ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

# Effect of γ-radiation on Structural, Thermal and Photoluminescence Properties of Biologically Important Copper (II)-picolinate Complex.

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**ABSTRACT**

Effect of γ-radiation on crystal structure, stability and photoluminescence properties of biologically important copper(II)-picolinate (**1**) complex, [Cu(pic)($H_2O$)] (pic=picolinate), had been examined. IR, power XRD and TGA analysis revealed that complex **1** is highly stable even when subjected to the γ-irradiation at 5 and 300 kGy. Quenching of photoluminescence was observed upon γ-irradiation.

**Keywords:** Picolinic acid, Crystal structure, thermal stability, photoluminescence and γ-radiation.

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ISSN: 0975-8585

## INTRODUCTON

Picolinic acid is a biologically important compound found in animal liver and kidney [1]. Picolinic acid has numerous biomedical applications such as antimicrobial and therapeutic effects [2-5]. Earlier reports indicate that the dietary supplement of picolinic acid inhibits cell growth and blocks cell cycle in tumors [6]. Picolinic acid is also known to stimulate the programmed cell-death in cancer cells and interrupts the advancement of HIV [7, 8]. In addition to the therapeutic effects, picolinic acid enhances disease resistance in rice by defense gene activation [9]. Since metal picolinate complexes have significant physiological activity and are known to involve in development of metallopharmaceuticals, research on synthesis of metal-piconinate complexes is attracting much attention in recent years [10]. Picolinic acid exhibits monodentate and bidentate chelation through oxygen and nitrogen atoms from carboxyl and pyridine groups. In general, picolinic acid forms stable complexes with transition metal ions such as $Zn^{2+}$, $Fe^{2+}$, $Cu^{2+}$ etc [11]. Cu(II) is an important transition metal in biological systems and produce variety of complexes with picolinic acid for biomedical applications especially for anti-microbial and anti-inflammatory effects [12]. The Cu-N bonding in copper-picolinate complex stimulates the blood flow in experimental animals [13].

Current research on influence of pre and post exposure of high energy ionization on crystalline materials have wide range of applications in various fields like optical communications, lasers, drug delivery, light emitting diodes (LEDs) etc [14-16]. Hence, a key requirement is needed to the detailed study of several factors that affect the efficiency and timing of luminescence output. The present investigation is designed in such a way as to explore thermal properties, structural factors and luminescence behavior of 1D layered Cu(II)-picolinate complex before and after γ-irradiation.

## EXPERIMENTAL

All chemicals and solvents used were of Analytical Grade. Cpper sulphate dihydrate ($CuSO_4 \cdot 2H_2O$) was purchased from Merck-India and Picolinic acid (Pyridine-2-Carboxylic Acid, $C_6H_5NO_2$) was purchased from Acros organics. Complex **1** was prepared hydrothermally by known procedure reported by Colette et.al [17]. Elemental analysis of compound **1** as calculated (%) for $C_{12}H_{12}Cu_2N_2O_6$: C=35.42, N=6.84, H=2.92.Found C=35.47, N=6.89 and H=2.97. The IR spectra were recorded on a PerkinElmer "Spectrum Two" FT-IR spectrophotometer using KBr pellet method. Powder diffraction patterns were performed on "PANALYTICAL X'Pert Pro Powder X-ray diffractometer" with graphite monochromatic Cu $K_\alpha$ (λ=1.5406 Å) radiation. The thermogravimetric analysis (TGA) of complex **1** was done using "Melter Toledo TGA/DSC-1" apparatus in a temperature range between 30 and 1000 $^oC$ under nitrogen flow at a heating rate of 10 $^oC\ min^{-1}$. The C, H and N microanalysis was recorded with the "Thermo Scientific FLASH-2000" elemental analyzer. Luminescence spectrum of the solid sample was recorded at room temperature on "Perkin Elmer LS-55 Luminescence Spectrometer". γ-radiation studies were performed at room temperature using $^{60}Co$ gamma cell with a source capacity 3700 Ci at a dose rate of 2.95 kGy/ hr.

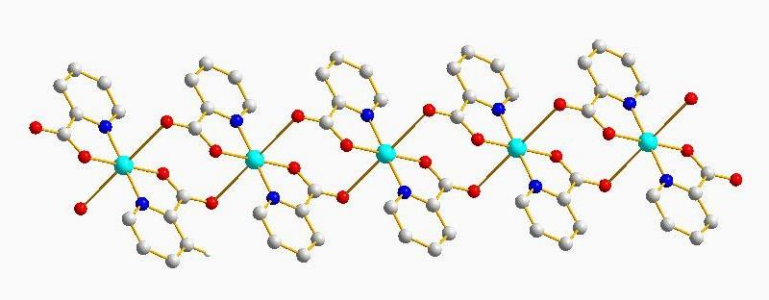
## RESULTS AND DISCUSSION

### Crystal structure of complex 1:

The crystal structure from single crystal X-ray analysis is shown in Fig. 1. The compound **1** crystallizes in the triclinic crystal system with space group *P*-1 (2) with cell parameters $a$ = 5.1282(1) Å, $b$ = 7.6475(1) Å, $c$ = 9.2326(1) Å, $\alpha$ = 74.84°, $\beta$ = 84.36°, $\gamma$ = 71.32°. Picolinic acid deprotonates into pincolinate under the experimental conditions and chelates to copper ions through the pyridine ring containing nitrogen atom and also through one of the carboxylate oxygen atoms yielding $Cu(pic)_2(H_2O)$ complex. The bond distance between Cu(II) and picolinate oxygen atom is 1.9625 Å (Cu-O, and Cu-O2) where as Cu(II) and picolinate nitrogen is 1.9625 Å (Cu-N1 and Cu-N2). It is observed that the bond lengths of Cu-N are longer than the Cu-O distance. Cu(II) ion in this complex exhibits a distorted octahedral geometry. The axial interactions i.e Cu atoms of one plane and carboxylate O-atoms of an adjacent plane with a Cu-O distances of 2.770 Å may lead the infinite extended 1-D layered structure.

ISSN: 0975-8585

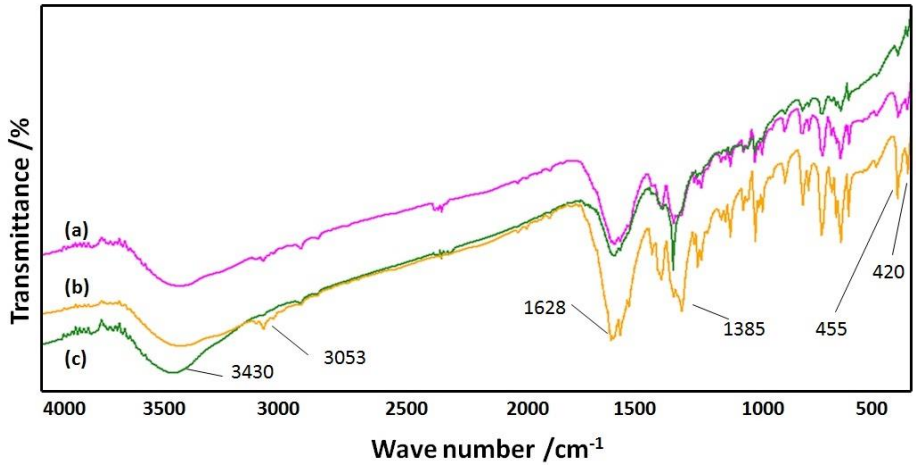
**Figure 1: Crystal structure of complex 1**



**Effect of γ-radiation on crystal structure**

Effect of γ-radiation on crystal structure was examined through IR spectroscopy. So the FT-IR spectrum of complex **1** is shown in Fig.2. A broad band centered at about ~3430 $cm^{-1}$ ascribed to the stretching vibrations of hydroxyl group from water molecule. The IR bands corresponding to the stretching vibrations of the C–H group is located at ~3053 $cm^{-1}$. The asymmetric stretching vibration mode of $COO^-$ is appears at ~1628 $cm^{-1}$ and the band associated to the symmetric stretching vibrational mode of $COO^-$ is appears at 1385 $cm^{-1}$. The absorption band found in the 420$cm^{-1}$ region is assigned to the Cu–O bond and 455 $cm^{-1}$ region is assigned to the Cu–N bond. As shown in Fig.2, no considerable change in peaks was observed in IR spectra of complex **1** after γ-irradiation at 5kGy (Fig.2b) and 300kGy (Fig.2c) doses. This results indicates that no profound influence of γ-rays on structure of complex **1**.

**Figure 2: FT-IR spectrum of complex 1 (a) before γ-irradiation (b) γ-irradiated at 5 kGy (c) γ- irradiated at 300 kGy.**

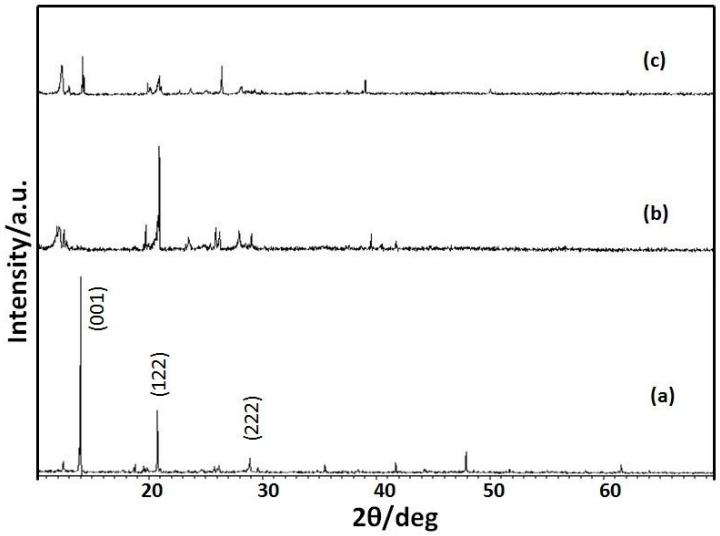



**Effect of γ-radiation on crystallinity:**

Powder X-ray diffraction patterns of un-irradiated and γ-irradiated samples of complex **1** are shown in Fig.3. In general, peak intensities or peak positions may themselves depends on one of the important factor i.e, structure factor, which in general is interrelated to the position of atoms and their scattering capacity in the unit cell. The atoms present in the crystalline materials may not in the same position, they might oscillate about an equilibrium position. On exposure to high energy ionizing radiation, atoms present in the crystal lattice may afflict from their mean position. Consequently, the scattering capacity and structure factor may disturbed. High energy ionizing radiation generally creates stress on the crystalline sites causing unit cell contraction. In the present study the lowering of intensities of diffracted peaks after subjecting to 5KGy radiation (Fig.3b) and 300kGy radiation (Fig.3c) indicates poor degree of crystallinity. Furthermore, the peaks corresponding to the higher 2θ values disappeared in case of irradiated sample (Fig.4b & 4c). It may be concluded that, both static and stress factors are responsible for the drastic changes in the powder diffraction patterns of γ-irradiated complex **1.**

ISSN: 0975-8585

**Figure 3: Powder XRD patterns of complex 1 (a) before γ-irradiation (b) γ-irradiated at 5 kGy (c) γ- irradiated at 300 kGy.**

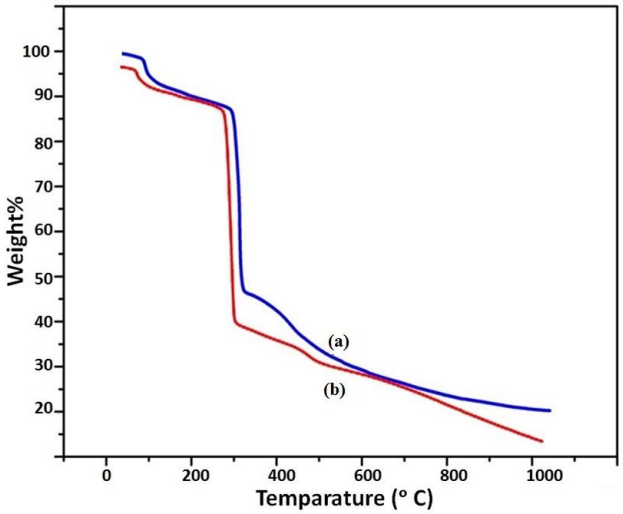



**Effect of γ-radiation on thermal stability:**

TGA analysis of complex **1** was carried out under $N_2$ atmosphere in the range 30-1000 °C was investigated to identify the thermal decomposition process. As shown in Fig.4 complex **1** exhibits two weight loss steps (Fig.4a). The first weight loss of 6.8% at 98 °C corresponds to release of two lattice water molecules. The second mass loss of 39.45% observed between 290 and 320 °C due to the loss of the ligand molecules from the complex **1** resulting in the collapse of framework.

In general, γ-irradiation may create chemical displacement, atomic or ionic imperfections and lattice defects in complexes. Moreover, the lattice imperfections created by high energy radiation (X-rays and γ-rays) does not affect the complexes unless it was a chemical damage. In complex **1** the weight loss analogous to the two steps up to 320 °C was observed in both unirradiated samples and samples irradiated at 300 kGy (Fig.4b). In case of irradiated samples the same thermal decomposition steps were observed at a lesser temperature as compared to unirradiated samples due to the breaking of some hydrogen bonds in the complex **1**.

**Figure 4: Thermo gravimetric Analysis of complex 1 (a) before γ-irradiation (b) γ-irradiated at 300 kGy.**



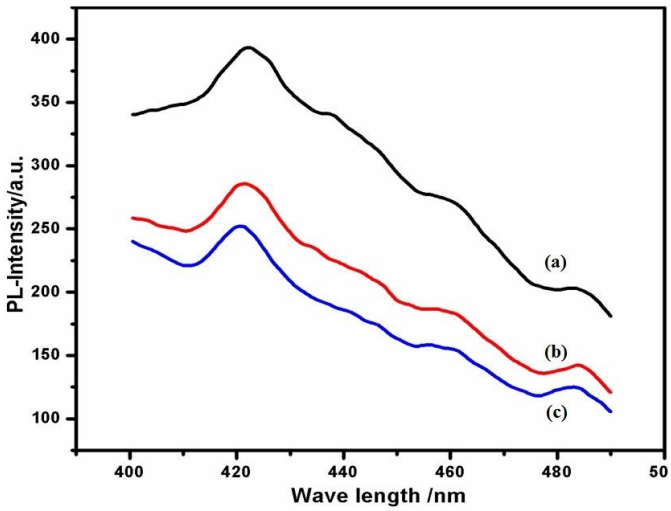

**Effect of γ-radiation on photoluminescence**

The photoluminescence (PL) spectra of complex **1** before and after γ-irradiation at 5 and 300kGy doses is shown in Fig.4. Complex **1** displayed a prominent blue emission at 424nm upon photoexcitation at 365nm. Generally transition metal complexes exhibit intense emission bands from red to blue region after photoexcitation at room temperature either due to metal to ligand charge transfer (MLCT) or from ligand to

metal charge transfer (LMCT). In case of complex **1**, the intense peak at 424 nm is ascribed to the spin allowed π-π* electron transition, which is analogous to the metal-ligand charge transfer (MLCT) transitions. In this case, picolinic acid bridged the metal ion in a non-conjugated manner resulting in is an effective way to obtain new blue emission materials.

The photoluminescence (PL) intensity of complex **1** decreased on compare to the 5 kGy (Fig.5b) and 300 kGy (Fig.5c) γ-irradiated samples. This may be assumed that γ-irradiation might have cause some prominent lattice imperfections in the crystalline sites of complex **1**, which favors non-radiative losses.

**Figure 5: Photoluminescence spectra of complex 1 (a) before γ-irradiation (b) γ-irradiated at 5 kGy (c) γ-irradiated at 300 kGy.**




## CONCLUSIONS

Influence of γ-radiation at 5 and 300kGy doses on crystal structure, crystal stability and photoluminescence (PL) properties of copper picolinate complex had been examined. FT-IR, Powder X-ray diffraction and TGA techniques were used to characterize the crystals. Complex **1** emits blue emission at 424nm after photoexcitation at 365nm. Quenching of photoluminescence was observed after γ-irradiation due to loss of non-radiative energy loss. Hence, further study is necessary to understand to prevent the relative deterioration of PL-spectra.

## ACKNOWLEDGEMENTS

This work was financially supported by the UGC-DAE-CSR, Kolkata.

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