The Crystal Structure of Benzimidazole Complex with Chloranilic Acid Hydrate Adduct

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The crystal structure of benzimidazole with chloranilic acid hydrate adduct crystallizes in monoclinic, space group $P2_1/c$, with unit cell parameters; $a = 4.4870(10)\text{\AA}$, $b = 18.8554(2)\text{\AA}$, $c = 16.6576(10)\text{\AA}$, $\beta = 91.4421(8)^\circ$, $V = 1408.86(4)\text{\AA}^3$, and $Z = 4$. Water influences proton transfer in the adduct, contributes to generation of H-bonds, and links chloranilic acid molecules through O-H...O interactions to form a zigzag channel that entraps benzimidazole through N-H...O, C-H...O, and C-H...Cl interactions.

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Proton transfer realized through intermolecular H-bonds enables charge and energy transfer in biological systems, particularly in enzymes.¹ Protonation of the donor from acidic acceptors are generally a route for the formation of ion pair adducts. Chloranilic acid (CLA) exhibits electron-acceptor properties on one hand and acidic properties leading to formation of H-bonds on the other hand, and usually utilized as a template for generating tightly bound self assemblies with various organic bases, and also as a model compound for investigating hydrogen transfer motions in O-H...N and N-H...O hydrogen bond systems.² Benzimidazole (BIZ) is an organic base, and has H-bond donor site as well as acceptor site. The synthesis and spectroscopic studies, as well as crystallographic studies^{3,4} of charge transfer complexes formed between CLA and BIZ derivatives have been reported and the knowledge utilized in the field of drug-receptor binding mechanisms in medicinal chemistry. However, there is no report on BIZ complex with CLA, and is being pursued by our group. Our attempt to obtain such a complex resulted in the formation of BIZ with CLA hydrate adduct. As per our interest in studying proton transfer complexes, we found it prudent to report the role played by water in influencing proton transfer in the adduct, as well as contributing to increased number of H-bonds. The complex was

obtained by dissolving a 1:1 mixture of BIZ (0.24 g, 2 mmol) and CLA (0.42 g, 2 mmol) in 20 ml methanol and allowed to evaporate slowly at room temperature. Suitable crystals were obtained after two weeks and characterized through X-ray diffraction at 150 K. Crystal data and details of data collection are given in Table 1. The structure solution was carried out with direct methods using the programs SIR 92 or superflip within the CRYSTALS software suite, and refined by full-matrix least-squares methods based on F^2 .

The chemical structure of BIZ/CLA·H₂O adduct is shown in

Table 1 Crystal and experimental data

Chemical formula: C ₇ H ₇ N ₂ ⁺ ·C ₆ O ₄ HCl ₂ ⁻	
Formula weight = 345.14	
T = 298 K	
Crystal system: Monoclinic	Space group: $P2_1/c$
$a = 4.48700(10)\text{\AA}$	
$b = 18.8554(2)\text{\AA}$	$\beta = 91.4421(8)^\circ$
$c = 16.65760(10)\text{\AA}$	
$V = 1408.86(4)\text{\AA}^3$	$Z = 4$
$D_{\text{calc}} = 1.627\text{ g/cm}^3$	
Radiation: Cu K_α radiation ($\lambda = 1.5418\text{\AA}$)	
$\mu(\text{Cu } K_\alpha) = 4.407\text{ mm}^{-1}$	$F(0\ 0\ 0) = 704$
Crystal size = $0.11 \times 0.12 \times 0.32\text{ mm}^3$	
No. of reflections collected = 28888	
No. of independent reflections = 2963	
θ range for data collection: $3.5 - 76.7^\circ$	
Data/Restraint/Parameters = 2963/0/200	
Goodness-of-fit on $F^2 = 1.001$	
R indices [$I > 2\sigma(I)$]: $R1 = 0.0235$, $wR2 = 0.0614$	
R indices (all data): $R1 = 0.0237$, $wR2 = 0.0616$	
$(\Delta/\sigma)_{\text{max}} = 0.001$	
$(\Delta\rho)_{\text{max}} = 0.31\text{ e}\text{\AA}^{-3}$	$(\Delta\rho)_{\text{min}} = -0.20\text{ e}\text{\AA}^{-3}$
Measurement: Oxford Diffraction (Agilent) SuperNova diffractometer	
Program system: CRYSTALS	
Structure determination: Superflip	
CCDC deposition number: 1006904

Fig. 1 Chemical structure of the BIZ·CLA hydrate adduct.

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Fig. 2 ORTEP view of the BIZ-CLA hydrate adduct with the atom labeling scheme. Displacement parameters are drawn at 50% probability level.

Fig. 1, while the atom numbering follows the scheme indicated in Fig. 2. The bond lengths and angles (Table 2S) in CLA and BIZ are not significantly different from those in neutral CLA⁵ and reported CLA complexes,⁶ as well as BIZ⁷ and its comparable complexes.⁸ The BIZ cation (C₇H₇N₂⁺) is protonated on N3 atom of the imidazole moiety through a proton transfer from an OH group of CLA. An interaction between adjacent layers of CLA exhibit a π - π stacking mode (Fig. 3S). The dihedral angle between the interacting CLA ring planes is only 1.22(7)° with an interplanar spacing between C10...C12 (3.383(16) Å) and C13...C15 (3.351(14) Å) (Fig. 3S), and a *centroid-to-centroid* separation of 3.619(8) Å. Water serves as a bridge between CLA molecules through O-H...O hydrogen bonding to form a *zigzag* channel (Fig. 4), and links CLA with BIZ molecules entrapped within the *zigzag* channel (Fig. 5S). Water links CLA molecules through bifurcated H-bond between O-H of water and O atom of carbonyl group of CLA [O3-H10...O1ⁱⁱⁱ ($d_{\text{O3}\cdots\text{O1}'} = 2.759(12)$ and $d_{\text{H10}\cdots\text{O1}'} = 1.93$ Å), and that between O-H of CLA and O of water [O2-H7...O3ⁱ ($d_{\text{O2}\cdots\text{O3}} = 2.632(12)$ and $d_{\text{H7}\cdots\text{O3}} = 1.84$ Å), as well as that between O-H of water and oxygen (O2⁻) of CLA [O3-H9...O2⁻ ($d_{\text{O3}\cdots\text{O2}^-} = 3.119(12)$ and $d_{\text{H9}\cdots\text{O2}^-} = 2.53$ Å), and O3-H9...O1ⁱ interactions ($d_{\text{O3}\cdots\text{O1}'} = 2.801(12)$ and $d_{\text{H9}\cdots\text{O1}'} = 2.04$ Å). In the chloranilate anion (C₆HCl₂O₄⁻), an intramolecular H-bond involving O2-H7 and O1 ($d_{\text{O2}\cdots\text{O1}} = 2.670(12)$ and 2.25 Å) occurs, and are not significantly different from those in reported CLA hydrate complexes.⁹ The BIZ molecules are entrapped within the *zigzag* channel by N-H...O hydrogen bonding [N3-H8...O3ⁱⁱ ($d_{\text{N3}\cdots\text{O3}} = 2.790(12)$ and $d_{\text{H8}\cdots\text{O3}} = 1.93$ Å) that involves N3-H8 of BIZ cation and O3 atom of water, as well as N1-H1 of BIZ cation and O2⁻ of chloranilate anion [N1-H1...O2⁻ ($d_{\text{N1}\cdots\text{O2}^-} = 2.675(13)$ and $d_{\text{H1}\cdots\text{O2}^-} = 1.81$ Å)]. The N1-H1...O2⁻ is shorter than N3-H8...O3, and could be attributed to the effect of O2⁻ being more polar than O atom of water. Additional interactions enhancing the entrapment of BIZ molecules are interactions between C-H groups of phenyl moiety of BIZ cation and O atom of a carbonyl group of chloranilate anion (C2-H2...O1^{iv}; $d_{\text{C2}\cdots\text{O1}} = 3.026(16)$ Å and 2.40 Å), and that with O atom of OH group of chloranilate anion (C6-H5...O2⁻; $d_{\text{C6}\cdots\text{O2}^-} = 3.414(15)$ Å and 2.56 Å) [symmetry codes: [(i) $-1+x, 3/2-y, -1/2+z$ (ii) $1-x, -1/2+y, 1/2-z$ (iii) $1+x, y, z$ (iv) $-x, 1-y, -z$ (v) $2+x, 3/2-y, 1/2+z$].

Fig. 4 Packing structure of BIZ-CLA hydrate showing the inter- and intramolecular interactions in the *ac*-plane. Symmetry codes: (i) $-1+x, 3/2-y, -1/2+z$ (ii) $1-x, -1/2+y, 1/2-z$ (iii) $1+x, y, z$ (iv) $-x, 1-y, -z$ (v) $2+x, 3/2-y, 1/2+z$.

Furthermore, the C-H...Cl interactions ($d_{\text{C2}\cdots\text{Cl}} = 3.417$ (13) Å and $d_{\text{H2}\cdots\text{Cl}} = 3.04$ Å) involving the Cl of chloranilate anion with a donor group (C2-H2) of the imidazole moiety contribute to the stability of H-bond network within the *zigzag* channel. A summary of the H-bond geometry is given in Table 3S.

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