



A Study of Metal Complexes of 2-picolinic Acid

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ABSTRACT

The metal (II) complexes of picolinic acid are prepared in non-aqueous medium and its complexes are characterized by spectral studies (Infra-red spectroscopy, UV-Visible spectroscopy, ¹H-NMR spectroscopy and ESR spectroscopy), conductance, magnetic susceptibility and thermal analysis. On heating, the complexes decompose at temperature above 260°C. It revealed that all the complexes were stable. The FT-IR evidenced the C=O, C=C-complexes along with corresponding ligands. Thermogravimetric study showed that there is no water molecule in the complexes. The electrochemical behavior of all metal complexes was investigated. From the electronic spectra the geometries of cobalt, nickel and copper is found to be Octahedral, Octahedral, and Distorted octahedral respectively. The complexes of the ligand are evaluated for anti-microbial activity hostile to fungal and bacterial strains. The nickel (II) complex reveals excellent inhibition against the selected four bacterial strains compare with other complexes.

Keywords: Metal (II) complexes, Picolinic acid, Cyclic voltammetry, Antimicrobial activity.

INTRODUCTION

Picolinic acid is a chelating agent composed of elements in their human body. The zinc dipicolinate dietary additives are favored due to their articulate significance of instigating zinc into the body. The mineral manganese is essential for human's life and it plays vital role for the plant growth. It act as a main energy source for the redox mechanism in photosystem (I) and (II). Deficiency of manganese leads to the osteoarthritis and osteoporosis. The hard ferromagnetic mineral is cobalt and well know cobalt complex is Vitamin-B₁₂. It is used in the treatment of anaemia because it enhance the production of red blood cells. The naturally abounded

micro nutrient is nickel which increases the hormonal activities and also affects the lipid metabolisms. The copper mineral needed for human's health which involves in the various natural process of human's body. Copper based complexes are widely reported for wound healing and prevents the infection after tuscles and bones and its level can regulated by the liver. Its complexes commonly utilized for acne, Alzheimer and tooth plaque. The trace mineral zinc involves in the DNA creation, supports the body immunity, cell growth, protein synthesis and heals the damage tissues. Excess of zinc can reduce the absorption of copper and iron.

A literature review on the subject of picolinic



acid coordinate to the metal through nitrogen and carboxylate oxygen are most prominent¹⁻⁴. The antimicrobial activities^{5,6} of some metal complexes of the mixed ligands were reported⁷⁻¹⁵. The electrochemical studies and the biological activities of the Cu (II) complex with picolinic acid and Co (II) complex imides were reported respectively¹⁶. Similarly, the homogeneous H₂ evolution from the H₂O of cobalt complexed with picolinic acid¹⁷ also reported. The homogeneous electrocatalytic reduction of water in aqueous medium of nickel (II) complex with picolinic acid¹⁸ is reported in the previous reviews. In subject to this paper, we have been examined the conglomeration, properties of cobalt, manganese, nickel, copper and zinc complexes with picolinic acid were studied and furthermore, the electrochemical behavior and antimicrobial activities also studied.

MATERIALS AND METHODS

Materials

The chemicals utilized for the preparation of the five picolinic acid complexes are standard grade and are ethanol, diethyl ether, the ligand picolinic acid, five metal carbonates and the perchloric acid were procured from the Ponmani & Co Chemicals, Trichy, Tamilnadu, India.

Synthesis of five metal(II) perchlorate

The five different perchlorates of cobalt, manganese, nickel, copper and zinc were complexed by simple precipitation method. Ten grams of each of the metal carbonates (Cobalt (II) carbonate, Manganese (II) carbonate, Nickel (II) carbonate, Copper (II) carbonate, and Zinc Carbonate) treated with fourteen milliliters of 70% aqueous perchloric acid and then re-crystallized with water. All the complexes were concocted by treating the one mole

of each metal (II) perchlorate and 3 moles of ligand are dissolved in ethanol and refluxed for six hours. The solutions are concentrated then cooled, the excess ligand in the reaction mixture is removed by washing with the diethyl ether. Finally synthesized five complexes are crystallized.

Characterization of Five Complexes and their Anti-microbial activity

The FT-IR spectra of synthesized five perchlorate complexes were screened by mixing three chlorates with the KBr in the shimadzu24 make of FT-IR 8400S. The electronic spectra of three complexes were screened in the ethanol and methanol solvent with make of a Hitachi U-3400 spectrophotometer. Likewise, the ¹H-NMR spectrumvivors were investigated with the help of cyclic voltammetry instrument device VSP(SNO147). Tetrabutyl ammonium perchlorate is used as a supporting electrolyte.

Antimicrobial screening of the ligand and its five complexes have been investigated inimical to three fungal and four bacteria by using agar diffusion method.

RESULTS AND VALIDATION

Physicochemical Studies

Molar conductance of the prepared complexes was assigned by the following composition. From the conductance studies, we came to know about the complexes be an adherent to 1:2 electrolyte¹⁹ where the anions are present outside the coordination sphere. Magnetic moments, μ_{eff} and melting point of metal complexes are shown in Table 1. μ_{eff} of metal ions are confined to the predicted values. On heating, the complexes decompose at temperature above 260°C. It revealed that all the complexes were stable.

Table 1: Physicochemical properties of metal complexes

Complex	Conductance values Ohm ⁻¹ cm ² mol ⁻¹	Type of Electrolyte	μ_{eff}	Melting Point°C	Colour
[MnL ₃] ²⁺ (ClO ₄) ₂	171.89	1:2	6.02	260	White
[CoL ₃] ²⁺ (ClO ₄) ₂	186.6	1:2	4.9	260	Brown
[NiL ₃] ²⁺ (ClO ₄) ₂	202.23	1:2	2.9	290	Light Blue
[CuL ₃] ²⁺ (ClO ₄) ₂	193.07	1:2	1.9	310	Dark Blue
[ZnL ₃] ²⁺ (ClO ₄) ₂	172.19	1:2	-	280	White

L=Picolinic acid

IR Spectroscopy

The spectra of ligand reveal a sharp band at 1742 cm⁻¹ is corresponds to the C=O

stretch of carboxylic acid²⁰. The stretch found at 1675 cm⁻¹ is attributed to the C=N of pyridine ring and the O-H stretch of the acid group is found at

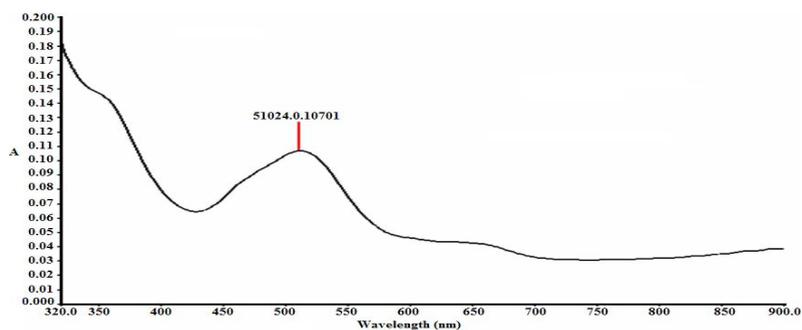
Electronic Spectra of Metal Complexes²⁵

The copper perchlorate complex reveals the band at $19,607\text{ cm}^{-1}$ is assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition having an

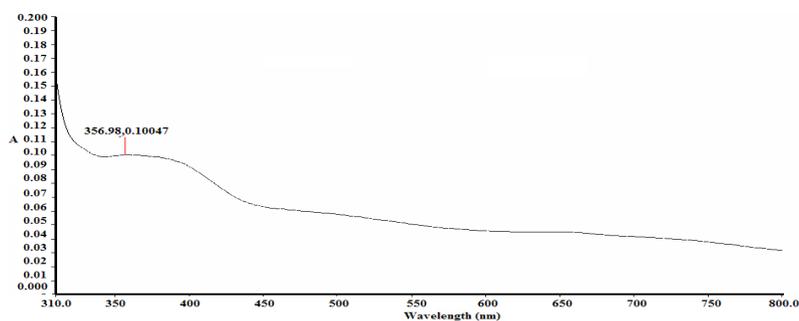
octahedral geometry. The perchlorate due to Jahn-Teller distortion. Similarly, copper perchlorates exhibits a band at $15,290\text{ cm}^{-1}$ with a distorted octahedral geometry.

Table 3: Electronic spectra of metal complexes

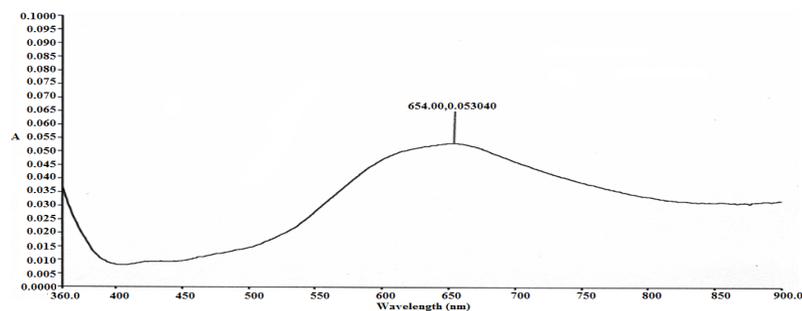
Complex	Medium	Assignment	Stereochemistry
$[\text{CoL}_3]^{2+}(\text{ClO}_4)_2$	Ethanol	$19,607\text{ cm}^{-1} {}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	Octahedral
$[\text{NiL}_3]^{2+}(\text{ClO}_4)_2$	Ethanol	$28,089\text{ cm}^{-1} {}^3A_{2g} \rightarrow {}^3T_{1g}(P)$	Octahedral
$[\text{CuL}_3]^{2+}(\text{ClO}_4)_2$	Ethanol	$15,290\text{ cm}^{-1} {}^2E_g \rightarrow {}^2T_{2g}$	Distorted octahedral



(i)



(ii)

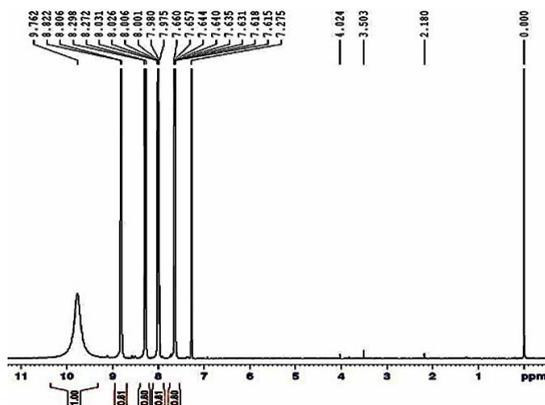


(iii)

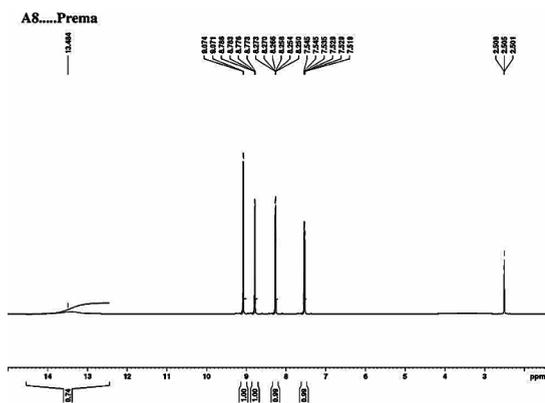
Fig. 3. Electronic spectra of (i) Cobalt (II) perchlorate, (ii) Nickel (II) perchlorate, (iii) Copper (II) perchlorate complexes**¹H NMR Spectral studies**

The spectrum of the ligand which has been taken in CDCl_3 , shows different peaks at 7.6-8.8 ppm

corresponding to the aromatic protons. The peak at 9.76 ppm was assigned to hydrogen of carboxylic acid group.

Fig. 4. ¹H-NMR spectrum of ligand

Zinc (II) perchlorate complex is extracted from DMSO-*d*₆. Signals correspond to 7.5-9.07 ppm for aromatic protons. 13.48 ppm corresponds to carboxylic acid hydrogen. This group is involved in coordination. This peak in complex shifted to low field signal. The presence of carboxylic acid proton in the NMR spectrum of Zinc (II) complex reveals that the not ionization of -COOH (acid) group. The shift in the position of that proton in the spectrum of the complex in comparison with that of the ligand suggest that the electron density around the proton is changed due to the coordination of carbonyl oxygen (C=O) of the acid group and due to absence of hydrogen bonding.

Fig. 5. ¹H-NMR of Zinc (II) perchlorate complexTable 4: ¹H-NMR of Ligand and Zinc(II) perchlorate complexes

Compound	Aromatic ring proton (ppm)	Carboxylic acid proton (ppm)
Ligand ²⁺	7.6-8.8	9.76
[ZnL ₃](ClO ₄) ₂	7.5-9.07	13.48

L = Picolinic acid

Thermal Analysis

Manganese (II) perchlorate complex was stable up to 258.2°C which indicates that there is no water molecule in the complex^{26,27}. In the analysis of TGA curve, the moisture is removed of about 5.8% (cal 5.77%) at 258.2°C which is associated by an endothermic peak with 296°C on the DTA curve shows that the complex defrosts in prior to decomposition, which indicates that melting of the perchlorate ion. In the first stage of degradation, at 307.4°C it is observed that there is loss of perchlorate ions and decomposition of the pyridine ring with an experimental value of about 38.3% (cal 39.6%) thereby associated by an exothermic peak with 439.2°C and 510.1°C followed by decomposition of the ligands. In the second stage of degradation, at 657.5°C it correlated to the decomposition of the ligands with an experimental value of about 31.1% (cal 32%). The weight of the final residue is stable which is accompanied by Manganese oxalate with 21% (cal 22.9%). The Cobalt (II) perchlorate complex is stable up to 197.6°C which indicates that there is no water molecule in the complex. An endothermic peak at 211.5°C corresponds to the melting of perchlorate ions. Decomposition occurs at an exothermic peak which was found at 311.8°C. There occurs a systematic drop in the weight of the complex at the terminal stage of about 537.4°C. The curve appears at Nickel (II) perchlorate complex intimates that the complex is stable up to 304.1°C which indicates that it has no water molecule. The initial stage of degradation arise at 304.1°C losses one perchlorate with moisture 17.3% (cal 15.9%), an exothermic peak with 335.3°C, 457.8°C and 503.5°C exhibits the ligand decompositions. The weight of the last residue that metal oxide is formed.

Cyclic Voltammetry studies

The cyclic voltammogram of ligand and all metal complexes are recorded in 0.001M electrolyte containing DMF. All the metal (II) perchlorate were scanned in the limit of -2V to +2V at the scan rate 20 mV/s, except manganese(II) perchlorate complex. The scan rate of this complex is 10 mV/s. The measurable parameter of a quasi-reversible system is ΔE_p . This would be greater than 0.59V for quasi reversible process. The ligand exhibits

irreversible reduction peak around at -0.69V with irreversible oxidative peak at 1.31V. Manganese (II) perchlorate complex exhibits one electron reduction corresponding to $Mn(II) \rightarrow Mn(I)$ at $E_{1/2}$ value of -0.784V. ($\Delta E_p=65mV$) and irreversible oxidation peak at 1.152V reveals that $Mn(II) \rightarrow Mn(III)$ oxidation²³. Cobalt (II) perchlorate complex exhibits an irreversible reduction at -0.4699 V corresponding to $Co(II) \rightarrow Co(I)$ On the oxidative response, it exhibits an irreversible oxidation at 0.8485 V reveals that $Co(II) \rightarrow Co(III)$ oxidation. Nickel (II) perchlorate complex exhibit quasi reversible²⁸ one electron reduction corresponding to $Ni(II) \rightarrow Ni(I)$ at $E_{1/2}$ values of -0.534V $\Delta E_p=129 mV$, and an irreversible oxidative response at $E_{pa}=0.769V$ reveals that $Ni(II) \rightarrow Ni(III)$ oxidation²³. Copper (II) perchlorate complex exhibits irreversible reduction at = -0.4019 and -1.7525V corresponding to $Cu(II) \rightarrow Cu(I)$ an $Cu(I) \rightarrow Cu(0)$ reduction and an irreversible oxidation occurs with the peak value of = 1.133V attributed to $Cu(II) \rightarrow Cu(III)$ oxidation²⁴. Zinc (II) perchlorate complex exhibits quasi reversible one electron reduction corresponding to $Zn(II) \rightarrow Zn(I)$ at $E_{1/2}$ values of -0.840V, ($\Delta E_p=77 mV$) and an irreversible oxidation peak at =1.022V attributed to $Zn(I) \rightarrow Zn(0)$ We concluded that , most of the complexes display one electron reduction and irreversible oxidation potential range 0.76 V to 1.1V. The reduction waves with $E_{1/2}$ values in the range of 0.53V to 0.84V is assigned to the $M(II) \rightarrow M(I)$ reduction. Therefore, the cyclic voltammogram of all complexes show metal centered process. The potentials are summarized in the Table 6.

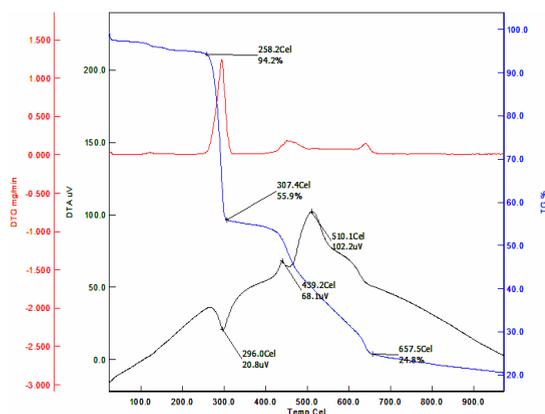


Fig. 6. TGA and DTA of Manganese(II) perchlorate complex

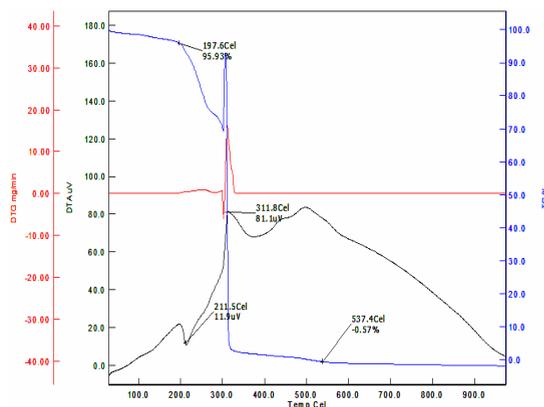


Fig. 7. TGA and DTA of Cobalt(II) perchlorate complex

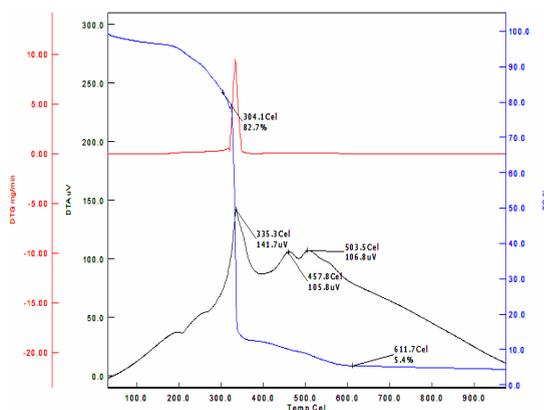


Fig. 8. TGA and DTA of Nickel(II) perchlorate complex

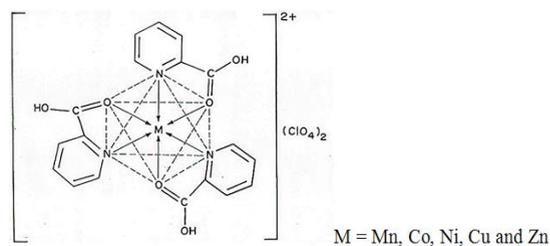
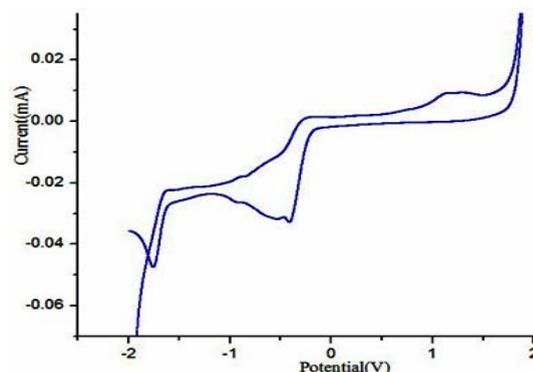
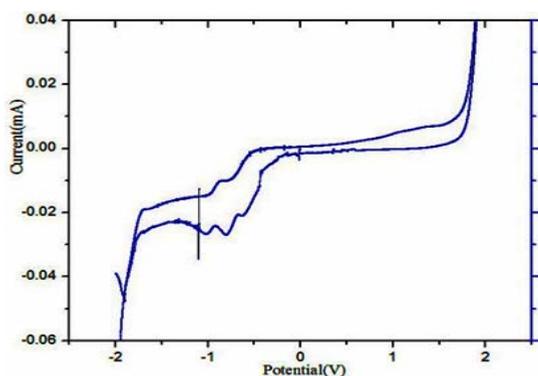


Fig. 9. Structure of Metal(II) perchlorate complexes

Fig. 10. Cyclic voltammogram of $[CuL_3]_2(ClO_4)_2$

Fig. 11. Cyclic voltammogram of $[ZnL_3]^{2+}(ClO_4)_2$

Antimicrobial Activity

It has been investigated that the antifungal activity of the mixture of metal complexes was inimical to 3 fungal pathogens by the assay of disc-diffusion and their outcomes are shown in Table 6. Comparative inhibitions of the non-complexed ligand with their complexes concludes that the Cobalt (II) perchlorate complex has less activity against *Aspergillus niger*. Copper (II) complex has very less activity against *Aspergillus niger* and *Aspergillus flavus*, but having a good activity against *Aspergillus terreus*.

Table 5: CV study of metal complexes

Compound	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	ΔE_p (mV)	E_{pa} (V)
Ligand		-0.690			1.310
$[MnL_3]^{2+}(ClO_4)_2$	-0.752	-0.817	-0.784	65	1.152
$[CoL_3]^{2+}(ClO_4)_2$		-0.4699	-		0.8485
$[NiL_3]^{2+}(ClO_4)_2$	-0.4702	-0.599	-0.534	129	0.769
$[CuL_3]^{2+}(ClO_4)_2$	-	0.4019	-	-	1.119
		1.7525			
$[ZnL_3]^{2+}(ClO_4)_2$	-0.8786	-1.022	0.8016	-0.840	77

Table 6: Antifungal activity of metal complexes

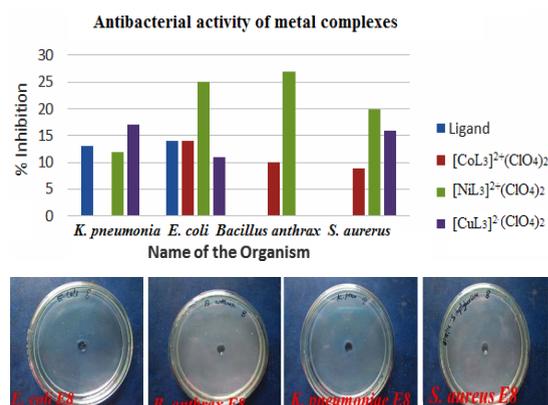
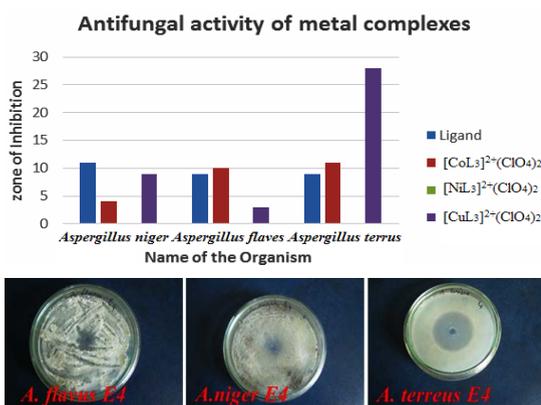
Name of organism	Ligand	$[CoL_3]^{2+}(ClO_4)_2$	$[NiL_3]^{2+}(ClO_4)_2$	$[CuL_3]^{2+}(ClO_4)_2$
<i>Aspergillus niger</i>	11	4	-	9
<i>Aspergillus flavus</i>	9	10	-	3
<i>Aspergillus terreus</i>	9	11	-	28

Table 7: Antibacterial activity of metal complexes

Name of organism	Ligand	$[CoL_3]^{2+}(ClO_4)_2$	$[NiL_3]^{2+}(ClO_4)_2$	$[CuL_3]^{2+}(ClO_4)_2$
<i>K. pneumonia</i>	13	-	12	17
<i>E. coli</i>	14	14	25	11
<i>Bacillus anthrax</i>	-	10	27	-
<i>S. aureus</i>	-	9	20	16

From the anti-bacterial analysis, a moderate activity is imparted. Whereas, in Nickel (II) perchlorate complex it exhibits a higher activity in opposition to three bacterial

microorganism. The Cobalt (II) complex has moderate activity against three pathogens. Copper (II) complexes has good activity against *K. Pneumonia* and *S. aureus*.



CONCLUSION

The spectral studies of the metal(II) perchlorate complexes revealed that the ligand exhibits a mode of coordination through the oxygen of carbonyl and nitrogen of the pyridine ring. The spectral studies evidence that the octahedral geometry of the complex is manifested. A thermal study revealed that all the complexes have no water molecule. The CV studies revealed that the complex of nickel exhibits the quasi-reversible one electron transfer reduction process. Manganese (II) and Zinc (II) complexes reported the reversible one electron reduction process and Copper (II)

and Cobalt (II) complexes exhibit an irreversible reduction and oxidation process. The ligand and complexes possesses better activity against fungal and bacterial strains.

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Conflict of interest

Both the authors declares no conflict of interests.

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