International Journal of
Advances in Scientific Research and Engineering (ijasre)

E-ISSN : 2454-8006

DOI: http://doi.org/10.31695/IJASRE.2018.33015

Volume 4, Issue 12
December - 2018

Synthesis and Structural Analysis of Ammonium Orotate Hydrate Crystal

Priyanka Singh and Kafeel Ahmad Siddiqui

Department of Chemistry

National Institute of Technology

Raipur, G.E. Road Raipur-492010, Chhattisgarh

India

ABSTRACT

Single crystals of the title molecular salt, $NH_4^{+}\cdot C_5H_3N_2O_4^{-}\cdot H_2O$*, were isolated from the reaction of orotic acid, Dysprosium (III) Nitrate in a 1:1 molar ratio in 5 ml water 25% ammonia solution by hydrothermal reaction at 120°C for 3 days. In the crystal, the cations and anions are positioned alternately along an infinite helical chain and linked together through* $N-H\cdots O$ *hydrogen bonds between carboxylate oxygen and carbonyl oxygen of orotate ion. The water molecules of crystallization link the chains into (101) bilayers, with the cations organized in an isotactic manner.*

Keywords: *Ammonium Ion, Orotic acid, Hydrate Synthesis analysis, Structural Analysis.*

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1. INTRODUCTION

The supramolecular association in proton-transfer adducts containing molecules are of biological interest [1]. Further, Orotic acid monohydrate, the only effective precursor in the biosynthesis of pyrimidine nucleobases. Since in OrH ion, the carboxylate anion and carbonyl group is a versatile H–bond acceptor while imino group is an H–bond donor, these peripheral groups are expected to interact with each other or with ancillary ligands via hydrogen bonding, of pyrimidyl ring [2].

We report here hydrothermal synthesis for orotate ammonium hydrate crystal in which $N-H\cdots O$ and $O-H\cdots O$ hydrogen bonds are instrumental in deciding overall crystal packing.

2. EXPERIMENTAL PROCEDURE

2.1 Materials and Methods

All chemicals of reagent grade were commercially available and were used without further purification.

2.2 Crystallography

Single crystal of **1** (size 0.34 x 0.30 x 0.10 mm) was mounted on a Bruker Apex DUO CCD area-detector, equipped with graphite monochromator and MoKα radiation source (λ = 0.71073Å). The unit cell dimensions and intensity data were measured at 100(2)K. The structure was solved by the direct methods, and refined by full matrix least square treatment based on F^2 with anisotropic thermal parameters for the non-hydrogen atoms using Bruker APEX (Bruker 2009) for data collection and SAINT (Bruker, 2009) for cell refinement, Bruker SAINT (data reduction), SHELXS-97 (structure solution) [3a], SHELXL-97 (structure refinement) [3b,3c], and Bruker SHELXTL (molecular graphics) programs [3d]. A multi-scan absorption correction (SADABS) was applied. Hydrogen atoms were included in geometrically calculated positions using a riding model and were refined isotropically. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre www.ccdc.cam.ac.uk/data_request/cif upon quoting CCDC code **1876630**.

Crystal structure refinement and unit cell parameters of complex **1** are given below**:**

Molecular formula = $C_5H_9N_3O_5$; Crystal System =Orthorhombic; Space group = Pbca; a (Å)= 12.624(2); b(Å) = 6.5137(11); c(Å) = 18.635(3); α(◦)= 90.00; β(◦) = 90.00; γ(◦) = 90.00; Cell Volume (Å^3) = 1532.3(4)3; Z = 8; Z'= 0; R-Factor (%) = 3.4;

Wavelength (Å) = 0.71073; Temperature (K) = 100(2); D_{calc} (Mg/m3) =1.657; Absorption coefficient (mm^{-1}) = 0.148; F(0 0 0) = 800; Crystal size (mm^3) = 0.34 x 0.30 x 0.10; Theta range for data collection (°) = 2.19 to 25.96; Index ranges = -15< h >10; -8< k >7; -22< l >22; Reflections collected = 7902; Absorption correction = Multi-Scan; Maximum and minimum transmission = 0.9512 & 0.9853; Refinement method = Full-matrix least-squares on F2; Data/restraints/parameters = 1487/0/142; Goodness-of-fit (GOF) on F2 = 1.094; Final R indices [I >2r(I)] = R1 = 0.0340 , wR2 = 0.0922; R indices (all data) = R1 = 0.0360 , wR2 = 0.0906; Largest diff. peak, hole, e/$Å^3$ = 0.311, -0.373

2.3 Synthesis of $NH_4^{+\cdot}$ $C_5H_3N_2O_4^{-\cdot}$ H_2O (1)

In a 10 ml Teflon reaction vessel 0.5 mmole Orotic Acid, 0.5 mmole $Dy(NO_3)_3.5H_2O$ and 5 ml 25% ammonia solution was taken. The reaction vessel was then placed in a stainless steel reactor and heated at 120°C in a high precision programmed oven at the heating rate of 20°C /hour for a period of 72 hours. After heating the reaction vessel was cooled at the same rate as it was heated. The light clear solution thus obtained was filter and kept for crystallization at room temperature. After 20 days air stable light colorless block shaped crystals suitable for X-ray diffraction was collected from same reaction mixture. The single crystal X-ray analysis shows the non-bonding of Dy ions.

3. Supramolecular Structure of $NH_4^{+\cdot}$ $C_5H_3N_2O_4^{-\cdot}$ H_2O (1)

The title compound crystallizes in the orthorhombic space group P*bca*, with one orotate anion (Or^-), one ammonium cation (NH_4^+) and one water molecules of crystallization (Figure 1).

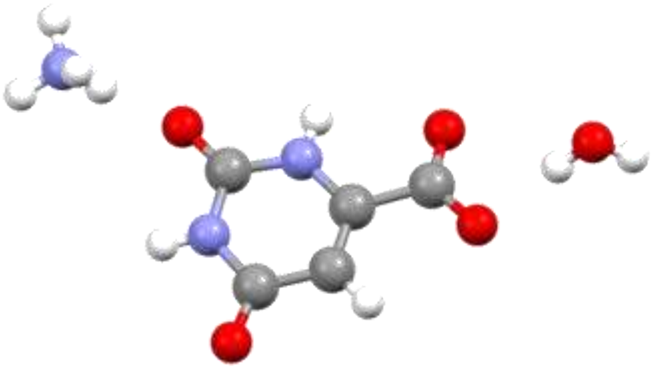
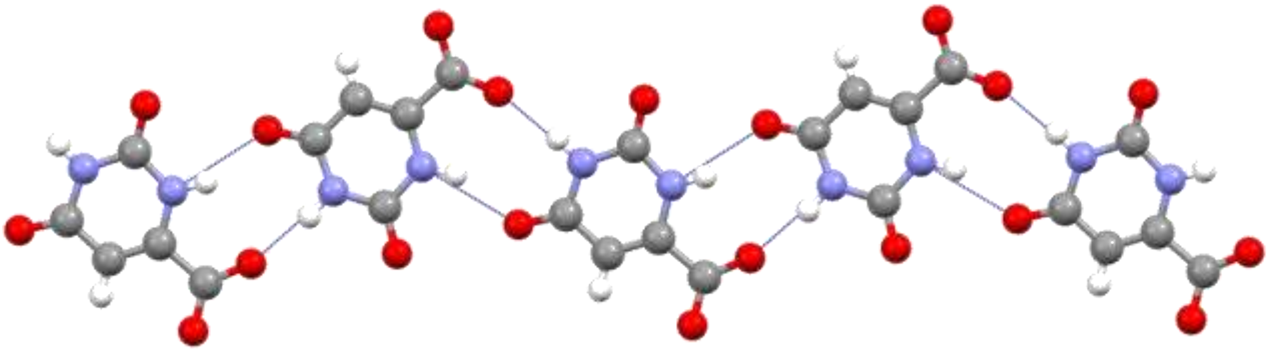
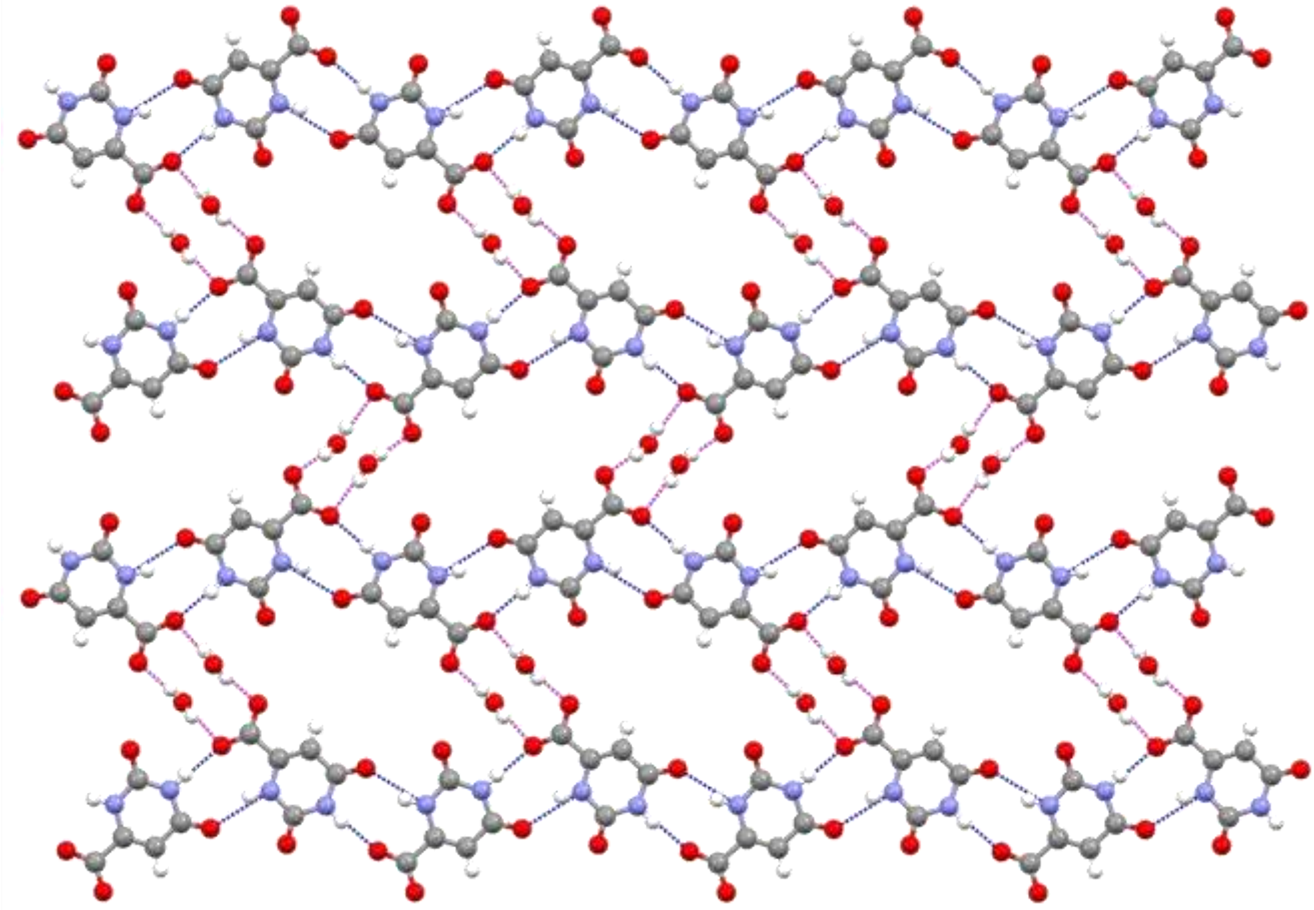


Figure-1- Asymmetric Unit in 1.

The noncovalent interactions between pyrimidyl nitrogen (N2) and carbonyl oxygen (O4) of one orotate unit and carboxyl oxygen (O2) and pyrimidyl nitrogen (N1) of nearby orotate anion results in the formation of 1D hydrogen bonded bimolecular structure. The thus formed dimer propagate to form 1D hydrogen bonded zig-zag chain involving N–H…O synthons as node (Figure 2a). The nearby 1D sheets are connected by centrosymmetric lattice water molecules through O-H⋯O hydrogen bond resulting 2D hydrogen bonded network along *b* axis (Figure 2b).



(a)



(b)

Figure-2a- 1D sheet through N-H¨O hydrogen bond. (b) The nearby 1D sheets are connected by centrosymmetric lattice water molecules through O-H¨O hydrogen bond resulting 2D hydrogen bonded network.

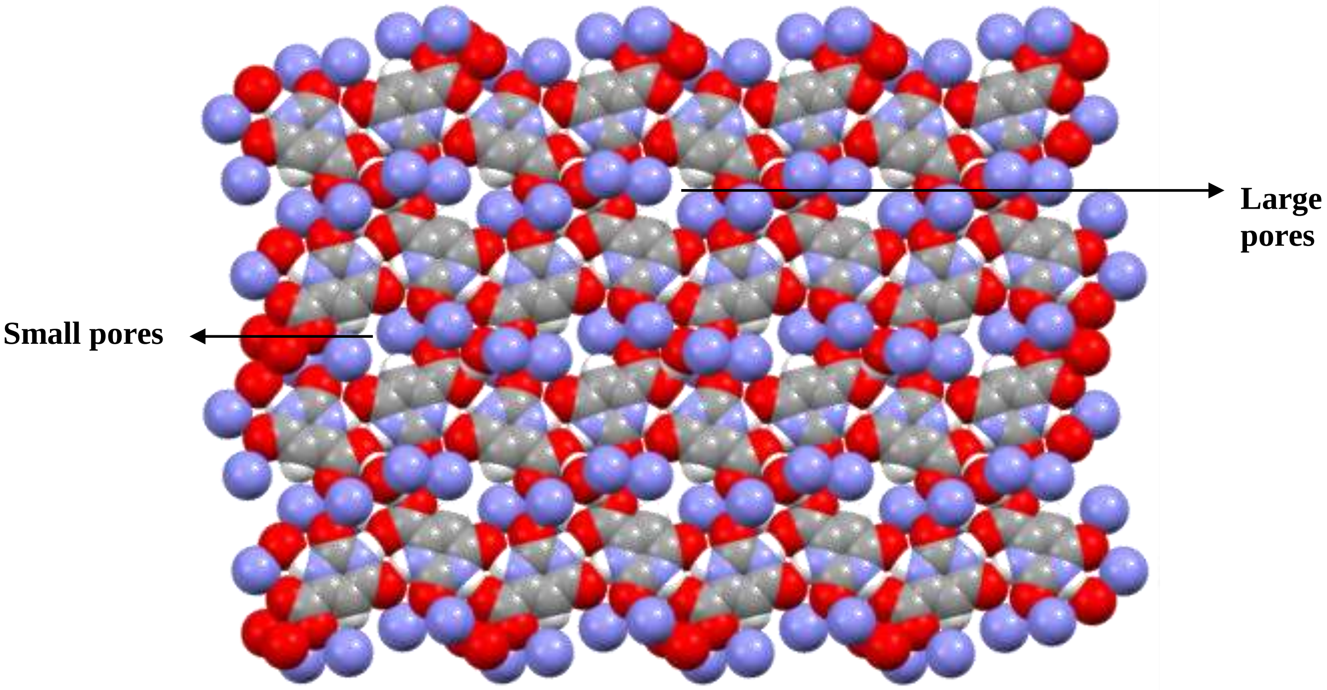


Figure 2c. 2D hydrogen bonded network with pores.

DOI: 10.31695/IJASRE.2018.33015

The ammonium ions interact with nearby two orotate anions results in the formations of three molecule aggregate involving N^+-H$\cdots$$O^-$ supramolecular synthons (figure 3a). The hydrogen bonding parameters are listed in table 1.

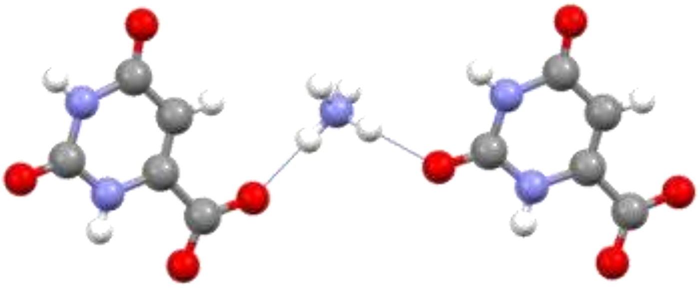


Figure 3a. Three molecule aggregate formed by ammonium ion and two orotate ions.

Table 1: Conventional Hydrogen bonding parameters for 1 (Å) and (◦)

D-H$\cdots$A	d(H$\cdots$A)	d(D$\cdots$A)	<(DHA)
N2–H2…O2	1.923(9)	2.794 (1)	170.11(2)
N1–H1…O4	2.033(3)	2.851(1)	154.38(2)
O1w–H2w1…O2	2.008(2)	2.839(1)	168.84(2)
O1w–H1w…O1	1.915(2)	2.784(1)	171.50(2)
N3–H1…O3	1.96(2)	2.870(1)	179.77(2)
N3–H3…O1	1.98(2)	2.915(1)	172.83(2)

The ammonium ions interact with carbonyl oxygen (O3) and carboxylate oxygen (O3) of nearby 1D chain to form a hydrogen bonded 2D network (Figure 3b).

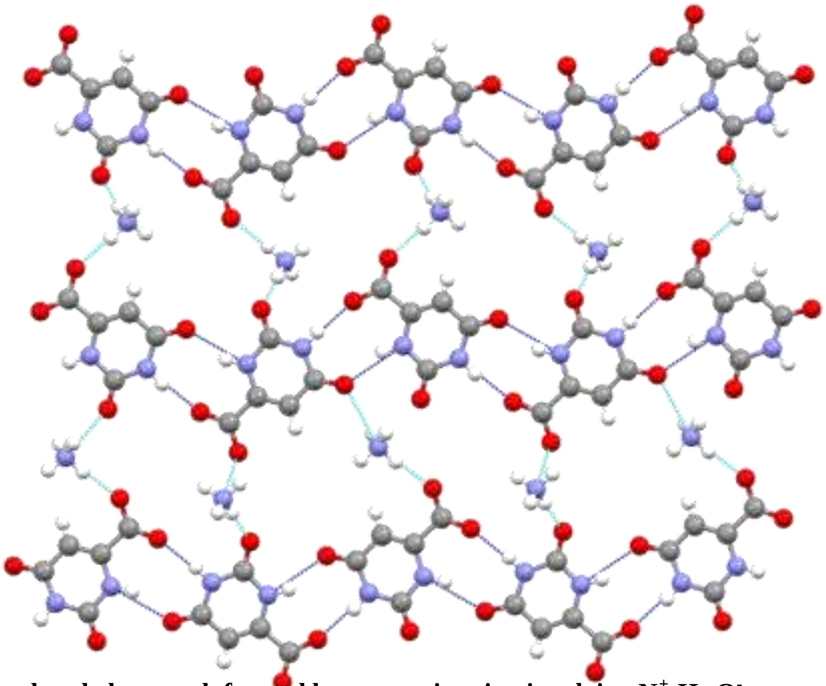


Figure 3b. 2D hydrogen bonded network formed by ammonium ion involving N^+-H$\cdots$$O^-$ supramolecular synthons.

One of the hydrogen (H2) atom of ammonium ion in 2D sheet interact with oxygen of lattice water (O1w) results in the formation of an overall 3D hydrogen bonded network (Figure 4). The lattice water shows [2+1] hydrogen bonding pattern [4].

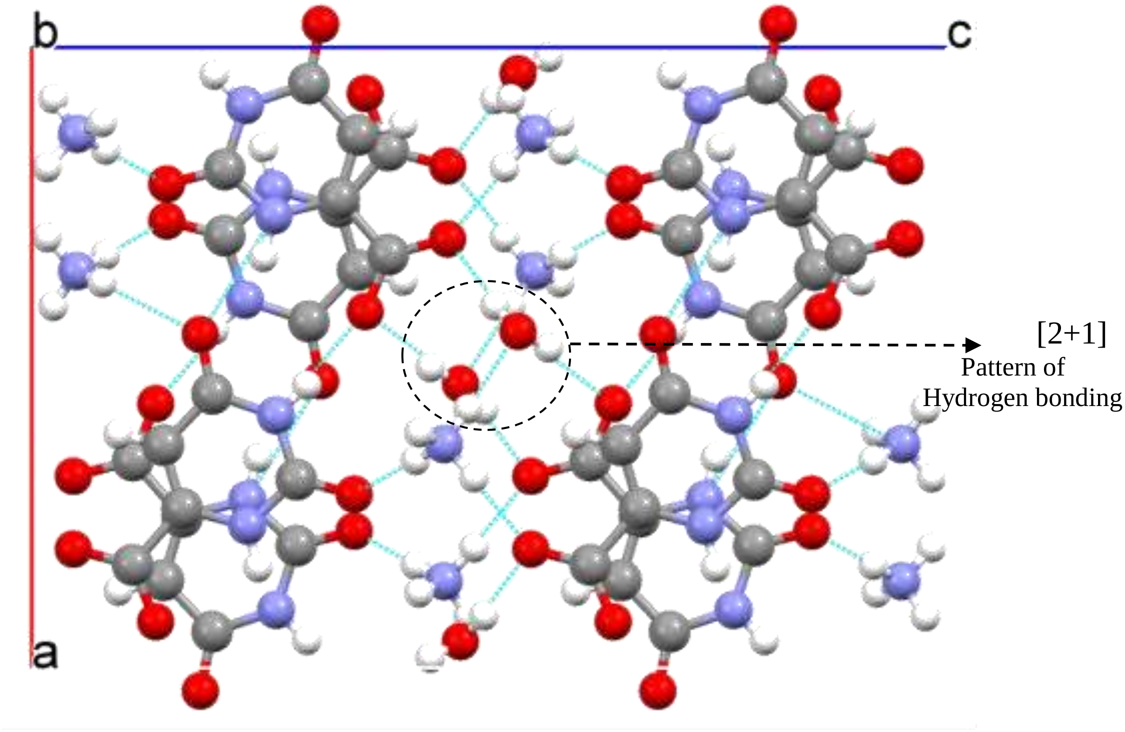


Figure4. 3D hydrogen bonded network (view down crystallographic *b* axis).

4. CONCLUSIONS

We have synthesized first ammonium orotate monohydrate crystal. The ammonium ion and lattice water molecule interplay with orotate anion to form 3D hydrogen bonded supramolecular structure. The reported crystal provides a platform for proton-transfer adducts in biological interest as orotic acid is only effective precursor in the biosynthesis of pyrimidine nucleobases

Acknowledgement

Dr Kafeel Ahmad Siddiqui is thankful to Director and Dean (R&C), National Institute of Technology Raipur, India, for award of a "Research Seed Grant Project" (Sanction Order No. NITRR/Dean(R&C)/2017/8300 dated 23/05/2017) to support "Crystal Engineering Research".

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