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Synthesis, Physical Characterization and Biological Activity of Some Schiff Base of Cu (II), Zn (II), and Cd (II) Metal Complexes

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Abstract: **pyridine-2,6-diylbis(azan-methan-1-yl) diphenol and Schiff's base complexes of Cu, Zn and Cd meta have been successfully synthesized. The Schiff base metal complexes showed gripping co-ordination chemistry. Schiff base ligand of metal complexes has Structural grammatical relation of organic molecule showed considerable biological connection. Further, coordination of a biomolecules to the metal ions significantly alters the effectiveness of the biomolecules. In view of the antimicrobial activity ligand (pyridine-2,6-diylbis(azan-methan-1-yl) diphenol [HBDAP], metal complexes with Cu (II), Zn (II) and Cd (II) have been synthesized and found to be potential antimicrobial agents. An attempt is also made to correlate the biological activities. The thermal stability and degradation of the metal complexes were investigated by thermogravimetric analysis. The complexes have been by elemental analysis, spectra. The structural assessment of the complexes has been carried out based on, infrared spectra and elemental analysis.**

Index Terms: **Biological activity, TGA, SEM, Elemental Analysis**

I. INTRODUCTION

Schiff bases are the condensation products of primary amines with carbonyl compounds and were first reported by Hugo Schiff (Cimerman Z, et al.,2000) . The Schiff bases ligand has been found extensive use in the field of research and field of interest now a day. The Schiff bases compounds are recognized due to the presence of azomethine group (-CH=N) which is formed by reacting either by aldehyde or ketone with compounds containing amine group (Chakraborty H.,1994).Schiff bases have gained importance in medicinal and pharmaceutical fields due to a broad spectrum of biological activities like anti-inflammatory (Reddy P.,at al,2011; Sathe B. S., 2011), analgesic (Chinnasamy R. P,et al., 2010) [5], antimicrobial (Venkatesh P,2011), anticonvulsant (Chaubey A. K. and Pandeya S. N.,2012), antitubercular (Aboul-Fadl T.,et al.,2003), anticancer (Miri R., et al.,2013), antioxidant (Wei D., et al.,2006), anthelmintic (Avaji P. G., et al.,2009), and so forth. Apart from biological activities, Schiff bases are also used as catalysts, intermediates in organic synthesis, dyes, pigments, polymer stabilizers, and corrosion inhibitors (Li S., et al.,1999). The Schiff bases derived from amino acids form stable complexes with transition metals and also inhibit the growth of bacterial and fungal strains after complexation ([Reddy P. S. N., et al.,1987). Studies enlightened that metal complexes show greater biological activity than free organic compounds (Chohan Z. H.,1997). Augmentation of biological activity was reported by implementation of transition metals into Schiff bases (Ershad S., et al., 2009). The homobimetallic complexes of tin have been synthesized and their antimicrobial activities were studied and reported which gave good results for complexes than ligand (Pervaiz M., et al.,2015). A series of transition metal complexes containing Mn, Fe, Co and Re were prepared and their structural characterization was carries by using various instrumental techniques (Vinod S.S., et al.,2006). The synthesis of Schiff base derivatives Ni, Co, Cu and Zn complexes was also proposed and reported along with their structural elucidation as well as anti-corrosion utilization (Nassar A.M., et al.,2015). Schiff bases played an influencing role in development of coordination chemistry and were involved as key point in the development of inorganic biochemistry and optical materials (Tisato F., et al.,994) . Keeping in mind the above discussed situation, the following aims have been achieved in the current research work, Synthesis of Schiff base as ligand derived from amino acid, Synthesis of Schiff base derivative complexes with different metals antimicrobial activities of the synthesized ligand and complexes pyridine-2,6-diamine and 2-hydroxybenzaldehyde compounds are capable to form complexes with transition metal ions in the form Schiff bases. The obtained chemical analysis data showed the formation of [M: L] ratio. The complexes of copper (II), zinc (II) and cadmium (II) have been prepared and investigated using different chemical techniques, such as; elemental analysis, magnetic measurements, infrared, TGA, EDX values. The work concentrates

on the synthesis and biological activity of Schiff bases and their complexes. This work reveals synthesis of new structural design of Schiff base Cu (II), Zn (II) and Cd (II) complexes. All the compounds were prepared through in-situ reaction. The preparation is that the overall time for the synthesis has been considerably reduced. The synthesized Schiff ligands and their copper (II), zinc (II) and cadmium (II) complexes are novel as well as their antimicrobial. The prepared metal complexes exhibit several advantages such as eco-friendliness, low cost, metal affinity and moisture absorbing nature and proved better pharmaceutical results than the reported ones.

II. MATERIAL MATHOD

All the purchased chemicals were analytical grade and used without further purification. Solvents were purified and dried according to literature method (Perrin D.D., Purification of Laboratory Chemicals,20010). All chemicals were obtained from Sigma–Aldrich chemical used without purification. 2, 6 Diamino-pyridine and o- hydroxyl benzaldehyde., remaining all chemical solvents were purchased from Spectro Chem.Ltd.

II. EXPERIMENTAL

A. Synthesis of (pyridine-2,6-diylbis(azan-methan-1-yl) diphenol [HBDAP]

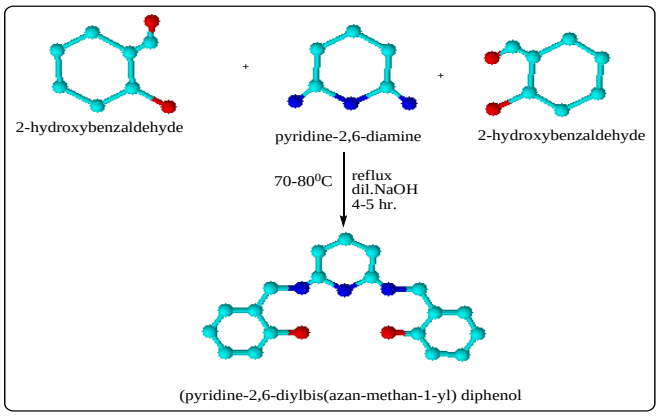


Fig.1. Synthesis of (pyridine-2,6-diylbis(azan-methan-1-yl) diphenol [HBDAP]

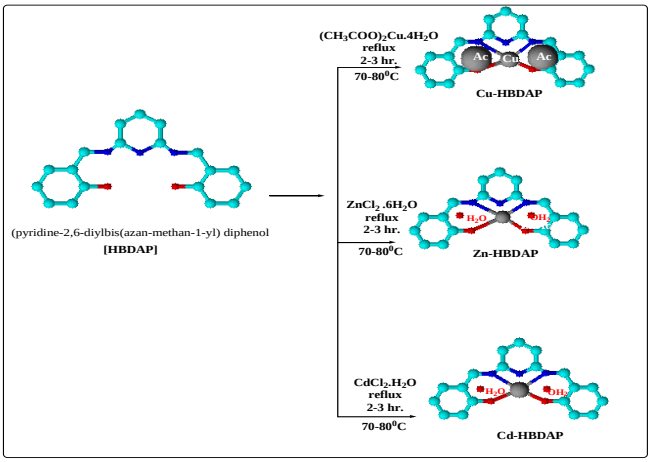


Fig.2. Synthesis of Schiff's base complexes of Cu, Zn and Cd metal.

B. Synthesis of metal complexes

The equimolar quantity of pyridine-2,6-diamine $C_5H_7N_3$ (0.01 M) and 2-hydroxybenzaldehyde $C_7H_6O_2$ (0.01 M) in anhydrous ethanol solvent in catalytic amount dil. NaOH. The reaction mixture was heated at reflux with stirring for 4–5 h and then poured in ice cold water finally colored solid were obtained by filtration and it crystallized in ethyl alcohol.The ligand was taken in ethanol and stirred gently for 30 minutes to give a homogeneous suspension. Schiff base [HBDAP] was added to copper (II) perchlorate hexahydrate solution.

III. RESULT AND DISSCUSSION

A. Physio-chemical characterizations and geometrical configuration of the complexes

The stoichiometry of the ligand and its complexes were confirmed by their elemental analysis. The metal / ligand ratio was found to be 1:1 has been arrived at by estimating the metal and nitrogen contents of the complexes. Elemental analysis of ligand and its Cu (II), Zn (II) and Cd (II) complexes show good agreement with the proposed structures of the ligand and its complexes. Apart from this, biological activity of the ligands and its complexes were studied. Table 1

Compound	Molecular Formula	Molecular Weight	M.P	Cal. Elemental Analysis Calculated					BM	Yield%
				M	C	H	N	O		
HBDAP(L)	$C_{19}H_{15}N_3O_2$	317.35	258	----	71.91	4.76	13.24	10.08	--	74.38
CuL_2	$C_{19}H_{13}CuN_3O_2$	378.87	>360	14.76	61.30	4.06	11.29	8.60	1.07	79.11
ZnL_2	$C_{19}H_{13}ZnN_3O_2$	380.03	236	15.66	60.65	4.02	11.17	8.50	0.00	64.09
CdL_2	$C_{19}H_{13}CdN_3O_2$	427.74	198	15.61	60.69	4.02	11.17	8.51	3.36	72.65

B. Infrared spectra

The ligand and metal complexes were characterized mainly using the azomethine and primary amine ($–NH_2$) bands. The appearance of a broad strong band in the IR spectra of the ligand in 3400 -3350 cm-1 is assigned to N-H stretching vibrations of

the primary amine group. In the complexes, this band is shifted to lower frequency indicating that the ligand was coordinated to metal ions through the nitrogen atoms of the NH_2 group (Ghames A., et al.,2005). The spectrum of the ligand shows two different –C=N bands in the region 1590-1550 cm^{-1}, which is shifted to lower frequencies in the spectra of all the complexes (1570-1520 cm^{-1}) indicating the involvement of –C=N nitrogen in coordination to the metal ion (Thankamony M and Mohanan.K.,2007). Assignment of the proposed coordination sites is further supported by the appearance of medium bands at 450- 400 cm^{-1} which could be attributed to υM-N respectively (Thomas M, et al.,1995).

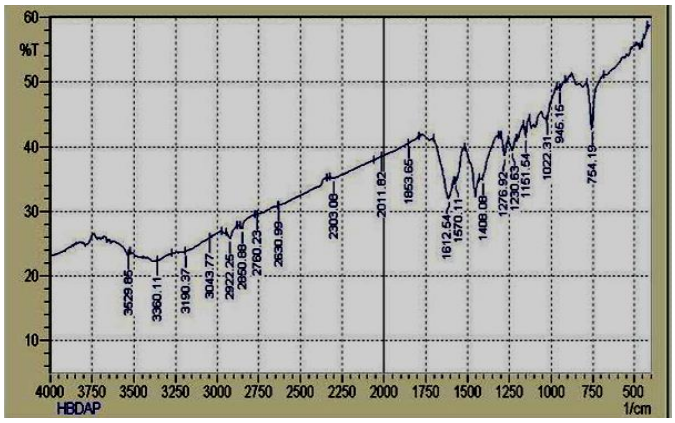
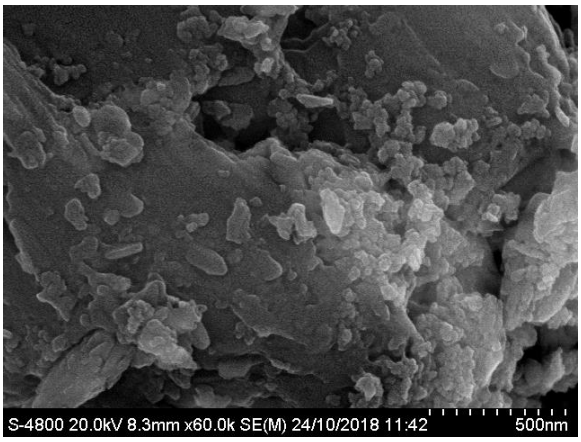


Fig.3.Proposed structure IR of Schiff base [HBDAP]

The ligand and metal complexes were characterized mainly using the azomethine and primary amine (–NH_2) bands. The appearance of a broad strong band in the IR spectra of the ligand in 3400 - 3350 cm-1 is assigned to N-H stretching vibrations of the primary amine group. In the complexes, this band is shifted to lower frequency indicating that the ligand was coordinated to metal ions through the nitrogen atoms of the NH_2 group (Ghames A., et al.,2005). The spectrum of the ligand shows two different –C=N bands in the region 1590-1550 cm^{-1}, which is shifted to lower frequencies in the spectra of all the complexes (1570-1520 cm^{-1}) indicating the involvement of –C=N nitrogen in coordination to the metal ion (Thankamony M and Mohanan.K.,2007). Assignment of the proposed coordination sites is further supported by the appearance of medium bands at 450- 400 cm^{-1} which could be attributed to υM-N respectively (Thomas M, et al.,1995).

C. SEM

Figure shows the SEM images of Schiff base ligand [HBDAP] and their Cu (II), Zn (II) and Cd (II) complexes. The SEM image indicates that the surface morphology of the plate-type was agglomeration of grains. The size and porous structure of the ligands were drastically changed after the complexation. The complexation revealed uniform, regular, amorphous and layered structure and this efficiently supported the antimicrobial, anti-inflammatory and total antioxidant activities.



D. Thermogravimetric analysis

TGA of the transition metal complexes were carried out from ambient temperature to 500 °C in Nitrogen atmosphere having heating rate 10 °C per minute. The kinetic parameters of all the transition metal complexes by Freeman and Carroll methods have been determined and computerized software is essential for processing the enormous amount of data involved in this analysis and represented graphically by Microsoft Excel.

E. Biological activity

The free ligand and its metal complexes were tested against the bacterial species *Staphylococcus Aureus*, Bacillus subtilis, Pseudomonas *aeruginosa*, and *Escherichia coli*. Chloramphenicol as a standard antibacterial agent or reference was evaluated for their antibacterial activity and the result was compared with the free ligand and its metal complexes. The comparison of the biological activities of the synthesized compounds and some known antibiotic shows the following results:

1. The free ligand and its metal complexes show positive effect towards *Staphylococcus aureus* more than standard.
2. The free ligand and Ni (II) complex show higher antibacterial effect than that of standard.
3. The copper (II), zinc (II) and oxovanadium (IV) complexes have more biological activity than ligand, Nickel and standard. Such increased activity of the metal chelates can be explained based on chelation theory. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of π electrons over the whole chelate ring and enhances the penetration of the complexes into lipid membranes and blocking of the metal binding sites in the enzymes of microorganisms. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organisms.

Table II. Characteristic IR bands (cm-1) of the compounds studied

Compound	υ(C=O)	Free-OH	Azo methine υ (C=N)	Aromatic Disubstitu edring	Pyridine Ring Defor mation	υ(C-O)	υ(M-O)	υ(M-N)	Ar. (C-H)	(OAc)
HBDAP(L)	3529	3535	1612	754	1151	1276	945	--	3043	1408
CuL_2	--	--	1570	756	1151	1230	956	--	3041	1408
ZnL_2	--	--	1622	756	1151	1228	--	844	--	1452
CdL_2	3529	3529	1612	754	1151	1230	--	--	--	--

Table 3 Antimicrobial data of metal complexes

Compound	S. aureus	B. Pumulis	E. coli	P. Vulgaris	A. Niger	C.albicans
ABDAP	1	1	6.24	6.1	2	1.5
Cu- ABDAP	1	1	1	1	1	1
Zn- ABDAP	14.42	12.32	11.24	13.31	1	14.99
Cd- ABDAP	1	1	1	1	11.26	1
Chlormphenical	14.72	11.92	10.39	15.43	2	2
Amphotericin B	5	5	5	5	14.27	10.22

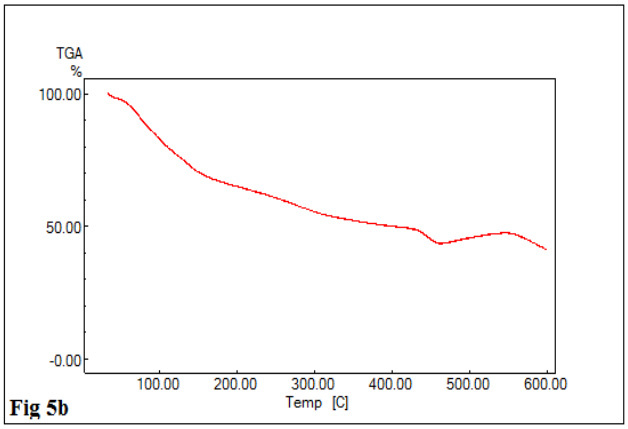


Fig.5. TGA Analysis curve of Cu Metal complexes

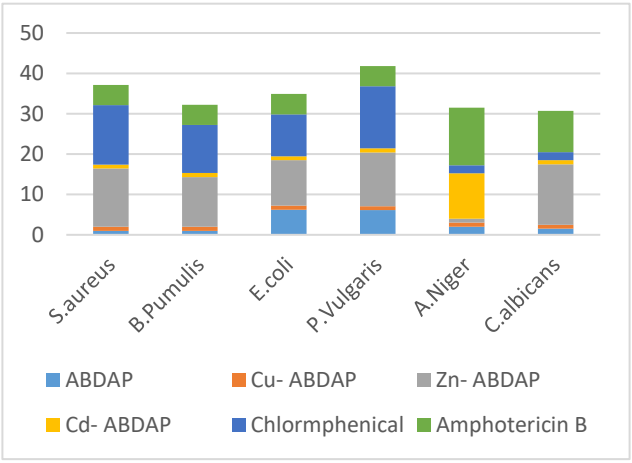


Fig.6 Graphical representation of antimicrobial activity

CONCLUSION

The spectral data show that the Schiff base exist as tetradentate ligand by bonding to the metal ion through the phenolic nitrogen and azomethine nitrogen. The analytical data show the presence of one metal ion per ligand molecule and suggest a mononuclear structure for the complexes. On the basis of chelation theory, metal complexes have more biological activity than free ligands.

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