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Novel Salen Based Azo Conjugated Ligand For Chemosensing And Its Antibacterial Studies

L. Alphonse [a], P.Tharmaraj[a*] C.D. Sheela[b] and M. Priyadharsani[c]

[a] Department of Chemisty, Thiagarajar college, Madurai, Tamil Nadu, India.
[a*]Department of Chemistry, Thiagarajar College, Madurai, Tamil Nadu, India.
[b] Department of Chemistry, The American College, Madurai, Tamil Nadu, India.
[c] Department of Chemistry, Fatima College, Madurai, Tamil Nadu, India.

ABSTRACT

The new novel azo benzene derivative is expected to exhibit variety of characteristics such as biological and sensing properties.The main aim of the present work is to synthesis ligand (PABMTB) derived from [2-hydroxy-5-(p-tolyldiazenyl) benzaldehyde] and o-phenlenediamine. An intense focus is given to the formation of copper complex due to their wide range of application as functional material in biomedical field. The synthesized ligand was characterized by various physical and chemical methods of analysis such as UV-Vis, FTIR, CV and ^{1}H-NMR Spectral studies.Biological activity of the ligand and complex were analyzed with four different bacteria and the metal complex is found to have good antibacterial activity compared to ligand.

KEYWORDS: Salicylaldehyde, Diazotisation, Azo derivative and Biological activity

***Corresponding Author**

P. Tharmaraj

Department of Chemistry

Thiagarajar College

Theppakulam-625 009, (Madurai), India.

E-mail: ab24ml@gmail.com , rajtc1962@gmail.com

Mobile No: 9442555836

INTRODUCTION

Infectious diseases caused by the microorganisms are the majorthreat to the global health care. Recent statistics suggest that 47% ofhospital deaths are caused by infectious pathogens. Bacterial infections are commonly treated with antibiotics which are known to target the growth process of the bacteria and damage the cellular structure of microorganisms. In recent years, metals and metal oxide nanoparticles such as Au, Ag, Cu, Pt, Pd, ZnO, TiO_2, Bi_2O_3, CuO, and Fe_2O_3 etc., are reported to have excellent antibacterial properties.[1] Schiff base metal complexes display wide range of biological applications such as anticancer, antibacterial, antivirus and antifungal agents.[2-3] They have been evaluated against several pathogenic fungi and bacteria with promising results.Transition metals have numerous and unique biological, chemical and physical properties due to the availability of 'd' electrons in valance shells. Much attention has been focused on copper complexesdue to its various biological activities out of which antibacterialis paramount.[4]

The Coordination chemistry of transition metal complexes with azo ligands is an important and fascinating branch of chemistry. Coordination compounds that include azo ligands play a pivotal role in industry, technology and life processes.[5-8] Copper forms planar 1:1 complexes and polyazo copper complexes are used as direct dyes.[9] Recently, metal complex dyes have been introduced into many high-technological frontier applications as key functional materials.[10-12] Here, we present the synthesis, spectral characterizationand fluorescence study of ligand derived from diazotised *p*-toluidine coupled with salicylaldehydeand o-Phenylenediamine, and the formed ligand is introduced to form complex with metal ion.

The biological activity of the ligand and its metal complex has been investigated.The antibacterial property of copper complex on agar plates was investigated in the present study. The antibacterial activity of complex was evaluated against four bacteria strains (*K. Pneumoniae, Stapyh. epidermis, Stapyh. Pyogenes and Proteaus*). These results show that copper complex has an antibacterial activity and suggest its potential application as antibacterial agent.The aim of the present study therefore is to evaluate the antibacterial properties of Copper (II) complex comparing with free ligandPABMTB.[13] Thesolid Cu(II) complex and the ligand (PABMTB)are characterized by IR, ^{1}H NMR, CV, UV and fluorescence studies.[14]

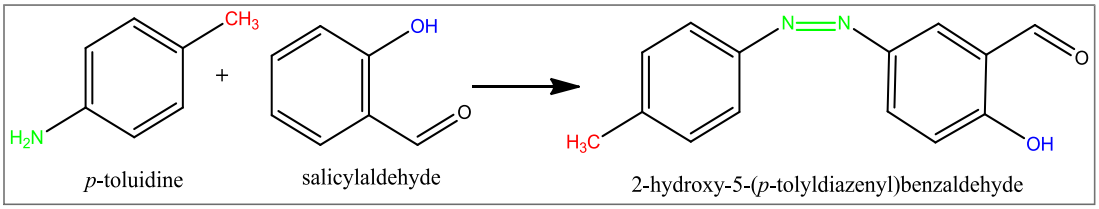
EXPERIMENTAL

Materials:

AR grade P-Phenylenediamine, P-Dimethyl aminobenzaldehyde, $NaNO_2$, NaOH, Dimethylsulfoxide, Salicylaldehyde and organic solvents were used.

Synthesis of 2 -hydroxy-5-(p-tolyldiazenyl) benzaldehyde (HTDBA):

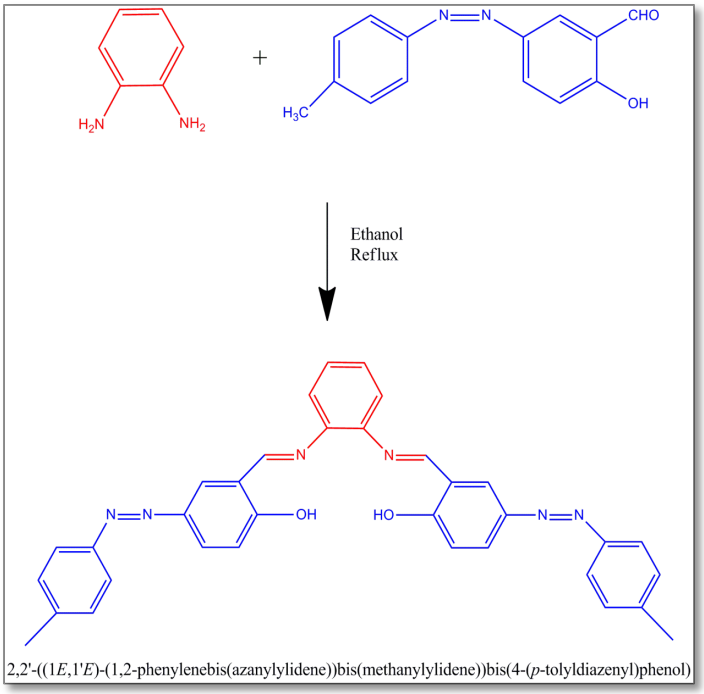
The *p*-toluidine (6.40g) was mixed with HCl (6ml) in distilled water (30ml) and $NaNO_2$ (2.8g) in water below 5°C. The diazotised *p*-toluidine was coupled with salicylaldehyde in the alkaline media. The pH during the coupling was kept fixed between7-9. The progress of the reaction was monitored by TLC.A dark brown color precipitate starts separating out, it was filtered and dried. This is given in **Scheme 1.**



Scheme 1: Synthesis of HTDBA

Synthesis of Ligand (PABMTB):

To **HTDBA** about (1 g) of o-Phenylenediamine dissolved in ethanol was added and refluxed for 8 hrs. Gradually a black precipitate starts separating out. The ligand ABMTB was filtered and dried. This reaction details is given in **Scheme 2.**

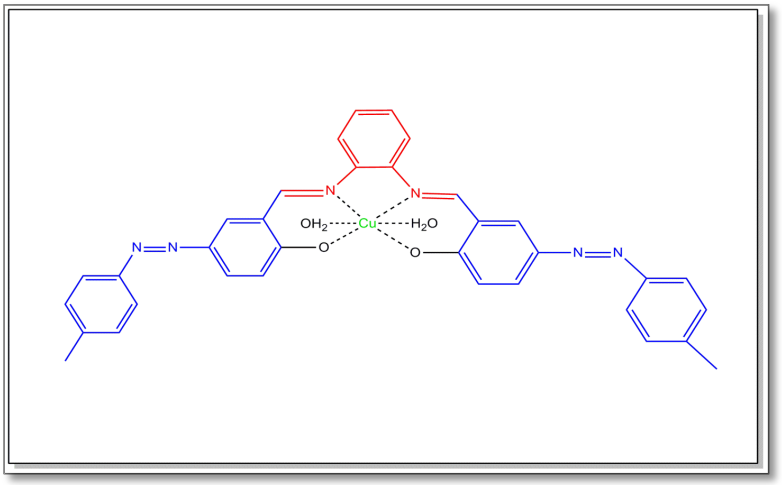


Scheme 2: Synthesis of ligand PABMTB

Synthesis of Cu(II) complex:

The metal complex was synthesized by addition of solution of copper (II) chloride (1mmol) to the solution of ligand (2mmol). The resulting mixture was stirred for 2 h and the complex were precipitated by filtration and washed with ethanol. Yield 67-75%. This is given in

Scheme.3.



Scheme.3. Copper (II) Complex of the ligand (PABMTB)

RESULTS AND DISCUSSION

The metal(II) complex of copper(II) of [$ML_2.H_2O$] type were obtained in good yield through the reaction of (PABMTB) with the corresponding metal salt. The ligand and metal(II) complexes were characterized through IR, elemental analyses, electronic absorption, NMR spectral data and arrived their structure. The analytical data and physical properties of the ligand and metal (II) complex are listed in the table 1. Elemental analysis, Spectral and conductance data suggest that the molecular formula[$ML.H_2O$] for copper(II) complex. The magnetic moment of the complex is consistent with octahedral geometry around central metal ion

Table.1. Physical characterization, analytical, molar conductance data of the ligand (PABMTB) and its metal (II) complex

Compounds	F.W. (g/mol)	Color	Calculated (Found) (%)					Δ_M (Ohm^{-1} cm^2 Mol^{-1})
			C	H	N	O	Cu	
(PABMTB) ($C_{34}H_{28}N_6O_2$)	552.63	Dark brown	73.90	5.11	15.21	5.29	-	-
[(Cu)PABMTB)$H_2O)_2$] ($C_{39}H_{38}CON_6O_3$)	701.23	Greenish black	66.70	5.45	11.97	6.83	9.05	1.81

Spectral Characterization

In the UV–Visible spectrum of the ligand, weaker and broader absorption bands in the range of 300–400 nm were observed. These transitions bands could be attributed to the n-π* transitions due to the presence of n electrons on the –CH=N– or –N=N– chromophore groups. The sharp band located at 341 nm is due to the presence of π→π* transition of the of the trans form of azobenzene shown in Fig.1.

Solvent effect

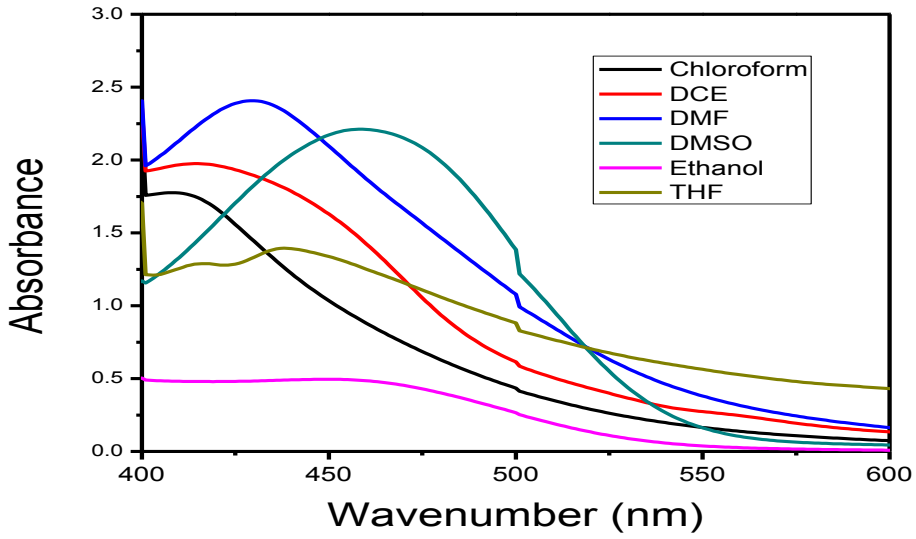


Fig.1. Electronic Spectra of [PABMTB] with solvents

The Uv-Vis absorption spectra were recorded using different solvents namely DMF, DMSO,Chloroform,Ethanol andTHF.The concentration range is kept constant at 10^{-5} M.The bands at

431 and 457nm shows bathochromic shift(Positive solvatochromism) upon decreasing solvent polarity.It is due to the dipole moment change and increase in conjugation.

Effect of Cations

The Ligand (PABMTB) was studied with various metals likeMg^{2+},Co^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+}.Among the cations copper has a significant effect with the ligand.The presence of absorption band at 828 nm shows a bathochromic shift is due to the formation of[Cu(PABMTB) (H_2O)].Other metals like cobalt,Nickel,Magnesium,Manganese has no effects with the azo ligand. A distinct colour change from dark brown to black occurs due to the complexation of the ligand with cu^{2+}shown in Fig. 2 and 3.

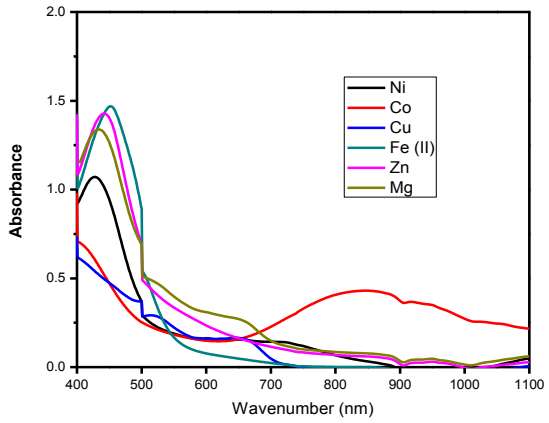


Fig.2. Electronic spectra of [PABMTB] with Different metals salt

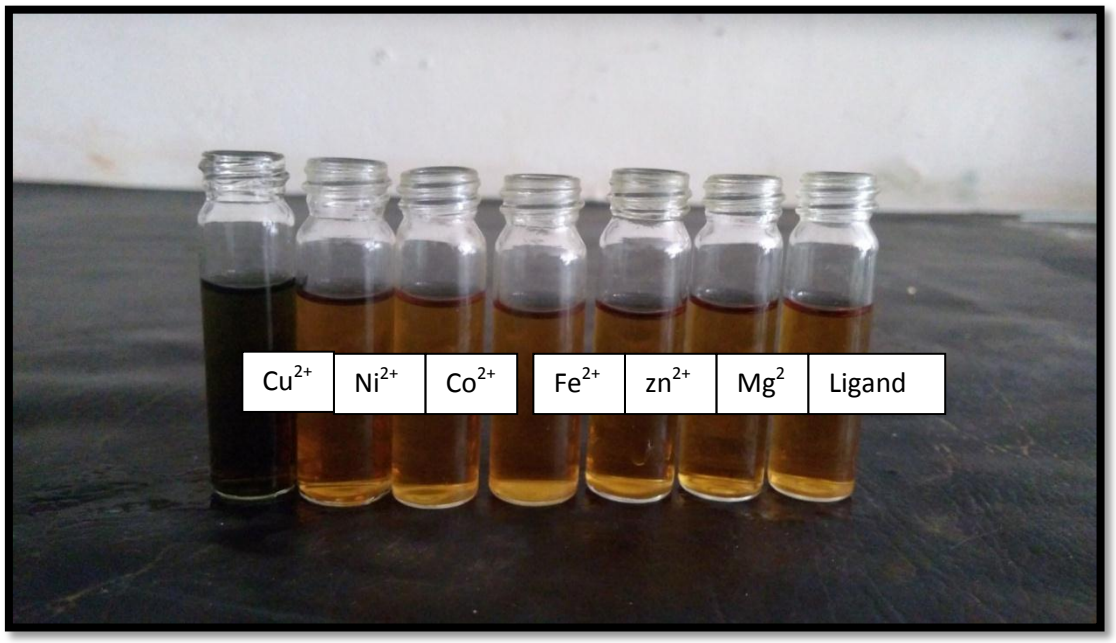


Fig. 3. Copper (II) complex showing distinct colour change from the ligand

Characterization of Ligand (PABMTB):

The ligand(PABMTB) was characterized using ^{1}H NMR data. ^{1}H NMR was recorded using DMSO as the solvent.(N-CH) has a characteristic peak at 8.35 (δ).The aromatic protons has resonated in the range of (7.0-7.8)(δ). A sharp peak at 2.5 (δ) is due to the presence of (CH_3) group.

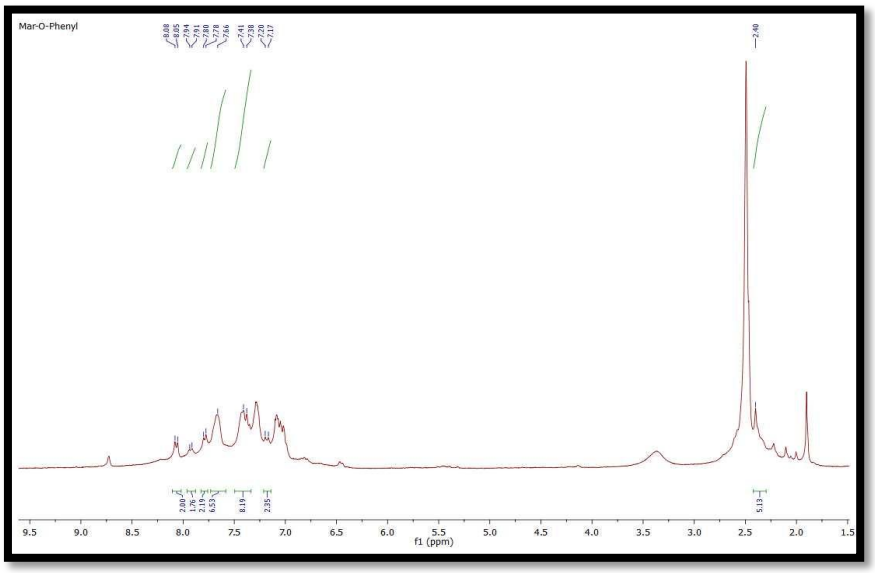


Fig.4. NMR spectrum of ligand (PABMTB)

Characterization of Cu(II) complex:

The metal(II) complex of copper(II) of [$ML_2.H_2O$] type were obtained in good yield through the reaction of (PABMTB) with the corresponding metal salt. The ligand and metal(II) complexes were characterized through IR, elemental analyses, electronic absorption, and NMR spectral data and arrived their structure. The analytical data and physical properties of the ligand and metal(II) complex are listed in the table1. Elemental analysis, Spectral and conductance data suggest that the molecular formula[$ML.H_2O$] for copper(II) complex.The magnetic moment of the complex is consistent with octahedral geometry around central metal ion.

Table.2. Physical characterization, analytical, molar conductance data of the ligand (PABMTB) and its metal(II) complex

Compounds	*F.W. (g/mol)*	*Color*	*Calculated (Found) (%)*					Δ_M*(Ohm^{-1} cm^2 Mol^{-1})*
			C	*H*	*N*	*O*	*Cu*	
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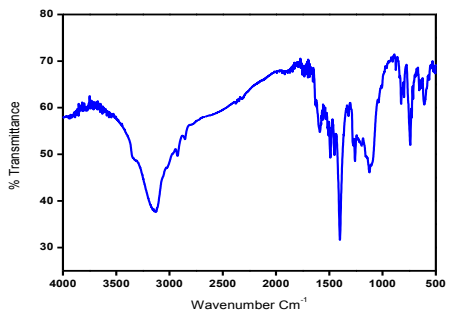
INFRARED SPECTRAL STUDIES:

The IR spectra of the free ligand and metal complex were carried out in the range 4000-400 cm^{-1} and the spectral data are listed in Table.3. A broad band centered at 3220 cm^{-1} is the characteristic of ν (OH). The IR spectrum of the ligand shows a broad band at 3160cm^{-1} which is due to ν (N-H) stretching vibration. A peak at 810 is due to (C-H) Bending. The band at 1472 cm^{-1}is assigned to ν(C -N) stretching and a band at 3220 cm^{-1} and two weak bands at 1528 cm^{-1} and 1498 cm^{-1} shows the presence of phenolic ν(OH) and ν(N = N) respectively. The FT-IR spectra are depicted in Fig.5 and 6. IR spectrum of the Metal(II) complex shoe significant variations compared with the free ligand. The broad band around 3160 cm^{-1} for the complex suggests the coordinated water in copper metal complex.[15-18]

Table.3. IR spectral data of ligand (PABMTB) and its metal(II)complex ***(cm^{-1}).***

Compounds	*ν*(C-H)	**ν (C-N)**	**ν (N-H)**	**ν (-OH)**	**ν (N=N)**
PABMTB($C_{22}H_{20}N_4O_2$)	810	1472	1610	3220	1528
[Cu(PABMTB)(H_2O)]	898	1398	1628	3160	1498



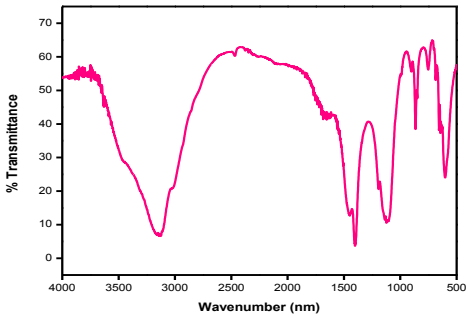


Fig.5. IR Spectra of ligand [PABMTB] **Fig.6. IR Spectra of Cu(II) Complex**

Electrochemical behaviour of ligand and metal complex

Cyclic voltammetry (CV) is popular for its relative simplicity and its high information content. It is used most often as a diagnostic tool for elucidating the electron transfer process at the scan rate of 100 mV s^{-1} (-2.0 to 1.6V). The electrochemical behaviour of the ligand was performed in Ethanol solution at room temperature with tetrabutylammonium perchlorate(TBAP) as supporting electrolyte; glassy carbon as working electrode; Pt wire as auxiliary electrode; Ag/AgCl as reference electrode in order to monitor spectral and structural changes accompanying electron transfer. The Cyclic Voltamogram of ligand shows a broad reduction peak 0.4 V.[19-21]

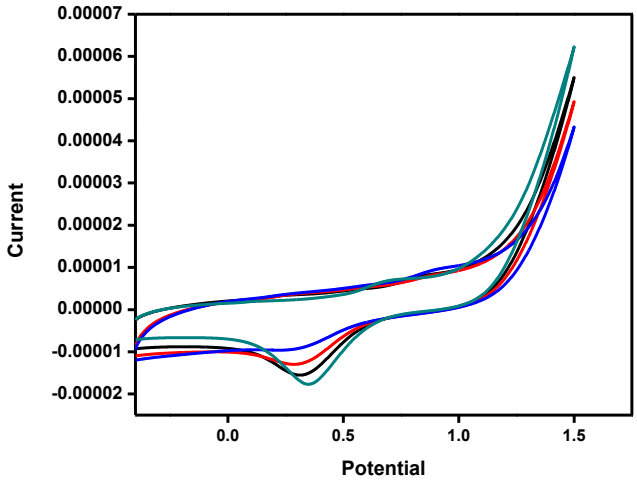


Fig.7. Cyclic voltammetry of ligand of PABMTB

BIOLOGICAL STUDIES

All the newly synthesized compounds were tested *in vitro* by well diffusion method against the bacteria ***K.Pneumoniae, Stapyh.epidermis, Stapyh.Pyogenes and Proteaus***Amikacin and Ketoconazole were taken as the standard for antibacterial studies. Every bacterial strain was incubated in Nutrient Broth (NB) at 37^0C for 24 hours. The wells each of 5 nm were made in Muller-Hinton agar using cork borer. The stock solution was prepared in 10^{-3} mL^{-1} concentration (DMSO) and then 100µl of the solution was transferred into each well. The plates were incubated for 24 hours at 37^0C and examined for clear inhibition of the zone around the well.The inhibition zone was developed and measured. The antimicrobial studies reveal that the complexes are resistant towards the bacteria *Stapyh.Pyogenes* and shows good activity with other organisms.

All the tested compounds showed a remarkable biological activity against different types of bacteria species. On comparing the biological activity of the ligand and its metal(II)complex with the

standard, it is inferred that, the metal(II)complexes shows potential antibacterial activity against all the bacterial strains.

Table.4. Antimicrobial activity data of the ligand and metal (II) complex (Zone of inhibition in nm)*

Compounds	K.Pneumoniae	Stapyh.epidermis	Staph.Pyogenes	proteus
PABMTB (L)	12	10	12	9
[Cu(PABMTB)(H_2O)$_2$]	15	12	16	13
Standard	19	19	22	19

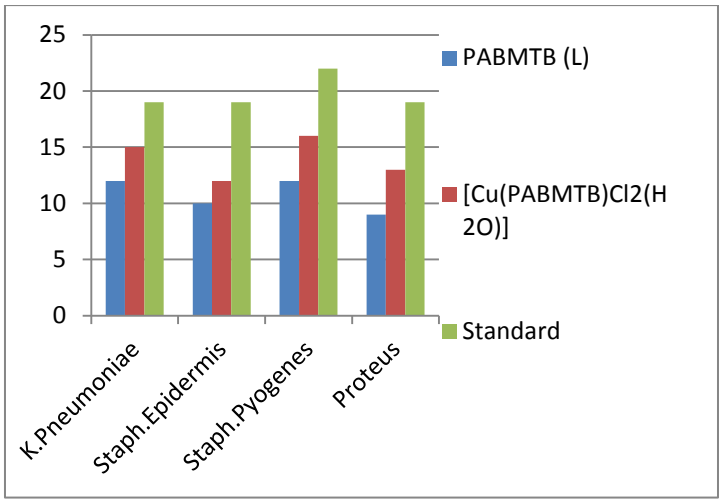


Fig.8. Bio spectrum of the ligand and its complexes for antimicrobial activity

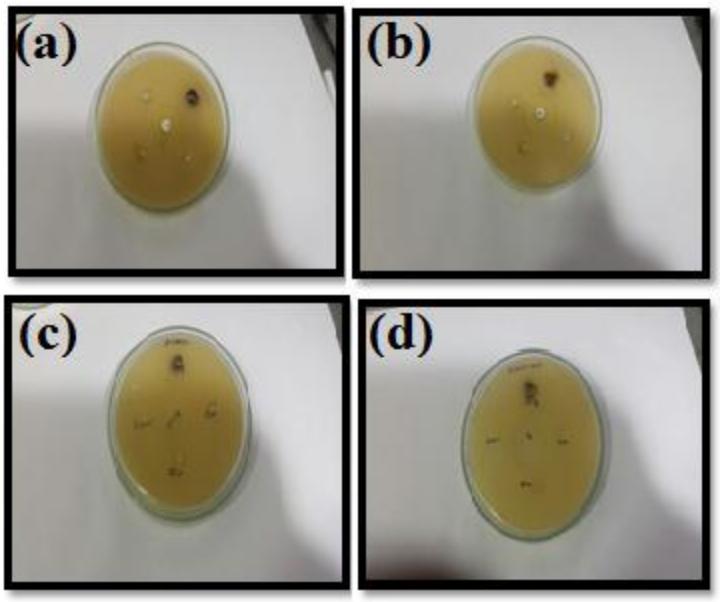


Fig.9. Inhibition Zones formed for (a). *Pneumoniae, (b). Stapyh.epidermis, (c). Stapyh.Pyogenes and (d). Proteaus*

CONCLUSION

In the present study, a novel o-phenylenediamine based ligand was synthesized and characterized by various spectral techniques. Sensing properties of the ligand was studied with

different metal cations and copper (II) showed significant effect with the synthesized ligand. Copper (II) complex was prepared and it is said to possess octahedral geometry with the conductance value of 1.81. Biological activity of the ligand and complex were analysed with four different bacteria and the metal complex is found to have good antibacterial activity compared to the ligand.

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REFERENCES

1. Khan BehlolAyaz Ahmed, Siva Bala Subramaniyan, Sanaulla Farisa Banu, Jacalin-copper sulfide nanoparticles complex enhance the antibacterial activity against drug resistant bacteria via cell surface glycan recognition, Coll and Surf B: Biointer**.,** 2018**;** 163: 209-217.
2. Abdel-Nasser MA, Alaghaz, Mohamed Zayed E, Synthesis, spectroscopic, molecular structure, antioxidant, antimicrobial and antitumor behavior of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of O_2N type tridentate chromone-2-carboxaldehyde Schiff's base ligand, J. Mol. Stru., 2014; 1141: 368-381.
3. Ali Mohammed Yimer, Chemical Synthesis, Spectral Characterization and Antimicrobial Studies on Complexes of Ni(II), Cu(II) and Zn(II) with N, N-di (o-hydroxybenzenoylmethylene) Ethylenediamine, Am. J. of BioSci. Special Issue: Chem Bio., 2014; 2 (6-1): 22-34.
4. SupunKatugampala, Inoka C. Perera, Chandrika Nanayakkara and Theshini Perera, Synthesis, Characterization and Antimicrobial Activity of Novel Sulfonated Copper-Triazine Complexes, Bioinorg. Chem and Appl., 2018: 1-7.
5. Ashraf, MA, Mahmood K, Wajid A, Synthesis, characterization and biological activity of Schiff bases, IPCBEE., 2011**;**10: 1-7.
6. Brodowska K, Lodyga-Chruscinska, Schiff bases - Interesting range of applications in various fields of science, J. Mol. Stru., 2014**;** 68:129-134**.**
7. Cozzi PG, Metal–Salen Schiff base complexes in catalysis: practical aspects, Chem. Soc. Rev., 2004; 33 (7): 410-421.
8. Garnovski AD, Nivorozhkin AL, Minkin VI, Ligand environment and the structure of schiff base adducts and tetracoordinated metal-chelates, Coord. Chem. Rev., 1993; 2: 1-69.
9. Gupta KC, Sutar AK, Catalytic activities of Schiff base transition metal complexes, Coord. Chem. Rev., (2008); 252 (12-14):1420-1450.

10. Gupta KC, Sutar AK, Lin CC, Polymer-supported Schiff base complexes in oxidation reactions, Coord. Chem. Rev., 2009; 253(13-14):1926–1946.
11. Akelah A, Rehal A, Kenawy ER, Zeid MS, Abou MS, Catalytic activity of polymer–montmorillonite composites in chemical reactions, J. Appl. Polym. Sci., 2006**;** 101:1121–1129.
12. Drago RS, Gaul J, Zombeck A, Straub DK, Preparation, Characterization, and Catalytic Studies of Iron and Cobalt Complexes Supported by ONNO – Tetradentate Schiff-Base Ligands, J. Am. Chem. Soc., 1980;102:1033–1038.
13. Andreea Stanila, Cornelia Braicu,Raluca Pop, Antibacterial Activity of Copper and Cobalt Amino Acids Complexes, Not Bot HortiAgrobo., 2011**;** 39(2): 124-129.
14. Ahmed AA, Benguzzi SA, EL-Hadi AL, Synthesis, characterization, molecular modeling and biological activity of mixed ligand complexes of Cu(II), Ni(II) and Co(II) based on 1,10-phenanthroline and novel thiosemicarbazone, Inorg. Chim. Acta., 2013; 407: 58-68**.**
15. Solankee A, Thakor I, Synthesis of pyrazolines, isoxazolines and aminopyrimidines as biological potent agents, Indian. J. Chem., 2006; 45B: 517-522.
16. Vijayanthimala R, Nirmala A, Swathy CH, Synthesis, characterization and Microbial Study of Complexes of Cu(II) and Ni(II) with thiosemicarbazone, J. Chem. Pharm. Res., 2011; 3: 682-688.
17. Kulkarni APG, Avaji G, Bagihalli SA, Patil PS, Badami, Synthesis, spectral, electrochemical and biological studies of Co(II), Ni(II) and Cu(II) complexes with Schiff bases of 8-formyl-7-hydroxy-4-methyl coumarin, J. Coord. Chem., 2009; 62: 481-492.
18. Raman N, Mitu L, Sakthivel A, Pandi MSS, Studies on DNA cleavage and antimicrobial screening of transition metal complexes of 4-aminoantipyrine derivatives of N_2O_2 type, J. Iran. Chem. Soc., 2009; 6: 738-748.
19. Kannappan R, Mahalakshmi R, Rajendran TM, Venkatesan R, Sambasiva Rao P, Magnetic, catalytic, EPR and electrochemical studies on binuclear copper(II) complexes derived from 3,4-disubstituted phenol, Proc. Indian Acad. Sci (Chem. Sci)., 2003; 115: 1-14.
20. Kadam RM., Sastry M.D, Bhide MK, Chavan SA, Yakhmi JV, Khan O, An EPR study of spin correlations and existence of ordered and disordered phases in $(NBu_4)_2Mn_2[Cu(opba)]_3{\cdot}6DMSO{\cdot}1H_2O$, Chem. Phys. Lett., 1997; 281: 292-296.
21. Warad DU, Satish CD, Kulkarni VH, Bajgur CS, Synthesis, structure and reactivity of zirconium(IV), vanadium(IV), cobalt(II), nickel(II) and copper(II) complexes derived from carbohydrazide schiff base ligands, Indian J. Chem., 2000; 39: 415-420.