) complexes possess 1:2 stoichiometry between the metal and ligand.

Magnetic moment studies

Measurement of magnetic moment data helped to identify the geometry of the complexes. The results are given in Table 1.8. Chromium(III), cobalt(II) and nickel(II) complexes were assigned octahedral geometry since they exhibited magnetic moment values 3.54BM, 3.75BM and 2.82BM respectively. The copper chelate showed 1.75BM and a square planar geometry was found to be suitable for it. For the zinc complex diamagnetic nature was observed and this result matched with the fact that Zn(II) ion has d^{10} configuration. Tetrahedral geometry was therefore suggested for it.

Molar conductance studies

For all the complexes, the molar conductance data was measured in DMSO medium. The values obtained were in the range $10-16\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ and hence it was concluded that in all the complexes counter ions were not present outside the coordination sphere. Therefore non-electrolytic behaviour was assigned for them.

IR spectral studies

In the IR spectra of the complexes, the downward shift of the vibrational frequencies of the azomethine bond, compared to that in the ligand CTHMT2YBA, strongly confirmed the coordination of imine nitrogen to metal in all complexes. Additional bands in the region $3200\text{-}3300\text{cm}^{-1}$ were attributed to the coordinated water molecules in all the chelates. Again the new M-S and M-N bonds showed their presence in the complex as characteristic peaks in the low field region. On comparing the symmetric and asymmetric stretching vibrations of the carboxylate group in ligand and the complexes, it can be concluded that the COOH group is not participating in coordination with the metal ion. The IR spectral data is given in Table 1.9.

NMR spectral studies

The non-involvement of carboxylate group in coordination is well elucidated by the $^1\text{Hnmr}$ spectral studies of the complexes. In the proton magnetic resonance spectrum of all the chelates, there was a characteristic peak at 11.5δ as found in the pmr spectrum of the ligand. At the same time the signal obtained at 12.92δ in the case of Schiff base spectrum, was disappeared in the spectra of chelates, which clearly indicates the coordination of sulphur atom in the thiocarbamoyl hydrazide part of the ligand to the central metal ion.

Electronic spectral studies

Intra ligand electronic transitions and d-d transitions were obtained from the electronic spectra of the complexes. The shifting of these bands to longer wavelength region was a clear indication of complexation. There were three bands in the electronic spectrum of Cr(III) chelate at 26809 , 38986 and 40404cm^{-1} , which were characteristic of

${}^4A_2(F) \rightarrow {}^4T_2$, ${}^4A_2(F) \rightarrow {}^4T_2(F)$ and ${}^4A_2 \rightarrow {}^4T_1(P)$ electronic transitions of an octahedral field. ${}^3A_2 \rightarrow {}^3T_2$ and ${}^3A_2 \rightarrow {}^3T_1(F)$ electronic transitions in Ni(II) complex gave two absorption bands at 30303 and 40160 cm^{-1} respectively and octahedral geometry was assigned for the complex. In the Cu(II) complex, for which a square planar geometry was assigned, ${}^2B_1 \rightarrow {}^2A_1$ and ${}^2B_1 \rightarrow {}^2B_2$ transitions were shown at 27285 and 35026 cm^{-1} respectively. The absorption bands observed at 26882 cm^{-1} for Zn(II) complex was due to the L \rightarrow M charge transfer transition.

Thermogravimetric studies

The Cr(III) and Ni(II) complexes of CTHMT2YBA were found to be stable upto 60 $^{\circ}$ C. The decomposition of Cr(III) complex followed a definite three stage pattern. In the first stage (60-150 $^{\circ}$ C) two coordinated water molecules were lost. Two acetate groups and two CO₂ molecules are removed in the second stage. The third stage was due to the loss of rest of both the ligands and two bridged acetates. The decomposition of Ni(II) complex also resulted with a definite three stage pattern. The first was assigned to the loss of two water molecules. The second stage consisted of three substages. In the first substage two COOH groups were lost. Then two NH₂ groups and two phenyl groups were removed in the second and third substages respectively. The third stage corresponded to the loss of rest of both the ligands. The percentage mass losses according to the TG curves and the theoretical values were in good agreement for both the complexes. The mass loss from the pyrolysis was also found out. The results are explained in Part IV.

Based on the above explanations, the structures of the complexes of the Schiff base can be represented as in Figure 1.16. In all the chelates the Schiff base, CTHMT2YBA acts as monovalent bidentate ligand.

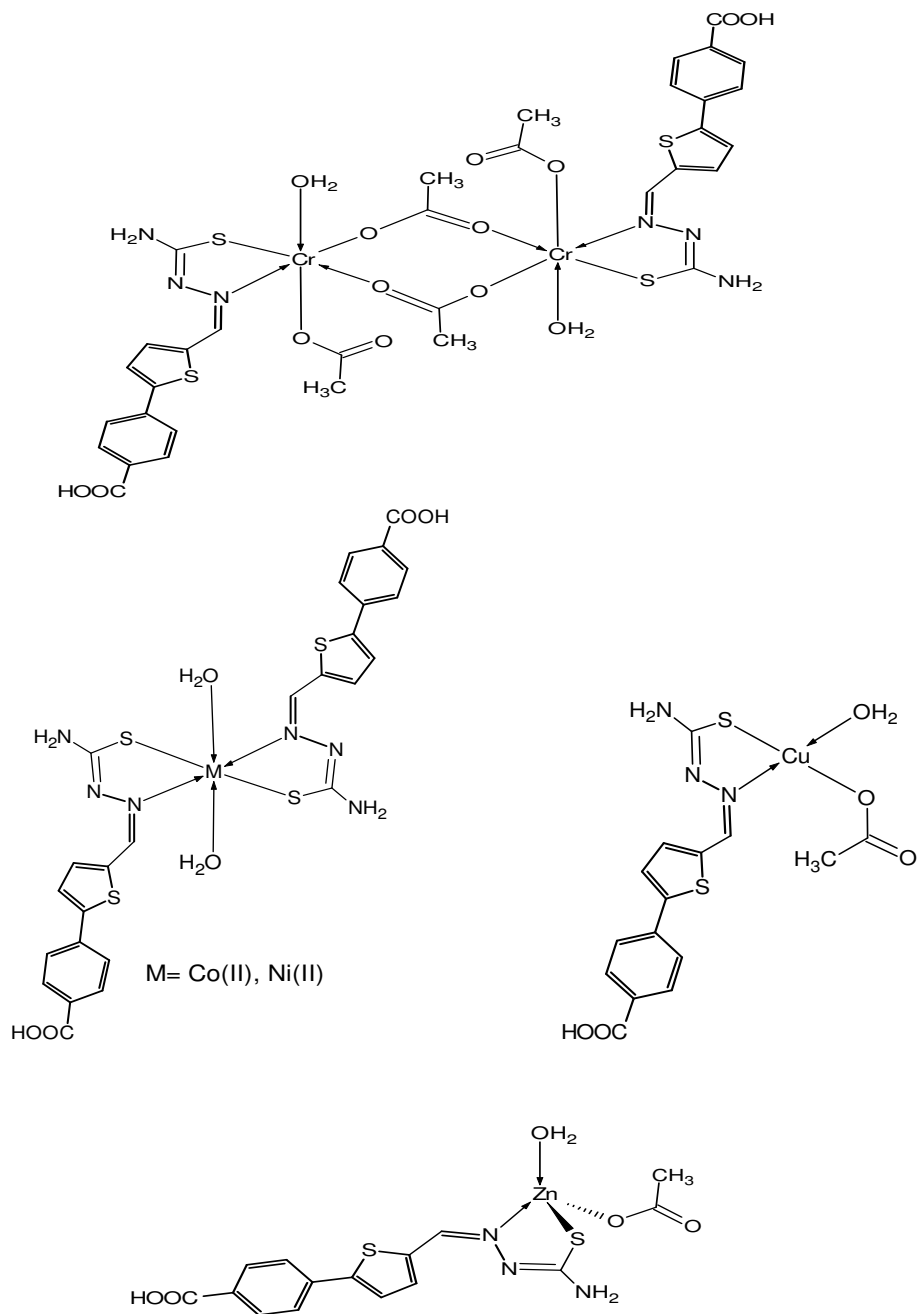


Fig.1.16 Structure of metal complexes of CTHMT2YBA

Table 1.8 Microanalytical, magnetic and conductance data of the ligand CTHMT2YBA 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
CTHMT2YBA (LH)	Pale brown	72	305	288	-	52.98 (51.15)	4.16 (3.60)	13.84 (13.70)	20.48 (20.98)	-	-	-
[CrLAc ₂ (H ₂ O)] ₂	Pale brown	68	492	>300	11.35 (10.57)	41.01 (41.46)	4.12 (3.66)	7.85 (8.54)	12.33 (13.01)	3.54	16	Octahedral
[CoL ₂ (H ₂ O) ₂]	Black	60	703	>300	7.86 (8.38)	43.86 (44.39)	4.10 (3.41)	12.45 (11.95)	19.03 (18.21)	3.75	12	Octahedral
[NiL ₂ (H ₂ O) ₂]	Pale Green	70	703	>300	9.18 (8.35)	43.58 (44.40)	4.21 (3.42)	12.66 (11.95)	19.16 (18.23)	2.82	10	Octahedral
[CuLAc(H ₂ O)]	Gray	78	445	>300	13.86 (14.29)	39.32 (40.49)	4.17 (3.37)	10.03 (9.45)	15.14 (14.40)	1.75	15	Square planar
[ZnLAc(H ₂ O)]	Off white	66	446	>300	15.51 (14.65)	41.08 (40.32)	4.23 (3.36)	8.65 (9.41)	13.89 (14.33)	D	12	Tetrahedral

Ac: Acetate, D: Diamagnetic

Table 1.9 Characteristic infrared absorption frequencies of CTHMT2YBA and its transition metal complexes

Complex	$\nu_{\text{N-H}}$	$\nu_{\text{H}_2\text{O}}$	$\nu_{\text{C-H(Ar)}}$	ν_{COO} (asym)	$\nu_{\text{C=N}}$	ν_{COO} (sym)	$\nu_{\text{C-O}}$	In plane bending	Out of plane bending	$\nu_{\text{M-N}}$	$\nu_{\text{M-S}}$
CTHMT2YBA (LH)	3490, 3369	-	3174	1695	1608	1577	1284	1006	814, 777	-	-
[CrLAc ₂ (H ₂ O) ₂]	3423, 3361	3321	3197	1689	1598	1544	1276	1097	808, 777	567	530
[CoL ₂ (H ₂ O) ₂]	3421, 3400	3284	3170	1689	1602	1570	1246	1007	810, 777	556	489
[NiL ₂ (H ₂ O) ₂]	3415, 3398	3296	3184	1685	1604	1570	1251	1076	827, 779	592	511
[CuLAc(H ₂ O)]	3421, 3360	3277	3159	1687	1598	1544	1286	1012	823, 773	596	492
[ZnLAc(H ₂ O)]	3415, 3392	3282	3170	1689	1598	1552	1278	1051	837, 781	551	501