Synthesis, Crystal Structure and Antimicrobial Activity of Poly [bis-μ-3,5-dinitro-2-oxidobenzoato) (py) Cu II]

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(Received on 10th May 2020, accepted in revised form 6th October 2020)

Summary: A novel Poly [bis-μ-3,5-dinitro-2-oxidobenzoato) (py) Cu II]/($C_{12}H_7CuN_3O_7$) was synthesized by a self assemble method at room temperature. The molecular structure was determined by single-crystal X-ray analysis. The compound crystallizes in the monoclinic system, space group P 2 1/c with lattice parameters of a = 10.2143, b = 5.1651 and c = 26.608, α = 90, β = 99.720, γ = 90, Z = 4, V = 1383.60 (18) Å^3.Pore size depicted from single crystal XRD data was 47Å. The central metal atom Cu (II) is coordinated with oxygen of carboxylates group and nitrogen atom of pyridine. The coordination polyhedron posses square pyramidal geometry is manifested by the N— Cu—O angle of 90°. The structure is composed of monomeric coordination units with the central copper (II) ion is not occupying a centre of symmetry.

Key words: Crystal Structure; Antimicrobial Activity; Pyridine; Crystallography; C—H…π interactions.

Introduction

Salicylic acid (SA) as a curative substance is well-known for centuries, derivatives of salicylic acid such as nitro, amino and halogen gives superior remedial performance than the parent compound [1]. One of the SA derivative e.g. aspirin is the most commonly used medicines for humans. Copper (II) coordination polymer of SA is very rare but have many applications such as anti-ulcer, anti-diabetic, anti-mutagenic, anti-cenvulsant, analgesic, anti-neoplastic and radio protective activity [2]. SA ability is to act as an oxygen donor and it forms complex with metal atoms. SA has been studied well from time to time but the study of coordination polymers with metal atoms and 3,5-dinitrosalicylic acid is also rare in solid state chemistry [3]. However, 3, 5-dinitrosalicylic acid is effectively applied for the glucose estimation in human urine. In addition dinitrosalicylic acid is an excellent protein precipitant and on this account can probably be used for the determination of blood sugar [4].

The chemistry of carboxylates and transition metal atoms has played a major role in the intangible progress of modern inorganic chemistry. Transition metals form complexes with carboxylates anion. Transition metal complexes with biochemically active ligands frequently show interesting physical and chemical properties, as a result they may find applications in biological systems [5]. Extensive structural and physicochemical studies of these compounds were important for increasing the understanding of the bonding and electronic interactions between proximate metal centers. Metal–organic frameworks with salicylic acid ligand and nitrogen-containing ligands were found to display multipoint diverse structure types such as discrete clusters and one dimensional (1D) chain compound. However, substituted salicylic acid such as 3,5-dinitrosalicylic acid ligand is much less applied compared with salicylic acid ligand [6]. The chemistry of copper compounds has been extensively investigated and the relationship between the structure and reactivity, ranging from industrial catalysis to biomedical activity, is of major importance [7]. The active form of aspirin was also suggested to be a copper complex, formed in vivo. Metal complexes are generally more active than drug themselves [8]. Copper (II) carboxylates and benzoates have been extensively studied because carboxylates anions posses different bonding modes that are related to their properties e.g basicity of anion, position of substituent on the aromatic ring [9]. In present study, Cu(II) form 1D polymer with 3,5-dinitrosalicylic acid and pyridine, which was characterized by different techniques. $C_{12}H_7CuN_3O_7$ Experimental %C = 38.58, H = 2.63, N = 9.06.Calculated %C = 39.0, H = 1.90, N = 11.01.

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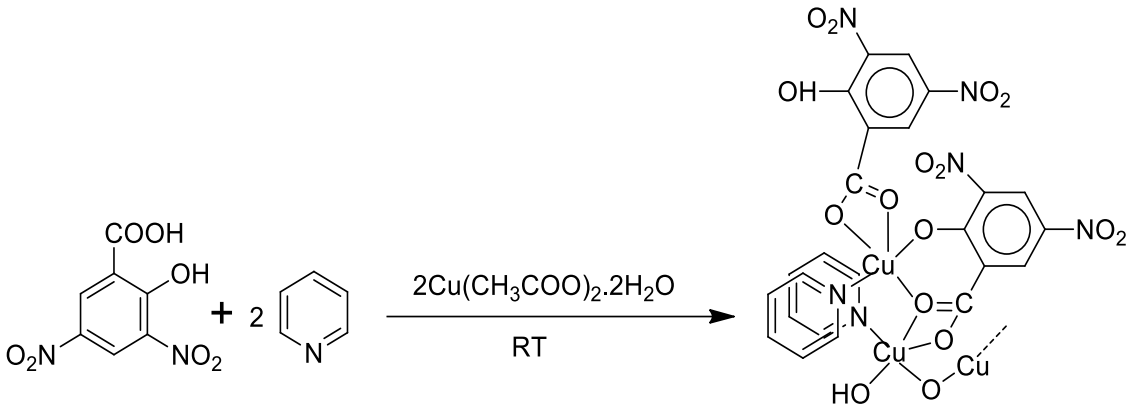

Scheme-1: Synthesis of Poly [bis-μ-3,5-dinitro-2oxidobenzoato) (py) Cu II].

Experimental

Materials and methods

All reagents and material used is of analytical grade to avoid further purification. Cu $(CH_3COO)_2.2H_2O$ and C_5H_5N were purchased from E. Merck, Darmstadt (Germany). 3,5- Dinitrosalicylic acid and Methanol was purchased from Sigma Aldrich (India). Ingle Crystal XRD were carried out on a Bruker APEX II CCD diffractometer at 296(2) K with Mo Kα radiation (λ =1.54 A˚). Nicolet 5700 FT-IR spectrophotometer was used to measured IR in the region (4000—600 cm^{-1}). LIBRA S-22 UV/Vis spectrophotometer (200— 800 nm) is used to record electronic spectra of complex. Melting points was resolute from a Gallen Kamp instrument. AVANCE AV-500 instrument records ^1H NMR spectra in DMSO. CHNS were run on a Thermoscientific analyzer.

Synthesis of Poly [bis-μ-3,5-dinitro-2oxidobenzoato) (py) Cu II]

Round bottom flask was used to prepared complex of title compound (**1**). Methanolic solution of 1:1 equimolar quantities of 3,5-Dinitrosalicylic acid (0.03 M) and copper acetate (0.05 M) in the presence of 2 mL pyridine (2.5 mM) was stirrer strongly about 20 min. The solutions turn green when mixed with each other, after two to three days at room temperature green colour crystals appeared. Flowery crystals of the title compound were further analyzed with single X-ray crystal structure (Scheme-1).

Green crystalline solid, yield = 60 %, m.p = 296∼298°.IR (KBr cm^{-1}) νmax 1614, 1584, 1525, 1480, 1432, 1342, 3092 and 3430.^{1}HNMR in DMSO of the compound 1 showed doublet at δ ppm 8.833 ∼8.826 for C-H aromatic protons, singlet at δ ppm 8.585 for N=CH/HC=O, doublets at 8.469 ~ 8.462, two triplet at 7.820 and 7.411 for Ar─H proton. Two triplets are 3.312 and 2.490 for O─CH_2.

Crystallography

Crystals having proper size and shape were selected and analyzed by single crystal X-ray diffraction technique. Single crystal of compound (**1**) was mounted on a thin glass fiber at room temperature. All measurements were made on Bruker Kappa *APEX*-II CCD diffractometer with graphite monochromatic Mo-Kα radiation. The structure Fig.1 was solved by direct method and refined by using *SHELXL* 2013(Sheldrick, 2013).

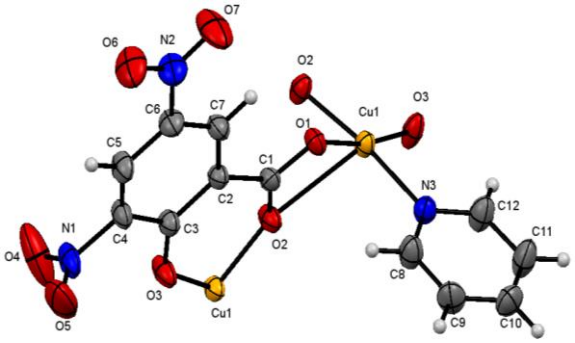

Fig. 1: Molecular structure of Poly [bis-μ-3,5-dinitro-2oxidobenzoato) (py) Cu II]. Ellipsoid is drawn.

The CIF file of compound have been assigned CCDC number 1435801 and can be obtained free of charge on application to CCDC 12 Union Road, Cambridge CB21 EZ, UK. (Fax: (+44) 1223 336-033; email: data_request@ccdc.cam.ac.uk).

Antimicrobial testing

Preliminary in vitro tests for antimicrobial activity of compounds (**1)** have been carried out by disk diffusion method. The antimicrobial activities of compounds (**1**) against two bacterial strains i.e Staphylococcus albus (G+ve) and Escherichia coli (G-ve) as well as one fungal strain Rhizopus stolonifer have been investigated at a concentration of 50 µg/disc. These microorganisms were taken as representative organisms for testing antimicrobial activity. Diluted DMSO was used as negative control and to dissolve cefixime and terbinafine 10 µg/disc were used as positive control. The disks with the tested compounds and the blank (DMSO) were added on to petri dishes inoculated with the tested microbial strains. After incubation at 28 °C for 24-36 h, the diameters of the zones of inhibition were determined and DMSO was found to be inactive under the conditions applied.

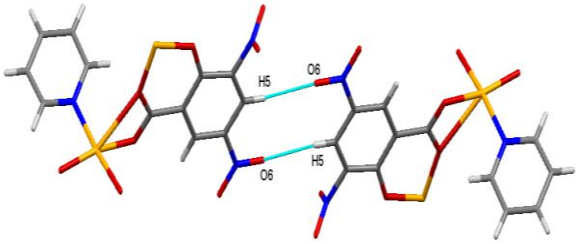

Fig. 2: Dimeric interactions *via H* (5)···*O*(6) and *O*(6)···*H*(5) in compound **(1).**

Results and Discussion

X-ray diffraction analysis

Compound crystallized as a green flower like solid in a monoclinic system having space group P 2 1 / c. Experimental detail are listed in Table-1. X-ray diffraction analysis was performed to ensure the final structure and to study their three-dimensional patterns. The complete crystal data are narrated in table and ORTEP views are shown in Fig. 2. Selected bond lengths and geometrical parameters are listed in Table-2.The infinite one dimensional chain structure has also been observed via several non-bonding interactions Fig. 3 showed pyridine rings are in the form of a wall. Since hydrogen bonding is a gateway to molecular organization and even to crystal engineering, it was considered appropriate to use a hydroxyl group in an ortho position as a suitable probe in the present study. Hydrogen bond interactions are also shown in Table-3. Moreover, reviewers suggest, that hydrogen bonding with coordinated carboxylates oxygen atom should result the elongation in the axial Cu–O bond in trans-bis Werner-type copper (II) complexes [10, 11]. Synthesis of title compound (**1**) was also confirmed by H-NMR values.

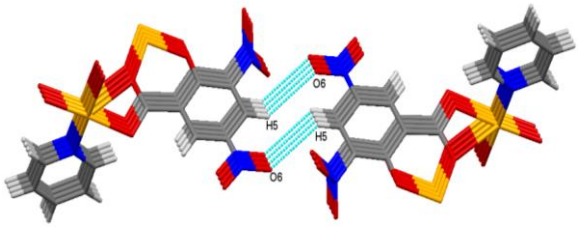

Fig. 3: Supramolecular wall-like pattern of title compound (**1)** through multiple C–H···π interactions.

Table-1: Experimental detail of compound (**1**).

	SHELXL
Crystal data	
Chemical formula	$C_{12}H_7CuN_3O_7$
M_r	**368.75**
Crystal system, space group	**Monoclinic, $P2_1/c$**
Temperature (K)	**296**
***a*, *b*, *c* (Å)**	**10.2143 (9), 5.1651 (3), 26.608 (2)**
β (°)	**99.720 (4)**
V (Å^3)	**1383.60 (18)**
Z	**4**
Radiation type	**Mo $K\alpha$**
μ (mm^{-1})	**1.62**
Crystal size (mm)	**0.38 × 0.22 × 0.16**
Data collection	
Diffractometer	**Bruker Kappa Apex-II**
Absorption correction	**Multi-scan**
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	**12746, 3298, 2696**
R_{int}	**0.033**
$(\sin \theta/\theta)_{max}$ (Å^{-1})	**0.658**
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	**0.034, 0.088, 1.02**
No. of reflections	**3298**
No. of parameters	**208**
H-atom treatment	**H-atom parameters constrained**
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	**0.69, -0.35**

Spectroscopic studies

The IR spectrum of the compound Fig. 4 showed very weak absorption band in the area 3098 and 3430 cm^{-1}, belonging with O–H vibrations of methanol molecules and O–H of protonated carboxylic group. The disappearance of O-H and C-H stretching peaks indicate the successful conversion of ligand into its respective copper coordination polymer. Carboxylates stretching frequencies were found as doublets m as(COO^-) at 1614 and 1605 cm^{-1}, and ms(COO^-) at 1480, and 1432 cm^{-1}.The difference between the asymmetric and symmetric stretching vibrations (Dm = mas(COO^-) - ms(COO^-)) of 134 and 173 cm^{-1} [7]. The nitro-group stretching frequencies were found, mas(NO_2) at 1584 and ms(NO_2) at 1342 cm^{-1}, indicates that the 3,5-dinitrosalicylate anions coordinated as a bidentate chelating, or bridging carboxylic group (see the crystal structure).

Table-2: Selected geometric parameters (Å).

Cu(1)—O(3)^{i}	1.8967 (16)	C(2)—C(7)	1.392 (3)
Cu(1)—O(2)^{i}	1.9213 (16)	C(2)—C(3)	1.422 (3)
Cu(1)—O(1)	1.9885 (15)	C(3)—C(4)	1.426 (3)
Cu(1)—N(3)	1.994 (2)	C(4)—C(5)	1.363 (3)
O(1)—C(1)	1.258 (3)	C(5)—C(6)	1.384 (4)
O(2)—C(1)	1.270 (3)	C(5)—H(5)	0.9300
O(2)—Cu(1)^{ii}	1.9213 (16)	C(6)—C(7)	1.374 (3)
O(3)—C(3)	1.294 (3)	C(7)—H(7)	0.9300
O(3)—Cu(1)^{ii}	1.8966 (16)	C(8)—C(9)	1.368 (4)
O(4)—N(1)	1.191 (3)	C(8)—H(8)	0.9300
O(5)—N(1)	1.208 (3)	C(9)—C(10)	1.369 (4)
O(6)—N(2)	1.222 (3)	C(9)—H(9)	0.9300
O(7)—N(2)	1.217 (3)	C(10)—C(11)	1.372 (4)
N(1)—C(4)	1.469 (3)	C(10)—H(10)	0.9300
N(2)—C(6)	1.456 (3)	C(11)—C(12)	1.376 (4)
N(3)—C(12)	1.338 (3)	C(11)—H(11)	0.9300
N(3)—C(8)	1.340 (3)	C(12)—H(12)	0.9300
O(3)^{i}—Cu(1)—N(3)	91.00 (8)	C(4)—C(5)—C(6)	117.6 (2)
O(2)^{i}—Cu(1)—N(3)	173.65 (8)	C(4)—C(5)—H(5)	121.2
O(1)—Cu(1)—N(3)	94.37 (8)	C(6)—C(5)—H(5)	121.2
C(1)—O(1)—Cu(1)	106.68 (14)	C(7)—C(6)—C(5)	121.4 (2)
C(1)—O(2)—Cu(1)^{ii}	131.40 (14)	C(7)—C(6)—N(2)	119.1 (2)
C(3)—O(3)—Cu(1)^{ii}	127.86 (14)	C(5)—C(6)—N(2)	119.4 (2)
O(4)—N(1)—O(5)	124.4 (3)	C(6)—C(7)—C(2)	120.8 (2)
O(4)—N(1)—C(4)	117.7 (3)	C(6)—C(7)—H(7)	119.6
O(5)—N(1)—C(4)	117.8 (3)	C(2)—C(7)—H(7)	119.6
O(7)—N(2)—O(6)	123.5 (2)	N(3)—C(8)—C(9)	123.0 (2)
O(7)—N(2)—C(6)	118.2 (2)	N(3)—C(8)—H(8)	118.5
O(6)—N(2)—C(6)	118.4 (2)	C(9)—C(8)—H(8)	118.5
Cu(1—O(1)—C(1)—O(2)	12.5 (3)	O(5)—N(1)—C(4)—C(3)	115.5 (3)
Cu(1—O(1)—C(1)—C(2)	-167.06 (17)	C(3)—C(4)—C(5)—C(6)	2.5 (4)
Cu(1)^{i}—O(2)—C(1)—O(1)	172.75 (15)	N(1)—C(4)—C(5)—C(6)	-178.0 (2)
Cu(1)^{i}—O(2)—C(1)—C(2)	-7.7 (3)	C(4)—C(5)—C(6)—C(7)	-1.8 (4)
O(1)—C(1)—C(2)—C(7)	6.6 (3)	C(4)—C(5)—C(6)—N(2)	176.9 (2)
O(2)—C(1)—C(2—C7	-172.9 (2)	O(7)—N(2)—C(6)—C(7)	2.4 (4)
O(1)—C(1)—C(2—C3	-173.7 (2)	O(6)—N(2)—C(6)—C(7)	-178.2 (3)
O(2)—C(1)—C(2—C3	6.7 (4)	O(7)—N(2)—C(6)—C(5)	-176.4 (3)
Cu(1)^{i}—O(3)—C(3)—C(2)	-8.9 (4)	O(6)—N(2)—C(6)—C(5)	3.1 (4)
Cu(1)^{i}—O(3)—C(3)—C(4)	172.43 (18)	C(5)—C(6)—C(7)—C(2)	0.3 (4)
C(7)—C(2)—C(3)—O(3)	-178.7 (2)	N(2)—C(6)—C(7)—C(2)	-178.4 (2)
C(1)—C(2)—C(3)—O(3)	1.6 (4)	C(3)—C(2)—C(7)—C(6)	0.6 (4)
C(7)—C(2)—C(3)—C(4)	0.0 (3)	C(1)—C(2)—C(7)—C(6)	-179.8 (2)
C(1)—C(2)—C(3)—C(4)	-179.6 (2)	C(12)—N(3)—C(8)—C(9)	-0.2 (4)
O(3)—C(3)—C(4)—C(5)	177.2 (3)	Cu(1)—N(3)—C(8)—C(9)	-179.8 (2)
C(2)—C(3)—C(4)—C(5)	-1.6 (4)	N(3)—C(8)—C(9)—C(10)	0.7 (5)
O(3)—C(3)—C(4)—N(1)	-2.3 (4)	C(8)—C(9)—C(10)—C(11)	-1.1 (5)
C(2)—C(3)—C(4)—N(1)	178.9 (2)	C(9)—C(10)—C(11)—C(12)	1.0 (5)
O(4)—N(1)—C(4)—C(5)	113.2 (3)	C(8)—N(3)—C(12)—C(11)	0.0 (5)
O(5)—N(1)—C(4)—C(5)	-64.0 (4)	Cu(1)—N(3)—C(12)—C(11)	179.7 (2)
O(4)—N(1)—C(4)—C(3)	-67.3 (4)	C(10)—C(11)—C(12)—N(3)	-0.5 (5)

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2; (ii) −*x*+1, *y*−1/2, −*z*+1/2.

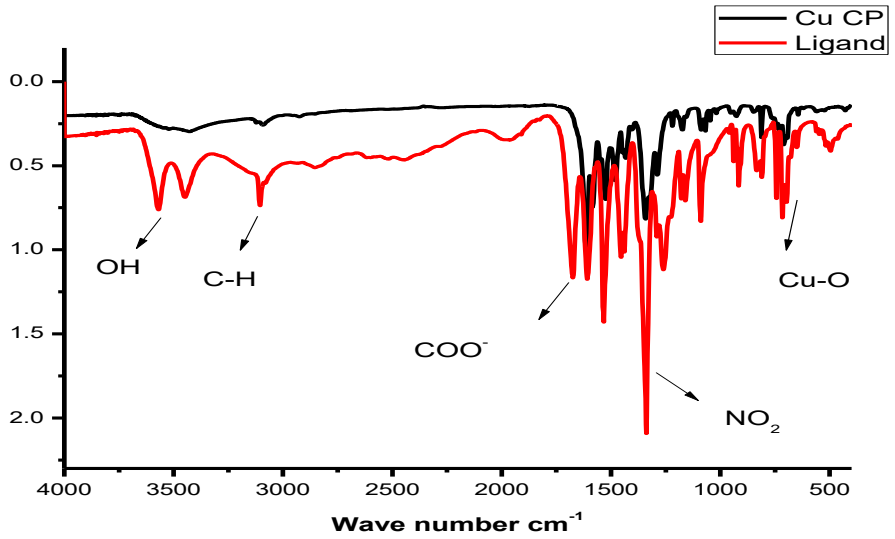

Fig. 4: FTIR spectra of Poly [bis-µ-3,5-dinitro-2oxidobenzoato) (py) Cu II].

Table-3: Selected hydrogen-bond parameters.

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
C(5)H(5)···O(6)[i]	0.93	2.59	3.356 (3)	140.3
C(8)—H(8)···O(1)	0.93	2.52	3.033 (3)	115.2
C(9)—H(9)···O(7)[ii]	0.93	2.57	3.235 (3)	129.1
C(12)—H(12)···O(3)[iii]	0.93	2.32	2.856 (3)	116.2

Symmetry code(s): (i) -*x*, -*y*+1, -*z*; (ii) -*x*, *y*-3/2, -*z*+1/2; (iii) -*x*+1, *y*+1/2, -*z*+1/2.

The electronic spectrum of the compound Fig.5 showed a weak asymmetric band at around 700 nm and a shoulder band at about 240 nm. The band at about 700 nm is due to d–d transitions. The asymmetry of this d–d band is in connection with known structure showing one type of coordination polyhedral of the copper atoms. The other band may be assigned as a charge-transfer 300-330 nm and π-π* transition takes place in the range of 200-250 nm.

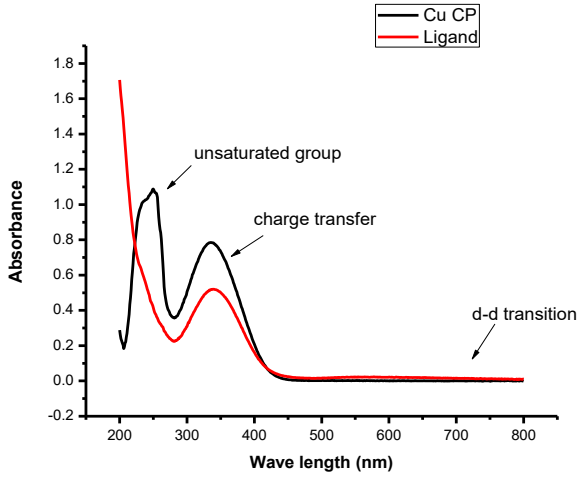

Fig. 5: UV/Visible spectra of Poly [bis-μ-3,5-dinitro-2oxidobenzoato) (py) Cu II].

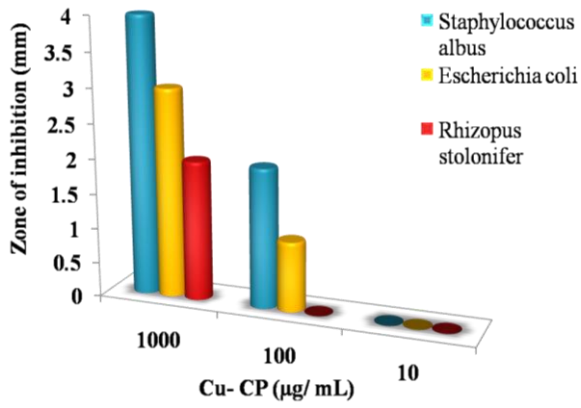

Fig. 6: Graphical Representation of Antimicrobial Activity of Poly[bis-μ-3,5-dinitro-2oxidobenzoato) (py)Cu II].

Antimicrobial Activity

In this study the antibacterial activity of the compound was observed using disc diffusion method against two bacterial and one Fungal strain. Compound (**1**) showed moderate activity against bacterial and fungal strains. Results are listed in Table-4, while graphical results are shown in Fig.6. Zones were measured in mm while cefixime and terbinafine were used as reference drugs. DMSO was used as negative control.

Table-4: Antimicrobial Activity of Title Compound (**1**).

Bacterial strain	Staphylococcus albus (G + ve)	Escherichia coli (G-ve)	Rhizopus stolonifer
	Zone of inhibition		
Compound (1)	4	3	2
DMSO	---	---	---
Cefixime	12	10	--
Terbinafine	--	--	12

Conclusion

A novel copper compound (**1**) ($C_{12}H_7CuN_3O_7$) was synthesized at room temperature by a self-assemble method and characterized with single-crystal X-ray Diffraction, UV-visible, IR and NMR techniques. ORTEP image showed π-π* interactions and pores in the structure may lead to applications of compound (**1**) in catalysis and separation. While antimicrobial activity of title compound (**1**) is moderate.

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