International Journal of Recent Trends in Engineering & Research
ISSN : 2455-1457 Impact Factor : 3.344

Synthesis, Characterization and antimicrobial activity of transition metal (II) complexes of schiff bases derived from 2-aminophenol and vanillin

Padma Sikarwar[1], Sapna Tomar[2] and A.P.Singh[3]
[1]Department of Chemistry, B.R.E.I., Bichpuri (Campus) Agra – 283105
[2, 3] Department of Chemistry, F.E.T., R.B.S. College, Bichpuri (Campus) Agra–283105

Abstract: Some new transition metal complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Schiff base ligand derived from condensation of 2-amino phenol with vanillin. Both the ligands/complexes were characterized on the basis of elemental analysis, ^{1}H- and ^{13}C-NMR, IR and UV-visible spectral data. The invitro antibacterial and antifungal activities of the complexes were tested using number of bacteria species such as E. coli, Staphylococcus aureus and fungal species such as Aspergillus nidulence and candida albicans. The complexes were formed in moderate yields and they are of various colours and have sharp melting points. The purity and composition of the schiff bases and the metal(II) complexes were established by elemental analysis which suggests a metal : ligand ratio of 1:2. The IR spectra revealed that the complexes coordinated through azomethine nitrogen and methoxy oxygen of the ligands. Further conclusive evidence of the coordination of the schiff bases with the metal ions was shown by the appearance of new bands due to ν(M-N) and ν(M-O) in the metal complexes. Based on the electronic spectral transitions, an octahedral structure has been assigned to all the complexes except Zn(II) complexes which has been assigned tetrahedral structure. Measured molar conductance showed that the complexes are non electrolytes and are soluble in protic solvents like methanol and ethanol. Some complexes showed good antibacterial activities against the tested bacteria, therefore the possible use of the complexes as antibiotic can be suggested.

Keywords: Synthesis, characterization, antimicrobial studies, schiff base vanillin, 2-aminophenol.

I. INTRODUCTION

The synthesis of schiff base ligands and their metal complexes have been extensively studied because of their interesting biological activities[(1-4)]. Schiff bases have been reported to possess antimicrobial[(5-9)], antiviral[(10)], anticancer[(11-14)] and anti-inflammatory activity[(15)] The imine functional functional group (HC=N) is believed to be responsible for the biological activity of schiff base compounds. Vanillin is a phenolic aldehyde organic compound with the molecular formula $C_8H_8O_3$. It is the primary component of the extract of the vanilla bean. Vanillin Schiff bases have been demonstrated to possess polyvalent metal ions[(16)] . Condensation product of vanillin with amines confers biological activity; as well as having good complexation ability with metal ions[(17-19)].). In this study, we present the synthesis, characterization and antimicrobial activity of a series of ONO schiff base ligands derived from condensation of o-aminophenol with vanillin and their metal(II) complexes.

Experimental Section

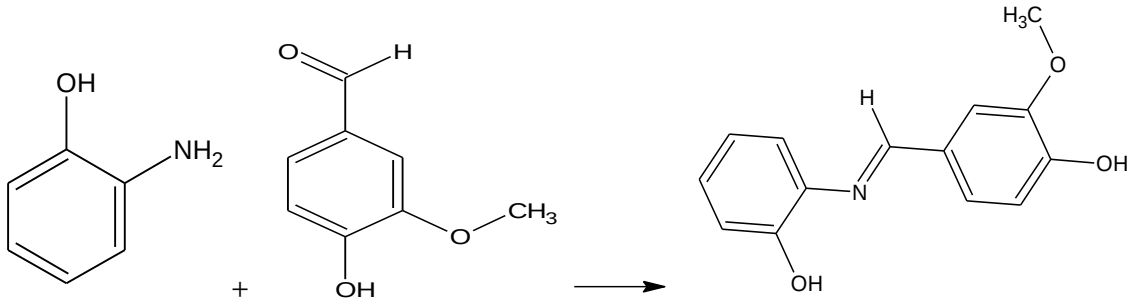
All the chemicals and solvents used were of Analar (AR) grade and were used without further purification. They are vanillin, 2-aminophenol, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $Cu(CH_3COO)_2.H_2O$, $Zn(CH_3COO)_2.2H_2O$, methanol, ethanol, petroleum ether, chloroform, benzene, ethylacetate and acetone. The percentage (%) Co, Ni, Cu and Zn were determined by EDTA complexometric titration[(20)]. The elemental analysis, CHN, was done on Vario MICRO VI.6.2 elemental analysis system GmbH.

Melting points of all compounds were determined using Griffin melting point apparatus. The solubility of the complexes was determined in some polar and non polar solvents such as water, methanol, ethanol, petroleum ether, chloroform, benzene, ethyl acetate and acetone. Molar conductivity was measured by using metler P 163 conductivity meter in methanol solution (10^{-3} M) at 25^0C. The H^1 and C^{13}-NMR spectra were recorded in deuterated DMSO-d6 with $SiMe_4$ as internal standard on Bruker Avance NMR equipment operating at 400 MHz. The mid-infrared absorption frequencies (4000-700 Cm^{-1}) were recorded on a Perkin Elmer Spectrum 100 FTIR equipped with universal attenuated total reflectance (ATR) accessory while the Far-infrared (700-30 cm^{-1}) spectra were recorded in nujol mull on a Perkin Elmer Spectrum 400 FT-IR. The UV/Visible spectra were obtained from Perkin Elmer Lambda 25 spectrophotometer.

Synthesis of the Schiff base ligands:

The schiff base ligand was synthesized as described by Raman et al., 2004[21]. This was done by the condensation of 20 ml of vanillin (0.03gm, 10mmol) with 2-amino phenol (0.022gm, 10mmol) in ethanol (1:1 molar ratio). The mixture was then refluxed for 3h. The product obtained was filtered, washed in distilled water, dried and preserved in a desiccator containing $CaCl_2$.

Yield ; 39%, M.P.; 340, colour; black.



2- amino- phenol vanillin

Synthesis of the complexes:

An ethanolic (10 ml) solution of schiff base ligand (20 mmol) was added drop wise to 10 ml of the metal(II) salts [10 mmol, 0.024 gm of $CoCl_2.6H_2O$, 0.024 gm of $NiCl_2.6H_2O$, 0.02 gm of $Cu(CH_3COO)_2.H_2O$ and 0.022 gm of $Zn(CH_3COO)_2.2H_2O$] in boiling ethanol (78.3^0C). The reaction took place in 1:2 mole ratio of metal(II) : HL. The reaction mixture was refluxed for 3 hr on a water bath and the volume of solution was reduced to half of the initial volume. The product obtained was filtered, washed with water, diethyl ether and then dried in a vacuum over $CaCl_2$[22,23].

II. RESULT AND DISCUSSION

The microanalysis of the ligands and their metal(II) complexes are presented in Table 1. From the data obtained, it appears that the compounds analyzed as $[M(L\text{-}L)X_2]$ indicating a 1:2 mole ratio (M:L). The results revealed that the %C, H and N are in good agreement with the proposed structures (Figure 2 & 3). The analytical data along with some physical properties are summarized in table 1. The schiff base ligand (HL) on interaction with Co(II), Ni(II), Cu(II) and Zn(II) formed complexes with moderate yields (29%-52%). All the complexes are air stable and have sharp melting points ($150\text{-}240^0$C) except the ligand which melted above 340^0C. The sharp melting point indicates that the complexes are probably pure. The lower value of the molar conductivity indicates the non electrolytic behavior of these complexes, since a value in the range 75-90 Scm^2 mol^{-1} is expected for a 1:1 electrolytic. Solubility test

revealed that the complexes of Co(II), Ni(II) and Cu(II) are soluble in all the solvents used except water and petroleum ether. In addition the Cu(II) complexes were soluble in petroleum ether.

Table1:Physical characteristic and analytical data for the schiff base ligand and the metal(II) complexes

Compound	Colour	Yield%	M.P .(^{0}C)	Molar mass	Λ_M (Ω^{-1} cm^2 mol^{-1}	Microanalysis, % Found (Calculated) C	H	N	M
Ligand ($C_{14}H_{13}NO_3$)	Black	34%	>340	243.25	0	68.25 (69.32)	4.88 (5.41)	6.46 (5.51)	-
$[Co^{II}(L_2)]Cl_2$ $Co(C_{14}H_{13}NO_3)_2$	Brown	43%	190	543.98	$1.5x10^{-2}$	62.35 (62.15)	4.55 (4.80)	6.41 (5.34)	10.24 (10.08)
$[Ni^{II}(L_2)]$ Cl_2 $Ni(C_{14}H_{13}NO_3)_2$	Brown	29%	180	545.21	$6.5x10^{-3}$	47.14 (60.88)	4.91 (4.82)	7.49 (5.87)	10.82 (10.74)
$[Cu^{II}(L_2)](CH_3COO)_2$ $Cu(C_{14}H_{13}NO_3)_2$	Brown	52%	190	550.06	0	47.99 (61.13)	4.64 (4.77)	7.45 (5.09)	11.09 (10.78)
$[Zn^{II}(L_2)]$ $Zn(C_{14}H_{13}NO_3)_2$	Red	33%	140	551.93	$3.7x10^{-3}$	60.15 (61.31)	4.52 (4.74)	4.79 (5.10)	11.52 (11.86)

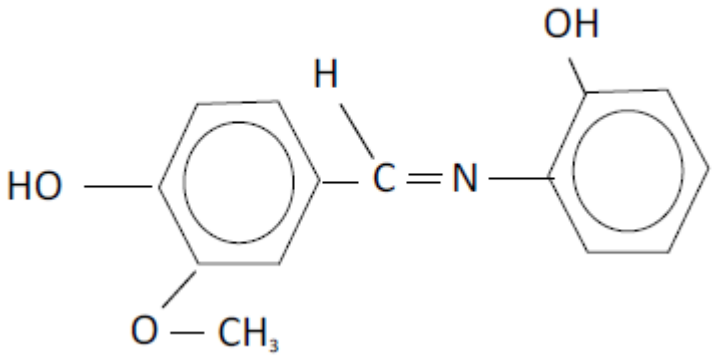


Fig 1: Proposed structure of schiff base

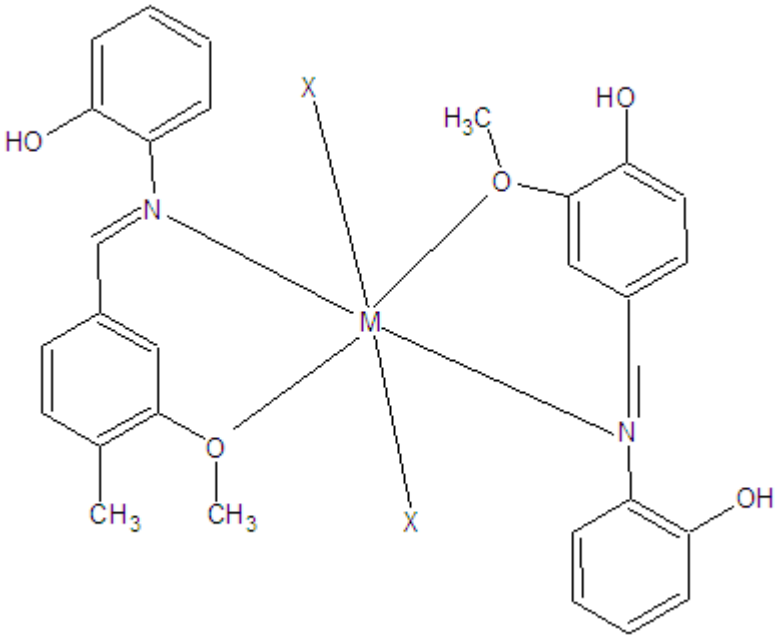


Fig 2: Proposed structure of the metal complexes M = Co(II), Ni(II) or Cu(II)

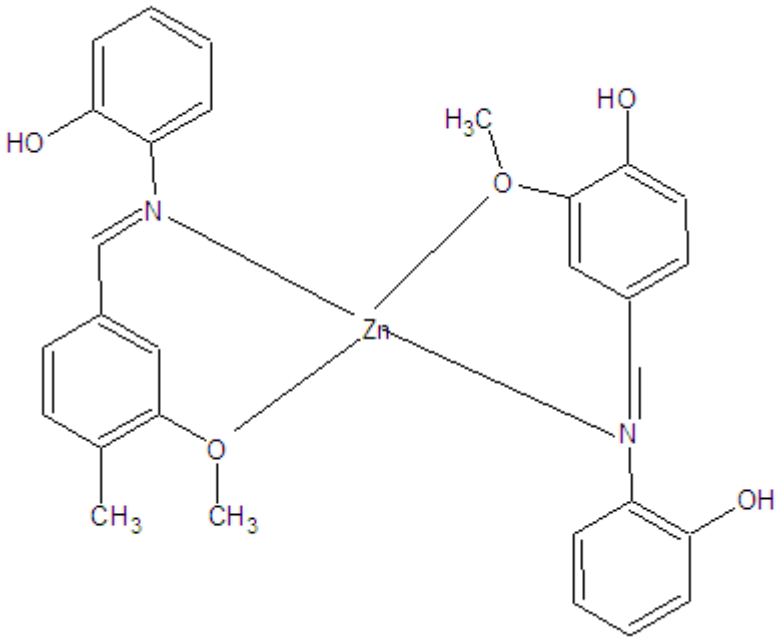


Fig 3: Proposed structure of Zn(II) complex

IR Spectra of Schiff base ligand:

The selected vibrational frequencies for the Schiff base ligand and its metal complexes are presented in Table 2. Very strong band at 1568cm^{-1} is characteristics of the azomethine nitrogen present in the Schiff base ligand[24]. This was shifted to 1551-1595 cm^{-1} in the complexes, which indicates the coordination of the metal to the azomethine nitrogen. The metal complexes showed broad bands at 3260-3407 cm^{-1} which is characteristic of ν(OH).

This indicates that the phenolic –OH group does not participate in bond formation with the metals. The infrared spectrum of the Schiff base ligand showed strong bands at 1487, which was assigned to ν(C-N) stretching. This was shifted to 1491-1587 cm^{-1} region in all the complexes. The spectral bands of the complexes at 1280-1289 were assigned to ν(C-O) which did not show considerable shift from the region 1290 $cm^{-1}$of the ligand. Thus it is suggested that the oxygen atoms of terminal methoxy and hydroxyl group are not coordinated to the metal ions. V(M-N) and ν(M-O) were observed in the far infrared region. These bands are absent in the spectra of the ligand.The ν(M-N) was observed at 529-979cm^{-1} as new bands. This occurrence indicates that there is coordination between the metal and the lone pair of electron on the nitrogen atom of the ligands. Also bands observed at 443-583 cm^{-1}, indicates the formation of M-O bond for the complexes[25].This support the coordination mode of ligand through oxygen atom of the methoxy group.

UV-Visible Studies:

The electronic transition study of the Co(II), Ni(II), Cu(II) and Zn(II) complexes were recorded at 280 – 650 nm using methanol as a solvent. The absorption regions, band assignment and the proposed geometries of the complexes are given in table 3. The orgel diagram for d^7configuration for Co(II) shows the three bands at 12116, 14996 and 23967cm^{-1} assigned for , $^4A_{2g}(F)\rightarrow{}^4T_{1g}(P)$, $^4A_{2g}(F)\rightarrow{}^4T_{1g}(F)$ and $^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$. The electronic transition observed for Co(II) complex suggest the octahedral geometry[26].

The appearance of a band at 23051 cm^{-1} assigned to $^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$ transition favors an octahedral geometry for Ni(II) complex. Copper(II) has a (d^9)configuration and showed only one transition at 23812cm^{-1} assigned to the $^3A_{2g}\rightarrow{}^3T_{2g}$ transition ,which is in good agreement with distorted octahedral configuration around the copper(II) ion. Though three transitions are expected in this case, they are very close in energy and often appear in the form of one broad band envelope[27]. The bands observed in the complex at 22997 cm-1 is tentatively assigned to the spin allowed d-d transitions. This is consistent with a tetrahedral geometry. Based on the microanalysis, IR and Electronic spectral data the proposed structures for the Schiff base ligand and the complexes are shown in Figures 1– 3.

NMR STUDIES:

The NMR spectral data for the ligands are presented in the table 3. The Schiff base ligands exist in enol form; as indicated by the non-splitting of the methine proton (figure 4) and the appearance of the phenolic protons[28-30] . The phenolic hydroxyl proton in the aldehyde moiety of the ligands absorbed downfield as a broad singlet at 14.44 - 13.77 ppm; while the broad signal at 9.79 - 9.77 ppm was attributable to the hydroxyl proton of the ortho-aminophenol moiety. The broadness of the signals was due to a strong hydrogen bonding between the imine N and the hydroxyl protons. On the other hand, the azomethine proton, HC=N, appeared as a strong singlet at 8.97 - 8.85 ppm, which was corroborated by the ^{13}C-NMR signal at 166.54 - 160.73 ppm. The purity of the ligands was indicated by the disappearance of the aldehyde and the amino protons; CHO (δ = 9 - 10 ppm) and NH_2 (δ = 3 – 4 ppm); in the ligands spectra. All the aromatic protons were accounted for and absorbed at 6.50 - 7.50 ppm. Lastly, the signals at 3.80 ppm and 56.55 - 56.24 ppm (^{13}C-NMR), correspond to the methoxyl protons of ligand resulting from vanillin.

Table 2: Relevant IR frequencies (cm^{-1}) of the schiff base ligands and their metal(II) complexes.

Compound	V(OH)phenolic	V(C-O)	V(C-N)	V(C=N)	V(O-CH_3)	V(M-N)	V(M-O)
Ligand	3398w	1288m	1487m	1568sh	2932w	-	-
$[Co^{II}(L_2)]Cl_2$	3407b	1280b	1512s	1587s	3405b	635m	572m
$[Ni^{II}(L_2)]\ Cl_2$	3359sh	1280vs	1487vs	1590vs	3464sh	596m	504m
$[Cu^{II}(L_2)](CH_3COO)_2$	3326m	1288vs	1491vs	1552w	3218w	529s	439m
$[Zn^{II}(L_2)]$	3260w	1291vs	1587vs	1590vs	2946w	979m	569b

b = broad m = medium s = strong vs = very strong sh = sharp w = weak

Table-3: H^1 NMR Spectral data of ligand and their metal complexes. δH (400MHz, $CDCl_3$)

Compound	1H, s, Ar-OH	1H, s, HC=N	1H, d	2H, dd	1H, t	3H, s, -OCH_3
Ligand ($C_{14}H_{13}NO_3$)	14.39, 9.79	8.82	7.61, 7.30, 6.45	6.86	7.25, 6.93	3.78
$[Co^{II}(L_2)]Cl_2$ $Co(C_{14}H_{13}NO_3)_2$	14.09, 9.77	8.84	7.43, 7.34, 6.46	6.91	7.18, 6.41	3.80
$[Ni^{II}(L_2)]\ Cl_2$ $Ni(C_{14}H_{13}NO_3)_2$	13.97, 9.78	8.85	7.49, 7.31, 6.46	7.31	7.13, 6.41	3.79
$[Cu^{II}(L_2)](CH_3COO)_2$ $Cu(C_{14}H_{13}NO_3)_2$	14.38, 9.77	8.96	7.44, 7.32, 6.44	7.34	7.32, 6.45	3.81
$[Zn^{II}(L_2)]$ $Zn(C_{14}H_{13}NO_3)_2$	14.37, 9.77	8.84	7.45, 7.32, 6.45	7.36	7.30, 6.41	3.80

Table-4: C^{13} NMR Spectral data of ligands and their metal complexes. δC (400MHz, $CDCl_3$)

Compound	Ar-OCH3	Ar-N=C	Ar-OH	Ar - C	CH=N
Ligand ($C_{14}H_{13}NO_3$)	152.12	148.96	147.37	128.52–123.29	163.26
$[Co^{II}(L_2)]Cl_2$ $Co(C_{14}H_{13}NO_3)_2$	164.63	134.76	151.32	128.52–123.29	165.64
$[Ni^{II}(L_2)]\ Cl_2$ $Ni(C_{14}H_{13}NO_3)_2$	164.68	134.87	151.07	128.52–123.29	165.35
$[Cu^{II}(L_2)](CH_3COO)_2$ $Cu(C_{14}H_{13}NO_3)_2$	163.90	134.82	151.09	128.52–123.29	165.05
$[Zn^{II}(L_2)]$ $Zn(C_{14}H_{13}NO_3)_2$	164.12	134.89	151.12	128.52–123.29	162.77

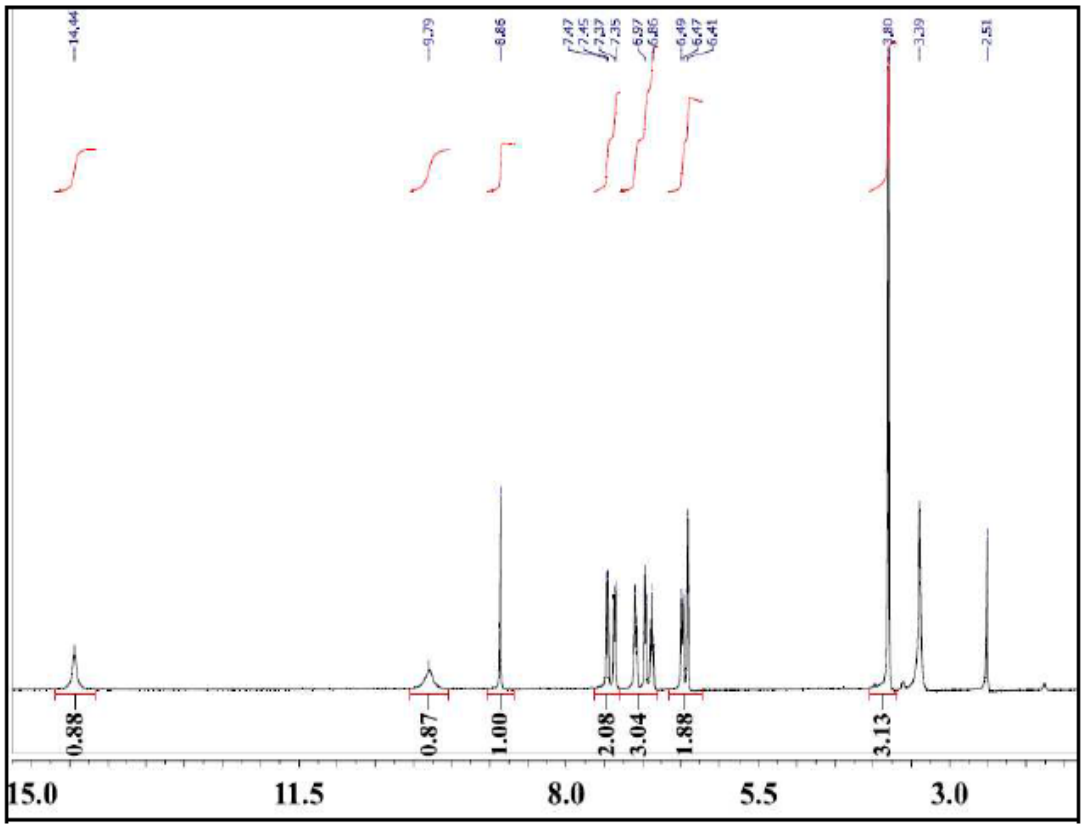


Figure 4: ^{1}H-NMR spectrum for ligand

Antimicrobial Activity:

Antibacterial Activity

The newly synthesized ligands and their metal complexes were screened for their antibacterial activity against Staphylococcus aureus and E.coli bacterial species using the agar well diffusion method. 10–24 hour bacterial solution containing ~10^4–10^6 colony forming units (CFU)/mL were used. The test sample's (1 mg/mL in DMF) concentration (100 µL) was introduced in the petric disc. New petric dishes were incubated immediately at 37°C for 24 h activities was determine by measuring the diameter of zones showing complete inhibition (mm). Growth inhibition was compared with the standard drug.

Table-5: Antibacterial screening data of ligand and their metal complexes

Compound	Average % inhibition after 48 h. (conc. in ppm)			
	Staphylococcus aureus (gram +ve)		E. coli (gram –ve)	
	500	1000	500	1000
Ligand ($C_{14}H_{13}NO_3$)	29	43	30	36
$[Co^{II}(L_2)]Cl_2$ $Co(C_{14}H_{13}NO_3)_2$	43	52	41	54
$[Ni^{II}(L_2)]$ Cl_2 $Ni(C_{14}H_{13}NO_3)_2$	43	50	41	45

$[Cu^{II}(L_2)](CH_3COO)_2$ $Cu(C_{14}H_{13}NO_3)_2$	42	51	42	56
$[Zn^{II}(L_2)]$ $Zn(C_{14}H_{13}NO_3)_2$	41	51	41	38
Amoxycillin (antibacterial)	83	100	81	99

Antifungal Activity

Antifungal activities of all compounds were studies against two fungal cultures Candida albicans and Aspergillus nidulence fungal species. Sabouraud dextrose agar was seeded with 10^5 mL^{-1}fungal spare suspension and transferred to petric plates. Dishes soaked in 20 mL (10 µg/mL in DMF) of the entire agar surface. The plates were incubated at 32°C for 24 h. the results were recorded as zones of inhibition (mm) and compared with the standard drug Streptomycin.

Table-5: Fungicidal screening data of ligand and their metal complexes.

Compound	Average % inhibition after 48 h. (conc. in ppm)			
	Candida albicans		Aspergillus nidulence	
	500	1000	500	1000
Ligand ($C_{14}H_{13}NO_3$)	5	9	5	10
$[Co^{II}(L_2)]Cl_2$ $Co(C_{14}H_{13}NO_3)_2$	7	14	7	15
$[Ni^{II}(L_2)]$ Cl_2 $Ni(C_{14}H_{13}NO_3)_2$	7	11	7	16
$[Cu^{II}(L_2)](CH_3COO)_2$ $Cu(C_{14}H_{13}NO_3)_2$	9	16	10	12
$[Zn^{II}(L_2)]$ $Zn(C_{14}H_{13}NO_3)_2$	7	16	7	11
Streptomycin (antifungal)	16	18	16	18

III. MINIMUM INHIBITORY CONCENTRATION

Compounds showing antibacterial activity over 8% were selected for minimum inhibitory concentration studies. The MIC was determined using the disc diffusion technique by prepared uses containing 500 and 1000 µg/mL of the compounds (Figure 1).

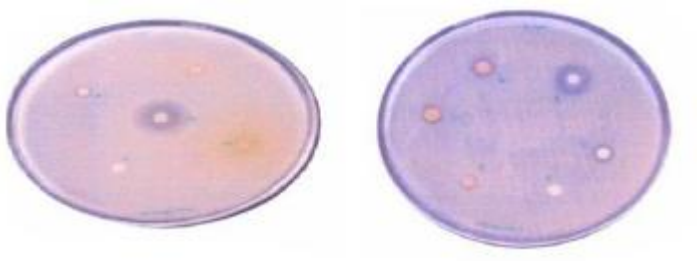


Fig 5: showing zone of inhabitation against S. aureus, and E. coli

IV. CONCLUSION

In this paper the synthesis of a Schiff base ligand derived from condensation of vanillin with 2-aminophenol and its metal(II) complexes have been described. The Schiff base ligand coordinated through its azomethine nitrogen and oxygen atom of methoxy group of the vanillin. This is supported by infrared spectral data. The electronic spectral band observed are consistent with an octahedral geometry for Co(II), Ni(II) and Cu(II) complexes while Zn(II) complex adopt a tetrahedral geometry. The complexes were formed in 1:2(metal: ligand) ratio as confirmed by the microanalysis. The molar conductivity data of the complexes in methanol indicated that they are non electrolytes. All the complexes are air stable and soluble in protic solvents like methanol and ethanol. The in vitro antimicrobial study shows that the complexes have higher activities compared to the free ligand.

REFERENCES

i. Shayma, A.S., Yang, F. and Abbas, A.S.; Europ. J. Scient. Res., 33 (4), 702 (2009).
ii. Rajib, L.D., Mahuya, M., Lovely, R. and Jay, D.M.; Ind. J. Chem., 47(A), 207 (2008).
iii. Harlal, S. and Varshney, A.K.; Bioinorg. Chem. Appl., 23245, 1 (2006).
iv. Sonmez, M. and Sekerci, M.; Polish. J. Chem., 76, 907 (2006).
v. Reddy, V. Patil, N. and Angadi, S.D.; E. J. Chem., 5(3), 577 (2008).
vi. Valent, A., Melnik, M., Hudecova, D., Dudova, B., Kivekas, R. and Sundberg, M.R.; Inorg. Chem. Acta., 340, 15 (2002).
vii. Samanta, B., Chakraborty, J., Choudhury, C.R., Dey, S.K., Dey, D.K., Batten, S.R. and Jensen, P.; S. Mitra Struct. Chem., 18, 33 (2007).
viii. Şabik, A.E., Karabork, M., Ceyhan, G., Tumer, M. and Digrak, M.; Int. J. Inorg. Chem., 2012, 11 (2012).
ix. Singh, U.I., Singh, R.K.B., Devi, W.R. and Singh, C.B.; J. Chem. Pharm. Res., 4(2), 1130 (2012).
x. Singh, S.P., Shukla, S.K. and Awasthi, L.P.; Current Science, 52(16), 766 (1983).
xi. Sathisha, M.P., Revankar, V.K. and Pai, K.S.R.; Metal Based Drugs, 2008, 11 (2008).
xii. Coluccia, M., Nassi, A., Boccarelli, A., Giordano, D., Cardellichio, N., Locker, D., Leng, M., Sivo, M., Intini, F.P. and Natile, G.; J. Inorg. Biochem., 77(1-2), 31 (1999).
xiii. Kandeel, M.M., Ali, S.M., Abed, E.K.A., ElALL, Abdelgawad, M.A. and Lamie, P.F.; J. Chem. Pharm. Res., 4(9), 4097 (2012).
xiv. Arjmand, F., Sayeed, F. and Muddassir, M.; J. Photochem. Photobiol., 103, 166 (2001).
xv. Bawa, S. and Kumar, S.; Indian J. Chem. Sect. B: Org. Chem. Incl. Med. Chem., 48B (1), 142 (2009).
xvi. Magdy, W., Sabaa, R.M., and Emad, H.O.; Europ. Polym.J., 45(11), 3072 (2009).
xvii. Ali, S.M., Azad, M.K., Jesmin, M., Ahsan, S., Rahman, M.M., Khanam, J.A., Islam, M.N. and Shahriar, S.M.; Asian Pacific J. Trop. Biom., 1, 438 (2012).
xviii. Zhu, W., Huang, Z., Li, J., Chen, Y. and Yan, Q.; Chin. Chem. Magaz., 9(4), 18 (2007).
xix. Sallomi, I.J. and Al-Zeadan, W.A.; J. Educ. Scienc., 24 (4) (2011).
xx. Vogel, A.I.; A text book of practical organic chemistry including qualitative organic Analysis (4th edition), Longman group limited, London, 264 (1978).
xxi. Raman, N., Ravichandran, S. and Thangaraja, C.; J. Chem. Sci., 116(4), 215 (2004).
xxii. Sekhar, E.V., Jayaveera, K.N. and Srihari, S.; J. Chem. Pharm. Res. 4(12), 5121 (2012).
xxiii. Neelakantan, M.A., Esakkiimmal, M, Mariappan, S.S., Dharmaraja, J. and Jeyakumar, T.; Ind. J. pharm. Scien., 72(2), 216 (2010).
xxiv. Raman, N., Ravichandran, S. and Thangaraja, C.; J. Chem. Sci., 116(4) 215 (2004).
xxv. M Hamrit; S Djebbar-Sid; O Benli-Baitichy; MA Khan and GM Bouet. Journal of synthesis and reaction in Metal Organic Chemistry. 2000, 30 (10): 1884.
xxvi. Suresh, M.S. and Prakash, V.; Int. J. Phys. Sci., 5(14), 2203 (2010).
xxvii. Pal, T.K., Alam, M.A. and Paul, S.R.; J. Bangl. Acad. Sci., 34(2), 153 (2010).
xxviii. Joshi, K.T., Pancholi, A.M., Pandya, K.S. and Thakar, A.S.; J. Chem. Pharm. Res., 3(4), 741(2011).
xxix. Vijayaganthila, R., Nirmala, A. and Swanthy, C.H.; J. Chem. Pharm. Res., 3(3), 635 (2011).
xxx. Wanger, A., Schwalbe, R., Steele-Moore, L. and Goodwin, A.C.; Antimicrobial Susceptibility Testing Protocols, Taylor and Francis group, London, 6 (2007).

