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Synthesis and Characterization of 3 [Cu(C₅H₆N₂)2(CO₃).H₂O] Using Slow Method * A.Sinthiya ** M. Renuga Devi *** A. Priyankamary **** S.Alfred Cecil raj ***** S. R. Bheeter ****** Sudhadevi Antharjanam

* Department of Physics, St. Josephs College (Autonomous), Tiruchirappalli 620 002, TamilNadu, India.

** Department of Physics, St. Josephs College (Autonomous), Tiruchirappalli 620 002, India.

*** Department of Physics, St. Josephs College (Autonomous), Tiruchirappalli 620 002, Tamil Nadu, India.

**** Department of Physics, St. Josephs College (Autonomous), Tiruchirappalli 620 002,Tamil Nadu, India.

***** Department of Chemistry, St. Josephs College (Autonomous), Tiruchirappalli 620 002, India

****** Sophisticated Analytical Instrument Facility (SAIF),Indian Institute of Technology Madras, I.I.T. Campus,Chennai – 600036, India.

ABSTRACT

Single crystal of $3[Cu(C_5H_6N_2)_2(CO_3).H_2O]$ with blue colored needle shaped crystals with size dimension $0.3 \times 0.2 \times 0.15$ 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 534.9J/g and the determined entropy of fusion is 2.5841 J/g °C with calorimetric constant 2.1155. The TGA curve shows that the residue of 1.085mg of CuO become constant at 940°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 C,N,O and Cu.

Keywords : Single crystal X-ray diffraction study, T = 297(2)K, mean sigma(c-c) = 0.009Å, R = 0.0282, wR = 0.0733, R_{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 CuCO₃ Cu (OH)₂.H₂O.

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 $CuCO_3Cu(OH)_2$. H₂O (1.7048 g) in 99.9% pure distilled water and mixture was prepared at 30°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:

 $\begin{array}{ll} 6\ C_{5}H_{6}N_{2}+3\ CuCO_{3}\ Cu\ (OH)_{2}\ .H_{2}O \rightarrow & 3\ Cu\ (C_{5}H_{6}N_{2})_{2}(CO_{3}).H_{2}O \\ +\ 3\ Cu\ O+\ 3H_{2}O \end{array}$

Single crystal X-ray diffraction

Single crystal X-ray diffraction study shows that the blue colored needle like crystals with size dimension 0.3×0.2×0.15 mm at T = 297(2)K, shows that the structure of title compound has monoclinic system, space_group = C2/m, a = 25.7800(5) Å ,b = 15.8910(4)Å, c = 9.6480(2)Å, alpha = 90.00°, beta = 97.9670(10)°, gamma= 90.00°, cell volume= 3914.35(15)Å3, Z=4,cell measurement theta_min= 2.56,cell_measurement theta max = 28.5, mean sigma(c-c) = 0.009Å, R = 0.0282, wR = 0.0733, $R_{int} = 0.0347$, and Data-parameter ratio = 10, through multi scan absorption method. The title compound, hexa (4-aminopyridine)tris copper(II)carbonate tri hydrate, C₃₃H₃₆N₁₂O₆Cu₃.3H₂O or 3[Cu (C₅H₆N₂)₂(CO₃).H₂O] contains six 4-aminopyridines, three copper carbonates and three water molecules. The copper carbonates and water molecules lie on the (0 1 0) 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/m symmetry. The coordination environment of all four copper atoms differs considerably. While all four metal atoms have a regular square plane coordination through pyridine nitrogens and carbonate oxygens, atoms Cu1, Cu3 and Cu4 further have weak fifth and sixth coordination through carbonate oxygens with the Cu-O distances varying from 2.477 Å to 2.611 Å. Cu2 has only a weak fifth coordination with Cu-O distance of 2.763(3)Å 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 [1 0 2] direction to form infinite chains. The bond angle of N-H-N amine group for the ligand are in the range of 118,121 and 123. The average bond distance of the amine group with each carbon atom is 1.32Å. 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°, the 4-aminopyridine ligand forms structure with each Cu3,Cu2 and Cu1. The carbonate anions link the copper atoms. We can see the bite angle of Cu3-O6-C18, Cu3-O7-C19 and Cu4-O8-C19 are 108.7,110.5 and 105.05 and are distorted from the ideal 109.5° angle . But the bite angle of Cu2-O5-C18 and Cu4-O9-C19 are 74.74 ° and 77.78 ° respectively. Similarly the bite angle of Cu2-O3-C7 is 132.25 °. The packing is stabilised throug three dimensional N-H...O and O-H...O hydrogen bonds. The H atoms of the water molecule are located in the difference map and refined with O-H and H...H distance restraints of 0.82Å to 0.88Å and 1.38Å respectively. The remaining H atoms were positioned geometrically (C-H in 0.93Å and N-H in 0.86Å) and refined using a riding model with U_{iso}(H)=1.2 U_{eq} (C,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.



ignue 2. The crystal packing of the title compound, Hydrogen bonds are shown as dotted lines. Figure 3 shows the FTIR spectra of title compound was recorded in the region of \pm 400-4000 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 with100 mW power and with the scanning range of 50-4000cm⁻¹.



Figure 3: FTIR spectrum



Figure 4: FT-Raman Spectrum

FTIR and FT-Raman spectra

numbering (-x,y,1-z; x,-y,z; 1-x,y,-z;)

Table 1: Vibration modes of titled compound

Modes of vibration of ligand 4-aminopyridine	Bands assigned to FTIR spectra (cm ⁻¹)	Bands assigned to FT-Raman Spectra (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 b ₂ modes of benzene		663
degenerate e _{av} modes of benzene	430	
C-H stretching vibrations	Not clearly identified	2724,2846,2945, and 3078
C-NH ₂ stretching vibrations	1391	1287
C-NH ₂ in-plane	525	
C-NH ₂ out-of-plane		280
N-H stretching	3396 and 3211	3214 and 3076
NH ₂ scissoring mode	1566	1530
Wagging NH, mode	830	815
NH ₂ twisting mode	579	663
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 4.03300mg. Figure 5 shows the DSC curve of the titled compound. it shows that the crystalline material undergoes solid – solid phase transition at 182 °C and the material has the melting point at 207 °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 534.9J/g and the entropy of fusion is 2.5841 J/g $^{\circ}$ 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, i.e., the water was driven off up to 162 $^{\circ}$ C - 210 $^{\circ}$ C, then horizontal line in the curve indicates the existence of the zone of a new compound. The second step, the curve diverges in O₂ 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 $^{\circ}$ C to 313 $^{\circ}$ C, there is a

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residue keeping constant mass. The third step in decomposition reaction, the small difference was due to the difference in the nature/composition of CuO_2 formation. This is due to the particle size, surface area, lattice defects or to the other physical characteristics of ($CuCO_3$) formed. The residue is CuO of 1.085mg which is only become constant at 940°C.

Figure 7 shows the typical Temperature-Time schedule and it shows that below 33°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 µm of the titled compound. The peaks shows that presence of C,N,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

Conclusion

Using Single crystal X-ray diffraction method the titled compound was indexed in monoclinic system with space group C2/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 534.9J/g and the entropy of fusion is 2.5841 J/g[°]C with calorimetric constant 2.1155. The TGA process completes in three steps with residue of CuO of 1.085mg which is only become constant at 940°C. Temperature-Time schedule shows that below 33°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 C,N,O and Cu.

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