## Synthesis and Characterization of 3 [ $\left.\mathrm{Cu}\left(\mathrm{C}_{5} \mathrm{H}_{6} \mathrm{~N}_{2}\right) 2\left(\mathrm{CO}_{3}\right) \cdot \mathrm{H}_{2} \mathrm{O}\right]$ Using Slow Method *A.Sinthiya ** M. Renuga Devi *** A. Priyankamary ${ }^{* * * *}$ S.Alfred Cecil raj ${ }^{* * * * *}$ S. R. Bheeter ****** Sudhadevi Antharjanam

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## ABSTRACT

Single crystal of $3\left[\mathrm{Cu}\left(\mathrm{C}_{5} \mathrm{H}_{6} \mathrm{~N}_{2}\right)_{2}\left(\mathrm{CO}_{3}\right) \cdot \mathrm{H}_{2} \mathrm{O}\right]$ with blue colored needle shaped crystals with size dimension $0.3 \times 0.2 \times 0.15 \mathrm{~mm}$ has monoclinic system, space group C2/m. FTIR and FT-Raman spectra conforms the vibrational modes of titled compound. From DSC curve, the area of the melting peak is calculated as 252.845 KmW , the obtained enthalpy of fusion is $534.9 \mathrm{~J} / \mathrm{g}$ and the determined entropy of fusion is $2.5841 \mathrm{~J} / g^{\circ} \mathrm{C}$ with calorimetric constant 2.1155 . The TGA curve shows that the residue of 1.085 mg of CuO become constant at $940^{\circ} \mathrm{C}$. Time-Temperature transformation diagram for the solidification reaction indicates that the slow cooling through the martensitic transformation range reduces stress associated with the crystallographic change. The EDAX spectrum conforming the presence of $\mathrm{C}, \mathrm{N}, \mathrm{O}$ and Cu .

## Keywords : Single crystal X-ray diffraction study, T = 297(2)K, mean sigma(c-c) = $0.009 A, R=0.0282, w R=0.0733, R_{\text {int }}=0.0347$, Data-parameter ratio $=10$

## Introduction

4-Aminopyridine (Fampridine) is clinically used in the treatment of Lambert-Eaton myasthenic syndrome and multiple sclerosis. It prolongs action potentials by blocking potassium channels, thereby increases transmitter release at the neuromuscular junction(Judge \& Bever, 2006: Schwid et al. 1997; Strupp et al. 2004)[1,2,3].Hydrogen bonding plays a key role in the molecular recognition(Goswami \& Ghosh, 1997)[4]. This report concerns the X-Ray structure Analysis, FTIR and FT-RAMAN spectrum, DSC/TGA analysis and EDAX pattern of the title compound. Earlier works were carried out regarding this metal-organic compound structure using slow diffusion technique with two reacting solutions [5,6]. But our attempt was through slow evaporation method at room temperature with new material $\mathrm{CuCO}_{3}$ $\mathrm{Cu}(\mathrm{OH})_{2} \cdot \mathrm{H}_{2} \mathrm{O}$.

## Experimental process:

All the reagents used for the preparation of sample are analytical grade and the solutions are prepared using pure de-ionized distilled water. A solution of 4 -aminopyridine ( 0.3768 g ) in $99.9 \%$ pure distilled water ( 20 ml ) was added to a solution of $\mathrm{CuCO}_{3} \mathrm{Cu}(\mathrm{OH})_{2} . \mathrm{H}_{2} \mathrm{O}(1.7048 \mathrm{~g})$ in $99.9 \%$ pure distilled water and mixture was prepared at $30^{\circ} \mathrm{C}$. After three days very small sized blue colored needle shaped crystals were formed at the surface of the solution and it was filtered and was dried
at the room temperature. The chemical reaction taking place in the growth process is:
$6 \mathrm{C}_{5} \mathrm{H}_{6} \mathrm{~N}_{2}+3 \mathrm{CuCO}_{3} \mathrm{Cu}(\mathrm{OH})_{2} \cdot \mathrm{H}_{2} \mathrm{O} \rightarrow 3 \mathrm{Cu}\left(\mathrm{C}_{5} \mathrm{H}_{6} \mathrm{~N}_{2}\right)_{2}\left(\mathrm{CO}_{3}\right) \cdot \mathrm{H}_{2} \mathrm{O}$ $+3 \mathrm{CuO}^{2}+3 \mathrm{H}_{2} \mathrm{O}$

## Single crystal X-ray diffraction

Single crystal X-ray diffraction study shows that the blue colored needle like crystals with size dimension $0.3 \times 0.2 \times 0.15$ mm at $\mathrm{T}=297(2) \mathrm{K}$, shows that the structure of title compound has monoclinic system, space_group $=\mathrm{C} 2 / \mathrm{m}, \mathrm{a}=25.7800$ (5) $\AA, b=15.8910(4) \AA, \mathrm{c}=9.6480(2) \AA$, alpha $=90.00^{\circ}$, beta $=$ $97.9670(10)^{\circ}$, gamma $=90.00^{\circ}$, cell volume $=3914.35(15) \AA^{3}$, $\mathrm{Z}=4$,cell measurement theta_min= 2.56 ,cell_measurement theta $\max =28.5$, mean sigma $(c-c)=0.009 \AA, \quad R=0.0282$, $\mathrm{wR}=0.0733, \mathrm{R}_{\text {int }}=0.0347$, and Data-parameter ratio $=10$, through multi scan absorption method. The title compound, hexa (4-aminopyridine)tris copper(II)carbonate tri hydrate, $\mathrm{C}_{33} \mathrm{H}_{36} \mathrm{~N}_{12} \mathrm{O}_{9} \mathrm{Cu}_{3} \cdot 3 \mathrm{H}_{2} \mathrm{O}$ or $3\left[\mathrm{Cu}\left(\mathrm{C}_{5} \mathrm{H}_{6} \mathrm{~N}_{2}\right)_{2}\left(\mathrm{CO}_{3}\right) \cdot \mathrm{H}_{2} \mathrm{O}\right]$ contains six 4 -aminopyridines, three copper carbonates and three water molecules. The copper carbonates and water molecules lie on the ( 010 ) mirror planes. Of the four metal positions in the asymmetric unit two are in the mirror plane and other two are at points with $2 / \mathrm{m}$ symmetry. The coordination environment of all four copper atoms differs considerably. While all four metal atoms have a regular square plane coordina-
tion through pyridine nitrogens and carbonate oxygens, atoms Cu1, Cu3 and Cu4 further have weak fifth and sixth coordination through carbonate oxygens with the $\mathrm{Cu}-\mathrm{O}$ distances varying from $2.477 \AA$ to $2.611 \AA$. Cu2 has only a weak fifth coordination with Cu -O distance of $2.763(3) \AA$ The bond lengths and angles of 4 -aminopyridinium cation agree with those previously reported (Chao \& Schempp, 1977; Anderson et al. 2005)[7,8]. All amino pyridine moieties are perpedicular to copper carbonate plane. The asymmetric unit as well its equivalents extend along [llll 102 2 direction to form infinite chains. The bond angle of N-H-N amine group for the ligand are in the range of $118^{\circ}, 121^{\circ}$ and $123^{\circ}$. The average bond distance of the amine group with each carbon atom is $1.32 \AA$. The C-O-O bite angle with the metal varies from 53.07 to 58.70 . With N-C-N bite angle variation from 157,171 and $180^{\circ}$,the 4 -aminopyridine ligand forms structure with each $\mathrm{Cu} 3, \mathrm{Cu} 2$ and Cu 1 . The carbonate anions link the copper atoms. We can see the bite angle of Cu3-O6-C18, Cu3-07-C19 and Cu4-O8-C19 are 108.7,110.5 and 105.05 and are distorted from the ideal $109.5^{\circ}$ angle. But the bite angle of Cu2-O5-C18 and Cu4-09-C19 are $74.74^{\circ}$ and $77.78^{\circ}$ respectively. Similarly the bite angle of Cu2-O3-C7 is $132.25^{\circ}$. The packing is stabilised throug three dimensional $\mathrm{N}-\mathrm{H} . . . \mathrm{O}$ and $\mathrm{O}-\mathrm{H} . . . \mathrm{O}$ hydrogen bonds. The H atoms of the water molecule are located in the difference map and refined with $\mathrm{O}-\mathrm{H}$ and $\mathrm{H} . . . \mathrm{H}$ distance restraints of $0.82 \AA$ to $0.88 \AA$ and $1.38 \AA$ respectively. The remaining H atoms were positioned geometrically (C-H in $0.93 \AA$ and $\mathrm{N}-\mathrm{H}$ in $0.86 \AA$ ) and refined using a riding model with $\mathrm{U}_{\text {iso }}(\mathrm{H})=1.2 \mathrm{U}_{\text {eq }}(\mathrm{C}, \mathrm{N})$. Figure 1 shows the atom numbering of the formula unit of the compound with atoms represented $50 \%$ probability ellipsoids and figure 2 represents the packing of the molecule with hydrogen bonds represented as dotted lines.


Figure 1: Tie formala unit of the title compound rquestates as sohe probability etlipspitas ind the moon trumbering( $(-x, y, 1-\Sigma, x,-y, z, \mid-x, y,-z)$


Figore 2. The crystal jacking of the tithe compousc, Hywrogn bond ane shoum as dottedlints

Figure 3 shows the FTIR spectra of title compound was recorded in the region of $\pm 400-4000 \mathrm{~cm}^{-1}$ using Perkin-Elmer Fourier transform infrared spectrometer, model SPECTRUM RXI, using KBr pellets. Figure 4 shows the FT-Raman spectra of the title compound was recorded with BRUKER RFS 27 : stand alone model, raman spectrometer with fourier transform equipped with Nd:YAG laser source giving output at 1064nm line with 100 mW power and with the scanning range of $50-4000 \mathrm{~cm}^{-1}$.


Figure 3: FTIR spectrum


Figure 4: FT-Raman Spectrum

## FTIR and FT-Raman spectra

Table 1: Vibration modes of titled compound

| Modes of vibration of ligand 4-aminopyridine | Bands assigned to FTIR spectra $\left(\mathrm{cm}^{-1}\right)$ | Bands assigned to FT-Raman Spectra ( $\mathrm{cm}^{-1}$ ) |
| :---: | :---: | :---: |
| C-N stretching vibration | 1566 and 1263 | 1287 |
| C-C-C trigonal bending mode | 1019 | 1019 |
| C-C-C ring breathing mode | 830 | 858 |
| C-C-C in-plane bending mode | 576 | 566 |
| non - degenerate $\mathrm{b}_{2}$, modes of benzene | ---- | 663 |
| degenerate $e_{2 v}$, modes of benzene | 430 | ---- |
| C-H stretching vibrations | Not clearly identified | 2724,2846,2945, and 3078 |
| C-NH, stretching vibrations | 1391 | 1287 |
| C-NH2 in-plane | 525 | ----- |
| C-NH2 out-of-plane | -- | 280 |
| N-H stretching | 3396 and 3211 | 3214 and 3076 |
| $\mathrm{NH}_{2}$ scissoring mode | 1566 | 1530 |
| Wagging $\mathrm{NH}_{2}$ mode | 830 | 815 |
| $\mathrm{NH}_{2}$ twisting mode | 579 | 663 |
| $\mathrm{NH}_{2}$ torsion mode | ---- | 280 |
| Lattice vibration | ---- | 80 |

## DSC-TGA analysis

The differential scanning calorimeter and the thermaogravimetric analysis (DSC/TGA) were performed on a STD Q600 V20.9 Build 20 instrument for the sample of 4.03300 mg . Figure 5 shows the DSC curve of the titled compound. it shows that the crystalline material undergoes solid - solid phase transition at $182^{\circ} \mathrm{C}$ and the material has the melting point at $207^{\circ}$ C. According to Lindemann (1910), the melting is caused by instability in the crystal lattice structure due to vibrations $[9,10,11]$. As the temperature increases, the material achieves its melting point and starts to change from solid to
liquid. The area of the melting peak is 252.845 KmW , the enthalpy of fusion is $534.9 \mathrm{~J} / \mathrm{g}$ and the entropy of fusion is 2.5841 $\mathrm{J} / \mathrm{g}{ }^{\circ} \mathrm{C}$ with calorimetric constant 2.1155 . The TGA curve is shown in Figure 6. The process completes in three steps. The first step, which is dehydration, ie., the water was driven off up to $162^{\circ} \mathrm{C}-210^{\circ} \mathrm{C}$, then horizontal line in the curve indicates the existence of the zone of a new compound. The second step, the curve diverges in $\mathrm{O}_{2}$ atmosphere because the oxygen reacts with evolved CO, giving a second oxidation reaction which is highly exothermic and so raises the temperature of the un-reacted sample. From $210^{\circ} \mathrm{C}$ to $313^{\circ} \mathrm{C}$, there is a
residue keeping constant mass. The third step in decomposition reaction, the small difference was due to the difference in the nature/composition of $\mathrm{CuO}_{2}$ formation. This is due to the particle size, surface area, lattice defects or to the other physical characteristics of $\left(\mathrm{CuCO}_{3}\right)$ formed. The residue is CuO of 1.085 mg which is only become constant at $940^{\circ} \mathrm{C}$.

Figure 7 shows the typical Temperature-Time schedule and it shows that below $33^{\circ} \mathrm{C}$ there is no information. This indicates that the occurrence of diffusion less process known as martensitic transformation. This conform that the crystal has pure crystalline order without any impurities. Figure 8 shows the Time-Temperature transformation diagram for the solidification reaction of the titled compound. This indicates that the slow cooling through the martensitic transformation range reduces stress associated with the crystallographic change.


## Energy dispersive X-ray spectroscopy (EDAX)

The structure of crystalline solid, whatever is its dimension, can be characterized by several means such as X-ray diffraction and microscopy, for micro- and nanomaterials, use of
electron microscopy is necessary[12]. Figure 9 and 10 shows the EDAX spectrum for the selected area at $5 \mu \mathrm{~m}$ of the titled compound. The peaks shows that presence of $\mathrm{C}, \mathrm{N}, \mathrm{O}$ and Cu . The presence of Au is due to the coating made during the sample preparation for EDAX spectrum. Table 2 shows the atomic \% and mass \% of the elements C,N,O and Cu in the prepared crystals.



## Conclusion

Using Single crystal X-ray diffraction method the titled compound was indexed in monoclinic system with space group $\mathrm{C} 2 / \mathrm{m}$. FTIR and FT-Raman spectra the present investigation conforms the vibrational spectra of 4 -aminopyridine. From DSC curve, the area of the melting peak is 252.845 KmW , enthalpy of fusion is $534.9 \mathrm{~J} / \mathrm{g}$ and the entropy of fusion is $2.5841 \mathrm{~J} / \mathrm{g}^{\circ} \mathrm{C}$ with calorimetric constant 2.1155. The TGA process completes in three steps with residue of CuO of 1.085 mg which is only become constant at $940^{\circ} \mathrm{C}$. Temperature-Time schedule shows that below $33^{\circ} \mathrm{C}$ there is no information and Time-Temperature transformation diagram for the solidification reaction indicates that the slow cooling through the martensitic transformation range reduces stress associated with the crystallographic change. The EDAX spectrum conforming the presence of $\mathrm{C}, \mathrm{N}, \mathrm{O}$ and Cu .

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