JACJOSHAM

JAC JOURNAL OF SCIENCE, HUMANITIES AND MANAGEMENT

Vol. I No. 2 JUNE 2014 ISSN 2347 - 9868

Bi-Annual

Published by

JAYARAJ ANNAPACKIAM COLLEGE FOR WOMEN (AUTONOMOUS)

(Nationally Accredited at 'A' Grade by NAAC in III Cycle

Periyakulam - 625 601, Theni Dt. Tamilnadu -

CONTENT

SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL SCREENING OF METAL COMPLEXES OF SCHIFF BASE DERIVED FROM 2-AMINO-1,3,4 THIADIAZOLE-5-THIOL

M.Kalanithi

Department of Chemistry, Jayaraj Annapackiam College for Women, Periyakulam-625601, Tamilnadu, India. E mail: kalacharle@gmail.com

M.Rajarajan

Department of Chemistry, Cardamom Planters' Association College, Bodinayakkanur-625513, Tamilnadu, India.

P.Tharmaraj

Department of Chemistry, Thiagarajar College, Madurai-625009, Tamilnadu ,India.

Abstract

A novel Schiff base 2-(N-3-formylchromone) imino-1,3,4-thiadiazole-5-thiol [L]was obtained through the condensation of 2-amino-1,3,4 thiadiazole-5-thiol with 3-formyl chromone. The Co(II),Ni(II),Cu(II) and Zn(II) metal complexes of the ligand L were synthesized. The compounds were characterized by ^{1}H, ^{13}C NMR, UV-Vis, IR, Mass, EPR, molar conductance and magnetic susceptibility measurements. Tetrahedrally distorted square planar geometry was suggested for the Cu(II) complex and distorted tetrahedral geometry was proposed for Co(II), Ni(II) and Zn(II) complexes. The antimicrobial activity against the species Pseudomonas aeruginosa, Escherichia coli, Staphylococcus aureus, Bacillus subtilis, Candida albigans and Aspergillus niger was screened and compared to the activity of the ligands. Fluorescent nature of the ligand was shown by emission spectrum.

Key words: *Schiff base, 3-formylchromone, 2-amino-1,3,4 thiadiazole-5-thiol, transition metal complexes, antimicrobial activity*

1. Introduction

Schiff bases are considered as promising ligands due to their coordinating ability with metal ions. The metal complexes of Schiff bases find a variety of applications in biological [1] and catalytic fields[2]. The 3-formylchromone and its

derivatives with π electron conjugation system were found to possess non-linear optical property [3] and antimicrobial activity [4-6]. These derivatives also serve as intermediates to many products of fine chemical industries such as pharmaceuticals, agrochemicals and dyestuffs [7]. Thiadiazoles are the important heterocyclic compounds with special applications in the medicinal field [8]. The activities such as anticonvulsant, antidepressant, analgesic, antiinflammatory, antiplatelet, antimalarial, antimicrobial, antimycobacterial and antitumoral of thiadiazoles were explored by a review study [9]. Our present approach is to develop a novel Schiff base from a thiadiazole derivative and hence a new ligand system obtained from 3-formyl chromone and 2-amino-1,3,4 thiadiazole-5-thiol was fabricated. The synthesis, structural elucidation and antimicrobial activity of the ligand(L) and its metal(II) complexes were reported in this paper.

2. Experimental

The UV–Visible spectra of the ligand and metal complexes were recorded using a JASCO V-530 spectrophotometer. The IR spectra in KBr discs were recorded on a SHIMADZU FT-IR 8400 S spectrophotometer. Fluorescence spectra were performed on ELICO SL174 spectroflurometer using DMF solvent. Elemental analyses were performed at SAIF, CDRI-Lucknow. The metal contents of the complexes were estimated by incinerating them to oxides [10]. NMR spectrum was recorded using a Bruker DRX-300 MHz NMR spectrometer. EI mass was recorded by JEOL-GC MATE-2 at IIT, Madras-Chennai. EPR spectrum was recorded by Varian E-112 spectrometer at X-band, using TCNE with 100 kHz modulation frequency and 9.1GHz microwave frequency at SAIF, IIT Bombay, India. Magnetic susceptibility of the complexes was measured by MSB mark 1 Sherwood U.K at Thiagarajar College, Madurai. Effective magnetic moments were calculated using the formula $\mu_{eff} = (2.828\chi_M T)^{1/2}$, where χ_M is the corrected molar susceptibility. The diamagnetic corrections were made by Pascal's constant and $Hg[Co(SCN)_4]$ was used as a calibrant. Molar conductance of the complexes (10^{-3} M) was measured in DMF at room temperature using a Systronic conductivity bridge type.

2.1. Synthesis of Schiff base 2-(N-3-formylchromone) imino-1,3,4-thiadiazole-5-thiol (L)

A hot solution of 3-formylchromone (1.74 g, 10 mmol) and 2-amino-1,3,4 thiadiazole-5-thiol (1.33 g, 10 mmol) in ethanol was refluxed with stirring for 4 h . On cooling, the yellow precipitate obtained was filtered out and washed with ethanol and dried. The yield obtained was 60 %. 2-amino-1,3,4 thiadiazole-5-thiol is partially soluble in ethanol and exhibits keto-enol tautomerism in DMSO [11].

2.2. Synthesis of Cu (II) complex

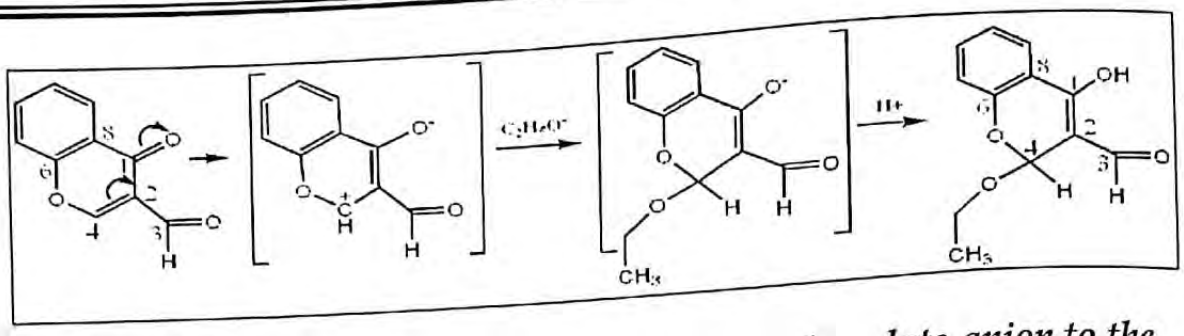
A hot solution of Schiff base (L) (1.008 g, 3 mmol) in ethanol was added to a solution of $CuCl_2$ $2H_2O$ (0.510 g, 3 mmol) in ethanol and stirred. The brown colored complex precipitated in a microcrystalline form was filtered and washed with hot water, ethanol and dried in vacuum.

2.3. Synthesis of Co (II), Ni (II) and Zn(II) complexes

To the hot solution of Schiff base (L) (1.008 g, 3 mmol) in ethanol, a solution (3 mmol) of metal chloride (M = Co(II), Ni(II) and Zn(II)) in ethanol was added and refluxed with stirring for 3 h. The solution was concentrated to one third of its volume and refrigerated for one day. A solid product obtained was filtered, washed with hot water, ethanol followed by petroleum ether and dried in vacuum.

3. Results and Discussion

The synthesis of Schiff base was carried out using ethanol as solvent in hot condition. It was found that an ethanolat-anion [6] was added to a molecule of 3-formylchromone in position 4. This was confirmed by ^{1}H NMR, ^{13}C NMR and mass spectrum. The probable mechanism of the addition is represented in Scheme 1. The physical data, the elemental analyses, and molar conductance of the ligand and complexes are given in Table 1 and Table 2. The complexes are partially soluble in chloroform and acetonitrile but soluble in polar coordinating solvents such as DMF and DMSO. The molar conductance of complexes in 10^{-3} M DMF solution are in the range 09-12 Ω^{-1} cm^2mol^{-1} indicating that, these chelates are non electrolytes [12] . Elemental analyses, spectral, mass and conductance data suggest the molecular formula [M(L)Cl] for Co(II),Ni(II), Cu(II) and Zn(II) complexes. The yield of the complexes was 50-60%.



Scheme 1. The mechanism of the addition of an ethanolate-anion to the 3-formylchromone molecule

Table 1. Physical data of Schiff base ligand(L) and its metal(II) complexes

S.no.	Ligand/complexes	Colour	Formula weight g/mol	MP(°C)
1	$C_{14}H_{15}O_3N_3S_2$(L)	Yellow	336.42	165-167
2	[Co(L)Cl]	Green	429.95	268-270
3	[Ni(L)Cl]	Brown	428.96	273-275
4	[Cu(L)Cl]	Brown	433.95	249-251
5	[Zn(L)Cl]	Yellow	434.95	280-282

Table 2. Microanalytical data of Ligand and its metal (II)complexes

S.no.	Ligand/complexes	Elemental analysis(%) found (Calcd)				M % found (Calcd)	Λ_M m^2 mol^{-1}
		C	H	N	S		
1	$C_{14}H_{15}O_3N_3S_2$(L)	49.75 (49.83)	4.36 (4.48)	12.35 (12.45)	18.97 (19.01)	-	-
2	[Co(L)Cl]	39.00 (39.03)	3.15 (3.28)	9.64 (9.75)	14.74 (14.89)	13.56 (13.68)	08
3	[Ni(L)Cl]	39.01 (39.05)	3.15 (3.28)	9.64 (9.76)	14.74 (14.89)	13.53 (13.63)	12
4	[Cu(L)Cl]	38.59 (38.62)	3.20 (3.24)	9.61 (9.65)	14.62 (14.73)	14.49 (14.59)	09
5	[Zn(L)Cl]	38.34 (38.46)	3.10 (3.23)	9.50 (9.61)	14.54 (14.67)	14.85 (14.95)	11

3.1. ^1H and ^{13}C NMR Spectral studies

2-(N-3-formylchromone) imino-1,3,4-thiadiazole-5-thiol (L)

The ^1H NMR spectrum was recorded in DMSO for the ligand and the structure was confirmed by the following signals : 13.15 δ (H, s, OH); 9.33 δ (H, s,

azomethine proton); 6.88-7.93 δ (4H, m, aromatic protons); 3.52-3.58 δ (2H, q, OCH2); 1.17-1.22 δ (3H, t, -CH_3). The structure of the ligand is shown in Figure 1. The ^{1}H NMR spectrum is shown in Figure 2.

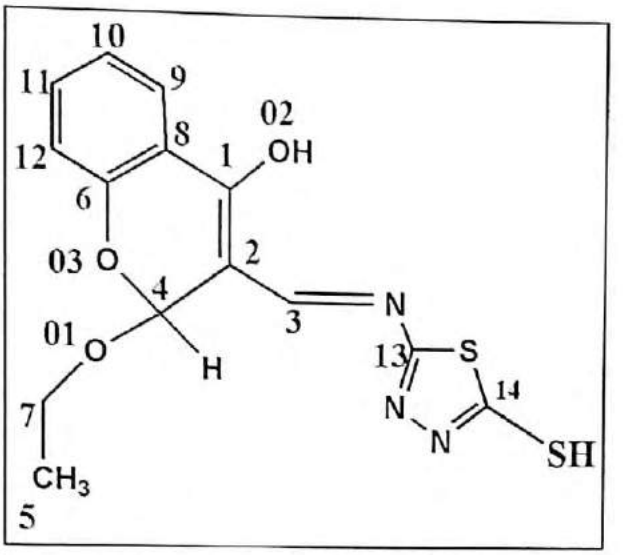


Figure 1. Structure of the Schiff base ligand 2-(N-3-formylchromone) imino-1,3,4-thiadiazole-5-thiol (L)

The ^{13}C NMR (DMSO, δ): δ=16.84(CH_3, -C_5); 55 (CH_2, -C_7); 116-125 (C_8-C_{12}); 179 (CH=N, C_3); 154 (O-CH-O, C_4); 186 (C_{13}); 161-160 (C_1); 132-133(C_{14}) .The ^{13}C NMR spectrum is presented in Figure 3.

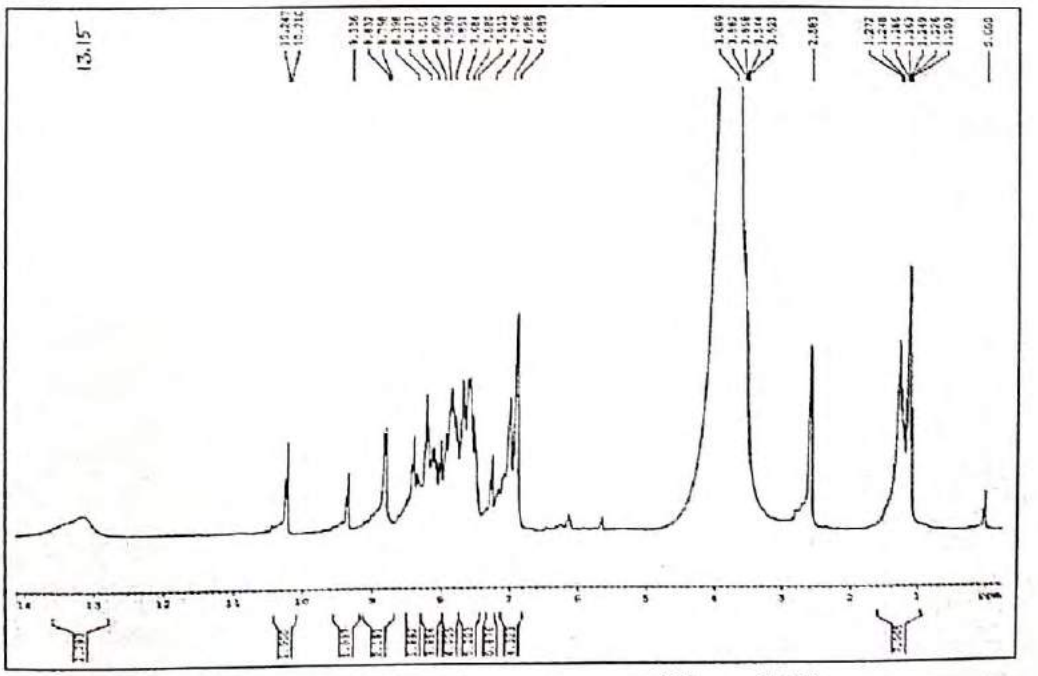


Figure 2 ^{1}H NMR spectrum of ligand (L)

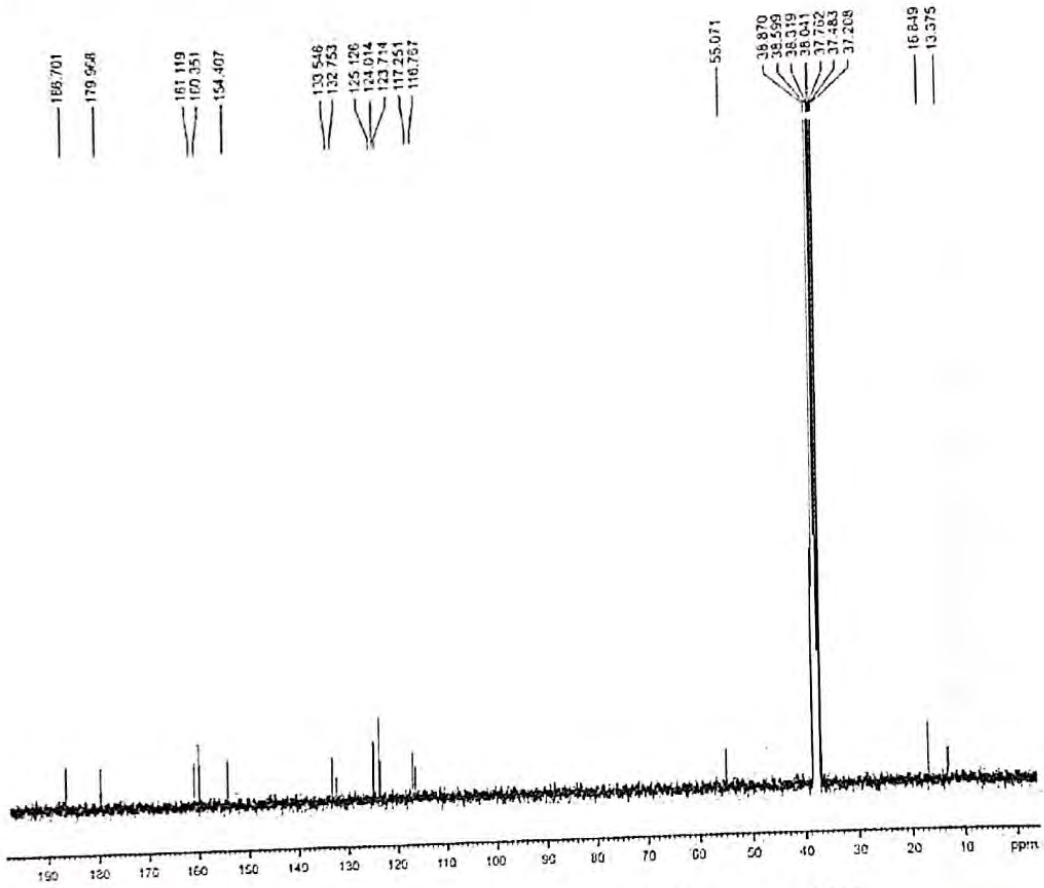


Figure 3. 13 C NMR spectrum of the ligand(L)

3.2. IR spectral studies

The spectral data for ligand (L) and the complexes are presented in the Table 3.The formation of Schiff base was confirmed by the absence of parent bands at 1740 and 3340, 3450 cm^{-1} originally attributed to ν(C=O) of aldehyde and the ν(NH_2) group of 3-formylchromone and heterocyclic amine respectively. A new band at 1643 cm^{-1} was observed confirming the azomethine linkage [13] of the Schiff base. The spectrum shows a band at 3120 cm^{-1} which is assigned to ν(OH) stretching vibration and the low value may be due to intermolecular hydrogen bonding between OH and azomethine nitrogen. The band at 1606 cm^{-1} was assigned to ν(CH=N) of thiadiazole ring. The band at 1265 cm^{-1} was assigned to ν(C-O) of the enolic OH group [14]. The stretching vibration at 759 cm^{-1} is due to ν(C-S) [15] of the thiadiazole ring was observed in the spectrum.

In comparison with the ligand the ν(C=N) due to azomethine vibration is shifted to a lower frequency (10-25 cm^{-1}) in the metal complexes indicating the coordination of azomethine nitrogen to the metal(II) ion [16]. A shift in the band at 1606 cm^{-1} of the heterocyclic ring (6-12 cm^{-1}) in complexes suggesting the coordination via thiazole nitrogen [17] (N→M). The participation of deprotanated OH group is confirmed by the blue shift (1270-1286 cm^{-1}) of ν(C-O) in the complexes. In all the complexes the ν(C-S) remains unchanged indicating that the endocyclic sulphur does not involve in coordination. In addition, the IR spectra of complexes show new non ligand bands at 416-495 cm^{-1} and 530-595 cm^{-1} assigned to ν(M-N) and ν(M-O) vibrational modes [18] respectively. From the above discussions it was suggested that the ligand behaves as a monobasic tridentate ligand coordinated to the metal(II) ions via the azomethine N, thiadiazole N and enolic O.

Table 3. IR spectral data of the ligand and its metal(II) complexes(cm^{-1})

Compounds	ν(C=N)	ν(C=N) ring	ν(C-O)	ν(M-N)	ν(M-O)
$C_{14}H_{15}O_3N_3S_2$(L)	1643	1606	1265	-	-
[Co(L)Cl]	1632	1616	1270	443	530
[Ni(L)Cl]	1620	1600	1273	430	550
[Cu(L)Cl]	1637	1615	1276	495	595
[Zn(L)Cl]	1625	1594	1272	416	540

3.3. Magnetic susceptibility and electronic spectral studies

The absorption bands of the ligand in DMF were appeared at 383 nm (26109 cm^{-1}) and 421 nm (23752 cm^{-1}) due to n - π* and π - π* transitions. The molar intensity of the ligand is higher in DMF than in chloroform [19]. The absorption spectra of complexes were recorded in DMF and in chloroform. The molar intensities are less in chloroform than in DMF. The absorption bands of the ligand and the complexes recorded in DMF with the molar absorption coefficients(ε) are given in Table 4. The cobalt(II)complex exhibit two low intensity bands in 670 nm (14925 cm^{-1}) and 610 nm (16393 cm^{-1}) which are closer and it can be assigned tentatively to $^4A_2(F) \rightarrow {}^4T_1(P)$ transition for the tetrahedral geometry[20]. Nickel(II) complex shows low intensity absorption band in 684 nm (14619 cm^{-1})due to $^3T_1(F) \rightarrow {}^3T_1(P)$ transition characteristic of tetrahedral geometry [21]. A broad band in 706 nm

region (16666 cm^{-1}) was observed for copper(II) complex which can be tentatively assigned to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition suggesting tetrahedrally distorted square planar [6].

For cobalt (II) complex the magnetic moment is found to be 4.28 B.M. which is an indicative of distorted tetrahedral geometry [22]. The Ni(II) complex reported herein is high spin with a magnetic moment value of 2.91B.M which indicates that, the complex of Ni(II) is probably distorted tetrahedral [23].The magnetic moment value of 1.75 B.M for copper complex falls within the range normally observed for distorted square planar Cu(II) complexes[24].The magnetic moment of the zinc(II) complex shows the diamagnetic behavior of the complex.

Table 4. Electronic spectral data of the Schiff base (L) and metal (II) complexes in DMF

Compound	Λ_{max} (cm^{-1}) ε (L mol^{-1} cm^{-1})	Transition	Geometry	μ_{eff} (BM)
$C_{14}H_{15}O_3N_3S_2$(L)	26109(5000) 23752(3316)	n - π* π - π*	-	-
[Co(L)Cl]	14925 (2620)	$^4A_2$ (F) → $^4T_1$ (P)	Distorted Tetrahedral	4.28
[Ni(L)Cl]	14600(45)	$^3T_1$(F) → $^3T_1$(P)	Distorted Tetrahedral	2.91
[Cu(L)Cl]	16666(706)	$^2B_{1g} \rightarrow {}^2A_{1g}$	Tetrahedrally Distorted Square planar	1.75

3.4. Mass spectral studies

The EI mass spectra of ligand (L) and its complexes are recorded. The molecular ion peak for the ligand was observed at 336 m/z. The molecular ion peak is in good agreement with the suggested molecular formula indicated from elemental analyses. The molecular ion peak for [Cu(L)Cl] was observed at 433.88 m/z confirming the stoichiometry of the complex. The molecular ion peaks of Co(II), Ni(II) and Zn(II) complexes were observed at 430,429 and 435 respectively, suggesting the molecular formula [M(L)Cl]. The mass spectrum of the ligand and the copper complex are depicted in Figure 4 and Figure 5.

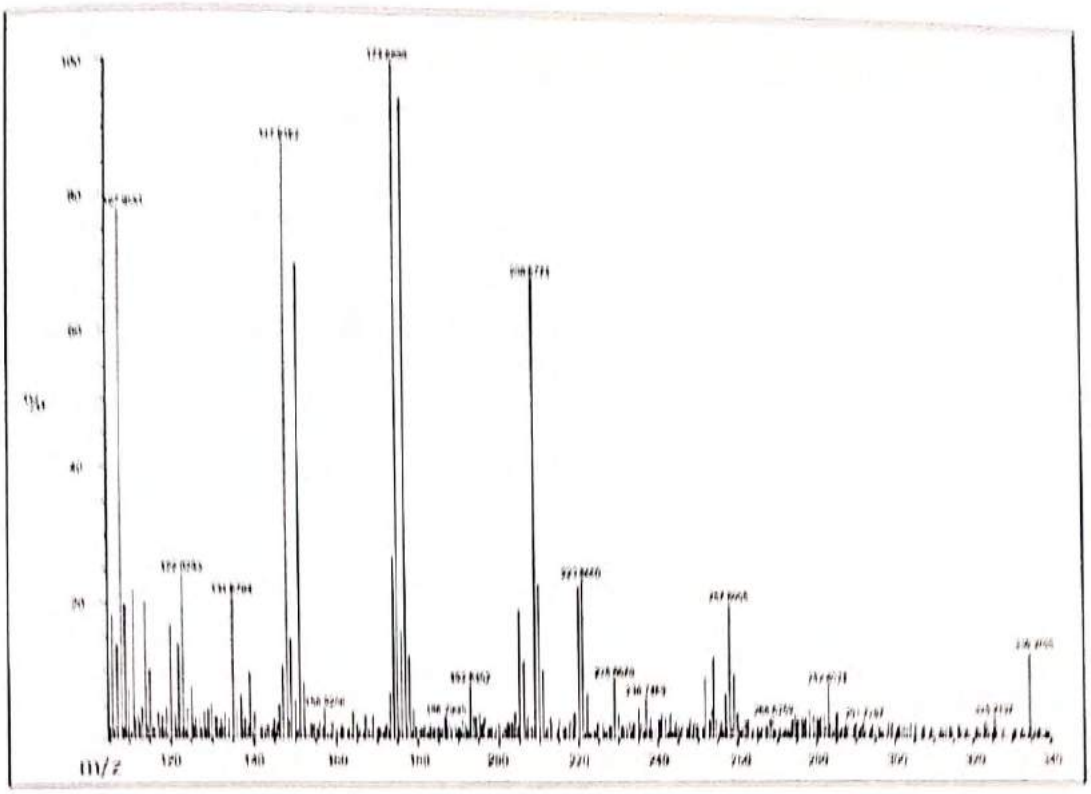


Figure 4 Mass spectrum of the ligand

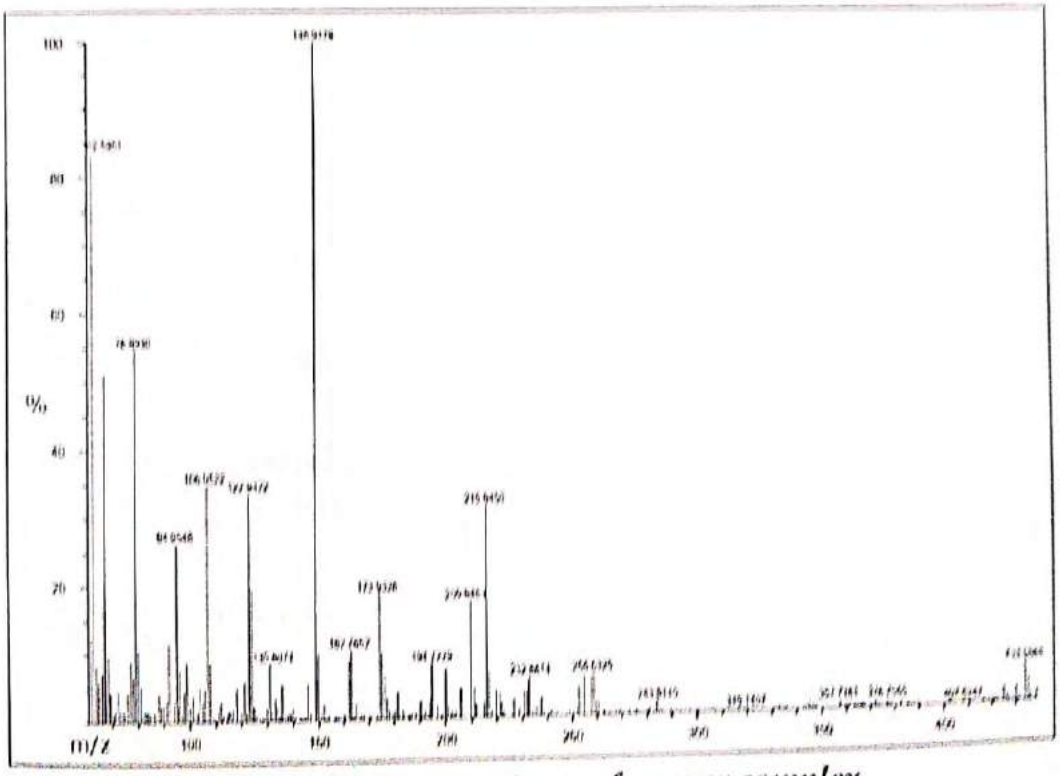


Figure 5 Mass spectrum of copper complex

3.5. EPR spectral studies

The EPR spectral parameters of the copper(II) complex was recorded in DMSO solution at room temperature and 77 °K. The room temperature spectrum of complex shows no splitting pattern, however in the LNT spectrum well defined four hyperfine lines in the parallel region corresponding to the electron spin – nuclear spin interaction were observed. The EPR spectrum of the complex is given in Figure 6. The EPR parameters are summarized in Table 4. The trend $g_{\parallel} > g_{\perp} > g_e$ (2.0027) shows that the unpaired electron localized in the d_{x2-y2} orbital characteristic of tetrahedrally distorted square planar geometry in Cu(II) complex [22]

The $g_{\parallel} / A_{\parallel}$ ratio can be used as an empirical convenient of distortion from square-planar structure [25]. The values of the $g_{\parallel}/ A_{\parallel}$ ratio for copper complex (from ca. 160) indicate nearly square-planar environments with tetrahedral distortion [26]. The EPR parameters $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ and the energies of d–d transition were used to evaluate the bonding parameters α^2, β^2. $\alpha^2 = 0.5$ indicates complete covalent bonding and $\alpha^2 = 1$ suggests complete ionic bonding. The observed value of α^2 and β^2 of the complexes is less than unity (0.9794) which concludes that the complexes have negligible ionic character for in-plane σ bonds and in-plane π bonds. The orbital reduction factors $K_{\parallel}$ and $K_{\perp}$ were calculated using the expressions reported [27]. Likewise, according to Hathaway, for pure σ bonding $K_{\parallel} \approx K_{\perp} \approx 0.77$, for in-plane π bonding $K_{\parallel} < K_{\perp}$, and for out-of-plane π bonding $K_{\parallel} > K_{\perp}$. The $K_{\parallel}$, $K_{\perp}$ value in complexes is in agreement with the relation $K_{\parallel} > K_{\perp}$ which indicates the presence of out-of-plane π bonding.

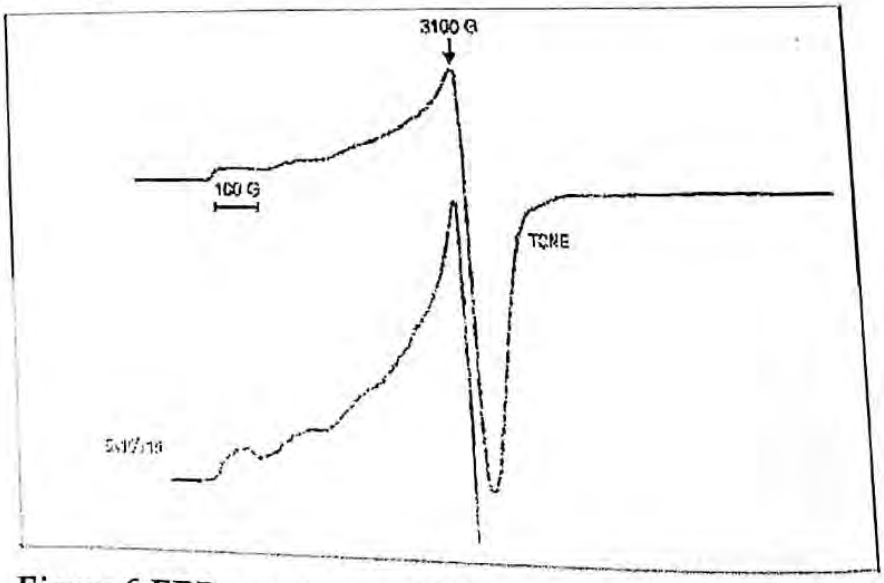


Figure 6 EPR spectrum of [Cu(L)Cl] at 77 K in DMSO

Table 5. EPR spectral parameters of copper(II) complex

complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (10^{-4} cm^{-1})	$A_{\perp}$ (10^{-4} cm^{-1})	α^2	β^2	$K_{\parallel}$	$K_{\perp}$
[Cu(L)Cl]	2.31	2.08	144	22.50	0.799	0.979	0.777	0.689

On the basis of above discussion which is based upon elemental analysis, molar conductance, magnetic susceptibility measurement, IR, electronic, EPR spectral studies, and mass spectra the following structure is proposed for the complexes.

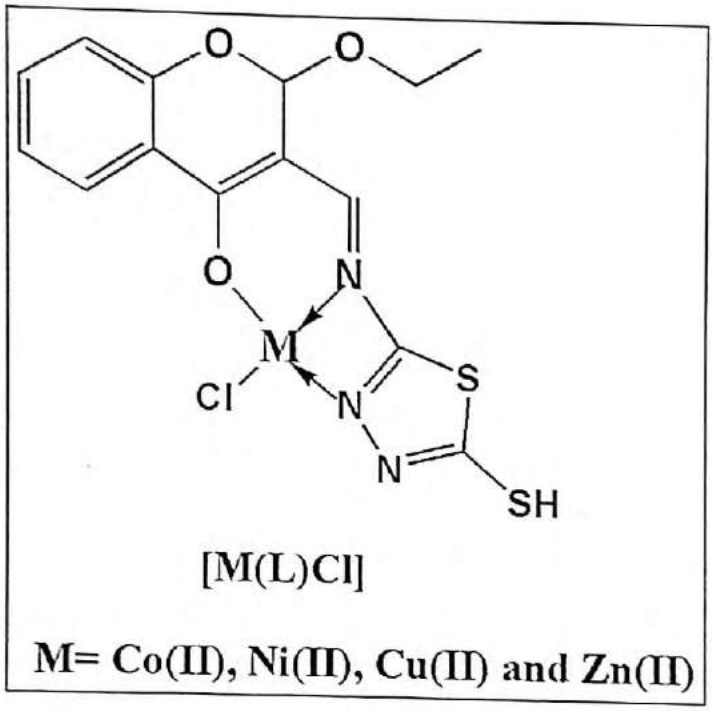


Figure 7. Proposed structure of the complexes

3.6. Fluorescence studies

The emission spectrum was recorded in DMF. The Schiff base (L) was characterized by an emission band around 502 nm upon photo excitation at 510 nm. The complexes do not show emission bands. The spectrum is shown in Figure 8.

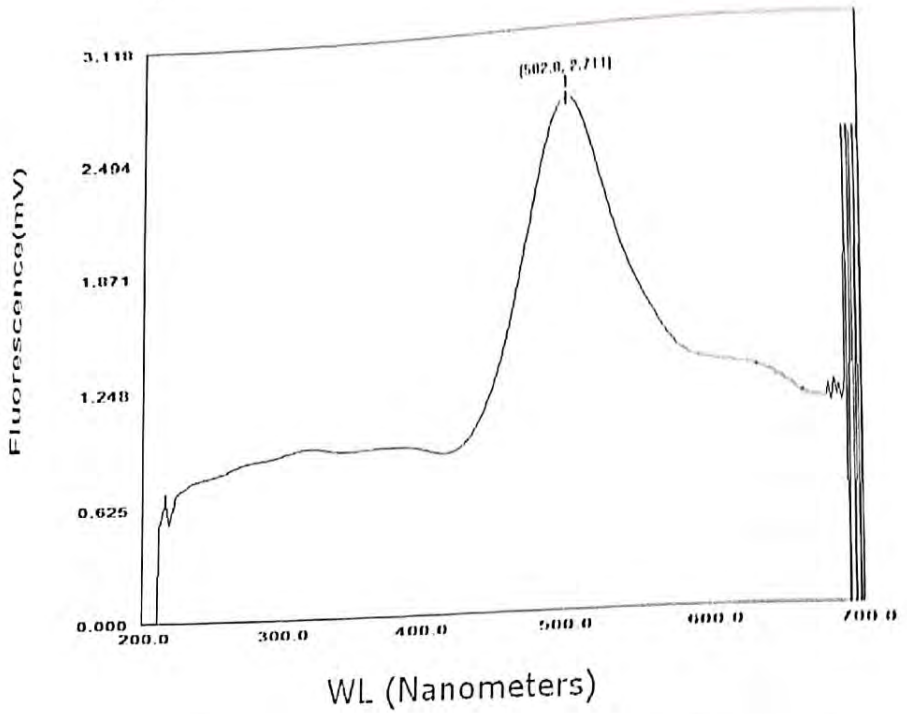


Figure 8. Emission spectrum of the ligand

3.7. Antimicrobial activity

The *in vitro* antibacterial and antifungal activity tests for all the synthesized compounds were performed by well diffusion method [15].The ligand and the complexes were tested for their in *vitro* antibacterial activity against *Pseudomonas aeruginosa, Escherichia coli,* (Gram negative) and *Staphylococcus aureus and Bacillus subtilis* (Gram positive) and the antifungal activity against *Candida albigans and Aspergillus niger.* The concentration of the solution taken was 100 µg/mL. The plates were incubated at 35°C for 24 h. Amikacin and ketokonazole were used as positive control for bacteria and fungus respectively.

The growth of inhibition zones in mm after incubation is shown in Table 6. The synthesized complexes exhibit exhibit higher antimicrobial activity than the ligand and some complexes show enhanced antifungal activity than the standard drug ketokonazole..The metal complexes increase the lipophilic nature of the metal ion and enhance the permeation of drug through the lipoid membrane [28]. The copper complex shows very less activity than the other complexes because of the poor solubility of copper complex in DMSO [29]. The synthesized compounds are

found to be effective antifungal agents. This could be attributed to the fact that the compounds were more susceptible towards the fungal cells than bacterial cells.

Table 6 Antimicrobial activity of ligand (L) and its metal(II) complexes. (Zone of inhibition in mm)

Compounds	S. aureus	E. coli	P.aeruginosa	B. subtilis	A. niger	C. albigans
$C_{14}H_{15}O_3N_3S_2$ (L)	12	04	11	09	11	10
[Co(L)Cl]	13	09	14	15	13	15
[Ni(L)Cl]	16	13	15	11	14	17
[Cu(L)Cl]	12	10	09	10	-	13
[Zn(L)Cl]	15	12	14	17	11	18
Amikacin	18	19	20	22	-	-
Ketokonazole	-	-	-	-	17	18
DMSO	-	-	-	-	-	-

The Schiff base coordinates to the metal ion through thiadiazole ring nitrogen, azomethine nitrogen and phenolic group and acts as a tridentate ligand. On the basis of elemental analyses, molar conductance, magnetic susceptibility measurement, IR, electronic, EPR spectral studies, and mass spectra, the metal ions exhibit four coordination with tetrahedrally distorted square planar for Cu(II) complex and distorted tetrahedral for other complexes.. The thiol group has not participated in the coordination. The synthesized compounds are potent against bacterial and fungal pathogens. The antifungal activity shows promising results and may lead to synthesis of suitable drugs in future.

4. Conclusion

The formation of 2-(N-3-formylchromone) imino-1,3,4-thiadiazole-5-thiol (L)is confirmed from NMR and mass spectral data. The Schiff base act as tridentate ligand. The metal(II) ions are coordinated to azomethine nitrogen, thiadiazole ring nitrogen and enolic oxygen. The EPR parameters of copper(II) complexe suggest that the complex has distorted square planar coordination. The process of chelation

dominantly affects the biological activity of the complexes that are potent against pathogens. The inhibition activity against *Candida albigans* show promising results. The copper(II) complex [Cu(L)Cl] shows reduced antimicrobial activity due to its partial solubility in DMSO with formation of suspension.

5. References

1. Kumar, S.; Dhar, D.N.; Saxena, P.N. Synthesis, Characterization, and Antimicrobial Studies of N, O Donor Schiff Base Polymeric Complexes, *Journal of Scientific And Industrial Research* 68,2009, pp 181-187.
2. Gupta, K.C.; Sutar, A.K. *Coord. Chem. Rev.* 2008, 252, 1420-1450.
3. Kalanithi, M.; Kodimunthiri, M.; Rajarajan, M.; Tharmaraj, P. Synthesis, characterization and biological activity of some new VO(IV), Co(II), Ni(II), Cu(II) and Zn(II) complexes of chromone based NNO Schiff base derived from 2-aminothiazole ,*Spectrochim. Acta Part A*,2011, 82, pp 290-298.
4. Khan, KM.; Ambreen, N.; Hussain, S.; Perveen, S.; Choudhary, MI. Schiff bases of 3-formylchromone as thymidine phosphorylase inhibitors ,*Bioorg. Med. Chem.* 2009, 17, pp 2983 -2988.
5. Khan, KM.; Ambreen, N.; Mughal, UR.; Jalil, S.; Perveen, S.; Choudhary, MI. 3- formylchromones : potential anti-inflammatory agents, *Eur. J. Med. Chem.* 2010, 45, pp 4058- 4064.
6. Rosu, T.; Pahontu, E.; Maxim, C.; Georgescu, R.; Stanica, N.; Almajan, GL.; Gulea, A.Synthesis,characterization and antibacterial activity of some new complexes of Cu(II),Ni(II),Mn(II) with Schiff base derived from 4-amino-2,3-dimethyl-1- phenyl3pyrazolin-5-one, *Polyhedron*, 2010, 29, pp 757-766.
7. Harnisch, H. *Liebigs Ann. Chem.* Chromon-3-carbaldehyde,1973, pp 765, 8-14.
8. Sweety, D.; Asif Iqbal, CM.; Saravanan, J.; Mohan, S. *World Journal of Pharmaceutical Research* 2013, 2, pp 3199-3208.
9. Kushwaha, N.; Swatantra, K.; Kushwaha, S.; Rai, AK. Biological activities of thiazole derivatives : A review, *Int.J. Chemtech Res.*, 2012, 4(2), pp 517-531.
10. Angellici R. J. 1969. Synthesis and Techniques in Inorganic Chemistry, W.B. Saunders Company.

11. Luoni, P. O.; Vera, L.; Astudillo, C.; Guzman, M.; Lopez, P. O. Synthesis of metallic azo derivatives of 2-amino-5-mercapto-1,3,4- thiadiazole. *J. Chil.Chem.Soc.*2007, 52, pp 1120- 1122.
12. Geary, WG. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds.*Coord Chem Rev.* 1971,7, pp 81-122.
13. Kulkarni, A.; Patil, SA.; Badami, PS. DNA cleavage and in vitro antimicrobial studies of Co(II),Ni(II) and Cu(II) complexes with ONNO donor Schiff bases : synthesis,spectral characterization and electrochemical studies, *J Enzyme Inhib Med Chem.* 2010, 25(1), pp 87-96.
14. Ya-Li Sang; Xue-Song Lin. *J Coord Chem.* 2010, 63, pp 315-322.
15. Chandra, S.; Jain, D.; Sharma, AK.; Sharma' P. Coordination Modes of a Schiff Base Pentadentate Derivative of 4-Aminoantipyrine with Cobalt(II), Nickel(II) and Copper(II) Metal Ions: Synthesis, Spectroscopic and Antimicrobial Studies.*Molecules* 2009, 14, pp 174-190.
16. Valarmathy, G.; Subbalakshmi, R. Synthesis, spectral characterisation, electrochemical, and fluorescence studies of biologically active novel Schiff_ base complexes derived from E-4-(2-hydroxy-3- methoxybenzlideneamino)-N-(pyrimidin-2-yl)benzenesulfonamide *Turk J Chem.* 2014, 38, pp 521-530.
17. Alexandru, M.G.; Velickovic, T.C.; Jitaru1, I.; Sipka, S.G.; Draghici, C. Synthesis, characterization and antitumor activity of Cu(II), Co(II), Zn(II) and Mn(II) complex compounds with aminothiazole acetate derivative, *Cent.Eur.J.Chem.* 2010, 8, pp 639-645.
18. Tas, E.; Kilic, A.; Durgun, M.; Kupecik, L.; Yilmaz, I.; Arslan,S. Cu(II), Co(II), Ni(II), Mn(II), and Fe(II) metal complexes containing N,N'-(3,4-diaminobenzophenon)-3,5- But²-salicylaldimine ligand: Synthesis, structural characterization, thermal properties, electrochemistry, and spectroelectrochemistry, *Spectrochim. Acta A* 2010, 75, pp 811- 818.
19. Kasumov, VT.; Koksal, F.; Aslanoglu, M.; Yerli, Y. Synthesis, spectroscopic characterization and reactivity studies of oxovanadium(IV) complexes with bulky N,N'- polymethylenebis(3,5-t Bu_2salicylaldimine)ligands, *Spectrochim. Acta A*, 2010, 77, pp 630- 637.

20. Dhanaraja, CJ.; Nair, MS. Synthesis, characterization, and antimicrobial studies of some Schiff-base metal(II) complexes, *J Coord Chem.* 2009, 62, pp 4018-4028.
21. West, DX.; Nassar, AA.; El-Saied, FA.; Agad, MI. Nickel(II) complexes of 2-aminoacetophenone N(4)-substituted thiosemicarbazones,*Transition Met. Chem.* 1988, 23, pp 423- 427.
22. Arish, D.; Nair, MS. Synthesis, Characterization, Antimicrobial and nuclease activity studies on some Schiff base metal complexes *J Coord Chem.*, 2010, 63, pp 1619-1628.
23. Nakamoto, K. *Infra-red and Raman Spectra of Inorganic and Coordination Compounds;* John Wiley & Sons: New York, 1978.
24. Wilkinson, G.; Gillard, DR.; McCleverty, AJ. *Comprehensive Coordination Chemistry;* Pergamon Press: New York, 1987.
25. Romanowski, SMM.; Tormena, F.; Santos, VA.; Hermann, MF.; Mangrich, AS. Solution studies of copper(II) complexes as a Contribution to the study of the Active site of Galactose oxidase,*J. Braz. Chem. Soc.*, 2004,15, pp 897-903.
26. Sakaguchi, U.; Addidon, AW. *J. Chem. Soc., Dalton Trans.*, 1979, 600 -608.
27. Hathaway, BJ. *Structure and Bonding;* Springer Verlag: Heidelberg, 1973.
28. Raman, N.;Selvan, A. Studies on DNA binding,electrochemical activation,DNA photocleavage and biopotency of N and O donor bidentate ligands with Cu(II),Co(II) and Zn(II), *J Coord Chem.* 2011, 64, pp 534-553.
29. Creaven, BS.; Devereux, M.; Foltyn, A.; McClean, S.; Rosair, G.; Thangella, VR.; Walsh, M. Quinolin-2(1H)-one-triazole derived Schiff bases and their Cu(II) and Zn(II) complexes: possible new therapeutic agents, *Polyhedron* 2010, 29, pp 813-822.