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Synthesis, characterization and antimicrobial activity of Ni(II) and Zn(II) complexes with amino acids and heterocyclic amine

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ABSTRACT

Mixed ligand complexes of Ni(II) and Zn(II) have been synthesized and characterized with amino acids and heterocyclic amine. The synthesized complexes were characterized on the basis of elemental analysis, conductometric, magnetic moment measurements, electronic spectra analysis, and FTIR spectral studies. The complexes are found to be colored, electrolytic and diamagnetic in nature. Our results indicate that the Ni(II) complexes are octahedralgeometry, while Zn(II) complexes are tetrahedral structure. The synthesized complexes showed remarkable antimicrobial activity.

Keywords: Mixed ligand complexes; Electronic spectra; Amino acids; Heterocyclic amine; Antimicrobial activity.

INTRODUCTION

Co-ordination compounds show different characteristic properties that depend on the metal ion to which they are bound. The metal complexes have wide applications in various fields of human interest that depend on the nature of the metal and type of the ligand [1,2].Transition metals play a vital role in biological systems such as respiration, nitrogen fixation, photo- synthesis and cell division [3]. The importance in the mechanism for storage, transport and accumulation of transition metals in living organisms depends on the presence of transition metals in human blood plasma[4,5]. The mixed ligand complexes are revealing valuable information about the elucidation of enzymatic processes of biological relevance [6,7]. These complexes are well-known to be biologically active against pathogenic microorganisms [8,9]. Amino acids are form complexes with metal atoms and exhibit significant enzymatic and biological activities [10].Antimicrobial activities of Ni(II) and Zn(II) ions have been reported [11]. The synthesis, spectrochemical properties, structure, stability, thermochemical study, and characterization of Ni(II) complexes with histidine, glycine, alanine, and other amino acids have previously been reported [12-15].

The synthesized Ni(II)-cysteine complex and studied its antineoplastic activity against ehrlich ascites arcinoma (EAC)cells in swiss albino mice have been described [16]. This information's have inspired us to search for new coordination compounds having pronounced bacterial activities. In this connection we synthesized some Ni(II)

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complexes with amino acid and heterocyclic amine bases and studied anti-bacterial and anti-fungal properties against four and three pathogenic bacteria and fungi.

The observed Ni(II) and Zn(II)complexes are soluble in DMF and DMSO; low molar conductance values indicate that they are non-electrolytes. The Zn(II) complexes showed good biological and exhibit enhanced activities as compared to their parental ligands [17].The complexes of Ni(II) and Zn(II) showed good bactericides and fungicides [18]. In the present study, we synthesized and characterized of the mixed ligand complexes of Ni(II) and Zn(II) with amino acids such as glycine and β-alanine that played primary ligands and heterocyclic amine such as 8-hydroxyquinolinewhich was act secondary ligand.

MATERIALS AND METHODS

1.1. Reagents and Chemicals

Nickel chloride, $NiCl_2.6H_2O$ (Thomas & Baker, ≥97%), Zinc chloride, $ZnCl_2$ (≥97%) obtained from May &Baker (England). All the ligands were purchased from BDH (England). Solvents were purified and dried according to standard procedures.

2.2. Physical Measurements

The melting or decomposition temperature of all the prepared metal complexes was observed in an electro thermal melting point apparatus model SMP30. It was not possible to measure the melting points beyond 390°C. The sherwood scientific magnetic susceptibility balance was used for the present study. Infrared spectra (KBr) were recorded in a shimadzu FTIR- 8400 (Japan) spectrophotometer in the range of 4000-400 cm^{-1}. The absorbance's of the complexes were noted on shimadzu spectrophotometer (modelUV-1800).

2.3. General Method for the Preparation of the Complexes

An ethanolic solution of Ni(II) chloride and Zn(II) chloride (5 mM and 5 mM) and ethanolic potassium hydroxide solution (just dissolved) of amino acids (for Ni(II) complexes glycine and β-alanine 10 mM and for Zn(II) complexes glycine and β-alanine 5 mM) were mixed and gently heating with stirring for half an hour but no precipitate was observed. Then secondary ligand(8-hydroxyquinoline) in calculated ratio was added to the resulting mixture and heat on a magnetic regulator hot plate with constant stirring. The volume of the solution was reduced to one half and allowed to cool. The precipitate formed and were filtered washed several times with ethanol and then dried in desiccators over anhydrous $CaCl_2$.

2.4. Antibacterial and antifungal screening

The antibacterial and antifungal activities of the complexes were tested against the bacterial species: Gram positive (*Bacillus cereus* and *Staphylococcus aureus*) and Gram negative (*Escherichia coli* and *Shigella sonnei)* and the fungal species: *Candida albicans*, *Saccharomyces cerevisiae* (Human Pathogens) and *Aspergillus niger* (Plant Pathogens). These studies were carried out using diffusion method [19,20]. Ciprofloxacin and fluconazole were used as the standard antibacterial and antifungal agents. All the complexes dissolved in DMSO were used for study.

RESULTS AND DISCUSSION

3.1. Elemental analysis and conductivity measurement

The physical properties of the Ni(II) and Zn(II) complexes were tabulated in table 1. Their structures have been proposed on the basis of conductivity and magnetic moment measurements. The molar conductance of 10^{-3} M solution of the complexes in DMSO was measured at room temperature. The molar conductance values ranged from 7.4 to 35.5ohm^{-1} cm^{2} mol^{-1} indicates that the compounds are non-electrolytes [21].

3.2. Magnetic moment and electronic spectra

The observed effective moment (μ_{eff}) values of the Ni(II) and Zn(II) complexes at room temperature are given in table 1. The complexes under investigations were found to be diamagnetic [22-24] have shown the presence of no unpaired electron. The electronic spectra of all complexes were recorded in 10^{-3} M DMSO at room temperature. The electronic spectra of [Ni(Gly)$_2$(8-HQ)] and [Ni(β-Ala)$_2$(8-HQ)] complexes were shown 340, 409 and 340, 408 nm respectively, and these are suggestive of octahedral geometry around Ni(II) ion [25,26]. In Zn (II) complexes, d^{10} orbital is completely filled that's why it does not show any d-d electronic transition but exhibit charge transfer spectra [27]. The [Zn(Gly)(8-HQ)] and [Zn(β-Ala)(8-HQ)] complexes were shown339, 399 and 336, 398 nm due to the L → M charge transfer transition that correspond to tetrahedral structure[28,29]. The all data of electronic spectra of Ni(II) and Zn(II) complexes as shown in table 2 and Fig. 2.

3.3. FTIR studies

FTIR spectrums of the Ni(II) and Zn(II) complexes were shown in table 3 and Fig.3. The complexes 1 to 4 shows υ(N-H) and 1 to 2 shows υ(-NH_2) bands respectively from 3395-3645 cm^{-1} and 3365-3375 cm^{-1} which is significantly lower than the free ligand (amines band 3500 cm^{-1} and amino band 3395-3645 cm^{-1}) that clearly suggest the coordination of amines group through nitrogen atoms of amine bases. The complexes display bands in the regions of 1485-1590 and 1220-1360 cm^{-1} due to υ(C=O) and υ(C-O) respectively, significantly lower than that of free ligand 1760 cm-^{1} for υ(C=O)and 1220 cm^{-1} for υ(C-O)respectively indicating the coordination of metal ion through its carboxylate anion. The disappearance of the υ(O-H) mode observed in the free amino acid molecule clearly indicate the loss of proton for O-H group upon coordination, revealing that acids are di-negative bi-dentate ligand coordinating through the carboxylate anion. The presence of metal nitrogen bonding in the complexes is evident from the appearance of υ(M-O) bands at 645-850 cm^{-1} in the spectra of the complexes and υ(M-N) appearance at 500 to 525 cm^{-1}.

3.4. Antibacterial and antifungal screening

Metal complexes play an important role in regulating biological activities. The antimicrobial activity is depending on the nature of metal ions and cell membrane of the microorganisms [30]. The antibacterial and antifungal screening results as shown in Table 4 and 5. All the complexes showed remarkable antimicrobial activities and the good zone of inhibition observed. The produced zone of inhibition by each complex was measured in mm.

Table 1: Analytical data and physical properties of the complexes

No.	**Complex, molecular wt.**	**Color and decomposition temp. (±5^{0}C)**	**Molar Conductance (ohm^{-1} cm^2 mol^{-1})**	**Magnetic moment μ_{eff} (B.M.)**	**Analysis, % found(cal.)**				
					Metal	C	H	N	O
a	[Ni$(Gly)_2$(8-HQ)], 350.97	Light green, 272	07.4	Dia	16.79 (16.72)	44.53 (44.49)	4.09 (4.02)	12.07 (11.98)	22.83 (22.79)
b	[Ni$(β\text{-}Ala)_2$(8-HQ)], 379.01	Light green, 380	35.4	Dia	15.54 (15.48)	47.62 (47.54)	4.85 (4.79)	11.14 (11.09)	21.18 (21.10)
c	[Zn(Gly)(8-HQ)], 283.60	Light green, 170	08.9	Dia	23.14 (23.06)	46.65 (46.57)	3.64 (3.56)	9.86 (9.88)	16.99 (16.93)
d	[Zn(β-Ala)(8-HQ)], 297.62	Light green, 165	30.5	Dia	22.03 (21.97)	48.51 (48.43)	4.11 (4.06)	9.49 (9.41)	16.22 (16.13)

Table 2: Data for the determination of UV-visible spectral bands

No.	**Complex**	**Band -1**	**Band -2**
a	[Ni$(Gly)_2$(8-HQ)]	409	340
b	[Ni$(β\text{-}Ala)_2$(8-HQ)]	408	340
c	[Zn(Gly)(8-HQ)]	399	339
d	[Zn(β-Ala)(8-HQ)]	398	336

Table 3: Data for the determination of FTIR Spectroscopy in cm^{-1}

No.	**Complex**	**υ(N-H)**	**υ(-NH_2)**	**υ(C=O)**	**υ(C-O)**	**υ(M-O)**	**υ(M-N)**
a	[Ni$(Gly)_2$(8-HQ)]	3637.87	3367.86	1575.54	1228.34	647.96	503.00
b	[Ni$(β\text{-}Ala)_2$(8-HQ)]	3642.24	3370.24	1571.38	1222.72	650.37	500.81
c	[Zn(Gly)(8-HQ)]	3400.02	-	1497.07	1347.98	841.02	516.99
d	[Zn(β-Ala)(8-HQ)]	3399.16	-	1493.32	1359.88	848.36	520.04

Table 4: Antibacterial activity of the synthesized complexes

Complex	**Zone of inhibition, diameter in mm**			
	Bacillus cereus	***Staphyllococeus aureus***	***Escherichia coli***	***Shigella sonnei***
[Ni$(Gly)_2$(8-HQ)]	22	30	30	15
[Ni$(β\text{-}Ala)_2$(8-HQ)]	20	20	16	20
[Zn(Gly)(8-HQ)]	10	10	10	16
[Zn(β-Ala)(8-HQ)]	6	6	6	10
Ciprofloxacin	30	40	30	40

Table 5: Antifungal activity of the synthesized complexes

Complex	Zone of inhibition, diameter in mm		
	Candida albicans	*Asperglllus niger*	*Saccharromyces cerevaceae*
[Ni(Gly)$_2$(8-HQ)]	18	22	20
[Ni(β-Ala)$_2$(8-HQ)]	16	16	22
[Zn(Gly)(8-HQ)]	14	15	12
[Zn(β-Ala)(8-HQ)]	6	12	16
Fluconazole	12	12	12

Where, Gly=Glycine, β-Ala= β-Alanine, 8-HQ=8-Hydroxyquinoline.

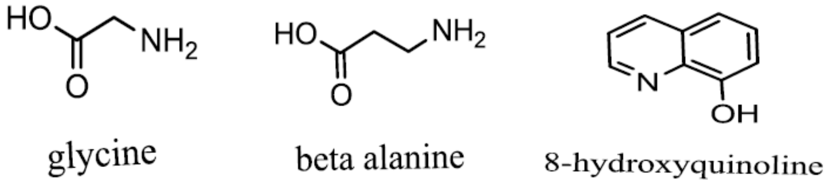

Figure 1: Structures of the ligands

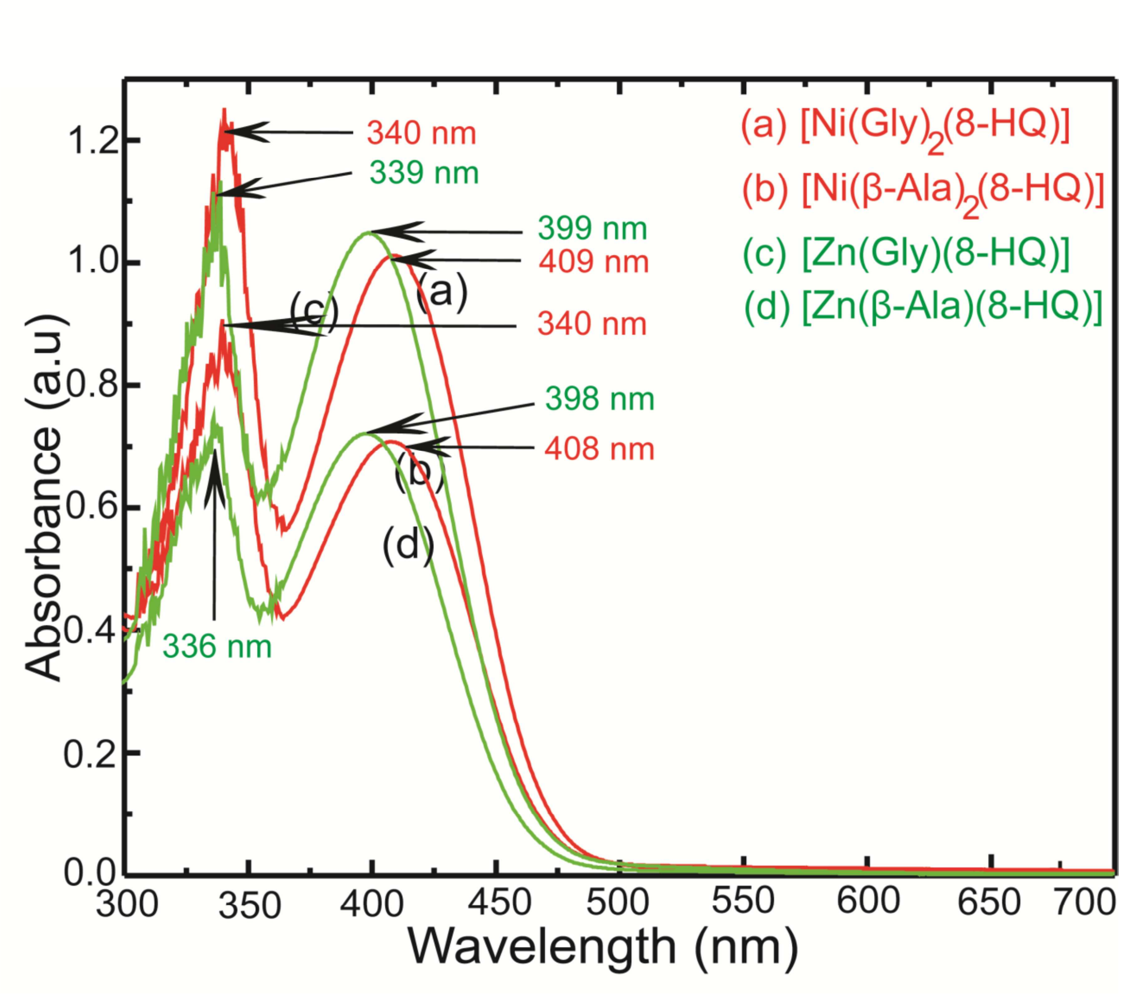

Figure 2: UV/VIS absorption spectra achieved from the complexes of [Ni(Gly)$_2$(8-HQ)], [Ni(β-Ala)$_2$(8-HQ)], [Zn(Gly)(8-HQ)], and [Zn(β-Ala)(8-HQ)]

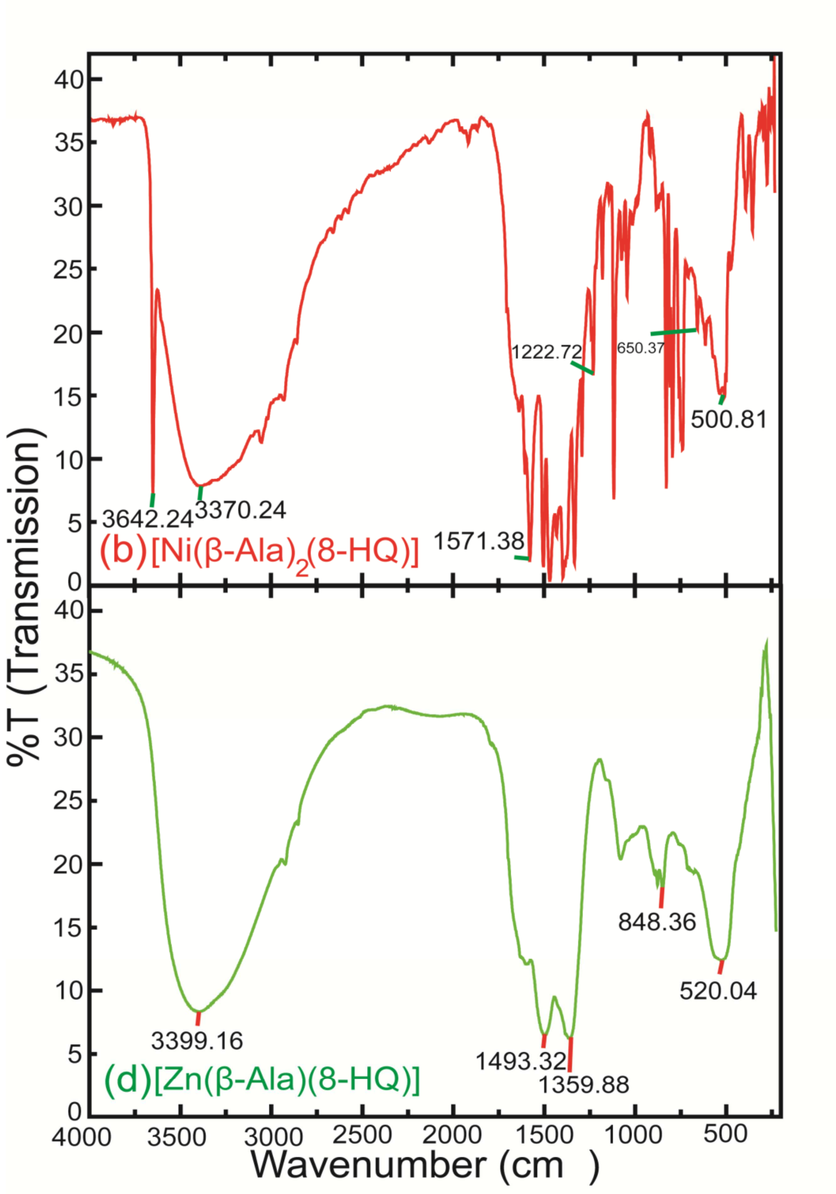

Figure 3: FTIR spectra of the complexes [Ni(β-Ala)$_2$(8-HQ)], and [Zn(β-Ala)(8-HQ)]

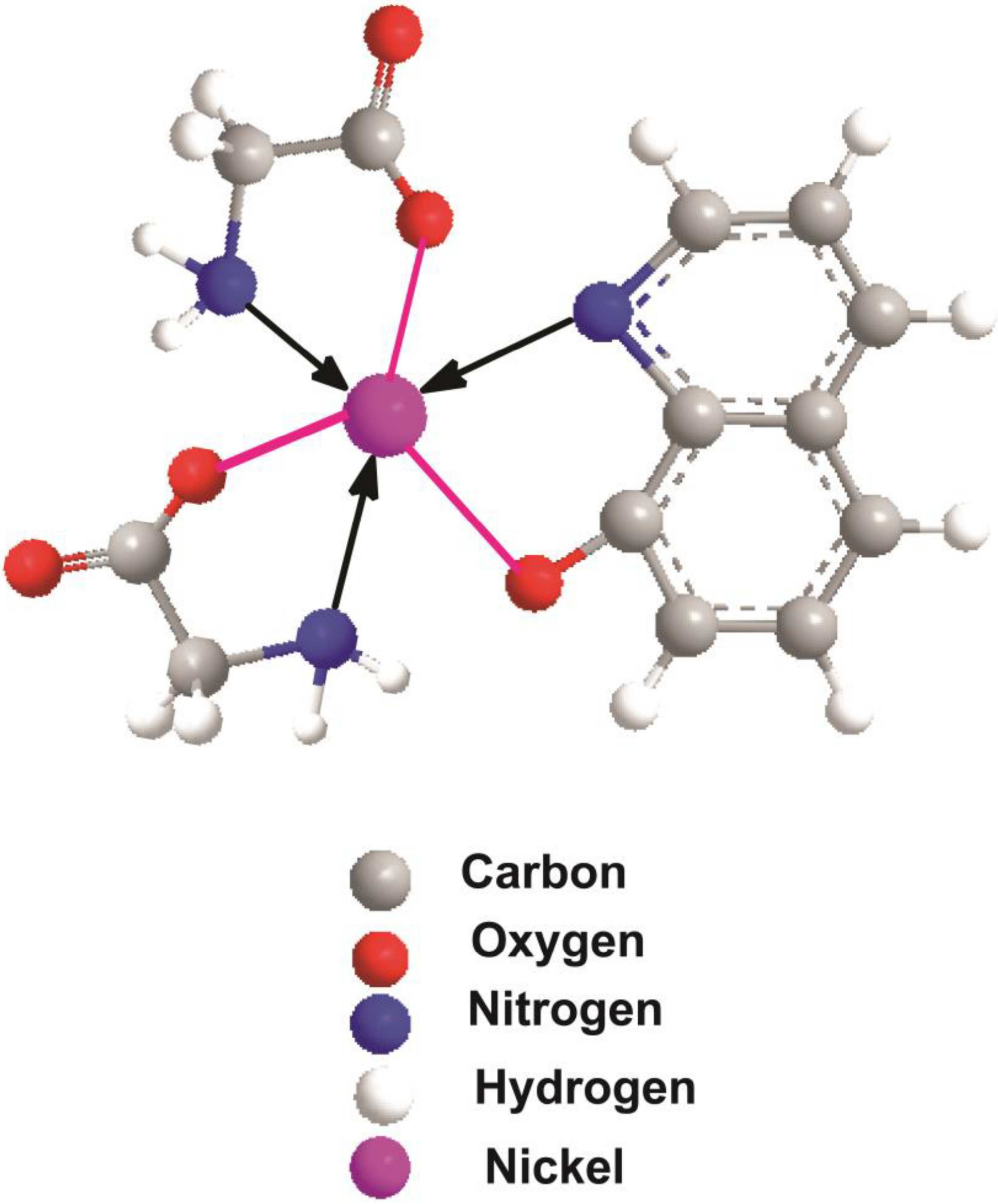

Figure 4: Probable 3-D structure of the complex [Ni(Gly)$_2$(8-HQ)]

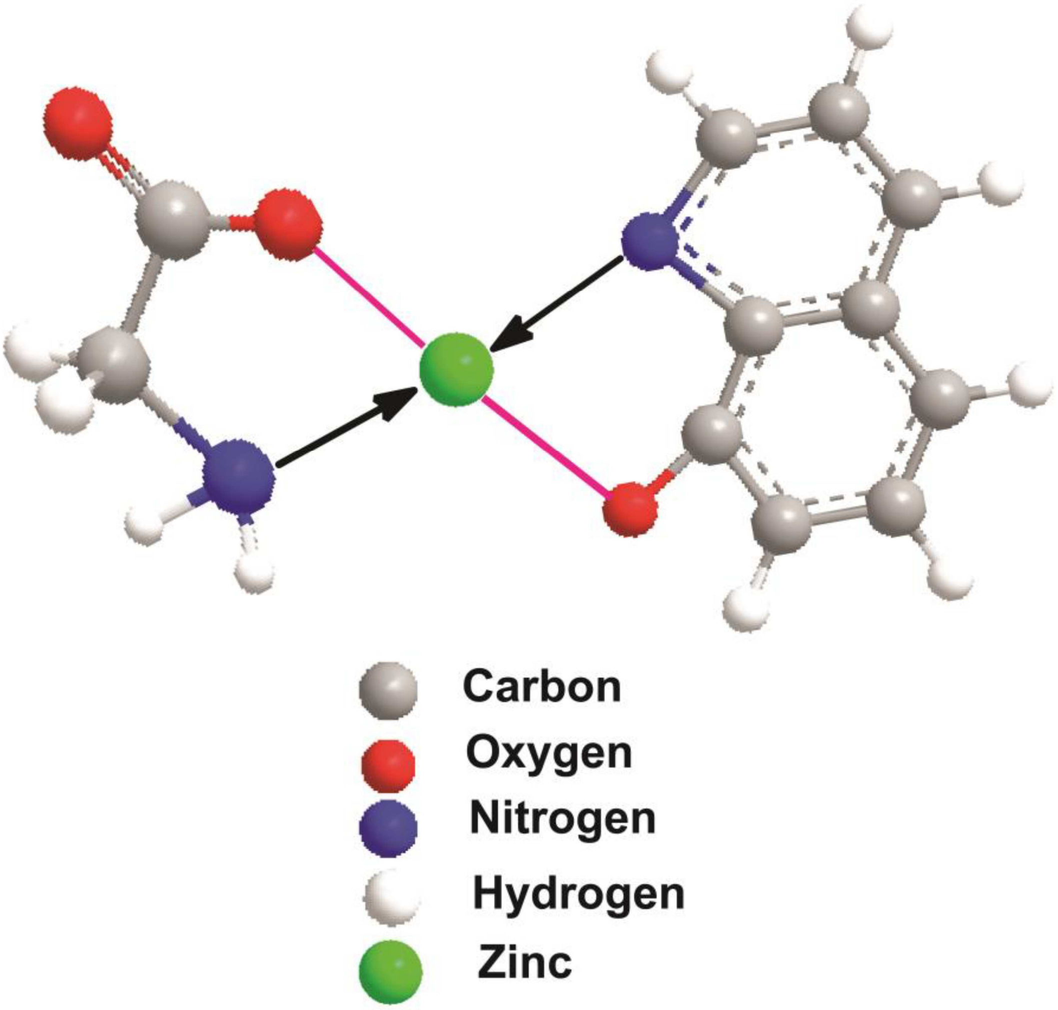

Figure 5: Probable 3-D structure of the complex [Zn(Gly)(8-HQ)]

CONCLUSION

Conductivity measurement indicated that the compounds are non-electrolytes. Magnetic susceptibility measurement showed that the complexes are diamagnetic. The electronic spectral data are in conformity with the transitions of octahedral for Ni (II) and tetrahedral for Zn (II) structure respectively. The IR spectral data indicated that the ligands coordinate to the metal through O and N atoms. All the complexes revealed remarkable antimicrobial activity. Based on the above analysis we have been proposed the structure of [Ni(Gly)$_2$(8-HQ)], and [Zn(Gly)(8-HQ)] complexes as shown in Fig. 4 and Fig. 5.

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