A Novel Hydrogen-Bonded Duplex Made up of Water Molecules and Halide Ions in the Sandwich Inclusion Structures of $(C_{10}H_8N_3S)^+\cdot X\cdot 2H_2O$ [X=Cl^-, Br^-]

Ponraj Prabakaran,# Somasundaram Murugesan, Jebamony Justin Robert, Pathus Panneerselvam, Packianathan Thomas Muthiah,*
Gabriele Bocelli,† and Lara Righi†
Department of Chemistry, Bharathidasan University, Tiruchirppalli 620 024, India
†*CSSD-CNR, University of Parma, Viale delle Scienze 431001, Parma, Italy*

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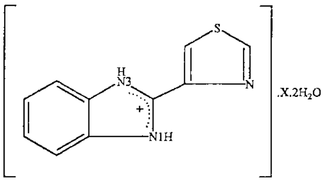
The X-ray crystal structures of thiabendazolium halide dihydrates $(C_{10}H_8N_3S)^+\cdot X\cdot 2H_2O$ [X = Cl^-, Br^-] **1**, **2** reveal a novel hydrogen-bonded duplex consisting of alternate edge-sharing $(H_2O\cdot X)_2$ quadrilaterals and $(2H_2O\cdot X)_2$ hexagons; notably these duplexes exist as host lattices and sandwich thiabendazole molecules into two different supramolecular architectures by similar N···X and N···O hydrogen bonds.

For the last few decades a lot of studies have been focused on hydrate inclusion compounds in which either hydrogen-bonded water molecules or to combine with ions constitute a wide variety of structures have been hitherto reported.[1] The hydrogen bonding involving water molecules and halide ions is a widespread phenomenon among hydrated halide salts and of current interest too.[2a] Of our recent investigations devoted to hydrogen bonding patterns exhibited by some drug molecules,[3] we have come across a striking example of a unique supramolecular ladder motif made up of water molecules and halide ions. Thiabendazole [2-(thiazol-4-yl)-1*H*-benzimidazole] is used as an anthelmintic in the treatment of parasitic diseases and also a fungicide.[4] As a part of our research programme, we have already demonstrated the metal chelating ability[5] as well as hydrogen bonding patterns[3b] of thiabendazole molecule in different crystalline environments. Herein, we report the sandwich inclusion structures of thiabendazolium halide dihydrates **1**, **2** which possess an infinite hydrogen-bonded duplex formed by a pair of centrosymmetrically related water–halide chains.



1, 2 [X=Cl^-, Br^-]

Single crystal X-ray diffraction studies[6a,b] showed that the structures **1** and **2** have similar geometrical features at the single molecular level but entirely different structures at the supramolecular level. The N1 atoms at benzimidazole moieties of thiabendazole molecules in **1** and **2** are protonated. The benzimidazole and thiazole ring systems are nearly coplanar, the dihedral angle between them being 5.41(11)° in **1** and 8.89(12)° in **2**. The C–C bond connecting the two ring systems [1.449(3) Å in **1** and **2**] is the same length, within experimental error, as that in neutral thiabendazole [1.442(10) Å]. These values suggest appreciable delocalization across this bond.[7]

The halide ions in **1** and **2** bridge two water molecules at the lattice through O···X hydrogen bonds [O1W–H···Cl^-= 2.35(4) Å, 163(4)°; O2W–H···Cl^-= 2.41 Å, 177(4)°; O1W–H···Br^-= 2.49(5) Å, 170(4)°; O2W–H···Br^-= 2.59(6) Å, 174(5)°] making hydrogen-bonded fragments (O1W···X···O2W). These fragments again self-assemble in a cooperative manner to form a linear and infinite hydrogen-bonded chain via O···O hydrogen bonds [O1W–H···O2W= 1.92(4) Å, 175(4)° in **1**; 2.03(5) Å, 167(5)° in **2**]. This hydrogen-bonded chain pairs with that of centrosymmetrically related chain through O···X cross-linking hydrogen bonds [O2W–H···Cl^-= 2.33(5) Å, 176(4)°; O2W–H···Br^-= 2.64(5) Å, 172(4)°] forming a duplex, a new and unique supramolecular framework structure. We refer the term 'duplex' as a linear hydrogen-bonded double chain which being cross-linked by symmetrical hydrogen bonds. In these duplexes, there is an infinite ladder-like arrangement containing alternate edge-sharing $(H_2O\cdot X)_2$ quadrilaterals and $(2H_2O\cdot X)_2$ hexagons (Figure 1). This ladder type water–halide structure is quite different from those observed in the case of quaternary ammonium salts characterized by Harmon et al.[2b] where each water molecule forms one hydrogen bond to halide ion and one to another water molecule. In this case, one water molecule hydrogen bonds to two halide ions while the other bridges the water and halide. To the best of our knowledge, there has been no report describing a linear hydrogen-bonded double chain in the form of such an ordered supramolecular anionic-water host lattice.

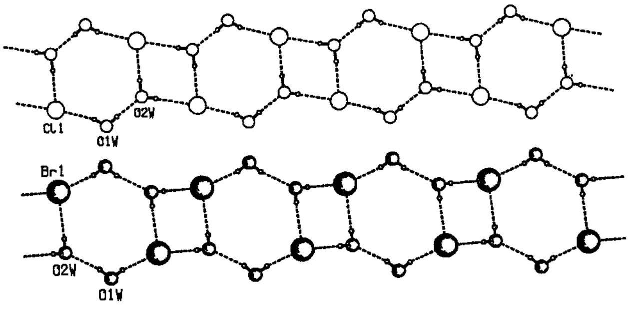


Figure 1. Hydrogen-bonded duplexes observed in **1**, **2** (a) The distances (Å) and angles (°) involving non-hydrogen atoms of the quadrilaterals and hexagons are O2W···Cl = 3.226(5), O2W···$Cl^{(i)}$= 3.281(5), Cl···O2W···$Cl^{(i)}$ = 103.1(1), $O2W^{(i)}$···Cl···O2W = 77.0(1) and O1W···$O2W^{(ii)}$ = 2.748(5), O1W···Cl = 3.149(5), O2W···Cl = 3.226(5), $O2W^{(ii)}$···O1W···Cl = 117.5(1), Cl···O2W···$O1W^{(iii)}$ = 127.3(1), O1W···Cl···$O2W^{(i)}$ = 110.3(1) respectively. (b) The distances (A) and angles (°) involving non-hydrogen atoms of the quadrilaterals and hexagons are O2W···Br = 3.503(3), O2W···$Br^{(iv)}$ = 3.374(4), Br···O2W···$Br^{(iv)}$ = 99.6(1), $O2W^{(iv)}$ ···Br···O2W = 80.3(1) and O1W···$O2W^{(v)}$ = 2.785(4), O1W···Br = 3.361(2), O2W···Br = 3.503(3), $O2W^{(vi)}$···O1W···Br = 120.7(1), Br···O2W···$O1W^{(v)}$ = 122.2(1), O1W···Br···$O2W^{(iv)}$ = 98.0(1) respectively. Symmetry codes: (i) -x,-y,-z (ii) x,y,z+1 (iii) x,y,-1+z (iv) -x,3-y,-z (v) -1+x,y,z and (vi) 1+x,y,z.

It is interesting to note that the fragment (O1W···X···O2W) is almost linear [O1–Cl^-–O2= 170.2(1)°] in **1** and highly bend [O1–Br^-–O2= 97.9(1)°] in **2**, leading to the formation of planar and twisted-ladders in **1** and **2** respectively. The N1-H groups of thiabendazole molecules in **1** and **2** are involved in N···X intermolecular hydrogen bonds [N1–H···Cl^-= 2.30(3) Å, 154(3)°; N1–H···Br^-= 2.63(3) Å, 150(3)°] while N3–H groups make N–O intermolecular hydrogen bonds with water molecules [N3–H···O1W= 1.88(4) Å, 176(3)° in **1**; 1.95(3) Å, 173(3)° in **2**]. The range of values for hydrogen bonding parameters observed in these structures agree with the recent statistical survey[8] of hydrogen bonding interactions between halide anions and organic H-bond donors OH, NH and N^+H.

The two structures **1**, **2** dominated by the presence of duplexes can be best described as sandwich inclusion structures in which the hydrogen-bonded duplexes act as the host lattice and thiabendazole molecules as the guest. The duplexes in **1** and **2** sandwich the thiabendazole molecules by similar N···X and N···O intermolecular hydrogen bonds, but through two different modes. In structure **1**, the duplexes are not stacked but anchored side by side through an array of thiabendazole molecules, which are sandwiched. The duplexes are almost kept parallel to the *bc* plane (Figure 2a). In structure **2**, the duplexes are stacked along the *c*-axis and anchored one over one by an array of thiabendazole molecules, which are sandwiched (Figure 2b). These remarkable differences at the supramolecular level may reasonably arise from the geometrical discrepancies involved in the hydrogen-bonded fragments (O1W···X···O2W) in **1** and **2** which in turn originates from the hydrogen bond strength and the mode of crystal packing in water–halide compounds. Thus, it can be foreseen that the enhancement of further studies in this direction on the hydrate inclusion compounds with appropriate halide anion recognizing molecules and proper hydrogen bond donor and acceptor stoichiometries will bring forth new and interesting supramolecular structures.

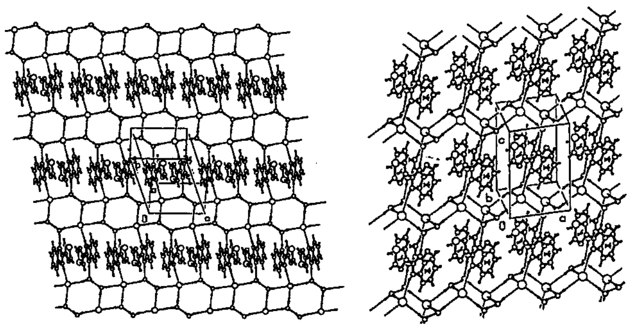


Figure 2. Crystal packing diagrams showing the two different types of supramolecular architectures in **1** and **2** by similar N-H···X and N-H···O hydrogen bonds.

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References and Notes

\# Present address: RIKEN Tsukuba Institute, 3-1-1 Koyadai, Tsukuba, Ibaraki 305-0074, Japan.

1 a) G. A. Jeffrey, “An Introduction to Hydrogen Bonding,” Oxford University Press, New York (1997). b) G. A. Jeffrey and W. Saenger, “Hydrogen Bonding in Biological Structures,” Springer, Berlin (1991). c) F. Xue and T. C. W. Mak, *Acta. Crystallogr., Sect. B*, **56**, 142 (2000).

2 a) K. M. Harmon, A. C. Webb, K. E. Shaw, and S. H. Gill, *J. Mol. Struct*., **523**, 39 (2000). b) K. M. Harmon and A. C. Webb, *J. Mol. Struct*., **508**, 119 (1999).

3 a) S. Murugesan and P. T. Muthiah, *Acta Crystallogr., Sect. C*, **54**, 763 (1997). b) S. Murugesan, P. Prabakaran, and P. T. Muthiah, *Acta. Crystallogr., Sect. C*, **54**, 1905 (1998). c) J. J. Robert and P. T. Muthiah, *Acta Crystallogr., Sect. C*, **54**, 539 (1998).

4 “The Merck Index,” 10th ed. by M. Windholz, Merck & Co. Inc., NJ (1983).

5 B. Umadevi, P. T. Muthiah, X. Shui, and D. S. Eggleston, *Inorg. Chim. Acta*, **234**, 149 (1995).

6 Thiabendazole (obtained from Merck, Sharp & Dohme Inc. U.S.A.) was dissolved in water and methanol. The solution was warmed for 30 minutes over a water bath and mixed with dilute HCl and HBr solutions separately. The final solutions were subjected to slow evaporation of solvent at the room temperature. Pale-yellow thin-plate shaped crystals appeared after a few days. a) Crystal data for **1**: $(C_{10}H_8N_3S)^+.Cl^-.2H_2O$, M = 273.74, triclinic, $P\bar{1}$, a = 8.360(4), b = 9.541(5), c = 8.162(10) Å, α = 99.1(1), β = 100.8(1), γ = 89.7(1)°, V = 631.2(9) Å^3, Z = 2, D_c = 1.440 g/cm^3, T = 293(2)K, μ(Cu Kα) = 4.196 mm^{-1}, R = 0.0444, R_w = 0.1386 for 2288 data with $F \geq 2\sigma$ (F). b) Crystal data for 2: $(C_{10}H_8N_3S)^+.Br^-\cdot 2H_2O$, M = 318.2, triclinic, $P\bar{1}$, a = 7.492(1), b = 9.349(1), c = 9.793(1) Å, α = 74.3(1), β = 85.5(1), γ = 72.7(1)°, V = 630.5(1) Å^3, Z = 2, D_c = 1.676 g/cm^3, T = 293(2)K, μ(Mo Kα) = 3.419 g mm^{-1}, R = 0.0321, R_w = 0.0723 for 2204 data with $F \geq 2\sigma(F)$. Structures were solved by direct methods using SIR97 and refined with SHELXL97. All hydrogen atoms were located from difference fourier maps and refined. PLATON97 was used for graphics and computations.

7 B. L. Trus and R. E. Marsh, *Acta Crystallogr., Sect. B*, **29**, 2298 (1973).

8 M. Mascal, *J. Chem. Soc., Perkin Trans. 2*, **1997**,1999.