Chapter X

Crystal structure of catena-poly [(Hmal) (mal) copper (II)-μ-nitrato]: 
bis (2-amino-4, 6-dimethoxypyrimidinium) monohydrate

10.1. Introduction

Copper is the third most abundant trace nutrient essential for normal functioning of plants, animals, humans, and most microorganisms. In humans, it is present as 80-120 mg and 2 to 15 ppm in other biological materials, depending on the type of the tissue. It is found primarily in the bloodstream, as a co-factor in various enzymes, and in copper-based pigments. Some examples of copper dependent metalloproteins and metalloenzymes are Cytochrome C oxidase, Dopamine - hydroxylase, Monoamine oxidase, Ceruloplasmine, Urate oxidase, Lysyl oxidase, Superoxide dismutase. It is incorporated into a variety of proteins, which perform specific metabolic functions. Copper and its amino acid complexes are being used as anti-inflammatory and antirheumatoid arthritic agents, other drugs against these diseases are believed to function by release of copper from serum albumin. It has also been demonstrated to be an effective antibacterial and also as an antiplaque agent. The crystal structure of malonato-bridged hexamethylenetetramine coordination polymers containing Mn (II) and Cu (II), malonate-based copper (II) coordination compounds, copper complex of bis [(2-aminoethyl)aminomethyl]malonate, [Cu(mal)(bipym).H₂O], [Cu₂(mal)₂(H₂O)₂(4,4'-bpy)]²⁺, [Cu₄(mal)₄(H₂O)₄(2,4'-bipy)₄].2H₂O, [(H₂bpe) [Cu(mal)₂]ₙ.4nH₂O [bpe=(4-pyridyl)-ethylene] and Cu(mal)₂(H₂O)₂](H₂O)₂(H₂DACH)²⁺ [DACH=1,4-diazacycloheptane] have been reported in the literature. From our laboratory crystal structures of [2[AMPYH]. [(Cu (H₂O) (mal)₂)].2H₂O] and 2 [2[AMPYH] . [ZnBr (Hmal) (mal)];2H₂O ] AMPYH = 2-amino-4, 6-dimethylpyrimidinium have been reported. In this chapter, the crystal structure of catena-poly [bis (hydrogen malonato) copper (II)-μ-nitrato]: bis (2-amino-4, 6-dimethoxypyrimidinium) monohydrate [CUAMPY] has been discussed in detail.

10.2. Experimental section

10.2.1. Preparation
A hot methanolic solution of Cu(NO$_3$)$_2$.3H$_2$O (60.4 mg in 5ml methanol) was added to a methanolic solution of malonic acid (53 mg in 5ml methanol). The mixture was warmed in a water bath for 20 minutes. The ligand 2-amino-4, 6-dimethoxy pyrimidine (77.6 mg dissolved in 20 ml methanol) was added to this mixture. The resultant solution was again warmed in water bath for another 20 minutes and then kept at room temperature. After a few days blue colored crystals were obtained.

10.2.2. X-ray data collection

The data set was collected on Bruker Kappa APEXII diffractometer$^{57}$ provided with a graphite monochromated MoKα radiation. Preliminary cell parameters were determined by collecting 5906 intense and centered reflections. The recorded data (θ range=1.0º-31.7º) was corrected for polarization and Lorentz effects. The absorption correction was performed by multi-scan method using SADABS$^{58}$. 

10.2.3. Structure solution and refinement

Among the reflections of the type hkl, there is no systematic absence. This indicates that the cell is primitive. The data set of the compound showed the following systematic absences.

(i) 0k0 type of reflections with k odd absent, revealing 2$_1$ screw parallel to b-axis.

(ii) h0l type of reflections with l odd absent, revealing the presence of c-glide perpendicular to b-axis.

Hence the space group P2$_1$/c was assigned unambiguously. The structure was solved by direct method using SHELXS97 and was refined using SHELXL97$^{59}$. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were placed in the idealized locations and refined as riding. The water molecule was found to be disordered. The hydrogen atoms (H1w and H2w) corresponding to the major component have been identified from the difference Fourier map. The minor component could not be located. The final R value was 0.0488 for 5925 reflections I >2σ (I). The geometric calculations were performed by PLATON97$^{60}$. The crystal data and refinement parameters are listed in Table 10.1. The fractional atomic coordinates for all the non-hydrogen atoms with the equivalent isotropic temperature factors are given in Table 10.2.
10.3. Results and discussion

The ORTEP view of the title compound CUAMPY is shown in Figure 10.1. In the crystal structure of catena-poly [(Hmal)(mal) copper (II)-μ-nitrate]: bis (2-amino-4, 6-dimethoxypyrimidinium) monohydrate, [Cu(NO$_3$)$_{2n}$ (Hmal) (mal)]. 2(C$_6$H$_{10}$N$_3$O$_2$). H$_2$O, the asymmetric unit contains pairs of protonated 2-amino-4, 6-dimethoxypyrimidinium cations (A and B), pairs of hydrogen malonate ions, Cu$^{2+}$ cation, nitrate anion and a water molecule in the lattice. The coordination environment around copper is distorted octahedral with hydrogen malonate and malonate ions occupying the basal plane. The ions form a folded six-membered chelating ring and are coordinated to the central metal atom via two oxygens [bis (η$^5$-bidentate)] and the remaining oxygens act as acceptors in hydrogen bonding. The copper ions are symmetrically bridged by nitrate anions forming a –Cu(mal)$_2$ – NO$_3$- linear polymeric chain. The bond distances [Cu-O6 = 1.978 (2) Å, Cu-O8 = 1.923(2) Å, Cu-O10 =1.969(2) Å, Cu-O12 = 1.914(2) Å and Cu-O2A = 2.584(3) Å] agree with the reported values$^{221}$. In the present study, 2-amino-4, 6-dimethoxypyrimidine moieties are protonated, which is evident from the enhancement in internal angle at N1A & N1B positions [C2A-N1A-C6A= 120.1(2)$^\circ$ and C2B-N1B-C6B= 120.5(2)$^\circ$] when compared to that of the unprotonated atom N3A and N3B [C2A-N3A-C4A= 116.3(2)$^\circ$ and C2B-N3B-C4B=, 116.1(2)$^\circ$] atoms. The bond distances and angles of the non-hydrogen atoms are listed on Table 10.3.

10.3.1. Hydrogen Bonding

The 2-amino-4, 6-dimethoxypyrimidinium cations are not coordinated to copper but are hydrogen bonded to malonate oxygens. The carboxylate oxygens (O11 O12 and O7 O8 ) of the malonate ions interacts with protonated pyrimidine nitrogen atoms (N1A and N1B) and the 2-amino groups (N2A-H2A2 and N2B-H2B2) through a pair of N-H…O hydrogen bonds, forming R$_2^2$(8) ring motif$^{7,10,65}$. The cyclic hydrogen-bonded R$_2^2$(8) motifs are also observed in organic crystal structures of trimethoprim hydrogen malonate$^{115}$, trimethoprim 3,5-dinitrosalicylate$^{118}$ and PMN nitrobenzoate salts$^{45}$. In addition, the uncoordinated oxygen (O9 and O11) atoms of the chelated malonate ring interacts with 2-amino group (N2-H2A1) and methoxy group (C7A) of cation A via N-H…O and C-H…O hydrogen bonds [R$_2^2$(13) ring motif]. The combination of metal coordination motif [(Hmal) (mal) + Cu] and organic motifs
[R$_2^2$(8) and R$_2^2$(13)] generates a new hybrid motif leading to a sheet like structure as shown in Figure 10.2. Similar type of hybrid motif has been reported from our laboratory in the crystal structure of bromo bis (malonato) zinc (II): bis (2-amino-4, -dimethylpyrimidinium) dihydrate$^{220}$. The carboxyl oxygen atom (O9) and the carboxylate oxygen atom (O5) of the malonate ions form O-H…O hydrogen bonds leading to supramolecular chain along c-axis (Figure 10.3). Further one of the hydrogen atom (H1W) of the water molecule forms a bifurcated O-H…O hydrogen bonds with the nitrate anions (O2A and O3A). The other hydrogen atom (H2W) acts as a donor to the methoxy oxygen atom (O3) of the pyrimidinium cation of molecule B. The crystal structure is also stabilized by weak C-H…O hydrogen bonds (Figure 10.4). In addition, aromatic stacking interactions are observed between the pyrimidinium cations (molecule A) with perpendicular separation 3.369 Å, a centroid-to-centroid distance 3.5847(14) Å and slip angle of 19.99°. In molecule B, the pyrimidinium cations (molecule B) stack with perpendicular separation of 3.324 Å, a centroid-to-centroid distance of 3.6153(13) Å and slip angle of 23.17°. The values are in agreement with the aromatic stacking interactions$^{76}$. The hydrogen bonding geometries are given in Table 10.4.

10.4. Supplementary Materials

The atomic coordinates and the isotropic displacement parameters for all the hydrogen atoms, the anisotropic displacement parameters for all the non-hydrogen atoms, the bond distances and bond angles involving the hydrogen atom and the torsion angles for CUAMPY is given in Table A 1.10.1(Appendix 1), Table A 2.10.1(Appendix 2), Table A 3.10.1(Appendix 3) and Table A 4.10.1(Appendix 4). The least squares plane calculations (Appendix 5. txt & Table A 5.10.1) and Fo-Fc Table [CUAMPY.FCF] for the compound is given in the CD attached at the end of the thesis.

Foot note:

Based on one of the examiners query, regarding the charge as well as location of water hydrogens in the crystal structure of catena-poly[bis(hydrogen malonato) copper (II)-µ-nitrat]: bis (2-amino-4, 6-dimethoxypyrimidinium) monohydrate, the H5 atom has been removed from O5 atom of the malonate ligand to balance the charge on the metal atom. The present crystal structure, catena-poly [(Hmal) (mal) copper (II)-µ-nitrat]: bis (2-amino-4, 6-dimethoxy.pyrimidinium) monohydrate, the O1w molecule was found to be disordered. The water hydrogens corresponding to the major component have been identified from the difference Fourier map. The minor component could not be located. The appropriate tables are included.