

SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF SOME TRANSITION METAL COMPLEXES OF NOVEL SCHIFF BASE LIGANDS DERIVED FROM CURCUMIN MOIETY

¹Saritha T.J., ²P.Metilda

¹Research Scholar, Department of Chemistry and Research, ²Assistant Professor, Department of Chemistry and Research Nesamony Memorial Christian college, Marthandam, Tamilnadu-629165, India.

Affiliated to Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli, Tamilnadu-627012

Abstract : Schiff bases are considered as a very important class of organic compounds which have wide applications in many biological aspects. Transition metal complexes of Schiff bases are one of the most adaptable and thoroughly studied systems. In this paper, two novel Schiff-base ligands derived from (a) [Curcumin & 2-Aminopyrimidine (**L**₁)] (b) [Curcumin & semicarbazide (**L**₂)] and its transition metal complexes [Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)] were synthesized. All the synthesized compounds have been characterized by elemental analysis, IR, UV, magnetic measurement, molar conductance, NMR and TG/DTA analysis. On the basis of elemental and spectral studies, four coordinated geometry has been assigned complexes for **L**₁ and six coordinated geometry has been assigned to complexes of **L**₂.

Keywords - Curcumin, 2-Aminopyrimidine, Semicarbazide, Transition metal complexes.

1. INTRODUCTION

Today the research in coordination chemistry plays a vital role in the development of inorganic chemistry. Schiff bases are considered as privileged ligand in coordination chemistry as they easily form stable complexes with most transition metal complexes. Schiff bases derived from an amino and carbonyl groups are an important class of compounds that contains azomethine nitrogen ie; >C = N linkage which is essential for biological activity. Curcumin has been widely used as a yellow pigment to color food, drugs and cosmetics, and it is also interesting from a pharmaceutical point of view because of its potential use as a drug or model substance for treatment of various diseases. The most interesting effects are probably its potential use against cancer, HIV-infections, cystic fibrosis, and as an immune-modulating agent (Arbiser et.al., 1998). The strong chelating ability of diketones has been widely investigated towards a great number of metal ions; therefore, curcumin could be of great importance in the chelate treatment of metal intoxication and overload. Curcumin exhibits potential therapeutic application against several chronic diseases including cancer, inflammatory, neurological, cardio-vascular and skin diseases (Aggarwal et.al., 2003). Curcumin can chelate metal ions and form metallo-complexes showing greatly effects than curcumin alone (Kanhathaisong et.al., 2011). In view of the biological significance of the parent compounds, two Schiff base ligands were prepared by the condensation of Curcumin with 2-aminopyrimidine and semicarbazide, and its metal complexes have been synthesized and characterized on the basis of various physicochemical and spectroscopic methods.

II. EXPERIMENTAL

Materials and methods

All the chemicals and solvents used in the preparation of ligands and their metal complexes were of A.R grade. Curcumin, 2-Aminopyrimidine and semicarbazide were purchased from Sigma-Aldrich. Metal salts like Zn(II), Cu(II), Ni(II), Co(II) and Mn(II) chlorides and the solvents were purchased from Merck. All reagents were analytical grade producers (Aldrich) and used without further purification. Chemical analysis of Carbon, Hydrogen and Nitrogen was performed using a Elementar Vario EL III CHN analyzer. IR spectra of the ligand and complexes were recorded in the range of 4000 - 400cm⁻¹ on a Shimadzu FTIR-470 Infrared spectrophotometer by KBR disc technique. UV-Visible spectra was recorded using Shimadzu 1601 UV-Visible spectrophotometer using Et-OH as the solvent in the range of 200-700nm. ¹H-NMR spectra were recorded in DMSO-d₆ on a Bruker Avance 111,400 MHz Spectrometer.

2.1 Synthesis of Schiff base ligands - [4,4'-(1E,3Z,5Z,6E)-3-hydroxy-5-(pyrimidin-2-ylimino) hepta-1,3,6-triene-1,7-diyl] bis (2-(methoxyphenol)) [**L**₁] and 2-[5-hydroxy-1,7-bis(4-hydroxy-3-methoxyphenyl)-hepta-1,4,6-triene-3-ylidene]hydrazine carboxamide [**L**₂]

Curcumin (0.01 mol) was dissolved in 20 ml methanol and stirred well at room temperature. Then methanolic solution of 2-Aminopyrimidine (0.01 mol) was added to the prepared curcumin solution. The obtained orange coloured mixture was stirred and refluxed at 60°C in presence of catalytic amount of glacial acetic acid (1-2 drops) for about 6 hrs. After cooling, the resulting orange fine precipitate was filtered and washed well with distilled ethanol repeatedly to remove any unreacted chemicals. The obtained orange crystals were then dried at room temperature. The same procedure was adopted for the preparation of L₂.

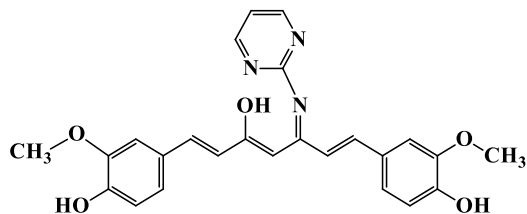


Figure 1: Structure of Schiff base ligand (L₁)

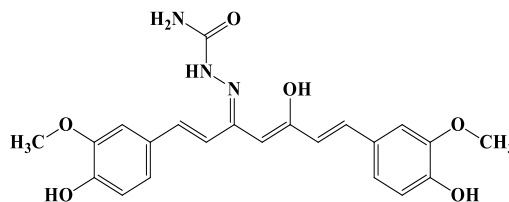


Figure 2: Structure of Schiff base ligand (L₂)

2.3 Synthesis of Schiff base metal complexes.

To the hot solution of schiff base ligands (0.01 mol) in methanol (20ml) was added a hot methanolic solution (10ml) of respective metal chlorides (0.005 mol) drop by drop in 2:1 (ligand: metal) molar ratio. pH of the solution was maintained just below the value of hydrolysis of the metal ion using alcoholic ammonia. The reaction mixture was magnetically stirred and refluxed for 4 hrs at 60°C. The coloured precipitate was filtered and washed by cold ethanol to remove the residue reactants. Finally the obtained powder was dried to get the complexes.

III. RESULTS AND DISCUSSIONS

The analytical data and some physical properties of the ligand (L₁) and its metal complexes are noted in table 1. The data shows that the complexes are formed in the ratio 2:1 (L:M). The schiff base ligand L₁ and its metal complexes are stable at room temperature and soluble in almost all organic solvents like DMSO, DMF, EtOH, MeOH etc.

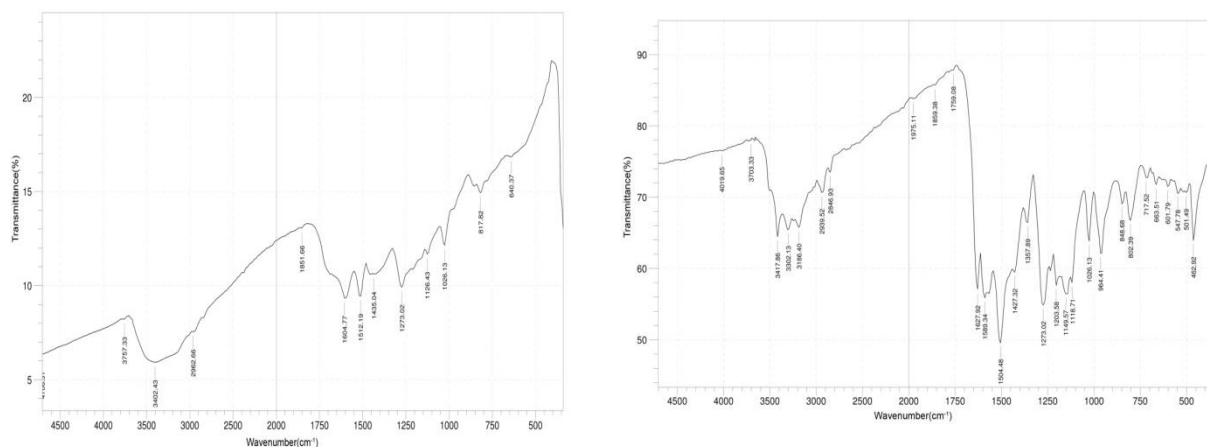
Table: 1 Analytical data and some physical properties of the ligand (L₁) and metal complexes

Compounds	Empirical Formula	Colour & yield	Mol.wt	Analytical data(%)				Molar conductance $\Omega^{-1}\text{cm}^{-1}\text{mol}^{-1}$
				C	H	N	M	
HPMP	C ₂₅ H ₂₃ N ₃ O ₅	Orange (82%)	445.47	67.40 (67.41)	5.16 (5.20)	9.41 (9.43)	---	---
[Mn(HPMP) ₂]	MnC ₅₀ H ₄₄ N ₆ O ₁₀	Black (67%)	943.86	63.57 (63.63)	4.68 (4.70)	8.88 (8.90)	5.68 (5.82)	8.5
[Co(HPMP) ₂]	CoC ₅₀ H ₄₄ N ₆ O ₁₀	Black (68%)	947.85	63.22 (63.36)	4.59 (4.68)	8.89 (8.87)	6.18 (6.22)	9.2
[Ni(HPMP) ₂]	NiC ₅₀ H ₄₄ N ₆ O ₁₀	Brown (65%)	947.61	63.31 (63.37)	4.54 (4.68)	8.86 (8.87)	6.19 (6.10)	9.3
[Cu(HPMP) ₂]	CuC ₅₀ H ₄₄ N ₆ O ₁₀	Green (68%)	952.46	63.02 (63.05)	4.55 (4.66)	8.78 (8.82)	6.59 (6.67)	9.1
[Zn(HPMP) ₂]	ZnC ₅₀ H ₄₄ N ₆ O ₁₀	Dark red (66%)	954.30	62.89 (62.93)	4.61 (4.65)	8.73 (8.81)	6.82 (6.85)	9.0

*Calculated values are given in paranthesis

3.1 IR Spectral analysis

IR spectrum of ligand showed a sharp peak at 3757 cm⁻¹ indicating the phenolic -OH stretching with a broad band at a range from 3200-3500 cm⁻¹, which is due to the $\nu(\text{OH})$ group (in enol form). [Parekh and Patel, 2006]. The IR spectrum of the ligand recorded in KBr (solid state) exhibited a medium intensity band at 1604 cm⁻¹ assignable to C=N bond of the azomethine group [Al-Mohanna et.al., 2005]. A medium band at 1512 cm⁻¹ is regarded as an aromatic $\nu(\text{C}=\text{C})$ stretching vibration. A band in the region 1435 cm⁻¹ show the presence of an aromatic ring. The IR spectrum also displayed a band at 1435cm⁻¹, which can be attributed to $\nu(\text{C}=\text{N})$ of the pyrimidine ring [Sonmez et.al, 2005].

Figure 3: IR spectrum of (a) ligand (L₁) and (b) [Cu(L₁)₂]

The band at 1604cm^{-1} is due to azomethine group $\nu(\text{C}=\text{N})$ of the ligand undergoes a shift to higher frequency by about $25\text{-}40\text{ cm}^{-1}$ in the spectra of all the metal complexes. The shift of this group frequency in the spectra of the metal complexes suggests the coordination of azomethine nitrogen atom to metal atom. Apart from all the above frequencies, vibrations characteristic of the curcumin moiety has been observed in the range, $1200\text{-}1450\text{ cm}^{-1}$ and $635\text{-}860\text{ cm}^{-1}$. The appearance of low intensity non-ligand bands in the region $550\text{cm}^{-1}\text{-}530\text{cm}^{-1}$ and $465\text{cm}^{-1}\text{-}455\text{cm}^{-1}$ in all the complexes are assigned to stretching frequency of $\nu(\text{M-O})$ and $\nu(\text{M-N})$ bands respectively [Cukurovali, 2002]. On the basis of these observations, it can be concluded that the ligand is coordinated to the metal ion in a bidentate fashion through the azomethine nitrogen and the enolic -OH of curcumin moiety.

Table 2: IR spectral data of the ligand (L₁) and its complex (cm^{-1})

Compounds	$\nu(\text{O-H})$	$\nu(\text{C=O})$	$\nu(\text{CO})_{\text{phenol}}$	$\nu(\text{OCH}_3)$	$\nu(\text{C=N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
L ₁	3402	1512	1273	1026	1604	---	---
[Mn(L ₁) ₂]	3332	1481	1342	1010	1635	555	462
[Co(L ₁) ₂]	3363	1512	1273	1006	1627	540	462
[Ni(L ₁) ₂]	3387	1597	1273	1026	1627	570	462
[Cu(L ₁) ₂]	3302	1504	1273	1025	1627	547	462
[Zn(L ₁) ₂]	3394	1512	1265	1026	1627	540	462

3.2 Electronic Spectral analysis

Electronic spectral studies of all these complexes were recorded in EtOH in the region of $200\text{-}700\text{ nm}$. In the spectra of the Schiff base ligand, the absorption band observed around 327.81 nm were assigned to a benzene $\pi \rightarrow \pi^*$ transition and the band around 427.63 nm were assigned to $n \rightarrow \pi^*$ transition associated with the azomethine ($\text{C}=\text{N}$) chromophore [Maurya et al., 2003]. These transitions are also found in the spectra of the complexes, but they are shifted towards longer wavelength from ligand to complex, indicating coordination of ligand to metals through the azomethine moiety. The intense charge transfer band due to the ligand totally masks the weak forbidden d-d bands of the manganese(II) complex. The magnetic moment value of the complex is found to be 5.88 BM indicating a high-spin complex with five unpaired electrons. These observations support the assumption of a tetrahedral geometry for the manganese(II) complex [Sing et al., 2001]. The absorption band at 596.23 nm in the cobalt(II) complex corresponding to ${}^4\text{A}_2\text{g} \rightarrow {}^4\text{T}_1\text{g}$ transition, which is characteristic of a tetrahedral geometry around the cobalt(II) ion. The magnetic moment value of the cobalt(II) complex (4.36 BM) gives added support to this observation [Mohan et al., 2007]. Nickel(II) complex is diamagnetic and it exhibits two absorption bands at 738.46 nm and 535.13 nm assignable to ${}^1\text{A}_1\text{g} \rightarrow {}^1\text{A}_2\text{g}$ and ${}^1\text{A}_1\text{g} \rightarrow {}^1\text{B}_1\text{g}$ transitions respectively. These values are consistent with a square-planar geometry [Sathyanarayana, 2001]. The electronic spectrum of the copper(II) complex exhibits broad bands centered at 728.24 nm and 425.16 nm corresponding to

${}^1B_{2g} \rightarrow {}^1A_{1g}$, & ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transitions and its magnetic moment value of 1.86 BM suggests square-planar geometry around the metal ion [Daniel et.al., 2008]. The completely filled d-orbital in zinc(II) complex and the absence of LFSE values are mainly responsible for the less extensive coordination chemistry of zinc(II). However, the zinc(II) ion is flexible with respect to a number of ligands that can be adopted in the coordination sphere. Analytical data and molar conductance value of zinc(II) complex adequately support the formulation of this complex. The four coordination sites are occupied by the O, N donors of the ligand in a bidentate fashion. It has been reported that tetrahedral geometry [Todor et.al., 2000] is the most preferred structure for four-coordinated zinc(II) complexes.

Table 3: Electronic Spectral data of ligand (L₁) and its metal complexes

Compounds	Absorption bands (cm ⁻¹)	Tentative assignments	Geometry	(μ _{eff}) B.M
L ₁	427,327	n-π*, π-π*	-	-
[Mn(L ₁) ₂]	428, 285	${}^4A_{2g} \rightarrow {}^4T_{1g}$	Tetrahedral	5.88
[Co(L ₁) ₂]	596, 432	${}^4A_{2g} \rightarrow {}^4T_{1g}$, ${}^4A_{2F} \rightarrow {}^4T_{1F}$	Tetrahedral	4.36
[Ni(L ₁) ₂]	738, 535	${}^1A_{1g} \rightarrow {}^1A_{2g}$, ${}^1A_{1g} \rightarrow {}^1B_{1g}$	Square planar	D
[Cu(L ₁) ₂]	728, 425	${}^1B_{2g} \rightarrow {}^1A_{1g}$, ${}^2B_{1g} \rightarrow {}^2A_{1g}$	Square planar	1.86
[Zn(L ₁) ₂]	423, 221	INCT	Tetrahedral	D

3.3 ¹H-NMR Spectral analysis

The ¹H-NMR spectrum of the ligand was recorded in DMSO-d₆. The ligand also showed one singlet at δ 8.21 ppm which was attributed to the azomethine (-C=N-) proton [Dehghanpour et.al., 2006]. The peak at δ 12.41 ppm in ¹H-NMR spectrum of the ligand assigned for the enolic -OH group of curcumin moiety. The ¹H-NMR spectrum of the parent ligand showed a singlet signal at very downfield at δ 5.42 ppm, which was attributed to two phenolic -OH protons in curcumin [Tümer et.al., 2006]. The Spectrum of the ligand shows a peak at δ 3.84 ppm is accounted to -OCH₃ group of curcumin moiety. The ¹H-NMR spectrum of the ligand revealed multiplets at δ 6.84–7.56 ppm, corresponding to aromatic protons [Naeimi et.al., 2007]. The peak at δ 12.41 ppm in ¹H-NMR spectrum of the ligand assigned for the enolic -OH proton of curcumin moiety disappeared in the zinc complex representing the deprotonation of the enolic group due to coordination with Zn(II), and confirmed the bonding of oxygen to the metal ions (C-O-M) [Majumder et.al., 2006]. Moreover, coordination of nitrogen atom of the ligand to Zn(II) was indicated by a shift of the imine carbon proton signal to downfield region δ 8.42 ppm in comparison with that of the free ligand, inferring coordination through the azomethine nitrogen atom of the ligand [[Majumder et.al., 2006], suggesting deshielding of the azomethine proton and proving its contribution to the covalent bond formed with the metal slight downfield shift is observed in all other signals of the zinc complex.

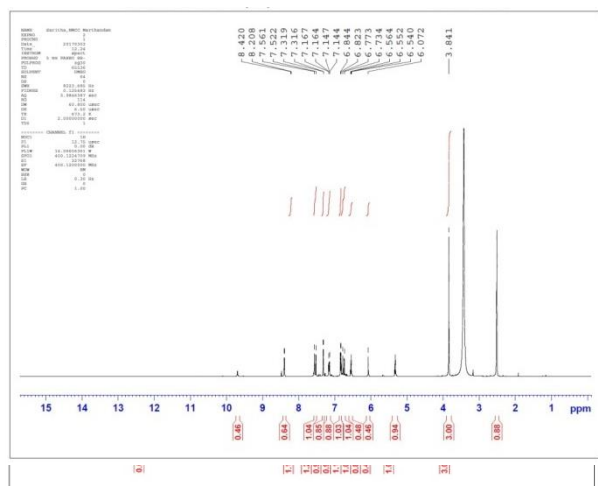


Figure 4: ¹H-NMR spectra of (a) ligand (L₁) (b) [Zn(L₁)₂]

3.4 Mass spectral analysis

The mass spectra of synthesized Ligand (L_1) and its complexes were recorded and the molecular ion peaks obtained confirm the proposed formulae. The mass spectrum of ligand shows an $[M^+]$ ion peak at $m/z = 445.38$ (91.86 %) corresponding to the $(C_{25}H_{23}N_3O_5^+)$ ion was given in Fig 5. The observed peaks are in good agreement with their empirical formula as obtained from the analytical data. The zinc(II) complex showed molecular ion peak, $[M^+]$ at $m/z = 952.35$, in accordance with the proposed structure of the complex. The peaks at m/z values of 239, 529, and 764 corresponds to the loss of various fragments from the complex, respectively. The mass spectrum of the zinc(II) complex confirmed the stoichiometry of the complex.

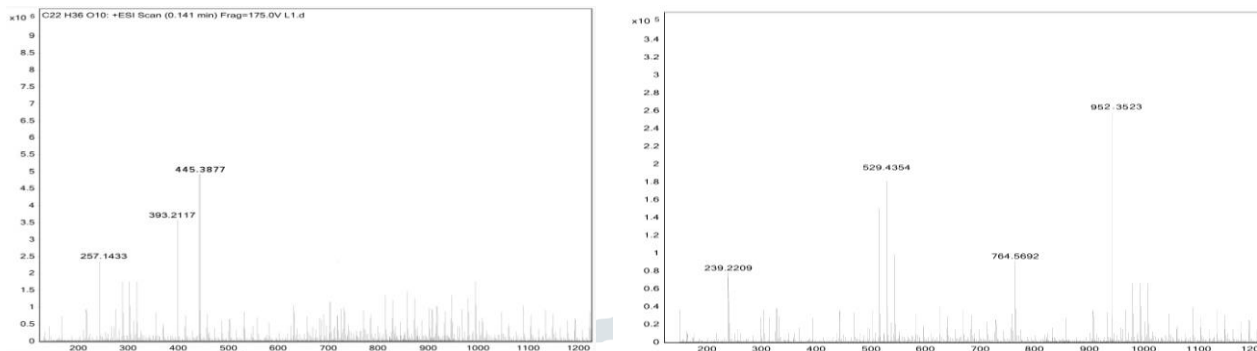


Figure 5: Mass spectra of (a) Ligand (L_1) (b) $[Cu(L_1)_2]$

3.5 Thermal (TGA/DTA) studies

The thermal behaviour of the copper(II) complex was examined using TG and DTA methods, in the temperature range of 40°C to 800°C at a heating rate of $10^\circ\text{C}/\text{min}$. The thermogram indicates that the complex is stable up to 210°C and then decomposes in two stages. The TG curve of Cu(II) complex exhibited no mass loss upto 270°C indicating the absence of lattice and coordinated water (Munde et al., 2009). The first stage of decomposition occurred in the temperature range of 230°C to 380°C with a mass loss of 18.91% (calculated value, 20.82%). This percentage loss was assigned to the loss of an aminopyrimidine moiety from the ligand. The DTG curve indicated a peak at 283.09°C . The second stage of decomposition started at 390°C and continued upto 700°C with DTG peak at 347.41°C . The second stage decomposition of the complex occurred with a mass loss of 75.58% (calculated value 76.65%) and is consistent with the complete decomposition of the complex, i.e; elimination of ligand moiety and oxidation to CuO. [Mohan et al., 2007]. Apart from providing valuable insight into the thermal stability of the complex, this study also helped in characterizing the Cu(II) complex.

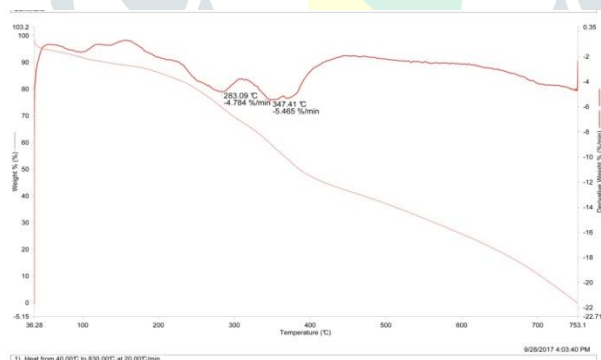


Figure 6: TG/DTA spectrum of $[Cu(L_1)_2]$ complex

Thus from the various physicochemical and spectral studies the proposed structure of metal complexes is shown in Fig:7-8.

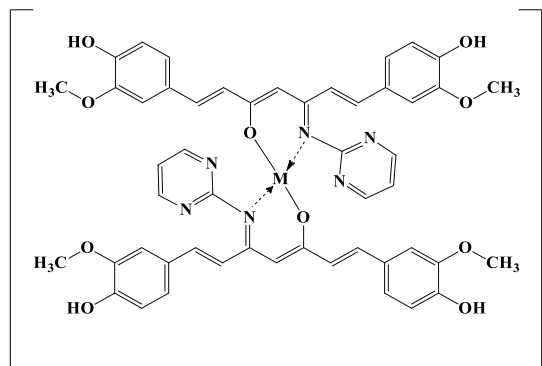


Figure 7: Structure of Schiff base metal complexes of Ni(II) with square planar geometry

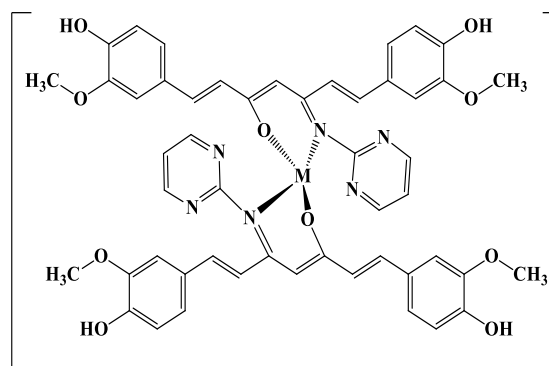


Figure 8: Structure of the Schiff base metal complexes of Mn(II), Co(II) and Zn(II) with tetrahedral geometry Cu(II) and

3.6 Elemental analysis of L₂

The analytical data and some physical properties of the ligand (L₂) and its metal complexes are noted in table 3. The data shows that the complexes are formed in the ratio 2:1 (L:M). The schiff base ligand L₂ and its metal complexes are stable at room temperature and soluble in almost all organic solvents like DMSO, DMF, EtOH, MeOH etc.

Table: 4 Analytical data and some physical properties of the ligand (L₂) and its metal complexes

Compounds	Empirical Formula	Colour & yield	Mol.wt	Analytical data(%)				Molar conductance $\Omega^{-1}\text{cm}^{-1}\text{mol}^{-1}$
				C	H	N	M	
L ₂	C ₂₂ H ₂₃ N ₃ O ₆	Orange (78%)	425.43	62.03 (62.11)	5.28 (4.45)	9.76 (9.88)	---	---
[Mn(L ₂) ₂]H ₂ O	MnC ₄₄ H ₄₆ N ₆ O ₁₃	Brown (72%)	921.81	57.21 (57.33)	5.12 (5.03)	9.05 (9.12)	5.88 (5.96)	15.5
[Co(L ₂) ₂]H ₂ O	CoC ₄₄ H ₄₆ N ₆ O ₁₃	Black (65%)	925.80	57.10 (57.08)	5.04 (5.01)	9.01 (9.08)	6.28 (6.37)	14.9
[Ni(L ₂) ₂]H ₂ O	NiC ₄₄ H ₄₆ N ₆ O ₁₃	Brown (69%)	925.56	57.02 (57.10)	5.10 (5.01)	9.06 (9.08)	6.22 (6.34)	24.7
[Cu(L ₂) ₂]H ₂ O	CuC ₄₄ H ₄₆ N ₆ O ₁₃	Green (78%)	930.41	56.76 (56.80)	4.88 (4.98)	9.10 (9.03)	6.76 (6.83)	30.7
[Zn(L ₂) ₂]H ₂ O	ZnC ₄₄ H ₄₆ N ₆ O ₁₃	Brown (76%)	932.25	56.58 (56.69)	4.91 (4.97)	9.04 (9.01)	7.04 (7.01)	31.6

*Calculated values are given in paranthesis

3.7 IR Spectral analysis

The IR spectrum of the ligand (HMHC) shows a broad band of medium intensity at 3471 cm^{-1} due to (NH) (that may be overlapping with hydrogen bonded O - -H stretching vibrations [Chauhan, 1993]. IR spectrum of the free ligand exhibited a medium intensity band at 3215 cm^{-1} which can be assigned to the (N-H) stretching vibrations of the indole ring system [Revankar et.al., 2000]. The IR spectrum of the Schiff base shows characteristic medium intensity band at 1604 cm^{-1} which is attributed to the $\nu(\text{C}=\text{N})$ vibration of the azomethine group [Srinivasan 2001]. A medium band at 1512 cm^{-1} is regarded as an aromatic $\nu(\text{C}=\text{C})$ stretching vibration. A band in the region 1434 cm^{-1} shows the presence of an aromatic ring. In the spectra of Schiff base complexes, disappearance of carbonyl band and a new strong sharp band that appears at 1635 cm^{-1} region is attributed to the $\nu(\text{C}=\text{N})$ band, confirming the formation of the Schiff base metal(II) complexes.

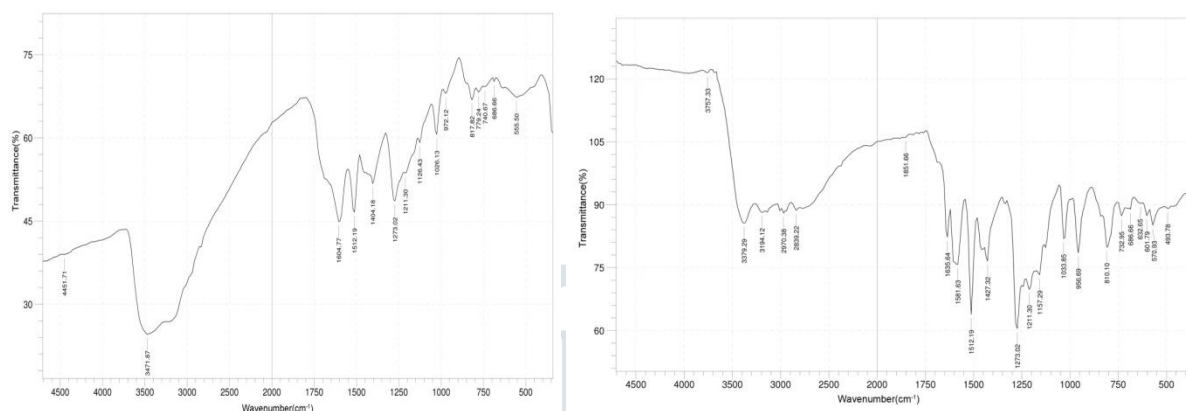


Figure 9: IR spectrum of (a) ligand (L_2) and (b) $[\text{Cu}(L_2)_2]\text{H}_2\text{O}$

In the spectra of complexes, the band due to -NH and (C–O) (phenolic) band shifted to higher frequency by $11\text{--}60\text{ cm}^{-1}$, indicating that nitrogen and phenolic oxygen are directly linked to metal [Mutikainen et.al., 2006]. The band at 1720 cm^{-1} is shifted to lower frequency by about $10\text{--}40\text{ cm}^{-1}$ in the spectra of all the complexes, indicating the involvement of C=O group of semicarbazide in co-ordination. The appearance of low intensity non-ligand bands in the region $580\text{ cm}^{-1}\text{--}530\text{ cm}^{-1}$ and $465\text{ cm}^{-1}\text{--}455\text{ cm}^{-1}$ in all the complexes are assigned to stretching frequency of $\nu(\text{M-O})$ and $\nu(\text{M-N})$ bands [Panchal et.al., 2004] respectively. These bands were absent in the spectra of the free ligands, thus confirming participation of the O and N in the coordination.

Table 5: IR spectral data of the ligand (L_1) and its complex (cm^{-1})

Compounds	$\nu(\text{O-H})$	$\nu(\text{C}=\text{C})$	$\nu(\text{CO})_{\text{phenol}}$	$\nu(\text{OCH}_3)$	$\nu(\text{C}=\text{N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
L_2	3471	1512	1273	1026	1604	---	---
$[\text{Mn}(L_2)_2]\text{H}_2\text{O}$	3356	1512	1273	1026	1627	547	462
$[\text{Co}(L_2)_2]\text{H}_2\text{O}$	3348	1527	1265	1026	1627	540	462
$[\text{Ni}(L_2)_2]\text{H}_2\text{O}$	3387	1512	1273	1033	1635	570	462
$[\text{Cu}(L_2)_2]\text{H}_2\text{O}$	3379	1512	1273	1033	1635	570	493
$[\text{Zn}(L_2)_2]\text{H}_2\text{O}$	3387	1512	1273	1026	1635	570	470

3.8 Electronic Spectral analysis

In the spectra of the Schiff base ligands, the absorption band observed around 288 nm were assigned to a benzene $\pi \rightarrow \pi^*$ transition and the band around 423 nm were assigned to $n \rightarrow \pi^*$ transition associated with the azomethine (C=N) chromophore [Lever, 1984]. The UV spectrum of the ligand gave a characteristic bands at 219 nm and 227 nm which corresponds to the enol form of the ligand. The electronic spectrum of Cu(II) complex derived from the ligand (HMHC) showed three bands at 635 , 428 , and 284 nm . The observed broad band in the case of present Cu(II) complex of ligand can be assigned ${}^2B_{1g} \rightarrow {}^2E_g$, ${}^2B_{2g}$, and ${}^2A_{2g}$ transitions suggesting octahedral geometry of Cu(II) complexes. The magnetic moment value of Cu(II) complex is 1.91 BM , therefore octahedral structure can be assigned to Cu(II) complex [Litkowska et.al., 1999]. The Co(II) complex of the ligand under present study has showed three bands at 638 , 576 and 448 nm due to ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$, ${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}(\text{F})$ and ${}^4T_{1g}(\text{F}) \rightarrow$

${}^4T_{2g}(P)$ transitions, respectively. These transitions suggest octahedral geometry for Co(II) complex. The UV-visible absorption bands along with magnetic moment value (4.56 B.M) suggest a low-spin Co(II) complex with octahedral geometry [Kohout et.al., 1999]. The electronic spectrum of Ni(II) complex of the ligand under present investigation exhibited three bands in the region 676, 530 and 444 nm which are assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions. All these observations favour the octahedral geometry for Ni(II) complex [Masoud et.al., 1991]. The value of magnetic moment in case of Ni(II) complexes at room temperature was calculated and found to be 3.10 B.M that is in the range of a high spin electronic configuration [Pathak et.al., 2001]. Electronic absorption spectra of Mn(II) octahedral complex are expected to show four spin allowed transitions. The four narrow absorption bands approximately around 555, 423, 334, and 296 nm were assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}(4G)$, ${}^6A_{1g} \rightarrow {}^4E_g(4G)$, ${}^6A_{1g} \rightarrow {}^4E_g(4D)$, and ${}^6A_{1g} \rightarrow {}^4T_{1g}(4P)$ transitions, respectively, for octahedral Mn(II) complex [Nethaji et.al., 2006]. The spectrum of Zn (II) complex exhibited only one band at 424 nm which was assigned to a ligand \rightarrow metal charge transfer. The zinc(II) complex were found to be diamagnetic as expected and therefore, their magnetic properties could not be investigated. The charge transfer band at 214 nm was assigned due to transition ${}^2E_g \rightarrow {}^2T_{2g}$ possibly in an octahedral environment [Selwood, 1956].

Table 6: Electronic Spectral data of ligand (L₂) and its metal complexes

Compounds	Absorption bands (cm ⁻¹)	Tentative assignments	Geometry	(μ_{eff}) B.M
L ₂	423, 288	n- π^* , π - π^*	-	-
[Mn(L ₂) ₂]H ₂ O	555,425,334,296	${}^6A_{1g} \rightarrow {}^4T_{1g}(4G)$, ${}^6A_{1g} \rightarrow {}^4E_g(4G)$, ${}^6A_{1g} \rightarrow {}^4E_g(4D)$, ${}^6A_{1g} \rightarrow {}^4T_{1g}(4P)$	Octahedral	5.88
[Co(L ₂) ₂]H ₂ O	638, 576, 448	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$	Octahedral	4.56
[Ni(L ₂) ₂]H ₂ O	676, 530,444	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Octahedral	3.10
[Cu(L ₂) ₂]H ₂ O	635,428, 284	${}^2B_{1g} \rightarrow {}^2E_g$, ${}^2B_{2g}$, and ${}^2A_{2g}$	Octahedral	1.91
[Zn(L ₂) ₂]H ₂ O	424,214	${}^2E_g \rightarrow {}^2T_{2g}$, INCT	Octahedral	D

3.9 ¹H-NMR Spectral analysis

The ¹H-NMR spectrum of the ligand was recorded in DMSO-d₆. In NMR spectra of ligand, two peaks appeared in the range δ 8.64 ppm assignable to the azomethine proton and second in the range δ 13.58 ppm for hydroxyl proton of Curcumin moiety [Munde et.al., 2010]. The Schiff base shows the presence of amide proton (-CONH-) signal at δ 9.63 ppm [Sivasankaran et.al., 2010]. The NH₂ protons were observed around δ 7.02 ppm as singlet. The Schiff base ligand shows a peak at δ 1.29 ppm as singlet is due to the presence of CH₂. The six methyl protons of curcumin were observed as singlet around δ 3.64 ppm [Ching et.al., 2012]. Also a set of multiplets observed in the range δ 6.58–6.98 ppm can be ascribed to the aromatic protons [Silverstein et.al. 1991]. The peak at 13.58 ppm in ¹H-NMR spectrum of the ligand assigned for the -OH proton of curcumin moiety disappeared in the zinc complex representing the deprotonation of the enolic group due to coordination with Zn(II), and confirmed the bonding of oxygen to the metal ions (C-O-M) [Majumder et.al., 2006]. The disappearance of the signal in δ 9.63 ppm confirms the coordination of -CONH- function of quinolinone moiety and its involvement in complexation with metal ion through oxygen atom of carbonyl function. Slight downfield shift is observed in all other signals of the zinc complex. ¹H-NMR spectrum of Ligand (L₂) and its Zn(II) complex is shown in fig: 10.

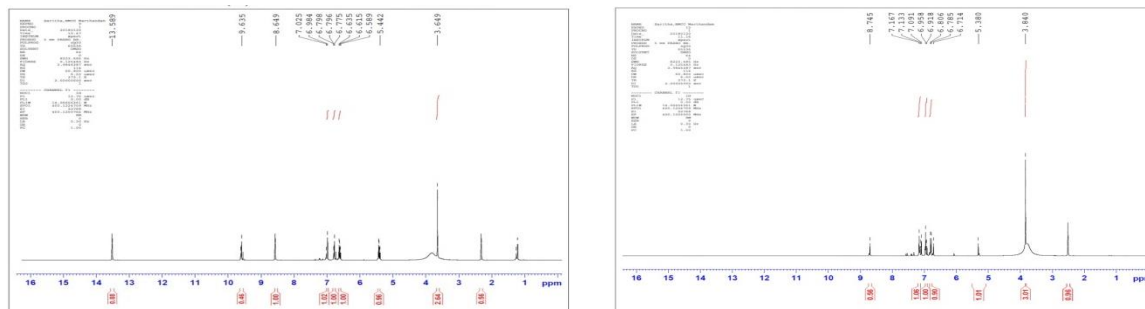


Figure 10: ¹H-NMR spectra of (a) ligand (L₂) and (b) [Zn(L₂)₂]H₂O

3.10 Mass spectral analysis

The mass spectra of synthesized Ligand (HMHC) and its complexes were recorded and the molecular ion peaks obtained confirm the proposed formulae. The mass spectrum of Ligand shows an $[M^+]$ ion peak at $m/z = 424.16$ (92.82 %) corresponding to the $(C_{22}H_{23}N_3O_6)^+$ ion. Also, the spectrum exhibits $m/z = 386.23$ and 238.24 corresponding to various fragments of the ligand molecule. The mass spectrum of the zinc(II) complex confirmed the stoichiometry of the complex. The zinc(II) complex showed molecular ion peak at $m/z = 928.36$, in accordance with the proposed structure of the complex (fig:11). The peaks at m/z values of 215.15, 348.38, 486.24 and 572.06 corresponds to the loss of various fragments of the complex, respectively.

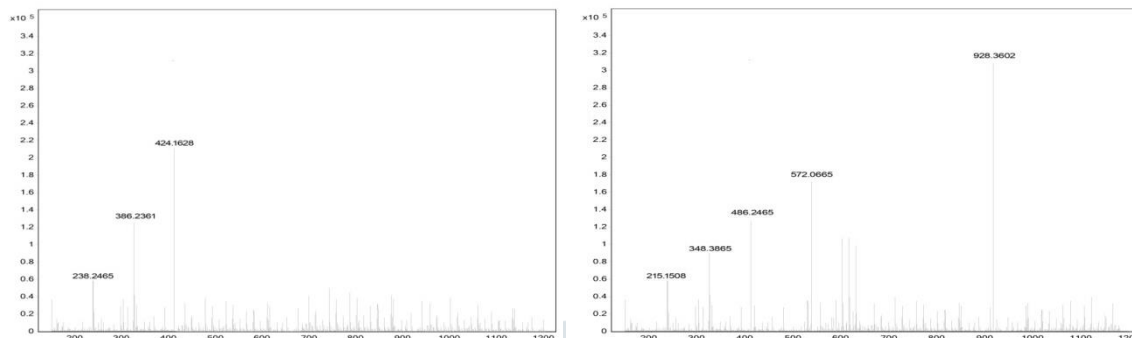


Figure 11: Mass spectra of (a) ligand (L_2) and (b) $[Cu(L_2)_2]H_2O$

3.5 Thermal (TGA/DTA) studies

Thermal decomposition studies of inorganic metal complexes has been received considerable attention recently because it can be used in the structural and kinetic investigation of coordination compounds. The TG-DTA curves of Cu(II) complex show mainly four stages in the decomposition process. The DTA curves showed a weight loss initially in the range of $69.83^\circ C$ with a mass loss of 5.92% indicates the presence of a lattice water molecule (Nikolaev et.al., 1969). The TG curve of Cu(II) complex exhibited no mass loss between $70-300^\circ C$ confirms the absence of coordinated water molecules (Modi et.al., 2007). Weight loss at decomposition temperature is in the range of $310^\circ C$ (27.22%) and $425.76^\circ C$ with a mass loss of 15.20% which corresponds to the loss of amide and chloride molecules. The decomposition temperature in the range of $584.67^\circ C$ with a mass loss of 49.69% which corresponds to the loss of remaining organic moiety of the ligand and finally the complex is converted into its metal oxide [Nami et.al., 2014].

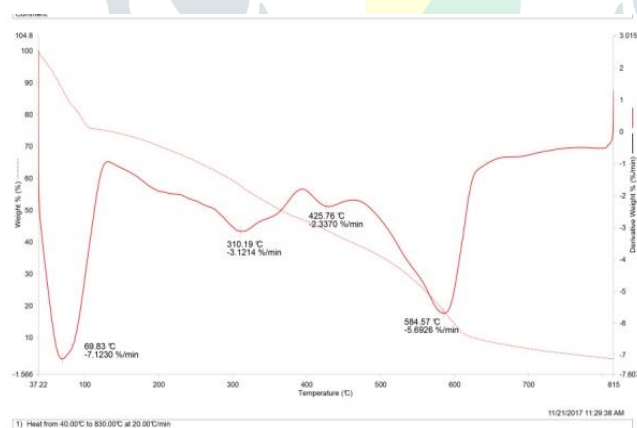


Figure 12: TG/DTA spectrum of $[Cu(L_2)_2]H_2O$ complex

Thus from the various physicochemical and spectral studies the proposed structure of metal complexes is shown in Fig:13.

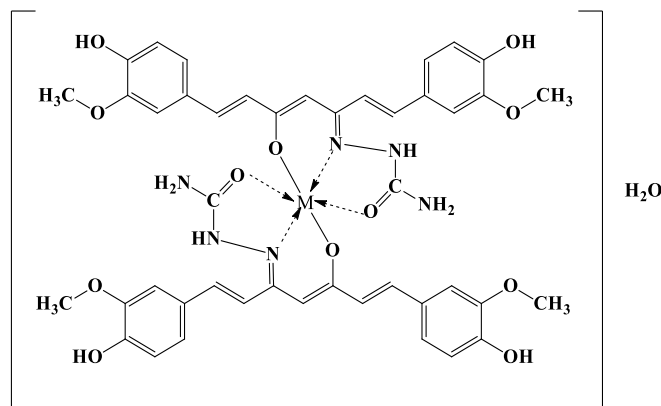


Figure: 13 Structure of the Schiff base metal complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with octahedral geometry

IV. CONCLUSION

In this study, Two novel Schiff base ligands (Curcumin with 2-Aminopyrimidine & semicarbazide) was synthesized. They formed stable complexes, 2:1 (L:M ratio) with transition metal ions such as Zn(II), Cu(II), Ni(II), Co(II) and Mn(II). The synthesized compounds were characterized by the elemental analysis, molar conductance, magnetic measurement, EPR, TG/DTA, IR and electronic spectral analysis. IR spectral data shows that the ligand coordinating to metal atom via azomethine nitrogen and enolic oxygen atoms. In the analysis of ligand L₁ and its complexes, electronic spectral studies revealed square planar geometry for Cu(II) and Ni(II) complexes, whereas Mn(II), Co(II) and Zn (II) posses tetrahedral geometry. Electronic spectral studies of ligand L₂ and its complexes revealed that all the complexes possess octahedral geometry.

V. ACKNOWLEDGEMENT

The authors acknowledge the department of chemistry and reaserch Nesamony Memorial Christian College, Marthandam, K.K. Dist for the facilities provided, STIC, Cochin – 22, SAIF IIT- Mumbai for recording various spectral analysis datas.

REFERENCES

- [1] Aggarwal, BB, Kumar, A, Bharti, AC, 2003, *Anticancer Res.* 23, 363–398.
- [2] Al-Mohanna, MAF, Rabia, MKM, Aly, GY, 2005, 'Synthesis, characterization and electrochemical studies of ternary complexes of lanthanum(III) and cerium(III) with some naphthylidene amino acids and imidazoles. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, 35, 801–809.
- [3] Arbiser, JL, Klauber, N, Rohan, R, Leeuwen, RV, Huang, MT, Fisher, C, Flynn, E, Byers, HR, 1998, *Mol. Med.*, 4, 376–383
- [4] Chauhan, HPS, 1993, 'Organotin(IV) derivatives of o-hydroxyacetophenone glycine', *Indian J. Chem.*, 32A, 157.
- [5] Ching, CL, Gwaram, NS, Ali, HM, Khaledi, H, Abdulla, MA, Hadi, AHA, Lin, TK, Ooi, CL, 2012, 'Antibacterial evaluation of some Schiff bases derived from 2-acetyl pyridine and their metal complexes', *Molecules*, 17, 5952–5971
- [6] Cukurovali, A, Yilmaz, I, Ozmen, H, Ahmedzade, M, 2002, 'Cobalt(II), copper(II), nickel(II) and zinc(II) complexes of two novel Schiff base ligands and their antimicrobial activity', *Transition Met. Chem.*, 27, 171–176.
- [7] Daniel, VP, Murukan, B, Kumari, BS, Mohanan, K, 2008, 'Synthesis, spectroscopic characterization, electrochemical behaviour, reactivity and antibacterial activity of some transition metal complexes with 2-(N-salicylideneamino)-3-carboxyethyl-4,5-dimethylthiophene', *Spectrochim. Acta*, 70, 403–410.
- [8] Dehghanpour, S, Mahmoudkhani, A.H, Amirnasr, A.M, 2007, 'Synthesis and characterization of [Cu(Phca2en)(PPh3)X] (X= Cl, Br, I, NCS, N3) Complexes. Crystal structures of [Cu(Phca2en)(PPh3)Br] and [Cu(Phca2en)(PPh3)I]', *Struct. Chem.*, 17, 255.
- [9] Kanhathaisong S, Rattanaphani S, Rattanaphani V, Manyum T. A spectroscopic investigation of the complex of turmeric dye with copper(II) in aqueous solution. *J. Sci. Technol.*, 2011; 18: 159–165.
- [10] Kohout, J, Hvastijova, M, Kozisek, J, Diaz, JG, Valko, M, Jager, L & Svoboda, I, 1999, 'Cyanamidonitrate-copper(II) complexes of imidazole ligands: X-ray crystallography and physical investigation', *Inorg Chim. Acta.*, 287, 186-192.

- [11] Litkowska, H, Krzyminiowska, VP & Paryzek, WR, 1999, 'Metal-template synthesis and characterization of a nitrogen-oxygen donor Schiff base macrocyclic system', *Monatshefte Fur Chemie*, 130, 243-247.
- [12] Majumder, A, Rosair, GM, Mallick, A, Chattopadhyay, N, Mitra, S, 2006, 'Synthesis, structures and fluorescence of nickel, zinc and cadmium complexes with the N,N,O-tridentate Schiff base N-2-pyridylmethylidene-2-hydroxy-phenylamine', *Polyhedron*, 25(8), 1753-56.
- [13] Maurya, RC, Sharma, P & Sutradhar, D, 2003, 'Synthesis, magnetic and spectral studies of some mixed-ligand complexes of Cu(II) involving diphenic acid and pyridine or aniline derivatives', *Synth. React. Inorg. Met-org. Chem.*, 33(4), 669-682.
- [14] Masoud, MS, Hindawy, AM & Soayed, AS, 1991, 'Structural chemistry of azo complexes', *Trans. Met. Chem.*, 16, 372-376.
- [15] Modi, C, Patel, S, Patel, M, 2007, 'Transition metal complexes with uninegative bidentate Schiff base', *J. Therm. Anal. Calorm*, 82, 441.
- [16] Mohanan, K, Cheriyan, M, 2007, Synthesis and characterization of the complexes of cobalt(II), nickel(II), copper(II) and zinc(II) with 2-(2-carboxyphenylazo)-1,3-diketones, *Asian J. Chem.*, 19, 2831-2838.
- [17] Munde, AS, Jagdale, AN, Jadhav, SM, Chondhekar, TK, 2010, 'Synthesis, characterisation and thermal study of some transition metal complexes of an asymmetrical tetradentate Schiff base ligand', *J. Serb. Chem. Soc.*, 75, 349-359.
- [18] Mutikainen, I, Kannappan, R, Tanase, S, Tureinen, U, Reedjik, J, 2006, *Polyhedron*, 25, 1646.
- [19] Naeimi, H, Safari, J, Heidarneshad, A, 2007, Synthesis of Schiff base ligands derived from condensation of salicylaldehyde derivatives and synthetic diamine, *Dyes Pigm.*, 73(2), 251-253.
- [20] Nami, SAA, Husain, A, Ullah, I, 2014, 'Self assembled homodinuclear dithiocarbamates: One pot synthesis and spectral characterization', *Spectrochim. Acta Part A*, 118, 380-388.
- [21] Nethaji, M, Philip, V, Suni, V, Kurup, MRP, 2006, 'Structural and spectral perspectives of a novel thiosemicarbazone synthesized from di-2-pyridyl ketone and 4-phenyl-3-thiosemicarbazide', *Spectrochim. Acta Part A*, 63(1), 174-181.
- [22] Nikolaev, AV, Logrinenko, VA, Myachina, LI, 1969, *Thermal Analysis*, academic press, Newyork, 2, 779.
- [23] Panchal, PK, Patel, MN, Parekh, HM, 2006, 'Synthesis and Antifungal activity of oxovanadium(IV) complexes with Schiff bases', *J. Pharm. Chem.*, 40(9), 494-97.
- [24] Parekh, HM, Patel, MN, 2006, 'Preparation of Schiff's base complexes of manganese(II), cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) and their spectroscopic, magnetic, thermal and antifungal studies', *Russ. J. Coord. Chem.*, 32, 431-436.
- [25] Pathak, R, Prasad, R, Thankachan, PP & Thomas, MT, 2001, Synthesis of aryl substituted azomethine complexes of iron-, cobalt- and copper(II), *J. Ind. Chem. Soc.*, 78, 28-31.
- [26] Revankar, VK, Sathisha, MP, Pai, KSR, 2008, Synthesis, Structure, Electrochemistry, and Spectral Characterization of Bis-Isatin Thiocarbohydrazone Metal Complexes and Their Antitumor Activity Against Ehrlich Ascites Carcinoma in Swiss Albino Mice, *Met. Based Drugs*, 1-11.
- [27] Sathyanarayana, DN, 2001, 'Electronic Absorption Spectroscopy and Related Techniques', University Press, Hyderabad.
- [28] Selwood, PW, 1956, *Magnetochemistry*, Interscience, New York, London.
- [29] Silverstein, RM, Bassler, GC, Morill, TC, 1991, 'Spectrometric identification of organic compounds, 5th ed., John Wiley and Sons, New York.
- [30] Sing, NK & Sing, SB, 2001, 'Complexes of 1-isonicotinoyl-4-benzoyl-3-thiosemicarbazide with manganese(II), iron(III), chromium(III), cobalt(II), nickel(II), copper(II) and zinc(II)', *Transition Met. Chem.*, 26, 487-495.
- [31] Sivasankaran Nair, M & Selwin Joseyphus, R, 2010, 'Synthesis, characterization and biological studies of some Co(II), Ni(II) and Cu(II) complexes derived from indole-3-carboxaldehyde and glycyglycine as Schiff base ligand', *Arabian Journal of Chemistry*, 3, 195-204.
- [32] Sonmez, M, Sekerci, M, 2005, 'The template synthesis, characterization and thermal investigation of new heterocyclic binucleating Schiff base complexes', *Synth. React. Inorg.-Met. Org. Chem.*, 34, 1551-1561.
- [33] Srinivasan, S, Rajagopal, G, Athappan, PR, 2001, Synthesis, spectral and redox properties of metal complexes of macrocyclic tetraaza chiral Schiff bases, *Trans. Met. Chem.*, 588-593.
- [34] Todor, D, Carmay, LJ, 2000, 'Tetrahedral Vs Octahedral Zinc Complexes with Ligands of Biological Interest: A DFT/CDM Study', *Am. Chem. Soc.*, 122, 11146-11153.