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Mixed ligand complexes: Synthesis, characterization and antibacterial activity investigation

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Abstract

Some mixed ligand complexes of Zn (II) and Cd (II) derived from phthalic acid, oxalic acid, succinic acid and nitrogen containing heterocyclic bases were prepared and had been characterized on the basis of their melting point studies, conductivity, magnetic measurements along with their infrared spectra and electronic spectroscopic studies. All complexes showed tetrahedral structure with moderate outcome of antimicrobial activity against some human pathogenic bacteria.

Keywords: Transition metals, mixed ligand complexes, FT-IR, electronic spectra, antimicrobial activity

Introduction

In the state of research, it is a well-known fact that mixed ligand complexes play a vital role in the biological systems [1, 3]. These complexes are significantly established to be biologically active against several pathogenic microorganisms [4, 5].

The organic bi-dentate ligands are the important class of ligand in coordination chemistry and find extensive applications in different fields [6]. The ligands contain donor atoms like nitrogen, oxygen and carbonyl groups as like organic acids such as oxalic acid, succinic acid and phthalic acid. Therefore, its interaction with metal ions yield complexes of different geometries and are found to be biologically active [7, 8].

In recent years, there has been renewed interest in the synthesis and study of mixed ligand transition metal complexes [9]. The utility aspects of these complexes have received their share of attention as their applications in diverse fields [10]. Some metal ligand complexes are found to be catalyzing different organic reactions such as oxidation, reduction, oxidative cleavage, hydroformylation etc. Some shows catalysis like activity in decomposition of hydrogen peroxide as well [11]. O-phthalate anion is a well-known versatile ligand, which has been extensively used in the design of coordination compounds due to the variety of its bonding abilities. As a result of the two ortho-carboxylic groups, the ligand has the capacity to chelate as well as to bridge up to seven metal centers at once [12] forming mono and polynuclear complexes.

Survey of existing literature reveals that, phthalic acids are widely used as centrifugal molding aids for concrete [13]. It can be used to make an antifreeze compound which showed good corrosion inhibiting properties for cast aluminum, cast iron, steel, brass and copper. This compound is also useful for automobile engines [14]. Phthalic acid and its derivatives also used as anticorrosive, antideposit and biocide agent for protection of aqueous heating and cooling systems. Carter and co-workers have done extensive works on thermal absorption of phthalic di-esters in rats [15]. The complexes of Zinc with phthalic acid act as an anticorrosive coating compound and marine growth inhibitors [16]. Succinic acid is a precursor to some specialized polyesters and also a component of some alkyd resins. It is used in the food and beverage industry primarily as an acidity regulator.

Organic compounds containing a pyridine ring play an important role in many biological reactions [17, 20]. Complexes containing pyridine ring (cyclic nitrogen) display significant anticancer activity as well as reductions in the tumor size have been reported [21].

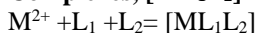
Keeping these facts in mind we report here in several new mixed ligand complexes of Zinc and Cadmium ions with phthalic acid, oxalic acid, succinic acid and nitrogen containing heterocyclic bases. These complexes have been prepared and characterized on the basis of different physical measurements.

2. Experimental

All the chemicals used were purchased from Merck and Loba chemicals Ltd. Melting points of all were determined on a digital melting point apparatus. All the products with authentic samples were characterized by comparison of melting points and spectroscopic data (UV-Visible Spectroscopy and FT-IR).

The magnetic susceptibility of the complexes was measured at room temperature using a Gouy balance and the wavelength of absorbance was determined by UV-Visible spectrophotometer [JASCO 503] using a quartz cuvette using ethanol as the reference. The IR spectrums were recorded on FT-IR spectrophotometer [JASCO, FT-IR/4100] Japan using dry KBr as the standard reference. All the steps of antimicrobial activity test were carried out at Microbiology Laboratory, Department of Textile, Khaza Yunus Ali University, Sirajgonj, Bangladesh.

2.1. General Method for the Preparation of the M(II) Complexes, [ML₁L₂]



[Where, M = Zn (II) and Cd (II); L₁ = Deprotonated phthalic acid, Deprotonated oxalic acid, Deprotonated succinic acid and; L₂ = Pyridine and Dimethylglyoxime]

2.1.1. Synthesis procedure for mixed ligand complexes derived from phthalic acid and pyridine

To a hot solution of H₂Pht (0.83g, 5 mmol) and pyridine (3 mL) in water, a solution of zinc acetate/cadmium chloride (5 mmol) in water (10 mL) was added slowly. The mixture was heated at reflux for 1 hour and left to stand at room temperature in an open flask. The precipitate produced was collected by filtration, washed with ethanol first then acetone and hot water and finally dried in a vacuum desiccator over anhydrous CaCl₂.

2.1.2. Synthesis procedure for mixed ligand complexes derived from dicarboxylic acid and dimethylglyoxime (DMG)

1mmol aqueous solution of metal salt in distilled water was prepared and ligand DMG (1mmol) and dicarboxylic acid (1mmol) in ethanol were dissolved for preparing 1:1 ligand solution of DMG and dicarboxylic acid. This mixture of ligand solution was added into metal salt solution drop wise with constant stirring up to 30 minutes. This reaction mixture was condensed for one hour using magnetic stirrer at room

temperature. The obtained complex was filtered, washed with ethanol first then hot water followed by acetone and finally dried in a vacuum desiccator over anhydrous CaCl₂.

2.1.3. For comparative study, we have also prepared [Cd (suc) (py)₂] reported earlier by J. Akhter [22] by the following procedure:

1 mmol ethanolic solution of Cd (II) salt and deprotonated succinic acid (1 mmol) was mixed as the first ligand with constant stirring but hence no precipitation was found. Then 25 mL of ethanolic KOH solution of secondary ligand (pyridine) in calculated ratio was added to the resulting mixture and heated on a magnetic stirrer with constant stirring. The volume of the reaction mixture was reduced to one half and then allowed to cool. The precipitate found was filtered, washed with ethanol and then dried in desiccators over anhydrous CaCl₂.

2.2. Antimicrobial activity

The metal complexes were screened for *in vitro* antimicrobial activity in DMSO against gram-negative *Pseudomonas aeruginosa*, *Escherichia coli* (*E. coli*) and gram-positive *Staphylococcus aureus* strains by Kirby Bauer's disc diffusion method. 24 hours old culture a uniform suspension of test organism was prepared in a test tube which contained the sterile saline solution. Sterile nutrient agar then was added in each Petri dishes. The dishes were related to ensuring the uniform mixing of the microorganism in the agar medium which was allowed to solidify finally.

Sterile Whatmann filter-paper discs were dipped in the solution of each compound and placed on the labelled plates. The DMSO was used as a control of the solvent and Kanamycin was used for standard compound. Plates were kept in the refrigerator for 30 minutes for diffusion and incubated at 37°C for 24 hours.

The diameters of the zone of inhibition around each disc were measured by scale while results were recorded in terms of mm. The observed data of antimicrobial activity of all the compounds are tabulated in (Table- 4).

3. Results and Discussion

The analytical and physical data (color, melting point, molar conductivity and magnetic moment) of the complexes are given in (Table-1). The melting or decomposition temperatures of all the prepared Zn(II) and Cd(II) metal complexes were observed in an electro thermal melting point apparatus model 0.AZ6512. In these cases, it was not possible to measure the melting points beyond 300 °C. The molar conductances of 1×10⁻³ M solution of the complexes in DMSO were measured at 30 °C. These values indicate that the compounds are non-electrolytic in nature [23-24]. All the synthesized compounds of Zn (II) and Cd (II) are found to be diamagnetic. These complexes have μ_{eff} values (near 0 B.M.) showing the presence of no unpaired electron.

Table 1: Physical Properties of the Zn (II) and Cd (II) Metal Complexes

S.N.	Complexes	Color	Melting point or Decomposition Temp/(±5 °C)	Molar Conductance(ohm ⁻¹ cm ² mol ⁻¹)	μ _{eff} B.M.
1	[Zn (DPA) (py) ₂]	white	>300	15	0.88
2	[Zn(oxa)(py) ₂]	white	>300	31	0.65
3	[Cd (DPA) (DMG)]	White	>300	14	0.74
4	[Cd (suc) (DMG)]	Off white	>300	18	0.73

[Where, DMG =Dimethylglyoxime; Py = Pyridine; DPA = Deprotonated phthalic acid; Suc =Deprotonated succinic acid; Oxa = Deprotonated oxalic acid]

3.1. IR Spectral Studies

The IR spectra of Zn (II) and Cd (II) metal compounds have shown in Fig 1, Fig 2, Fig 3 and Fig 4 respectively. Characteristic bands of carboxylate groups in the usual region

of 1608-1553 cm^{-1} for asymmetric stretching and in 1405-1399 cm^{-1} region for symmetric stretching are observed. Their positions and intensities are similar to those reported for other phthalates [25, 30] and carboxylate complexes [31, 33]. The complexes display band in the region of 1638-1627 cm^{-1} and 1244-1217 cm^{-1} due to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ respectively, significantly lower than that of free ligand $\nu(\text{C}=\text{O})=1760 \text{ cm}^{-1}$ and near about $\nu(\text{C}-\text{O})=1220 \text{ cm}^{-1}$ respectively indicating the coordination of metal ion through its carboxylate anion [34]. The absorption band is obtained in complex containing phthalic acid as a ligand, it shows $-\text{C}=\text{C}-$ stretching at 1600-1470 cm^{-1} , i.e., aromatic ($-\text{C}=\text{C}-$) stretching but this peak is absent in the complex containing oxalic acid and succinic acid

as a ligand [9]. The C-N stretching and O-H stretching of water molecules are at 1422 cm^{-1} and 3541-3071 cm^{-1} [35], respectively.

The in-plane and out-plane ring deformation modes of heterocyclic amines were observed at 680 cm^{-1} and 620 cm^{-1} respectively undergoing a positive shift in mixed ligand complexes confirming their coordination through nitrogen [34]. The presence of metal nitrogen bonding in the complexes is the evidences from the appearance of $\nu(\text{M}-\text{N})$ modes at 481-419 cm^{-1} in the spectra of the complexes and $\nu(\text{M}-\text{O})$ appearance at 629-518 cm^{-1} . All the observations of IR data have been tabulated in Table-2.

Table 2: IR Spectral Data for the Zn(ii) and Cd(ii) Metal Compounds in cm^{-1}

S.N.	Complex	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{COO}^-)_{\text{asy}}$	$\nu(\text{COO}^-)_{\text{sym}}$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
1	[Zn (DPA) (py) ₂]	1637	1217	1448	1580	1395	560	481
2	[Zn (oxa) (py) ₂]	1639	1220	1446	1602	1384	518	419
3	[Cd (DPA)(DMG)]	1603	1220	1446	1603	1414	653	444
4	[Cd (suc) (DMG)]	1638	1220	1447	1601	1364	629	419

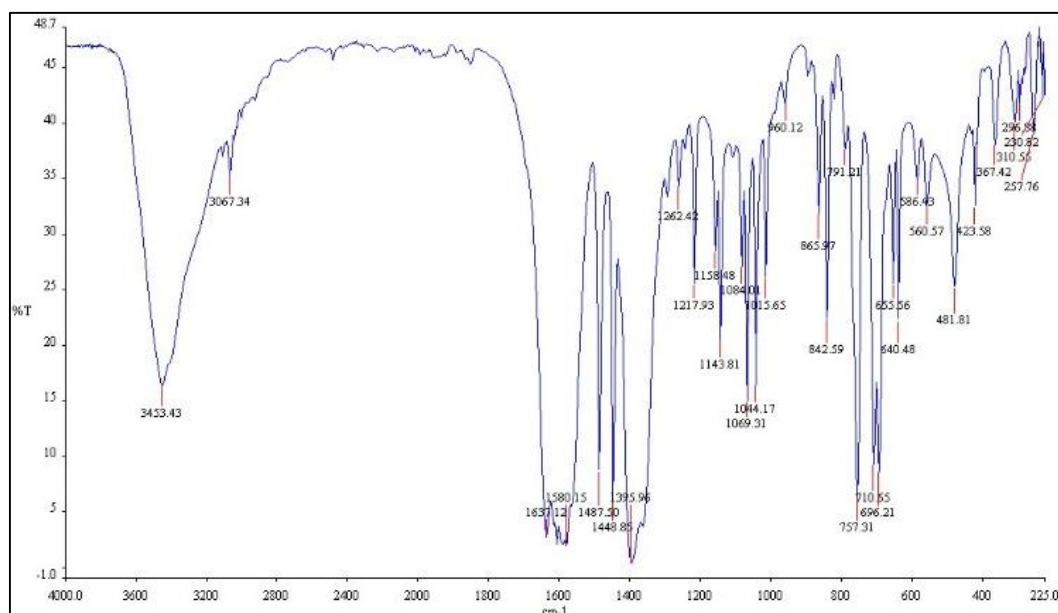


Fig 1: FTIR spectrum of the complex [Zn (DPA) (py) ₂].

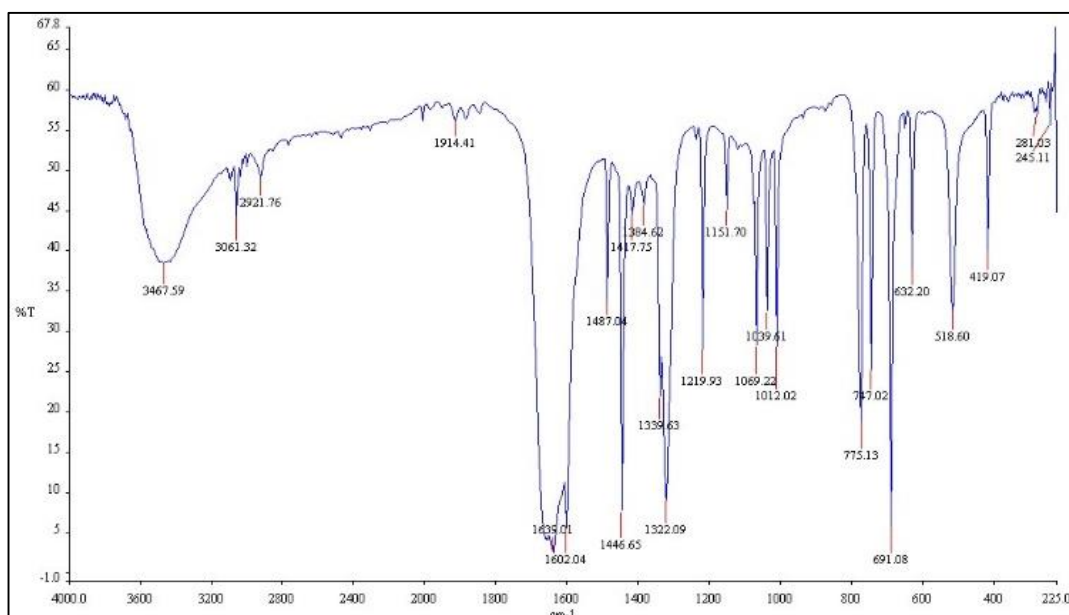


Fig 2: FTIR spectrum of the complex [Zn (oxa) (py) ₂].

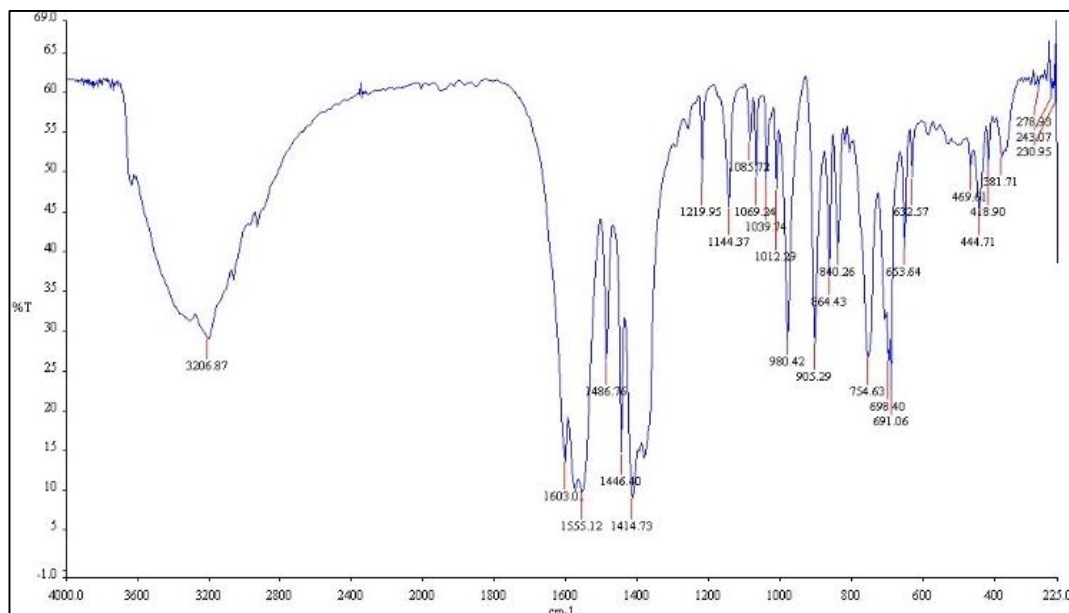


Fig 3: FTIR spectrum of the complex [Cd (DPA) (DMG)].

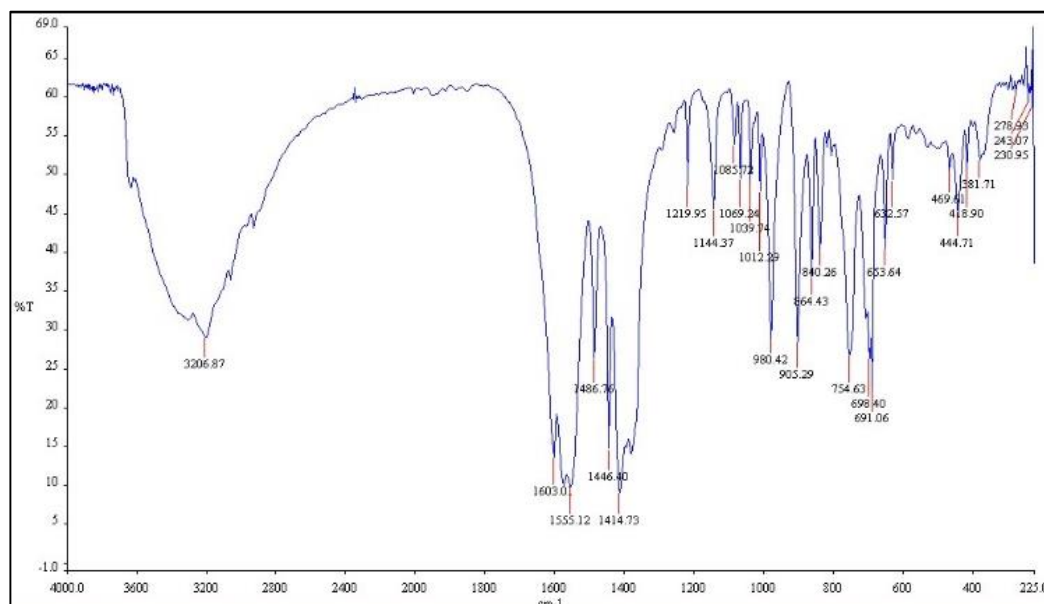


Fig 4: FTIR spectrum of the complex [Cd (suc)(DMG)].

3.2. UV-visible spectra studies

The electronic spectra of synthesized complexes were measured in DMSO solvent, which are given in Fig 5, Fig 6, Fig 7, and Fig 8. The Zn (II) and Cd (II) complexes show only charge transfer transitions, which may be formed due to charge transfer from ligand to metal and vice-versa, no d-d transition are possible for d^{10} of Zn (II) and Cd (II) complexes [36]. The electronic spectra of Zn (II) and Cd (II) complexes

exhibits a broad absorption band in the region of 320-340 nm, which due to L→M charge transfer. In the UV-region, the complex of Zn (II) and Cd (II) showed one strong absorption band at 265 nm (Table-3) which may be assigned to benzene ring for $\pi \rightarrow \pi^*$ transition [37, 40]. The spectra of the Zn (II) and Cd (II) complexes exhibited bands due to ligand $\pi \rightarrow \pi^*$ and L→M charge transfer [41, 44] indicated the tetrahedral structure of these Zn(II) and Cd(II) complexes.

Table 3: UV-visible Spectral Bands for the Zn (II) and Cd (II) Metal Complexes

S. N.	Complexes	λ_{\max}	Assignments
1	[Zn (DPA)(py) ₂]	263,340	$\pi \rightarrow \pi^*$, L→M charge transfer
2	[Zn (oxa)(py) ₂]	265,320	$\pi \rightarrow \pi^*$, L→M charge transfer
3	[Cd (DPA)(DMG)]	271,320	$\pi \rightarrow \pi^*$, L→M charge transfer
4	[Cd (suc)(DMG)]	270,340	$\pi \rightarrow \pi^*$, L→M charge transfer

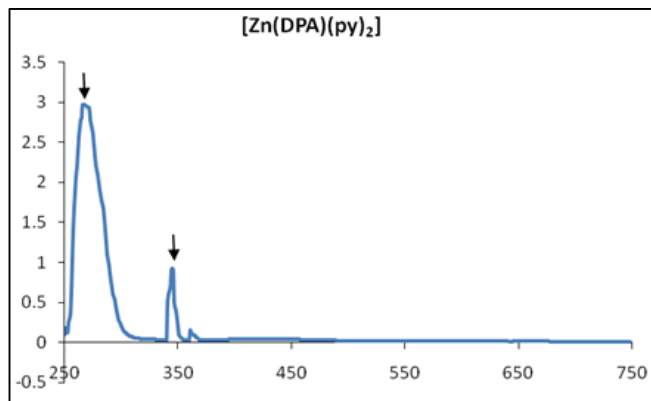


Fig 5: UV-VIS spectrum of the complex [Zn (DPA) (py)₂]

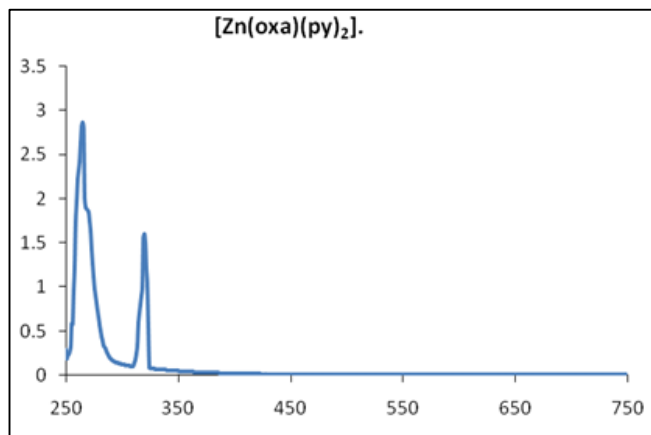


Fig 6: UV-VIS spectrum of the complex [Zn (oxa) (py)₂].

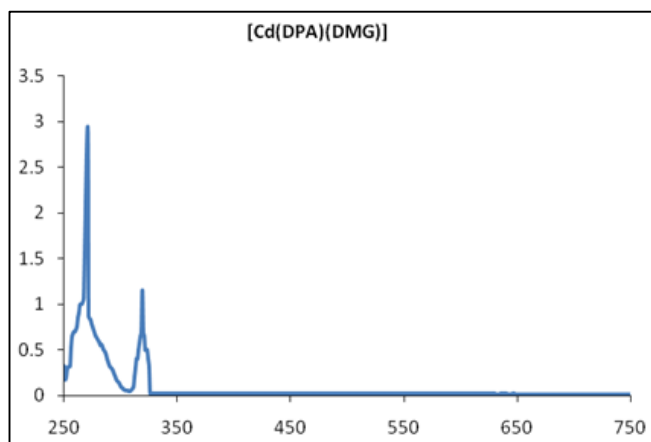


Fig 7: UV-VIS spectrum of the complex [Cd (DPA) (DMG)].

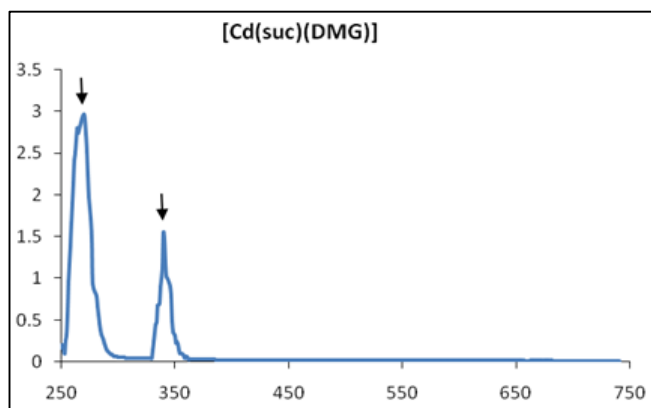


Fig 8: UV-VIS spectrum of the complex [Cd (suc) (DMG)].

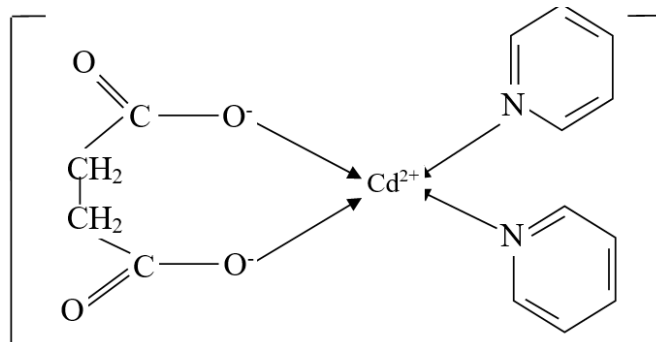


Fig 9: The probable structure of the complex [Cd(suc) (py)₂].

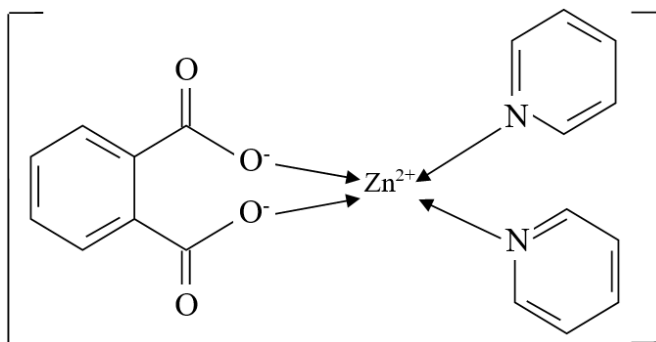


Fig 10: The probable structure of the complex [Zn (DPA) (py)₂].

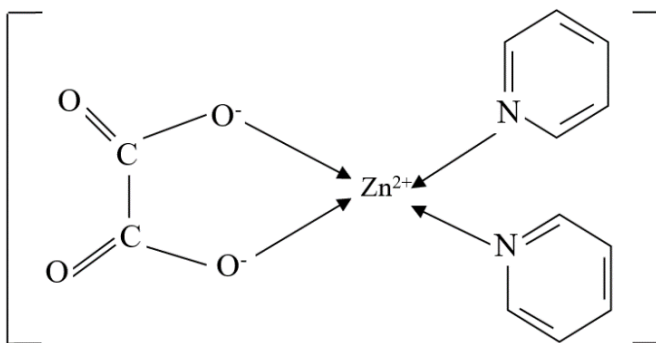


Fig 11: The probable structure of the complex [Zn (oxa) (py)₂].

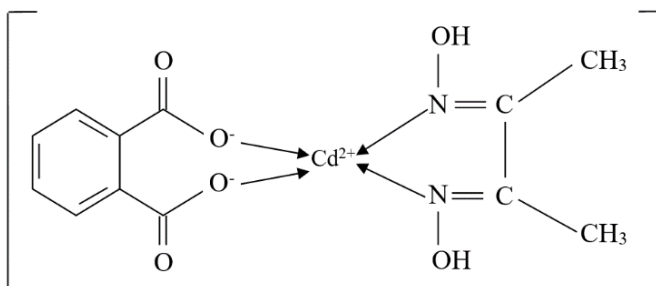


Fig 12: The probable structure of the complex [Cd(DPA)(DMG)].

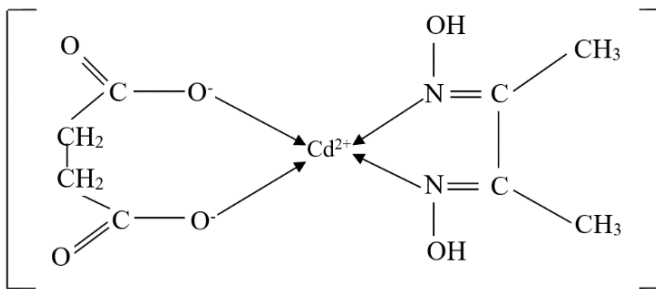


Fig 13: The probable structure of the complex [Cd(suc)(DMG)].

3.3. Antimicrobial Activity Studies

The potency of the metal complexes was evaluated against three bacteria. The diameter of the zone inhibitor (mm) was used to compare the antimicrobial activity of the test compounds. Results of the antimicrobial activity are presented in (Table-4). Mixed ligand [Cd (suc) (DMG) complex termed as SN-1 showed comparable activity with that of [Cd (suc) (py)₂] against *S. aureus* and *E. coli*. Among all synthesized Cd and Zn complexes, [Zn (oxa) (py)₂] complex marked as SN-4, showed higher antibacterial activity against *p. aeruginosa*

when compared with standard K-30 and [Cd (suc) (py)₂] complex. On the other hand, SN-5 compound showed comparatively less antibacterial activity against these three microorganisms, this is may be due to reduction of polarity of metal ion mainly because of chelation, which increases the lipophilic properties of the complexes. That is why the complexes show antimicrobial responses. That is to postulate that, the inhibitory activity of the complexes will increase as the concentration increases and the activity of the ligands increases upon chelation^[1, 45, 46].

Table 4: Antibacterial Screening Results of All Complexes

Bacteria	Gram Staining	Diameter of zone inhibition (in mm)					
		SN-1 100 µg/disc	SN-2 100 µg/disc	SN-3 100 µg/disc	SN-4 100 µg/disc	SN-5 100 µg/disc	K 30 µg/ disc
<i>Staphylococcus aureus</i>	+ve	20	15	25	12	10	35
<i>Escherichia coli</i>	-ve	21	20	23	21	14	30
<i>Pseudomonas aeruginosa</i>	-ve	12	23	20	25	-Ve	15

[Here, SN-1 = [Cd (suc) (DMG)], SN-2 = [Cd (DPA) (DMG)], SN-3 = [Cd (suc) (py)₂], SN-4 = [Zn (oxa) (py)₂], SN-5 = [Zn (DPA) (py)₂]

On the basis of the above characterizations, the probable structures of all obtained complexes are presented in the Fig 9 to Fig 13

4. Conclusions

The Mixed ligand complexes of Zn (II) and Cd (II) ions Cd²⁺ were synthesized and characterized by their conventional physical and chemical analyses. The complexes were obtained as white coloured powder form and they were stable at room temperature. The possible geometries of all synthesized complexes of Zn (II) and Cd (II) are tetrahedral structures and these are four coordinated metal ligand complexes. All synthesized complexes were tested for their antimicrobial activity against three pathogenic bacteria. [Zn(oxa)(py)₂] complex showed higher antibacterial activity against *P. aeruginosa* when compared with standard K-30 and [Cd(suc)(py)₂]. Further studies of this zinc complex may explore its clinical implications in the world life threatening infection.

5. References

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