Chapter XI

Crystal structure of bis (2-amino-4, 6-dimethylpyrimidinium) tetrachlorocobaltate (II) monohydrate

11.1. Introduction

Cobalt does not freely occur in nature, but compounds of cobalt occur naturally in many forms. Small amounts of it are found in most rocks, soil, water, plants, and animals. In nature, it is frequently associated with nickel. Mammals require small amounts of cobalt which is the basis of vitamin B$_{12}$. Vitamin B$_{12}$ (cobalamine) is found in eggs, meat, poultry, shellfish, milk, and milk products. Cobalamin acts as an oxygen carrier, decreases blood cholesterol and metabolizes fat. It is essential for red blood cell formation and to keep the nerve cells healthy. Cobalamin along with folate may be given to help reduce side effects in cancer patients. Cobalt-60, an artificially produced radioactive isotope of cobalt, is an important radioactive tracer and cancer-treatment agent. It is used for sterilization of food (cold pasteurization), medical supplies and medical wastes. It also finds application in industrial radiography. Many metal-organic crystal structures involving cobalt complexes have been reported in literature. The crystal structures of Bis(2-aminopyridinium)tetrachlorocobalt(II)$_{222}$, Bis(imidazolium)tetrachlorocobaltate(II)$_{223}$, μ-Amido-μ-nitrito-bis[tetraaminecobalt(III)] tetrachloride dihydrate$_{224}$, Bis[(2-chloroethyl)diisopropylammonium]tetrachlorocobaltate(II)$_{225}$, Bis(2,2':6',2''-terpyridyl)cobalt(III)chloride$_{226}$, and 3,3'-Dimethyl-1,1'-methylenedimidazolium tetrachlorocobaltate (II)$_{227}$ have been reported. In this chapter, the crystal structure of 2-amino-4, 6-dimethylpyrimidinium tetrachlorocobaltate (II) monohydrate is discussed.
11.2. Experimental section

11.2.1. Preparation

A hot methanolic solution of CoCl$_2$.6H$_2$O (59 mg dissolved in 5ml methanol) was added to a methanolic solution of malonic acid (28.5 mg in 5ml methanol). The mixture was warmed in a water bath for 20 minutes. The ligand 2-amino-4, 6-dimethylpyrimidine (63.25mg dissolved in 20ml of methanol) was added to this mixture. The resultant solution was warmed in a water bath for 20 minutes. The solution turns turbid. To get the clear solution drops of conc HCl was added. The solution was again warmed in water bath for another 20 minutes and then kept at room temperature for crystallisation. After a few days blue colored prismatic crystals were obtained.

11.2.2. X-ray data collection

The data were collected on Bruker Kappa APEXII diffractometer$^{57}$ provided with a graphite monochromated MoKα radiation. Preliminary cell parameters were determined by collecting 5247 intense and centered reflections. The recorded data (θ range= -1.5º -31.5º) were corrected for polarization and Lorentz effects. The absorption correction was performed by multi-scan method using SADABS$^{58}$. 

11.2.3. Structure solution and refinement

Among the reflections of the type hkl, there is no systematic absence. This indicates that the cell is primitive. The X-ray data set revealed no systematic absences. The E-statistics analysis revealed centrosymmetric distribution and hence the space group P-1 was assigned. This was further confirmed by successful structure solution and refinement. The structure was solved by SHELXS97 and refined by SHELXL97$^{59}$. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were placed in the idealized locations and refined as riding. The hydrogen atoms for water molecule were located from the difference Fourier map and were refined freely with isotropic displacement parameters. The final R value was 0.0314 for 5138 reflections I >2σ (I). The geometric calculations were performed by PLATON97$^{60}$. The crystal data and refinement parameters are listed in Table 11.1. The fractional atomic
coordinates for all the non-hydrogen atoms with the equivalent isotropic temperature factors are given in Table 11.2.

11.3. Results and discussion

The ORTEP view of the title compound, COAMPY is shown in Figure 11.1. The asymmetric unit contains protonated 2-amino-4,6-dimethylpyrimidinium cations (A and B), tetrachlorocobaltate ion and uncoordinated water molecule. The anion \([\text{CoCl}_4]^{2-}\) displays distortion from ideal tetrahedral geometry with variable Cl-Co-Cl bond angles \([\text{Cl}1\text{-Co-Cl}3= 109.46(2)^\circ, \text{Cl}1\text{-Co-Cl}4= 107.09(2)^\circ, \text{Cl}2\text{-Co-Cl}3= 112.29(2)^\circ, \text{Cl}2\text{-Co-Cl}4= 109.08(2)^\circ, \text{Cl}3\text{-Co-Cl}4= 110.99(2)^\circ\text{ and Cl}1\text{-Co-Cl}2= 107.74(2)^\circ]\). The bond distances \([\text{Co-Cl}1= 2.2737(15) \text{ Å, Co-Cl}2= 2.2780 (15) \text{ Å, Co-Cl}3= 2.2383(15) \text{ Å and Co-Cl}4= 2.2664(15) \text{ Å}]\) are closer to the overall average value of 2.2725 Å reported\(^{227}\). In the present study, 2-amino-4, 6-dimethylpyrimidine moieties are protonated at N1A and N1B positions. This is evident from the increase in the internal angle from 115.5(3)^\circ [C2-N1-C6] in neutral 2-amino-4, 6-dimethylpyrimidine to 122.04(14)^\circ [C2A-N1A-C6A=122.04(14)^\circ] and 121.38(14)^\circ[C2B-N1B-C6B] respectively. The bond distances and angles of the non-hydrogen atoms are listed on Table 11.3.

11.3.1. Hydrogen bonding

The protonated (N1A) cation and 2-aminogroup (N2A-H2A2) interacts with (Cl1 and Cl4) chlorine atoms of the coordinated cobalt chloride anion via N-H…Cl hydrogen bonds to form the eight meembered R\(_2^2\)(8) ring motif. In molecule B, the protonated N1B atom and 2-aminogroup (N2-H2B2) interacts with the water molecule (O1W) and Cl2 atom via N-H…O and N-H…Cl hydrogen bonds[R\(_2^2\)(8)]. The 2-aminogroup of pyrimidine (N2-H2A1) is centrosymmetrically paired with unprotonated pyrimidine moiety (N3B) via N-H…N hydrogen bonds forming an eight membered R\(_2^2\)(8) ring motif. Similarly amino group (N2-H2B1) of molecule B is centrosymmetrically paired up with unprotonated pyrimidine molecule A (N3A). The base pairing involving N2-H…N3 hydrogen bonds has been reported in some of the aminopyrimidine-carboxylate complexes\(^{45,74}\). In addition water molecule (O1W) bridges the
two chlorine atoms (Cl2 and Cl3) via O-H…X [X= Cl] hydrogen bonds [O1W-H1W…Cl3= 3.285(3) Å and O1W-H1W…Cl2=3.290(3) Å]. The O-H…Cl interactions have also been noticed in crystal structure of 5,7-dimethyl-1,2,4-triazolo[1,5-a] pyrimidinium tetrachlorocobaltate(II) monohydrate. The anion shares the edges of the octagon with water molecule occupying the apical positions. The octagons link the hydrogen bonded aminopyrimidine (A and B) alternatively to generate a supramolecular chain as shown in Figure 11.2. In addition C-H…Cl interactions involving the methyl group (C7A, C7B and C8A) and chlorine atom (Cl3 and Cl4 atom) are also observed. The crystal structure is further stabilized by stacking interactions (perpendicular separation 3.377 Å, centroid-to-centroid distance 3.922(3) Å and slip angle 22.96°) involving the pyrimidine moieties of molecule A and molecule B. The hydrogen bonding geometries are listed in Table 11.4.

11.4. 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 COAMPY is given in Table A 1.11.1, Table A 2.11.1, Table A 3.11.1, Table A 4.11.1 and Table A 5.11.1. The least squares plane calculations (Appendix 5. txt & Table A 5.11.1) and Fo-Fc Table [COAMPY.FCF] for the compound is given in the CD attached at the end of the thesis.