Turkish Journal of Chemistry

http://journals.tubitak.gov.tr/chem/

Research Article

Turk J Chem
(2014) 38: 521 – 530
© TÜBİTAK
doi:10.3906/kim-1301-83

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

Valarmathy GOVINDARAJ*, **Subbalakshmi RAMANATHAN**
PG and Research Department of Chemistry, Seethalakshmi Ramaswami College, Tiruchirappalli,
Tamil Nadu, India

Received: 01.02.2013 • **Accepted:** 23.07.2013 • **Published Online:** 11.06.2014 • **Printed:** 10.07.2014

Abstract: A new Schiff base was prepared from 2-sulphanilamidopyrimidine and 2-hydroxy-3-methoxybenzaldehyde in ethanolic media and it was complexed with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) ions. The synthesised ligand and complexes were characterised by IR, UV, ^{1}H and ^{13}C NMR, elemental analysis, cyclic voltammetry, EPR, molar conductance, and magnetic susceptibility. The reasonable shifts in FT-IR and NMR spectral signals of the complexes with respect to the free ligand confirm good coordination of the Schiff-base ligand with the metal through imine nitrogen and oxygen atoms of Schiff base moiety. The Schiff-base ligand and the complexes were screened for antimicrobial activity and fluorescent behaviour. From the analytical and spectral data, the stoichiometry was found to be 1:2 for all the complexes. An octahedral structure was proposed. All the complexes were found to be active against bacteria and fungi.

Key words: Schiff base, 2-sulphanilamidopyrimidine, 2-hydroxy-3-methoxybenzaldehyde, metal complexes, biological activity, fluorescent behaviour

1. Introduction

Sulpha drugs are chemotherapeutic agents whose molecular structures contain 4-aminobenzenesulfonamide moiety.[1] The antimicrobial activity of these drugs is thought to come from the structural resemblance between sulfanilamide group and p-amino benzoic acid where the sulpha drug mimics this metabolite and blocks folic acid synthesis in bacteria, thereby causing cell death.[2] Many sulpha drugs like sulphadiazine, sulphamethoxazole, and sulphamerazine possess SO_2NH moiety as an important toxophoric function.[3] It has been reported that biologically active compounds show greater activity when administered as metal complexes than as free compounds.[4] The efficacy of sulpha drugs can be enhanced upon coordination with a suitable metal ion.[5] Schiff-base compounds containing an imino group (–RC=N–) are usually formed by the condensation of a primary amine with an active carbonyl group. Schiff bases are regarded as privileged ligands.[6] Schiff bases and their metal complexes are very popular due to their diverse chelating ability.[7] They play important roles in both synthetic and structural research because of their preparative accessibility and structural diversity.[8] Metal complexes of Schiff bases are extensively studied due to their synthetic flexibility, selectivity, and sensitivity towards a variety of metal atoms.[9] Schiff bases are used as pigments and dyes, catalysts, intermediates in organic syn-

---

*Correspondence: valarchola@gmail.com

thesis, and polymer stabilisers.[10] A number of Schiff base molecules show biological antibacterial, antifungal,[11] antidiabetic, antitumour, antiproliferative, anticancer, anticorrosion, and anti-inflammatory activities.[12–14]

The topical application of metal complexes of sulphadiazine has recently revived the usefulness of these compounds in medicine.[15] Indeed metal sulphadiazine complexes are now widely used to prevent bacterial infection during burn treatments.[16] The interest in metal-based sulphonamides was stimulated by the successful introduction and preparation of Ag(I) and Zn(II) sulphadiazine complexes to prevent various bacterial infections.[17]

Paralleling the same idea, this paper records the synthesis and characterisation of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes derived from 2-sulphanilamidopyrimidine and 2-hydroxy-3-methoxybenzaldehyde. The structures of the ligand and its metal complexes were characterised by IR, UV, ^{1}H and ^{13}C NMR, elemental analysis, cyclic voltammetry, ESR, molar conductance, and magnetic susceptibility measurements. The biological activities were also studied against gram-positive and gram-negative bacterial and fungal organisms for the Schiff-base ligand and their complexes. The structure of the Schiff-base ligand confirmed in the present work is given in Figure 1.

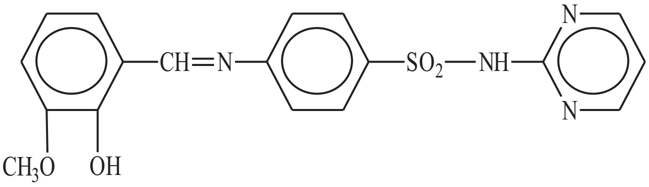


Figure 1. Structure of the ligand.

2. Results and discussion

The Schiff-base ligand was synthesised by using equimolar quantities of 2-sulphanilamidopyrimidine and 2-hydroxy-3-methoxybenzaldehyde and the complexes using metal acetates according to the following equation:

$$M(CH_3COO)_2.nH_2O + 2L \xrightarrow[reflux]{ethanol\backslash DMF} ML_2(H_2O)_2 + 2CH_3COOH + nH_2O$$

The metal complexes derived varied in colour. All the complexes were stable, nonhygroscopic, and coloured solids. The physical characteristics and microanalytical data of the ligand and metal complexes are given in Tables 1 and 2.

Table 1. Physical characteristics of Schiff base ligand and complexes.

S. no.	Ligand/ complexes	Colour	Molecular formula	MP °C	Yield %	μ_{eff} (BM)	CN
1	L	Orange	$C_{18}H_{16}N_4O_4S$	203	75	-	-
2	$[MnL_2(H_2O)_2]$	Sandalwood	$C_{36}H_{34}N_8O_{10}S_2Mn$	235	65	5.6	6
3	$[CoL_2(H_2O)_2]$	Nut brown	$C_{36}H_{34}N_8O_{10}S_2Co$	240	65	4.5	6
4	$[NiL_2(H_2O)_2]$	Brown yellow	$C_{36}H_{34}N_8O_{10}S_2Ni$	245	55	3.2	6
5	$[CuL_2(H_2O)_2]$	Green	$C_{36}H_{34}N_8O_{10}S_2Cu$	234	75	1.95	6
6	$[ZnL_2(H_2O)_2]$	Yellow	$C_{36}H_{34}N_8O_{10}S_2Zn$	226	65	dia	6

Table 2. Microanalytical data of Schiff base ligand and complexes.

S. no.	Ligand/ complexes	Elemental analysis (%)(Calcd)found				M % (Calcd) found	$\wedge_m$ m^2 mol^{-1}
		C	H	N	S		
1	L	(56.25) 56.20	(4.17) 4.10	(14.58) 14.51	(8.33) 8.32	-	-
2	[$MnL_2(H_2O)_2$]	(50.41) 50.41	(3.97) 3.96	(13.07) 13.0	(7.47) 7.43	(6.42) 6.41	16.7
3	[$CoL_2(H_2O)_2$]	(50.48) 50.45	(3.95) 3.95	(13.01) 12.99	(7.43) 7.43	(6.86) 6.84	3.44
4	[$NiL_2(H_2O)_2$]	(50.19) 50.15	(3.95) 3.91	(13.01) 13.00	(7.44) 7.42	(6.82) 6.82	6.0
5	[$CuL_2(H_2O)_2$]	(49.91) 40.91	(3.93) 3.91	(12.94) 12.93	(7.39) 7.39	(7.35) 7.34	7.86
6	[$ZnL_2(H_2O)_2$]	(49.80) 49.79	(3.92) 3.91	(12.91) 12.90	(7.38) 7.38	(7.54) 7.54	2.9

2.1. Molar conductance and magnetic susceptibility measurements

The observed molar conductances of all the complexes in 10^{-3} MDMF solution were 2.9–16.7 ohm^{-1} cm^2 mol^{-1}, showing their nonelectrolytic nature.[18] This in turn suggests that the water molecules are coordinated with the metal ions and present inside the coordination sphere in all the complexes.[19] The magnetic data for Co^{II} and Ni^{II} complexes are consistent with octahedral geometry around the metal ion for both complexes. The magnetic moment value of 1.95 BM for the Cu(II) complex lies in the range expected for the d^9 system, which contains one unpaired electron with octahedral geometry.[20] Zn(II) complexes were found to be diamagnetic as expected. The observed magnetic moment value of 5.60 BM for the Mn(II) complex suggests an octahedral geometry. The probable structure of the complexes proposed in the present work is given in Figure 2.

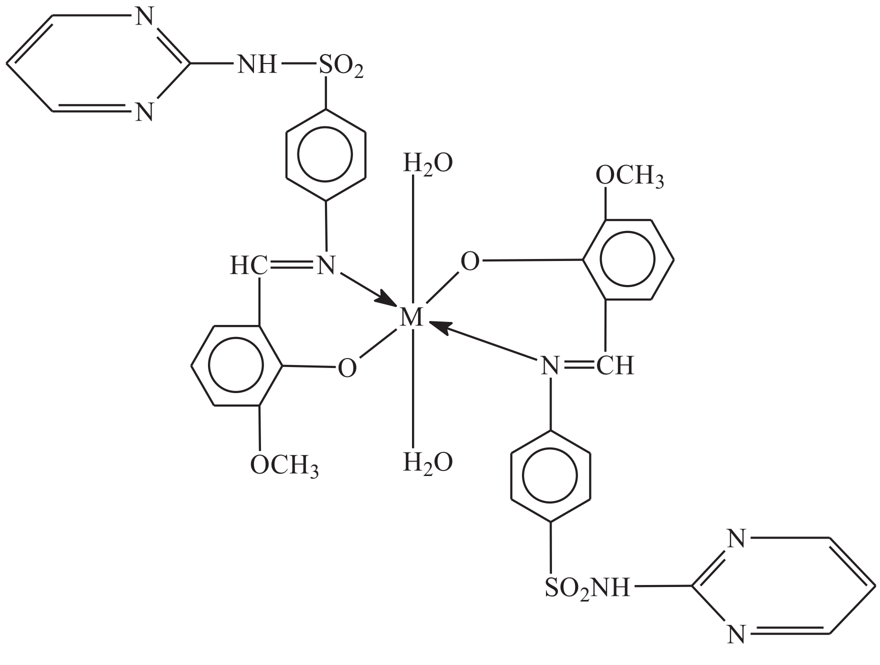


Figure 2. Structure of the complex.

2.2. Infrared spectra

The infrared spectral data of the Schiff base and its metal complexes are recorded in Table 3. The Schiff base showed a strong absorption band at 1582 cm^{-1} characteristic of ν(C=N), whereas the broad band at 3423 cm^{-1} was characteristic of hydrogen bonded ν(O-H) stretching vibrations.[21] The azomethine ν(>C=N) band at 1582 cm^{-1} in the Schiff base is shifted to higher frequency in Co(II), Mn(II), Ni(II), Cu(II), and Zn(II) by 15, 23, 12, 10, and 12 cm^{-1}, respectively, which indicated the coordination of azomethine nitrogen on complexation.[22] The disappearance of phenolic (OH) at 3423 cm^{-1} in all the complexes suggests the coordination of phenolic oxygen after deprotonation.[23] The linkage with the oxygen atom is further supported by the appearance of a band in the region around 420–464 cm^{-1}, which may be assigned to ν (M–O).[24] Further evidence of the coordination of the N atom of the Schiff base with the metal atom was shown by the appearance of a new weak frequency band at 512–578 cm^{-1} assigned to the metal nitrogen ν(M–N).[25] These new bands were observed only in the spectra of the metal complexes and not in the Schiff base, which confirmed the participation of the donor groups. The bands in the ligand due to ν_{as} (SO_2) and ν_s(SO_2) appear at 1155 cm^{-1} and 1332 cm^{-1}, respectively. These bands remain almost unchanged in the complexes, indicating that this –SO_2 group is not participating in coordination.[26] This is confirmed by the unchanged ν(S–N) and ν(C–S) modes appearing around 945 cm^{-1} and 843 cm^{-1}, respectively. The ring nitrogen (=N–) of the Schiff base does not take part in coordination, supported by the unchanged band at around 1275 cm^{-1}.

Table 3. IR and electronic spectral data.

Ligand/ complexes	IR spectral data, cm^{-1}				Electronic spectral data, (nm) cm^{-1}
	γ (O–H)	γ (C=N)	γ (M–O)	γ (M–N)	
L	3423	1582	-	-	(300, 348) 33333, 28601
[$MnL_2(H_2O)_2$]	3426	1597	520	447	(255, 272, 292) 39205, 36639, 34230
[$CoL_2(H_2O)_2$]	3440	1605	512	464	(262, 271) 38165, 36777
[$NiL_2(H_2O)_2$]	3450	1594	531	412	(255, 260, 271) 39064, 38329, 36846
[$CuL_2(H_2O)_2$]	3446	1591	524	442	(294, 302, 401) 33976, 33065, 24915
[$ZnL_2(H_2O)_2$]	3399	1594	531	431	(261, 272) 38283, 36774

2.3. Electronic spectra

The electronic spectrum of the ligand shows 2 high intensity bands at (300 nm) 33,333 cm^{-1} and (348 nm) 28,901 cm^{-1}, indicating $n \to n*$ and $\pi \to \pi^*$ transitions, respectively, of the ligand moiety.[27] The electronic spectrum of the Mn(II) complex shows a band at (255 nm) 39,205 cm^{-1} assignable to $M \to L$ charge transfer spectra and the bands at (272 nm) 36,639 and (292 nm) 34,230 cm^{-1} are due to $^6A_{1g} \to {}^4T_{2g}$(D) and $^6A_{1g} \to {}^4E_{g(G).}^{28}$ The electronic spectra of the Co(II) complex displays bands at (262 nm) 38,165 and (271 nm) 36,777 cm^{-1}. The former band corresponds to intraligand transition of the organic moiety[29] and the latter corresponds to $^4T_{1g}$(F) $\to$ $^4T_{1g}$(P), suggesting octahedral geometry of this complex. The Ni(II) complex shows absorption bands at (255 nm) 39,064, (260 nm) 38,329, and (271 nm) 36,846 cm^{-1}. The high intensity bands at 39,064 and 38,329 cm^{-1} are relatively attributed to L $\to$ M charge transfer transitions, whereas the band at 36,846 cm^{-1} may be due to $^3A_{2g} \to {}^3T_{2g}$.[30] The Cu(II) complex displays bands at (292 nm) 33,976, (302 nm) 33,065, and (401 nm) 24,915 cm^{-1}. The first 2 bands are attributed to intraligand transition and the third band, at 24,915 cm^{-1}, corresponds to $^{2}E_{(g)} \rightarrow {}^{2}T_{2g}$. The Zn(II) complex displays high intensity bands at (261 nm) 38,283 and (272 nm) 36,774 cm^{-1}. This may be due to ligand → metal charge transfer spectra.[31]

2.4. ^{1}H NMR and ^{13}C NMR spectra

The ^{1}H NMR spectra of the Schiff base and its complexes were recorded in DMSO (d_6). The azomethine proton (–CH=N–) in the Schiff base at δ = 8.5 ppm shifted downfield in metal complexes. This confirms the coordination by azomethine nitrogen.[32] The aromatic protons in the Schiff base appeared in the range at δ 6.8 to 8.1 ppm and metal complexes in the range δ 6.5 to 8.5 ppm.[33] The disappearance of the phenolic –OH proton signal at δ 12.2 ppm confirms the coordination by phenolic oxygen to metal ion. The ^{13}C NMR spectral data (imine at δ 160.0 ppm, aromatic C–OH at δ 119.1 ppm, CH pyrimidine at δ 157.9 ppm) for the ligand and (imine at δ 158.04 ppm, aromatic carbon at δ 129.4, CH pyrimidine at δ 158.0 ppm) for the complexes support the proposed structure.

2.5. Cyclic voltammetry

Electrochemical cyclic voltammetry measurements were performed at room temperature in an airtight 3-electrode cell by using a glassy carbon electrode with 0.071 cm^2 surface area as a working electrode, while a platinum wire served as the counter electrode and a Ag/AgCl in a saturated KCl solution as the reference electrode. The electrochemical reaction was charged with DMF solution of all the complexes (1×10^{-4} M) and tetrabutyl ammonium perchlorate (0.1 M) as supporting electrolyte.[34] Measurements were made over a potential range between –1.7 V and +1.7 V for Mn(II), Co(II), and Ni(II) complexes and between –1.1 V and +1.1 V for complexes Cu(II) and Zn(II) with a scan rate of 0.1 V s^{-1}. Voltammetric parameters for all compounds are summarised in Table 4. Generally the electrochemical properties of the complexes depend on a number of factors, such as chelate ring/size, axial ligation, degree and distribution of unsaturation, and substitution pattern in the chelate ring.[35] Each voltammogram shows one electron irreversible oxidation wave at a positive potential. The general reaction involved in the process is assigned to one electron oxidation of the metal centre except zinc.[36] The observed cyclic voltammograms are characterised as irreversible due to the absence of a marked reduction in the peak height of the reverse scan.

Table 4. Redox potential for the complexes.

Complexes	Ep_c(v)	Ep_a(v)	Ipc (μA)	Ipa (μA)	Remarks
$[MnL_2(H_2O)_2]$	-	1.058	-	20	Irreversible
$[CoL_2(H_2O)_2]$	-	1.501	-	15	Irreversible
$[NiL_2(H_2O)_2]$	-	0.463	-	4.5	Irreversible
$[CuL_2(H_2O)_2]$	-	1.398	-	11.7	Irreversible
$[ZnL_2(H_2O)_2]$	–1.357	-	–44.3	-	Irreversible

2.6. EPR spectra

The room temperature spectra of powdered samples were recorded at 9450 MHz. Both parallel and perpendicular features of Cu are resolved in the spectra, which are characteristic of axial symmetry. The g_{11} and $g_{\perp}$ component for the complex were calculated as 2.22 and 2.04. The g value of the Cu(II) complex is found to be 2.1095, confirming the presence of unpaired electrons in the dx^2-y^2 orbital of Cu(II). The g value is very close to those reported for a number of distorted Cu(II) complexes. Moreover, the observed g value is less than 2.3, suggesting a covalent nature of metal–ligand bonds in the complex.[37] The lines of this type usually observed are due either to the intermolecular spin exchange, which may broaden the lines, or to the occupancy of the unpaired electron in the degenerate orbital. The nature and pattern of the EPR spectra suggest an almost octahedral environment around the Cu(II) complex.

2.7. Fluorescence spectra

The photoluminescence properties of the azo Schiff base ligand and their complexes were studied at room temperature for 10^{-4} M solution for all compounds in DMSO solution. Excitation and emission slit widths were set at 10 nm with a scan speed of 500 nm/min. The excitation spectra of the ligand show a maximum at 300 nm and show an emission peak at 338 nm. Generally azo Schiff base systems exhibit fluorescence due to intraligand $\pi \rightarrow \pi^*$ transitions. Fluorescence spectra of the ligand solutions as 10^{-4} M in DMSO obtained with the excitation at 300 nm (Figure 3). The metal complex of Mn(II) exhibits the weakest quenching. The strongest quenching was obtained for the Cu(II) complex (Figure 4). These results show that the ligand has potential for trace analysis of some transition metals by fluorometric method. The fluorescence data of the complexes are summarised in Table 5.

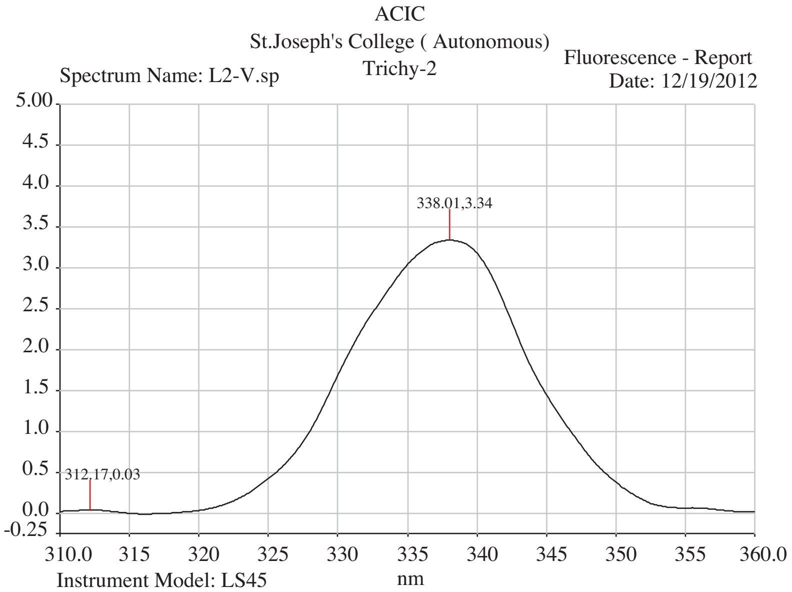


Figure 3. Fluorescence spectra for the ligand.

2.8. Antimicrobial activity

The antibacterial activity and antifungal activity of the Schiff-base ligand and its manganese, cobalt, nickel, copper, and zinc complexes were tested by disc diffusion technique.[38,39] Various gram-positive and gram-negative bacterial organisms such as gram-negative bacteria *Pseudomonas aeruginosa* and *E. coli*, gram-positive bacteria *Staphylococcus aureus* and *Klebsiella aerogenes*, and fungi *Aspergillus niger* and *Mucor* were used to find out the antimicrobial activity (Table 6). Filter paper discs of diameter 6 mm were used and the diameters of zones of inhibition formed around each disc after incubating for 72 h at 25–30 °C were recorded. Results were compared with those of the standard drug ciprofloxacin for bacteria and nystatin for fungi at the same concentration. All the new complexes showed remarkable biological activity against bacteria and fungi[40] (Figures 5a–c). From the results it is clear that the metal complexes have greater antimicrobial activity than the parent ligand.

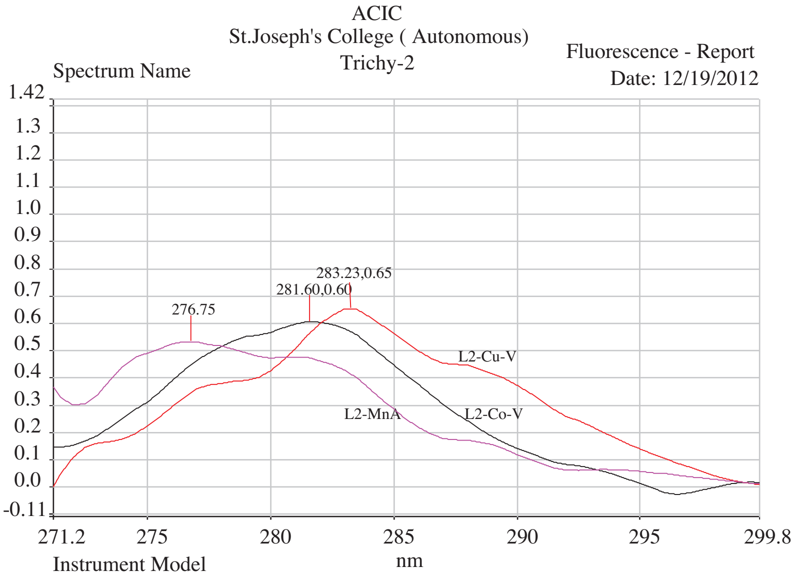


Figure 4. Fluorescence spectra of Mn(II),Co(II), and Cu(II) complexes.

Table 5. Fluorescence characteristics of ligand and complexes.

Complexes	Excitation wavelength λ_{max} (nm)	Fluorescence wavelength λ_{max} (nm)	Quantum yield
L	300	338	0.88
$[MnL_2(H_2O)_2]$	261	276	0.94
$[CoL_2(H_2O)_2]$	270	281	0.96
$[NiL_2(H_2O)_2]$	255	271	0.94
$[CuL_2(H_2O)_2]$	270	283	0.95
$[ZnL_2(H_2O)_2]$	260	274	0.94

In conclusion, the coordination ability of the newly synthesised azo Schiff base was proved in complexation reactions with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) ions. IR, UV, ^{1}H NMR, and magnetic measurements of the ligand and its complexes confirm the suggested coordination of the ligand through azomethine linkage. Based on these facts, an octahedral structure has been proposed for all complexes. The process of chelation dominantly affects the biological activity of the complexes that are potent against pathogens. In general, all the synthesised complexes can serve as potential photoactive materials, as indicated by their characteristic fluorescence properties.

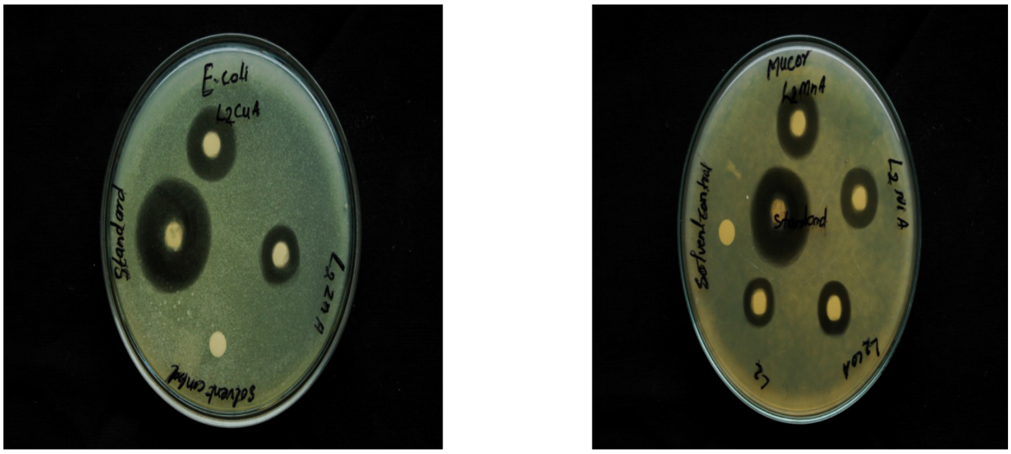
3. Experimental

All chemicals used were of analytical reagent (AR) grade and of the highest purity available. Solvents were purified and dried according to the standard procedures. All metal (II) compounds were used as acetate salts. IR spectra of the complexes were recorded in KBr pellets with a PerkinElmer RX1 FT-IR spectrophotometer in the 4000–400 cm^{-1} range. The electronic spectra were recorded in DMF on a PerkinElmer Lambda 35

Table 6. Antimicrobial activity of Schiff base ligand and complexes.

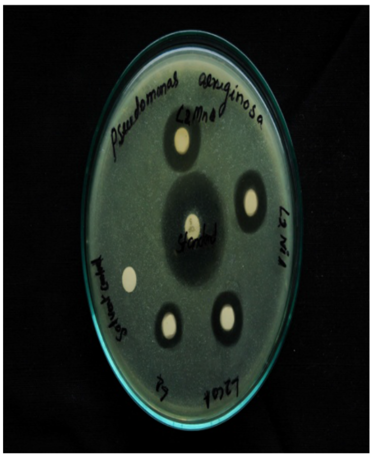
Ligand and complexes	*Staphylococcus aureus*	*Klebsiella aerogenes*	*E. coli*	*Pseudomonas aeruginosa*	*Mucor*	*Aspergillus niger*
Ligand (L)	++	+++	+++	++	++	++
$[MnL_2(H_2O)_2]$	+++	+++	+++	+++	+++	+++
$[CoL_2(H_2O)_2]$	+++	+++	+++	++	+++	+++
$[NiL_2(H_2O)_2]$	+++	+++	+++	++	+++	+++
$[CuL_2(H_2O)_2]$	+++	+++	+++	++	++	+++
$[ZnL_2(H_2O)_2]$	+++	+++	+++	+++	++	+++

Standard = ciprofloxacin 5 g/disc for bacteria; nystatin = 100 units/disc for fungi. Highly active = +++ (inhibition zone > 15 mm); moderately active = ++ (inhibition zone > 10 mm); slightly active = + (inhibition zone > 5 mm); inactive = – (inhibition zone < 5 mm)



a) Activity of Cu(II) and Zn(II) complex against gram positive bacteria E.coli

b) Activity of ligand and Mn(II),Co(II), Ni(II) complexes against fungus Mucor



c) Activity of ligand and Mn(II),Co(II), Ni(II) complexes against fungus Pseudomonas aeruginosa

Figure 5. a) Activity of Cu(II) and Zn(II) complex against gram-positive bacterium *E. coli.* b) Activity of ligand and Mn(II),Co(II), and Ni(II) complexes against fungus *Mucor.* c) Activity of ligand and Mn(II),Co(II), and Ni(II) complexes against fungus *Pseudomonas aeruginosa.*

spectrophotometer in the 190–1100 nm range. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz FT-PMR spectrometer (DMSO-d$_6$). Elemental analysis of the ligand and complexes was performed using an Elementar Vario EL CHN rapid analyser. Cyclic voltammetric measurements for the complexes were obtained using a Princeton Applied Research Multichannel VersaSTAT-II. The X-band EPR spectra were recorded on a Bruker ESP X-band EPR spectrometer using powdered samples at a microwave frequency of 9450 MHz. Magnetic susceptibilities were measured on an automagnetic susceptibility meter (MSB-Auto) at room temperature. Melting points were determined using a melting point apparatus (Elico) and are uncorrected. Conductivity measurements for the complexes were carried out on an Elico Conductivity Bridge and a dip conductivity cell using dimethyl formamide as solvent. Fluorescence spectra were detected using a PerkinElmer LS 45 spectrofluorometer.

3.1. Synthesis of Schiff-base ligand: E-4-(2-hydroxy-3-methoxybenzlideneamino)-N-(pyrimidin-2-yl)benzenesulfonamide(L)

The Schiff base was prepared by the condensation of equimolar amounts of 2-sulphanilamidopyrimidine and 2-hydroxy-3-methoxy benzaldehyde in a minimal quantity of ethanol. The resulting mixture was then refluxed on a water bath for 5 h. The pale orange coloured solid mass separated out on cooling was filtered, washed, and dried over anhydrous $CaCl_2$ in a desiccator. The purity of the ligand was checked by melting point, TLC, and spectral data. The ligand is insoluble in some common organic solvents like acetone and benzene, and soluble in polar solvents like DMF and DMSO.

3.2. Synthesis of metal complexes

Metal complexes were synthesised by mixing the hot solution of ligand (0.004 mol) in a minimal quantity of dimethyl formamide and ethanolic solution of metal acetates (0.002 mol). The resulting mixture was then refluxed in a water bath for 6 h. The complexes obtained in each case were cooled, filtered, and washed with ethanol several times to remove any excess of the ligand. Finally the complexes were washed with anhydrous diethylether and dried in a desiccator.

Acknowledgements

The authors express their gratitude to UGC-SERO, Hyderabad, for financial assistance. The authors express their gratitude to the Secretary, Seethalakshmi Ramaswami College, for providing laboratory facilities and faculty members, PG and Research Department of Chemistry, Seethalakshmi Ramaswami College, Tiruchirappalli, Tamilnadu, India.

References

1. Maurya, R. C.; Patel, P. *Spectrosc. Lett.* **1999**, *32*, 213–236.
2. Westcott, S. A. *Transition Met. Chem.* **2005**, *30*, 411–418.
3. Singh, H.; Srivastava, V. K.; Shukla, S. N.; Srivastava, M. K.; Upadhayay, M. K. *Indian J. Chem.* **1994**, *33A*, 350–351.
4. De Clercq, B.; Verpoort, F. *Macromolecules* **2002**, *35*, 8943–8949.
5. Goldstein, M.; Barton, J. K.; Goldberg, J. M.; Kumar, C. V.; Turro N. J. *J. Am. Chem. Soc.* **1986**, *10*, 2081–2088.
6. Mirkhani, V.; Moghadam, M.; Tangestanninejad S.; Baltork, M. P.; Rasouli N. *Catal. Commun.* **2008**, *9*, 219–223.

7. Bera, P.; Saha, N.; Kumar, S.; Baneeja, D.; Bhattacharya, R. *Transition Met. Chem.* **1999**, *24*, 425–428.
8. Espinet, P.; Esteruelas, M. A.; Ore, L. A.; Sarrano, J. L.; Sola, E. *Coord. Chem. Rev.* **1992**, *117*, 215–220.
9. Spinu, C.; Kriza, A. *Acta Chim. Slov.* **2000**, *47*, 179–185.
10. Thakar, B. T.; Barvalia, R. S. *J. Coord. Chem.* **2000**, *63*, 1597–1610.
11. Valarmathy, G.; Subbalakshmi, R. *Asian J. Chem.* **2013**, *25*, 2077–2079.
12. Kumar, G.; Kumar, D.; Devi, S.; Johari, R.; Singh, C. P. *Eur. J. Med. Chem.* **2010**, *45*, 3056–3062.
13. Vanco, J.; Marek, J.; Travnicek, Z.; Racanska, E.; Muselik, J.; Svajlenova O. *J. Inorg. Biochem.* **2008**, *102*, 595–605.
14. Wermuth, C. G. *J. Med. Chem.* **2004**, *47*, 1303–1314.
15. Guo, Z.; Sadler, P. *J. Angew Chem. Int. Edn. Engl.* **1999**, *39*, 1512–1531.
16. Narang, K. K.; Pandey, J. P. *Synth. React. Inorg. Met. Org. Chem.* **1994**, *21*, 73–78.
17. Bult, A. *Met. Ions Biol. Syst.* **1982**, *1*, 261–265.
18. Geary, W. J. *Coordin. Chem. Rev.* **1971**, 81.
19. Chinuusamy, V.; Natarjan, K. *Synth. React. Inorg. Met.Org. Nanomet. Chem.* **1993**, *23*, 889.
20. Maurya, R. C.; Misha, D. D.; Rathore, R.; Jain S. *Synth. React. Inorg. Met. Org. Chem.* **1994**, *24*, 427–437.
21. Sharda, L. N.; Ganokar, M. C. *Indian J. Chem.* **1988**, *27A*, 617–619.
22. Chattopadhyay, P.; Sinha, C. *Indian J. Chem.* **1995**, *34A*, 76–78.
23. Sahni, S. K. *Transition Met. Chem.* **1979**, *4*, 73–76.
24. Singh, H. R.; Agarwala, B. V. *Transition Met. Chem.* **1993**, *18*, 577–579.
25. Rao, T. R. *Synth. React. Inorg. Met. Org. Chem.* **1993**, *32*, 419–436.
26. Maurya, R. C.; Patel, P. *Spectroscop. Lett.* **1999**, *32*, 213–236.
27. Ghargava, B. P.; Bembi, R.; Tyagu, M. *J. Indian Chem. Soc.* **1983**, *60*, 214–217.
28. Lee, J. D. *Concise Inorganic Chemistry*; 5th Edition, Blackwell Science Publishers: Oxford, UK, 1999.
29. Singh, H. R.; Agarwala, B. V. *J. Indian Chem. Soc.* **1988**, *65*, 591–593.
30. Maurya, R. C.; Patel P. *Spectroscop. Lett.* **1999**, *32*, 213–236.
31. Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, Netherlands, 1984.
32. Singh, H. R.; Agarwala, B. V. *J. Indian Chem. Soc.* **1988**, *65*, 591–593.
33. Agarwala, B. V.; Hingorani, S.; Puri, V.; Khetrapal, C. L.; Nagangowda, G. A. *Transition Met. Chem.* **1994**, *19*, 25–27.
34. Mabbot, G. A. *J. Chem. Educ.* **1983**, *60*, 697.
35. Vijayaraj, A.; Prabu, R.; Suresh, R.; Sangeetha Kumari, R.; Kaviyarasan, V.; Narayanan. V. *Bull. Korean Chem. Soc.* **2012**, *33*, 3581–3588.
36. Ali, M. A.; Tan, A. L.; Mirza, A.; Santos, J. A.; Abdullah, A. H. *Transition Met. Chem.* **2012**, *37*, 651–659.
37. Karvembu, R.; Balasubramanian, K. P.; Chinnusamy, V.; Natarajan, K. *Indian J. Chem.* **2005**, *44A*, 2450–2454.
38. Rahman, A.; Choudhary, M. I.; Thomsen, W. J. *Bioassay Techniques for Drug Development*; Harwood Academic Publishers: Amsterdam, Netherlands, 2001.
39. *Indian Pharmacopoeia* **1996**, *IIA*, 105.
40. Gomathi, V.; Selvameena, R. *Asian J. Chem.* **2013**, *25*, 2083–2086.