SYNTHESIS, STRUCTURAL CHARACTERIZATION, THERMAL AND ANTIMICROBIAL EVALUATION OF BINUCLEAR Cu(II), Ni(II) AND VO(IV) SCHIFF BASE COMPLEXES

S. Vedanayaki, D. Sandhanamalar, P. Jayaseelan and R. Rajavel*

Department of Chemistry, Periyar University, Salem – 636 011, Tamil Nadu, India

E-mail: varshuvishal@gmail.com

Abstract

A binuclear Schiff base, H_2L, ligand was synthesized by reaction of 5-bromo-3-fluorosalicylaldehyde and benzidine in the molar ratio 1:1 forms stable complexes with transition metal ions such as Cu(II), Ni(II) and VO(IV). The elemental analysis, conductivity, IR, electronic, ^{1}H NMR, electrochemical and magnetic susceptibility measurements and thermal studies were used to characterize the isolated ligand and its metal complexes. EPR spectra provided further information to confirm the binuclear structure and the presence of magnetic interactions. The ligand acts as dibasic with two N_2O_2 tetradentate sites and can coordinate with metal ions to form binuclear complexes. The ^{1}H - NMR data reveal that the Schiff base exists in enol – iminic form. The bonding sites are the nitrogen atoms of the azomethine groups and oxygen atoms of the phenolic groups. Substitution in the phenyl ring of the complexes produces shift in the azomethine $\upsilon(C=N)$ stretching vibrational frequency. The electrochemical properties of the Cu(II) complexes were investigated. Thermal behavior of selected complexes has been studied by thermogravimetric and differential thermal analysis. The electrolytic behavior of complexes indicates the presence of counter ions. On the basis of electronic spectral data and magnetic susceptibility measurements, suitable geometry has been proposed for each complex. The Schiff base ligand and its metal complexes were tested against four pathogenic bacteria (*S. aureus* and *B. subtilis*) as Gram-positive bacteria and (*E. coli* and *K. pneumoniae*) as Gram-negative bacteria and one pathogenic fungi (*A. fumigatus*) to assess their antimicrobial properties.

Keywords: Schiff base complexes; Spectroscopy; Electrochemistry; Thermal analysis; Antimicrobial activity

Introduction

Schiff bases are formed by the condensation of a primary amine and an aldehyde or a ketone under specific conditions. The resultant functional group, $R^1HC=N-R^2$, is called an imine and is particularly for binding metal ions via the N atom lone pair, especially when used in combination with one or more donor atoms to form polydentate chelating ligands. Metal complexes of Schiff bases derived from substituted salicylaldehyde and various amines have been extensively investigated [1]. Such complexes present many applications in catalysis and oxygen storage devices [2]. Schiff base complexes have also been shown to exhibit a broad range of biological activities, including antifungal, antibacterial, antimalarial, antiviral, anti-inflammatory and antipyretic properties [3-8]. The interest in Schiff base complexes as analytical reagents is increasing since they enable simple and inexpensive determinations of different organic and inorganic substances [9].Various mono- and dialdehydes/ketones have been employed to condense with amines to explore multidentate binucleating Schiff bases to design a variety of binuclear transition metal complexes [10-12]. In view of recent interest in the thermal behavior and biological activities of the metal-ligand chelates involving Schiff base ligands [13, 14], we started to study the thermal behavior and biological activities of Schiff base complexes derived from tetradentate ligands involving an N_2O_2 donor atoms.

This paper describes the synthesis, spectral, magnetic and thermal studies of Schiff base derived from 5-bromo-3-fluorosalicylaldehyde and benzidine and its binuclear Cu (II), Ni(II) and VO(IV) complexes. Indeed, the biological activity of the ligand and its complexes were screened against selected kinds of bacteria and fungi.

Experimental

Materials

Cu $(ClO_4)_2.6H_2O$, Ni $(ClO_4)_2.4H_2O$ (Loba Chemicals), $Cu(CH_3COO)_2.H_2O$, $Ni(CH_3COO)_2.4H_2O$, $VOSO_4.H_2O$ (E . Merck) and 5-bromo-3- fluoro salicylaldehyde was purchased from Sigma-Aldrich and were

used without further purification. Solvents were A.R.grade and were used after purification by the standard methods as described in the literature [15, 16].

Instruments

C, H, N micro analysis was carried out with a Perkin-Elmer 2400II elemental analyser. Copper was determined by iodometric procedure and Nickel was determined by gravimetric methods using dimethylgyloxime as precipitating agent. Vanadium was determined following the method described by Fries J and Getrost H [17]. The FT-IR spectra (4000–400 cm^{-1}) of the compounds were recorded as KBr disc using FT-IR spectrophotometer with solid KBr disc. The electronic spectra were recorded at 300 K on a Perkin-Elmer Lambda 40 (UV-Vis) spectrometer using HPLC grade DMSO as solvent in the range 200–800 nm. ^{1}H NMR spectra was recorded on a Bruker 300 MHz FT-NMR spectrometer using tetramethylsilane as an internal standard. The molar conductance values at room temperature were measured in DMF (10^{-3} moldm^{-3}) on an Elico digital direct conductivity meter model CM-180. The magnetic studies were carried out at room temperature on a Gouy balance calibrated with Hg [Co(SCN)$_4$]. EPR spectra of compounds were recorded on a Bruker model EMX plus, X-band spectrometer (9.86 GHz) with 100 kHz modulation frequency. Thermal analyses (TGA and DTA) were measured from room temperature to 900 °C at a heating rate of 10 °C/min in N$_2$ atmosphere using SDT Q600 V8.3 Build101. The purity of the ligand and its complexes were checked by TLC.

Synthesis of the Schiff base ligand

A solution of 5-bromo-3-fluorosalicylaldehyde (2 mmol) in methanol (30 ml) was slowly added over a solution of benzidine (1 mmol) in the same solvent (30 ml). The reaction mixture was heated to reflux for 2 h at 80 °C. The resulting diimine precipitated as an orange solid was filtered off and washed with methanol. The Schiff base ligand so obtained was dried over anhydrous CaCl$_2$ in a dessicator.

Synthesis of metal complexes

The Ni(II), Cu(II) and VO(IV) complexes were synthesised by the addition of appropriate metal acetate / perchlorate / sulphate (2 mmol) in ethanol (30 ml) to the hot solution (60 °C) of Schiff base (2 mmol) in the same solvent (30 ml). The resulting mixture was refluxed on a water bath for 3 h were upon the complexes

precipitated. They were collected by filteration and purified by washing with ethanol, diethylether and dried over anhydrous $CaCl_2$.

Antimicrobial Activities

The standardized disc-agar diffusion method [18] was followed to determine the activity of the synthesized compounds against the sensitive organisms S. *aureus* and *B. subtilis* as Gram-positive bacteria, *E. coli* and *K. pneumoniae* as Gram-negative and the fungi *A. fumigatus*. The antibiotic *Ampicillin* was used as standard reference in the case of bacteria and *Fluconazole* was used as a standard antifungal reference.

The tested compounds were dissolved in DMSO (which has no inhibition activity), to get concentration of 2 and 1 $mgmL^{-1}$. The test was performed on medium potato dextrose agar (PDA) which contains infusion of 200 g potatoes, 6 g dextrose and 15 g agar [19, 20]. Uniform size filter paper disks (three disks per compound) were impregnated by equal volume (10 µL) from the specific concentration of dissolved test compounds and carefully placed on incubated agar surface. After incubation for 36 h at 27 °C in the case of bacteria and 48 h at 24 °C in the case of fungi, inhibition of the organisms which evidenced by clear zone surround each disk was measured and used to calculate mean of inhibition zones.

Results and discussion

The resulting solids are intensely coloured and stable in air. The ligand is partially soluble in common organic solvents but the complexes are soluble only in DMF and DMSO. The melting points are sharp indicating the purity of the prepared Schiff base and its metal complexes. Elemental analysis, conductivity, spectroscopic, magnetic moments, and thermal analysis were employed to determine the structural characterization of the ligand and their complexes are in well agreement with the expected values.

Elemental analysis

The elemental analysis is in good agreement with that calculated for the proposed formula as shown in Table 1.

Compound	Molecular formula	Colour	Yield (%)	M.P (°C)	Elemental analysis, found (Calc.) [%]			
					C	H	N	M
# H$_2$-BrFsalbz	C$_{26}$H$_{16}$O$_2$N$_2$F$_2$Br$_2$	Orange	80	240	52.95 (53.24)	2.65 (2.73)	4.68 (4.77)	–
1 [Cu(BrFsalbz)]$_2$	C$_{52}$H$_{28}$O$_4$N$_4$F$_4$Br$_4$Cu$_2$	Brown	60	>250	48.10(48.14)	2.13 (2.16)	4.26 (4.32)	9.82 (9.87)
2 [Ni(BrFsalbz)]$_2$	C$_{52}$H$_{28}$O$_4$N$_4$F$_4$Br$_4$Ni$_2$	Light green	62	>250	48.53 (48.59)	2.14 (2.18)	4.28 (4.36)	9.02 (9.09)
3 [Cu(BrFsalbz)]$_2$·4ClO$_4$	C$_{52}$H$_{28}$O$_{20}$N$_4$F$_4$Cl$_4$Br$_4$Cu$_2$	Dark brown	65	>250	36.82 (36.87)	1.62 (1.65)	3.26 (3.30)	7.52 (7.56)
4 [Ni(BrFsalbz)]$_2$·4ClO$_4$	C$_{52}$H$_{28}$O$_{20}$N$_4$F$_4$Cl$_4$Br$_4$Ni$_2$	Green	70	>250	37.12 (37.14)	1.58 (1.66)	3.29 (3.33)	6.86 (6.90)
5 [VO(BrFsalbz)]$_2$·2SO$_4$	C$_{52}$H$_{28}$O$_{14}$N$_4$F$_4$Br$_4$S$_2$V$_2$	Dark blue	65	>250	41.70 (41.76)	1.78 (1.87)	3.70 (3.74)	6.79 (6.82)

Molar conductivity measurements

Conductivity measurements were carried out in 10^{-3} mol/dm^3 DMF solution at 25 °C. The room temperature molar conductivity values are given in Table 3. The molar conductance values of the complexes 1 and 2 indicate that they are non-electrolytic except for the perchlorate and sulphate complexes which are in the range characteristic of 1:4 and 1:2 electrolytes respectively [21].

Table 3. Electronic spectral data and magnetic moment values of the metal complexes

Complex	Electronic spectral bands (nm)	Tentative assignments	Magnetic moments, μ_{eff} B.M.	Molar conductance (ohm^{-1}cm^{2}mol^{-1}) in DMF
1	592	$^2B_{1g} \rightarrow {}^2A_{2g}$	1.62	8.2
2	525	$^1A_{1g} \rightarrow {}^1A_{2g}$	Diamagnetic	10.2
3	585	$^2B_{1g} \rightarrow {}^2A_{2g}$	1.65	266
4	526	$^1A_{1g} \rightarrow {}^1A_{2g}$	Diamagnetic	248
5	588	$^2B_{2g} \rightarrow {}^2E$	1.80	132

^{1}H NMR Spectra

The ^{1}H NMR spectra of the free ligand was recorded in DMSO-d_6. The free ligand exhibits sharp low field signals for the two phenolic protons between 13.34 and 13.30 ppm. This shows that the Schiff base forms intramolecular hydrogen bonds [22] involving the phenolic proton and the azomethine nitrogen atom, thus implying a phenol-iminic structure (Figure 1). Signal for the methine proton of the azomethine group −N=C(H)− was observed between 8.4−8.7 ppm. In the region of 7.6−6.8 ppm were assigned to chemical shifts for protons of the aromatic ring. The total number of protons present in the Schiff base exhibited signals of the protons in their expected regions and these data are in good agreement with that previously reported for similar compounds [23]. It was also observed that DMSO did not show any coordinating effect on the ligand.

Figure-1: Synthesis of the Schiff base ligand.

Figure 1. Synthesis of the Schiff base ligand
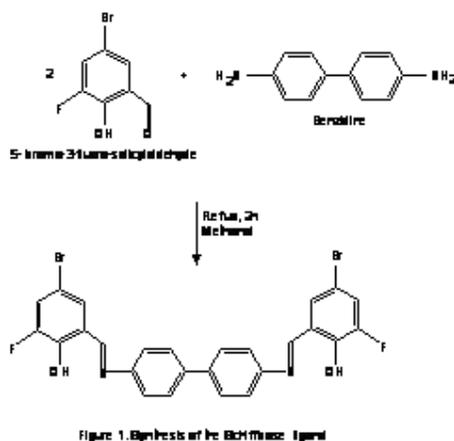
IR spectral studies

The IR spectral data of the Schiff base and its complexes are listed in Table 2. IR spectra of metal complexes of the Schiff base ligand are compared with that of the Schiff base in order to determine the coordination sites that may involved in chelation. The O−H stretching frequency of the ligand exhibits broad weak intensity band in the 2500−3500 cm^{-1} range, which is assigned to the intra molecular hydrogen bond O−H··N=C [24]. This band disappeared in the spectra of the complexes. A strong sharp absorption band around 1621 cm^{-1} in the spectrum of the Schiff base ligand can be assigned to the C=N stretching. In all the complexes,

this band is shifted to lower frquencies in the range 1611–1590 cm^{-1} upon complexation with the metal, which can be attributed to the coordination of the imine nitrogen to the metal centre [25, 26].

Table 2. Infrared spectral data of the ligand and its metal complexes (cm^{-1}) and their assignments.

Ligand/Complex	(C=N)	υ(C–O)	υ(O–H...N)	υ(M–O)	υ(M–N)	Other bands
H_2L	1621	1330	3130	–	–	–
1	1608	1311	–	541	462	–
2	1610	1312	–	525	446	–
3	1611	1315	–	535	460	1142, 1070, 623; ClO_4 groups
4	1611	1314	–	528	452	1130, 1054, 620; ClO_4 groups
5	1590	1310	–	515	442	1122; SO_4 and 980; υ(V=O)

The frequency of the aromatic carbon and phenolic oxygen of the free ligand at 1075 cm^{-1} was shifted to lower frequency ($\Delta\upsilon$ = 10–25 cm^{-1}) in the binuclear compexes, suggesting the participation of phenolic – OH group in chelation. The binuclear complexes have medium bands in the region of 1104–1182 cm^{-1} and weak bands at 1020–1093 cm^{-1} (antisymmetric stretch) and a sharp band at 620–626 cm^{-1} (symmetric bending) range featuring typical characteristics of uncoordinated perchlorates [27, 28]. The band at 980 cm^{-1} is assigned to υ(V=O) this band is observed as a new peak for the compexes and is not present in the spectrum of the free ligand. Finally, the appearance of two non-ligand bands in the two ranges 500–550 cm^{-1} and 440–465 cm^{-1} in all the complexes could be assigned to the stretching frequencies of υ(M–O) and υ(M–N) respectively [29]. Therefore, from the IR spectra, it is concluded that H_2L behaves as a tetradentate ligand with ONNO donor sites coordinating to the metal ions via the azomethine N and deprotonated phenolic O atoms.

Electronic spectral and magnetic susceptibility measurements

UV-Vis spectra provide the most detailed information about the electronic structure. UV-Visible spectra of the free ligand and the metal complexes were recorded at 300 K in HPLC grade DMSO solution. The UV-Vis spectrum of the Schiff base ligand (H_2L) exhibits two charge transfer (CT) bands at 260 nm and 325 nm attributed to π–π* and n– π* transition within the Schiff base ligand. In the spectrum of the complexes, the CT

band at 260 nm remains as such, in agreement with the π–π* transition of the Schiff base ligand. Another band at 350–365 nm is detected in the spectrum of the complexes. The band observed at 325 nm observed in the spectrum of the free ligand (H_2L) is red shifted to 350−365 nm in complexes in the form of ligand to metal charge transfer (LMCT) transition. Similarly much weaker and less well defined broad bands are found in the spectrum of the complexes at 520−650 nm which are assigned to the d-d transitions. The absorption spectrum of copper complexes 1 and 3 show a broad band at 592 and 585 nm attributed to $^2B_{1g} \rightarrow {}^2A_{2g}$ transition which is well within the range of 595−555 nm expected for square planar CuO_2N_2 chromophore [30]. The magnetic moment (μ_{eff}) of the complexes **1** and **3** at room temperature were 1.62 and 1.65 B.M., respectively. The lower values of magnetic moments at room temperature are consistent with square planar geometry around the metal ions. In general, the low magnetic moment values of binuclear copper complexes are attributed to the anti-ferromagnetic moment interaction between two central Cu(II) metal ions; this is an indication of the formation of binuclear Cu(II) complex [31].

The electronic spectra of the binuclear Ni (II) complexes show bands at 525 and 530 nm may be assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition, indicating a square planar environment around the nickel(II) [32] which is confirmed by the diamagnetic properties of the complexes.

The binuclear vanadyl complex exhibits only one band in addition to the intense charge transfer band, in the 581 nm region owing to the $^2B_{2g} \rightarrow {}^2E$ transition characteristic of square pyramidal geometry. The magnetic moment data of the VO (IV) complex was 1.80 B.M., which confirms the binuclear structure of the complex [33].

Electron spin resonance spectra

The X-band EPR spectrum of [Cu (BrFsalbz)]$_2$ complex recorded at LNT (Fig. 2) consists of an axial symmetrical signal with $g_{\parallel}$ at 2.178 and $g_{\perp}$ at 2.050. In the square planar complexes the unpaired e⁻ lies in the ($d_{x^2-y^2}$) orbital giving $^2B_{1g}$ as the ground state with the $g_{\parallel} > g_{\perp} > g_e$ (2.0023 free spin value) [34]. From the observed value of Cu (II) complex, it is clear that $g_{\parallel} > g_{\perp}$. These data are in agreement with those obtained from the electronic spectra and confirms the square planar geometry of the complex.

From the values of the g factors it may be determined the geometric parameter G, representing a measure of the exchange interaction between the Cu(II) centers in polycrystalline compounds following the formula, $G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$ [35]. If G < 4, it is considered the existence of exchange interaction between the Cu (II) centers and if G > 4, the exchange interactions are neglected. Thus in the case of complex **1,** the geometric parameter G = 0.2808 confirms the existence of interactions between the Cu(II) centers.

Thermal analysis (TGA and DTA)

Thermogravimetric analyses for complexes $[Cu(BrFsalbz)]_2$ and $[Ni(BrFsalbz)]_2$ were obtained to give information concerning the thermal stability of the complexes. The results of thermal analysis showed good agreement with the theoretical formula as suggested from the elemental analysis. Thermal analyses of the complexes were carried out within the temperature range from ambient temperature up to 900 °C. The correlation between the different decomposition steps of the compounds with the corresponding weight losses are discussed in terms of the proposed formula of the compound.

The thermogravimetric analysis of Cu (II) complex indicated three stages of decomposition involving the loss of bromine atoms, ligand moiety and oxidative degradation of the remainder to CuO. The complex was stable up to 240°C. The first stage of decomposition started at this temperature and completed at 456°C. A mass loss of 30.39% (calcd: 30.55%) was observed corresponding to the loss of four bromine and four fluorine atoms of the complex. The second stage of decomposition took place in the temperature range 456 − 572°C. The mass loss of 53.68% (calcd: 54.68%) which occurred in this region accounts for the elimination of the ligand moiety. The final decomposition stage occurred in the range 572 − 900 °C was consistent with the oxidative decomposition of the complex, leading to the formation of metal oxide, CuO. These steps are accompanied by exothermic peaks at 223, 442 and 506 °C and endothermic peaks at 305, 379, 553 °C respectively.

Thermal decomposition process of Ni (II) complex appeared in three stages. The initial weight loss occurred in the range of 278−544 °C with mass loss of 30.60% (calcd: 30.55%), in which four bromine and four fluorine atoms are removed. The second stage continued from 545−747 °C indicating the decomposition of remaining organic moiety with a mass loss of 52.79% (calcd: 54.68%). Above 749 °C, the complex started to

decompose slowly, then more rapidly up to 900 °C with the formation of metal oxide, NiO. It is clear from these data that these mass losses are accompanied by exothermic peaks at 347, 472, 554, 646, 748 °C and endothermic peaks at 333, 496, 529, 616, 733 °C respectively. Apart from evaluating the thermal stability of the metal complexes, these studies also helped to characterize the complex.

From the interpretation of elemental analysis, infrared, electronic spectra, EPR, magnetic measurements and molar conductivity, it is possible to draw up the tentative structures of the transition metal complexes. Figure 2 depicts the representative structure of the metal complexes.

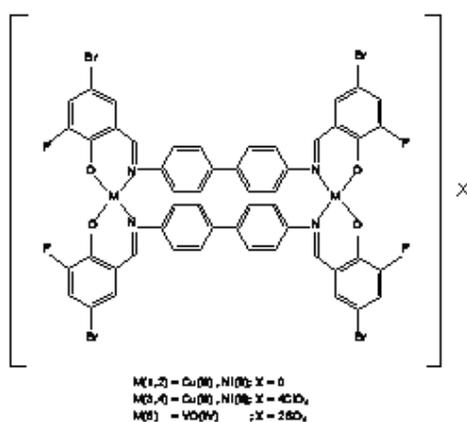**Figure-2: Proposed structure of Schiff base metal complexes.**

M(1,2) = Cu(II), Ni(II); X = 0
M(3,4) = Cu(II), Ni(II); X = 4ClO₄
M(5) = VO(IV)   ; X = 2SO₄

Figure 2. Proposed structure of Schiff base metal complexes
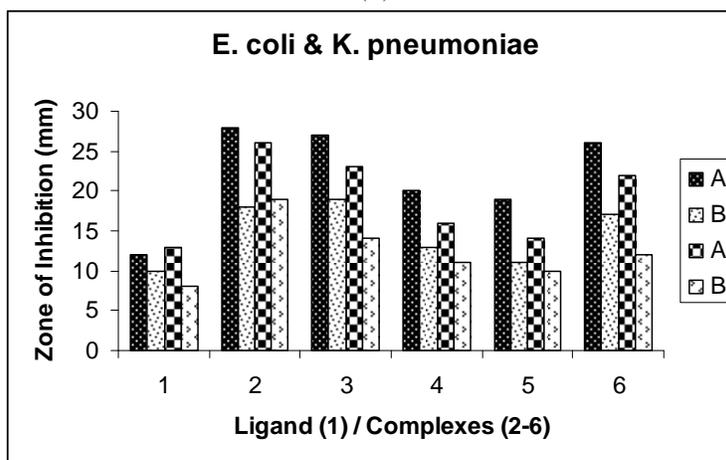
Antimicrobial Activity

To contribute in the field of bioinorganic chemistry, the Schiff base ligand, H_2L and its metal complexes were evaluated for antimicrobial activity against two strains Gram-positive bacteria (*S. aureus* and *B. subtilis*), Gram-negative bacteria (*E. coli* and *K. pneumoniae*) and fungi (*A. fumigatus*). The obtained antimicrobials are presented in Table 4. It shows that all metal complexes exhibit antimicrobial activity and enhanced on comparing with the parent Schiff base. Complexes **1, 2** and **5** showed high activity than complexes **3** and **4**. These complexes showed a high activity in Gram-positive, Gram-negative bacteria and intermediate activity for fungi in high and low concentrations. The activity of the Schiff base ligand and its metal complexes increases as the concentration increases because it is a well known fact that concentration plays a vital role in increasing the degree of inhibition. The structure of the tested compounds seems to be the principal factor influencing the

antimicrobial activity. The presence of anionic groups outside the coordination site exerts a number of changes on antimicrobial activity of the tested complexes. So, in case of **5**, the presence of SO_4^{2-} and VO^{2+} moiety induced a visible increase of their action against all bacterial and fungi species taken in the study. Complexes **3** and **4** show moderate activity against all bacterial and fungi species, probably due to the presence of more bulkier ClO_4^- anion [36]. Other factors such as solubility, conductivity and dipole moment, which affected by the presence of metal ions, may also be possible reasons for increasing the biological activity of the metal complexes as compared to the ligand. Keeping in view, these compounds may be used for formulating novel chemotherapeutic agents.
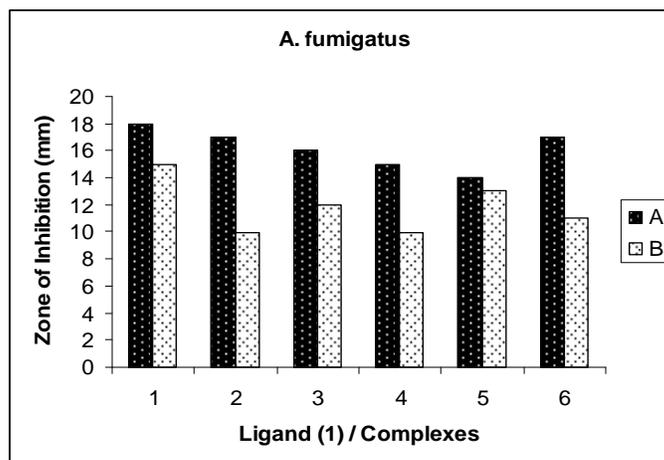
Figure-3: Antimicrobial activities of Schiff base ligand and its metal complexes.
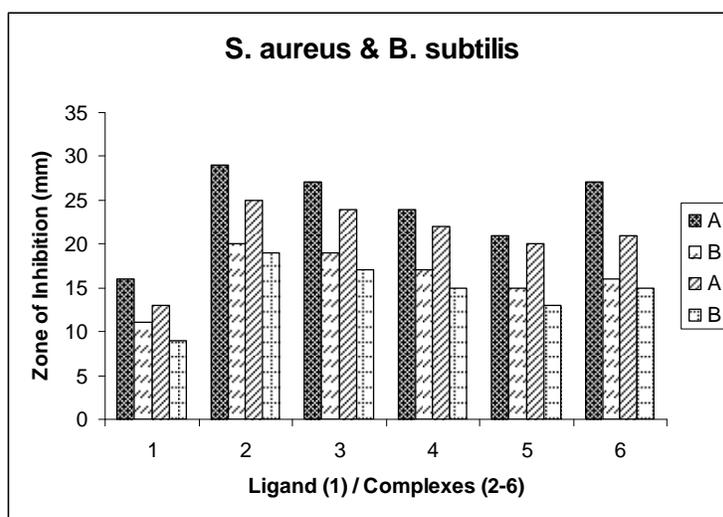
(A)

(B)

(C)

Table-4: Antimicrobial activity of the Schiff base, H_2 L, ligand and its Cu(II), Ni(II) and VO(IV) complexes against different bacteria and fungi.

Ligand / Complex	Zone of Inhibition (Mean)[a] (mm)									
	Gram-positive bacteria				Gram-negative bacteria				Fungi	
	S. aureus		*B. subtilis*		*E. coli*		*K. pneumoniae*		*A. fumigatus*	
	A	B	A	B	A	B	A	B	A	B
H_2L	16	11	13	9	12	10	13	8	18	15
1	29	20	25	19	28	18	26	19	17	10
2	27	19	24	17	27	19	23	14	16	12
3	24	17	22	15	20	13	16	11	15	10
4	21	15	20	13	19	11	14	10	14	13
5	27	16	21	15	26	17	22	12	17	16

[a] Calculated from three values. The concentration of A is 2 mgmL^{-1} and B is 1 mgmL^{-1}

Conclusion

In the present study, the Schiff base, H_2L, ligand is dibasic with two sets of N_2O_2- tetradentate sites. The Schiff base was allowed to react with Cu(II), Ni(II) and VO(IV) ions in 1:1 molar ratio (ligand:metal ion) to form the binuclear complexes. For this ligand, copper(II) and nickel(II) exhibit a square planar geometry while oxovanadium(IV) exhibits square pyramidal geometry. The bonding sites are the azomethine nitrogen atoms and the phenolic oxygen atoms. The thermal results allowed acquiring the information concerning the stoichiometry of Cu(II) and Ni(II) complexes. The antimicrobial activity of compounds shows that they are

most effective against selected bacterial strain and the results are comparable to the commercially available compounds.

Acknowledgement

Ms. S.Vedanayaki acknowledges University Grants Commission (UGC), New Delhi for the financial assistance through the Faculty Development Program (FDP).

References

1. J. Estreados santos, E.R. Dockal, E.T.G. Cavalheiro, J. Therm. Anal. Cal, 2003, Vol 79, pp243.

2. N. Chantarasiri, T. Tuntulani, P. Tongraung, R. Seangprasert-kit-Magee, W. Wannatong, Eur. Poly. J, 2000, Vol 36, pp695.

3. R. Pignatello, A. Panicol, P. Mazzone, M. Pinizzotto, A. Garozzo, P. Furneri, Eur. J. Med. Chem. 1994, Vol 29, pp781.

4. V.Mishra, S.N. Pandeya. S. Anathan, Acta. Pharm. Turc, 2000 Vol 42, pp139.

5. C. Wang, X. Wu, S. Tu, B. Jiang, Synth. React. Inorg. Met.-Org. Nano-Met. Chem, 2009, Vol 39, pp78.

6. S.K. Bharti, S.K. Patel, G. Nath, R. Tilak, S.K. Singh, Trans. Met. Chem, 2010 Vol 010, pp9412.

7. G.G. Mohamed, M.H. Soliman, Spectrochim. Acta Part A, 2010, Vol 76, pp341–347.

8. N.K. Singh, S.B. Singh, Ind. J. Chem, 2001, Vol 40, pp1070.

9. G. Wang, J.C. Chang, Synth. React. Inorg. Met.-Org. Chem, 1994, Vol 24(4), pp623–630.

10. B.J.A. Jeragh, A.E. Disssouky, J. Coord. Chem, 2005, Vol 58, pp1029-1038.

11. P. A. Vigato, S. Tamburini, Coord. Chem. Rev, 2004, Vol 248, pp1717-2128.

12. S.M.E. Khalil, K.A. Bashir, J. Coord. Chem, 2002, Vol 55, pp681-696.

13. A.A. Soliman, W. Linert, Thermochim. Acta, 1999, Vol 338, pp67–75.

14. A. Anthonysamy, S. Balasubramanian, Inorg. Chem. Commun, 2005 Vol 8, 908–911.

15. D.D. Perrin, W.L.F. Armarego, D.R. Perrin., Purification of Laboratory Chemicals, 2nd edn. Pergamon Press 1981.

16. A. Gordon, R. Ford, S. Khimika., A Hand Book of Practical Data, Techniques and References, John Wiley, Moscow 1976.

17. J. Fries, H. Getrost., Organic Reagents for Trace Analysis, Merck Darmstadt, 1977, pp394–405.

18. A.W. Bauer, W.W.M. Kirby, J.C. Sherris, M. Turck, Am. J. Clin. Pathol, 1966, Vol 45, pp493.

19. D.C. Gross, S.E. De Vay, Physiol. Plant. Pathol, 1977, Vol 11, 13.

20. H. William, V. Stephen., Theory and Application of Microbiological Assay, Academic Press, San diego1989, pp320.

21. W.J. Geary, Coord. Chem. Rev, 1971, Vol 7, pp81–122.

22. N.M.D. Brown, D.C. Nanhebel, Tetrahedron, 1968, Vol 24, pp5655.

23. A.H. Kianfar, L. Keramat, M. Dostani, M. Shamsipur, M. Roushani, F. Nikpour, Spectrochim. Acta Part A, 2010, Vol 77, pp424–429.

24. D.N. Kumar, B.S. Garg, Spectrochim. Acta A, 2006, Vol 59, pp141–147.

25. M. Dolaz, M. Tumer, M. Digrak, Trans. Met. Chem, 2004, Vol 29, pp528.

26. K. Nakamoto., Infrared and Raman Spectra of Inorganic and Coordination Compounds,s Wiley, New York 1997.

27. C. Lodeiroa, J.L. Capelob, E. Bertoloc, R.Z. Bastidad, An. Org. Allg. Chem, 2004, Vol 630, pp1110–1115.

28. S. Karabocek, N. Karabocek, A. Armuteu, Trans. Met. Chem, 2006, Vol 31, pp459–464.

29. A. Syamal, M.R. Maurya, Indian. J. Chem A, 1985, Vol 24A, pp836.

30. R.N. Prasad, M. Agarwal, S. Sharma, Indian. J. Chem A, 2004, Vol 43, pp337–340.

31. R.L. Carlin, A.J. Vandryneveldt., Magnetic Properties of Transition Metal Compounds, Springer-Verlag, New York 1997.

32. A.A.A. Emara AAA, Adly OMI, Trans Met Chem, 2007, Vol 32, pp889.

33. Tumer M, Erdogan B, Koksal H, Serin S and Nutku MY, Synth React Inorg Met Org Chem, 1998, Vol 28, pp529.

34. Hathaway BJ, Billing DE, Coord Chem Rev, 1970 Vol 5, pp43–207.

35. Lever APB, Lewis J, J Chem Soc, 1963, pp2552–2556.

36. Rosu T, Negoiu M, Pasculescu S, Pahontu E, Poirier D, Gulea A, Eur J Med Chem, 2010, Vol 45, pp774–781.

Corresponding Author:

R. Rajavel*

Department of Chemistry,

Periyar University, Salem – 636 011,

Tamil Nadu, India

E-mail: *varshuvishal@gmail.com*