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RESEARCH ARTICLE

CHARACTERIZATION OF NOVEL Co(II)TRANSITION METAL COMPLEX OF ONO DONOR LIGAND DERIVED FROM GLUTARALDEHYDE AND L-HISTIDINE AND ITS SCREENING FOR TOXICITY AGAINST FUNGAL AND BACTERIAL SPECIES

***Ajith Sinthuja, S.**

Department of Chemistry, Holy Cross College (Autonomous), Nagercoil – 629004

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ABSTRACT

Coordination complex with metal ion Co(II) has been synthesized from the Schiff base (L) derived from glutaraldehyde and L-histidine. Both the ligand and the complex synthesized were characterised by elemental analyses, magnetic susceptibility, molar conductance, IR, UV-Vis, ^{1}H-NMR spectral studies, X-ray diffraction study, SEM study and thermal studies. On the basis of the above studies, it is proposed that the ligand is suggested to act in a tetradentate manner coordinating through both carbonyl oxygen and amino nitrogen atoms. The antimicrobial activities of the ligand and its complex were screened by Disc Diffusion method. The activity data shows that the metal complex is more potent than the parent Schiff base ligand against bacterial and fungal species.

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INTRODUCTION

The Schiff base ligands and their corresponding metal complexes have been expanded enormously and include a vast area of organometallic compounds and various aspects of bio inorganic chemistry (Osman, 2006). Schiff base ligands have been reported to show a variety of biological actions by virtue of the azomethine linkage, which is responsible for various antibacterial, antifungal, herbicidal, clinical and analytical activities (Rai and Puja Anand, 2012). Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest. Earlier work reported that some drugs showed increased activity, when administered as metal complexes rather than as organic compounds (Costamagna *et al*., 1992). Depending upon the nature of the metal centre, these chiral complexes are able to promote a variety of enantio selective transformations. It has been reported that the structure of the substituent bonded to the imino nitrogen affects the coordination geometry of the complex (Ahmed and Akhtar, 1983). 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 (Ajith Sinthuja and Sudhakumari, 2013). This may be attributed to their stability, biological activity (Krishnakutty *et al*., 2008) and potential applications in many fields such as oxidation catalysis and electrochemistry (Djebbar *et al*., 1998). These investigations emphasised the great relevance of these systems in basic and applied chemistry, molecular materials, microelectronics, sensors and so on. Their bimetallic cores have also been recognized as the active sites of many metalloenzymes (Hamada, 1997). Chelating ligands containing O,N and S donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to the metal ions. In this present research work, the results of the studies on the Co(II) metal complex of a Schiff base derived from glutaraldehyde and L-histidine has been reported. Tentative structure has been proposed on the basis of analytical, spectral, magnetic and conductance data. The Schiff base and its metal chelate were also screened for their antibacterial and antifungal activities against some species of pathogenic fungi and bacteria.

MATERIALS AND METHODS

Chemicals

Reagents such as Glutaraldehyde, L-Histidine and metal(II) nitrate were of Merck products. The solvents were purified by standard methods (Chohan *et al*., 2001).

**Corresponding author: Ajith Sinthuja, S.*
Department of Chemistry, Holy Cross College (Autonomous), Nagercoil – 629004

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 complex was determined at room temperature in DMSO (10^{-3}) on SYSTRONICS digital conductivity meter. Magnetic susceptibility of the complex was measured by Guoy balance using Copper sulphate as calibrant. IR spectra of the Schiff base and its complex 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 MH_z)of the samples in DMSO-d_6 were recorded on by employing TMS as internal standard at NIIST Trivandrum. Powder XRD was recorded on a computer controlled X-ray diffractometer system JEOL JDX 8030 at NIIST Trivandrum. Thermal behaviour of the sample was recorded in a thermal analyzer at NIIST Trivandrum. SEM study of the complex was performed in CUSAT, Kochi.The melting points of the ligand and the complex were recorded in open capillaries on a capillary melting point apparatus. Double distilled water was used throughout the experimental work.

Antibacterial and Antifungal evaluation

Antimicrobial activity of the tested samples were determined using a modified Kirby-bauer disc diffusion method. 100 µl of the tested bacteria/fungi were grown in 10 ml of fresh media until they reached a count of approximately 108 cells/mL for bacteria or 105 cells/ml for fungi.100 µl of microbial suspension was spread onto agar plates corresponding to the broth in which they were maintained. Isolated colonies of each organism that might be playing a pathogenic role were selected from primary agar plates and tested for susceptibility by disc diffusion method. Plates were inoculated with filamentous fungi, *Aspergillus niger* and *Aspergillus fumigates* at 25° C for 48 hours, Gram (+) bacteria *Staphylococcus aureus*, *Klebsiella sps* and Gram(-) bacteria *Escherichia* coli were incubated at 37° C for 48 hours and *Candida sps* was incubated at 30°C for 48 hours.

The diameters of the inhibition zones were measured in millimetres. Standard discs of chloramphenicol served as positive controls for antimicrobial activity but filter disc impregnated with solvent were used as a negative control. The agar used is Muller-Hinton agar that is rigorously tested for composition and pH. Further the depth of the agar in the plate is a factor to be considered in the disc diffusion method. This method is well documented and standard zones of inhibition have been determined for susceptible values. Blank paper discs with a diameter of 8.0 mm were impregnated with 10 µl of tested concentration of the stock solutions. When the filter paper disc impregnated with a tested chemical is placed on agar, the chemical will diffuse from the disc into the agar. The chemical and its molecular size will determine the size of the area of chemical infiltration around the disc. If an organism is placed on the agar it will not grow in the area around the disc if it is susceptibile to the chemical. This area of no growth around the disc is known as a “Zone of inhibition” or “clear zone”

Synthesis of Schiff base

The Schiff base ligand was prepared by reacting glutaraldehyde and L-histidine in 1:2 molar ratio by refluxing in distilled methanol. The mixture was refluxed for 1 hour. The reaction was examined by TLC with time to time till completion. The solvent was partially evaporated and the yellowish mass product was precipitated by cooling and filtered off, washed with distilled water dried, recrystallised and finally preserved in a desiccators.

Synthesis of Schiff base complex

Cobalt (II) nitrate was dissolved in 200 cm^3 of methanol. The filtered solution was added dropwise into 20cm^3 methanolic solution of the Schiff base ligand(H glu-his.$2H_2O$), the resulting mixture was refluxed and stirred for 8 hours. After refluxing, the volume of the solution was reduced to one third and the concentrate was cooled at 0ºC. The precipitated complex was filtered off, washed several times with cold ethanol and dried in vacuo over anhydrous $CaCl_2$.

RESULTS AND DISCUSSION

The metal complex gives satisfactory elemental analysis values and are in close agreement with the values calculated for expected molecular formulae assigned to the complex suggesting 1:1 stoichiometric ratio. The synthesized metal complex is normally stable at room temperature and hygroscopic in nature. The Schiff base ligand is soluble in common organic solvents like ethanol and methanol. The corresponding complex is soluble in DMSO. The results of elemental analysis with molecular formula are presented in

Table 1. The Co(II) complex is non-electrolytic in nature as the molar conductivity measurements in DMSO is found to be 11.31 ohm^{-1} cm^2 mol^{-1}. The complex is paramagnetic in nature and its magnetic moment is 5.32 BM.

UV-Visible Spectra

The UV-Visible spectra are often very useful in the evaluation of results furnished by other methods of structural investigation. The electronic spectral measurements were 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 of the Schiff base ligand and its complex were recorded in DMSO solution in the range of 200 to 800 nm regions. It is usually recorded as a plot of absorbance (A) versus wavelength (cm^1).Upon the electronic spectrum of the Schiff base ligand, an intense band centered at 275 nm was observed which is assigned to − - −* transition of the C=N chromophore. On complexation, this band was shifted to lower wavelength region at 235 nm suggesting the coordination of azomethine nitrogen with Co(II) ion. The spectra also shows other transitions in the range of 337 and 348 nm which can be assigned to n - −* transition.

Table 1. Analytical and physiochemical data of Glu- his Schiff base and its metal complex

Ligand/Metal Chelate	Empirical Formula	Colour	M:L ratio	Molar Cond. (Ohm^{-1} cm^{2} mol^{-1})	Elemental Analysis % Found (cal)			
					C Found (Cal)	H Found (Cal)	N Found (Cal)	M Found (Cal)
H Glu(His)$_2$ ligand	$C_{17}H_{22}N_6O_4$	Yellow	-	-	63.43 (63.40)	9.15 (9.18)	8.20 (8.17)	-
(Co Glu(His)$_2$.2H$_2$O)	$C_{17}H_{22}N_6O_4Co$	Pale red	1:1	11.31	47.67 (48.64)	8.19 (8.11)	6.58 (6.50)	13.91(13.85)

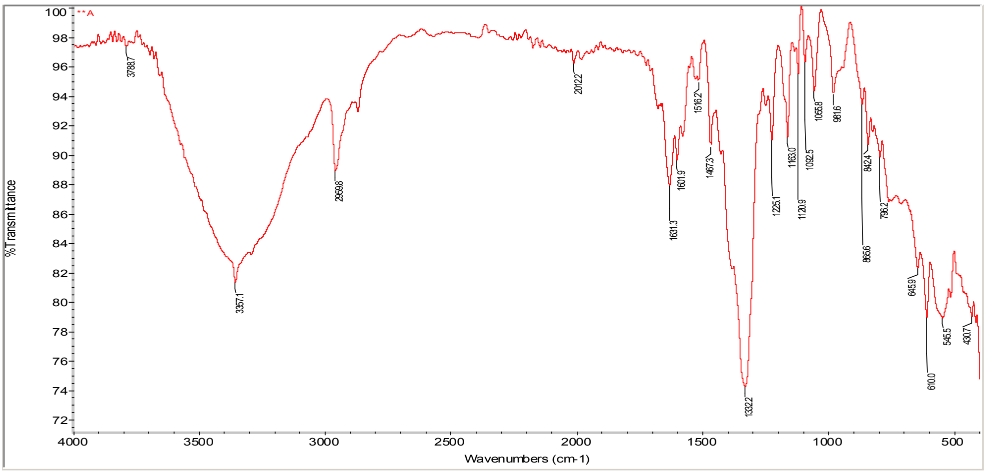


Fig. 1. IR spectrum of Glu-his Schiff base metal Complex

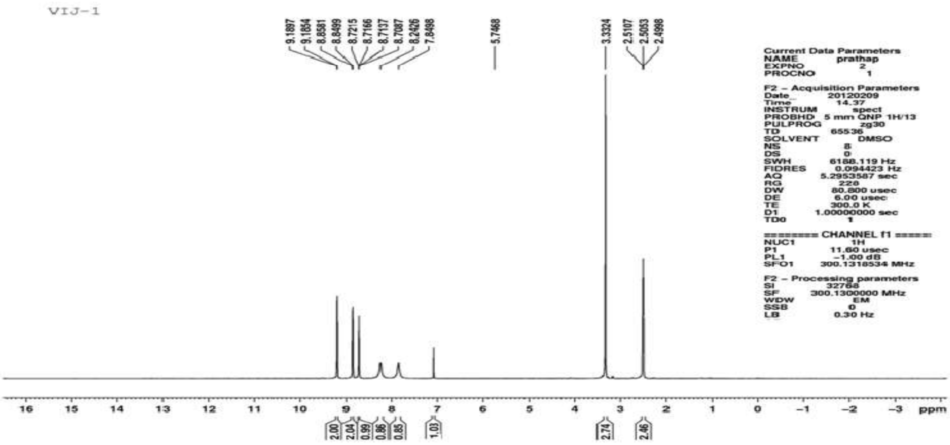


Fig. 2. ^{1}H NMR spectrum of Glu-his Schiff base Complex

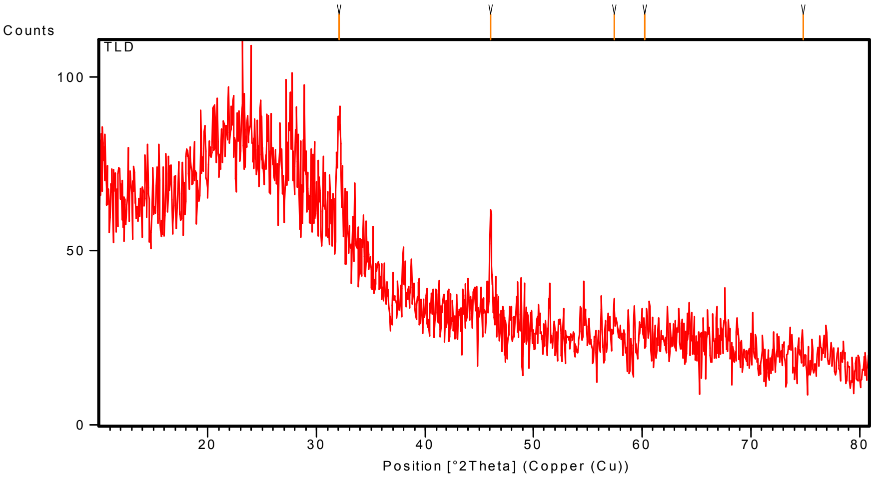


Fig. 3. Powder XRD pattern of the Glu-his Schiff base complex

The weak band in the region 400-500 nm is due to charge transfer band in the Co(II) complex which does not exist in the ligand H Glu $(His)_2$. However, the weak broad band in the region 500-600 nm is due to d-d transitions of the metal ion. Information concerning the geometry of the newly synthesized metal complex was obtained from the electronic and magnetic moment values.

Magnetic susceptibility measurement

The magnetic susceptibility measurement help to predict the possible geometry of the metal complex. In paramagnetic Co(II) complex often the magnetic moment (μ_{eff}) gives the spin only value ($\mu_{s.o}=(n(n+2)^{1/2}$ B.M) corresponding to the number of unpaired electron. The variation from the spin only value is attributed to the orbital contribution and it varies with the nature of coordination and consequent delocalization. The octahedral geometry of Co(II) complex has a magnetic moment, configurations ,stereochemistry, hybrid orbitals, number of unpaired electrons, and expected value as 5.32 BM, d^6, octahedral, sp^3d^2, 4, 5.39 BM. Thus the value of magnetic moment of a complex would give valuable insights into its constitution and structure. The magnetic moment of the Co(II) complex lies within the expected value for octahedral complexes.

Infra red spectra

Inorder to study the binding mode of the Schiff base to the metal in the complex, IR spectra of the free ligand was compared with metal complex. The IR spectra provide valuable information regarding the nature of functional group attached to the metal ion.The IR spectra of the ligand showed a broad band in the region 3300-3400 cm^{-1} which can be assigned to the intramolecular hydrogen bonded -OH groups. The appearance of this peak in the spectra of the complex indicates that the-OH group is from complexation. The spectrum of the ligand shows -C=N band in the region 1654 cm^{-1} which is shifted to lower frequency region 1631cm^{-1} in the spectrum of the corresponding metal complex indicating the coordination of –C=N nitrogen with Co^{2+} ion. Thus, the ligand acts as a tetradentate chelating agent, bonded to the metal ion through the two nitrogen atoms and two oxygen atoms of the two carboxylate ions. Assignment of the proposed coordination sites is further supported by their appearance of medium bands at 450-430 cm^{-1} which could be attributed to ν_{M-N} . In addition, the Co(II) complex shows a band at 545 cm^{-1} attributed to M-O frequency. The IR spectrum of the Schiff base complex is given in Fig 1.

^{1}H NMR Spectrum

The ^{1}H NMR Spectrum of the ligand H $Glu(His)_2$ recorded in DMSO solution shows a multiplet at 2.5, 1.8 ppm due to the methyl protons. Furthermore, the ^{1}H NMR Spectrum of the Schiff base complex (Co $Glu(His)_2 2H_2O$) exhibited signals at 8.4 and 7.8 ppm, that is attributable to CH=N- and –NH protons respectively. The azomethine proton signal in the spectrum of the corresponding complex is shifted downfield compared to the free ligand, suggesting the deshielding of the azomethine group due to the coordination with the Co^{2+} ion. There is no appreciable change in all other signals of the complex. The ^{1}H NMR spectrum of the Schiff base complex is given in Fig 2.

Powder XRD Study

X-ray diffraction data was recorded by using Cu Kα radiation (1.5406 Angstrom).The intensity data was collected over a 2θ range of 4-60°. The average crystallite size of the complex could be estimated with the help of Scherre's equation, using the diffraction intensity peak. All the diffraction peaks in the X-ray diffraction pattern of the Co(II) complex agreed with the reported standard data and no characteristic peak was obtained other than the oxide MO. The mean grain size of the particles was determined from the XRD line broadening measurement using the formula, Scherre's equation (1)

$$d_{XRD} = 0.9 \lambda \ / \beta \cos \theta \qquad (1)$$

Where λ is the wavelength(Cu Kα), β is the full width at half maxima (FWHM) and θ is the diffraction angle. A definite line broadening of the diffraction peak is an indication that the synthesized material is microcrystalline. The lattice parameter calculated was also in agreement with the reported value. The powder XRD shows that Co(II) complex has the crystallite size of 44 nm suggesting the microcrystalline nature. The powder XRD pattern of the Co(II) Schiff base complex is given in Fig. 3.

SEM study

SEM technique is extensively used for studying the morphological features of the Schiff base complex. The physical property and molecular architecture of the synthesized Co(II) Schiff base complex was studied by using scanning electron microscopy. Fig 4. shows the image of the synthesized CoO nanoparticles with an image magnification. The assembly was attached to a computer running a program to analyse the mean size of the particles in the samples. It should be noted that the particle diameter is always overestimated due to the distortion of SEM image.

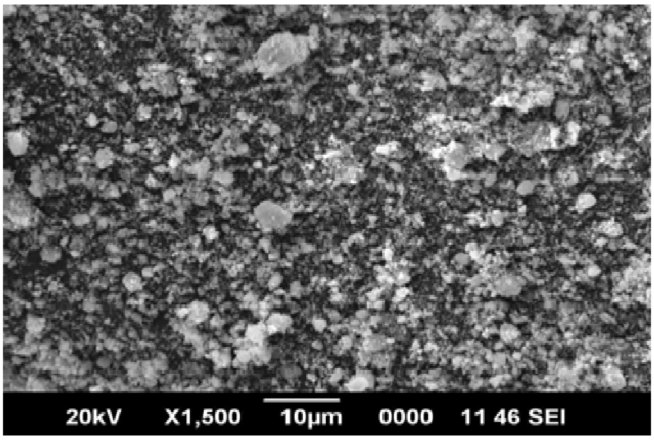
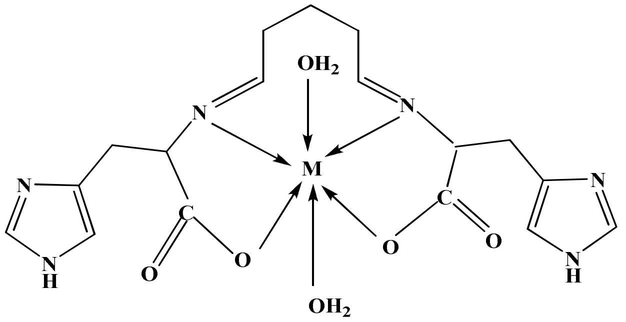


Fig. 4. SEM image of the Glu-his Schiff base complex

TGA study

In thermogravimetric analysis (TGA), the percentage mass loss at different steps have been recorded. The complex lose its weight in the temperature range 160-250^{o}C corresponding to two coordinated water molecules with an endothermic peak in DTA curve. After the total loss of water molecules, the decomposition occurs in the range 660-740^{o}C that indicates the decomposition of the ligand. The observed residue corresponds to the respective metal oxide. Based on the spectral and analytical characterization studies the expected geometry for the Co(II) complex is shown in **Fig.4**.

From the MIC values obtained ,it was found that the complex exhibited higher activity than the free ligand (Table 2). This may be ascribed to the increased lipophilic nature of the complex arising due to chelation. On chelation, the polarity of the metal ion get reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charges of metal ion with donor groups. Further, it increases the delocalization of electrons over the whole chelate ring, enhances the penetration of the complexes into lipid membranes and blocking of the metal binding sites in the enzymes of microorganisms.



where M is Co

Fig. 4. Structure of Glu-his Schiff base complex

Table 2. Antimicrobial activities of Glu-His Schiff base and its Co(II) complex by disc diffusion method (Zone inhibition in mm)

Compound	Microbial Species					
	E.coli	S.aureus	Kleb.sps	A.niger	A.fumigates	Candi.sps
Control	24.0	22.0	25.0	20.0	20.0	30.0
Schiff base	5.0	2.5	3.5	4.0	4.0	3.0
Metal complex	10.0	10.0	8.5	11.5	11.0	10.0

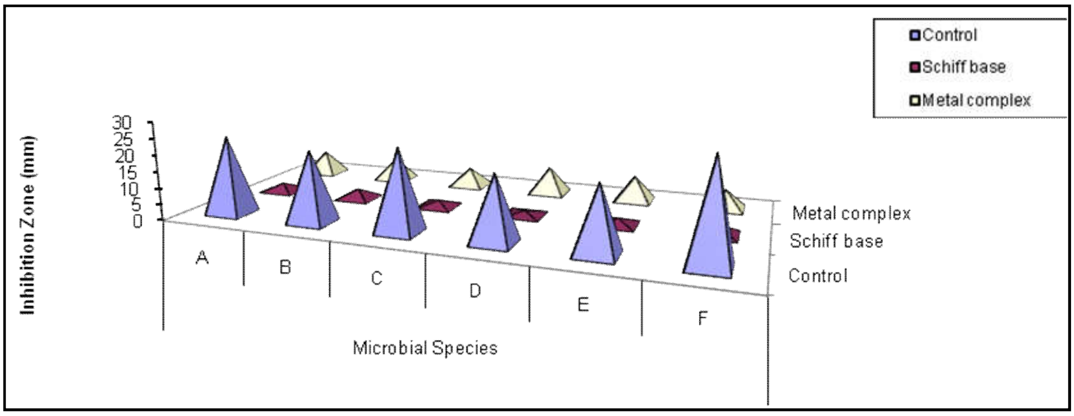


Fig. 5. Antimicrobial activities of Glu-His Schiff base and its Co(II) complex by disc diffusion method (Zone inhibition in mm)

A-Escherichia coli
B-Staphylococcus aureus
C-Klebsiella sps
D - Aspergillus niger
E - Aspergillus fumigates
F - **C**andida sps

Antimicrobial Study

The *In vitro* antimicrobial study of the investigated compounds were tested against the bacteria *Klebsiella sps, E.coli, Staphylococcus aureus* and fungi *Candida sps* , *Aspergillus niger* and *Aspergillus fumigates* by Disc diffusion method. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organism.

Conclusion

In this paper, the synthesis of a Schiff base ligand H Glu(His)$_2$ by the reaction of Glutaraldehyde and L-histidine has been reported. Co Glu(His)$_2$.2H$_2$O complex has been synthesized using the Schiff base ligand H Glu(His)$_2$ and characterized by spectral and analytical data. Based on these data, an octahedral geometry has been assigned to the Co(II) complex. The very low conductance value for the complex indicates the non-electrolytic nature of the complex. The synthesized Co(II) complex is found to be more bioactive and shows good antimicrobial property.

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