

# Bio-Active Phenylacetic Acid Complexes: Synthesis, Structure And Antimicrobial Activities

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## ABSTRACT

Cu(II) complexes due to their coordination properties and their biological activity these act as good chelating agents and have high pharmacological potential. Cu (II) with phenyl acetic acid and azide have been synthesized and characterized by IR, LC-MS, TG-DTA and UV confirms the coordination of ligands by oxygens of phenyl acetic acid and nitrogens of azide ligands. Complex is screened for anti microbial activity.

**KEY WORDS:** Phenyl acetic acid, Antimicrobial Activity.

## 1. INTRODUCTION

Coordination of metal with organic compounds causes drastic change in the properties of metal and ligand. Phenyl acetic acid and its derivatives are of much interest because of their biological activities. Phenyl acetic acid a type of plant hormone, and an active auxin molecule which plays a vital role in coordination of many growth and behavioural processes in the life cycle of plants. They have antibacterial activity against micro organisms. Pseudo halide ions like azides, thiocyanates, isocyanates are versatile ligands that can bind divalent metal ions ( $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ ) in a variety of ways of connecting transition metals in the solid state. Coordination of organic compounds with metal causes drastic change in the biological property of the ligand and also the metal moiety.

## 2. MATERIAL AND METHODS

IR spectra are obtained with a Shimadzu IR Prestige 21 FT-IR spectrophotometer. Electronic spectra are recorded on LABINDIA UV3000+ UV /VIS spectrophotometer. LC-MS spectra are recorded on AGILANT QQQ (ESI-MS). Mass spectrometer. TG-DSC spectra are obtained using SDT Q600 V20.9 BUILD 20.

**Synthesis of  $[\text{Cu}(\text{PAA})_3(\text{N}_3)_2]$  (1):** An aqueous (5 ml) solution of Copper perchlorate hexahydrate (0.185g, 0.5 mmol) is added to a methanolic solution (10ml) of Phenyl acetic acid (0.068g, 0.5 mmol) under stirring conditions at 60°C, blue solution is formed and then aqueous solution (5 ml) of  $\text{NaN}_3$  (0.03 g, 1.0 mmol) is added which turned to parrot green solution. After constant stirring at 60°C temperature for 30 minutes, the solution turned to greenish blue. The solution is filtered off, greenish blue precipitate is formed. The precipitate was washed with methanol to remove uncoordinated ligands. Yield is 0.168 g (59.4%). Anal.expt  $\text{C}_{26}\text{H}_{24}\text{CuN}_6\text{O}_6$ , Mol.Wt. 580.05, C 53.84, H 4.17, N 14.49 (observed) C 53.62, H 4.12, N 14.20 (calculated). Important IR bands (KBR disc  $\text{cm}^{-1}$ ) 3569, 2145, 1634, 1298  $\text{cm}^{-1}$ . Mass Peak (m/z): 416, 485, 551, 617.

**IR Spectrum of  $[\text{Cu}(\text{PAA})_3(\text{N}_3)_2]$ :** The Infrared spectrum exhibited bands in regions 3344, 3450  $\text{cm}^{-1}$  due to C=O of the free ligand. These bands are shifted to higher frequency 3569  $\text{cm}^{-1}$  on complexation with Cu(II). The C=O stretching in the infrared spectrum of Phenylacetic is assigned to the very intense infrared band observed at 1634  $\text{cm}^{-1}$  another intense band observed at 660  $\text{cm}^{-1}$  in the IR spectrum of Phenylacetic acid is assigned to a ring stretching deformation. However the  $\nu_{\text{as}}(\text{N}_3)$  modes appeared as strong peaks at 2051  $\text{cm}^{-1}$  respectively. The shift to higher frequencies of  $\nu_{\text{as}}(\text{N}_3)$  band at 2145  $\text{cm}^{-1}$  indicates the end-on bridging mode of azide. In addition, the  $\nu_s(\text{N}_3)$  modes appeared as a weak band at 1298  $\text{cm}^{-1}$  also indicates the terminal nature of azido group. Important peaks reported in table.1.

**Table.1. IR Spectrum of  $[\text{Cu}(\text{PAA})_3(\text{N}_3)_2]$**

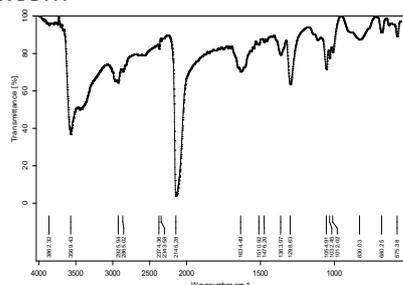
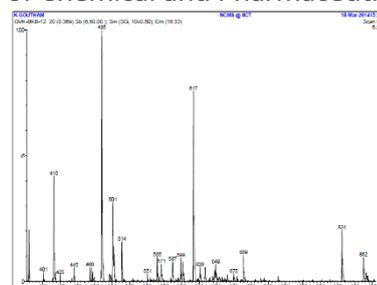
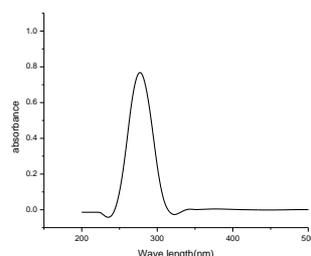
Complex	$\nu \text{ C=O}$	$\nu_{\text{as}}(\text{N}_3)$	Terminal azido group
	3344, 3450 $\text{cm}^{-1}$	2051 $\text{cm}^{-1}$	1298 $\text{cm}^{-1}$

**LC-MS Spectrum of  $[\text{Cu}(\text{PAA})_3(\text{N}_3)_2]$ :** Peak at 416 (m/z) is complex bound to two Phenylacetic acid and two azide ions refer to  $[\text{Cu}(\text{PAA})_2(\text{N}_3)_2]$ . Peak at 485 (m/z) at complex bound to fragments of two Phenylacetic acid and two azide ions. Peak at 551 (m/z) is complex bounded to three Phenylacetic acid and two azide ions refer to  $[\text{Cu}(\text{PAA})_3(\text{N}_3)_2]$ . Peak at 617 (m/z) corresponds to Cu bound to fragment of four PAA fragment and azide ions.

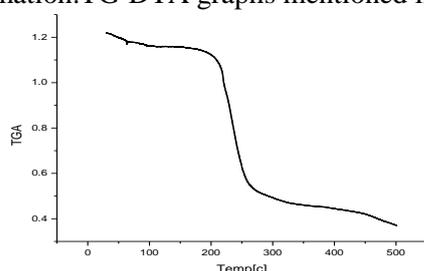
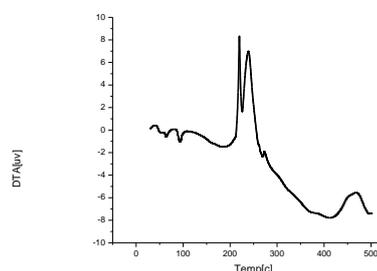
**Electronic Spectrum of  $[\text{Cu}(\text{PAA})_3(\text{N}_3)_2]$ :** The UV-VIS spectrum of the metal complexes is recorded in DMSO solution in the wavelength range 200–800 nm. The UV-VIS spectrum of Cu(II) complex displays a broad band at 360 nm attributable to d-d transition, which is compatible with complexes having square pyramidal structure. Important absorption band reported in table.2.

**Table.2. Electronic Spectrum of  $[\text{Cu}(\text{PAA})_3(\text{N}_3)_2]$**

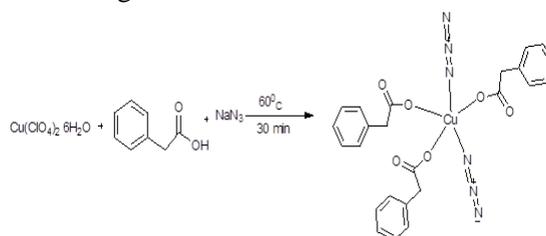
Complex	Absorbance	$\mu/\text{cm}^{-1}$	Assignment
	360	320	d-d

Figure.1. IR Spectrum of  $[\text{Cu}(\text{PAA})_3(\text{N}_3)_2]$ Figure.2. LC-MS Spectrum of  $[\text{Cu}(\text{PAA})_3(\text{N}_3)_2]$ Figure.3. Electronic Spectrum of  $[\text{Cu}(\text{PAA})_3(\text{N}_3)_2]$ 

**Thermo gravimetric Analysis of  $[\text{Cu}(\text{PAA})_3(\text{N}_3)_2]$ :** The thermal decomposition of the complex  $[\text{Cu}(\text{PAA})_3(\text{N}_3)_2]$  takes place in two stages  $\text{Cu}(\text{II})$  complex exhibits thermal stability up to  $200^\circ\text{C}$ , which confirms that this complex is free from any types of water molecules. In the first stage loss of three PAA ligands from the complex takes place in between  $50\text{--}220^\circ\text{C}$  with mass loss of 57.2% (obs 57.9%). This appeared as an exothermic peak in the DTA curve within the temperature range  $200\text{--}250^\circ\text{C}$ . In the second stage which occurs in the temperature range  $280\text{--}400^\circ\text{C}$  corresponds to the decomposition of azide ligand takes place with mass loss is recorded as 10.09% (obs 10.63%). This appeared as an exothermic peak within the temperature range maximum rate of mass loss is indicated by DTA peak at  $280\text{--}400^\circ\text{C}$ . Above this temperature, a weight loss has been occurred upto  $500^\circ\text{C}$ . This corresponds to Copper Oxide formation. TG-DTA graphs mentioned in Figs.4, 5.

Figure.4. TG Spectrum of  $[\text{Cu}(\text{PAA})_3(\text{N}_3)_2]$ Figure.5. DTA Spectrum of  $[\text{Cu}(\text{PAA})_3(\text{N}_3)_2]$ 

**Proposed Structure of  $[\text{Cu}(\text{PAA})_3(\text{N}_3)_2]$ :** In the title complex  $[\text{Cu}(\text{PAA})_3(\text{N}_3)_2]$   $\text{Cu}^{+2}$  was coordinated by three oxygens from three phenylacetic acid ligands, two N atoms from the azide ligands. Hence  $\text{Cu}^{+2}$  in the complex adopt perfect square pyramidal structure shows Fig.6.

Figure.6. Proposed Structure of  $[\text{Cu}(\text{PAA})_3(\text{N}_3)_2]$ 

**Antimicrobial Screening of  $[\text{Cu}(\text{PAA})_3(\text{N}_3)_2]$ :** The complex is screened *in vitro* for Antibacterial activity against *E.coli*, *S.aureus* and Antifungal activity against *R.Oligospor* by disc diffusion method. The *in vitro* Antimicrobial properties of the complex is tested against these gram-positive and gram-negative bacteria- *S. aureus*, *E.coli*, *P.aeruginosa* and fungi like *R.Oligospor*, complex presents very good results of Antibacterial activity and no Antifungal activity. The diameters of the inhibition zone are 3 and 2.5 mm for respectively for *S.aureus* & *E.coli* while no inhibition zone is found for *R.Oligospor*. The Antimicrobial activity of all the complexes are listed in table.3 and zone of inhibitions showed in figs.7,8.



Figure.7. Inhibition zones for complex against *S.aureus* and *E.coli*



Figure.8. Inhibition zones for complex against *R.Oligosporos*

Table.3. Inhibition zones for complex  $[\text{Cu}(\text{PAA})_3(\text{N}_3)_2]$

Bacteria	Inhibition zone (mm)
<i>E. coli</i>	2.5
<i>S.aureus</i>	3
Fungi	Inhibition zone (mm)
<i>R.Oligosporos</i>	Nil

### 3. RESULTS AND DISCUSSIONS

Transition metal complex of copper involving phenyl acetic acid as primary ligand and pseudo halide as secondary ligand is synthesized by self assembled method which were analysed by means of IR, LC-MS, UV and Thermo gravimetric analysis. The IR spectra show that Phenylacetic acid act as unidentate ligand coordinating with carboxylate ion. Electronic spectra confirm square pyramid geometry. The metal complex was screened for antimicrobial activities and evaluated against three different bacteria (*E. coli*, *S. aureus* & *P. aeruginosa*) and also fungi (*R.Oligosporos*) and the results showed that complex exhibit good antibacterial activity in comparison with standard drug streptomycin and totally inactive against fungi. Hence this new Bio Active Phenylacetic Acid complex endowed with potent antimicrobial activity which can be as drugs on further study.

### 4. CONCLUSION

In this article we are reported the synthesis of copper, Phenyl acetic acid Azide complex and their antimicrobial studies. The results for complex revealed that they are good in microbial activity.

### 5. ACKNOWLEDGMENTS

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### REFERENCES

- Burkhead K.D, Slininger P.J, Schisler D.A, Biological control bacterium *Enterobacter Colacae* S11:T:07 (NRRL B-21050) produces the antifungal Compound phenyl acetic acid in saboraud maltose broth Culture, *Soil Biol. Biochem.*, 30, 1998, 665-667.
- Burkhead K.D, Slininger P.J, Schisler D.A, Biological control bacterium *Enterobacter cloacae* S11:T:07 (NRRL B-21050) produces the antifungal compound phenylacetic acid, *Soil Biol Biochem.*, 30, 1998, 665-667.
- De Munno G, Lombardi M.G, Julve M, Lloret F and Faus J, Synthesis, crystal structure and magnetic properties of the first single azido-bridged copper(II) chain  $[\text{Cu}(\text{bpym}) (\text{N}_3)_2]_n$  (bpym + 2,2'-bipyrimidine), *Inorg. Chim. Acta*, 282 (2), 1998, 252-256.
- Depree C.V, Beckmann U, Heslop K and Brooker S, Monomeric, trimeric and polymeric assemblies of dicopper (II) complexes of a triazolate-containing Schiff-base macrocycle, *Dalton Trans.*, 2003, 3071.
- Lee J.G, Lee B.Y and Lee H.J, Accumulation of phytotoxic organic acids in reused nutrient solution during hydroponic cultivation of lettuce (*Lactuca sativa* L.), *Sci. Hortic.*, 110, 2006, 119-128.
- Mautner F.A, Landry K.N, Gallo A.A, Massoud S.S, Molecular Structure of Mononuclear Azido- and Diacyanamido-Cu(II) Complexes, *J. Molecular Structure*, 837, 2007, 72-78.
- Mukhopadhyay U, Bernal I, Massoud S.S, Mautner F.A, Syntheses, Structures and Some Electrochemistry of Cu(II) Complexes With Tris[(2-pyridyl)methyl] amine:  $[\text{Cu}\{\text{N}(\text{CH}_2\text{-py})_3\}(\text{N}_3)]\text{ClO}_4$  (I),  $[\text{Cu}\{\text{N}(\text{CH}_2\text{-py})_3\}(\text{NO}_2)]\text{ClO}_4$  (II) and  $[\text{Cu}\{\text{N}(\text{CH}_2\text{-py})_3\}(\text{NCS})]\text{ClO}_4$  (III), *Inorg. Chim. Acta.*, 357, 2004, 3673-3682.

Pizzeghello D, Zanella A, Carletti P, Nardi S, Chemical and biological characterization of dissolved organic matter from silver fir and beech forest soils, *Chemosphere*, 65, 2006, 190-200.

Sarkar S, Mondal A, Ribas, Drew M.GB, Pramanik K, Rajak K.K Mono, di and polynuclear Cu(II)–azido complexes incorporating *N, N, N* reduced schiff base, syntheses, structure and magnetic behavior., *Inorg. Chem. Acta.*, 358, 2005, 641-649.

Song Y, Massera C, Roubeau O, Gamez P, Lanfredi AM.M, Reedijk J, n unusual open cubane structure in a  $\mu(1,1)$ -azido- and alkoxo-bridged tetranuclear copper(II) complex,  $[\text{Cu}_4\text{L}_2(\mu(1,1)\text{-N}_3)_2]$  center dot  $5\text{H}_2\text{O}$  ( $\text{H}_3\text{L} = \text{N,N}'\text{-(2-hydroxylpropane-1,3-diyl)bis-salicylideneimine}$ ), *Inorg. Chem.*, 43,2004, 6842-6847.

Stamatatos T.C, Papaefstathiou G.S, Mac Gillivray L.R, Escuer A, Vicente R, Ruiz E, Perlepes S.P, Ferromagnetic Coupling in a 1D Coordination Polymer Containing a Symmetric  $[\text{Cu}(\mu_{1,1}\text{-N}_3)_2\text{Cu}(\mu_{1,1}\text{-N}_3)_2\text{Cu}]^{2+}$  Core and Based on an Organic Ligand Obtained from the Solid State, *Inorg. Chem.*, 46, 2007, 8843-8850.

Woodard, Willett R.D, Haddad S, Twamley B, Gomez-Garcia C.J, Coronado E. Structure of Two Azide Salts of a Copper(II) Macrocyclic and Magnetic Properties of  $\text{Cu(14ane)Cu(N}_3)_4$ , *Inorg. Chem.*, 43, 2004, 1822.