

Conventional and Microwave Synthesis, Characterization and Study of Microbiological Activity of Complexes of Ni (II) with [2-((Z)- (4-hydroxy-3-methoxy-5-((E)-thiazol-5- yldiazenyl)benzenylidene)amino)benzoic acid] (MThBABA)

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Abstract: A Schiff base and its complexes with Ni (II) have been synthesized by conventional methods & microwave synthesis which were characterized by elemental analysis, molar conductance, magnetic susceptibility, electronic spectra, IR and ESR spectroscopy. The metal complex is coloured, solid and non - hygroscopic in nature.

The ligand behaves as {bi negatively} tetradentate ligand coordinated to metal ions via azomethine (N), N=N and phenolic, carboxylic anionic(O).

On the basis of magnetic susceptibility values and electronic spectral analysis, the geometry of the complex was proposed to be octahedral. The molar conductivity data of complex suggests their nonelectrolytic nature. The ligand and metal complexes have analysed for their microbiological activity.

Index Terms: Co-ordination, Metal Complexes, Microbiological activity, Octahedral, Schiff base (MThBABA)

I. INTRODUCTION

Schiff base and its metal complex are occupying an important place in the field of coordination chemistry (Shirodkar et al., 2001) Nitrogen and other atoms such as oxygen (Djebbar et al., 1997), (Bhattacharya et al., 1998; Liu et al., 1996; Wu et al., 2001) are present as donor atoms in metal complexes of Schiff's

bases. Chelating ligands containing N, S and O donor atoms show biological and catalytic activities (Amir et al., 2002; Hamada, 1997; Vaghasiy et al., 2004). Many metal complexes are synthesized and are studied. In the detection of metal cations at the micro level schiff base are used (Jungreis & Thabet, 1969).

Microwave-assisted synthesis is a branch of green chemistry. It continues to develop at a very fast rate in organic, organometallic and coordination chemistry. Microwave-irradiated reactions are done under solvent free or less solvent conditions. Reduced pollution, low cost and better yield, shorter reaction time and simplicity in processing and handling are the advantages of Microwave-assisted synthesis. There are a few reports on the synthesis of metal complexes by microwave methods (Mahajan et al., 2009; Mishra et al., 2012; Mohanan et al., 2008; Sharma et al., 2010)

In the present paper, metal complex of Ni (II), with Schiff base ligand 2-(((Z)-4-hydroxy-3-methoxy-5-((E)-thiazol-5-yldiazenyl)benzylidene)amino)benzoic acid have been synthesized by conventional as well microwave method and both process are compared.

Elemental analysis, molar conductivity measurements, magnetic susceptibility, electronic spectra, IR, and ESR spectrum were done to identify and characterize the complexes.

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The ligand and their metal complexes were screened for microbiological activities.

II. MATERIALS AND METHODS

A. Chemicals

All chemicals employed in the present study were of analytical grade and were used without further purification, and purchased from Loba Chemie.

B. Apparatus

All glasswares used for experimental purpose were calibrated and made up of borosil glass. A digital pH meter ELICO LI- 127 was used for pH measurement.

Spectrophotometer model ELICO SL- 171 using quartz cells of 1cm path length was used for absorbance measurement. Element analyzer CHNO model Flash EA 1112 series gave percentage compositions of the elements (CHNO) of the ligand and its Ni(II) complex. ICPAES in an Iris Intrepid II XSP model instrument analyzed the metal contents of the complexes.

Perkin Elmer Spectrophotometer 8400 FTIR recorded IR of schiffs base and complex KBr discs. UV-Visible Spectrophotometer. ELICO SL -159 recorded the electronic Spectrum of complexes. E - 112 ESR Spectrometer at I.I.T. Mumbai was used to record the Electron spin resonance spectra (ESR) ELICO SL - 303 model conductometer is used for the molar conductivity measurements Gouy's method was used to find magnetic susceptibility using mercury tetraisothiocyanatocobaltate as the callibrant.

C. Conventional method of synthesis of ligand

[2-((Z)-(4-hydroxy-3-methoxy-5-((E)-thiazol-5-yl diazenyl)benzylidene)amino)benzoic acid

1) Preparation of azo compound (Diazotization Process)

2-Aminothiazol solution (0.005 moles) maintained below 5 °C was diazotized by adding sodium nitrite solution (0.005 moles) slowly and maintaining the temperature below 5°C for 30min. This cold diazonium salt was poured into ice cold vanilline (0.005 moles in 10% NaNO₃) solution very slowly and stirred. The red colour developed immediately, it was stirred till red crystals separated out, the crystals were filtered & washed with a saturated solution of sodium chloride.

2) Preparation of schiffs base by conventional method

In a round bottom flask 0.005 moles of azo compound is taken with 0.005 moles of 2-aminobenzoic acid, 50ml of pure alcohol was added, with few porcelain pieces. It is attached to a water condenser and reflux for 3 hours. After that mixture is poured into a beaker and left for overnight in the fridge.

The mixture is filtered, dried and recrystallized (Vogel, 1989). The product obtained is Greenish-brown crystals of schiffs base, 2-(((Z)-4-hydroxy-3-methoxy-5-((E)-thiazol-5-yl diazenyl)benzylidene)amino)benzoic acid. The reaction is shown in Fig. 1 In the entire paper ligand is represented by the Letter L.

Reaction's

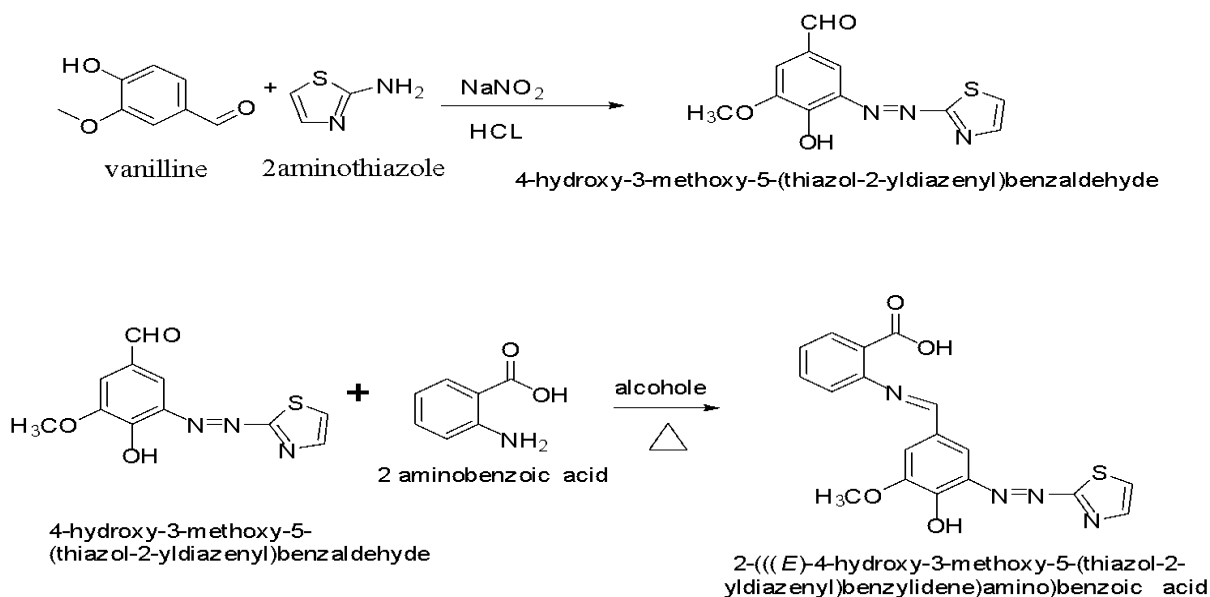


Fig. 1. Preparation of Schiff's Base

3) Preparation of schiffs base by microwave method

In a beaker 0.005 moles of azo compound is taken with 0.005 moles of 2-aminobenzoic acid, with few drops. It was then irradiated in the microwave oven at 1800 for 2 minutes. The reaction was completed in a short time (2 min) with higher yields.

4) Preparation of schiffs base ligand (MThBABA) by conventional method

The complex of Nickel was made by using hydrated NiCl_2 in ethanolic solution of ligand in molar ratio of 1:1 at pH 7.6 - 8.4. For 2 - 3 hrs the mixture was refluxed in a water bath. Dark brown colored solid was separated after cooling at room temperature. The resulting complex corresponding to the formula $[\text{Ni}_2 \text{L}_2 (\text{H}_2\text{O})_4]$ was washed with water and ethanol was then recrystallised (Vogel, 1989) and dried (yield 60 - 70%).

5) Preparation of schiffs base ligand (MThBABA) by microwave method

The ligand and the hydrated NiCl_2 were grinded in a 1:1 ratio then reaction mixture was taken in a 50 ml borosil beaker along with 3-4 ml of dry ethanol as a solvent then irradiated by the microwave oven at 700 Watts for 2 minutes. The reaction was completed in a short time (1-2 min) with higher yields. The resulting product was then recrystallized with ethanol and ether and finally dried under reduced pressure over anhydrous CaCl_2 in a desiccator. The progress of the reaction and purity of the product was monitored by TLC using silica gel G (yield: 91-92%).

D. Biological Studies

Cup plate method is used to determine antibacterial and antifungal activity of ligands and its Ni(II) complex. The stock solution of 2000 ppm of ligand and Ni (II) complex (dissolving 20 mg in 10 ml solvent carbon tetrachloride) was prepared on an active ingredient basis and was kept at room temperature till it was used. Sterile Sabouraud's agar plates for fungus *Candida albican* and Sterile Mueller Hinton agar plates for bacterial test cultures were seeded with 1ml of 24 hour old, 0.1 O.D. cultures. 0.2 ml of 48 hour old *Aspergillus* culture was used on surface spread on Sabouraud's agar plates. Wells were punched in the above media and compounds 50 μl were added.

Depending on their culture plates are incubated for 48 hours at 37°C / R.T. The area around the well was inhibited and measured in millimeters. Depending on the cultures the plates were incubated at 37°C / R.T. for 48 hours. The zone of inhibition around the wells was found in millimeters.

III. RESULT AND DISCUSSION

Metal complex $[\text{Ni}_2 \text{L}_2 (\text{H}_2\text{O})_4]$ is dark brown color, solid, non-hygroscopic and stable at room temp. The metal complexes exhibit 1:1 (metal-ligand) stoichiometry.

The Analytical and physical data of ligand and their metal complexes are recorded in Table - I.

A. Infra-red Spectral Analysis

Due to characteristics stretching frequency of functional group compound can be identified by IR which were recorded with a Perkin Elmer FTIR -8400S Spectrometer (4000-400 cm^{-1}) using KBr pellets.

The most important infrared spectra bands of the Ligand and investigated metal complexes in the present paper are summarized in Table- II. Figures of IR are shown in Fig. 2 and Fig. 3.

C=N stretching of azomethine group (Lever, 1973; Noorjahan et al., 2014) shows broad band at 1630 cm^{-1} in the IR spectrum due to ligand. Band was shifted to lower regions in IR of Ni (II) complexes at 1620 cm^{-1} suggesting the coordination of azomethine nitrogen to metal atom in complexes (Anitha et al., 2013; Priya D., & Kumar, H., 2010) is between azomethine nitrogen and metal atom. This was due to the donation of electron density from Nitrogen to metal.

A weak band around 3561 cm^{-1} due to intra molecular hydrogen bonded -OH group (Bellamy, 1954), (Anitha et al., 2013; Hasan et al., 2016; Silverstein & Webster, 1998) seen in the ligand is found to be absent in the case of binuclear Ni complexes indicating the dissociation of the phenolic proton on complexation and involvement of phenolic anionic oxygen in coordination. It is further supported by the fact that the strong band at 1275 cm^{-1} due to C - O (phenolic and carboxylic) in the ligand has been shifted to the 1316 cm^{-1} in the spectra of complexes (Anitha et al., 2013).

A band at 1620-1680 cm^{-1} is assigned to the C = O stretching frequency (Hasan et al., 2016; Omar, 2012), in the spectrum of free Schiff base, which is shifted by 20 to 60 cm^{-1} in the binuclear Ni complexes. The shifting of this band indicates the involvement of oxygen atoms from the hydroxyl group of COOH, which bonds with the metal ions (Hasan et al., 2016).

When we analysed only the spectrum of ligands, it did not show any peak at region 400-500 cm^{-1} in IR. But the complex shows a new peak at 400-500 cm^{-1} in the IR spectrum. The spectrum shows a band at 416 cm^{-1} due to stretching frequencies of $\nu(\text{M-O})$ (Anitha et al., 2013). Likewise we see another band at 458 cm^{-1} in IR spectrum. This is because of stretching frequencies of $\nu(\text{M-N})$ (Anitha et al., 2013) which proves that Oxygen and Nitrogen atoms are involved in coordination.

An additional band at 1160 cm^{-1} suggests that water molecules are coordinated to metal ion (Omar, 2012). Hence from IR spectra it is concluded that ligand behaves as {bi negatively} tetradentate ligand coordinated to metal ion via azomethine (N) N=N and phenolic, carboxylic anionic (O).

B. Molar Conductance

Molar conductance of binuclear nickel complex at room temperature (Λ_m) is 20 $\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ using DMF as a solvent (1×10^{-3} M) by using instrument as a ELICO Conductivity meter which have cell constant 1.0 cm^{-1} . Using the known molar

Table I. The Analytical and physical data of ligand and Metal complexes

Compounds (Colour) Molecular Weight	Reaction period Conventional Methods (Micro Methods)	M.P.	% Elemental Analysis Found (Calculated)					
			C	H	O	S	N	M
Ligand (greenish brown) 382.39	4 hours 79% (0.4 minutes 92%)	244	56.53 (56.54)	3.70 (3.69)	16.78 (16.79)	8.40 (8.39)	14.67 (14.65)	- -----
[Ni ₂ L ₂ (H ₂ O) ₄] (dark Brown) 882.16	3 hours 74 % (1.2 minutes 93%)	267	45.30 (45.31)	3.79 (3.78)	20.13 (20.12)	6.74 (6.72)	11.75 (11.74)	12.32 (12.30)

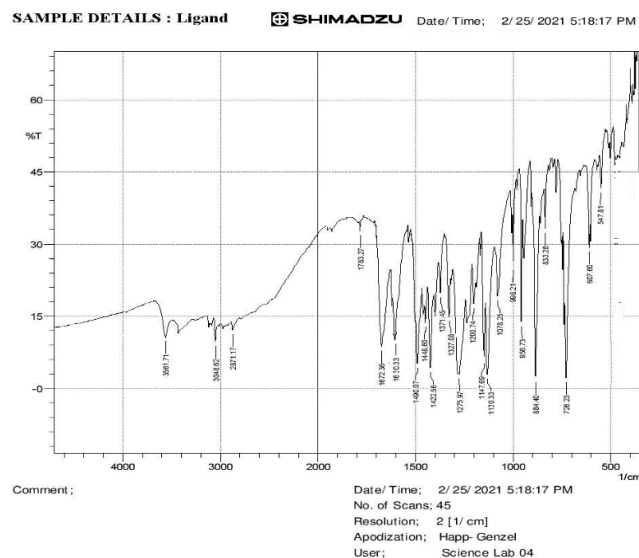


Fig. 2. IR Spectra of Ni Complex

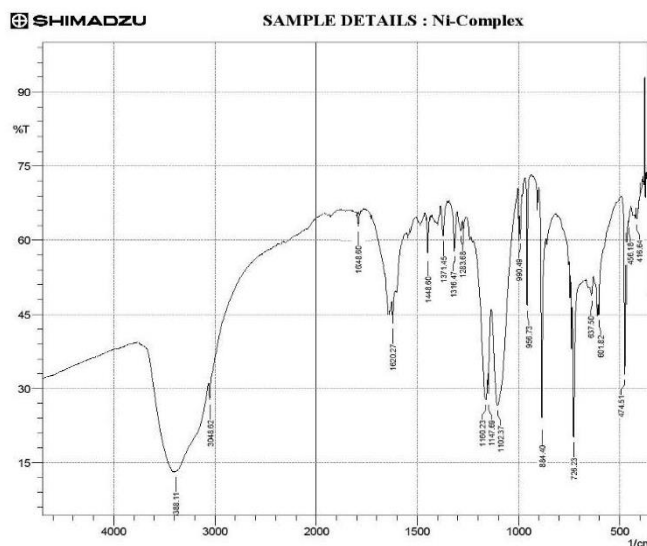


Fig. 3. IR Spectra of Ni Complex

conductivities (Omar, 2012; Sulekh & Umendra, 2005) these values were compared which shows the non - electrolytic nature (Priya, D. & Kumar, H., 2010) of the complexes.

C. Electronic spectra and magnetic susceptibility measurements of complexes

The electronic transition takes place in the UV-Visible electromagnetic region. ELICO SL - 159 UV-Visible

Spectrophotometer is used to record electronic spectra. The transition of metal ions occurs in a variety of structural environments. Hence the electronic structures are extremely varied and have been identified by UV-Visible spectroscopy. Data is shown in Table III and electronic spectra are shown in Fig. 4.

Table II. The Important IR bands of Ligand and Cu Complex

Compound	ν phenolic (-OH) cm^{-1}	$\nu(\text{C-O})$ stretching cm^{-1}	$\nu(\text{C=O})$ stretching cm^{-1}	$\nu(\text{C=N})$ cm^{-1}	$\nu(\text{M-N})$ cm^{-1}	$\nu(\text{M-O})$ cm^{-1}
Ligand	3561	1275	1672	1630	----	-----
$[\text{Ni}_2 \text{L}_2 (\text{H}_2\text{O})_4]$	---	1316	1648	1620	458	416

Table III. Electronic Spectra and Magnetic Moment of the Ni (II) Complex

Compound	Band, λ max (nm)	Band, λ max (cm^{-1})	Assignments	μ_{eff} (B.M.)
$[\text{Ni}_2 \text{L}_2 (\text{H}_2\text{O})_4]$	440	22727	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g} (\text{p})$	3.12
	640	15625	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g} (\text{f})$	
	680	14705.5	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g} (\text{f})$	

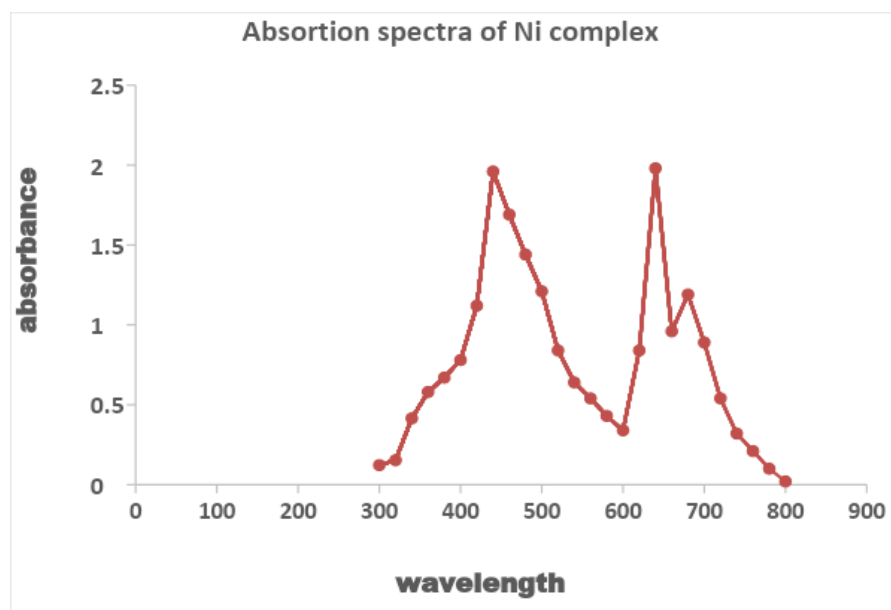


Fig. 4. Electronic Spectra of Ni Complex

The electronic absorption spectra of Ni (II) complex exhibit the three band around 22727.27 cm^{-1} (441 nm), 15847.86 cm^{-1} (640 nm), 15625.00 cm^{-1} (680 nm), at room temperature which could be attributed to d-d transition and may be assigned to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g} (\text{p})$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g} (\text{f})$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g} (\text{f})$ transition (Adhikary et al., 2015; Al-hamdani & Shayma, 2011; Qing Yu

et al., 2017; Bardakçı et al., 2015; Sulekh & Umendra, 2005) suggesting octahedral geometry. The magnetic moment value 3.12 B.M consistent with the octahedral Ni (II) complex (Priya D. & Kumar, H., 2010).

D. Electronic spin resonance (ESR) Spectra

Knowledge of unpaired electron and extent of delocalization is given by ESR spectrum. By using X - band at frequency 9.5 GHZ under the magnetic field strength 3400 gauss in DMF the ESR spectra of complexes have been taken at room temperature. The values of ESR parameters for Ni (II) complex shown in Table - IV.

criterion, in the present compounds g_{\parallel} indicate the existence of covalent character in metal - ligand bond (Maki & Mcgarvey, 1958).

The exchange coupling interaction has been explained by Hathaway expression $G = (g_{\parallel} - 2) / (g_{\perp} - 2)$. According to Hathaway expression if G value is more than four then exchange interaction not possible, But Ni (II) complex show

Table IV. E S R Parameters of the Complex

Metal complex	g_{\parallel}	g_{\perp}	g_{avg}	Δg	G
$[Ni_2 L_2 (H_2O)_4]$	2.306	2.076	2.1821	0.187	3.843

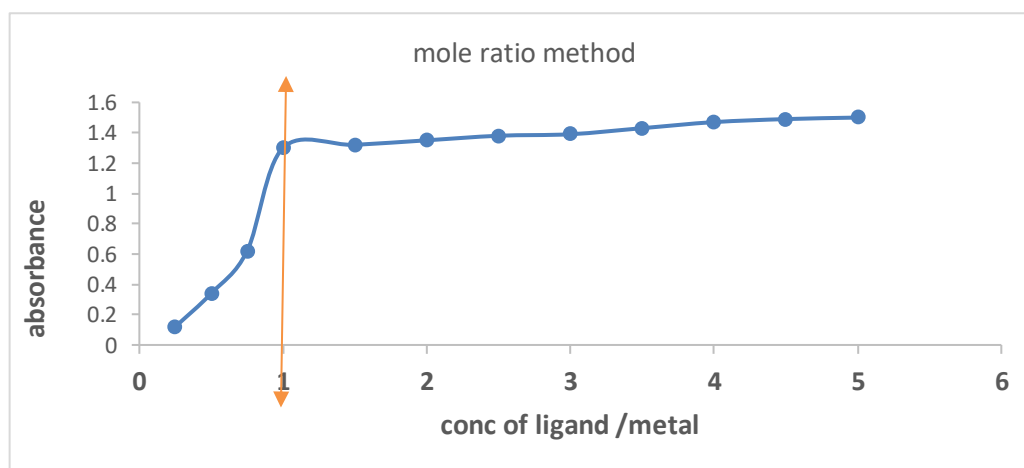


Fig. 5. Mole ratio method

Table V. Zone of inhibition of growth in millimeters after 48 hours of incubation

Compound	Antibacterial Activity				Antifungal Activity	
	S.a	C.d.	E.c	K.p	C.a	Asp.
Ligand	22	9	07	06	02	10
$[Ni_2 L_2 (H_2O)_4]$	30	11	10	12	03	13

ESR spectra of the complexes revealed two g values (g_{\parallel} and g_{\perp}). the trend ($g_{\parallel} > g_{\perp}$) shows that the unpaired electron is delocalized in $dx^2 - y^2$ orbital in the ground state of metal and spectra are characteristics of axial symmetry. The parameter g_{avg} was obtained by equation $[(g_{avg}) = 1/3 (g_{\parallel} + 2g_{\perp})]$. Kvelson & Neiman have reported that, $g_{\parallel} > 2.3$ is the characteristics of an ionic environment and $g_{\parallel} < 2.3$ indicates a covalent character in metal ligand bonding. Applying this

exchange interaction which suggest that complex have G value less than four indicating considerable exchange interaction the complexes (Abragam & Bleaney, 1970; Mishra et al.,2002).

E. Determination of composition of the extracted species

Composition of the complex was found to be 1:1 (Ni: L) Which was verified by using the Mole Ratio Method and Job's Continuous Variation Method (Makhijani et al.,2018) (Fig.5).

F. Proposed Structure of Complex

Analytical, magnetic, spectroscopic data and microbiology data suggests that the chelating nature of ligand forms stable complexes with Ni (II). Based on experimental evidence the probable structures of the complexes can be shown as Fig.6.

G. Biological Activity

Schiff base ligand and its binuclear Ni complex were analysed for antibacterial activity by cup plate method against "gram positive bacteria (staphylococcus aureus and corynebacterium diphtheria), gram negative bacteria Escherichia coli and Klebsiella pneumonia) and antifungal activity against Candila albicans and aspergillus species" (Omar Hamad Shihab Al-Obaidi, 2012)

From Table-V we can conclude that metal chelates of Ni (II) complex show higher antibacterial and antifungal activity as compared to free ligands.

This can be explained by using overtones concept and chelation theory.

There is an overlap of the ligand orbital and metal orbital also there is partial sharing of positive charges of metal ions with donor groups. This chelation reduces the polarity of the metal ion The delocalization of electrons over the whole chelate ring enhanced the lipophilicity of the complex. This magnified lipophilicity (Iniama et al., 2013; Pandeya et al., 1999) intensifies the penetration of the complexes into lipid membrane and blocking the metal sites on enzymes of microorganism

The respiration process of the cell is disturbed as metal complexes block the synthesis of proteins, which restricts further growth of the organism. The variation in the activity of different complexes against different organisms depends either on the

impermeability of the microbe's cells or difference in the microbe's ribosomes (Iniama et al., 2013),(Munde et al,2012).The microbiological activity was illustrated with a zone of inhibition which was measured in millimeters.

CONCLUSION

On the basis of above information we can conclude that ligand MThBABA [2-((Z)-(4-hydroxy-3-methoxy-5-((E)-thiazol-5-ylidiazenyl)benzenylidene)amino)benzoic acid] acts as bidentate, tetradentate ligand coordinated to metal ion via azomethine (N), N=N and phenolic, carboxylic anionic(O). Analytical data of complexes matches well with their molecular formula. Comparing IR value of free ligand and binuclear metal complex It was found that, nitrogen atom of azomethine and N=N, oxygen atom of phenolic and COOH of the tetradentate Schiff bases are involved in bond formation with Ni(II) ions which was confirmed by two new peaks in IR of binuclear complex (M-N and M-O). The ratio of metal to ligand is 1:1 which is proved by the job method and mole ratio method which further supports the binuclear complex. The electronic spectral and magnetic susceptibility measurements conclude that binuclear Ni (II) complex with MThBABA is octahedral in nature ESR spectra of complexes provide information about the extent of the delocalization of unpaired electrons. On the basis of these findings the structures have been proposed for the complex which is in good agreement with theoretical consideration (Fig. 6). The binuclear metal complex shows enhanced microbiological activities as compared to the ligand.

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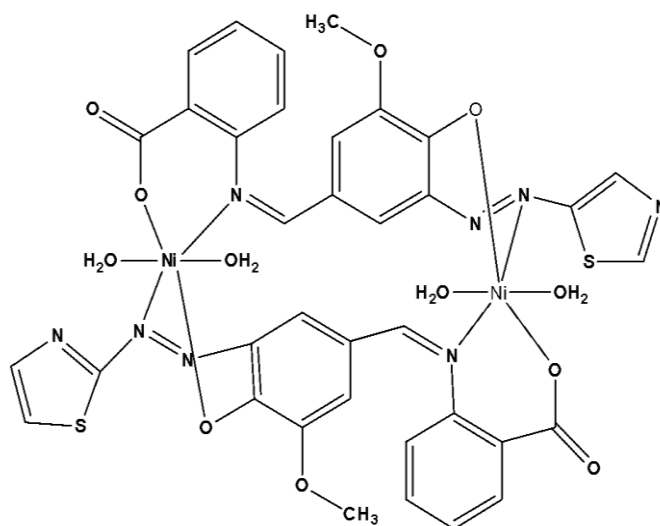


Fig. 6. Proposed Structure of Complexes

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REFERENCES

- Abraham, A., & Bleaney, B., (1970), EPR of Transition ions, Charedon, Oxford
- Adhikary, J., Chattopadhyay, S., Das, D., Dasgupta, S., Gabriel, A., Kundu, P., & Mukherjee S., (2015), Nickel (II) Complexes having different configurations controlled by N,N,O-donor Schiff-base ligands in presence of isothiocyanate as co-ligand: Synthesis, structures, comparative biological activity and DFT study. *Polyhedron*, 101, 93–102
- Al-hamdani, A.A., & Shayma, A.S., (2011) Synthesis, Characterization, Structural Studies and Biological Activity of a New Schiff Base- Azo Ligand and its Complexation with Selected Metal Ions, *Oriental Journal of Chemistry*, 27, (3): 835-845
- Amani, S., Alturiqi, Abdel-Nasser, M.A., Alaghaz ,Reda A. Ammar, & Mohamed E., Zayed, (2018), Synthesis, Spectral Characterization, and Thermal and Cytotoxicity Studies of Cr(III), Ru(III), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) Complexes of Schiff Base Derived from 5-Hydroxymethylfuran-2- Carbaldehyde Hindawi *Journal of Chemistry* Volume, Article ID 5816906, 17 pages
- Amir, M., Hasan, S.M., & Wadood, A., (2002), Synthesis and Antibacterial Activity of 1-Isonicotinyl-3- Methyl-4- (Substituted Phenyl Hydrazono)-2-Pyrazolin-5-one. *Oriental Journal of Chemistry*, 18 (2), 351-355.
- Anitha, C., Sheela, C.D., Tharmaraj, P, & Shanmugakala, R., (2013), Studies on synthesis and spectral characterization of some transition metal complexes oazo-azomethine derivative of diaminomaleonitrile, *International Journal of Inorganic Chemistry*, Volume Article ID 436275.
- Bardakçı, T., Altun, A., Golcuk, K., & Kumru M., (2015), Synthesis, structural, spectral (FT-IR, FT-Ra, and UVeVis) thermal and density functional studies on p-methylaniline complexes of Mn (II), Co(II), and Ni(II) bromides. *Journal of Molecular Structure*, 1100, 475-485.
- Basubramanyam, K.P, Karvembu, R., Chinnuswamy, V., K., & Natarajan; (2005), *Indian Journal of Chemistry*, 44A, 2450-2454.
- Bellamy, L.J., (1954). Infrared spectra of complexes molecules, Wiley, NewYork.
- Bhattacharya, P., Parr, J., Rossa, A.T., (1998). First synthesis of a unique dilead Schiff base complex, *Journal of Chemical Society, Dalton.*, 3149
- Djebbar, S.S. ,Benali, B.O., & Deloume, J.P., (1997). Synthesis, characterization and electrochemical behaviour of copper(II) complexes with linear and tripodal tetradentate ligands derived from Schiff, *Polyhedron*, 16, 2175.
- Hamada, Y.J. (1997), The development of chelate metal complexes as an organic electroluminescent material. *IEEE Trans. Electron Devices*. 44, 1208–1217
- Hasan, Md. R., Hossain, Md.A., Md. Salam A., & Uddin, Md.N. (2016). Nickel complexes of Schiff bases derived from mono/diketone with anthranilic acid: Synthesis, characterization and microbial evaluation, *Journal of Taibah University for Science* 10, 766–773 21.
- Iniama, Grace, E., Terungwa, I. , & Samson, O.O., (2013), Synthesis, Characterization and Antimicrobial Studies of Mn(II) Co(II) AND Zn(II) SCHIFF Base Complexes Derived from L-Arginine and 2- Hydroxy- Naphthaldehyde. *International Journal of Science and Research (IJSR)* ISSN (Online): 2319-7064
- Jungreis, E., & Thabet, S., (1969), Analytical Applications of Schiff bases. Marcell Dekker: New York; 5357675.
- Lever M.; (1973) *Anal. Chem. Acta*, 65, 311.
- Liu, C.M., Xiong, R.G., You, X.Z., Y.J. & Cheung, K.K. (1996). Crystal structure and some properties of a novel potent Cu₂Zn₂SOD model Schiff base copper(II) complex *Polyhedron*, 15, 4565-4571.
- Mahajan, K., Swami, M., & Singh, R.V. (2009). Microwave assisted synthesis, spectroscopic, thermal and antifungal studies of some lanthanide (III) complexes with a heterocyclic bishydrazone. *Russian Journal of Coordination Chemistry*, 35, 179-185.
- Makhijani, R, Barhate, V., & Navale, D., (2018). Development Of Extractive Spectrophotometric Determination Of Nickel (II) Using [N - (O-Methoxy Benzaldehyde)-2- Aminophenol](NOMBAP) As An Analytical Reagent. *International Journal of Scientific Research & Reviews*, 7(4), 2144-2151.
- Maki, A.H., & Mcgarvey, B.R., (1958). Electron Spin Resonance in Transition Metal Chelates. I. Copper (II) Bis-Acetylacetonate, *Journal of Chemical Physics*, 29, 31- 35.
- Mishra, A.P., Khare, M , & Gautam, S.K., (2002) Synthetic. Reaction. *Inorg. Metal Org. Chem.*, 32, 1485-1500
- Mishra, A.P., Mishra R., Jain R., & Gupta, S., (2012) , Synthesis of New VO(II), Ni(II) and Cu(II) Complexes with Isatin-3-Chloro-4-Floroaniline and 2-Pyridinecarboxylidene-4-Aminoantipyrine and their Antimicrobial Studies, *Mycobiology* , 40(1), 20–26.
- Mohanani, K., Kumari, B.S., & Rijulal, G., (2008). Microwave assisted synthesis, spectroscopic, thermal and antifungal studies of some lanthanide(III) complexes with a heterocyclic bishydrazone , *Journal of Rare Earths*, 29, 24-30
- Munde, A.S., Shelke, V.A., Jadhav, S.M., Kirdant, A.S., Vaidya, S.R., Shankarwar, S.G., & Chondhekar T.K. (2012).

- Synthesis, Characterization and Antimicrobial Activities of some Transition Metal Complexes of Biologically Active Asymmetrical Tetradentate Ligands. *Advances in Applied Science*, 3 (1),175-182.
- Noorjahan, Begum, T., Jaya, Raju, A., Mallikarjuna, Rao, R., Babu, R.K. & Sreeramulu, J., (2014). Synthesis, spectroscopic investigation and DNA binding studies of Pramipexole Schiff base metal complexes. *Journal of Pharmacy Research*, 8(3),366-373.
- Omar, Hamad Shihab Al-Obaidi. (2012). Binuclear CU(II) and Co(II) complexes of tridentate heterocyclic Schiff base derived from salicylaldehyde with 4-aminoantipyrine, *Bioinorganic Chemistry and Applications* Article ID 601879, 6 pages
- Pandeya, S.N., Sriram D., Nath G., & DeClercq E., (2012). Synthesis, antibacterial, antifungal and anti HIV activities of Schiff and mannich bases derived from isatin derivatives and N-[4-(4'chlorophenyl)thiazol-2-yl]thiosemicarbazide. *European Journal of Pharmaceutical Sciences*, 9:25–31.
- Priya, D., Kumar H., & Singh R.K., (2010). Complexes of nickel (II) with the Schiff bases derived from condensation of salicylaldehyde and bis-ni (amuh) 2cl2, *Rasayan Journal of Chemicals*, 3, 2, 266-270.
- Qing Y.H.F., Bian, He, Hui Yu., & Hong L.H., (2017). Ni(II) Complexes with Schiff Base Ligands: Preparation, Characterization, DNA/Protein Interaction and Cytotoxicity. *Molecules* 22(11), 1772.
- Sharma, K., Singh, R., Fahmi, N., & Singh R.V., (2010). Microwave assisted synthesis, characterization and biological evaluation of palladium and platinum complexes with azomethines. *Spectrochim Acta A*, 75, 422
- Shirodkar, S.G., Mane, P.S., & Chondhekar, T.K., (2010) Synthesis and fungitoxic studies of Mn(II), Co(II), Ni(II) and Cu(II) with some heterocyclic Schiff base ligands. *Indian Journal of Chemistry*, 40, 1114- 1117
- Silverstein, R.M & Webster, F.X.(1998). Spectrometric Identification of organic compounds, 6th ed. John Wiley & Sons, Newyork 87 [3.6.8.1]
- Sulekh, C. & Umendra, K., (2005). Spectral and magnetic studies on manganese(II), cobalt(II) and nickel(II) Complexes with Schiff bases, *Spectrochimica Acta Part A*, 61, 219–224
- Umendra, K., & Chandra, S., (2011). Synthesis, spectral and antifungal studies of some coordination compounds of cobalt(II) and copper(II) of a novel 18-membered octaaza [N8] tetradentate macrocyclic ligand. *Journal of Saudi Chemical Society* 15, 187–193 <https://doi.org/10.1016/j.jscs.2010.08.002>
- Vaghasiy, Y.K., Nair, R, Mayur, S., Baluja, S., & Shanda, S., (2004). Synthesis, structural determination and antibacterial activity of compounds derived from vanillin and 4-aminoantipyrine. *Journal of the Serbian Chemical Society* 69 (12), 991- 998
- Vogel, A.I., (1989) Practical Organic Chemistry, 5th Ed. Longman group limited London
- Wu, J. C., Tang, N., Liu, W.S., Tan, M.Y., Chan, A.S.C. (2001). Intramolecular hydrogen bond self-template synthesis of some new Robson-type macrocyclic ligands. *Chinese Chemical Letters*, 12, 757–760.
