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**Synthesis and Characterization with Antimicrobial activity of Ni(II) and Zn(II) Metal Complexes Containing Diphenyl Acetic Acid and Heterocyclic Amine Bases**

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**ABSTRACT**

Mixed-ligand metal complexes of Ni(II) and Zn(II) with Diphenylacetic acid and heterocyclic amines bases have been synthesized. The complexes of the following compositions were prepared  $[M(RCOO)(L)(H_2O)]_2Cl_2$ , where, M=Ni(II) and Zn(II)R=(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH, L=Quinoline, 2-picoline, pyridine, isoquinoline, 2-aminopyridine, α-pic=α-picoline, Py=Pyridine. Synthesized complexes were characterized on the basis of elemental (metal) analysis, conductivity measurements, magnetic measurements, infrared and UV spectral studies. The IR spectral data indicated that the ligand coordinated to the metal through O and N atoms. Magnetic moments are in good agreement with the square planer geometry of metal complexes. The present results revealed that the complexes are more microbial toxic than the free metal ions or ligands. The complexes showed strong to mode-rate activity against both Gram positive and Gram negative bacteria compared to standard Kanamycin indicating the higher zone of inhibition.

**Keywords:** Mixed ligand, Diphenyl acetic acid, Heterocyclic amines bases, Antimicrobial studies

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**INTRODUCTION**

The organic bidentate ligands find extensive application in different fields. They contain donor atoms like Nitrogen. Oxygen and Carboxyl groups, therefore their interaction with metal atom ions give complexes of different geometries and are capable to show biological activity [1]. The organic compounds containing carboxylic or dicarboxylic groups have both salt forming and coordinating properties. The resulting complexes are generally insoluble in polar solvents and soluble in non-polar solvents and hence are very important from analytical, industrial and pharmaceutical point of view. Metal ions co-ordinate with carboxylic acid groups also has antiseptic properties of films, fibres and fabrics. Studies on the metal complexes of heterocyclic amines have been carried out by several workers [2-12]. In the present investigation heterocyclic amines have been used in most of the cases as secondary ligands. Heterocyclic bases have a great importance in biological and industrial fields. Most of the heterocyclic bases are used as corrosion inhibitors [13] and as antibacterial, anticonvulsive, antifungal and antifouling agents. Their activity is generally enhanced when they are allowed to form complex with metal ions [14]. Thus their complexes with copper exhibit potent antitumor and bacterial activities [15,16]. It has great importance anti in Biological and industrial fields. In this research paper, We are going to report the synthesis and characterization of several new mixed ligand complexes of Ni(II) and Zn(II) metals with diphenyl acetic acid and heterocyclic amine bases.

## MATERIALS AND METHODS

### Reagent and chemicals

NiCl<sub>2</sub>·6H<sub>2</sub>O, ZnCl<sub>2</sub>·6H<sub>2</sub>O Diphenyl acetic acid, heterocyclic amine bases (Quinoline, isoquinoline,  $\alpha$ -picoline,  $\gamma$ -picoline, 2-amino pyridine), triethylamine supplied were Aldrids (Analytical reagent) grade.

### Physical measurements

The melting or decomposition temperatures of all the prepare complexes were observed in an electrothermal melting point apparatus model No. AZ6512. The SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance was used for the present investigation. Infrared spectra as KBr disc were recorded on Shimadzu IR-470, Perkin Elmer IR-883 and genesis series FTIRTM 9423-240-08061 spectrophotometer as KBr pellets in the region 4500-400 cm<sup>-1</sup> in the Department of Chemistry Rajshahi University, Rajshahi. Antibacterial Activity was investigated in the Department of Pharmacy, Rajshahi University, Rajshahi.

### GENERAL PROCEDURE FOR COMPLEX SYNTHESIS

Diphenyl acetic acid (2 mmol) was dissolved in absolute alcohol (30 mL) to which heterocyclic amine bases (2 mmol) (Quinoline, isoquinoline,  $\alpha$ -picoline,  $\gamma$ -picoline, 2-aminopyridine) was added. Then triethylamine (2 mmol) was added to the mixture and was stirred for 10 min. After that a solution of NiCl<sub>2</sub>·6H<sub>2</sub>O/Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2 mmol) dissolved in absolute alcohol was added to the mixture while stirring. The stirring was continued for 6 hours at 60°C and then cooled. Thus formed complexes were filtered, washed several times with alcohol and dried in vacuum desiccators over anhydrous CaCl<sub>2</sub>.

## RESULTS AND DISCUSSION

### Elemental analysis and conductivity measurements

The analytical data are given in Table 1 and the physical properties of the complexes are given in Table 2. The analytical data are in good agreement with the proposed empirical formula of the present complexes. This structure has been confirmed by conductivity, magnetic measurements, FTIR spectra and UV-visible spectral studies. Conductance of pure DMSO at 28°C is 4.0  $\mu$ S/cm. The molar conductance of 10<sup>-3</sup> M solution of the complexes in DMSO was measured at 28°C. The molar conductance values indicate that the complexes 1, 2, 4, 5 and 6 are non-electrolytes whereas the complex 3 is good 1:1 electrolyte.

### Infrared spectra

The spectral data of the complexes 1, 2, 3, 4, 5 and 6 are showed in Table 3. The complexes display bands at 1599-

**Table 1:** Analytical data and yields of the complexes, where, Py=Pyridine, Q=Quinoline, IQ=Isoquinoline, 2-Pic=2-Picoline, 2-APy=2-aminopyridine, DiPhAc=Diphenyl acetic acid

No.	Complexes	Y%	M%	C%	N%	H%
1	[Ni(DiPhAc)(Q)(H <sub>2</sub> O)] <sub>2</sub> Cl <sub>2</sub>	62	12.82	60.99	3.094	4.64
2	[Ni(DiPhAc)(2-pic)(H <sub>2</sub> O)] <sub>2</sub> Cl <sub>2</sub>	74	13.93	57.62	3.36	4.8
3	[Ni(DiPhAc)(Py)(H <sub>2</sub> O)] <sub>2</sub> Cl <sub>2</sub>	69	14.41	56.65	3.478	4.47
4	[Zn(DiPhAc)(2-pic)(H <sub>2</sub> O)] <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	73	14.44	53.33	4.67	4.44
5	[Zn(DiPhAc)(Q)(H <sub>2</sub> O)] <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	62	13.37	56.79	2.88	4.11
6	[Zn(DiPhAc)(2-APy)(H <sub>2</sub> O)] <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	76	14.41	50.55	6.21	4.21

**Table 2:** Physical properties of the complexes

Complex No.	Melting Point ( $\pm$ 0.5)	Molar conductance ohm-1 cm <sup>2</sup> mol <sup>-1</sup>	Colour	$\mu$ eff (B.M.)
1	>300	4.8	Pest	dia
2	>300°	6.9	Greenish	dia
3	>300°	13.6	Pest	dia
4	145-150	3.8	White	dia
5	150-155	4.0	White	dia
6	140-145	4.2	White	dia

1614  $\text{cm}^{-1}$  and 1617-1651  $\text{cm}^{-1}$  due to  $\nu_{\text{sym}}(\text{C}=\text{O})$  and  $\nu_{\text{asy}}(\text{C}-\text{O})$ , respectively, significantly lower than those of free diphenyl acetic acid  $\nu_{\text{sym}}(\text{C}=\text{O}) \sim 1700 \text{ cm}^{-1}$  and  $\nu_{\text{asy}}(\text{C}-\text{O}) \sim 1440 \text{ cm}^{-1}$  indicating the coordination of acid through its carboxylate anions. A broad band observed at 3400-3580  $\text{cm}^{-1}$  due to  $\nu(\text{OH})$  for free acids. The disappearance of the  $\nu(\text{OH})$  mode observed in the free acid molecule clearly indicates the loss of the protons from both O-H groups upon coordination, revealing that acid are negative monodentate ligand coordinating through carboxylate anions [6,17].

Further the presence of M-O bonding is evident from the appearance of  $\nu(\text{M}-\text{O})$  modes at 416-485  $\text{cm}^{-1}$  in the spectra of the complexes. The characteristic ring vibrations of the heterocyclic amines in the range 1400-1600  $\text{cm}^{-1}$  generally shown significant change on complexation [18] but in our present complexes present complexes there bands could not be distinguished because of overlapping with  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}-\text{O})$  stretching bands. The in-plane and out of plane ring deformation modes of the heterocyclic amines observed at  $\sim 500 \text{ cm}^{-1}$  and  $\sim 700 \text{ cm}^{-1}$ , respectively undergo a protein shift in mixed ligand complexes confirming thereby coordination through nitrogen [19]. The presence of  $\nu(\text{M}-\text{N})$  bonding in the complexes is also evident from appearance of  $\nu(\text{M}-\text{N})$  modes at 745-747  $\text{cm}^{-1}$  in the spectra of the complexes [20].

### UV-visible spectra

For Ni(II) and Zn(II) the UV-visible spectral data of the complexes 1, 2, 3, 4, 5 and 6 are given in Table 4. The complexes of Ni(II) gave three bands (bands I, II, III) in the region at 260-275, 300-320 and 420-440 nm respectively corresponding to the transition  $\text{A}1\text{g} \rightarrow \text{A}2\text{g}$ ,  $\text{A}1\text{g} \rightarrow \text{B}1\text{g}$  and  $\text{A}1\text{g} \rightarrow \text{Eg}$ , characteristics of square planar geometry of Ni(II) complexes [21].

The diamagnetism of the Ni(II) complexes indicates an essentially square planar environment around Ni(II), which is in agreement with their electronic spectra [22].

For the Zn(II) complexes (4, 5 and 6) absorption observed at 270 nm, 290 nm and 300 nm, respectively which is in good agreement with square planar structure only [23]. All Zn (II) complexes are diamagnetic as expected for the  $d_{10}$  configuration [24].

On the basis of elemental analysis, magnetic measurement, conductance measurement. FTIR spectra, UV-visible spectra and other physical properties, it can be concluded that the structure of the complexes 1-6 are square planar [23,25].

### Antibacterial activity of the complexes

The antibacterial activity of the synthesized complexes was determined by using the dose of 80  $\mu\text{g}/\text{disc}$ . The results of antibacterial activity measured in terms of zone inhibition have presented in Table 5. The complexes showed comparable/maximum sensitivity against both Gram positive and Gram negative bacteria and these obtained results

**Table 3:** Selected IR spectral data of the complexes 1-6 and their assignment

Complex No.	$\nu(\text{O}-\text{H})\text{cm}^{-1}$	$\nu_{\text{sym}}(\text{C}=\text{O})\text{cm}^{-1}$	$\nu_{\text{asy}}(\text{C}-\text{O})\text{cm}^{-1}$	$\nu(\text{MO})\text{cm}^{-1}$	$\nu(\text{M}-\text{N})\text{cm}^{-1}$	$\nu(\text{C}-\text{H})\text{cm}^{-1}$	$\nu(\text{Py})\text{cm}^{-1}$	$\nu(\text{Ph})\text{cm}^{-1}$
1	3414	1599	1617	385	746	3026	701, 644	1451, 1493
2	3419	1493	1618	386	747	3026	701, 747	1493, 1390
3	3414	1603	1635	395	745	3026	697, 645	1446, 1493
4	3468	1608	1647	392	741	3032	652, 702	1450, 1493
5	3487	1598	1647	395	745	3023	715, 703	1453, 1447
6	3487	1614	1651	386	746	3025	647, 702	1491, 1451

**Table 4:** UV-visible spectral band of the complexes 1-6 in Dimethylsulfoxide (DMSO)

No.	Complexes	Band I (nm)	Band II (nm)	Band III (nm)
1	[Ni(DiPhAc)(Q)(H <sub>2</sub> O)] <sub>2</sub> Cl <sub>2</sub>	270	320	440
2	[Ni(DiPhAc)(2-pic)(H <sub>2</sub> O)] <sub>2</sub> Cl <sub>2</sub>	260	300	425
3	[Ni(DiPhAc)(Py)(H <sub>2</sub> O)] <sub>2</sub> Cl <sub>2</sub>	275	320	420
4	[Zn(DiPhAc)(2-pic)(H <sub>2</sub> O)] <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	270	-	-
5	[Zn(DiPhAc)(Q)(H <sub>2</sub> O)] <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	290	-	-
6	[Zn(DiPhAc)(2-Apy)(H <sub>2</sub> O)] <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	300	-	-

were compared with antibiotic disc of kanamycin. Among the complexes,  $[\text{Zn}(\text{DiPhAc})(\text{Q})(\text{H}_2\text{O})_2](\text{NO}_3)_2$  showed very good activity against all organisms whereas  $[\text{Ni}(\text{DiPhAc})(\text{Q})(\text{H}_2\text{O})_2]\text{Cl}_2$ . However the synthesized compounds showed relatively higher or lower activity than kanamycin. It may be due to nature of metal ion, the nature of ligand and orientation of the ligand around the metal ion [26]. The higher activity of metal complexes may be due to the effect of metal ions on the normal cell membrane. The variation in the activity of different complexes against different organisms depends either on the impermeability of cells of the microbes or differences in the ribosomes of microbial cells [27].

## CONCLUSION

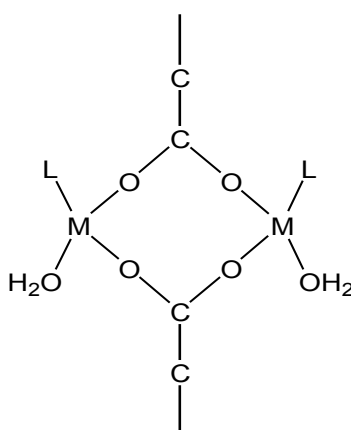
Mixed ligand complexes of Zn(II) and Ni(II) ions have been synthesized successfully and they were characterized by Uv-visible, FT-IR, Magnetic susceptibility, Molar Conductance, Elemental Analysis and others physical methods. The electronic spectral data are in good agreement with the transition of square planar metal complexes. Diamagnetic nature of the obtained metal complexes, indicate the  $d^{10}$  configuration of metal ions. The IR data confirmed the presence of M-N and M-O, M- $\text{H}_2\text{O}$  coordination mode of mixed ligand complexes. On the basis of the above investigations and other physical properties interpretations, the probable molecular structure of the metal complexes could be illustrated as shown below (Figure 1).

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**Table 5:** Antibacterial activity of Ni(II) and Zn(II) complexes

Bacteria	Gram Staining	Diameter of zone inhibition(mm)				K-30 µg/ disc
		$[\text{Ni}(\text{DiPhAc})(\text{Q})(\text{H}_2\text{O})_2]\text{Cl}_2$	$[\text{Ni}(\text{DiPhAc})(2\text{-pic})(\text{H}_2\text{O})_2]\text{Cl}_2$	$[\text{Zn}(\text{DiPhAc})(\text{Q})(\text{H}_2\text{O})_2](\text{NO}_3)_2$	$[\text{Zn}(\text{DiPhAc})(2\text{-Apy})(\text{H}_2\text{O})_2](\text{NO}_3)_2$	
<i>Bacillus cereus</i>	Positive	8	12	24	18	23
<i>Streptococcus aureus</i>	Positive	10	14	26	20	20
<i>Sarcina lutea</i>	Positive	7	15	23	22	22
<i>Escherichia coli</i>	Negative	8	13	22	24	22
<i>Shigella shiga</i>	Negative	9	14	25	21	24
<i>Pseudomonas aeruginosa</i>	Negative	10	16	26	23	23



**Figure 1:** Square planar structure of the complexes (1-6) Where, M=Ni(II), Zn(II), L=Quinolin, Isoquinoline, 2-amino pyridine, 2-picoline, pyridine

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