

Conventional and microwave Synthesis, Characterization & Study of Microbiological activity of Complexes of Co(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 (ligand) and its complex with Co (II) have been synthesized by conventional methods and microwave synthesis which were characterized by elemental analysis, molar conductance, magnetic susceptibility, electronic spectra and IR spectra. The metal complex is coloured, solid and non-hygroscopic in nature. The Schiff base acts as {bi negatively} tetradentate ligand co-ordinated to Co(II) through azomethine (N), N=N & phenolic, carboxylic anionic(O). On the basis of magnetic susceptibility values and electronic spectral analysis, geometry of complex was suggested to be octahedral. The molar conductivity data of complex suggests their non-electrolytic nature. The ligand and metal complex are analyzed for their microbiological activity.

Index Terms: Schiff base, MThBABA, Metal Complexes, octahedral and Microbiological activity

I. INTRODUCTION

Schiff base and its metal complex are occupying an important place in the field of coordination chemistry (Schiff, 1864). Nitrogen and other atoms such as oxygen (Kudrat and

Islam, 2015) are present as donor atoms in metal complexes of Schiff bases. Chelating ligands with N, S and O donor atoms show biological and catalytic activities (Kumar et al., 2009). Many metal complexes are synthesized and are studied. In the detection of metal cations at the micro level Schiff base are used. (Messori et al., 2000; Fanizzi et al., 1987)

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 (Yamada S., 1999; Mahajan et al., 2009; Sharma et al., 2010; Mohanan et al., 2008; Sun et al. 2010; Mishra et al., 2012)

In this paper, complex of Co (II), with Schiff base ligand 2-(((Z)-4-hydroxy-3-methoxy-5-((E)-thiazol-5-

ylidiazenyl) benzylidene) amino) benzoic acid have been synthesized by conventional as well micro wave 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. The ligand & their metal complexes were screened for microbiological activities.

II. MATERIAL AND METHOD

Chemicals:- All chemicals employed in the present study were of analytical grade and were used without further purification and purchased from loba chemie.

Apparatus:- All glasswares used for experimental purpose were calibrated and made up of borosil glass.

Following instruments were employed :- Digital pH meter ELICO LI- 127. Spectrophotometer model ELICO SL- 171 Element analyzer CHNO model flash EA 1112 PERKIN ELMER spectrophotometer 8400 FTIR UV-VIS spectrophotometer. Elico sl -159. Elico sl - 303 model conductometer. Gouy's method was used to find magnetic susceptibility (mercury tetraisothiocyanatocobaltate as the calibrant)

A. Conventional method of synthesis of ligand [2-((Z)-(4-hydroxy-3-methoxy-5-((E)-thiazol-5-ylidiazenyl) benzenylidene) amino)benzoic acid.

The cold diazotized 2-Aminothiazol solution (0.005 moles) was poured into this ice cold vanillin (0.005 moles in 10% NaNO₃) solution, very slowly with stirring. The red colour developed immediately, it was stirred till red crystals separates out. filtered it in a buchner. The product was washed with saturated solution of sodium chloride.

In a round bottom flask 0.005 moles of azo compound was taken with 0.005 moles of 2-aminobenzoic acid, 50ml of pure alcohol was added, with few porcelain pieces. It was attached to water condenser and refluxed for 3 hours. The mixture was poured into a beaker and left overnight in the fridge. Then mixture was filtered and dried. The product obtained was Greenish-brown crystals of schiffs base, 2-(((Z)-4-hydroxy-3-methoxy-5-((E)-thiazol-5-ylidiazenyl)benzylidene)amino)benzoic acid. The reaction is shown in Fig. 1. (Preparation of ligand)

In the entire paper ligand is represented by L

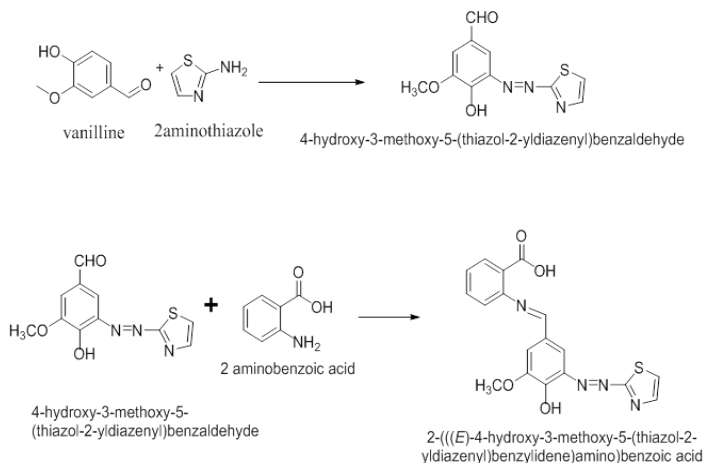


Fig. 1. (Preparation of ligand)

B. Preparation of cobalt complexes with Schiff base ligand (MThBABA) by conventional method.

The complex of cobalt was made by using hydrated CoCl₂ inn solution of ligand (Dissolved in ethanol) having molar ratio of 1:1 at pH 8.2 - 9.2. For 2-3 hours the mixture was refluxed on water bath. Dark brown colored solid was separated after cooling at room temperature. The resulting complex corresponding to the formula

[Co₂ L₂ (H₂O)₄] was washed with water and ethanol was then recrystallised (Vogel,1989) and dried (yield 60 - 70%).

C. Green method of preparation of schiff base & complex.

In a beaker ingredients (0.005 moles of azo compound & 0.005 moles of 2-aminobenzoic) were mixed and few drops of pure alcohol was added. 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.

The ligand and the hydrated CoCl₂ were grinded in a 1:1 (metal: ligand) ratio and taken in 50 ml borosil beaker along with 3-4 ml of dry ethanol as a solvent then irradiated by the microwave

Compounds (Colour)	% Elemental Analysis Found (Calculated)					
	C	H	O	S	N	M
Ligand (greenish brown)	56.53 (56.54)	3.70 (3.69)	16.78 (16.79)	8.40 (8.39)	14.67 (14.65)	- -----
[Co ₂ L ₂ (H ₂ O) ₄ (dark Brown)	45.31 (45.29)	3.79 (3.80)	20.12 (20.11)	6.73 (6.71)	11.74 (11.73)	12.33 (12.34)

oven at 700 Watts for 2 minutes. The reaction was completed in a short time (1-2 min) with higher yields. The

progress of the reaction and purity of the product was monitored by TLC using silica gel G (yield: 91–92%).

D. Biological Studies.

Antibacterial & antifungal activity of ligand & its Co(II) complex were assessed by Cup plate method. The 2000 ppm of ligand and Co(II) complex (dissolving 20 mg in 10 ml solvent carbon tetrachloride) was prepared on active ingredient basis was kept at room temperature till it was used.

Sterile (Sabourauds agar plates for fungus *Candida albicans* and Mueller Hinton agar plates for bacterial test cultures) plates were seeded with 1 ml of 24 hour old, 0.1 O.D.

cultures. 0.2 ml of 48 hour old *Aspergillus* culture was used on surface spread on Sabourauds agar plates. Wells were punched in the above media and compounds 50 μ l 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.

III. RESULTS AND DISCUSSION

A. Analytical and physical data

Metal complex $[\text{Co}_2 \text{L}_2 (\text{H}_2\text{O})_4]$ is dark brown color, solid, non hygroscopic and stable at room temperature. The metal complex exhibits 1:1 (metal-ligand) stoichiometry. The Analytical and physical data of ligand and their metal complexes are recorded in Table - I and Table- II.

Table - I: Analytical and physical data of ligand

Compounds (Colour)	Molecular weight	Reaction period Conventional methods	Reaction period Micro synthesis	M.P.
Ligand (greenish brown) Molecular	382.39	4 hours 79%	0.5 Minutes 92%	244
$[\text{Co}_2 \text{L}_2 (\text{H}_2\text{O})_4]$ (dark brown)	954.64	3 hours 76 %	1.4 Minutes 94%	272

Table - II: Percentage composition of elements in

ligand and cobalt complex

B. Infrared Spectral Analysis:

Compounds can be identified by the characteristic stretching frequency of functional group shown by IR Spectra, which were recorded by PerkinElmer FTIR -8400S Spectrometer (4000- 400 cm^{-1}) using KBr pellets.

The most important infrared spectra bands of the Ligand and investigated metal complex in the present paper are summarized in Table III and figures of IR Spectra are shown in Figure 2 and Figure 3.

C=N stretching of azomethine group shows broad band approximately at 1629 cm^{-1} in the IR spectrum of ligand. Band was shifted to lower regions in IR of Co (II) complex at 1604 cm^{-1} indicating coordination (Makhijani and Barhate, 2016; Anitha et al. 2013; Singh K. et al., 2013) between azomethine nitrogen & metal atom. The reason for shifting of band is 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; Silverstein and Webster, 1998; Singh et al., 2013; Anitha et al., 2013; Hasan et al., 2016; Hoda et al., 2013) seen in the ligand is found to be absent in the case of binuclear Co complexes proving the dissociation of the phenolic proton on complexation & involvement of phenolic anionic oxygen in coordination. It is further supported by the fact that the strong band at 1272 cm^{-1} due to C – O (phenolic and carboxylic) in the ligand has found to move to the 1327 cm^{-1} in the spectra of complexes (Anitha et al., 2013; Hoda et al., 2013)

A band at 1620–1680 cm^{-1} is assigned to the C = O stretching frequency (Singh et al., 2013; Hasan et al., 2016; Omar, 2012) in the spectrum of free Schiff base is approximately at 1672 cm^{-1} , which is shifted by 20 to 60 cm^{-1} in the binuclear Co complexes. The shifting of this band at 1628 indicates the involvement of oxygen atoms from the hydroxyl group of COOH, which bonds with the metal ions (Hasan et al., 2016)

When we analyze only spectrum of ligand. It does not show any peak at region 400-500 cm^{-1} in IR. But complex shows new peak at 400-500 cm^{-1} in IR spectrum. The spectrum shows band at 474 cm^{-1} due to stretching frequencies of $\nu(\text{M-O})$ (Anitha et al., 2013; Hasan et al., 2016; Omar, 2012). Likewise we see another band at 448 cm^{-1} in IR spectrum. This is because of stretching frequencies of $\nu(\text{M-N})$ (Anitha et al., 2013; Hasan et al., 2016; Omar, 2012) which proves that Oxygen and Nitrogen atom are involved in coordination.

An additional band at 1147 cm^{-1} suggests that water molecules are coordinated to metal ion (Omar,2012). Hence, from IR spectra it is inferred that ligand acts as {bi negatively} tetradentate ligand coordinated to metal ion through azomethine (N) , N=N and phenolic, carboxylic anionic(O)

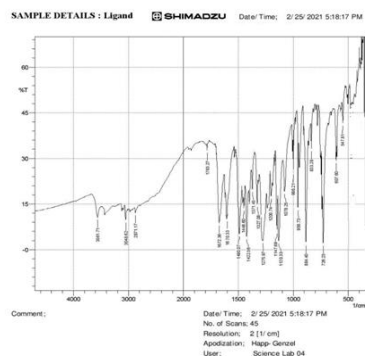


Fig. 2: IR Spectra of Schiff's base MThBABA

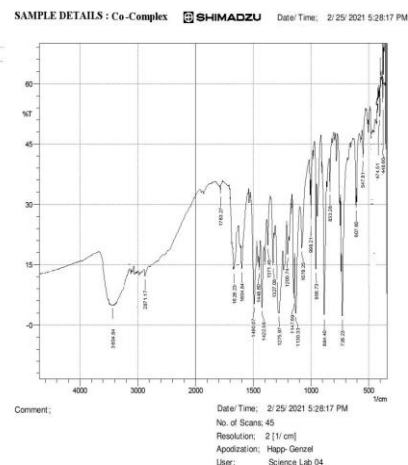


FIG. 3: IR SPECTRA OF CO COMPLEX

Table-III: The Important IR bands of Ligand and Co 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	1272	1672	1629	----	-----
$[\text{Co}_2\text{L}_2(\text{H}_2\text{O})_4]$		1327	1628	1604	474	448

C. Molar conductance

Molar conductance of binuclear cobalt complex at room temperature (Λ_m) is $10\text{ Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ using DMF as a solvent ($1 \times 10^{-3}\text{ M}$) by using instrument as a ELICO Conductivity meter which have cell constant 1.0 cm^{-1} . Using the known molar conductivities (Omar,2012; Hoda et al.,2013; Amani et al.,2018)these values were compared which shows the non-electrolytic nature of the complexes.

D. Electronic Spectra and Magnetic Susceptibility Measurements of Complexes:

The electronic transition takes place in UV-Visible region. ELICO SL - 159 UV-Visible Spectrophotometer is used to record electronic spectra. The transition metal ions has different types of structural environments. Hence the electronic structures are different and have been identified by UV-Visible spectroscopy. Data is shown in Figure 4 and electronic spectra is shown in Table IV

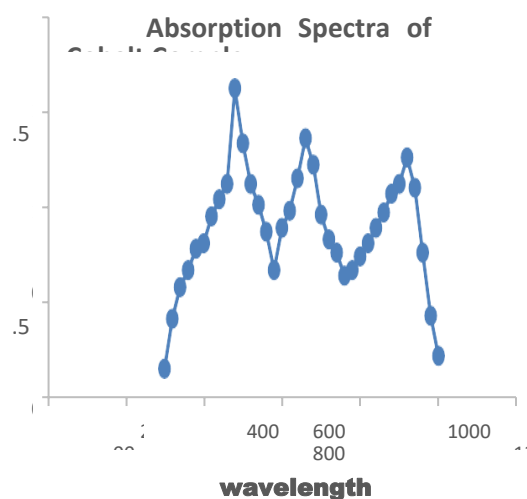


Fig. 4: Absorption Spectra of Co Complex

Table-IV: Electronic Spectra & Magnetic Moment of the Co (II)Complex

The electronic absorption spectra of Co (II) complex exhibit the three band around 10869.25cm^{-1} (920 nm),

	Band, λ max (nm)	Band, λ max (cm^{-1})	Assignments	μ_{eff} (B.M.)
v1	920	10869.25	$4\text{T}_{1g}(\text{f}) \rightarrow 4\text{T}_{2g}(\text{f})$	4.92
v2	660	15151.51	$4\text{T}_{1g}(\text{f}) \rightarrow 4\text{A}_{2g}$	
v3	480	20833.33	$4\text{T}_{1g}(\text{f}) \rightarrow 4\text{T}_{1g}(\text{p})$	

15151.5cm⁻¹ (660 nm), 20833.3cm⁻¹ (480 nm) at room temperature which could be attributed to d-d transition & may be assigned to ⁴T_{1g}(f) → ⁴T_{2g}(f), ⁴T_{1g}(f) → ⁴A_{2g} & ⁴T_{1g}(f) → ⁴T_{2g}(p) Transition (Omar,2012; Hoda et al.,2013; Amani et al.,2018; Umendra and Sulekh, 2011) suggesting octahedral geometry .

Co (II) has d7 has three unpaired electron Its observed magnetic moment value 4.95 B.M consistent with the octahedral Co (II) complex (Omar,2012; Hoda et al.,2013; Umendra and Sulekh, 2011). The observed magnetic moment are higher than the spin only value due to orbital angular momentum contribution in d7 system.(Umendra and Sulekh, 2011)

E. The ligand field parameters

The present binuclear complex the ratio $\nu_3 / \nu_1 = 2$ which lies in range 2-2.8 which is reported by most of octahedral cobalt complexes (Singh et al.,2013; Umendra and Sulekh, 2011). The various parameters such as *B* (interelectronic repulsion of the d-electrons in complex), β (The nephelauxetic effect), and *10Dq* are calculated according to the equation reported for octahedral Co(II) complex. $\nu_2 - \nu_1 = 10Dq$ and $\beta = B(\text{complex}) / B(\text{free ion})$ (Amani et al.,2018; Umendra and Sulekh, 2011) The β value less than one indicates that the appreciable covalent character of metal ligand *B* (complex) has decreased as compared to free ion due to delocalization of d electrons on the ligand which is in tune with covalent bonding (Amani et al.,2018), as can be seen in Table V.

Table V: Ligand Parameters of The Complex

Metal Complex	Dq cm ⁻¹	B cm ⁻¹	β	ν_3/ν_1
[Co ₂ L ₂ (H ₂ O) ₄]	428.2	225.13	0.244	2.0

F. Determination of Composition of the Extracted Species

Composition of complex was found to be 1:1 (Co : L) which was verified by using Mole Ratio Method and Job's Continuous Variation Method. (Fig 5)

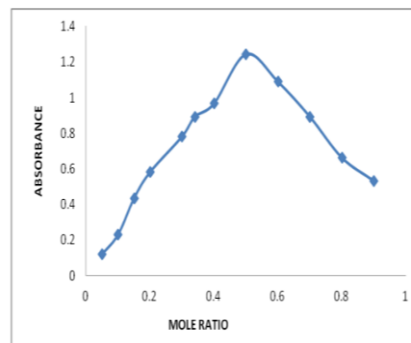


Fig.5: Mole ratio method

G. Proposed Structure of Complexes

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

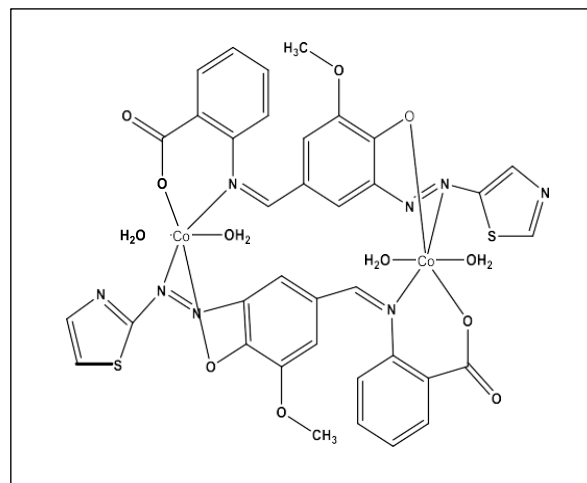


Fig.6: Proposed structure of Complexes

H, Biological activity.

Schiff base ligand and its binuclear Co complex were analyzed for antibacterial activity by cup plate method (Mattu et al.,2008) against “gram positive bacteria staphylococcus aureus, corynebacterium diphtheria” also “gram negative bacteria Escherichia coli , Klebsiella pneumonia” (Mattu et al.,2008) and antifungal activity against “Candida albicans and aspergillus species”(Mattu et al. ,2008)

From Table-VI we can conclude that metal chelates of

Co(II) complex show higher antibacterial and antifungal activity as compared to free ligands. This can be justified by using overtones concept and chelation theory. There is an overlap of the ligand orbital & metal orbital also there is partial sharing of positive charges of metal ion with donor groups. This chelation reduces the polarity of the metal ion. The electrons delocalize over the entire chelate ring thus enhance the lipophilicity of the complex. Due to magnified lipophilicity

(Mattu et.al, 2008) complex penetrates into lipid membrane & blocks the metal sites on enzymes of micro- organisms. As metal complex blocks the synthesis of proteins, which restricts further growth of the organism (Basubramanyamet al.,2005). The microbiological activity was illustrated with zone of inhibition which was measured in millimeters as shown in Table VI.

Table VI : Biological activity

	Cultures					
	S.a	Cd	E.c	K.p	C.a	Asp.
Ligand	22	08	06	06	02	09
[Co ₂ L ₂ (H ₂ O) ₄]	31	12	10	10	04	13

IV. CONCLUSION

On the basis of above information we can conclude that Schiff base ligand MThBABA [2-((Z)-(4-hydroxy-3-methoxy-5-((E)-thiazol-5-ldiazanyl)benzenylidene)amino)benzoic acid] shows as bi negatively, 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 Co(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 job method and mole ratio method which further supports binuclear complex. The electronic spectral and magnetic susceptibility measurements conclude that binuclear Co(II) complex with MThBABA is octahedral nature Ligand parameters of complex gives details about the extent of the delocalization of unpaired electron. The proposed structure for the complexes has been suggested based on these results & which also satisfies the theoretical consideration (Fig.6). The binuclear metal complex shows enhanced microbiological activities as compared to the ligand.

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