



Metal Complexes of Phenyl Glycine-o-Carboxylic Acid: Preparation, Characterization, Electrochemical and Biological Properties

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ABSTRACT

Metal complexes are the effective therapeutic compound and it became more emerging field in the drug discovery and delivery. A novel ligand phenyl-glycine-o-carboxylic acid was synthesized and further complexed with the metal(II) chlorides. The synthesized metal complexes was interpreted by FT-IR spectroscopy, Ultra Violet-visible, ¹H-NMR, molar conductance, magnetic susceptibility and thermogravimetric study. The electrochemical properties of the ligand and its complexes were inquired in DMF. Antibacterial and fungal activities of the phenyl-glycine-o-carboxylic acid (ligand) and metal complexes were analyzed by three fungal and four bacteria pathogens. The ligand has no activity against *Aspergillus terreus*, but nickel, copper and cobalt chloride complexes showed good activity against *Aspergillus terreus*. On anti-bacterial activity compare to ligands and other metal(II) complexes the cobalt (II) complex revealed greater inhibition effect on selected bacteria.

Keywords: Metal(II) complexes, Phenyl glycine-o-carboxylic acid, Cyclic voltammetry, Antimicrobial activity.

INTRODUCTION

The study of coordination complexes reported the more than centuries till now it plays significant role in many fields especially in the pharmacy and pharmacology fields. It related to the combinations of organic and inorganic chemistry concerning the synthesis, characterization and their applications. It mostly concern their structure, complexes were considered those compounds which do not obey the classical theory of valence.

The biological importance rich metal ions reported in divalent metals ions were cobalt, zinc, copper, manganese, and nickel owing the medicinal value all the five metals were selected for the this research. Naturally, the manganese obtained in daily life is only in trace amounts at different all forms. The human can 2 to 5 mg of vitamin B₁₂ and its derivatives, predominantly in the liver. Nickel gives the extraordinary binding potential for bone and skin which has played urged role in the skin pigmentations. Copper is extensively distributed in all human



resources. Zinc is a very predominant micro-nutrient. A number of human diseases are compatriotic with lowered blood zinc.

The metal and carboxylate ligand coordination behaviors has been explored by several researches. The neutral ligand was decided for the present investigation. Newly formulated neutral ligand phenyl glycine-o-carboxylic acid is derived from anthranilic acid. A literature survey reported that the characterization of complexes of anthranilate ligands manifest different modes of coordination in which carboxylate anion and nitrogen of amine group¹⁻⁴ and both the oxygen of carboxylic acid^{5,6}. The crystal structure of Lithium, Sodium, Thallium complexes of anthranoylanthranilic acid have meshed through the oxygen of carboxylate group with trihydrate water molecule was described⁷. An azomethine nitrogen and carboxylate oxygen of mannich base⁸ and Schiff base⁹⁻¹¹, obtained from anthranilic acid are documented. In this paper, we have given a detailed outline of the preparation, and interpretation of the synthesized metal complexes, furthermore, the electrochemical and biological behavior were studied. In addition to that, the antifungal and antibacterial efficacies of the ligand as well as synthesized five metal complexes were studied in comparative aspects.

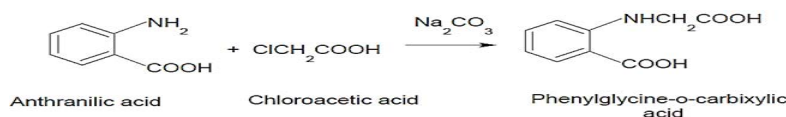


Fig. 1. Synthesis of ligand

Preparation of the metal complexes

Appropriate amount of each metal chlorides and the ligand phenyl-glycine-o-carboxylic acid are dissolved by the ethanol solvent individually and then proper ratio of both are mixed well in the 500 mL round bottom flask. After that, the whole contents in the RB flask highly refluxed with the aid of reflux condenser around six hours. Final mixture of solutions were again concentrated under water bath then, cooled followed by recrystallized the all five metal complexes. Thus, the complexes were prepared, and the excess ligand is separated by washing with ether and dried under vacuum and make into anhydrous with the help of calcium chloride environment.

Spectral methods

The FT-IR of all five metal complexes were

MATERIALS AND METHOD

Materials

All the metal(II) chlorides like cobalt, nickel, manganese, zinc, and copper are hydrated forms which was used in the complexation process and are Merck and Sigma Aldrich grades. Ethanol, diethyl ether, anthranilic acid, chloroacetic acid, anhydrous sodium carbonate, and animal charcoal are acquired from Sigma Aldrich products.

Preparation of ligand

15 g of anthranilic acid, 12 g of chloroacetic acid, 22 g of anhydrous sodium carbonate, and 200 mL of water are taken in one liter round bottom flask. Then reflux condenser is fitted and boil the mixture under reflux for about 3-4 hours. Then, cooled and acidified with the concentrated hydrochloric acid when a light brown precipitate of a ligand is obtained. After that, the mixture is allowed it to complexation overnight. Then it reaction mixture is filtered using the Buchner funnel and then wash with water. The collected solid compound is dissolved in hot water. To that the solution of a hot dilute acid is added followed by 1 g decolorizing animal charcoal is mixed then boil and again filtered. Finally, the crystals of the pure product are obtained.

measured with pellets of KBr using Shimadzu 24 FT-IR 8400S spectrometer between the ranges of 4000-400 cm^{-1} . Then, the electronic spectra of five metal complexes and their ligands were read by using Hitachi U-3400 spectrophotometer in the range of 1100-320 nm using cuvettes. The ¹HNMR was measured by BRUKER 400MHz spectrometer using TMS as an internal standard, CDCl_3 , and DMSO-D_6 as the solvent. The magnetic susceptibility measurements of the complexes were calculated using Gouy's balance at room temperature, and mercury tetrathiocyanato cobaltate(II) was used as a calibrant. The molar conductance was recorded on Toshniwall's conductivity meter in acetonitrile. All melting points in degrees Celsius were measured with a capillary device by using the Stuart melting point apparatus. The antimicrobial activity of ligand

and the metal complexes cobalt, copper, and nickel have been examined inimical to three fungal and four bacteria by using the Agar diffusion method. The 100 μL test solution in DMSO was added to the nutrient Agar plates and potato dextrose agar plates. The plates were incubated at 37°C for 24 h for bacteria and 28°C \pm 2°C for fungi. After 24 h the diameter (mm) of the incubation zone was recorded.

Outcomes & Validation

Electrical conductance

The electrical conductance is weighed and the values of the molar conductance are tabulated in Table 1. The conductance of cobalt(II) complex is 1:1 electrolytic in nature¹². From the all the spectral analysis and conductance results, cobalt(II) chloride

complex is assigned as $[\text{CoL}_3]^{2+} [\text{CoCl}_4]^{2-}$.

Magnetic susceptibility

The magnetic moment of the Manganese(II) chloride complex exhibits 5.93 B.M suggests that it exists in an octahedral geometry. The cobalt(II) chloride complex which is assigned to $[\text{CoL}_3]^{2+} [\text{CoCl}_4]^{2-}$ with an octahedral geometry has a μ_{eff} of 4.46 B.M which is supported by conductance data and the remaining values of five metal complexes are given in Table 1.

Melting behaviour

On heating, the complexes decompose at a temperature above 200°C. It is revealed that all the complexes are stable. Melting behavior is tabulated in Table 1.

Table 1: Physical parameters

Complex	Conductance $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$	Electrolytic nature	μ_{eff} B.M	Melting Point °C	Colour
$[\text{Mn}(\text{L})_2 \text{Cl}_2]$	57.21	1:0	5.93	252	Light Brown
$[\text{Co}(\text{L})_3]^{2+} [\text{CoCl}_4]^{2-}$	140.89	1:1	4.46	245	Light Green
$[\text{Ni}(\text{L})_2 \text{Cl}_2]$	59.71	1:0	3.01	355	Light Yellow
$[\text{Cu}(\text{L})_2 \text{Cl}_2]$	59.71	1:0	1.7	210	Dark Brown
$[\text{Zn}(\text{L})_2 \text{Cl}_2]$	17.06	1:0	-	295	Yellow

L = Phenyl glycine o-carboxylic acid

Infra-Red spectra of complexes

The infra-Red spectrum of ligand has a band at 3373 cm^{-1} is attributed to the OH group of carboxylic acids. The NH stretching vibrations is merged with the previous band. The band (1726 cm^{-1}) C=O of aliphatic acid. The band (1705 cm^{-1}) C=O of aromatic carboxylic acid. The band (1398 cm^{-1}) C-N stretching¹³. The strong band appears (1662 cm^{-1}) NH bending vibrations. The infra-red spectra of ligand are compared with the complexes confirming the complex formation. The shifting of bands from 3373 cm^{-1} to 3341 cm^{-1} , decreases the C-N stretching frequency to

1373 cm^{-1} . The asymmetric and symmetric stretch of the COO^- is not present proposes that the COOH is present in the complex and the shift of C=O stretch (1673 cm^{-1}) proposes that oxygen of C=O is bonded with the M-O bond. The sharp band (1726 cm^{-1}) is shifted to a higher frequency proposing that the aliphatic acid group is not combined with the metal ion. The bands at 3783 cm^{-1} indicate that both the hydroxyl group are present in the carboxylic acid. The new bands (605-575 cm^{-1}) Metal-Oxygen stretch and the band (557-527 cm^{-1}) are assigned to the M-N stretch of the complexes¹⁴⁻¹⁶.

Table 2: FT-IR data of the ligand and their five metal complexes

Compound	$\nu_{\text{O-H}}$ stretching for acid cm^{-1}	$\nu_{\text{C-O}}$ Aliphatic acid cm^{-1}	$\nu_{\text{C-O}}$ Aromatic acid cm^{-1}	$\nu_{\text{C-C}}$ ring cm^{-1}	$\nu_{\text{C-N}}$ stretching cm^{-1}	$\nu_{\text{N-H}}$ bending cm^{-1}	$\nu_{\text{M-O}}$ cm^{-1}	$\nu_{\text{M-N}}$ cm^{-1}
Ligand	3373	1726	1705	1573	1398	1662	-	-
$[\text{Mn}(\text{L})_2 \text{Cl}_2] \cdot 2\text{H}_2\text{O}$	3436	1738	1670	1581	1384	1620	597	532
$[\text{Co}(\text{L})_3]^{2+} [\text{CoCl}_4]^{2-}$	3400	1737	1666	1575	1380	1624	605	527
$[\text{Ni}(\text{L})_2 \text{Cl}_2]$	3524	1740	1668	1578	1378	1610	605	527
$[\text{Cu}(\text{L})_2 \text{Cl}_2]$	3789	1730	1673	1578	1378	1610	599	534
$[\text{Zn}(\text{L})_2 \text{Cl}_2]$	3374	1727	1663	1573	1395	1618	575	557

L = Phenyl glycine o-carboxylic acid

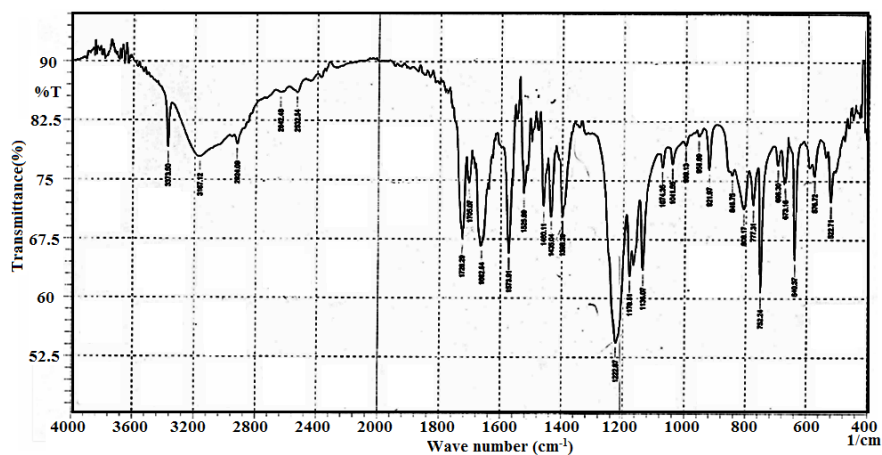


Fig. 2. Infrared Spectrum of Phenylglycine-o-carboxylic acid Ligand

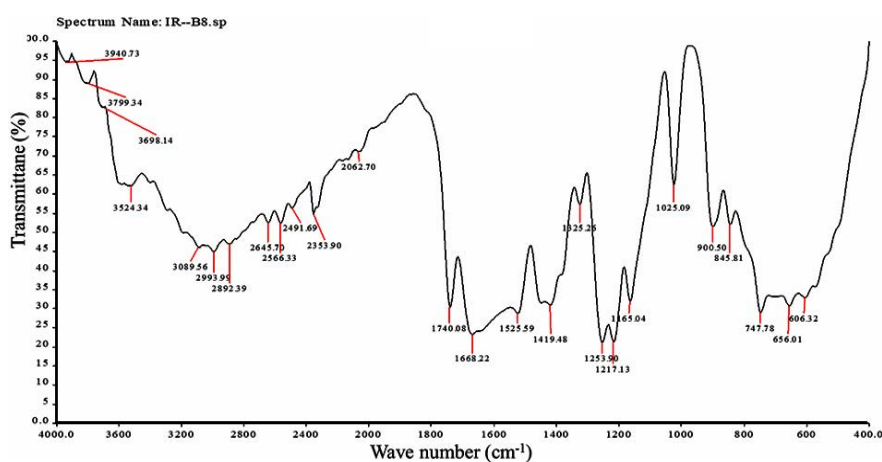


Fig. 3. Infrared Spectrum of Nickel(II) chloride Complex

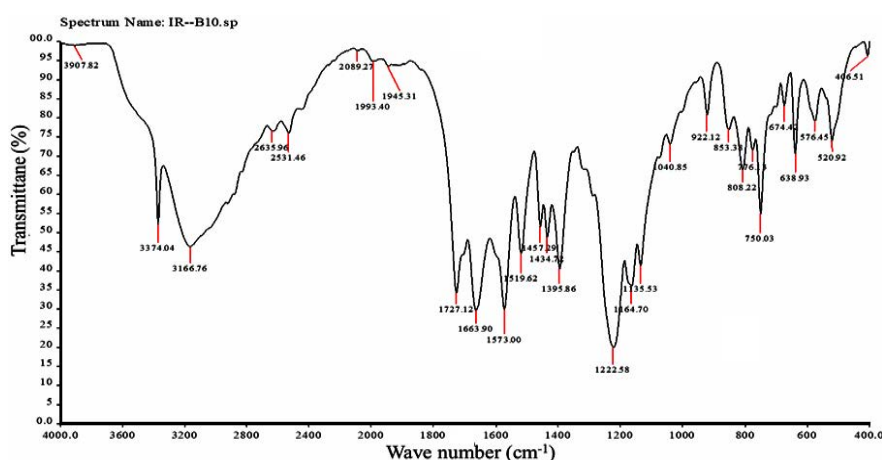


Fig. 4. Infrared Spectrum of Zinc(II) chloride Complex

Electronic spectra of five metal complexes

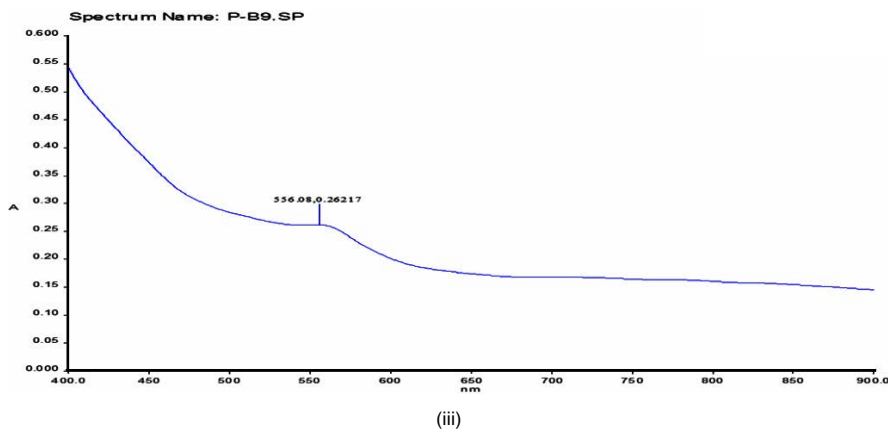
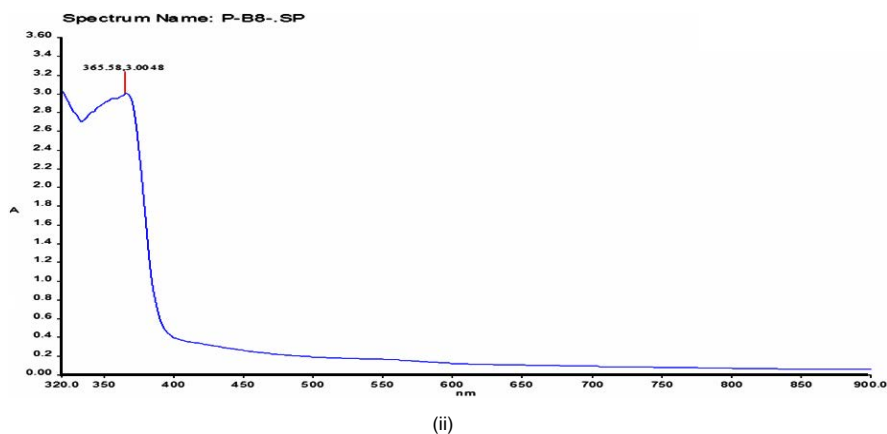
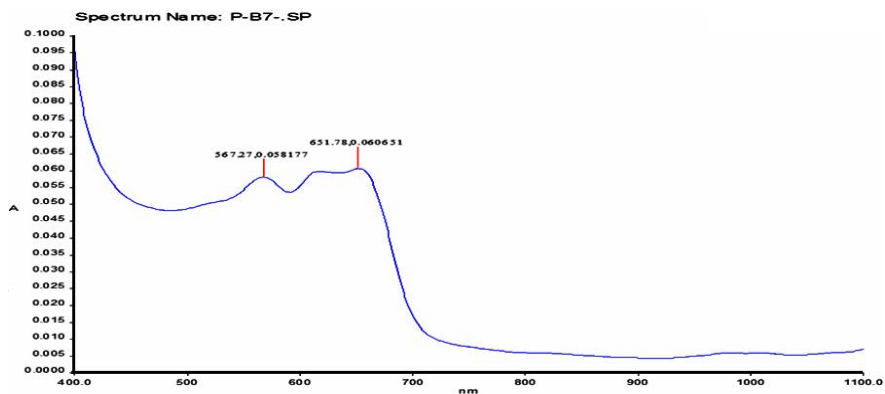
From the electronic spectral data the following assignment, structure and

coordination of nickel, copper, and cobalt complexes were proposed which was listed in the Table 3¹⁷.

Table 3: Electronic spectral data of three metal complexes

Complex	Medium	Adsorption (nm)	Assignment	Stereochemistry
$[\text{Co}(\text{L})_3]^{2+}[\text{CoCl}_4]^{2-}$	Methanol	651.78nm 567nm	$15,342 \text{ cm}^{-1} \text{ } ^4\text{A}_2 \rightarrow \text{}^4\text{T}_1(\text{P})$ $17,636 \text{ cm}^{-1} \text{ } ^4\text{T}_{1g} \rightarrow \text{}^4\text{T}_{1g}(\text{P})$	Tetrahedral and Octahedral
$[\text{NiL}_2\text{Cl}_2]\text{H}_2\text{O}$	Ethanol	365.58nm	$27,353 \text{ cm}^{-1} \text{ } ^3\text{A}_{2g} \rightarrow \text{}^3\text{T}_{1g}(\text{P})$	Octahedral
$[\text{CuL}_2\text{Cl}_2]$	Ethanol	712.83 nm	$14,044 \text{ cm}^{-1} \text{ } ^2\text{E}_g \rightarrow \text{}^2\text{T}_{2g}$	Distorted octahedral

L = Phenylglycine-o-carboxylic acid

**Fig. 5. Electronic Spectra of (i) Cobalt(II) chloride, (ii) Nickel(II) chloride, (iii) Copper(II) Chloride complexes**

¹H NMR spectral studies

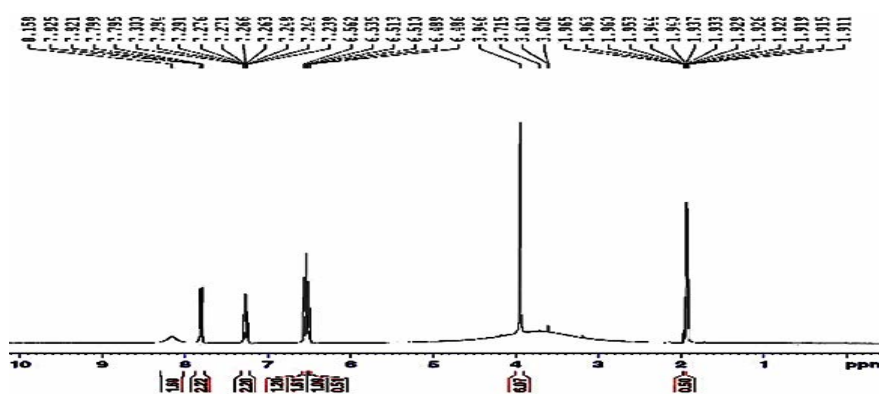
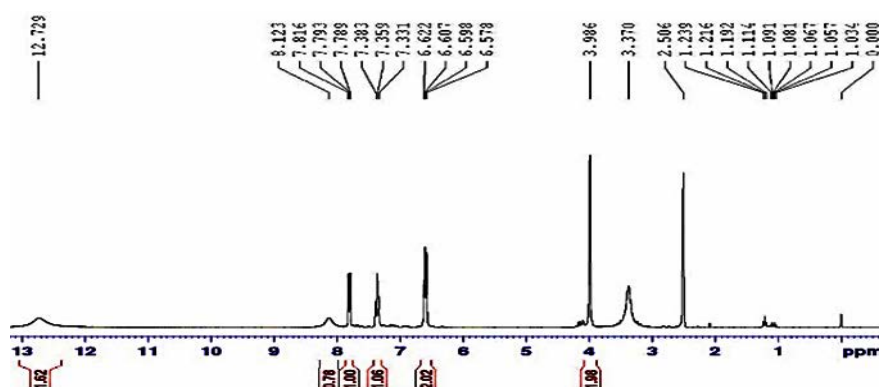
The spectrum of the complex is taken in DMSO-D₆. The spectrum of ligand reveals different peaks at 6.48-7.82ppm corresponding to aromatic proton¹³ and 3.94ppm corresponding to aliphatic CH₂ group 1.96ppm due to NH group. The peak at 8.15ppm assigns (2H) due to two carboxylic acid protons. In Zn(II) chloride complex shows different peaks at 6.53-7.84ppm corresponding to an aromatic proton, 3.98ppm corresponding to the aliphatic CH₂

group, and 2.50ppm assigned to the NH group of secondary amine. The peak at 8.25ppm responsible for -COOH (proton of carboxylic acid) attached to the aliphatic CH₂ group 12.6ppm responsible for -COOH (proton of carboxylic acid) bonded to an aromatic ring. The movement in the position of that proton in the spectrum of the complex suggests that the electron density around the proton is changed because of coordination bond of -C=O (carbonyl oxygen) in the acid functionality.

Table 4: ¹H-NMR of ligand and the metal complex of Zn(II)

Compound	Aromatic proton (ppm)	CH ₂ group (ppm)	NH Group (ppm)	COOH group Aliphatic (ppm)	COOH group Aromatic (ppm)
Ligand	6.48-7.82	3.94	1.96	8.15	8.15
[ZnL ₂ Cl ₂]	6.53-7.84	3.98	2.50	8.25	12.6

L = phenylglycine-o-carboxylic acid

**Fig. 6. ¹H-NMR of Phenyl Glycine-O-Carboxylic acid****Fig. 7. ¹H-NMR of Zinc(II) Chloride complex****Thermal analysis**

In Manganese(II) chloride complex, the curve depicts that the range between 100-120°C was due to the elimination of two lattice water molecules and loss of chloride around 230°C 16.1% (Cal 16.6%) assisted by an endothermic peak of

about 136.1°C and 195.9°C in the DTA curve revealed that the complex melts before decomposition. Further, it decomposes from 300-570°C with a weight loss of 67.9% (calc 70%) corresponding to the decomposition of the ligand combined with an exothermic peak of 446°C on the DTA curve

was observed. In Cobalt(II) chloride complex, it is stable up to 150°C^{19,20}. Above this temperature decomposes the cobalt(II) anion accompanied by an endothermic peak of 151.8°C on DTA showing melting of the complex. In the temperature range between 270-350°C, the anionic complex gets slowly decomposed, furthermore, the second stage of degradation occurs between the range of temperature from 350-580°C with 44.4% (cal 44.6%) mass loss and an exothermic peak with 441.7°C and 556.7°C on DTA are thereby, response to the ligand decomposition. The weight of cobalt oxide is estimated as 19% (cal 17.6%) are stable. The

curve of the Nickel(II) chloride complex depicts an initial weight loss of 14.2% (calc 14.8%) at 50-200°C leads to the separation of one lattice water and non-coordinated ligand, an endothermic peak with 76°C on DTA depicts that there is an occurrence of melting of the complex. The second stage from 250-550°C with the gradual decrease of mass loss of 73.8% (calc 79.7%) corresponds to the removal of two chlorine atoms and the remaining part and an exothermic peak with 384.5°C and decomposition occurs at 512.9°C. The weight of the final residue is about 12% (calc 10.5%) corresponding to stable nickel oxide.

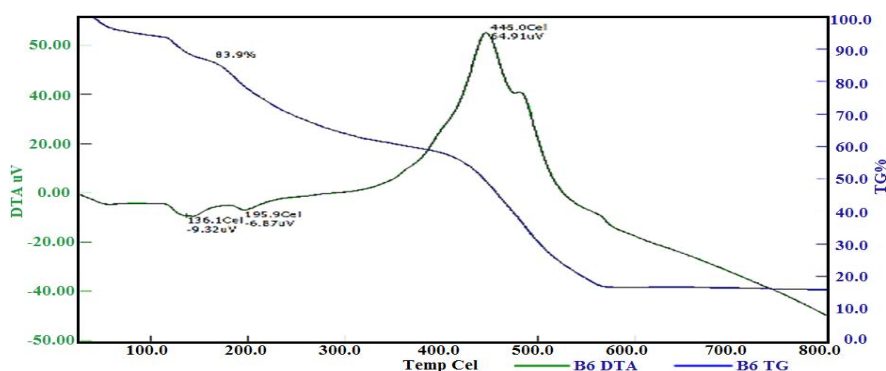


Fig. 8. DTA and TGA Manganese(II) Chloride complex

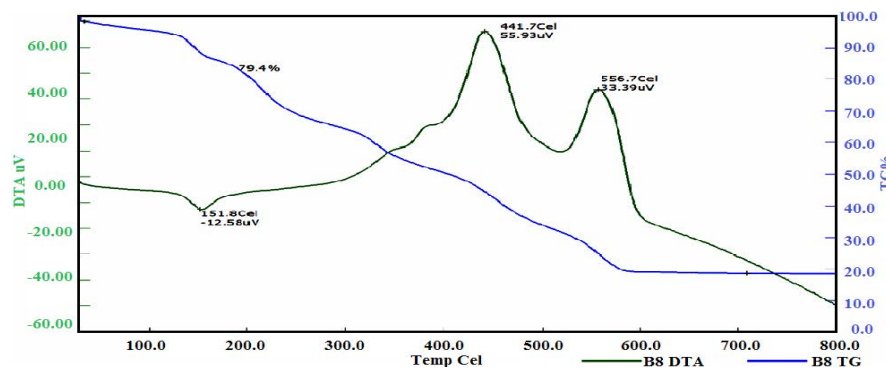


Fig. 9. DTA and TGA of Cobalt(II) Chloride complex

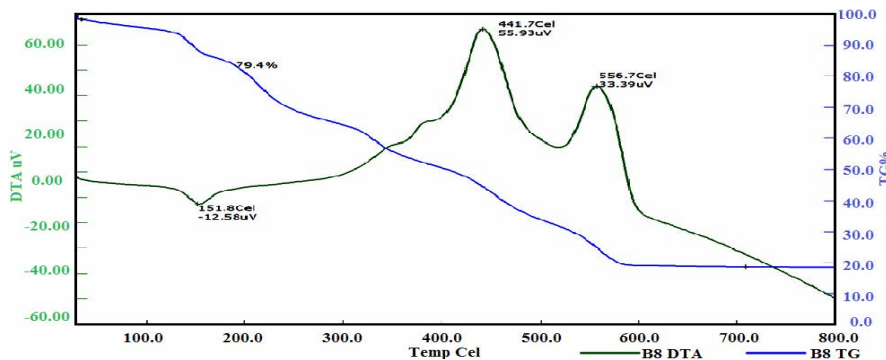


Fig. 10. DTA and TGA curve of Nickel(II) chloride

Structure of the complexes

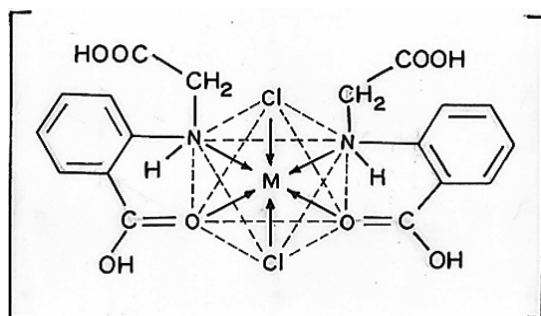


Fig. 11. Structure of metal(II) chloride complexes of phenyl glycine-O-carboxylic acid

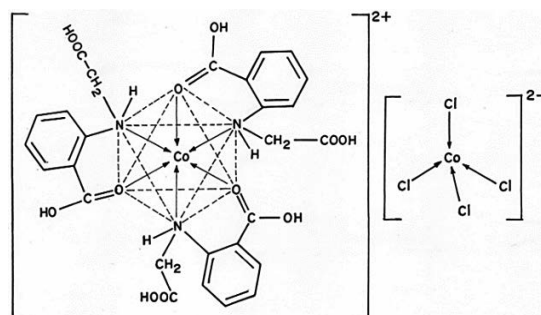


Fig. 12. Structure of $[\text{Co}(\text{L})_3]^{2+}[\text{CoCl}_4]^{2-}$ the complex of phenyl glycine-O-carboxylic acid

Electrochemical behaviour

The electron transfer property of ligand and all the complexes were studied in DMF solution except cobalt(II) chloride complex. It was studied in methanol. All were recorded in 0.001M electrolytes in the range of -2 to $+2$ volt potential in the 50 mV/s scan rate except manganese(II) complexes. The manganese(II) chloride complex was scanned at about 20 mV/s. The free ligand exhibits quasi reversible one-electron reduction at $E_{1/2}$ value is -0.907V ($\Delta E_p = 211$ mV) and two irreversible oxidation potentials at E_{pa} 0.566V and 1.221V . Manganese(II) chloride complex reveals the quasi reversible reduction²¹ with respect to $\text{Mn}(\text{II}) \rightarrow \text{Mn}(\text{I})$ at $E_{1/2}$ value of -0.765V ($\Delta E_p = 189\text{mV}$). Cobalt(II) chloride complex reveals an irreversible reduction and two irreversible oxidation. The first irreversible reduction is allotted to metal-based $\text{Co}(\text{II}) \rightarrow \text{Co}(\text{I})$, two oxidative responses at (E_{pa})= 0.738V and 1.536V were assigned to $2\text{Co}(\text{II}) \rightarrow 2\text{Co}(\text{III})$ oxidation. Nickel(II) chloride complex exhibits irreversible reduction related to $\text{Ni}(\text{II}) \rightarrow \text{Ni}(\text{I})$, quasi reversible one-electron oxidation corresponding to $\text{Ni}(\text{II}) \rightarrow \text{Ni}(\text{III})$ and it exhibits an irreversible oxidative response at (E_{pa}) = 1.349V

assigned to $\text{Ni}(\text{III}) \rightarrow \text{Ni}(\text{IV})$ oxidation. Copper(II) chloride complex displays quasi reversible one-electron reduction²² with respect to $\text{Cu}(\text{II}) \rightarrow \text{Cu}(\text{I})$ at $E_{1/2}$ value of -0.842V ($\Delta E_p = 200$ mV) and it exhibits an irreversible oxidative reduction at $E_{pc} = 0.0108\text{V}$. The Zinc(II) chloride exhibits quasi reversible one-electron reduction concerning $\text{Zn}(\text{II}) \rightarrow \text{Zn}(\text{I})$ at an $E_{1/2}$ value of -0.781V ($\Delta E_p = 161$ mV). From the results, it is conclude that, the metal complex zinc, copper and manganese are quasi reversible reduction, the reduction waves with $E_{1/2}$ in the range of 0.765V to 0.842V is assigned to $\text{M}(\text{II}) \rightarrow \text{M}(\text{I})$ reduction, Ni(II) complex exhibits quasi reversible oxidation and Cobalt (II) complex exhibits irreversible reduction and oxidation. The potentials are summarized in Table 5.

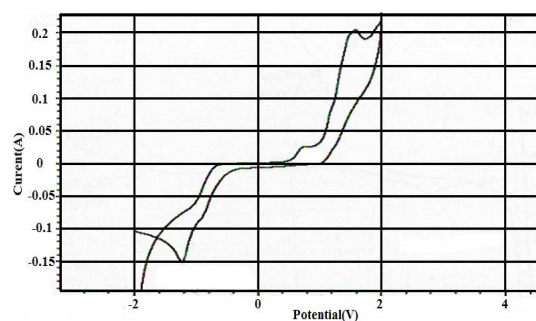


Fig. 13. CV of Cobalt(II) chloride complex

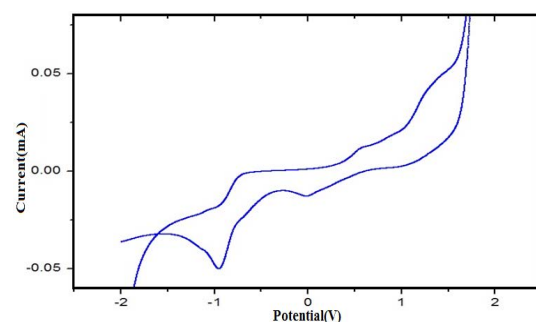


Fig. 14. CV of Copper(II) chloride complex

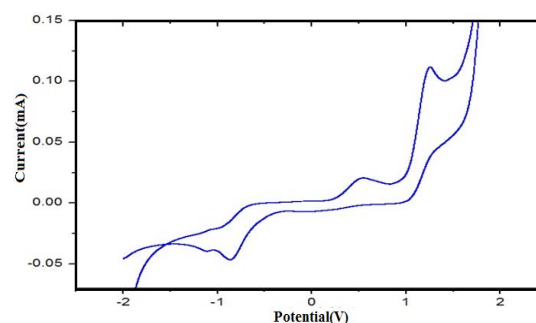


Fig. 15. CV of Zinc(II) chloride complex

Table 5: Cyclic voltammetry of Metal(II) complexes of PGA

Complexes	Reduction				Oxidation			
	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	ΔE_p (mV/s)	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	ΔE_p (mV/s)
Ligand	-0.8022	-1.014	-0.908	211	0.566 1.236	-	-	--
[Mn(L) ₂ Cl ₂] ₂ H ₂ O	-0.6707	-0.8603	-0.765	189	-	-	-	-
[Co(L) ₃] ²⁺ [CoCl ₄] ²⁻	-	-1.229	-	-	0.7381 1.536	-	-	-
[Ni(L) ₂ Cl ₂]	-	-0.7618	-	-	0.721 1.349	0.217	0.884	504
[Cu(L) ₂ Cl ₂]	-0.7420	-0.9426	-0.842	200	-	0.0108	-	-
[Zn(L) ₂ Cl ₂]	-0.6991	-0.8636	-0.781	161	-	-	-	-

L = Phenyl glycine o-carboxylic acid

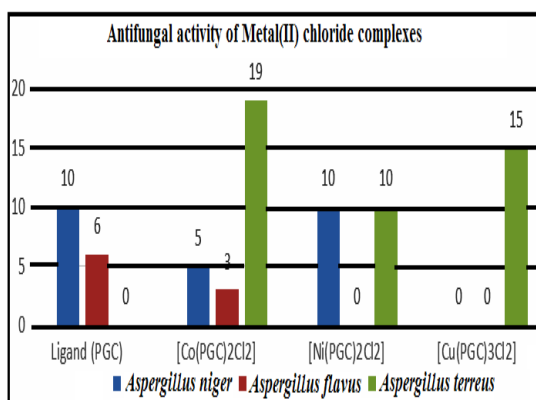
BIOLOGICAL ACTIVITY**Antifungal activity**

The antifungal activities of three metal complexes and their ligand has been examined was

inimical to 3 fungal pathogens-*Aspergillus niger*, *Aspergillus flavus*, and *Aspergillus terreus* by the Agar well diffusion method, and the outcomes are validated and tabulated in Table 6

Table 6: Antifungal activity of Metal(II) chloride complexes

Compound	Zone of inhibition (mm)		
	<i>Aspergillus niger</i>	<i>Aspergillus flavus</i>	<i>Aspergillus terreus</i>
Ligand (PGC)	10	6	-
[Co(L) ₃] ²⁺ [CoCl ₄] ²⁻	5	3	19
[Ni(PGC) ₂ Cl ₂]	10	-	10
[Cu(PGC) ₂ Cl ₂]	-	-	15



Antifungal activity of ligand compared with

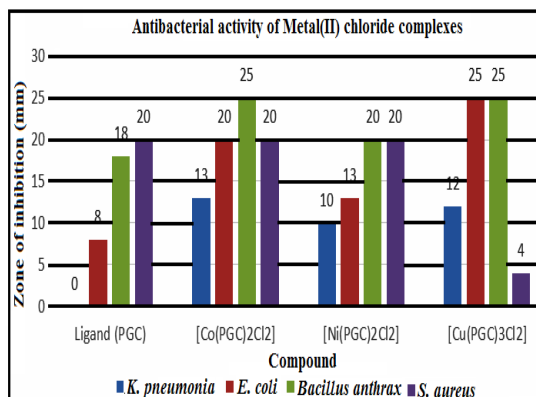
their metal(II) chloride complexes. The ligand has no activity against *Aspergillus terreus*, but copper, nickel and cobalt complexes showed good activity against *Aspergillus terreus*. Cobalt(II) complex reveals a better activity inimical to *Aspergillus niger* and *Aspergillus flavus*.

Antibacterial activity

Phenyl glycine-o-carboxylic acid and its complexes have been examined by the growth of bacteria such as *Klebsiella pneumonia*, *Escherichia coli*, *Bacillus anthrax*, and *Staphylococcus aureus*. The ligand has no activity against *Klebsiella pneumonia*.

Table 7: Antibacterial activities of three Metal(II) chloride complexes and the ligand

	Zone of inhibition (mm)			
	<i>K. pneumonia</i>	<i>E. coli</i>	<i>Bacillus anthrax</i>	<i>S. aureus</i>
Ligand (PGC)	-	8	18	20
[Co(L) ₃] ²⁺ [CoCl ₄] ²⁻	13	20	25	20
[Ni(PGC) ₂ Cl ₂]	10	13	20	20
[Cu(PGC) ₂ Cl ₂]	12	25	25	4



The ligand phenyl-glycine-o-carboxylic acid and their selected metal complexes depict a moderate activity inimical to *B. anthrax*. The metal complexes show fair activity against *E. coli*. The copper complex shows less activity against *S. aureus*. From the above outcomes, it is concluded that the phenyl-glycine-o-carboxylic acid and its metal complexes manifest a good activity inimical to the growth of various microorganisms.

CONCLUSION

The Phenyl-glycine-o-carboxylic acid

and its complexes has been concocted and signaled that the ligand is employed as a bidentate, where the carbonyl oxygen and nitrogen of the secondary amine are bound to the metal ion. The electrical conductance analysis illustrates, that the cobalt complex is in a 1:1 electrolyte. ¹H NMR spectral study elucidates that; the hydroxyl group of the carboxylic acid is not ionized. Remarkably, CV studies manifest that manganese(II), Copper(II) and Zinc(II) complexes flourish in a quasi reversible one-electron transfer reduction process whereas, the Cobalt(II) and Nickel(II) complexes flaunt an irreversible reduction and oxidation process. The ligand and the complexes make evident that it has a good antimicrobial activity inimical to the fungal and bacterial strains.

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Conflict of interest

No conflict of interest.

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