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Synthesis and Antimicrobial Screening of Novel Transition Metal Complexes of Co(II) and Zn(II) with Schiff base NNO functionalized Ligands

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ABSTRACT

Two Schiff base ligands L_1 and L_2 obtained by the condensation of Glutaraldehyde with L-alanine and L-valine were complexed with Co(II)and Zn(II) transition metal ions. Structural features were obtained from their elemental analyses, magnetic susceptibility measurements, molar conductance data, IR, UV-Vis, ^{1}H-NMR spectral studies, X-ray diffraction study, SEM analysis and thermal studies. The UV-Vis and magnetic susceptibility studies suggest an octahedral geometry around the central metal ions. IR datas show that the ligands behave as tetradentate ligands coordinating through both carbonyl oxygen and terminal nitrogen atoms. The molar conductance measurements indicate that the complexes are non-electrolytic in nature. The powder XRD data shows that the complexes are microcrystalline. The antimicrobial activities of ligands and its complexes screened by Disc Diffusion method shows that the metal complexes were more potent than the parent Schiff base ligands against one or more bacterial and fungal species.

KEY WORDS: Schiff base ligands; Metal complex; Spectral studies; Antimicrobial activity

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I. INTRODUCTION

Inorganic elements play crucial role in biological and medical processes, and it is evident that many organic compounds used in medicine do not have a purely organic mode of action, some are activated or bio transformed by metal ions metabolism .Many drugs possess modified toxicological and pharmacological properties in the form of metal complex and probably Schiff bases are versatile compounds possessing broad spectrum of biological activity and incorporation of metals in the form of complexes showed some degree ofantibacterial, antifungal , antitumor and anti-inflammatory activity[1]. Schiff base complex formation as intermediate in biochemical reactions have already been reported long time ago ,even before the general preparation of the Schiff base ligands [2]. Schiff base ligands are considered "privileged ligands" because they are easily prepared by the condensation of aldehydes with amines and are characterized by –N=CH- (imine) group which is important in elucidating the mechanism of transamination and racemisation reactions in biological systems [3]. During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donors[4]. These investigations emphasised the great relevance of these systems in basic and applied chemistry and catalysis, molecular materials, microelectronics, sensors and so on .Studies of new kinds of chemotherapeutic Schiff bases are now attracted the attention of biochemists. Keeping this end in view, we have undertaken the synthesis of some Schiff bases, which are potential ligands for transition metal ions to study their physiological properties and to study the complex biochemical processes involving these metal ions and Schiff bases . The present paper describes the synthesis , characterization and antimicrobial activities of Schiff bases obtained by the condensation of Glutaraldehyde with amino acids like L-alanine and L-valine and its metal ion chelate with Co(II) and Zn (II) ions.

II. EXPERIMENTAL

2.1 *Chemicals*

Reagents such as Glutaraldehyde, L-alanine, L-valine , metal (II) chloride and nitrate were of Merck products. The solvents were purified by standard methods[5].Double distilled water was used throughout the experimental work.

2.2 *Physical Measurements*

Microanalytical data of the compounds were recorded using a Vario EL III elemental analyzer at Sophisticated Analytical Instruments facility, CUSAT, Kochi. Ultraviolet spectra were recorded using Shimadzu double beam visible spectrophotometer in the visible region. The molar conductance of the metal complexes were determined in DMSO on SYSTRONICS digital

conductivity meter. Magnetic susceptibility of the complexes were measured by Guoy balance using Copper sulphate as calibrant. IR spectra in the range of 4000 to 400 cm^{-1} were recorded on a Perkin Elmer FT-IR spectrometer MODEL 1600 as KBR discs.^{1}H NMR spectra (300 MHz) of the samples in DMSO-d_6 were recorded by employing TMS as internal standard at NIIST Trivandrum. Powder XRD were recorded on a computer controlled X-ray diffractometer system JEOL JDX 8030 at NIIST Trivandrum. SEM images were recordedat Sophisticated Analytical Instruments facility, CUSAT, Kochi. Thermal behaviour of the samples were recorded in a thermal analyzer at NIIST Trivandrum. The invitro and invivo antimicrobial study of the compounds were tested against the bacteria *Klebsiellasps, Escherichia coli, Staphylococcus aureus* and fungi *Candida sps ,Aspergillus niger* and *Aspergillus fumigates* by Kirby-bauer Disc diffusion method. Standard discs of chloramphenicol served as positive controls for antimicrobial activity but filter disc impregnated with solvent were used as a negative control.

2.3 *Synthesis of Schiff Base Ligands*

The Schiff base ligands were prepared by reacting Glutaraldehyde with L-alanine and L-valine in 1:2 molar ratio by refluxing in distilled methanol for 1 hour. The reactions were examined by TLC with time to time till completion. The solvent was partially evaporated and the yellowish mass products obtained were precipitated by cooling and filtered off, washed with distilled water , dried, recrystallized and finally preserved in desiccators.

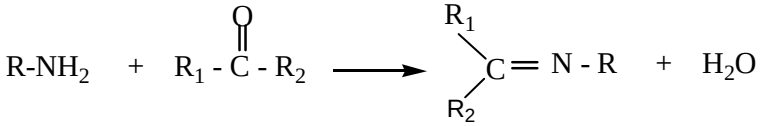
2.4 *Synthesis of Schiff Base Transition Metal Complexes*

Metal (II) chloride and nitrate were dissolved in 200 cm^3 of methanol. The filtered solutions were added dropwise into 20cm^3 methanol solutions of the Schiff base ligands, the resulting mixtures were refluxed , stirred for 8 hours and the concentrate were cooled at 0ºC. The precipitated complexes were filtered off, washed several times with cold ethanol and dried in vacuo over anhydrous $CaCl_2$.

III. RESULTS AND DISCUSSION

3.1. *Physical Properties and Elemental Analyses*:

The physical properties and results obtained from C.H.N. analyses and metal contents of the prepared compounds are presented in **Table 1**. The general reaction of an amine with a carbonyl compound can be represented as in **equation 1**:



where R_1 and R_2 are the organic moieties . The synthesized metal complexeswerein 1:1 stoichiometric ratio, stable at room temperature and hygroscopic in nature. The Schiff base ligandsand its complexes were soluble in DMSO . The Co(II) and Zn(II) complexeswere non-electrolytic in nature.

Table 1. Physiochemical data of Schiff bases and its metal complex

Ligand/Metal Chelate	Empirical Formula	Colour	M:L ratio	Molar Cond. (Ohm^{-1} cm^2 mol^{-1}	Elemental analysis % Found (calculated)			
					C	H	N	M
$HGlu(val)_2$	$C_{15}H_{30}N_2O_6$	Yellow	-	-	63.43 (62.11)	8.9 (9.3)	8.7 (9.5)	-
$CoGlu(val)_2.2H_2O$	$C_{15}H_{30}N_2O_6Co$	Pink	1:1	0.071	44.54 (45.26)	7.2 (7.6)	6.9 (7.1)	15.01 (15.96)
$ZnGlu(val)_2.2H_2O$	$C_{15}H_{30}N_2O_6Zn$	Pale Yellow	1:1	0.064	45.64 (44.35)	7.7 (8.0)	6.9 (7.3)	14.86 (15.20)
$HGlu(ala)_2$	$C_{11}H_{22}N_2O_6$	Yellow	-	-	67.89 (65.78)	9.6 (8.8)	8.6 (9.3)	-
$CoGlu(ala)_2.2H_2O$	$C_{11}H_{22}N_2O_6Co$	Pink	1:1	0.062	51.89 (52.68)	6.29 (6.49)	7.98 (8.19)	17.98 (18.58)
$ZnGlu(ala)_2.2H_2O$	$C_{11}H_{22}N_2O_6Zn$	Pale Yellow	1:1	0.077	54.67 (52.99)	6.97 (6.80)	7.62 (8.10)	17.52 (18.06)

3.2 *UV-Visible Spectra*

The UV-Visible spectra are often very useful in the evaluation of results furnished by other methods of structural investigation[6] and used for assigning the stereochemistry of metal ions in the complex based on the positions and number of d-d transition peaks. The electronic absorption spectra were recorded in DMSO solution in the range of 200 to 800 nm regions.The data obtained were correlated with magnetic moment values and ligand field parameters: splitting energy (10Dq), interelectronic repulsion parameter (B), and nephelauxetic ratio (β).The intense bands centered at 275 nm and 280 nm was assigned to π - π* transition of the C=N chromophore. On complexation, the bands were shifted to lower wavelength region at 235 nm and 250 nm suggesting the coordination of azomethine nitrogen with the metal ions. The spectrum also showed other transitions in the range of 337 and 348 nm which can be assigned to n -π * transition. In UV-Vis spectra, the weak bands at 400-500 nm were due to charge transfer band in the complex that does not exist in the

ligands. However, the weak broad bands at 500-600 nm were due to d-d transitions of Co(II) ion. The octahedral geometry of Co(II) complexes have magnetic moment values as 4.78 and 4.89 BM .The electronic spectra of Zn(II) complexes does not contain d-d transitions and was found to be diamagnetic as expected.

3.3 Infra Red Spectra

Infrared spectra (IR) are highly useful in identifying the nature of coordination sites, particularly in Schiff base complexes involving multidentate ligands and valuable information regarding the nature of functional group attached to the metal ion [7]. The IR spectra of the ligands showed a broad band in the region 3220-3550 cm^{-1}, assignable to intramolecular hydrogen bonded -OH groups. The spectrum of the ligands showed –C=N band in the region of 1655- 1660 cm^{-1} which was shifted to lower frequency in the spectra of the corresponding metal complex indicating the involvement of –C=N nitrogen in coordination to the metal ions. Accordingly, the ligands act as a tetradentate chelating agent, bonded to the metal ion through the four nitrogen atoms of the Schiff base. The medium bands at 550-460 $cm^{-1}$and 565 -575 cm^{-1} was attributed to M-N and M-O frequency (**Fig 1and 2)**.

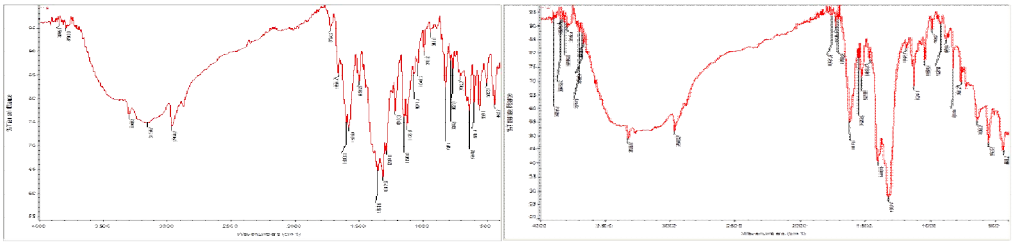


Fig.1:IR Spectra of$ZnGlu(val)_2.2H_2O$ and $CoGlu(val)_2.2H_2O$Schiff base complexes

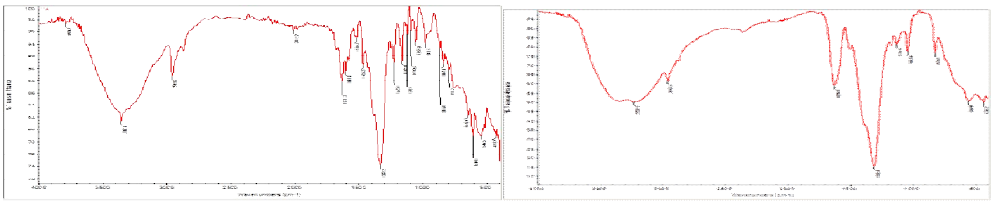


Fig.2: IR Spectra of $ZnGlu(ala)_2.2H_2O$ and $CoGlu(ala)_2.2H_2O$Schiff base complexes

3.4 ^{1}H NMR Spectra

The ^{1}H NMR Spectrum of the ligand H Glu(val)$_2$and H Glu(ala)$_2$ recorded in DMSO solution shows a multiplet at 2.6,2.4,1.6 and 1.8 ppm due to the methyl protons. Furthermore, the ^{1}H NMR Spectrum of the Schiff base complexes ZnGlu(val)$_2$.2H$_2$O, CoGlu(val)$_2$.2H$_2$O,ZnGlu(ala)$_2$.2H$_2$O and CoGlu(ala)$_2$.2H$_2$O exhibited signals at 8.4 ,8.8,8.1,8.7 ppm and 7.8 ,7.9,7.5,7.4 ppm attributable to CH=N- and –NH protons respectively. The azomethine proton signal in the spectrum of the corresponding complexes are shifted downfield compared to the free ligands, suggesting the deshielding of the azomethine group due to the coordination with the metal ions.

3.5 Powder XRD Study

X-ray diffraction data was recorded by using Cu Kα radiation (1.5406 Angstrom).The intensity data over 2θ range of 4-60^o agreed with the reported standard data and no characteristic peaks were obtained . The mean grain size of the particles was determined from the XRD line broadening measurement using Scherre's equation**(2)**

$$d_{XRD} = 0.9\,\lambda \,/\, \beta \cos\theta \qquad \textbf{(2)}$$

Where λ is the wavelength (Cu Kα), β is the full width at half maxima (FWHM) and θ is the diffraction angle. The powder XRD shows thatCoGlu(val)$_2$.2H$_2$O and ZnGlu(val)$_2$.2H$_2$O complexes has the crystallite size of 42 nm and 40 nm andCoGlu(ala)$_2$.2H$_2$O and ZnGlu(ala)$_2$.2H$_2$O complexes has the crystallite size of 41 nm and 46 nm suggesting the microcrystalline nature.**(Fig 3 and 4)**.

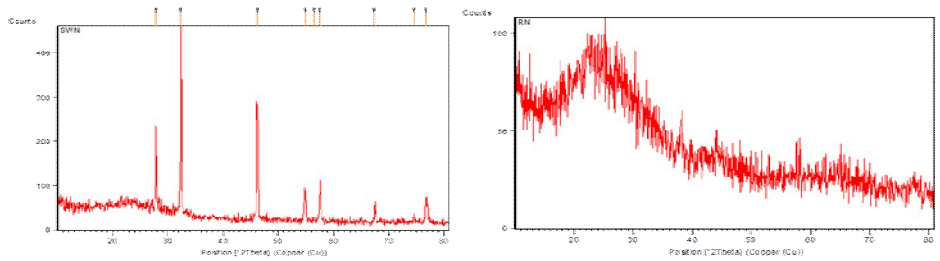


Fig. 3:PowderXRD pattern of the CoGlu(val)$_2$.2H$_2$O and ZnGlu(val)$_2$.2H$_2$O complexes

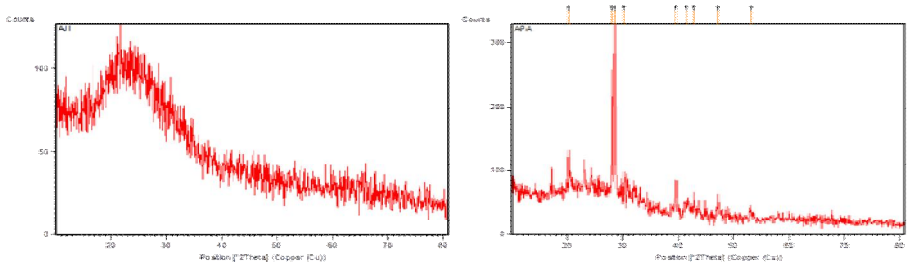


Fig. 4:Powder XRD pattern of the CoGlu(ala)$_2$.2H$_2$O and ZnGlu(ala)$_2$.2H$_2$O complexes

3.6 Scanning Electron Microscope

The scanningelectron micrographs taken at 20kV accelerating voltage with magnification from150x to 1000xreveal the morphology of the compounds. In SEM image macroscopic phase separation in dense layer , the domain size of about 100µm with void spaceswas noticed. The void spaces are certainly due to the result ofmacroscopic phase separation [8].The morphology showedthat the surface was spongy and soft with large macroscopic phase separation. The phase separation and the spongy nature was reduced due to the introduction of metalion. From SEM images, it was clear that there was a strong change in morphology ofSchiff base on complexation.**(Fig.5 and 6)**

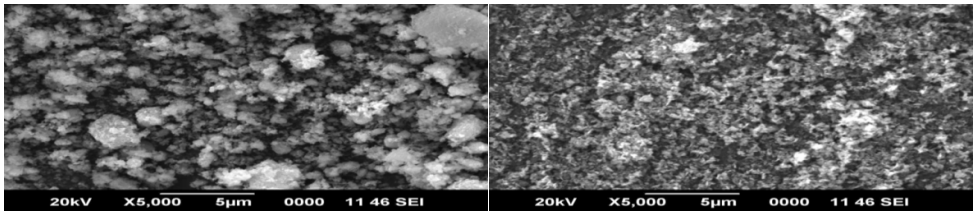


Fig. 5:SEM images of $CoGlu(val)_2.2H_2O$ and$ZnGlu(val)_2.2H_2O$ complexes

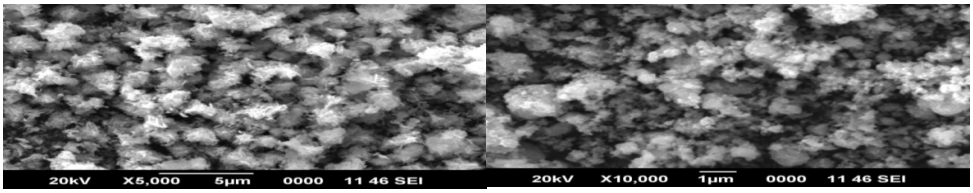


Fig. 6 :SEM images of $CoGlu(ala)_2.2H_2O$ and $ZnGlu(ala)_2.2H_2O$ complexes

3.7 Thermal Analysis

Thermogravimetric analyses were carried out from room temperature to 900°C .Calculated and experimental mass losses are comparable. The weight loss in the range 117–207°C with experimental mass loss of 2.35-2.55% in all the complexes indicates the loss of two coordinated water molecules (calculated value, 2.86%). This type of thermal behaviour is characteristic of coordinated water molecules. From 197°C to 463°C, a sharp decrease in weight indicated the loss of fragments from two Schiff base molecules from the complexes with experimental mass loss of 46.32-48.32% for all the complexes, respectively. In the final stage, in the 453-605°C temperature range, both decomposition products with experimental mass loss of 31.75–32.75% for the complexes and black residue were eliminated. Chemical analysis of the black final residue corresponds to the metallic oxide.

3.8. Antimicrobial Study

The qualitative screening of the susceptibility spectra of various microbial strains to newly synthesized compounds showed that all tested compounds exhibited antimicrobial effect quantified by the occurrence of a growth inhibition zone **Fig .7**.For all tested complexes, the diameters of the inhibition zones

were superior to those exhibited by the ligand.The lowest antimicrobial spectrum was noticed for the $ZnGlu(val)_2.2H_2O$ complex , while the largest inhibitions zones were exhibited by the $CoGlu(ala)_2.2H_2O$ complex.Tweedy's chelation theory offers an explanation for the increased antimicrobial activity of the metal complexes. In the chelated complex, the positive charge of the metal ion is partially shared with the donor atoms of the ligand and electron delocalization occurs over the whole chelate ring. In this way, the lipophilic character of the metal chelate is increasing and favouring its permeation through the lipid layers of the bacterial membranes and blocking the metal binding sites in the microorganism.

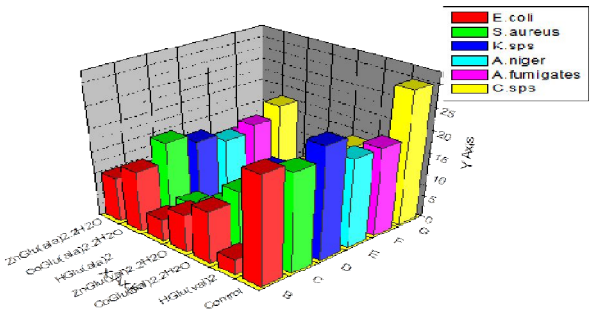
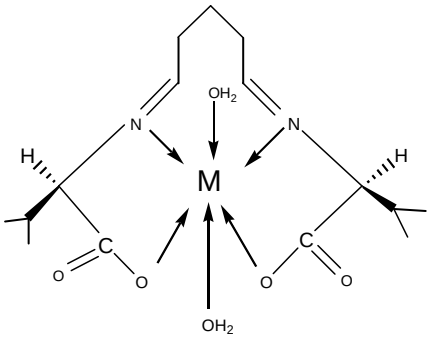


Fig .7: Antimicrobial activities of Schiff base ligands and its complexes by disc diffusion method (Zone inhibition in mm)

Based on the spectral and analytical data,the structure of the synthesized compounds are given below.



Where M is Co or Zn

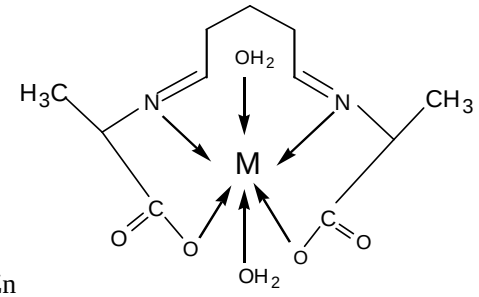


Fig .8: Structure of $HGlu(val)_2$ complexes

Fig.9: Structure of $HGlu(ala)_2$ complexes

IV. CONCLUSION

Four metal(II) complexes with the Schiff base derived by the condensation of Glutaraldehyde with L-alanine and L-valine have been synthesized and characterised. Data from IR spectra concluded that the ligand behaves as a tetradentate ligand. Electronic spectra and magnetic measurements indicate an octahedral geometry for the complexes. The results from the biological activity demonstrated that the newly synthesized

complexes could exhibit, in some cases, improved antimicrobial activity against both bacteria and fungi and can be used for the development of novel antimicrobial materials.

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